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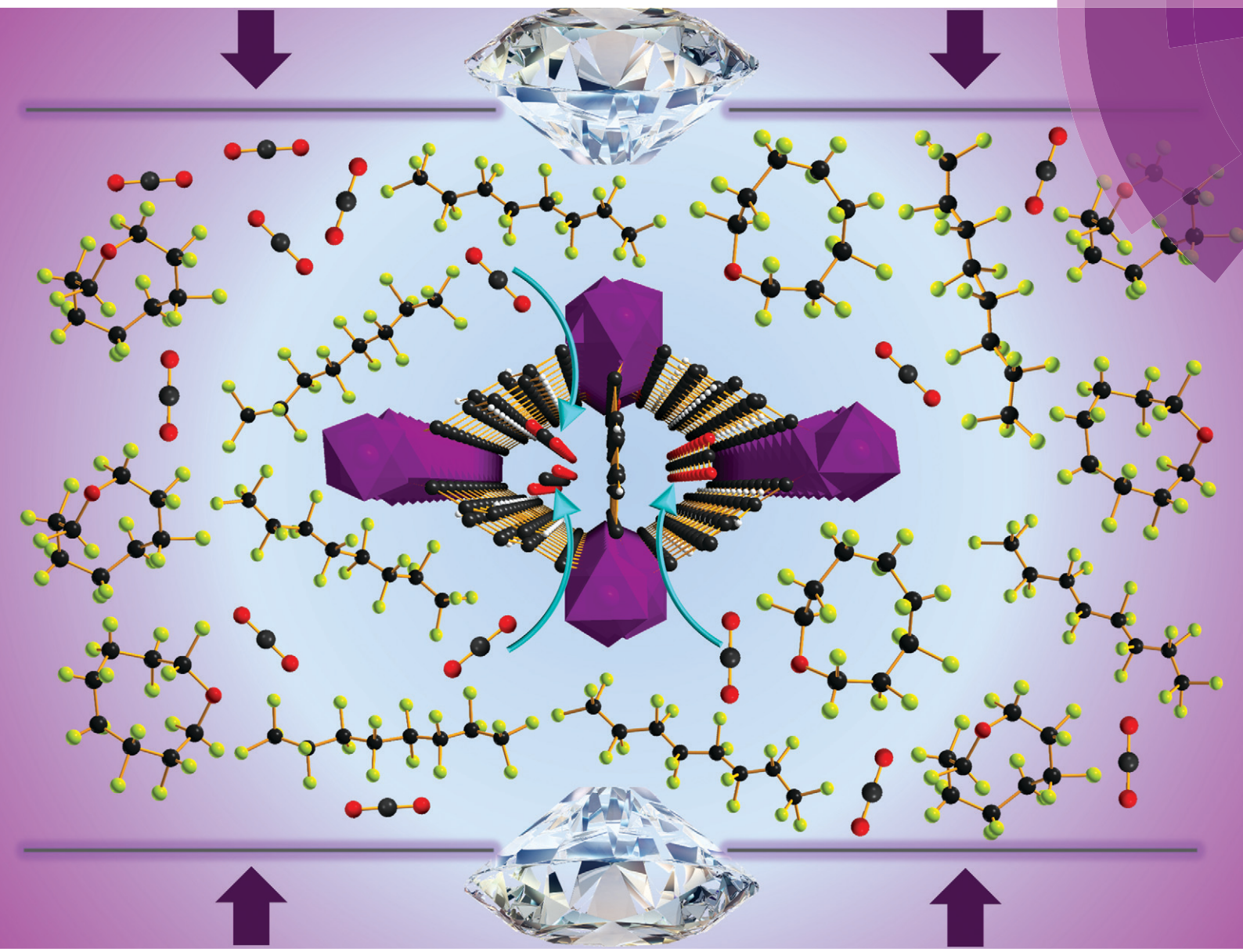

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Perfluorocarbon liquid under pressure: a medium for gas delivery†

Scott C. McKellar,[a] Jorge Sotelo,[a] John P. S. Mowat,[b] Paul A. Wright[b] and Stephen A. Moggach*[a]

A novel method for CO_2 delivery to a porous material is reported, wherein a perfluorocarbon containing dissolved CO_2 has been used as a pressure-transmitting liquid in a high-pressure single-crystal X-ray diffraction experiment. Pressure causes the gas to be squeezed out of the liquid into the host crystal, monitored *via* a single-crystal to single-crystal phase transition on uptake of CO_2.

