Inclusion Compounds

Methane and Carbon Dioxide Storage in a Porous van der Waals Crystal**

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The absorption properties of materials are emerging as a forefront issue of present-day research boosted by strategic industrial and environmental applications such as gas storage, selective gas recognition, and separation.[1] Molecular self-assembled materials and organic zeolites[2] are still to be explored extensively as a competing alternative in the field, although they are promising as a result of their unique features. In fact, they can be prepared simply by exploiting soft interactions: the ease of formation results in a surprising modularity of the preparation approach. The available space for absorbates can be engineered in the shape of nanochannels lined with an infinite number of receptors for targeted and selective physisorption. Selectivity is provided not only by the channel opening, as in conventional zeolites, but also by organic groups that focus specific interactions on the channel core and fabricate supramolecular structures that cooperatively stabilize gases that diffuse in. Relatively narrow channels with interacting walls provide greater stability and thus milder absorption conditions than those necessary in the widely reported large-cavity systems, as in the case of metal–organic frameworks.[3] Moreover, the network of soft interactions is often amenable to switching properties and to fabricating actuators, as reversible changes from an absorbing state to a close-packed inactive polymorph can be triggered by thermal, mechanical, or radiative stimuli.[4]

Herein we show the remarkable sorption properties of molecular crystals of tris-*o*-phenylenedioxycyclotriphosphazene (**1**; TPP)[5] with respect to important gases that participate in a network of soft interactions. In fact, methane and carbon dioxide, key gases in the global economy, could be incorporated with high efficiency in the novel adducts (60% and 100% occupation, respectively, of the available sites, guest–host molar fraction of up to 1.25) with neat selectivity over other gases. Unprecedented observations of the gases in van der Waals crystals and their topology could be provided by fast MAS NMR spectroscopy.

The empty-pore hexagonal structure was solved for the first time after isolation of diffraction-quality single crystals and showed no residual electron density in the large unoccupied volume, shaped as straight nanochannels with a minimum diameter of 4.6 Å (Supporting Information). Weak intermolecular interactions consolidate molecular stacks along the *c* axis (repeat period of 10.16 Å) and layers on the *a*–*b* plane ($a = 11.45$ Å), ensuring the stability of the assembly (Figure 1). The crystal density is low ($\rho_{calcd} = 1.321$ g cm^{-3}) and 25% of the volume is available to guests in the noncovalent architecture.

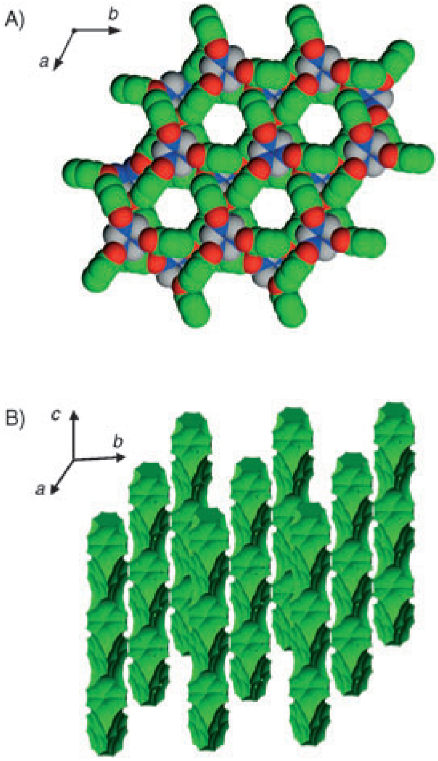

Figure 1. A) Crystal structure of **1** in the nanoporous hexagonal modification viewed along the channel axis: a double layer of molecules is presented; no residual electron density along the nanochannels is shown by Fourier difference maps, indicating the permanent porosity of the structure. B) Portion of the space described by the center of a sphere of 2.5 Å diameter exploring the empty nanochannels (3×3×3 array of unit cells).

