-Supplementary info file-

High compressibility of a flexible Metal-Organic-Framework

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1.- Experimental procedures

1.1.- NH_2-MIL-53 Synthesis. The NH_2-MIL-53(In) was synthesized using a hydrothermal procedure. Indium nitrate ($In(NO_3)_3 \cdot xH_2O$, Sigma Aldrich, purity 99.9 %) and 2-aminoterephthalic acid (Aldrich, 99%) were used as received. 5.3 mmol of indium nitrate and 8.3 mmol of 2-aminoterephthalic acid are dissolved in deionized water (20 mL). The reactants are placed in a Teflon-lined autoclave and heated for 5 h at 423 K in an oven under static conditions. The resulting yellow powders were filtered under vacuum and washed with acetone. In order to remove organic species trapped within the pores, the samples were activated. The activation process consists on exchanging the trapped linker with DMF at 423 K overnight.

1.2.- Characterization Techniques

High Pressure XRD experiments.- A symmetric diamond anvil cell was used to generate pressures. The diamond anvils had flat culets with diameters of 300 μm. A 100-μm hole serving as a sample chamber was drilled in the center of the indentation by an electric discharge machine. The sample chamber was large enough to avoid any peaks from gasket. Ruby chips were loaded in the sample chamber at different positions to calculate the pressure by measuring the wavelength shift of the R_1 ruby fluorescence line. X-ray diffraction experiments were conducted at beam line X17C at the national synchrotron light source (NSLS), Brookhaven National Laboratory. The X-ray beam (λ = 0.37677 Å) was focused on the sample by a pair of mirrors to increase the incident photon density to a dimension of 18×25 μm^2. X-ray diffraction measurements were performed to 38.8 GPa

Thermo-gravimetric analysis.- Thermal stability in air was studied using a thermobalance (Mettler Toledo, model TGA/SDTA851e) with an air flow of 60 ml/min at a heating rate of 5 K/min up to 873 K. The sample stayed at 333 K for 2 hours before the experiment to eliminate the adsorbed water.

DRIFTS.- Diffuse Reflectance Infra-red Fourier Transform spectra were recorded in a Bruker model IFS66 spectrometer, equipped with a high temperature cell with CaF_2 windows and a 633 nm laser. The spectra were collected after accumulation of 128 scans with a resolution of 4 cm^{-1}. A flow of helium at 10 ml/min was maintained during the measurements. Before collecting the spectra, the sample was pretreated in the equipment under helium flow at 423 K for 1 h. KBr was used as a background.

Gas adsorption isotherms.- High-pressure adsorption isotherm of CO_2 (purity of 99.995%) was determined using the volumetric technique with an apparatus from BEL Japan (Belsorp HP). Around 0.5 gram of NH_2-MIL-53(In) was placed in the sample container. Before measurement, the adsorbent was pretreated by increasing the temperature to 423 K at a rate of 10 K/min under vacuum and maintaining the temperature for two hours.

2.- Experimental results

2.1.- Thermo-gravimetric analysis.

The mass of NH_2-MIL-53(In) in an air atmosphere when the temperature is increased is shown in Fig. S-1. The sample does not lose a remarkable amount of mass up to 473 K. In the range of temperature between 473 and 650 K there is a continuous decrease in mass, where finally a 20 % of the mass is lost. At a temperature of 650 K there is an abrupt lost of mass. The remaining amount of solid corresponds to a 30 % in total weight.

