

Investigating the solid-state packing of metal-organic cages using atomic force microscopy and machine learning

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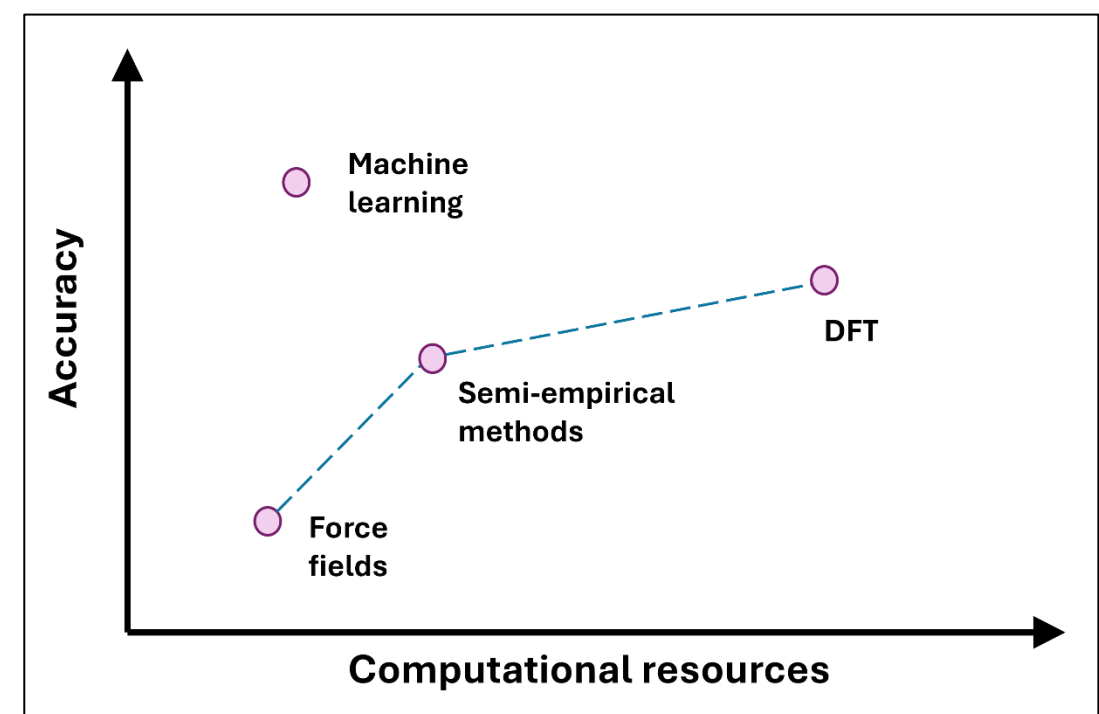
I. Introduction

Metal-organic cages (MOCs) are an emerging class of porous supramolecular materials with diverse applications, such as liquid-phase separations¹ and catalysis². However, their **solid-state** structures and properties have been *relatively underexplored*, mainly due to the **difficulty of growing and analysing high-quality crystalline MOCs**. Furthermore, there are currently limited computational tools available to explore them in this state, given their structural complexity.

We present a study that bridges experimental characterisation (using atomic force microscopy, AFM) and computational exploration (using both traditional force fields - UFF,³ GFN-FF⁴ - and machine learnt intermolecular potentials - MACE⁵). This set of results is an important step towards understanding the crystal engineering of new MOC-based materials.

II. Challenges

- Characterisation:
- Can be hard to obtain high quality crystals, and they may require many attempts and/ or the usage of advanced diffraction techniques.
- Computationally:
- Large number of degrees of freedom, complex, large systems;
 - MOCs contain both metals and non-metals – conventional methods can be computationally intensive.

