Effect of Crystal Size on the Water Intrusion/Extrusion Pressure and Negative Compressibility of the ZIF-8 Metal-Organic Framework

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Introduction

- Hypothesis: The behaviour of Heterogeneous Lyophobic Systems (HLSs) comprised of a lyophobic porous material and a corresponding non-wetting liquid is affected by a variety of different structural parameters of the porous material.
- Dependence on *exogenic* properties such as crystallite size is desirable for system tuning as they are much more facilely modified.
- The dependence of intrusion/extrusion pressures and intruded volume on crystallite size was explored, as well as the effect of crystallite size on negative compressibility of the ZIF-8 MOF.

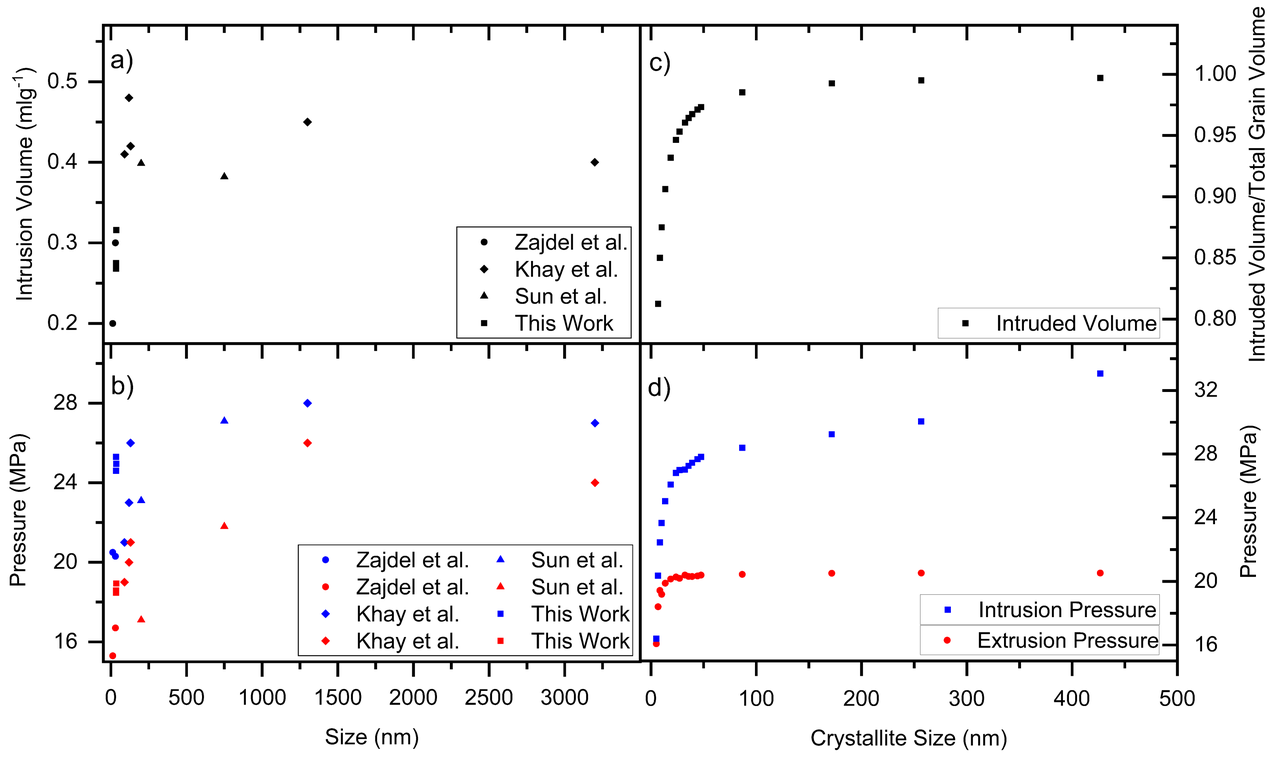

Figure 1 — Plots of a) gravimetric intrusion volume vs crystallite size and b) intrusion (blue) and extrusion (orange) pressure vs crystallite size.[1-4] c) and d) show the behaviour as determined by the stochastic model.

