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Tuning the Swing Effect by Chemical Functionalisation of Zeolitic Imidazolate Frameworks


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KEYWORDS Metal-organic frameworks; adsorption; porous materials; high-pressure crystallography; molecular simulation; density functional theory

Supporting Information Placeholder

ABSTRACT: (Many zeolitic imidazolate frameworks (ZIFs) are promising candidates for use in separation technologies. Comprising large cavities interconnected by small windows they can be used, at least in principle, as molecular sieves where molecules smaller than the window size are able to diffuse into the material while larger are rejected. However, “swing effect” or “gate opening” phenomena resulting in an enlargement of the windows have proven to be detrimental. Here, we present the first systematic experimental and computational study of the effect of chemical functionalisation of the imidazole linker on the framework dynamics. Using high-pressure (HP) single-crystal X-ray diffraction, density functional theory, and grand canonical Monte Carlo simulations, we show that in the isomorphic ZIF-8, ZIF-90 and ZIF-65 functional groups of increasing polarity (−CH3, CHO, −NO2) on the imidazolate linkers provide control over the degree of rotation and thus the critical window diameter. On application of pressure, the substituted imidazolate rings rotate resulting in an increase in both pore volume and content. Our results show that the interplay between the guest molecules and the chemical function of the imidazole linker is essential for directing the swing effect in ZIF frameworks and therefore the adsorption performance.

Introduction

Zeolitic imidazolate frameworks (ZIFs) are a class of chemically stable and commercial porous materials.1,4 Their structures are based on zeolite topologies, where imidazolate (Im, C3H3N2+) and Zn2+, Co2+, Li+ or B3+ ions replace the oxygen and Al3+/Si4+ species found in zeolites. Incorporating the Im linker increases the pore sizes compared to zeolites. The ZIF family contains over 100 frameworks which adopt zeolite topologies such as rho (ZIF-11), dft (ZIF-3) and cag (ZIF-4). These different topologies are made possible through functionalisation of the imidazole linker, which results in a change in pore size and surface chemistry.3 This has led to a plethora of applications of ZIFs in catalysis, drug delivery and gas storage.6,7 In order to fully exploit the potential of ZIFs it is necessary to fully understand the structural changes of the framework upon guest uptake and the resulting mechanical properties. There has been little work on the mechanical response for example. ZIF-4 (Zn(Im)2, Im = imidazolate) is known to desolvate to a dense form8 and ZIF-11 (Zn(blm), blm = benzimidazolate) has been studied to understand how solvent plays a role in stabilising the structure against mechanical stress in ball-milling.9

One of the ZIFs that has been widely studied is ZIF-8, (Zn(mIm)2, mIm = 2-methylimidazolate), which crystallises in the cubic space group I-43m (a=16.9856(16) Å, V=4900.5(8) Å3) and adopts the sodalite topology (Fig. 1a).4 At ambient pressure and temperature, ZIF-8 contains one central nano-sized pore per unit cell, with a volume of ~2500 Å3 and pore diameter of 11.6 Å. Connecting these large nanopores are eight six-membered ring (6MR) windows ca. 3.0 Å in diameter and six smaller four-membered ring (4MR) windows of ca. 0.8 Å (Fig. 1a, Table 1). Multiple studies have made use of these critically narrow 6MR windows for gas separation in e.g. membranes.10,15 However, H2/CH4 separation experiments (with kinetic diameters of 2.85 Å and 3.80 Å, respectively) illustrated that many molecules with kinetic diameters larger...
penetration of the hydrostatic medium into the pores was followed by compression at 0.90 GPA. At 1.47 GPA, a single-crystal to single-crystal phase transition took place to a previously unobserved phase (referred to as ZIF-8-HP), involving rotation of the mlm linker. The angle of rotation, \( \theta \), defined as the angle between the (100) plane and the mean plane passing through the mlm ring increased from 64.3° at ambient pressure to 89.7° at 1.47 GPA (Fig. 1b). This rotation resulted in an increase in the diameter of the 4MR and 6MR windows from 0.8 Å to 2.2 Å, and 3.0 Å to 3.6 Å, allowing more MeOH and EtOH molecules to enter the framework. Using a combination of grand canonical Monte Carlo (GCMC) simulations and in situ powder X-ray diffraction (PXRD), Fairen-Jimenez et al later demonstrated that the same phase transition took place upon gas adsorption at much lower pressure (for N\(_2\) at 77 K it can be observed at ~0.02 bar) due to the adsorption of additional molecules in the 4MR windows. Zhang et al showed that this phenomenon is dependent on the ZIF-8 particle size. In addition, the vibrational mode linked to the gate opening has been observed in the terahertz region (~50 cm\(^{-1}\)) and increase in pore volume and content compared to ZIF-8HP (~300 Å\(^3\) and 1087 e/uc compared to 100 Å\(^3\) and ~636 e/uc) predicted by ab initio density functional simulations. The effect of hydrostatic media on the compression of ZIF-8 has also been studied demonstrating that the framework has different compressibilities in different media.