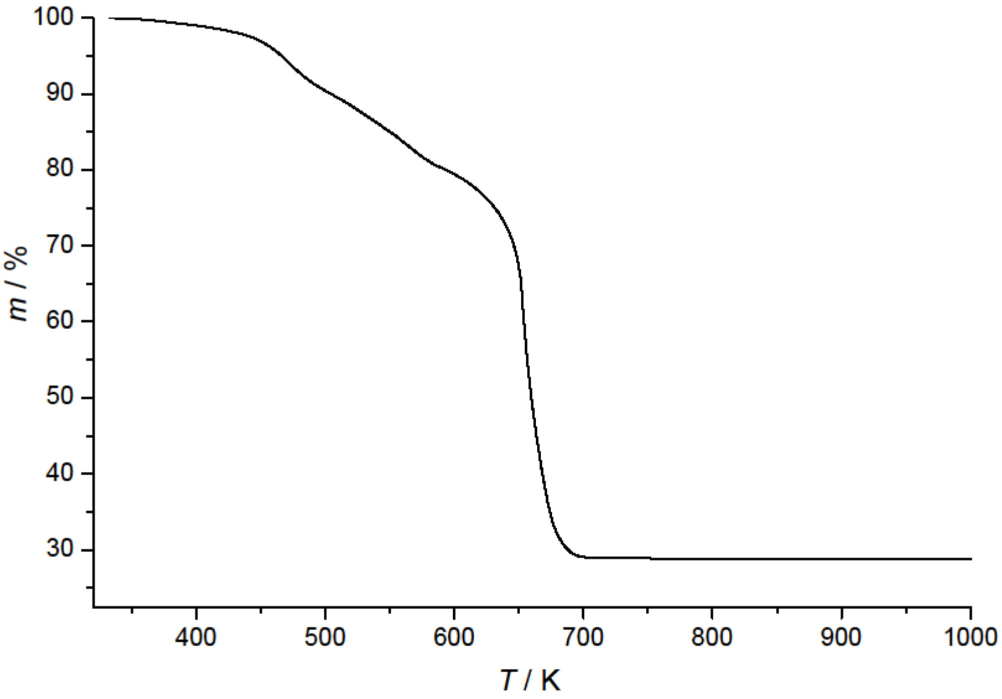

Fig S- 1 Thermal stability of NH_2-MIL-53 (In) in an air flow of 60 ml/min with a heating of 5 K/min.

2.2.- DRIFTS

In figure S-2 the infrared spectrum of NH_2-MIL-53(In) is depicted. In the high wavenumber region three sharp peaks can be distinguished. The peak at 3639 cm^{-1} corresponds to the hydroxyl stretching, and the two vibrations at 3490 and 3384 cm^{-1} are the symmetric and the asymmetric amine stretchings. These amine are non-coordinated and available for interactions with guest molecules.

