

Zeolitic imidazole frameworks: structural and energetics trends compared with their zeolite analogues†

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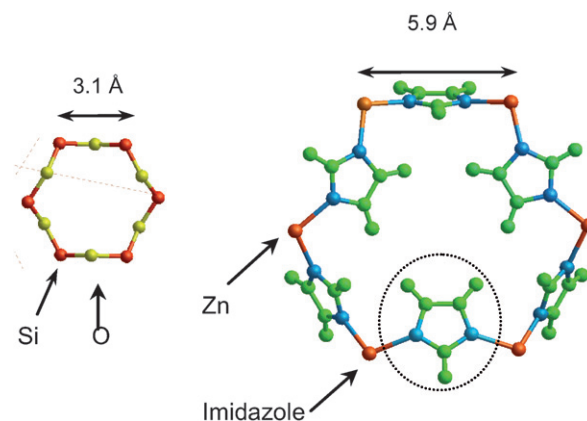
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We use periodic DFT calculations to compute the total energy of known zeolitic imidazole frameworks (ZIFs) together with those of hypothetical porous ZIFs. We show that the total energy of ZIFs decreases with increasing density, in a similar fashion to the alumino-silicate zeolites, but with a more complex energy landscape. The computational evaluation of the stability of hypothetical ZIFs is useful in the search for viable synthesis targets. Our results suggest that a number of hitherto undiscovered nanoporous topologies should be amenable to synthesis (CAN, ATN) and that even the most open framework types might be obtained with appropriately substituted ligands.

Introduction

Zeotypes are technologically important nanoporous inorganic materials with more than 180 framework topologies known to date.¹ In addition to the aluminosilicate zeolites, many other zeolite-like inorganic materials were discovered in the 1980s and 90s, such as the aluminium (AlPOs) and transition metal phosphates (MeAPOs).² More recently, during the last decade, intensive efforts have been made to develop a new class of zeolitic structures based upon hybrid metal–organic framework materials (MOFs). Such work is driven by the prospect of expanding pore sizes, enhancing their functionality, and finding new sorption and catalytic properties.³ A number of zeolitic architectures have been successfully synthesised as hybrid frameworks, either fortuitously⁴ or rationally.^{5,6} Among them, the synthesis of zeolitic imidazole frameworks (ZIFs) has recently gained considerable attention.⁶ ZIFs adopt crystalline architectures, where typically Zn²⁺ ions play the role of silicon and the imidazolate anions form bridges that mimic the role of oxygen in zeolites (Scheme 1). Currently about 20 distinct ZIFs have been synthesised, a subset of which possess the same framework topologies as zeolites. Most of the known ZIFs contain Zn or Co ions in combination with imidazolate or functionalized imidazolate anions. However, the factors that



Scheme 1 Zeolites versus ZIFs: the sequence of Si–O–Si bonds in zeolites (left) and of Zn–IM–Zn in ZIFs (right) is illustrated for a 6-membered ring.

determine which zeolite topologies will form as ZIFs, and which will not, have yet to be elucidated.

Computer simulations have been widely used in the zeolite area, for example to determine or predict their structures⁷ and to interpret adsorption properties.⁸ More recently, simulations have begun to play a role in the area of MOFs for structure prediction purposes and for characterising adsorption properties, as recently reviewed in ref. 9. In the case of ZIFs, first principles calculations based upon density functional theory (DFT) were successfully used to explore hypothetical ZIFs with dense topologies.¹⁰

The recent synthesis of the very large pore ZIF-20,^{6c} which has the LTA topology, suggests that other very large pore ZIFs might be viable. Thus, here, we utilise DFT methods to estimate the relative energies of a range of large pore hypothetical ZIFs such as FAU- and LTL-, together with those of known ZIFs including porous and dense structures. Taking a selection of zeolite topologies extracted from the existing IZA database of zeolite structures¹ and converting these topologies to ZIFs, we consider the structure and stability of these materials. The results shed quantitative light on some of the factors that control the structural diversity of this interesting new class of materials.