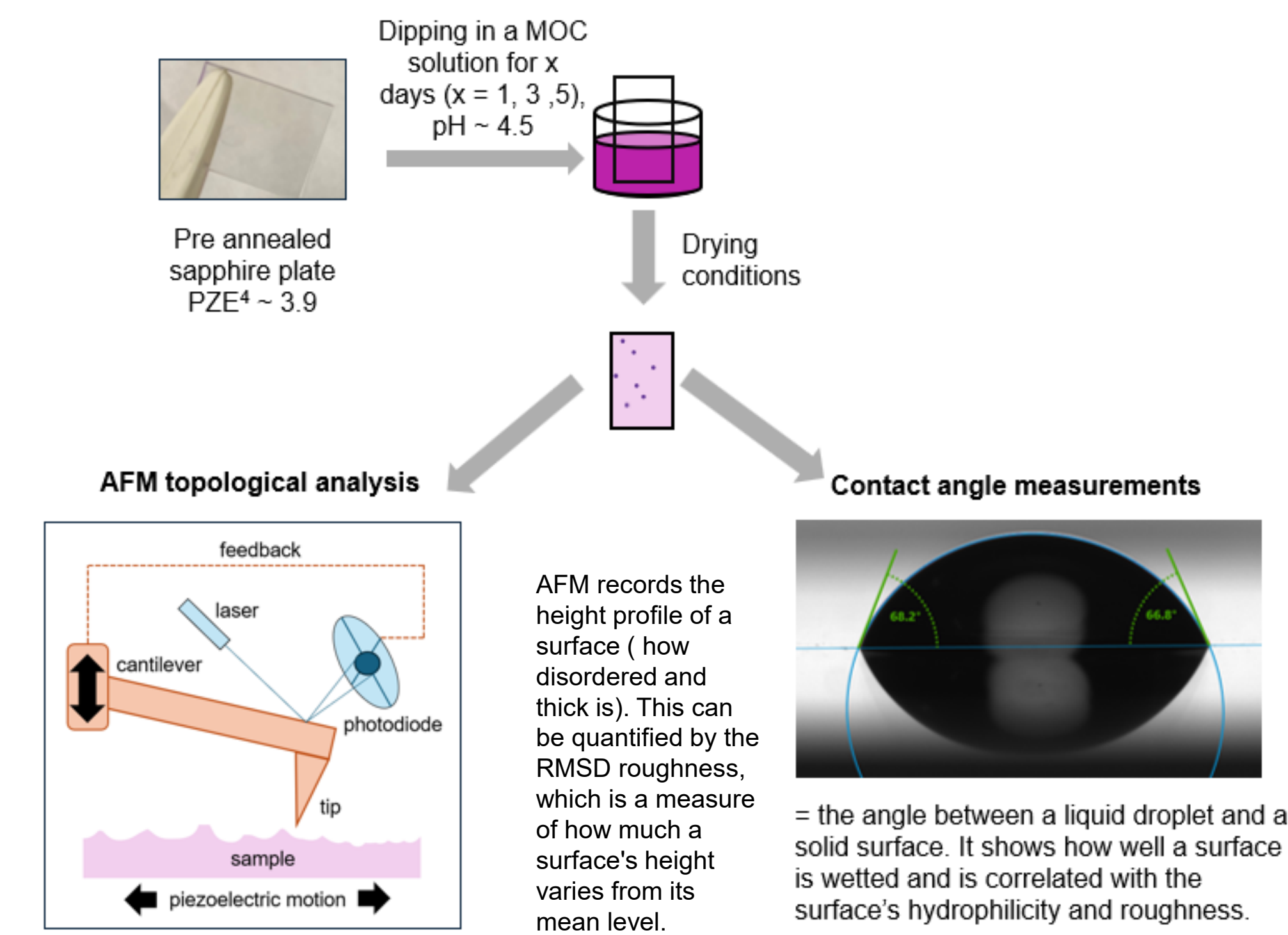


Main features of commonly used computational methods in the investigation of MOCs