Replacement of the -CH\(_3\) substituent on the mlm linker with either -CHO or -NO\(_2\) groups leads to the isosctructural and isosymmetric ZIF-90 (Zn(ICA)), ZIF-65 (Zn(nlm)), ZIF-65 displays an increased affinity for CO\(_2\), compared to ZIF-8 due to the NO\(_2\) functionality.

### Results and Discussion

However, the influence of the functionality on the framework dynamics and mechanical properties has not been systematically studied. Here, we present a combined high-pressure (HP) single-crystal diffraction and computational study on three isostuctural ZIFs: ZIF-8, ZIF-90 and ZIF-65 in order to understand the effect of imidazole functionality and guest molecule uptake on swing effect.

<p>| Table 1: Diameter of 4MR and 6MR windows in ZIF-8, ZIF-65 and ZIF-90 |
|-----------------|-----|-----|-----|-----|</p>
<table>
<thead>
<tr>
<th>ZIF</th>
<th>Lattice</th>
<th>Pore</th>
<th>( \theta )</th>
<th>4MR</th>
<th>6MR</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>16.9856(16)</td>
<td>2500</td>
<td>64.3</td>
<td>0.8</td>
<td>3.0</td>
</tr>
<tr>
<td>ZIF-90</td>
<td>17.0758(13)</td>
<td>2354</td>
<td>66.5</td>
<td>1.4</td>
<td>3.2</td>
</tr>
<tr>
<td>ZIF-65</td>
<td>17.3185(2)</td>
<td>2619</td>
<td>46.3</td>
<td>0.8</td>
<td>3.2</td>
</tr>
</tbody>
</table>

All diameters calculated in Mercurry, with 0.2 Å grid spacing.
accompanied by a steady increase in electron density in the pore to 3.10 GPa (from 280 to ~ 540 e/uc), whereby a plateau was reached and maintained to 4.77 GPa. This latter pressure marked the highest pressure point for which diffraction data could be collected and solved (Fig. 3). Above this pressure, the single crystal fractured and became amorphous. ZIFs are often observed to become amorphous on direct compression, and have been predicted to be rather unstable on applying pressure.28,29 The inclusion of solvent stabilises ZIF-65 to external pressure, which has been seen in other MOFs such as CuBTC and MOF-5.27,30

The structure of ZIF-65-HP does not resemble that of ZIF-8-HP or ZIF-90-HP (Fig. 3). Rotation of the organic linkers to smaller values of \( \theta \) was observed, compared to the latter two high pressure structures which coincided with an increase in \( \theta \). Interestingly, the intermolecular N...O distance (where N is contained within one NO2 headgroup and O within an adjacent NO2 headgroup (Fig. S3)) across the 4MR decreased by ~0.5 Å (Table S2). The fact that these -NO2 groups move towards each other suggest that unlike CH3...CH3 interactions the interaction between these groups are mildly favourable. This rationale is consistent with the observation that in certain geometries, stacking of NO2 groups leads to interaction energies comparable to C=O…H-C interactions.31,32 As a result of these high-pressure geometries, adsorption of guest molecules is improved due to the increased size of channels linking the central nanopore (Fig. 3), encouraging percolation of guest molecules between pores.