The absorbtion capacity of the nanoporous crystal was measured for a few gases, including Ar, N_2, O_2, H_2, CH_4, and CO_2, under isothermal conditions both by precision microbalance and pressure measurements (see Experimental Section). The molecular structure shows the highest sorption values with methane and carbon dioxide (Figure 2).

The isotherm for methane at 195 K traces a typical type I curve that at 1 atm has not yet reached the saturation value. The nanoporous crystal can store up to 0.7 mol of CH_4 per mol of **1** under these conditions. Based on a limit storage value of about 1.2 mol per mol (58 cm^3 g^{-1} at STP), beyond which the gas molecules interact directly with each other in the nanochannels by van der Waals close contacts,[6] we can conclude that a large part of the space available for guests is occupied at equilibrium, indicating a high storage capacity

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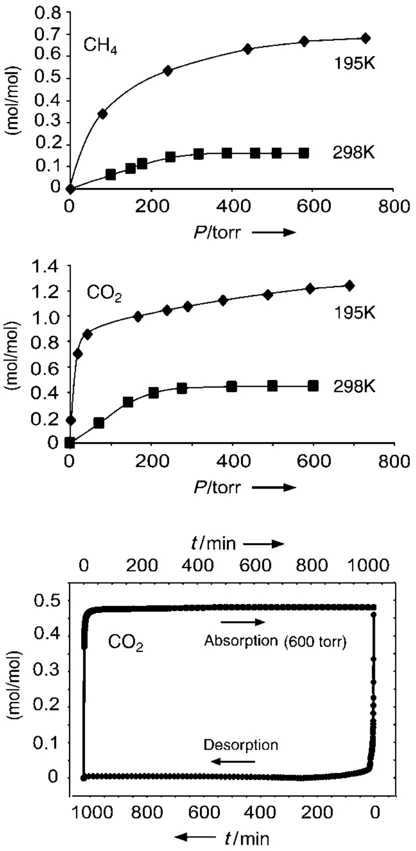

Figure 2. Absorption isotherms of CH_4 and CO_2 expressed as moles of gas per mole of **1** at 195 K and room temperature and microbalance measurements showing the absorption/desorption kinetics of CO_2 at room temperature.

and a large host–guest interaction. The uptake value of methane at 195 K is 2.4 wt%, which corresponds to 33.2 $cm^3 g^{-1}$ (at STP), and is comparable with, or exceeds, the values of inorganic zeolites containing 1D channels with a similar diameter.[7] Even under the mild conditions of ambient pressure and temperature, the efficiency of organic zeolite for methane storage (0.6 wt%) is as high as in conventional zeolites (e.g. in silicalite)[7b] and in metal complexes of comparable channel size ($\approx$0.8 wt% at 1 atm, 298 K).[8] The system appears to be very competitive, especially at low pressures, with respect to other recently proposed van der Waals crystals, in which high pressure (100 atm) is required to reach the saturation of the crystals.[9] This may be due to the peculiar open-pore structure of the hexagonal crystals of **1**, as was shown by single-crystal X-ray analysis.

The nanoporous architecture of **1** presents a surprisingly high storage capacity for CO_2, even at low pressures. In fact, it reaches 1.24 mol of CO_2 absorbed per mol of host at 195 K and 1 atm (12 wt% and 60.5 $cm^3 g^{-1}$ at STP), indicating the virtually complete filling of the available volume in the structure and more than two gas molecules per unit cell.[10] The storage capacity is also considerably high at ambient temperature, setting values of about 0.5 mol mol^{-1}: with a single CO_2 molecule occupying, on the average, the unit cell. The values match the absorption capacity of the most valuable materials of comparable channel size described in the literature.[11] Interestingly, the kinetics of absorption are very fast: after 14 min of contact between CO_2 and crystals of **1** at 600 torr, the saturation limit (4.3 wt%) is reached, as shown by precision microbalance measurements (Figure 2). The desorption process is equally fast and no hysteresis is present. CO_2 is rapidly absorbed by the crystals of **1** because of the small kinetic diameter of 3.3 Å and as a result of the loose steric fitting of the gas molecules inside the channels. Superior properties are shown especially under mild conditions, as the initial slopes of the sorption isotherms are very steep at low pressure, owing to the considerable stabilization in the organic zeolite.[7b, 11a] Carbon dioxide absorption values are considerably higher at room temperature than those recently reported for a molecular crystal of *tert*-butylcalixarene containing aromatic groups.[12]