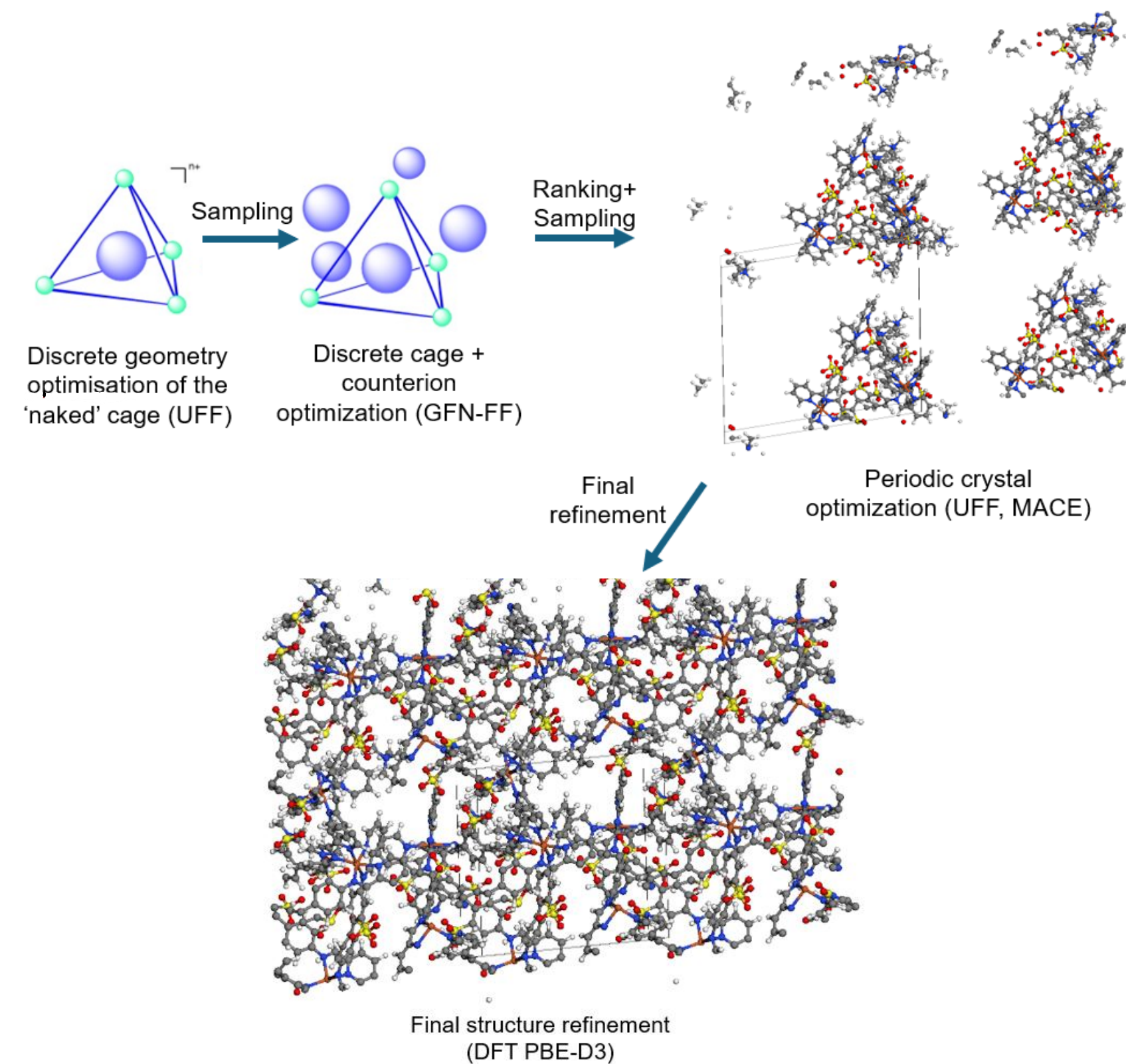
V. MOCs investigated



III. Characterisation methods



IV. Computational methods – crystal structure prediction (CSP) pipeline



VI. Results – topology analysis using AFM

