Supplementary Information for

Flexibility of ZIF-8 materials studied by ^{129}Xe NMR

Marie-Anne Springuel-Huet,*[a] Andrei Nossov,[a] Flavien Guenneau,[a] and Antoine Gédéon[a]

[a] *UPMC Uni Paris 06, Collège de France and CNRS, UMR 7574, Laboratoire de Chimie de la Matière Condensée, case 196, 4 place Jussieu, 75252 Paris Cedex 05, France; Tel: 33144275537;*

*To whom correspondence should be addressed. E-mail: marie-anne.springuel-huet@upmc.fr

Table of contents

Experimental section

- *Synthesis*. As mentioned in the acknowledgment, Dr. Aude Demessence (Institut de Recherche sur la Catalyse et l'Environnement de Lyon, Université Lyon I) has provided us with the sample. The synthesis of ZIF-8 nanoparticles was performed following the conditions previously reported by Cravillon et al. (*Chem. Mater*. 2009, **21**, 1410). A solution of $Zn(NO_3)_2.6H_2O$ (2.933 g, 9.87 mmol; 98% Sigma-Aldrich) in 200 mL of methanol (Aldrich, 99%) is rapidly poured into a solution of 2-methylimidazole (Hmim; 6.489 g, 79.04 mmol; 99% Aldrich) in 200 mL of methanol under vigorous stirring at room temperature. The mixture slowly turns turbid and after 1 h the nanocrystals are separated from the milky dispersion by centrifugation at 20000 rpm for 15 min. To remove the excess of unreacted acid and zinc nitrate species, ZIF-8 nanoparticles were readily redispersed in absolute ethanol and centrifuged. Three washing cycles of the redispersion in absolute EtOH/centrifugation were performed. The particles were subsequently dried under vacuum.

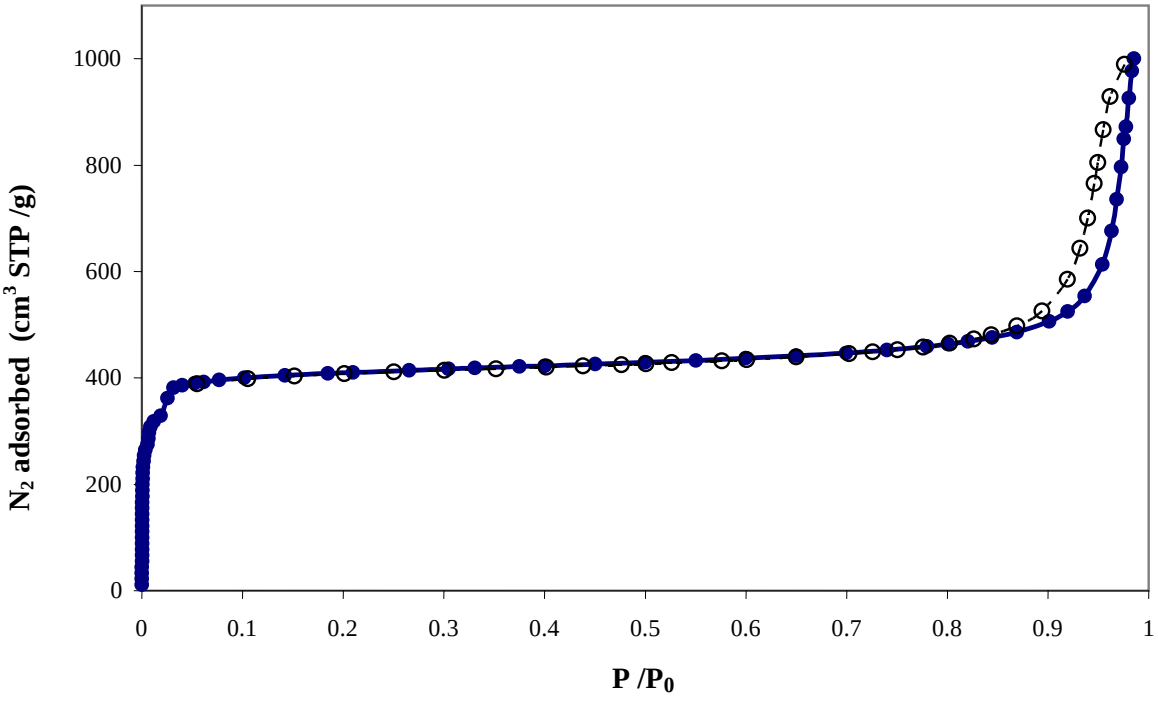
- *N_2 adsorption experiment*. The isotherms were measured at 77 K on a Micromeretics ASAP 2010 sorption after activation of the sample (ca. 130 mg) at 120°C for 12 h under primary vacuum.