The direct observation of gas molecules diffused to nanochannels is a challenge for solid-state NMR spectroscopy. The remarkable stability of the gases stored in the host allowed the easy manipulation of the samples and detection the spectra of the gases in the crystals under ambient conditions and in natural isotope abundance. The resonance of stored methane appears in the ^{13}C MAS NMR spectrum as a sharp signal at −9.4 ppm relative to TMS, notably upfield to any known resonance of methane (Figure 3a). Host signals are limited to three, as the high-symmetry arrangement of the hexagonal crystal cell is not lost upon gas loading.

Rare reports of methane observed by NMR spectroscopy have appeared in the literature, with ^{13}C NMR chemical shifts ranging from $\delta = -5$ up to -8 ppm:[13] in particular, methane stored in inorganic zeolites with channel diameters comparable to ours resonates at $\delta_C = -8$ ppm. The exceptional upfield shift to −9.4 ppm determined here is explained by the large magnetic susceptibility effect of the aromatic matrix, showing unequivocally that methane is filled into narrow crystal pipes lined with aromatic groups (Figure 3). Even more impressively, the upfield shift was apparent in the 30 ppm total range of the ^1H NMR spectrum, which was notably resolved at the high spinning speed of 15 kHz:[14] in this case an intense signal of the stored methane is detected at $\delta_H = -2.0$ ppm along with a weak signal for the gas-phase methane loaded in the sealed rotor at $\delta_H = -0.3$ ppm.[15] A direct comparison of the resonances of methane in the two states of free and included gas precisely measures the nucleus-independent upfield shift of $\Delta\delta_H = -1.7$ ppm ($\Delta\delta_H = \delta_{H(\text{stored gas})} - \delta_{H(\text{free gas})}$) as a result of the magnetic susceptibility of the aromatic groups directly surrounding the hydrogen atoms.[16] The quantitative analysis of the ^1H NMR spectrum could give, independently, the amount of the gas absorbed in the zeolite, confirming the high storage values obtained by the sorption isotherms (Figure 3b).

The ^{13}C MAS NMR spectrum of the sample containing CO_2 shows, in addition to the matrix carbon atoms, a signal for CO_2 stored in the nanoporous crystals (Figure 3d). However, the resonance is very close to that of one of the carbon atoms of the matrix, namely C_3; this drawback was overcome by performing a so-called Non Quaternary Suppression (NQS) experiment in which suitable irradiation conditions were found to suppress the protonated carbon atoms of the matrix.