Computational methods

Model building

In the first stage of our calculations, we constructed starting models of ZIFs, *i.e.* polymorphs with the Zn(IM)₂ chemical

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composition, possessing either experimentally determined structures or hypothetical ones, built as explained below. The crystallographic data of as-synthesized ZIFs were retrieved from the CCDC, eliminating extra-framework species and the imidazole substituents when required. These include two structures with dense topologies, *i.e.* cag- (ZIF-4),^{6d} and zni,¹¹ and eight known structural analogues of zeolites, *i.e.* BCT- (ZIF-1, ZIF-2),^{6d} DFT- (ZIF-3),^{6d} GIS- (ZIF-6),^{6d} SOD (ZIF-7, ZIF-8, ZIF-9),^{6d} MER- (ZIF-10),^{6d} and LTA (ZIF-20)^{6e} (See Table 1). Turning to hypothetical ZIF crystal structures, in view of the very large choice of topologies from the IZA database (and of course the even greater number of tetrahedral hypothetical nets),¹² we constrain our initial survey to a selection of zeotypes. They are listed in Table 2, denoted by their three-letter IZA codes. Our choice of zeolite topologies was guided by the intriguing fact that the majority of ZIFs synthesised to date possess uninodal nets, *i.e.* have one crystallographic tetrahedral site in their asymmetric unit. Having this in mind, we chose to construct hypothetical ZIFs having uninodal nets—ACO, ABW, AFI, ATN, ATO, CAN—and multimodal nets—LTL and AST (2 nodes), and FER (4 nodes). We also considered, despite its very large cell volume

(~26 000 Å³), the uninodal FAU-type model due to its remarkable low density and its hierarchical system of pores.

In order to construct suitable starting hypothetical models of ZIFs for simulations, we need to take each uninodal zeolite crystal structure and convert them to the targeted Zn and imidazole-based ZIFs. Here, we applied TOBUNPOROUS,¹³ a code written to: (i) replace each Si centre with a Zn ion; (ii) replace the bridging oxygen of the Si–O–Si bridge by a linking ligand, here imidazole; and finally (iii) scale the unit-cell dimensions appropriately. The method is a robust and reliable approach in the case of ZIFs, typically providing starting parameters for energy minimization within ±2% of experimental values. All hypothetical structures studied in this work are shown in Fig. 1.

Geometry optimization

In the second stage of the work, we performed energy minimization calculations to determine the equilibrium structures and the relative total energies of both the experimentally determined and hypothetical models using DFT methods, with the aim of identifying new and viable ZIFs topologies.

Table 1 Geometry optimized (upright) and experimentally determined (italic) parameters of ZIFs, simulated with the Zn(IM)₂ composition. (*) refer to structures that were originally synthesised with substituted imidazole, by contrast with all other structures made with non-substituted imidazole

ZIF code	Cell parameters <i>a, b, c</i> in Å			Cell angles α, β, γ in deg		<i>V</i> /Å ³	Density (<i>T/V</i> in nm ⁻³)	Total energy <i>E</i> (eV/Zn)	
zni	17.984	17.984	18.0547	97.23	97.23	138.55	3611.7	4.43	−3894.4283
	<i>17.738</i>	<i>17.738</i>	<i>17.738</i>	<i>97.11</i>	<i>97.11</i>	<i>138.80</i>	<i>3440.7</i>		
ZIF-1 (BTC)	9.995	15.397	15.180	90.00	98.55	90.00	2310.2	3.46	−3894.3362
	<i>9.740</i>	<i>15.260</i>	<i>14.936</i>	<i>90.00</i>	<i>98.62</i>	<i>90.00</i>	<i>2195.8</i>		
ZIF-2 (BTC)	9.67	24.16,	24.36	90.00	90.00	90.00	5691.6	2.81	−3894.2795
	<i>9.68</i>	<i>24.11</i>	<i>24.45</i>	<i>90.00</i>	<i>90.00</i>	<i>90.00</i>	<i>5706.6</i>		
ZIF-3 (DFT)	18.963	18.963	16.772	90.00	90.00	90.00	6031.4	2.65	−3894.2921
	<i>18.970</i>	<i>18.970</i>	<i>16.740</i>	<i>90.00</i>	<i>90.00</i>	<i>90.00</i>	<i>6024.1</i>		
ZIF-4 (cag)	15.423	15.404	18.438	90.00	90.00	90.00	4380.5	3.65	−3894.3527
	<i>15.395</i>	<i>15.307</i>	<i>18.426</i>	<i>90.00</i>	<i>90.00</i>	<i>90.00</i>	<i>4344.9</i>		
ZIF-6 (GIS)	16.804	16.776	16.814	112.85	112.82	103.42	3594.3	2.22	−3894.2878
	<i>16.549</i>	<i>16.549</i>	<i>16.459</i>	<i>111.97</i>	<i>111.97</i>	<i>104.58</i>	<i>3470.0</i>		
ZIF-20 (LTA)*	32.500	32.500	32.500	60.00	60.00	60.00	24273.6	1.98	−3894.2649
	<i>32.154</i>	<i>32.154</i>	<i>32.154</i>	<i>60.00</i>	<i>60.00</i>	<i>60.00</i>	<i>23506.4</i>		
ZIF-7 (SOD)*	14.231	14.309	14.283	107.22	106.40	107.15	2427.1	2.47	−3894.2442
	<i>14.275</i>	<i>14.275</i>	<i>14.274</i>	<i>107.26</i>	<i>107.26</i>	<i>107.26</i>	<i>2404.8</i>		
ZIF-8 (SOD)*	14.736	14.780	14.764	109.61	109.47	109.36	2474.7	2.42	−3894.2955
	<i>14.715</i>	<i>14.715</i>	<i>14.715</i>	<i>109.47</i>	<i>109.47</i>	<i>109.47</i>	<i>2452.6</i>		
ZIF-9 (SOD)*	22.913	22.910	15.880	90.12	90.02	119.95	7223.9	2.49	−3894.2473
	<i>22.94</i>	<i>22.944</i>	<i>15.747</i>	<i>90.00</i>	<i>90.00</i>	<i>120.00</i>	<i>7178.9</i>		
ZIF-10 (MER)	21.68	21.71	21.69	101.82	101.84	126.45	7312.7	2.19	−3894.3037
	<i>21.45</i>	<i>21.45</i>	<i>21.45</i>	<i>101.80</i>	<i>101.80</i>	<i>126.22</i>	<i>7105.4</i>		