Cage1, initial solution concentration 0.5 mM

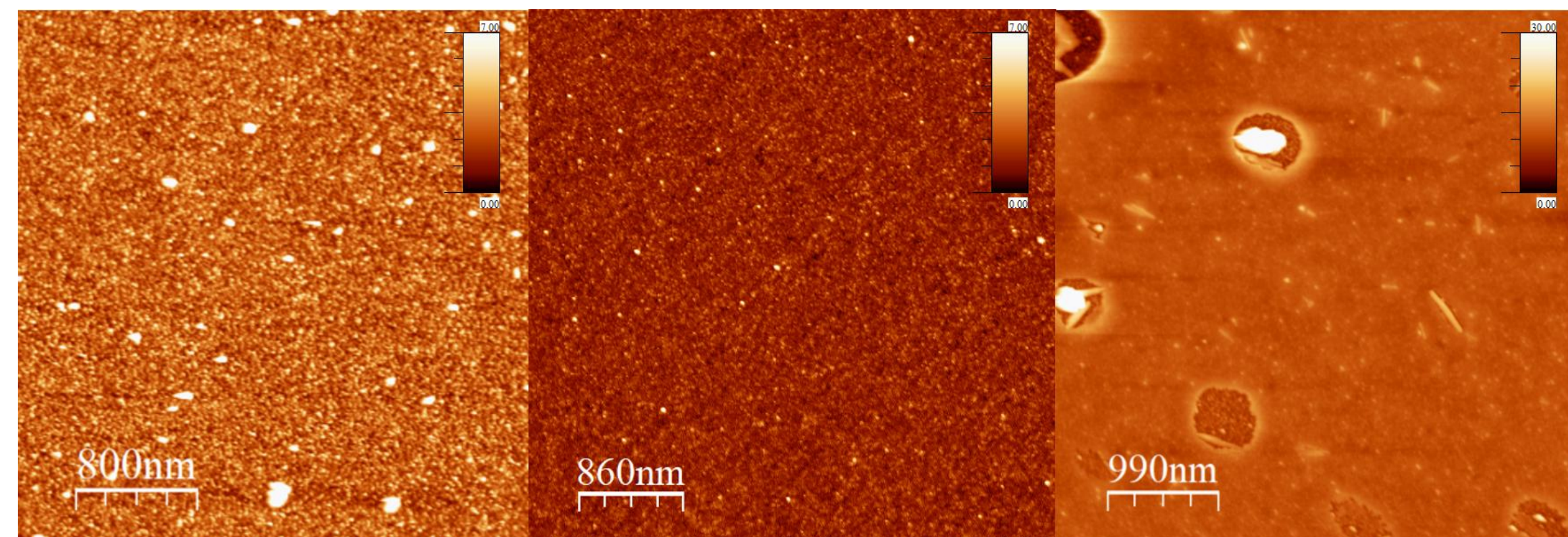


Figure 1 showing the topology of sapphire surfaces covered by Cage1 after 1, 3 and 5 days.

