

Supplementary information for:

Structural Transitions in MOF: View from Outside and Inside

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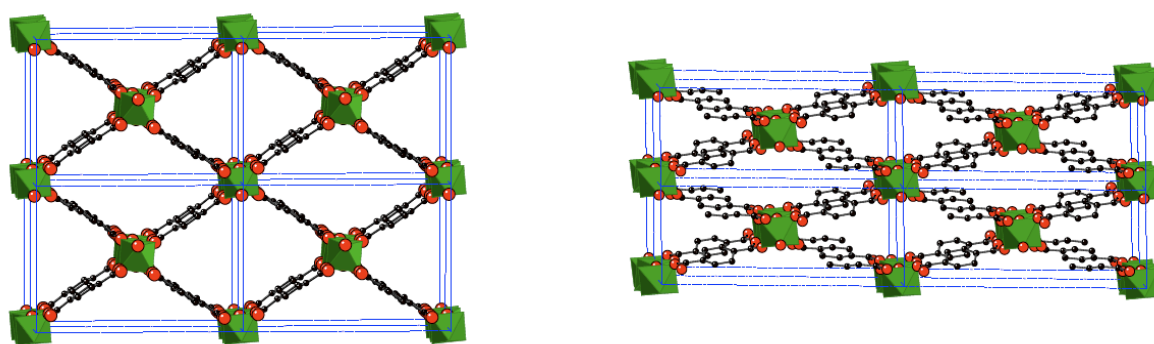


Figure S1: 2 x 2 x 2 supercell of the large-pore (**lp**, left) and narrow-pore (**np**, right) forms of the MIL-53 structure, viewed along the axis of the unidimensional channels^[1,2].

[1] C. Serre, F. Millange, C. Thouvenot, M. Nogués, G. Marsolier, D. Louer, G. Férey, *J. Am. Chem. Soc.* **2002**, *124*, 13519.

[2] C. Serre, S. Bourrelly, A. Vimont, N. Ramsahye, G. Maurin, P. L. Llewellyn, M. Daturi, Y. Filinchuk, O. Leynaud, P. Barnes, G. Férey, *G. Adv. Mater.* **2007**, *19*, 2246.