Table 2 Geometry optimized hypothetical ZIFs, simulated with the Zn(IM)₂ composition

ZIF code	Cell parameters <i>a b c</i> in Å			Cell angles $\alpha \beta \gamma$ in deg		<i>V</i> /Å ³	Density (<i>T/V</i> in nm ⁻³)	Total energy <i>E</i> (eV/Zn)	
ABW	13.732	13.655	13.887	91.23	105.34	135.77	1663.1	2.4	−3894.2588
ACO	16.627	16.655	16.785	109.48	109.44	108.63	3615.5	2.21	−3894.2124
AFI	26.875	26.915	16.574	90.02	89.99	119.88	10395.8	2.31	−3894.2396
AST	18.554	18.507	18.60	60.49	60.54	60.39	4565.1	2.19	−3894.2194
ATN	18.884	18.988	26.315	45.72	46.09	83.98	3297.5	2.42	−3894.3155
ATO	23.764	23.764	23.764	118.09	118.09	118.09	4761.3	2.52	−3894.2490
CAN	24.328	24.300	10.065	89.98	89.99	119.77	5173.7	2.32	−3894.2812
FAU	33.470	33.470	33.470	60.00	60.00	60.00	26513.3	1.81	−3894.2115
FER	24.466	24.396	24.539	79.96	110.67	144.95	7689.5	2.34	−3894.2199
LTL	35.638	35.635	14.762	90.00	90.00	120.00	16235.6	2.21	−3894.1936