- *^{129}Xe NMR experiments*. Before NMR experiments, the sample was evacuated under dynamic high vacuum (less than 10^{-2} Pa) at 150°C K overnight (heating rate 24 K/h). The variable-temperature experiments were performed using laser-polarized xenon

under continuous gas flow using a home-built system on a Bruker DSX 300 spectrometer between 373 and 138 K. The hyperpolarized ^{129}Xe was obtained by passing gaseous Xe/N_2/He mixtures, containing 1 % or 0.1 % Xe, through a cell, heated to *ca.* 430 K, that was containing rubidium vapour irradiated by a 794 nm laser inducing the optical pumping of rubidium. Then, the gas mixture was delivered using a 1/8" plastic tubing into the powdered sample and finally released to the atmosphere via an oil bath to avoid back flow of air.
Typically 2000 to 4000 scans, with a repetition time of 1 s, were recorded. The spectra were recorded every 2 to 5 K after the sample was allowed to equilibrate during a few tens of minutes.
The chemical shifts are referenced to that of gaseous xenon extrapolated to zero pressure (0 ppm).

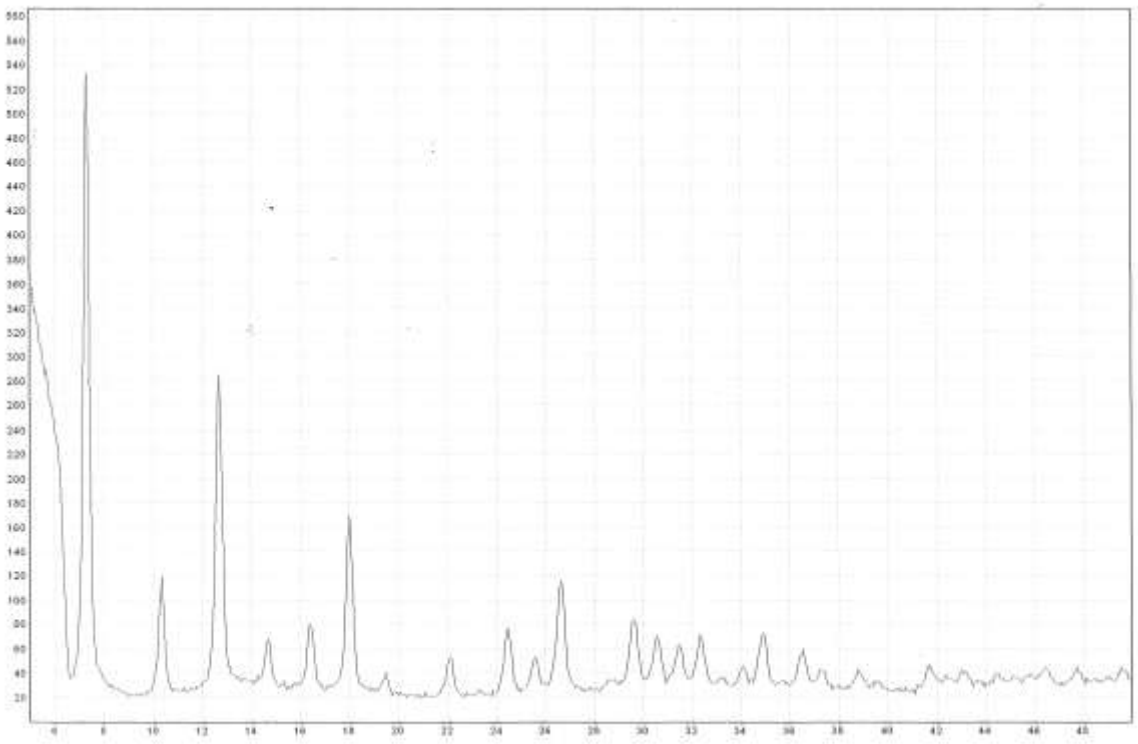
- *X-ray diffraction.* The X-ray powder diffraction pattern of the ZIF-8 sample has been measured using a Bruker D8 ADVANCE equipped with a LynxEye detector with Cu Kα radiation (Kα_1 = 1.540600 and Kα_2 =1.544390). The acquisition was performed in Bragg-Brentano mode with a variable-divergence slot.

Nitrogen sorption at 77 K



Adsorption: full symbols; desorption: empty symbols.
The Langmuir and BET surface area of the ZIF-8 sample are 1830 m^2/g. and 1100 m^2/g, respectively.

X ray diffraction



Heat of adsorption

The isosteric heat of adsorption were determined from the Xe adsorption isotherms (shown in Figure 3 of the Communication) using Van't Hoff relationship.