By using a mixture of 4:1 methanol:ethanol, we used a pressure transmitting medium that is hydrostatic to high-pressures (12 GPa) and can enter the pores of the ZIFs. In order to determine its role in the transformation of the AP to the HP structures, single point energy calculations were undertaken on guest-free ZIF-8, ZIF-90 and ZIF-65 as a function of ligand rotation. To begin with, geometry optimisation of the ambient pressure structures using the periodic CASTEP code (for full details see SI-1) were performed, giving values of \( \theta \) comparable to the ambient pressure values, measuring 63.4°, 55.5°, 50.2° for ZIF-8, ZIF-90 and ZIF-65 respectively compared to the ambient crystal structure values of 64.3°, 66.5° and 46.5°. Deviation in the latter two cases is ascribed to solvent presence in the pores in the experimental data. \( \theta \) was then varied (i.e. the Im linkers rotated) by 30°, in 5° increments, in both positive and negative directions relative to the equilibrium structure. Relative energies with respect to the equilibrium structure were calculated and are given in kJ mol\(^{-1}\) per imidazolate linker. Fig. 4 shows the results of the single point energy calculations (see Table S3 for more information). Relatively flat potential energy surfaces were revealed, indicating that energy penalty to rotate the linkers are very low. For ZIF-8 (which had a starting \( \theta \) of 64.3°), the energy penalty to the rotation of the mlm linker to the ZIF-8-HP phase (where \( \theta = 89.7° \)) was relatively small (~8 kJ mol\(^{-1}\)). However, the

![Graph showing the percentage change in unit cell volume and Imidazole linker rotation](image-url)

**Table 2:** 4MR and 6MR window diameters of ZIF-8, ZIF-65 and ZIF-90 at pressure. * marks the onset to the high-pressure phase.

<table>
<thead>
<tr>
<th></th>
<th>ZIF-8 in MeOH/EtOH</th>
<th>4MR diameter / Å</th>
<th>6MR diameter / Å</th>
<th>ZIF-65 in MeOH/EtOH</th>
<th>4MR diameter / Å</th>
<th>6MR diameter / Å</th>
<th>ZIF-90 in MeOH/EtOH</th>
<th>4MR diameter / Å</th>
<th>6MR diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure / GPa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>0.0</td>
<td>0.8</td>
<td>3.0</td>
<td>0.0</td>
<td>0.8</td>
<td>3.2</td>
<td>0.0</td>
<td>1.4</td>
<td>3.2</td>
<td></td>
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<tr>
<td>0.18</td>
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<td>3.0</td>
<td>0.11</td>
<td>1.0</td>
<td>3.2</td>
<td>0.34</td>
<td>2.4</td>
<td>3.4</td>
<td></td>
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<tr>
<td>0.30</td>
<td>0.6</td>
<td>3.0</td>
<td>0.30</td>
<td>1.0</td>
<td>3.2</td>
<td>0.88*</td>
<td>2.4</td>
<td>3.4</td>
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<tr>
<td>0.73*</td>
<td>0.6</td>
<td>3.6</td>
<td>0.73*</td>
<td>0.6</td>
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<td>1.47*</td>
<td>2.6</td>
<td>3.6</td>
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<td>1.40*</td>
<td>3.2</td>
<td>3.4</td>
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<td>1.0</td>
<td>3.6</td>
<td>1.95*</td>
<td>2.4</td>
<td>3.6</td>
<td></td>
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<tr>
<td>2.15*</td>
<td>4.0</td>
<td>3.6</td>
<td>2.15*</td>
<td>4.0</td>
<td>3.6</td>
<td>4.77*</td>
<td>4.0</td>
<td>3.8</td>
<td></td>
</tr>
<tr>
<td>2.94*</td>
<td>4.0</td>
<td>3.8</td>
<td>2.94*</td>
<td>4.0</td>
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<tr>
<td>4.77*</td>
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<td>4.3</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

**Figure 2:** Percentage change in unit cell volume, \( \Delta \) (MeOH/EtOH). Where AP \( \Delta \) al.1
same rotation by 25° in the opposite direction had a much larger
energy penalty, equating to ~160 kJ mol⁻¹. Due to steric hindrance
of the methyl groups, the rotation of the linker clearly has a definite
preference, and in order for the opposite rotation to occur, the
energies of adsorption would have to be very large, much larger than
what might be expected for adsorption of MeOH which is usually
in the order of tens of kJ mol⁻¹. For both ZIF-90 and ZIF-65, the potential energy landscape determined was relatively flat in comparison to ZIF-8, with only small
energy penalties of a few kJ mol⁻¹ regardless of the direction of rotation.
The difference in behaviour observed for negative linker ro-
tations is attributed to unfavourable CH⁻⁻CHO or -NO₂ head group
interactions in the case of ZIF-90 and ZIF-65, respectively. On compressing ZIF-90, the imidazole rings rotated by approximately
+20°. This equated to an energy penalty of just 6.1 kJ mol⁻¹. The
corresponding backward rotation equated to 7.5 kJ mol⁻¹. Similarly,
for ZIF-65, whilst the highest degree of rotation was -20° at
4.77 GPa, which equated to 25.6 kJ mol⁻¹, the corresponding for-
ward rotation was more favourable at 5.6 kJ mol⁻¹. For all three
frameworks, positive rotations are favoured in the absence of any
guests. The negative rotations observed in the HP experiments for
ZIF-65 therefore indicate a much greater guest-host interaction
than for ZIF-90 and ZIF-8.