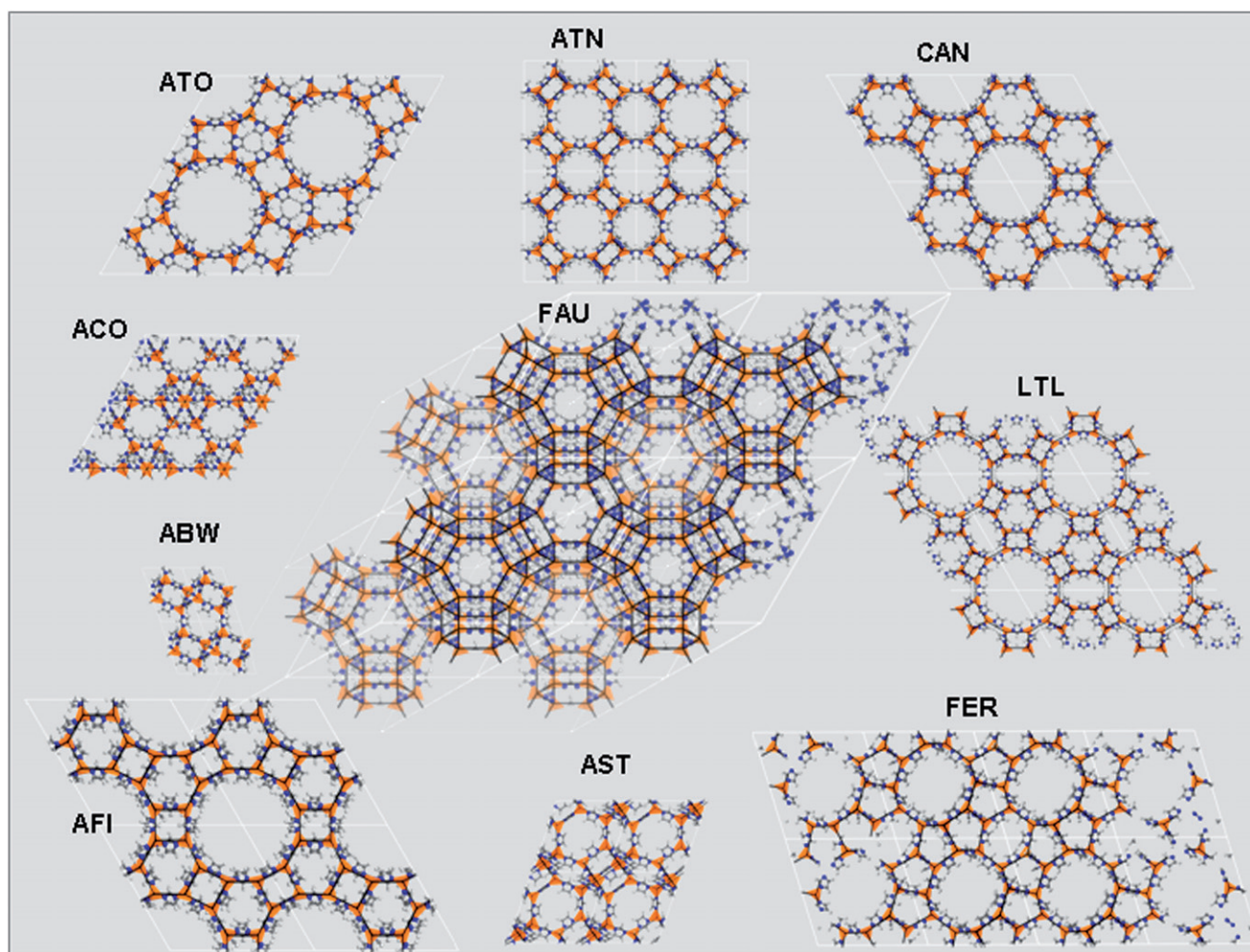


Fig. 1 Simulated energy minimized crystal structures of hypothetical ZIFs (N: blue, C: grey, H: white, and Zn: orange tetrahedra). The three-letter code refers to the nomenclature of zeotypes from IZA [1].

Our choice of DFT method is dictated and constrained firstly by the absence of flexible validated force fields for hybrid materials and secondly by the large unit cells considered here. DFT methods have proved to be efficient in addressing the energetics and structures of hybrid compounds.^{10,14} DFT calculations were carried out with the code SIESTA,¹⁵ which uses atom centered basis functions that are particularly efficient for total energy studies of very low density materials with very large unit cells. Periodic DFT calculations were carried out using the PBE exchange correlation functional within the GGA approximation. Energies of all structures in their primitive cells or unit cells were minimized by geometry optimization at constant pressure using the Broyden scheme, where both cell parameters and atomic coordinates were relaxed. No symmetry was imposed on the structure in the calculation and so the cell may relax to alternative Bravais lattice types. Double zeta plus polarisation basis sets were used throughout. Pseudopotentials for Zn, C and N were taken from a recent study of $\text{Zn}(\text{CN})_2$.¹⁶ The hydrogen pseudopotential and basis were taken from the SIESTA database.¹⁷ In each case, the geometry was relaxed until the residual forces were smaller than $0.015 \text{ eV } \text{\AA}^{-1}$, with a stress tolerance less than 1 GPa. The Hartree and exchange–correlation potentials were evaluated using a real-space mesh with a kinetic energy cutoff of 200 Ry, while the Brillouin zone was sampled

only at the Γ point (which is reasonable given these materials are insulators with a minimum cell parameter of 9.7 \AA and a maximum of $>32 \text{ \AA}$). Coordinates for all geometry optimized structures are given in the form of CIF files in the ESI.† Cell parameters and energies of all structures are reported in Tables 1 and 2.

