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A combined high-pressure diffraction and computational study on scandium MOFs

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Previous high-pressure experiments have shown that pressure-transmitting fluids composed of small molecules can be forced inside the pores of metal organic framework materials, where they can cause phase transitions and amorphization and can even induce porosity in conventionally non-porous materials.¹ Here we present a combined high-pressure diffraction and computational study of the structural response to methanol uptake at high pressure on a scandium terephthalate MOF (Sc₂BDC₃, BDC=1,4-benzenedicarboxylate)² and its nitro-functionalized derivative (Sc₂(NO₂-BDC)₃)³ and compare it to direct compression behaviour in a non-penetrative hydrostatic fluid, Fluorinert-77. In Fluorinert-77, Sc₂BDC₃ displays amorphization above 0.1 GPa, reversible upon pressure release, whereas Sc₂(NO₂-BDC)₃ undergoes a phase transition (C2/c to Fdd2) to a denser but topologically-identical polymorph. In the presence of methanol, the reversible amorphization of Sc₂BDC₃ and the displacive phase transition of the nitro-form are completely inhibited (at least up to 3 GPa). Upon uptake of methanol on Sc₂BDC₃, the methanol molecules are found by diffraction to occupy two sites, with preferential relative filling of one site compared to the other: grand canonical Monte Carlo simulations support these experimental observations and molecular dynamics simulations reveal the likely orientations of the methanol molecules, which are controlled at least in part by H-bonding interactions between guests. As well as revealing the atomistic origin of the stabilization of these MOFs against non-penetrative hydrostatic fluids at high pressure this study demonstrates a novel high pressure approach to study adsorption within a porous framework as a function of increasing guest content, and so to determine the most energetically favourable adsorption sites.

[1] Moggach, S. A.; Bennett, T. D.; Cheetham, A. K. *Angew.Chem. Int. Ed.* 2009, 48, 7087., [2] S. R. Miller, P. A. Wright, C. Serre et al. *Chem. Comm.* 2005, 3850., [3] S. R. Miller, P. A. Wright, T. Devic et al. *Langmuir* 2009, 25, 3618.

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