Supplementary Information for

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

Marie-Anne Springuel-Huet, Andrei Nossov, Flavien Guenneau, and Antoine Gédéon

$^a$ 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

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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$_2$O (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 K$\alpha$ radiation ($K\alpha_1 = 1.540600$ and $K\alpha_2 = 1.544390$). The acquisition was performed in Bragg-Brentano mode with a variable-divergence slot.

Nitrogen sorption at 77 K

![Nitrogen sorption at 77 K](image)

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.