Results and discussion

It is important to emphasize that the cell parameters of the energy-minimized structures of all the known ZIFs are in excellent agreement with the experimental data (Table 1), underlining the robustness of the energy minimizations.

Fig. 2 plots the calculated total energies of our set of known ZIFs structures as a function of their framework densities, expressed as the number of Zn sites per unit volume. The energy for each structure was normalized relative to the number of Zn atoms in the unit-cell and compared to the normalized total energy of the most stable dense polymorph, znl ,¹¹ taken here as the reference structure. We have computed eight known topologies in their pure imidazole forms, though some have only been prepared with substituted imidazolate anions. For example, the LTA topology is shown with the unsubstituted imidazole $\text{Zn}(\text{IM})_2$ composition, although it has been

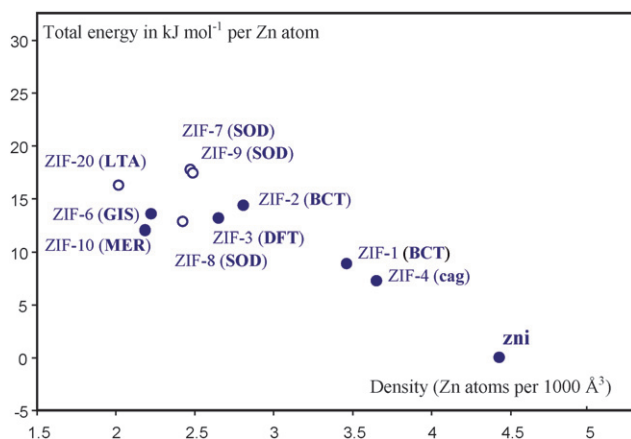


Fig. 2 Variation of calculated total energy of the known ZIFs with their framework density, expressed as the number of Zn sites per volume unit. (●) Pure imidazole ZIFs, (○) substituted imidazole ZIFs.

synthesized as ZIF-20 with purine.^{6c} Similarly, our pure imidazole (Zn(IM)₂) models of the sodalite ZIFs (ZIF-7, ZIF-8 and ZIF-9) are simplifications of the real materials due to our neglect of substituents on the imidazole ring ($-\text{CH}_3$, $-\text{C}_6\text{H}_4$).

To a reasonable approximation, it appears that two distinct groups of materials can be identified among the known structure types: a first group consisting of ZIFs synthesized with pure imidazole correspond to the most stable topologies (ZIF-1-2-3-4-6-10), and a second group of slightly less stable ZIFs, which are those experimentally only obtained with substituted imidazole (ZIF-7-9-20). ZIF-8, made with a substituted ligand, is the only exception to this grouping. This finding would support the view that certain architectures can be stabilized due to the interactions between the substituents on the imidazole ligands.

The variation in the total energy of the three SOD structures (ZIF-7-8-9) in the 12–17.5 kJ.mol⁻¹ range is illustrative of the impact of the ligand on the stabilisation of a given topology. The relative orientation of the imidazole molecules within the 6-rings is very different in ZIF-7 and -9 than in ZIF-8 where a regular “up” and “down” orientation is observed. While the latter is highly symmetrical and is the most stable one, the simulations reveal that the use of substituted imidazole in ZIF-7 and -9 allows the synthesis of metastable and distorted SOD structures, where the energetic cost of cooperative framework distortions may be compensated by stabilizing interactions between substituents.

One striking feature of the simulations is that there is a rather restricted variation of total energies for the known ZIF architectures, with less than 18 kJ mol⁻¹ separating the most stable structure (zni) from the least stable (ZIF-7;SOD). It is also noteworthy that the more dense structures found experimentally are the most stable ones, with the dense zni and cag- lying in the lower part of the energy/density plot. There is an approximately linear trend of total energies with density. Indeed, the variation in relative total energies of both the ZIFs and siliceous zeolites is remarkably, if coincidentally, similar, particularly given the approximate 10-fold difference in density. (Fig. 3).¹⁸ It is probable that the stabilisation of dense ZIF structures relative to more open ones might be even more pronounced than our calculations would suggest because the DFT method does not include the van der Waals interactions.

