A single-crystal imprints macroscopic orientation on xenon atoms†

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A porous single-crystal collects xenon atoms from the gas phase and orients them macroscopically, as highlighted by hyperpolarized xenon NMR.

Macroscopically oriented materials, either single-crystals, surfaces or films, are of very great interest because of their potential to retain spatial information and provide anisotropic responses. The effort put into obtaining materials endowed with an architecture of oriented atoms and molecules has resulted in the design of liquid crystal assemblies,[1] organic molecules assembled on surfaces in the form of mono and multilayers[2] and oriented porous materials with specific pore orientation on surfaces or in the bulk.[3] The use of organic single-crystals is quite attractive and offers the possibility of decorating target faces with a high degree of selectivity.[4] The self-assembly of organic molecules permits one to design and fabricate single-crystals with desired anisotropic surfaces.[5] For example, very recently, hexagonal single-crystals of L-cysteine have been used for anisotropic deposition onto given crystal faces.[6] However, single-crystal porosity has not yet been exploited in this context although it would offer the possibility of both face-selective absorption and anisotropic diffusion.

From a fundamental point of view the opportunity to spectroscopically observe oriented molecules or groups of atoms has led to the unravelling of single parameters from their complex average over space. NMR signals from the fluid phases—gas and solution—derive from the fast spontaneous dynamic averaging over several orientations. Confinement within restricted space, by the use of porous materials, is a method of obtaining the orientation of gases and molecules where the species can find alignment without losing all the degrees of freedom.[5] Here we have exploited an organic single-crystal to imprint its anisotropy on a gas and manipulate the spatial orientation of a gas with respect to the main magnetic field. This was made possible by encapsulating xenon gas in a microporous, molecular single-crystal and observing the xenon NMR resonances as a function of the orientation of the single-crystal with respect to the magnetic field. Hyperpolarized ^{129}Xe NMR,[7] due to its high sensitivity, opens up the way to collect xenon NMR signals from porous single-crystals. However, it has not yet been applied to organic single-crystals,[8] although it has been extensively exploited to study microporous and microcrystalline powders.[9]

Porous single-crystals of tris-*ortho*-phenylenedioxycyclotriphosphazene **1** could be grown to the size of a few millimeters by crystallization from a supersaturated benzene solution, followed by mild evacuation of benzene at 70 °C and 10^{-1} torr. X-Ray diffraction shows a $P6_3/m$ space group with unit cell parameters $a = b = 11.496(1)$ Å and $c = 10.129(1)$ Å;‡ the crystal packing and design strategy has previously been presented.[10] The X-ray diffraction experiment allowed us to recognize the orientation of the crystallographic axes with respect to the morphological habit of the crystals (Fig. 1). Crystal morphology can be described as hexagonal bipyramidal and contains open, parallel and independent nanochannels aligned along the *c* axis with a cross-section of 4.6 Å (see ESI†). The possibility of growing large single-crystals and the structural features make this system over others[9] a most suitable crystalline host for the present study.

The porous single-crystal was placed in a homogeneous magnetic field and exposed to a continuous flow of hyperpolarized xenon at 2% concentration in helium; a single intense signal was detected far downfield with respect to that of the free gas reference at 0 ppm. The *c* axis of the crystal was inclined at variable θ angles, from 0° to 90° with respect to the main magnetic field, and a spectrum was acquired at each given inclination (Fig. 2). The resonances move progressively from downfield to upfield spanning a notable 31 ppm range. The extreme values of the chemical shifts at 111.9 and 80.9 ppm correspond to the θ angles of 0° and 90°, respectively. Instead, rotation about the *c* axis does not affect the resonance

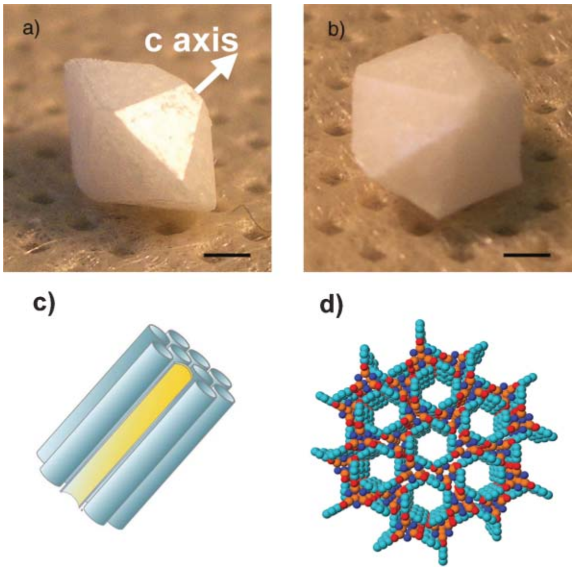

Fig. 1 Photographs of the nanoporous, van der Waals single-crystal of **1** with a hexagonal-base bipyramidal morphology viewed a) perpendicularly and b) along the *c* axis. The bar represents 1 mm. c) Schematic representation of the independent and parallel nanochannels aligned along the *c* axis of the single-crystal. d) Projection of the hexagonal crystal structure onto the (001) plane showing the nanochannels of 4.6 Å diameter.