Cage2, initial solution concentration 0.5 mM

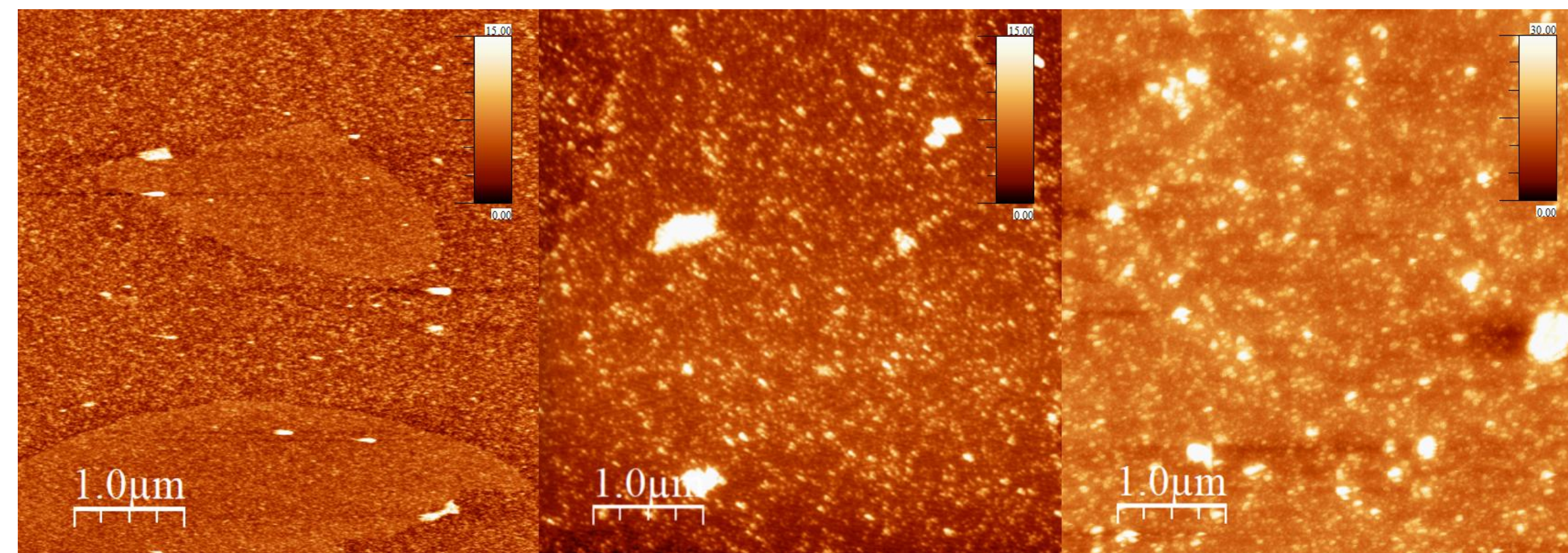
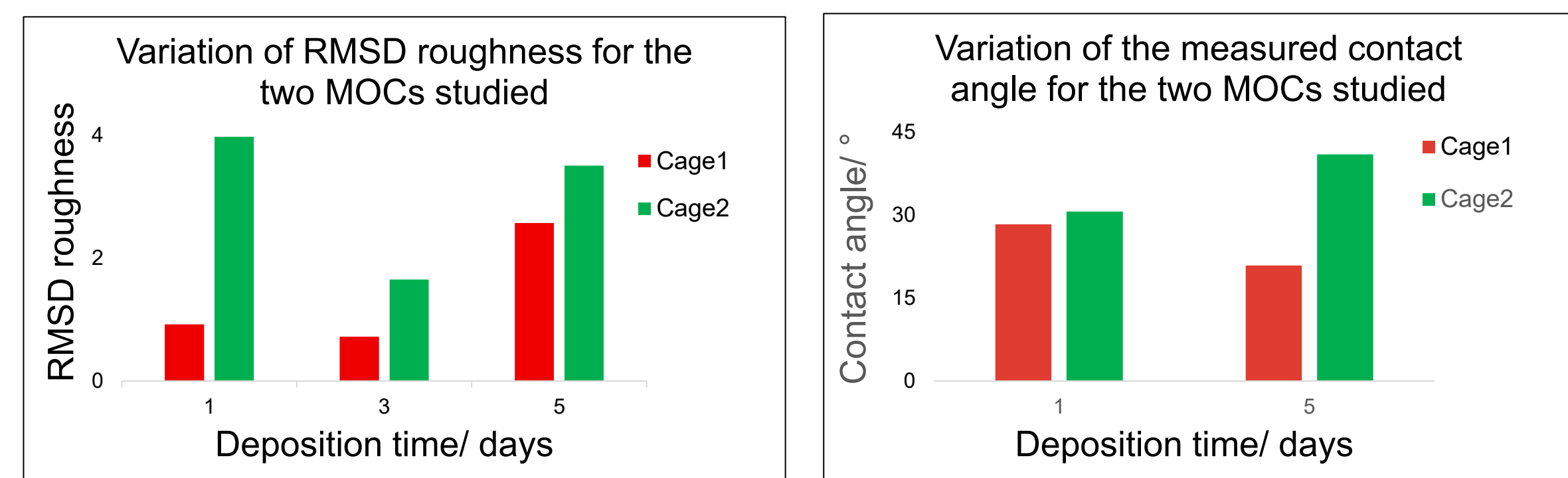


