

### 6.1 Conclusion

The flexibility of the 3-dimensional porous metal-organic framework  $(\text{Me}_2\text{NH}_2)[\text{In}(\text{ABDC})_2]$  has been discovered and explored by various crystallographic techniques. The removal of solvent ( $\text{H}_2\text{O}$  and DMF) from the framework of the as-synthesised MOF results in a large predominately 2-dimensional breathing effect resulting in large changes in the *b*- and *c*-axes, and occurring due to a twisting of the flattened tetrahedral geometry and a small knee-cap effect. This flexibility, contrary to almost all other reported breathing modes in metal-organic frameworks, appears to occur in continuous manner without defined phase transformations.<sup>1</sup> The continuousness of the effect allows for a potentially infinite range of different structures to be obtained, a property easily observed by studying the constantly changing diffraction pattern during water uptake. The continuum of structures is believed to arise due to the maintenance of favourable solvent-framework interactions over a wide range of residual solvent content in the pore. Exchanging this contained solvent, and thereby changing the strength of the solvent-framework interactions, results in substantial changes to the degree of flexibility of the framework, resulting in two different desolvated forms of the MOF after evacuation of the material. Polar solvents (DMF and acetone) appear to induce the pore closing on solvent removal, but removal of less polar solvents ( $\text{CHCl}_3$  and THF) results in much more limited dynamic motions, with the framework remaining in an open-pore structure. Evidence so far suggests that both of these forms are fully desolvated and unlike in MIL-53 no guest molecules are responsible for holding the poses closed.<sup>2, 3</sup> This suggests the existence of two thermodynamic minima for the structure which is rare but not without precedent.<sup>4</sup>

The solvent-dependence has a substantial impact on the gas adsorption properties of the MOF, changing the overall uptake, the adsorption profile and the relative  $\text{CO}_2$  vs  $\text{CH}_4$  selectivity. This has been shown by comparing the gravimetric gas uptakes of the framework after desolvation from the as-synthesised material with those of the previously published method involving  $\text{CHCl}_3$ -exchange followed by desolvation.<sup>5</sup> The fully desolvated as-synthesised MOF showed significantly lower uptake than the MOF after  $\text{CHCl}_3$  desolvation due the changes in the accessible pore space. The interactions maintaining the closed-pore form of the framework are believed to be strong, because even application of high relative pressure of  $\text{CO}_2$  ( $P/P_0 \approx 0.9$ ) does not reopen the structure, unlike the situation for many flexible MOFs.<sup>6-13</sup>

The continuousness of the breathing effect allows for a wide range of partially solvated materials to be produced and subsequently studied for gas sorption. These partially solvated materials show distinct steps in their gravimetric gas adsorption isotherms, which has been confirmed by multiple *in situ* crystallographic experiments to be due to a transition back to an open-pore form. The partially solvated materials are believed to be held closed only by solvent-framework interactions, which are weaker than the framework-framework or framework-cation interactions in the fully closed MOF. This results in the ability to undergo a transition back to an open-pore form at particular gating pressures, which appear to be dependent on the amount or type of solvent present. To the author's knowledge this type of behaviour has not previously been demonstrated in MOF literature. The *in situ* crystallographic experiments show that the MOF also exhibits continuous motions, along the known breathing trend line, particularly outside the gating region.

The solvent-dependence of the framework extends to the water adsorption properties, resulting in a continual expansion from the partially desolvated as-synthesised framework in its closed-pore form, but a defined transition to a new crystalline phase from the open-pore framework obtained from desolvation of the  $\text{CHCl}_3$ -exchanged MOF. This new phase involves coordination of two water molecules to half of the indium centres forming a new octahedral indium environment, and resulting in change of the space group symmetry from  $Fddd$  to  $C2/c$ . The transition drastically reduces the pore volume, and subsequent loading of  $\text{CO}_2$  has been shown by *in situ* crystallographic studies to result in a transition back to the open-pore form accompanied by an increase in the accessible void space. Similarly, the coordinated water molecules can be removed by heating of the MOF, implying they are not strongly bound. Further complexities in the solvent-framework dynamics are shown with the acetone-exchanged MOF which suggests the potential ordering of the solvent / cations in a different periodicity to the framework.

The framework exhibits several different points of modification including functional group transformations of the amine group, and cation exchange of the dimethylammonium ion. These modifications have been shown to occur in a single-crystal-single-crystal manner allowing accurate structural characterisation of the modified framework, which is rarely seen in MOFs.<sup>14</sup> The conversion of the amine to a methyl amide was optimised to give a quantitative conversion, and desolvation studies showed that the framework flexibility now occurs significantly in all 3 dimensions. A solvent-dependence is still present in the fully solvated MOF but the removal of different solvents now results in a single desolvated structure. Exchange of the dimethylammonium cation with a  $\text{Ag}^+$  ion also showed a change in the overall dynamics of the framework. The  $\text{Ag}^+$  ion is

coordinated to the amine group of the MOF, and points directly into the pore space, which may provide an open metal site for applications such as catalysis or gas sorption.

Overall this MOF system has proven to both be very interesting and very complicated. The combination of its rare dynamic behaviour and its ability to be chemically functionalised, both while remaining as a single crystals suitable for X-ray diffraction, make it a perfect system for studying the dynamic responses of MOFs.

## 6.2 Future Work

Many of the aspects covered in the thesis could be studied in further depth. These include: the desolvation and guest-uptake properties of the methyl amide-modified MOF coupled with gravimetric adsorption measurements, an accurate quantification of the exchange of the counter ion with  $\text{Ag}^+$ , and a more detailed analysis of the modulation effects in the acetone-exchanged single crystals.

The work described in this thesis, however, only scratches the surface of the wide range of potential experiments which could be carried out on  $(\text{Me}_2\text{NH}_2)[\text{In}(\text{ABDC})_2]$ . Chapters 3 & 5 have shown that the flexibility of the framework is highly dependent on both the contained solvent and the functionalization of the framework. A systematic adjustment of the contained solvent (polar to nonpolar), the amine functionality and the counterion could therefore be carried out while observing the structural effects via crystallographic techniques. This would hopefully generate an understanding of the role of the individual parts in the underlying mechanisms of the continuous breathing. Various spectroscopic techniques could also be introduced, e.g. *in situ* infrared spectroscopy, to understand the intermolecular interactions responsible. Inspiration for these experiments could be drawn from the many different publications studying MIL-53 by various techniques.<sup>15–22</sup>

Further information on why the framework breathes, the differences with different solvents and the two thermodynamically stable desolvated forms, could be gained through computational studies. Information on the extent of the materials breathing and the guest uptake properties could also be obtained via high pressure crystallographic studies using both penetrating and non-penetrating media. In addition the study of other frameworks showing similar networks but different metal

centres, or indium-based frameworks showing similar SBUs but different topologies, should be explored to see if breathing effects exist but have not yet been noticed. The knowledge gained by this work would hopefully lead to the ability to accurately tune and design the breathing effect, which would be greatly beneficial to both the design of new stimuli-responsive materials and any potential applications of this framework.

## 6.3 References

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