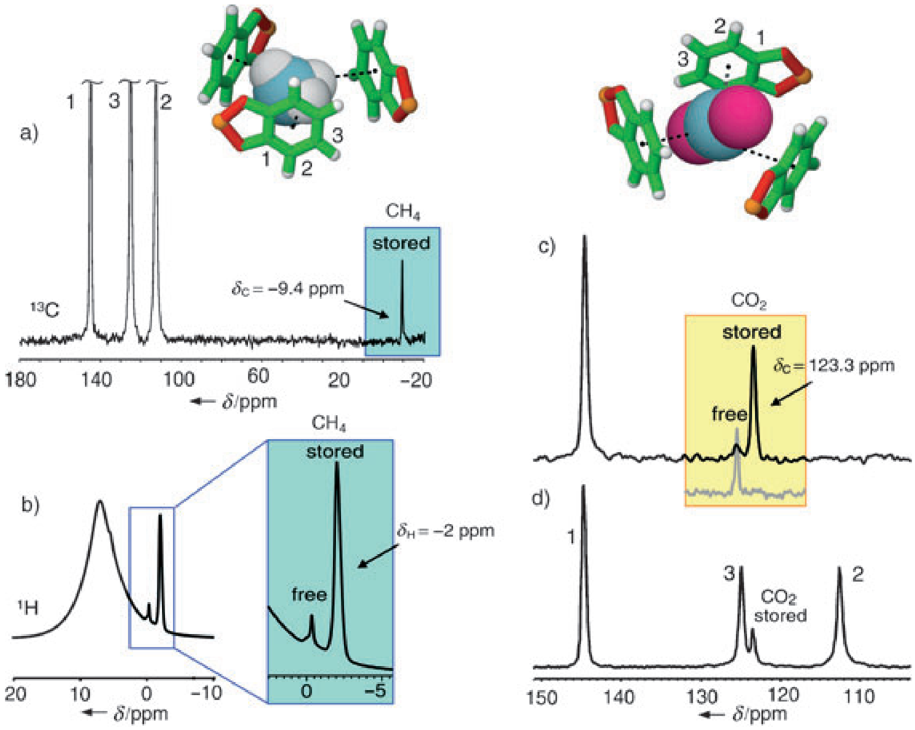

Figure 3. Fast magic-angle spinning (MAS) NMR spectra of gases stored in the van der Waals crystals. Methane stored in **1**: a) ^{13}C MAS NMR spectrum; b) ^{1}H MAS NMR spectrum showing the stored and free gas resonances (enlarged in the insert); the aromatic hydrogen atoms of the matrix appear as a wide signal centered at $\delta = 6.8$ ppm. Carbon dioxide stored in **1**: c) ^{13}C MAS NMR spectrum obtained by applying the Non Quaternary Suppression (NQS) filter compared with the free gas detected separately and d) single-pulse Excitation ^{13}C MAS NMR spectrum showing also the three matrix signals.

The filtered spectrum presents a neat signal at $\delta = 123.3$ ppm, which was assigned to the unprotonated carbon of CO_2 (Figure 3c). The resonance of carbon dioxide stored in the nanochannels is found at the highest field thus far reported in the literature: in particular, it appears much further upfield ($\delta = 133$ ppm) than the signals for bulk solid CO_2, CO_2 associated with calixarenes and cucurbit[5]uril, and free CO_2 gas.[15b,17] We measured the value of $\delta = 125.4$ ppm for pure gas-phase CO_2 under ambient conditions (insert of Figure 3c) and established, therefore, the remarkable upfield shift of $\Delta\delta_C = -2.1$ ppm for the stored gas with respect to the gas phase. The shift denotes the tight proximity of the gas molecules to the walls in the restricted aromatic environment and, in particular, reveals that the gas carbon atoms are located as closely as possible to the "sticky" walls.

Based on a detailed XRD single-crystal analysis of the architecture of the porous crystal, it was concluded that the aromatic paddles of **1** are aligned parallel to the channel axis at 4.0 Å distance, so that the π electrons of the phenylenedioxy units are prone to interactions with the gas species diffusing in (Figure 4).

NMR spectroscopy provides the guest arrangement by the spatial dependence of the magnetic susceptibility on the aromatic ring coordinates.[16] In the case of methane, a shielding effect of $\Delta\delta_H = -1.7$ ppm in the hydrogen spectrum corresponds to an accurate distance measurement of 2.9 Å from the center of an aromatic ring to the nucleus of one of the methane hydrogen atoms (Figure 4). The carbon nucleus of methane experiences a smaller shielding effect and is displaced a further 1.1 Å apart, falling at the center of the channel. Thus, methane is located at an equilibrium distance in close contact with the π-electron clouds that protrude for about 1.7 Å from the host paddles (Supporting Information).