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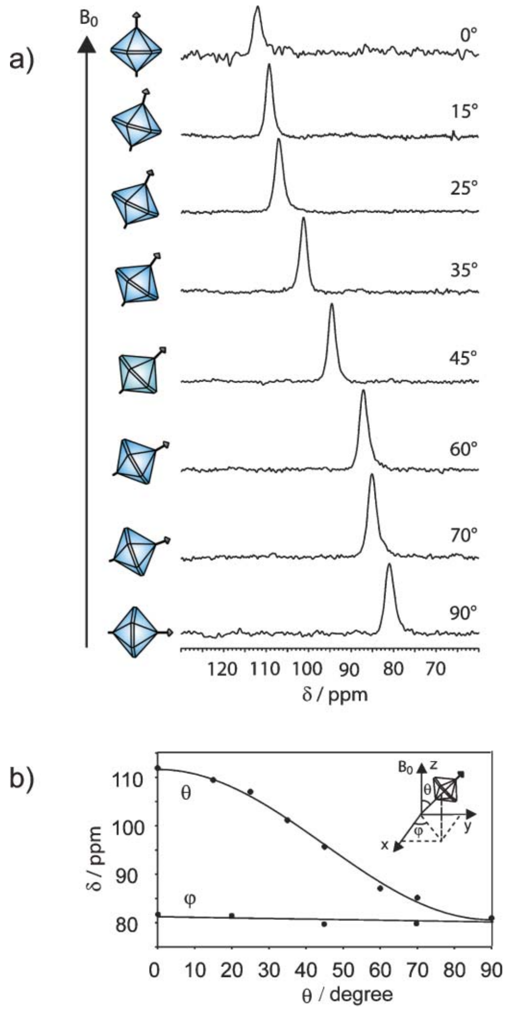

Fig. 2 a) Continuous-flow hyperpolarized ^{129}Xe NMR spectra of the porous, molecular single-crystal inclined at different orientations θ from 0° to 90° with respect to the magnetic field B_0. b) Chemical shifts of xenon diffused into the single-crystal at different orientations of both θ and φ. The chemical shift values have been fitted by the formula $\delta = \delta_{iso} + [(\delta_{xx} - \delta_{zz})(3\cos^2\theta - 1)]/3$ (the asymmetry parameter is zero).

frequencies demonstrating that the components of the tensors δ_{xx} and δ_{yy} have the same intensity and the confinement produced by the nanochannels is axially symmetric. This evidence demonstrates that the electron distribution of xenon changes from the spherical symmetry of the free gas, with the three main components of the tensors being equal, to a shape with axial symmetry. The axial symmetry of the shielding tensor is in agreement with crystal symmetry, and the tensor δ_{zz} component, detected at a θ angle of 0°, coincides with the *c* axis of the crystal. Each signal is a marker of the particular orientation of the single-crystal and of the electron distribution imprinted on the xenon atoms.

The presence of a single resonance in each spectrum indicates that all xenon nuclei experience the same environment, and neither different sites for xenon nor twinning of the crystal are present. Thus, we recognized, unambiguously, the main components of the xenon shielding tensors and assigned them, by direct observation, to the crystal reference system and to the morphology of the crystal.[11] Furthermore, the limit of extreme dilution of xenon that can be used by highly sensitive hyperpolarization techniques permitted us to obtain magnetic parameters of isolated xenon nuclei in the restricted space of the nanochannels without spurious contribution of xenon–xenon interactions. In fact, at room temperature, xenon equilibrium absorption at a pressure as low as 15.2 torr is 0.1 xenon moles per mole of **1**, indicating that each xenon atom is located at an average distance of about 50 Å from the next neighbor along the nanochannels (ESI†). The interaction energy of 23 kJ mol^{-1}, calculated at low xenon loading,[12] can be explained by the favorable topology of the channel walls offering multiple van der Waals interactions to the guest atom.

Variable temperature experiments were performed on the single-crystal placed, with respect to the main magnetic field, at the two limit orientations θ of 0° and 90° (Fig. 3).

At these orientations each component can be singled out. The crystal oriented with channels perpendicular to the main magnetic field shows a very marked dependence on chemical shift with temperature. With decreasing temperature the chemical shift moves downfield (from 80.0 ppm at 313 K to 109.6 ppm at 212 K). This is due to increasing interactions with other neighboring xenon atoms along the channels, since at lower temperature the concentration of absorbed xenon increases considerably, affecting the δ_{xx} (or δ_{yy}) component of the shielding tensor.[13] In fact, the xenon absorption isotherm at 210 K demonstrates a high Xe occupancy of 0.7 xenon moles per mole of **1** at operating conditions of 15.2 torr indicating about 70% of the complete loading of the channels (ESI†). From the crystal structure a complete filling is reached at 1 : 1 xenon moles per mole of **1**. The downfield shift was confirmed by performing the experiment at room temperature with the same crystal orientation but at increasing xenon concentrations: a more deshielded value of about 4 ppm has been observed for the increase in xenon concentration from 2% (15.2 torr) to 4% (30.4 torr) leading to xenon loading from 0.1 to 0.2 moles per mole of **1**, respectively. On