Figure 2 showing the topology of sapphire surfaces covered by Cage2 after 1, 3 and 5 days.

RMSD roughness and contact angle measurements



Both sets of data indicate that the system with Cage2 is consistently rougher (and less hydrophilic) than Cage1. Both MOCs show a decrease in the roughness for 3 days dipping time, suggesting the surfaces are in continuous change and achieve more coverage over time.

VII. Results - CSP

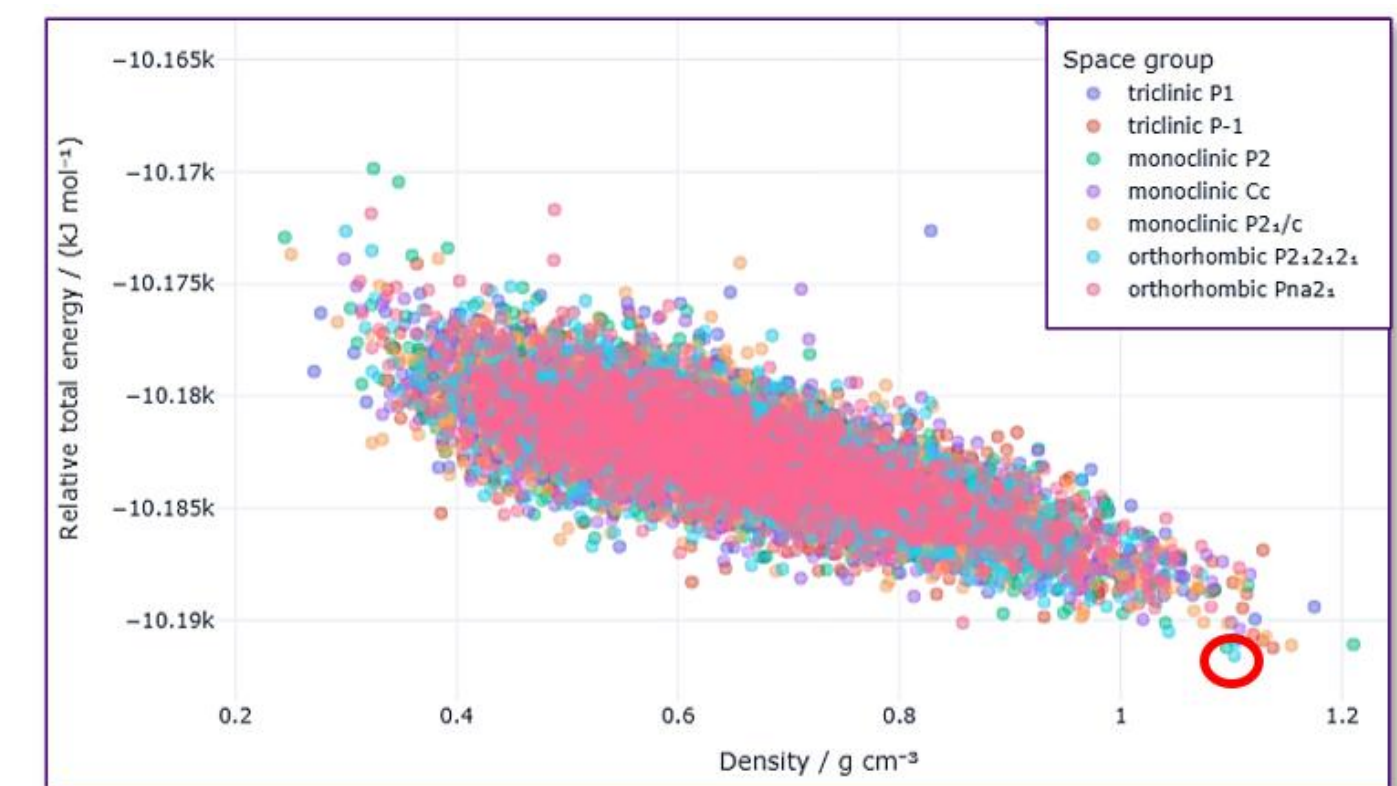


Figure 3 showing the distribution of packing modes in the energy landscape of Cage1, energy minimum encircled in red