The distance determinations are consistent with models of benzene/CH_4 dimers for which the energy minimum falls at 3.8 Å (from the methane carbon atom to the center of the aromatic ring) and indicate the formation of $\mathrm{CH}\cdots\pi$ interactions accounting for an attractive energy of 6 kJ mol^{-1}.[18] The distances also match a large number of examples of $\mathrm{CH}\cdots\pi$ interactions with energies of about 8.5 kJ mol^{-1}.[19] However, the elaboration of the absorption isotherms at variable temperatures to obtain the isosteric heat of absorption at a low pressure estimates a larger enthapy per mol of gas of 11 kJ mol^{-1}.[20] In fact, the tetrahedron of methane placed at the center of the channel behaves as a polydentate structure with a favorable topology for setting multiple interactions with the channel walls: $\mathrm{CH}\cdots\pi$ interactions can be established with two or even three host paddles at a time, designing a few stable configurations.[21] Nuclear magnetic relaxation rates in the extreme narrowing limit indicate that the configurations are explored dynamically. Indeed, given the properties of scarce directionality, $\mathrm{CH}\cdots\pi$ interactions generate shallow and proximal energy minima that do not fix methane to a single configuration, but trace easy ways for diffusion.[18] Thus, the zeolitic modification of **1** provides considerable stabilization to the

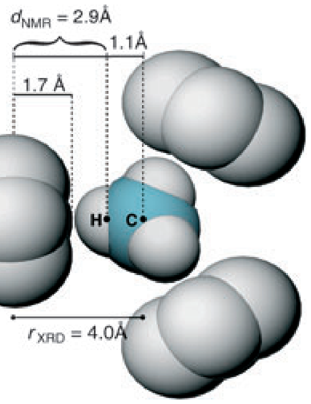

Figure 4. A single methane molecule at a particular site along the nanochannel of **1**, creating close contact interactions with the surrounding π receptors. The host–guest distances are determined by the effect of magnetic susceptibility on methane NMR resonances.

lightest of alkanes without sacrificing diffusivity in the crystal. Other kinds of local interactions are set with CO_2 for which the carbon nucleus comes closer to the aromatic groups, as proven by the large NMR upfield shift of $\Delta\delta_C = -2.1$ ppm. The carbon atom of CO_2 is pushed towards the walls at an equilibrium distance as short as 3.3 Å, with a stabilization energy amounting to 10.5 kJ mol^{-1} for a single interaction of CO_2 arranged parallel to the benzene plane.[22] This distance, shorter than the channel radius of 4.0 Å, explains the fast absorption/desorption rate and allows carbon dioxide to explore multiple aromatic receptors along the nanochannel walls.

Sorption/desorption cycles can be repeated many times in the porous molecular crystals as in conventional zeolites because, after the gas release, the open framework does not collapse to a close-packed structure, as commonly happens in molecular materials.[2h,23] The absorbing state of **1** can be switched off by thermal treatment at high temperature, and no absorption was observed for the closed-packed polymorph after prolonged exposure to the gases. However, the molecular system can be switched back to the active nanoporous form after exposure to benzene and mild evacuation.

O_2, N_2, and Ar are absorbed in amounts below 0.04 mol of gas per mol of **1** at 400 torr and room temperature. Also, hydrogen gas is not appreciably retained by the crystal at 77 K and 1 atm even if it probably explores the interior of the porous crystal. This selectivity is an attractive property since CO_2 and/or CH_4 can be removed from the gas phase by our molecular zeolite at low partial pressures and stimulates interesting perspectives for the purification of H_2. It was recently emphasized that the removal of small amounts of contaminant gases, primarily CO_2 and CH_4, from H_2 is a determining challenge for the real use of hydrogen as a fuel.[12] It is interesting to note that **1** can capture CH_4 as much as CO_2, contrary to other systems that cannot absorb CH_4 in comparable amounts.[24]