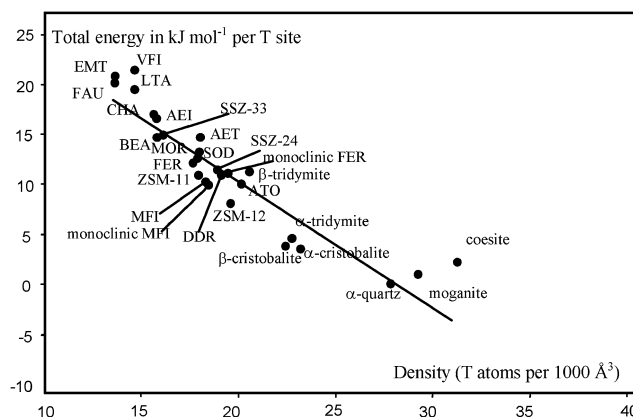


Fig. 3 Calculated total energy of the SiO₂ zeolites with their framework density. Reproduced by permission of ref. 18. Copyright American Chemical Society 1994.

In Fig. 4 we compare the energies of the hypothetical ZIF structures (in red) with those of the known architectures (in blue). While the energies of the hypothetical structures are generally higher than the known ones, the difference is not very great in several cases and we conclude that a number of other topologies should be accessible experimentally, even with unsubstituted imidazolates. This is especially the case for the two topologies, CAN and ATN, whose total energies fall within the range of the already synthesized structures. Indeed, ATN is among the most stable structures considered, with a total energy similar to that of the imidazole-containing ZIF-2 (BCT) and ZIF-10 (MER). The other hypothetical ZIFs, including the very large pore FAU- and LTL-type ZIFs, together with AST, ACO and AFI, have less favourable relative total energies. Nevertheless, as with zeolites, these lower density frameworks may be experimentally accessible through the modifications of the framework compositions, using here substituted ligands. In ZIFs, the substituted ligand can act as a secondary structure directing agent, as illustrated by the ~ 5 kJ mol⁻¹ difference between ZIF-7 and -8 which both possess the SOD topology. The very recent synthesis of the

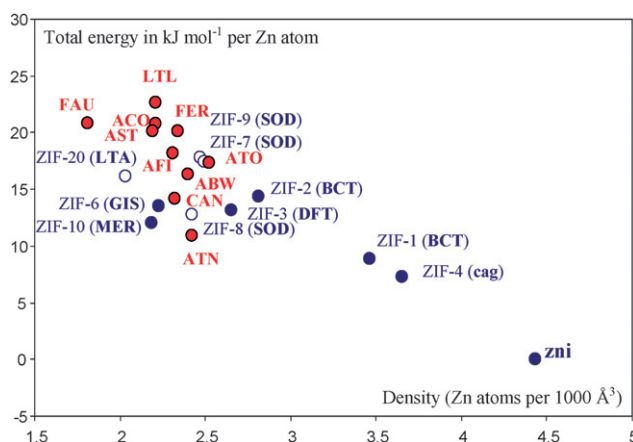


Fig. 4 Calculated total energy of hypothetical ZIF structures (red) compared to those of known ZIFs (blue). Density is expressed as the number of Zn sites per volume unit. (●) Pure imidazole ZIFs, (○) substituted imidazole ZIFs.

ACO topology¹⁹ with a mixture of 5-methylbenzimidazole and imidazole supports the above conclusions.

Conclusions

As with other systems that display polymorphism, kinetic control during synthesis is apparent from the rather small range of total energies that separate the known ZIFs that can be formed with unsubstituted imidazole (~15 kJ mol⁻¹). The role of thermodynamics is underlined by the fact that many of the unknown ZIFs have total energies that are as much as 23 kJ mol⁻¹ higher than the most stable system (zni). Nevertheless, we expect that strategies to stabilise the framework, such as substitution on the ligand or “templating”, may be applicable and provide routes to the less stable topologies. Future work will address this question by means of simulation. At this stage, we do not fully understand the synthetic factors that control which phase is formed. However, there is no doubt that a number of hitherto undiscovered topologies should be amenable to synthesis and that even the most open framework types might be obtained with appropriately substituted ligands. Furthermore, the possibility of discovering not-yet-synthesized zeolitic topologies remains very real, as exemplified by the fact that the most stable of all the ZIFs, zni, has a topology that is unknown as a silica polymorph, though it is known as the dense aluminosilicate, banalsite BaSi₂Al₂O₈.²⁰

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