Perfluorocarbons (PFCs) are a family of liquids which have long been recognised as useful due to their capacity for dissolving large volumes of gas.[1,2] They are colourless, odourless, chemically inert hydrocarbons in which the hydrogen atoms have been replaced with fluorine. First developed as corrosion inhibitors during World War II,[3] they now also have industrial applications as lubricants and coolants, with a wide range of linear, branched, cyclic or derivatised PFCs commercially available. The high solubility of respiratory gases such as CO_2 and O_2 in PFCs saw their usage expanded to biomedicine in the early 1990s with the launch of Flousol®, an emulsion of perfluorodecalin ($C_{10}F_{18}$) and perfluorotripropylene (C_9F_{20}). The solubility of O_2 in PFC liquids at 1 bar and 37 °C is typically 40–50% per volume of liquid, while that of CO_2 can exceed 200%. For comparison, the solubility of O_2 in water is 2.5 vol%.[4] PFCs attained 'cult status' in popular culture after the ground-breaking work of Clark demonstrated that mice could 'breathe' while submerged in oxygenated perfluorobutyltetrahydrofuran ($C_8F_{16}O$) liquid.[1] Solid porous materials with applications in gas storage and separation are of enormous interest across many disciplines of science, due in large part to current drives towards clean energy and reduction of CO_2 emissions.[5–8] Inherent in such research is the requirement to optimise the quantity of gas that can be stored in the material. Evaluation of gas storage capacities is usually performed using gravimetric or calorimetric analysis over a range of temperatures and pressures. However, in the alternative method outlined here, we have used high-pressure, single-crystal X-ray diffraction to show for the first time how a PFC containing high concentrations of dissolved gas can be used as a pressure-transmitting medium, allowing us to literally squeeze gas into a host crystal from the surrounding liquid and calculate the gas uptake in a single experimental step at room temperature.

Previous work has shown that when surrounded by a pressure-transmitting liquid in the sample chamber of a modified Merril–Bassett diamond anvil cell (DAC), the structural response of porous metal–organic frameworks (MOFs) to pressure can be highly sensitive to the liquid used to apply hydrostatic pressure to the sample.[9] For example, surrounded by a liquid small enough to penetrate the pores of the MOF, the framework can be super-filled, causing an expansion in unit cell volume as the liquid is squeezed into the void space. However, with larger media such as PFCs, the liquid is typically too large to penetrate the pore openings of most MOFs and thus direct compression of the framework occurs. These guest-dependant high-pressure results are an effective way to understand guest uptake and flexibility in porous MOFs, which have numerous potential related uses in applications such as gas storage,[10] molecular separation[11] and carbon capture.[5] In the work presented herein, the gas-dissolving capacity of PFCs has allowed us to investigate the application of these materials not just as media for compression experiments, but also as materials for pressure-induced gas delivery.

Our approach is fundamentally very simple; for a pressure-transmitting liquid, we selected Fluorinert™ FC-77 (Fig. 1a), a mixed PFC liquid comprised of perfluorooctane (C_8F_{18}) and perfluorooxacyclononane ($C_8F_{16}O$). FC-77 was chosen to demonstrate proof-of-concept since the liquid

[a] *EaStCHEM School of Chemistry and the Centre for Science at Extreme Conditions, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK. E-mail: s.moggach@ed.ac.uk*
[b] *EaStCHEM School of Chemistry, University of St Andrews, Purdie Building, St Andrews, KY16 9ST, UK*

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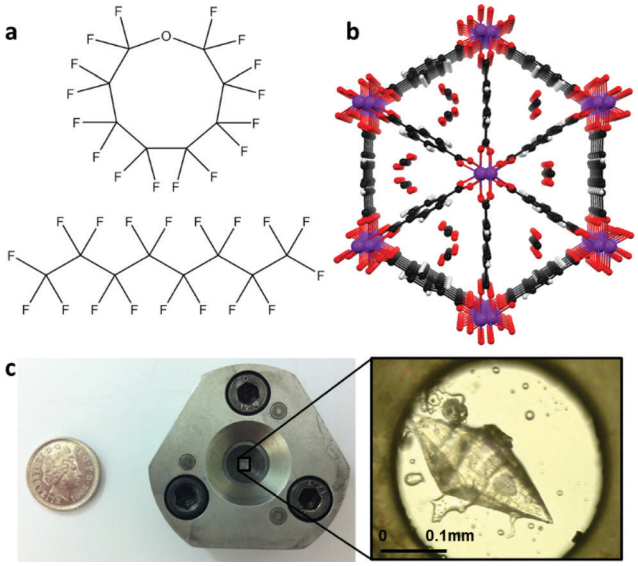

