# Supplementary Material (ESI) for Chemical Communications


# Supplementary Information

# A single-crystal imprints macroscopic orientation to xenon atoms

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**Experimental part**

Synthesis. Porous single-crystals of tris-o-phenylenedioxycyclotriphosphazene were crystallized from a supersaturated benzene solution at 80°C over 48 hours. The benzene removal was performed by heating the single crystals from 25 to 80°C at a rate of 5°C/h and at a pressure of $10^{-1}$-$10^{-2}$ torr.
X-ray diffraction analysis. The X-ray data collection of the nanoporous single-crystals were perfomed on an Oxford Xcalibur automated 4-circle diffractometer with k geometry equipped with a CCD detector and a Mo-target X-ray tube operating with a radiation wavelength λ of 0.71073 Å.
Hyperpolarized Xe NMR. Hyperpolarization $^{129}$Xe NMR experiments were performed by a home-built apparatus with a continuos flow set-up with a Bruker Avance 300 spectrometer operating at a Larmor Frequency of 83.02 MHz for $^{129}$Xe. A diode array laser delivering 16 W at 795 nm was applied. A stream of gas mixture containing 2% xenon, 2% nitrogen and 96% helium was used in most of the experiments and gas flow rates were optimized in between 200-300 $cm^3$/min. The polarization was about 5%. An home-made Teflon support endowed with a goniometer was inserted in a horizontal coil and rotated at chosen angles with respect to the magnetic field. The samples were equilibrated in the gas stream for at least 20 minutes before collecting the NMR spectra. The remarkable sensitivity of the hyperpolarized technique allowed the detection of xenon resonances in a single-crystal under ambient conditions and in natural isotope abundance.
Adsorption isotherm. Xenon absorption isotherms were determined by volumetric measurements equipped with precision manometers (±0.5 torr). Absorption equilibrium was reached within 30÷90 min.

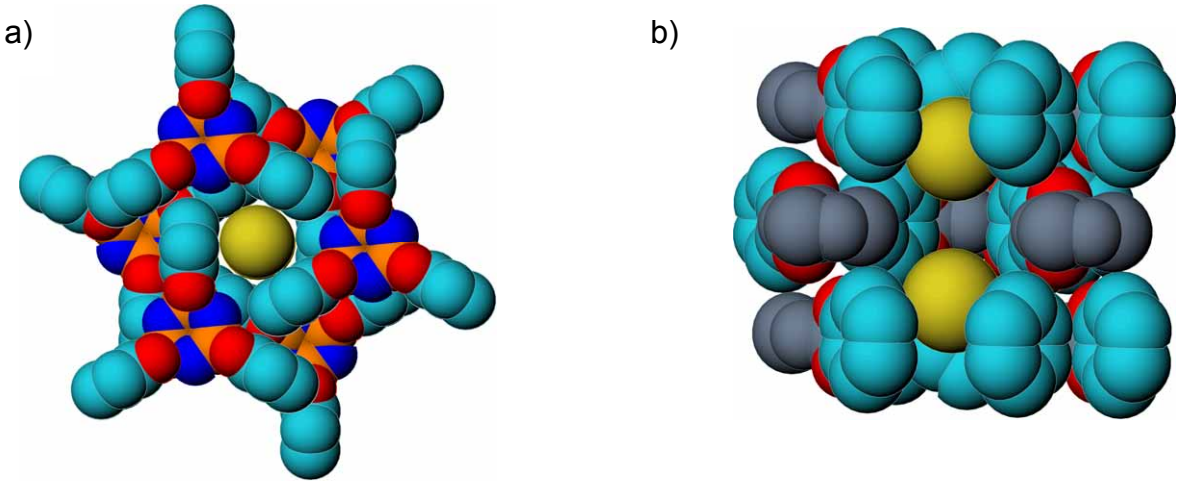


**Figure 1.** Crystal structure of the nanoporous crystals showing xenon diffusing in a single nanochannel view a) along the c axis and b) perpendicular to the c axis. The channel cross section is about 4.6 Å. The following van der Waals radii have been adopted: 1.7 Å for C (light blue), 1.5 Å for O (red), 1.5 Å for N (blue), 1.8 Å for P (orange) and 2.2 Å for Xe (yellow). A tight fitting can be observed between the xenon atom and the surrounding structure. The nanochannel is fully lined with phenylenedioxy moieties facing the channel axis. The nanochannels run parallel to the c axis of the crystal.

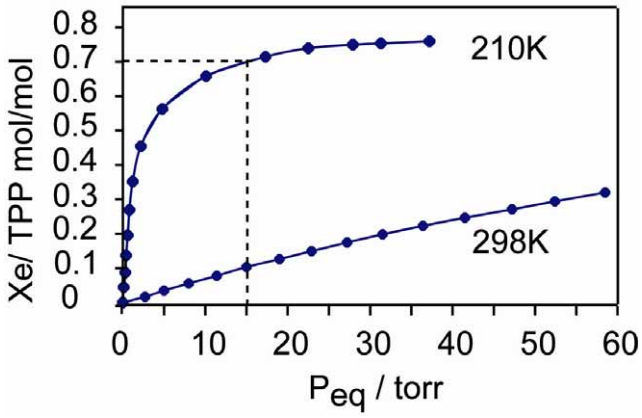


**Figure 2.** Xenon absorption isotherms at 210 K and at room temperature. At low temperature and at 15.2 torr partial pressure (2% Xe concentration), 0.7 xenon moles per mole of **1** are absorbed.