In conclusion, the molecular crystal of **1**, which exhibits permanent nanoporosity, can store large amounts of carbon dioxide and methane selectively over nitrogen, oxygen, and hydrogen, suggesting intriguing applications for fuel storage, hydrogen purification, and carbon dioxide removal from the air. In fact, by exploiting the weakly directional interactions borrowed by supramolecular chemistry, we discovered that the gases were bound by the soft molecular lattice to fabricate new gas–solid adducts. This represents a still rare case of gas sorption, as until recently, molecular systems were neglected relative to metal-organic or traditional zeolites. The novel frameworks with gases could be described in-depth by NMR spectroscopy, which accurately measures intermolecular distances and recognizes the specific interactions that contribute to the overall stabilization. The impressive upfield shifts caused by the aromatic ring currents on gas molecules at the van der Waals contacts provided an unconventional tool for understanding the preferred topology of the gases interacting with the inner surface of a porous crystal. The multiple receptors lining the channel walls and the tight fit with the guests recall the specificity of biological nanochannels.[25] Also, the relevant gas sorption capacity of the van der Waals crystals even at low pressures opens up applications to new generations of sensing materials that contain a variety of suitably engineered functional groups.

Experimental Section

X-ray structure determination: The single-crystal X-ray data collection of the nanoporous TPP was performed on an Oxford Xcalibur automated 4-circle diffractometer with k geometry equipped with a CCD detector and a Mo-target X-ray tube operating at 50 kV and 30 mA with a radiation wavelength λ of 0.71073 Å. The frames were integrated with the CrysAlis RED software package of Oxford Diffraction. Absorption correction was applied by using the program SADABS. The structure was solved by direct methods, and the subsequent difference Fourier synthesis and refinement was carried out with the JANA2000 software package. Crystal data of TPP: $C_{18}H_{12}N_3O_6P_3$, $M_r = 459.23$, crystal size $80 \times 80 \times 100\ \mu m^3$, hexagonal, space group $P6_3/m$, $a = b = 11.454(4)$, $c = 10.160(4)$ Å, $\gamma = 120°$, $Z = 2$, $V = 1154(1)$ Å^3, $\rho_{calcd} = 1.321\ g\,cm^{-3}$, $F(000) = 444$, $\lambda(Mo_{K\alpha}) =$ 0.71073 Å, $3.56° < \vartheta < 28.14°$, a total of 460 frames were collected with a scan width of 1 deg in ω and ϕ with an exposure time of 60 s per frame, $T = 298$ K, 8029 measured reflections, 922 ($R_{int} = 0.170$) independent reflections, $R_1 = 0.0882$, $wR_2 = 0.0128$ for 2167 observed reflections with ($I > 3\sigma$), GOF = 1.70, refinement method: full-matrix least-squares on F^2. CCDC-253 392 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).The simulated powder profile derived from single-crystal data reproduces the experimental X-ray powder pattern (Supporting Information).

Gas absorption: The preparation of adducts of **1** with gases and absorption isotherms were obtained by using the following instruments: a) a precision quartz microbalance system and b) gas adsorption manometry apparatus. The gravimetric apparatus is constituted by a quartz microbalance (Cahn 2000 balance) enclosed in a vessel (overall volume: 2000 cm^3) connected to a vacuum pump with a gas inlet and a pressure gauge. The nanoporous crystals of **1** (50 mg) were placed on the microbalance and the apparatus was evacuated at 10^{-3} torr. The system was pressurized at the desired gas pressure and the mass of the sample was monitored over time. The sensitivity is 0.1 μg. In the manometry apparatus, samples were degassed to below 10^{-3} torr. The gas pressure was determined by an active strain gauge (Edwards ASG) with a sensitivity of 0.1 torr. Adsorption equilibrium was usually reached within 150–200 min. The measurements were carried out at room temperature and 195 K. The determination of the maximum loadings in the case of methane was checked by ^{1}H MAS NMR.

Solid-state NMR spectroscopy measurements: ^{1}H and ^{13}C MAS NMR spectra were recorded at 7.04 Tesla static magnetic field on a Bruker Avance 300 apparatus at 300.13 and 75.5 MHz, respectively, and at a spinning speed of 15 kHz obtained with 4-mm zirconia rotors. Single-pulse excitation was applied; the application of the cross-polarization pulse sequence was found to be ineffective for recording the signals of gases. Spin-lattice relaxation times were measured by the inversion recovery method.

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