Fig. 1 Materials used to perform high-pressure, single-crystal X-ray diffraction experiments. a, Structure of Fluorinert™ FC-77; a mixed liquid consisting of perfluorooctane (C_8F_{18}) and perfluorooxacyclononane ($C_8F_{16}O$). b, Six-channel portion of the previously-determined monoclinic Sc_2BDC_3 crystal structure,[12] shown with partially-occupied adsorbed CO_2 molecules in the framework pores. Purple, black, red and white spheres denote Sc, C, O and H atoms respectively. c, Photograph of a modified Merril–Bassett diamond anvil cell (DAC) (depicted beside a five-pence coin for scale), with an expanded photomicrograph of the sample chamber containing a single crystal of Sc_2BDC_3 surrounded by CO_2-loaded FC-77 liquid.

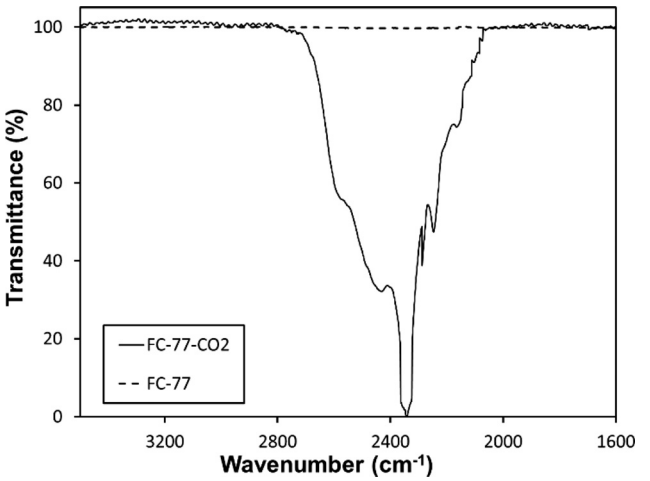

Fig. 2 IR spectra of native FC-77 (dashed line) and CO_2-loaded FC-77 (solid line). The presence of CO_2 in the liquid FC-77 is clearly visible from the characteristic asymmetric CO_2 stretch at ~2385 cm^{-1}.

remains hydrostatic up to GPa pressures[13] and because it has one of the highest gas-dissolving capacities of commercially available PFCs (56 ml O_2/100 ml FC-77 and 224 ml CO_2/100 ml FC-77 at 37 °C).[14] As a host compound, the MOF Sc_2BDC_3 (ref. 15) (Fig. 1b) (BDC = 1,4-benzenedicarboxylate) was used for two reasons. Firstly, Sc_2BDC_3 has small (<4 Å diameter) hydrophobic pore openings that can adsorb a range of small gas molecules such as CO_2, carbon monoxide and methane, but the pores are too small to accommodate the bulky FC-77 molecules. Secondly, it has been shown previously that CO_2 adsorption causes Sc_2BDC_3 to undergo a single-crystal-to-single-crystal phase transformation, characterised structurally by a slight rotation of the BDC linking molecules.[12,16] Though the transition is subtle, it is easily detectable due to an associated change in crystal system from orthorhombic to monoclinic. No other guest species has been observed to trigger the phase transition. Therefore for the purposes of this work, Sc_2BDC_3 has been used as a CO_2 sensor with the phase change serving as an elegant indicator of CO_2 uptake. CO_2 was dissolved in the FC-77 by bubbling CO_2 gas slowly through the liquid (see ESI†). The presence of CO_2 in the liquid was confirmed using IR spectroscopy (Fig. 2).

Initial X-ray diffraction data collected on a single crystal of Sc_2BDC_3 at ambient temperature and pressure confirmed that the framework pores of the orthorhombic parent phase were free of any guest species (*i.e.* residual mother liquor solvent). Diffraction data were then collected on the same crystal whilst immersed in CO_2-loaded FC-77 at ambient pressure and temperature, using a bespoke method[9] whereby a Sc_2BDC_3 crystal was stuck to the tip of a microloop inside a polyester capillary which was then filled with the PFC. This confirmed unambiguously that the face-centred orthorhombic symmetry of the as-prepared sample was maintained (*Fddd*; a = 8.755(<1) Å, b = 20.779(<1) Å, c = 34.407(<1) Å[15]), indicating that the dissolved CO_2 did not diffuse from the liquid into the crystal. A Sc_2BDC_3 crystal was then loaded into a DAC at 1.7 kbar, with the CO_2-loaded FC-77 as a hydrostatic medium (Fig. 1c). At this pressure, crystal structure solution confirmed that the sample had adopted the monoclinic form indicative of CO_2 uptake (*C*2/*c*; a = 8.6929(18) Å, b = 34.291(5) Å, c = 11.0714(19) Å, β = 111.014(13)°). Abridged crystallographic information for the ambient temperature/ambient pressure (1), ambient-pressure immersed (2) and high-pressure (3) crystal structures is provided in Table 1.