In order to locate the position of guest MeOH molecules, and to
quantify guest-host interactions for ZIF-8, ZIF-65 and ZIF-90,
grand canonical Monte Carlo (GCMC) calculations were carried
out (for full simulation details see SI-1). As GCMC simulations
require the frameworks to be rigid, both the ambient pressure (AP)
and the highest HP crystallographic structures were used as models
in separate GCMC simulations. In this way, the effect of changing
the linker orientation on the uptake of methanol into the pores can
be directly studied. During the simulations the energies and posi-
tions of the methanol molecules were stored, and from this, poten-
tial energy histograms constructed (Fig. 5). Compared to the AP
structures, the guest-host interaction energies for all HP structures
decreased, that is, became more favourable. The driving force for
HP phases, for all systems studied, is therefore to maximise the in-
teraction between the framework and the adsorbate – something
that was observed before for CH₂ in ZIF-8. To understand the effect that the guest-host interactions have on the
direction of rotation, GCMC simulations were also undertaken
on hypothetical structures of ZIF-90 and ZIF-65 where the linkers
were rotated by the same degree but in the opposite direction to
their HP experimental structures. For example, in ZIF-65-HP, the
linkers rotate by 20° compared to the AP phase, so the linkers in
the hypothetical structure (named ZIF-65-HYPO) were rotated by
+20°. Likewise, the ICA linkers in ZIF-90-HP rotate by ± 25°, so
the linkers in ZIF-90-HYPO were rotated by ±25°. Fig. 6 shows the
resulting methanol – framework interaction energy mapped onto
surfaces. The colour of the surface signifies the strength of the in-
teraction. In both ZIF-90-HYPO and ZIF-65-HYPO, the interaction
energy between methanol and the framework increases (i.e.
becomes less favourable) compared to the experimentally observed
structures a strong indication that the guest-framework energies
dictate the direction of ligand rotation. See SI-4 for more infor-
mation on the interaction energies.
Analysing the position of the methanol molecules in the pores sheds light on the differences of packing within the structures, and why each HP structure was preferred over their hypothetical counterpart. For ZIF65-HP (Fig. 6a) the most favourable interaction for methanol with the framework (-40 to -30 kJ mol$^{-1}$) was located just above the four-membered window, interacting strongly with the four overlapping NO$_2$ groups. The second strongest sites (-30 to -20 kJ mol$^{-1}$), are found percolating through the structure connecting adjacent pores through the 6MR. The third strongest site (-20 to -10 kJ mol$^{-1}$), can be found in the pore, as well as in the 6MR window, however these molecules have less favourable orientations to the second site. The final site (-10 to 0 kJ mol$^{-1}$), was found in the centre of the pore, accounting for the low interaction energy these methanol molecules experience with ZIF-65.

For ZIF-65-HYPO (Fig. 6b), there were no methanol –framework interactions below -30 kJ mol$^{-1}$, most likely due to the orientation of the framework which is now in a gate-opened structure. With the 4MR window open, this orientation does not allow good contact with methanol. The resulting most favourable sites having energies in the order of -30 to -20 kJ mol$^{-1}$. These sites, like in ZIF-65-HP, sit in the 6MR window thereby connecting the pores throughout the crystal lattice, but with less favourable interaction energies (by ca. 5 kJ mol$^{-1}$) than in ZIF-65-HP. The second site, blue (-20 to -10 kJ mol$^{-1}$), was also present in the 6MR window and in the central pore, but the mean interaction energy is again around -5 kJ mol$^{-1}$ less than ZIF-65-HP. The weakest binding site in ZIF-65-HYPO (-10 to 0 kJ mol$^{-1}$), occupied the centre of the pore, and the density was much higher than in ZIF-65-HP, which again illustrates that the structure of ZIF-65-HYPO is in a less favourable orientation for the uptake of methanol than ZIF-65-HP. In the case of ZIF-90, the hypothetical phase ZIF-90-HYPO also produced less favourable interaction energies with methanol than ZIF-90-HP. However, the interaction energies are much closer (-1 kJ mol$^{-1}$ difference) compared to ZIF-65, where the offset between each phase is ~3 kJ mol$^{-1}$.