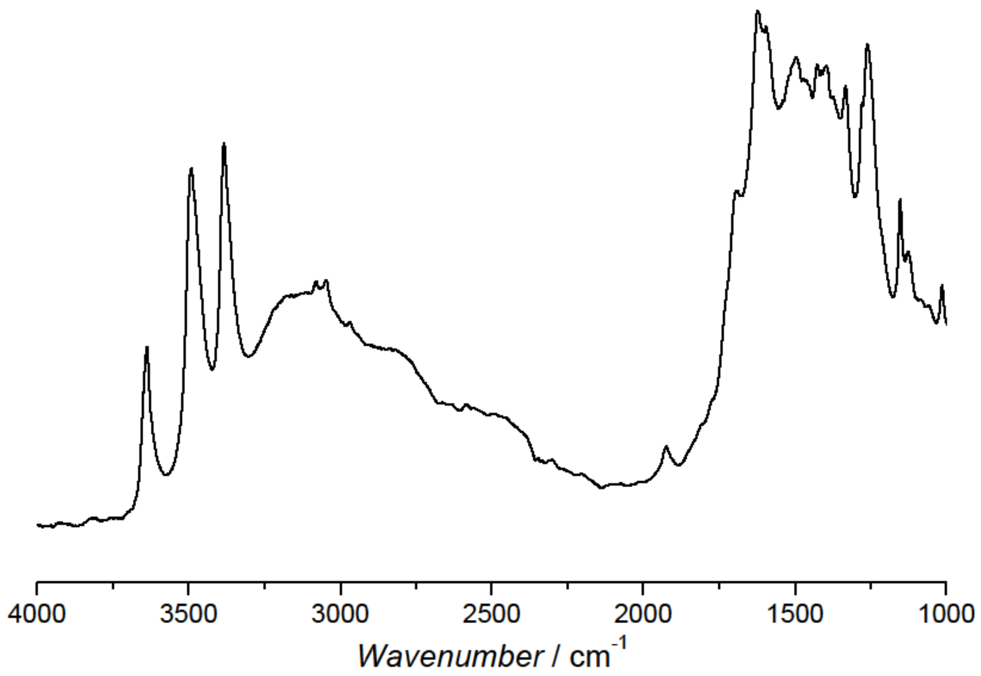

Fig S- 2 Infrared spectrum of NH_2-MIL-53(In) (measured at room temperature after activation at 373K under He)

2.3.- High pressure adsorption isotherms

Figure S-3 shows a CO_2 adsorption isotherm measured on NH_2-MIL-53(In) at 273 K. The adsorption isotherm has the same shape as that previously reported for NH_2-MIL-53(Al). The material starts in a narrow pore form and after adsorbing certain amount of carbon dioxide above 1.5 MPa a phase transition occurs, giving rise to a larger pore configuration and higher adsorbed amount. The uptake of this material is slightly lower in comparison with its aluminum counterpart.

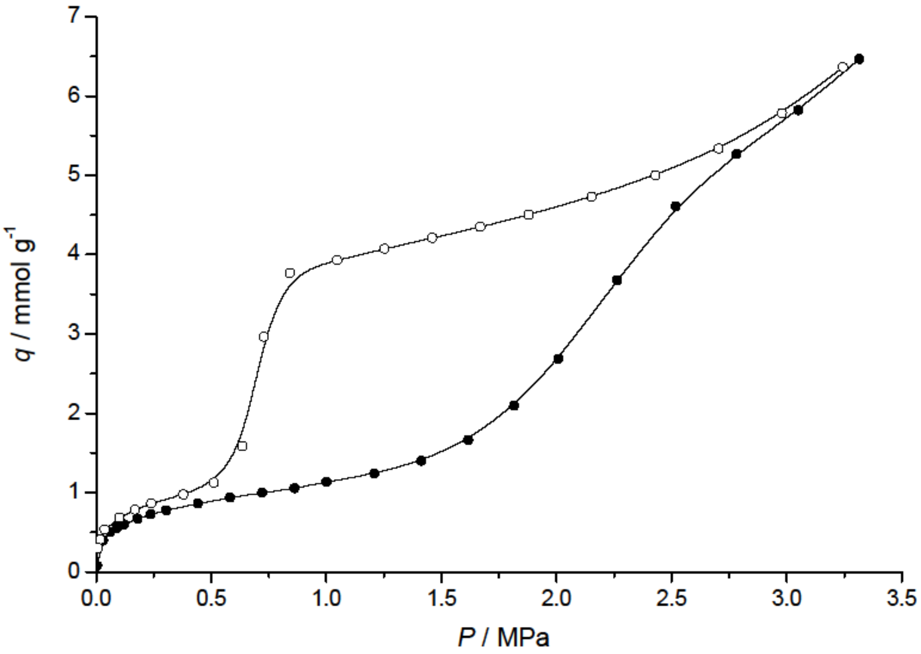

Fig S- 3 Carbon dioxide adsorption isotherm on NH2-MIL-53(In) at 273 K. Solid symbols represent adsorption and open symbols the desorption branch.

2.4.- Third-order Birch–Murnaghan equation of state.

The change in volume due to external pressure was fitted by a third order Birch-Murnaghan equation of state (Equation S1). From the fit the bulk modulus at $P = 0$ (K_0) and its derivative can be calculated.

$$P(V) = \frac{3K_0}{2}\left[\left(\frac{V_0}{V}\right)^{\frac{7}{3}} - \left(\frac{V_0}{V}\right)^{\frac{5}{3}}\right]\cdot\left[1 + \frac{3}{4}\left(K_0^{'} - 4\right)\left(\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right)\right] \qquad \textbf{Equation S1}$$