This result is, to the best of our knowledge, the first of its kind. It is known from previous work[17] that compression of Sc_2BDC_3 in FC-77 causes the framework to experience direct compression with no change in the crystal symmetry. Therefore, the observed orthorhombic-to-monoclinic phase transition is due entirely to the CO_2 uptake from the hydrostatic medium, and not due to structural rearrangement as a result of compression. This result (illustrated schematically in Fig. 3) shows that with the application of pressure, it is possible to squeeze gas from a PFC liquid into a porous framework as the system seeks to fill empty space and redistribute density upon contraction.

The CO_2 guest molecules in the framework at 1.7 kbar were treated in the crystallographic model using the *PLATON SQUEEZE* algorithm. The calculated pore content was equivalent to 4.5 molecules of CO_2 per Sc_2BDC_3 unit cell; a calculated uptake of 1.95 mmol g^{-1} at room temperature. This figure is somewhat lower than the maximum CO_2 adsorption capacity measured independently for Sc_2BDC_3 by Miller

Table 1 Abridged crystallographic data and structure refinement parameters for Sc_2BDC_3 at ambient temperature and ambient pressure (**1**), immersed in CO_2-loaded FC77 at ambient pressure (**2**) and at high-pressure in CO_2-loaded FC77 (**3**)

	1	2	3
Chemical formula	$C_{12}H_6O_6Sc$	$C_{12}H_6O_6Sc$	$C_{12}H_6O_6Sc \cdot 0.56(CO_2)$
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Fddd*	*Fddd*	*C*2/*c*
T (K)	293.0	293.0	293.0
a (Å)	8.785(6)	8.798(2)	8.7007(13)
b (Å)	20.810(14)	20.865(4)	34.271(3)
c (Å)	34.480(2)	34.551(6)	11.0753(12)
V (Å^3)	6303(7)s	6342(2)	3082.1(7)
Z	16	16	8
F (000)	2352	2352	1176
Radiation type	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.48	0.48	0.49
Crystal size (mm)	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1
Reflections collected	5977	1914	4125
Independent reflections	831	771	972
Data/parameters	823/88	765/88	906/83
R_{int}	0.059	0.109	0.093
ϑ_{max} (°)	20.8	20.8	22.7
$R[F^2 > 2s(F^2)]$, w$R(F^2)$	0.031, 0.064	0.049, 0.111	0.121, 0.329
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.32	0.76, −0.67	0.89, −0.76

et al.[12] In this previous work, at 304 K, the type 1 adsorption isotherm up to 50 bar showed a maximum CO_2 adsorption of ~4.5 mmol g^{-1}. However, gas uptake increased significantly at lower temperatures; the maximum uptake measured volumetrically was ~6.5 mmol g^{-1}, achieved at 1 bar at 195 K and at 0.006 bar (p/p_0 = 1) at 150 K. It is worth noting that use of the *SQUEEZE* algorithm is an estimate and is ideally performed on data sets with 100% completeness,[18] which is impossible in this instance due to shading by the DAC. However, we have previously shown that *SQUEEZE* can be used effectively in high-pressure datasets of MOFs to observe trends in pore content,[19] and accurately as a quantitative validation tool using guest species which can also be modelled crystallographically.[20]

The results obtained here would imply that there must be a barrier for diffusion of CO_2 molecules into the framework when trapped within the PFC. However it has also been shown recently that particle size can play a significant role in the gas adsorption mechanics in MOFs,[21] which could explain the disparity between previous adsorption work, conducted using polycrystalline material, and the diffraction results reported here, performed using single crystals. Unfortunately, an atomistic model could not be obtained for localised CO_2 sites within the MOF pores, therefore we could not determine whether the molecules retained the same geometry observed previously at 1 bar and 195 K. This is unsurprising considering the low data completeness and lower CO_2 uptake at 1.7 kbar observed here. In previous measurements, only polarised infrared spectroscopy has been able to shed light on the orientation of CO_2 molecules within Sc_2BDC_3 at room temperature.[22]