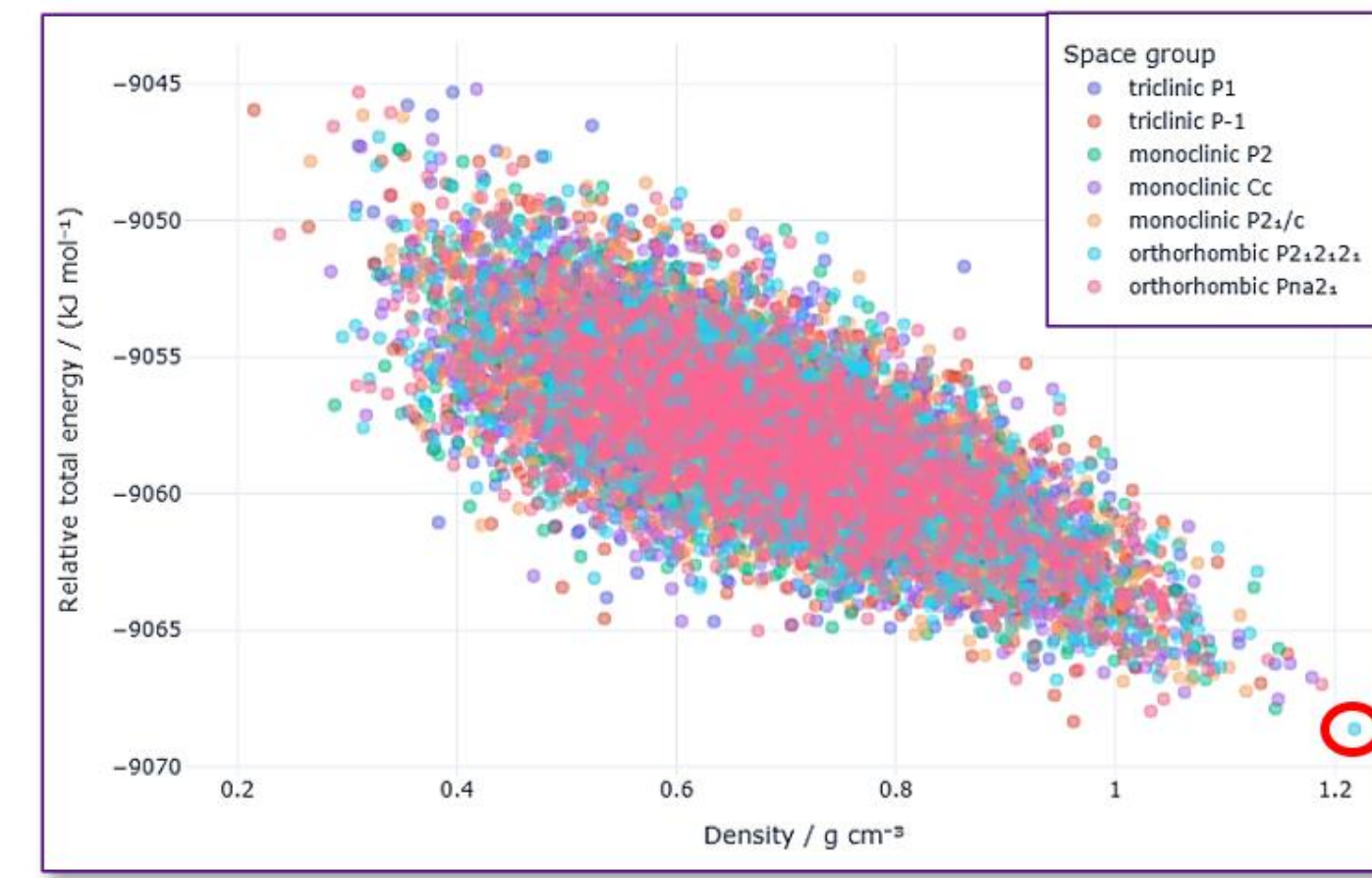
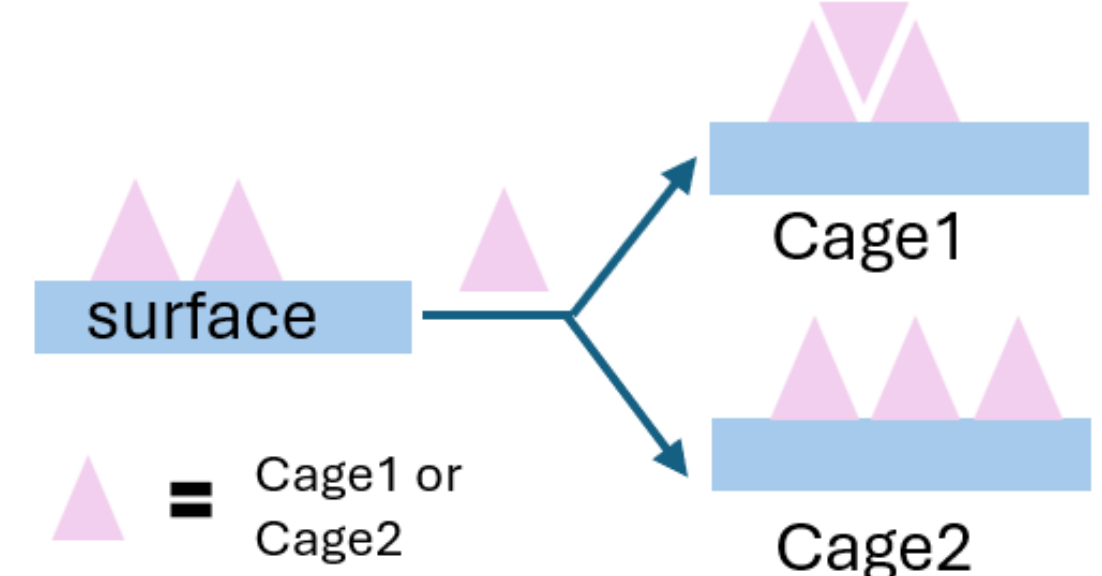


Figure 4 showing the distribution of packing modes in the energy landscape of Cage2, energy minimum encircled in red

The **CSP pipeline** indicates that the energy minimum of Cage1 is lower in energy than that of Cage2 but shows a lower density (i.e. it's slightly less well packed). This correlates with the Na⁺ counterion preferring to chelate to a discrete cage rather than diffusing throughout the periodic crystal, in contrast to the sulfate in Cage2.⁶

VIII. Summary

This study showed how two MOCs with identical topology and symmetry (tetrahedral M4L6) exhibit markedly different behaviour when layered on a polar surface. This is a key result, both qualitative and quantitative, which can be used alongside the rational design of new porous materials cross-linked with MOCs.



References

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