It is evident that the lowest energy sites (~30 to -20 kJ mol$^{-1}$) dictate the orientation of the linkers in the frameworks. These sites percolate from one pore to another through the 6MR windows and it is therefore clear that increasing the limiting pore diameters of these windows is important for adsorption of methanol through the extended pore network. Fig. 7 and Table 3 illustrate how for ZIF-90-HP and ZIF-65-HP the diameter of the 6MR windows is larger than for their rotated counterpart structures and ZIF-65-HYPO. For ZIF-65, the highly polar -NO$_2$: 4MR window can form very strong interactions with methanol, which it could not do if it formed a “gate opened” structure like ZIF-8 or ZIF-90, in addition to creating larger channels for the methanol to percolate through the structure.

![Figure 6: Framework-methanol interaction energy surfaces for (a) ZIF-65-HP, (b) ZIF-65-HYPO, (b) ZIF-90-HP and (d) ZIF-90-HYPO. The scale on the surface represents the interaction energy with blue = 10 kJ mol$^{-1}$ and red = -40 kJ mol$^{-1}$. Hydrogen atoms are omitted for clarity.](image)

![Figure 7: (a) ZIF-90-HP, (b) ZIF-90-HYPO, (c) ZIF-65-HP, (d) ZIF-65-HYPO. All viewed down the 100 direction. Purple shading represents the solvent accessible volume calculated with a probe size diameter of 3.4 Å (kinetic diameter of methanol) using Mercury. Note in (b) and (d) the smaller channels in the six membered ring windows.](image)

<table>
<thead>
<tr>
<th>Framework</th>
<th>$\theta$ / °</th>
<th>4MR window diameter / Å</th>
<th>6MR window diameter / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-90-HP</td>
<td>84</td>
<td>2.4</td>
<td>3.6</td>
</tr>
<tr>
<td>ZIF-90-HYPO</td>
<td>34</td>
<td>0.0</td>
<td>3.2</td>
</tr>
<tr>
<td>ZIF-65-HP</td>
<td>30</td>
<td>0.4</td>
<td>3.8</td>
</tr>
<tr>
<td>ZIF-65-HYPO</td>
<td>70</td>
<td>2.0</td>
<td>3.6</td>
</tr>
</tbody>
</table>

In summary, we have demonstrated that the functionality of the imidazole ring dictates the swing effect behaviour of sod ZIFs. By using an alcohol as the hydrostatic medium and by using groups of increasing polarity on the framework in our high pressure X-ray diffraction experiments, we have demonstrated control over the degree of rotation and thus the critical window diameters. We showed that ZIF-90 undergoes a phase transition to a ‘gate open’ HP phase, however the degree of rotation of the Im linker is less than that of ZIF-8. In addition, it was demonstrated that ZIF-65 undergoes a transition to a more ‘gate-closed’ structure upon applying high-
pressure. By carrying out DFT simulations of the framework response to ligand rotation, combined with GCMC simulations in the presence of methanol on the HIP structures of ZIF-65, ZIF-90 and ZIF-8, and their hypothetical counterparts where the direction of linker rotation is reversed, the guest-host interactions and framework rotation interactions have been deconvoluted. We have demonstrated the importance of guest-framework interactions in the swing-effect mechanism, and it is these interactions which dictate, for SOD topology ZIFs, the direction of the ligand swing. This study opens up the possibilities for exploring these swing-effect frameworks with respect to gas mixtures. Such studies will be invaluable in understanding the competition of guest uptake and how this affects the swing effect mechanism. By exploiting the control over guest – framework interactions, we can work towards creating bespoke molecular sieves.

ASSOCIATED CONTENT

Supporting Information
All computational and experimental methods can be found in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

Synthesis and methods for: high-pressure crystallography, DFT geometry optimization, DFT single point energy calculations, grand canonical Monte Carlo simulations; Crystallographic data of ZIF-90 and ZIF-65 at pressure; ZIF-65 geometry changes at pressure; Density functional theory calculations of linker rotations; Grand canonical Monte Carlo simulations of hypothetical ZIF phases.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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REFERENCES

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