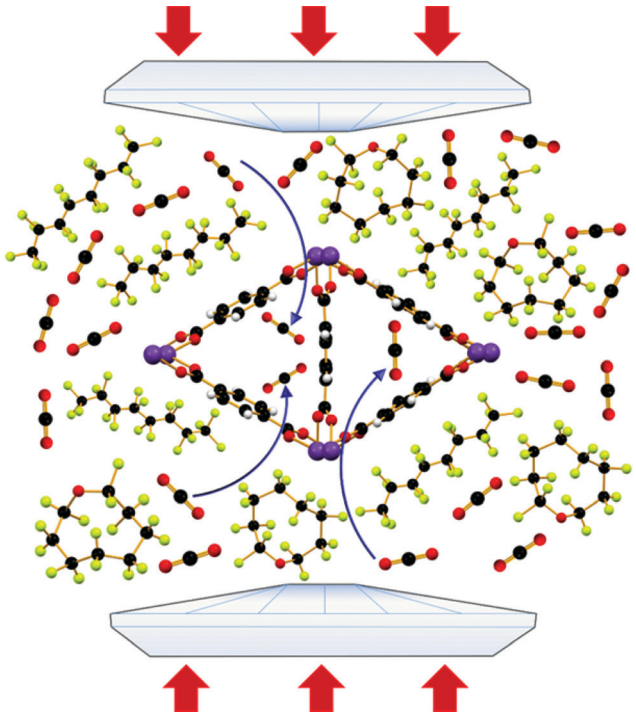

Fig. 3 Cartoon schematic of pressure-induced CO_2 loading of porous Sc_2BDC_3 from liquid FC-77. Colour scheme as in Fig. 1, with green spheres denoting F atoms. As pressure is applied to the Sc_2BDC_3 crystal in the sample chamber between two diamond culets, dissolved CO_2 in the liquid is squeezed into the previously empty framework. The molecules of the FC-77 are too large to penetrate the framework.

The pressure in the DAC was then increased to 4.4 kbar in an attempt to push the limit of CO_2 uptake from FC-77. At this pressure the Sc_2BDC_3 crystal fractured and the resolution of the data decreased rapidly (≈1.3 Å). Nevertheless, the sample could still be confirmed as being in the crystalline monoclinic phase. This work is the first example of a penetrating (CO_2) and a non-penetrating (FC-77) medium being used simultaneously, so it is therefore interesting to speculate on the competing effect of the two given the different structural response that can be produced in porous frameworks. Previous work[17] has shown that native Sc_2BDC_3 is not stable at pressures over ~4 kbar whilst under direct compression in Fluorinert™. However, super-filling of MOFs with penetrating guest molecules stabilises the frameworks to high pressures. It would therefore appear then, that even at low loadings of CO_2, the crystalline phase is stabilised to external pressure, preventing amorphisation. When comparing the unit cell parameters of the monoclinic Sc_2BDC_3 at 1.7 kbar to the data collected at 4.4 kbar, contraction of all the unit cell axes takes place – as opposed to lengthening along the more flexible directions as is common in super-filled frameworks – suggesting that the direct compression at higher pressures exerted by the FC-77 outweighs any effect of possible super-filling with CO_2. Given the low uptake of CO_2 previously calculated, and the fact that the sample is still crystalline at 4.4 kbar, it is easy to envisage that further filling of the pores with CO_2 molecules may occur, further

stabilising the crystalline monoclinic phase to amorphisation, but this requires further investigation.

Though this method of using PFCs for gas-loading crystalline compounds under pressure is by no means limited to MOFs (nor is the gas necessarily limited to CO_2), Sc_2BDC_3 is a useful material to demonstrate the application of the method since the use of porous MOFs as gas storage agents is currently a source of enormous interest in the research community.[23] This has been driven by advances in separation and carbon sequestration technologies[5,6] in line with global government targets for cleaner energy and the reduction of CO_2 emissions.[7,24] Innovative routes to CO_2 storage and the measurement of storage capacity is vital information for researchers considering scale-up and application of a particular MOF. Determination of the storage capacity *via* the construction of adsorption isotherms is usually performed using gravimetric or calorimetric analyses over a range of different temperatures and pressures,[12,25–29] often requiring gram-scale quantities of material. The results from our proof-of-concept study indicate that, in one experimental step, we can fill the pores with CO_2 and calculate the pore content with just one single crystal surrounded by FC-77 in a sample chamber of ~0.01 μL. Moreover, since our experiment is performed at room temperature, the structural response observed in the framework is more reflective of potential real-world gas storage material applications than the low temperatures used for adsorption isotherm construction, or indeed for standard X-ray diffraction experiments. We propose that as a method to quickly and efficiently probe the gas uptake and structural response of a material, pressure-induced gas loading from a PFC represents a unique approach and a complementary technique to classical gravimetric methods.

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