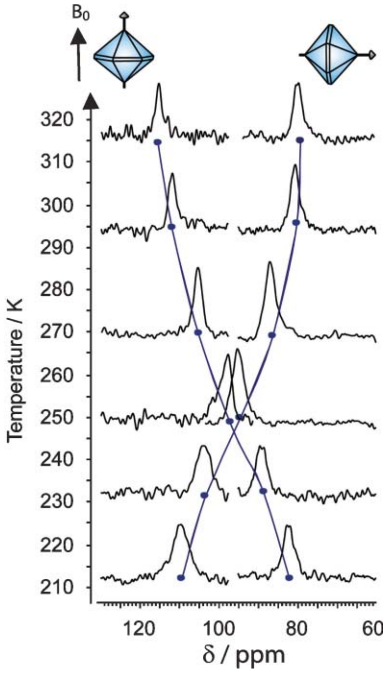

Fig. 3 Variable temperature continuous-flow hyperpolarized ^{129}Xe NMR spectra of a porous, molecular single-crystal inclined at two orientations θ of 0° and 90° with respect to the main magnetic field.

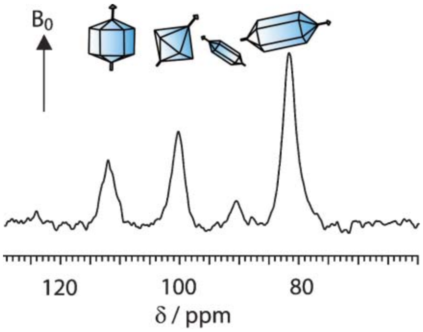

Fig. 4 Continuous-flow HP ^{129}Xe NMR spectrum of an ensemble of four porous molecular single-crystals of different morphologies with the *c* axis inclined at different orientations θ with respect to the magnetic field.

the other hand, when the crystal was set with the nanochannels aligned parallel to the main magnetic field, the chemical shift of the δ_{zz} component changed from 115.4 ppm at 313 K to the upfield value of 82.7 ppm at 212 K. Since at this orientation the resonance is insensitive to xenon concentration,[13] the change in chemical shift is totally due to the interactions of xenon with the channel walls. The upfield shift at low temperature indicates that xenon atoms experience weaker interactions with the walls, that are balanced by stronger interactions with neighboring xenon atoms as shown above by the perpendicular orientation experiment. The components of the xenon shielding tensor as a function of temperature were observed here, for the first time, by a single-crystal allowing their behavior to be measured independently. These observations provide the experimental data required to verify the theoretical predictions.[13] In addition, by the use of HP Xe NMR and a porous single-crystal we could observe, for the first time, macroscopically aligned and oriented chains of xenon atoms and manipulate their orientation in the space.

If a multiplicity of single-crystals were placed in the magnetic field and subjected to the hyperpolarized Xe NMR experiment, a xenon resonance for each single-crystal would be detected, depending on the specific orientation. Actually, a family of four single-crystals of different size and morphology were put in a glass tube and inserted into the probe head with their *c* axis at different θ orientations with respect to the main magnetic field. Four separate lines were detected simultaneously at 111.9, 100.1, 90.5 and 81.5 ppm (Fig. 4).

On the basis of the angular dependence of the chemical shift previously determined we can establish the crystal orientations (θ of 0°, 38°, 56° and 77°, respectively) that correspond to the θ values measured independently by a goniometer. For angles within 15° and 75° the NMR determination of the orientation angles could be as precise as $\pm 1°$. This experiment provides a novel tool to decode the orientation pattern of an ensemble, or an aggregate, of a finite number of porous crystals, simultaneously.

In conclusion, porous single-crystals obtained by self-assembly were proven to be excellent tools to reduce the entropy of gas species and manipulate their orientations. The condensation of gases and vapors onto surfaces is a well known process that produces ordered states of aggregation, but the macroscopic alignment of a gas in a bulk single-crystal is still a challenge. We succeeded in organizing rows of xenon atoms in macroscopically oriented aromatic nanochannels. This represents an exceptional example of gas observation in an organic single-crystal by NMR. The orientational information, brought about with a molecular single-crystal and transferred to a gas traveling along the straight and parallel tunnels, has been collected unambiguously by hyperpolarized ^{129}Xe NMR spectroscopy. This technique opens up the possibility of describing the orientation of the cavities in confining systems, and leads to the recognition of specific access surfaces on crystal faces. The perspective of using porous molecular single-crystals easily grown by self-assembly enables the massive alignment and orientation of a number of important gases, and the exploitation of the orientational properties of gases.

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Notes and references

‡ Crystallographic data for compound **1**: $C_{18}H_{12}N_3O_6P_3$, M = 459.23, hexagonal, $a = b$ = 11.454(5) Å, c = 10.160(5) Å, γ = 120°, U =1154.49 Å^3, T = 298(2) K, space group $P6_3/m$, Z = 2, μ(Mo-Kα) = 0.293 mm^{-1}, 949 reflections measured, R = 0.1920 wR = 0.3027. CCDC 625332. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612002d

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