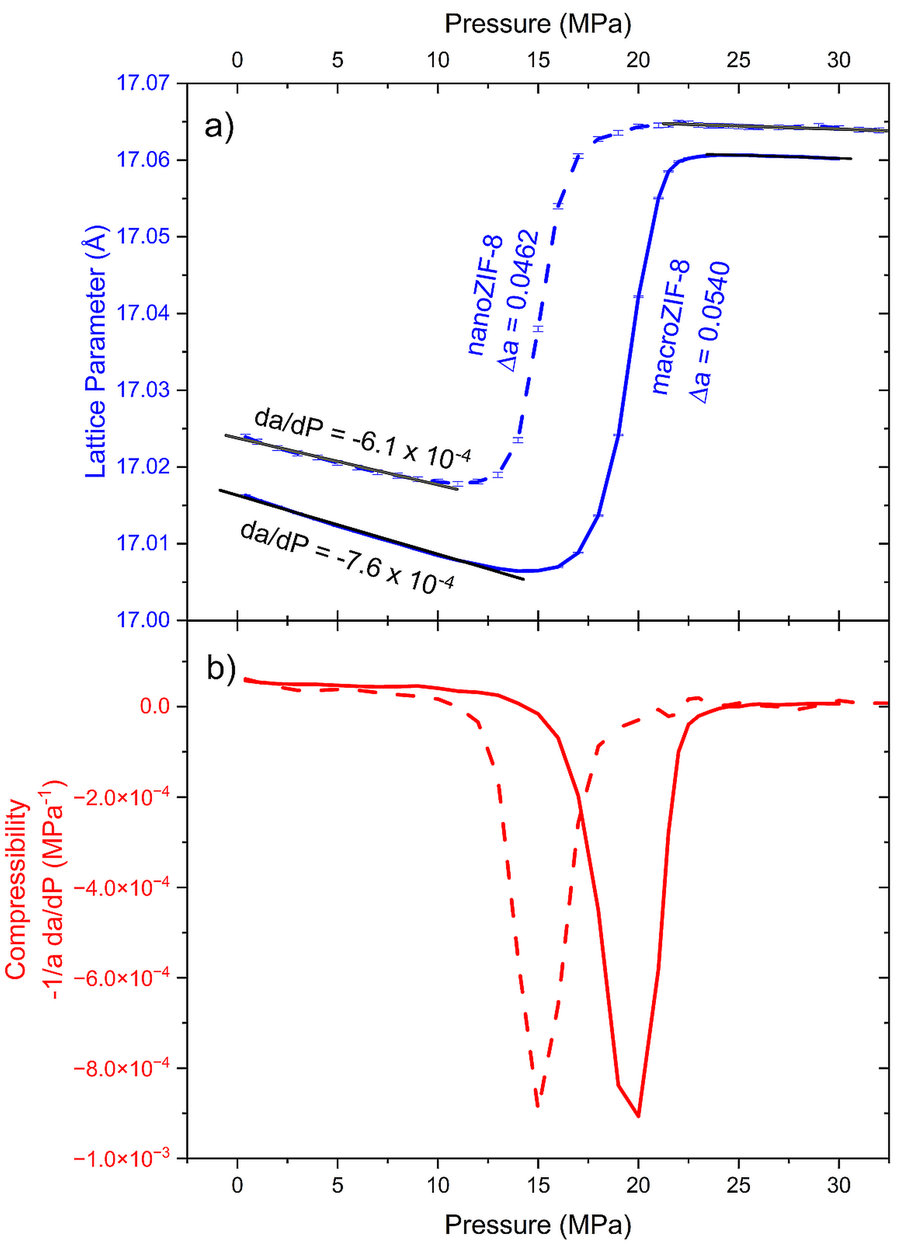

Figure 2 — a) Lattice parameter against applied pressure for macroZIF-8 (solid blue line) and nanoZIF-8 (dashed blue line) systems. b) the compressibility of macro/nanoZIF-8 (solid/dashed) relative to pressure.

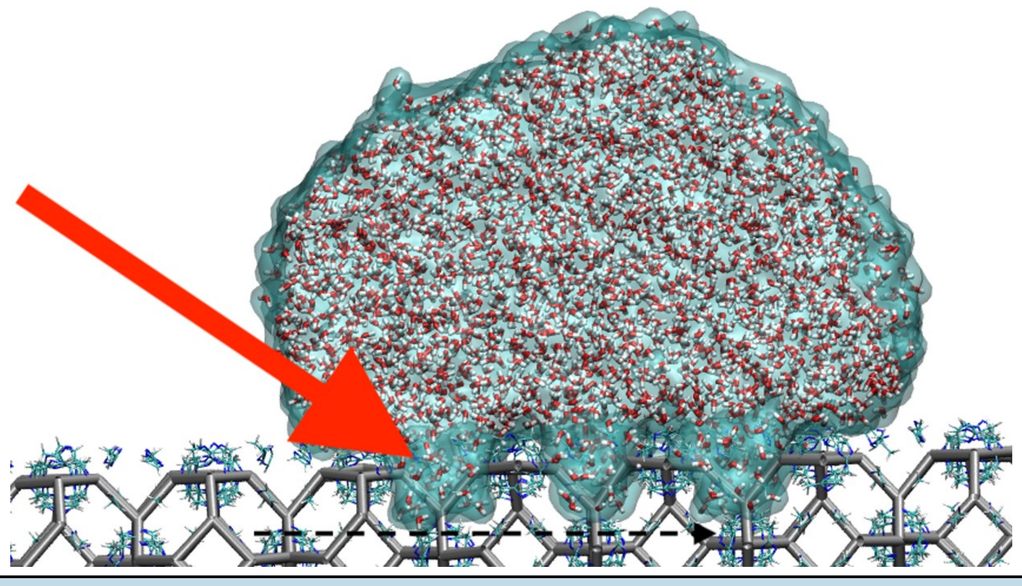

Figure 3—Water contact angle on the ZIF-8 surface. Despite the hydrophobicity of ZIF-8, confirmed by a contact angle > 90◦, surface half-cages are filled with water. This allows for hydrogen bonds between water in the surface cages and the bulk liquid.

Results and Conclusions

- Crystallite size can be used to tune intrusion and extrusion pressures for ZIF-8/water Heterogeneous Lyophobic Systems (HLSs), which is important for tailoring the system for specific applications.[4] Intrusion volume can also be tuned with crystallite size.
- The flexibility of ZIF-8 is dependent on crystallite size[5,6], as illustrated in figure 2 with pre-intrusion linearity (da/dP) differing between macro– and nanoZIF-8 (a difference of one order of magnitude).
- The incomplete surface cages of ZIF-8 are hydrophilic and readily filled at atmospheric pressure (figure 3), thus allowing for cross-cage hydrogen bonding to stabilise the intruded state and reduce the intrusion/extrusion pressures.[1]

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