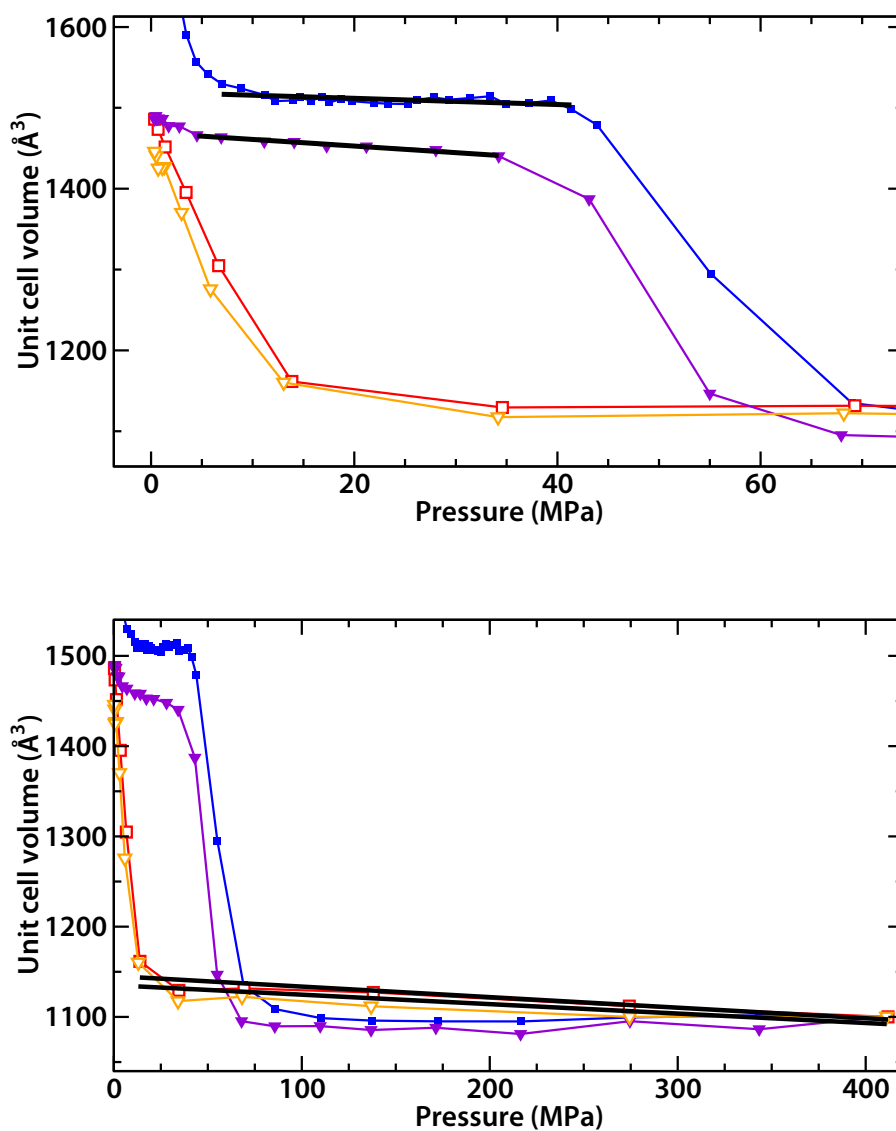
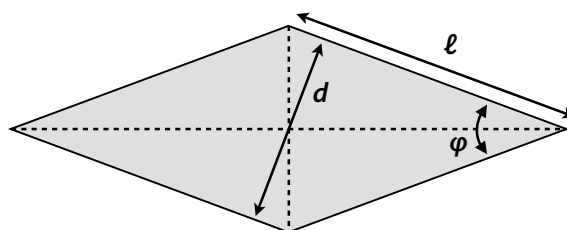


Figure S2: Fits of the linear deformation regimes of the mercury intrusion/extrusion data from which the bulk moduli of the **lp** (top graph) and **np** (bottom graph) phases of MIL-53 (Cr) were calculated. The blank-corrected experimental data is in color, and the black lines are the fits of the linear regions.

Description of the geometrical model for the interpretation of in situ XRD

In this section, we describe how a simple geometric model can be applied to the in situ X-ray diffraction patterns measured upon CO₂ adsorption and desorption in MIL-53 (Cr). Using this model, the slight variations in XRD peak positions upon CO₂ adsorption and desorption were linked to the evolutions of the unit cell volume of the material.

We have studied the peak around $2\theta \sim 4^\circ$ for the **lp** phase, which corresponds to the (101) crystallographic plane. For the **np** phase, we used the peak at $2\theta \sim 5^\circ$, which corresponds to the (110) plane (the unit cell is oriented differently, with the unidimensional channel axis being the *b* axis for the **lp** structure, and the *c* axis for **np**). The diffraction angle θ is linked to the interplanar spacing d by the Bragg law ($n\lambda = 2d \sin \theta$), and the interplanar spacing can be correlated to the unit cell volume V_c and our geometric order parameter, the lozenge angle φ :



To do that, we assume that linker length l is constant for each phase ($l_{\text{lp}} = 10.606 \text{ \AA}$, $l_{\text{np}} = 10.325 \text{ \AA}$), and that all deformation comes from the variation of the angle φ . Geometric considerations then lead for the **lp** structure to $\varphi = \arccos(d/l)$, $V_c = 2cld$ for the **lp** phase, and $V_c = 2dlb \sin \beta$ for the **np** structure. Evolution of diffraction peak position 2θ and lozenge angle φ with adsorption are shown below, while the unit cell volume for the **lp** phase is Figure 4 of the main text.

