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Supplementary Information for

Perfluorocarbon Liquid Under Pressure: A Medium for Gas Delivery

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S1. Materials

All starting materials and solvents were purchased from Sigma-Aldrich (UK) in high purity and used as received. Sc_2BDC_3 was synthesised using a previously described method.[1]

S2. Dissolving CO_2 in FC-77

5 mL of FC-77 was added to a small glass vial, which was sealed with a rubber cap and connected to a CO_2 canister via a syringe embedded in rubber tubing. The syringe was positioned directly in the FC-77 enabling the CO_2 gas to bubble through the solution, saturating the FC-77 with CO_2. A second syringe was used to pierce the rubber seal of the beaker containing the FC-77 to act as a pressure outlet. CO_2 was bubbled through the FC-77 for 1 hour before removing the syringe from the liquid whilst keeping it under a CO_2 atmosphere. CO_2 saturation was confirmed by infrared spectroscopy (see section S3 below). The carbonated FC-77 was used immediately for pressure experiments and kept within the sealed syringe to prevent loss of CO_2.

S3. IR spectroscopy

IR data were collected on both FC-77 and the CO_2 enriched sample of FC-77 on a PerkinElmer 65 spectrometer. The samples were placed in a rectangular sealed liquid cell mount holder and data collected from 1000-3600cm^{-1}.

S4. Single-crystal X-ray diffraction

Data collection, reduction and refinement

For the ambient-pressure diffraction experiment in a liquid, a crystal of Sc_2BDC_3 was stuck to the tip of a MiTeGen 100 μm Microloop™ using a small amount of Araldite™ epoxy resin. The loop was mounted on a goniometer head, and covered with a MicroRT™ polyester capillary. The capillary was stuck to the goniometer head and sealed around the base using Araldite™. When the epoxy resin was dry, the capillary was filled with CO_2-loaded FC-77 by injecting the liquid through the top of the capillary using a 0.6 mm needle. The resultant hole was sealed by melting a small amount of beeswax over the hole. Single-crystal X-ray diffraction data were then collected at room temperature on an Agilent SuperNova diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), equipped with an Atlas detector, with a step size and exposure time of 0.3 and 60 s respectively (Figure S1). The unit cell and crystal system (orthorhombic, a = 8.798(2), b = 20.865(4), c =

34.551(6) Å) confirmed that the structure was still in the orthorhombic ambient pressure and temperature phase. Refinements were carried out against $|F|^2$ using all data in CRYSTALS[2] starting from the ambient temperature and pressure coordinates previously determined (see above).

For the crystal collected at ambient pressure and temperature, single-crystal X-ray diffraction data were collected on a Bruker APEXII diffractometer (Bruker, 2002) with graphite-monochromated Mo *K*α radiation (λ = 0.71073 Å). These data were integrated using the programme SAINT[3], while the absorption corrections were carried out with the program SADABS[4]. Refinements were carried out against $|F|^2$ using all data in CRYSTALS. Pore volume and water content were calculated using the SQUEEZE algorithm within *PLATON*[5].

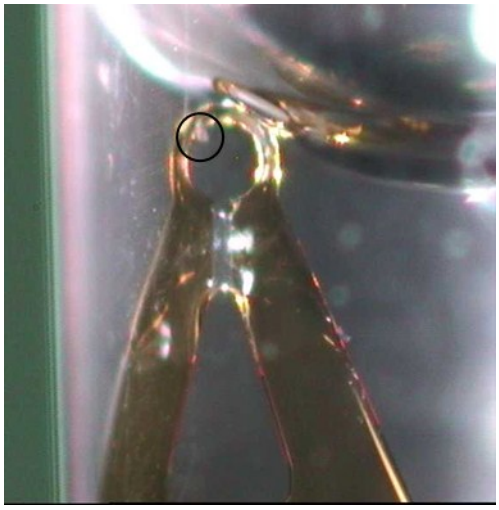

Figure S1. A single crystal fragment of Sc_2BDC_3 mounted on a MiTeGen 100 μm Microloop™ using Araldite™ epoxy resin. The crystal is circled in black.

High-pressure data collection and refinement

The high-pressure experiment was carried out using a modified Merrill-Bassett diamond anvil cell (DAC) equipped with 600 μm culet diamonds and a tungsten gasket.[6] A crystal of Sc_2BDC_3 and a chip of ruby (as a pressure calibrant) were loaded into the DAC with the CO_2-loaded FC-77 as a hydrostatic medium. The ruby fluorescence method was used to measure the pressure.[7] High-pressure single-crystal X-ray diffraction data were collected on a Bruker APEXII diffractometer (Bruker, 2002) with graphite-monochromated Mo *K*α radiation (λ =

0.71073 Å) in ω-scans in eight settings of 2θ and ϕ with a frame time and step size of 40 seconds and 0.5° respectively. This data collection strategy was based on that described by Dawson *et al.*[8] The data were integrated with SAINT using 'dynamic masks' to avoid integration of regions of the detector shaded by the body of the pressure cell. Absorption corrections for the DAC and sample were carried out with the programs SHADE[9] and SADABS, respectively. Refinements were carried out as described above but against $|F|^2$, using atomic coordinates for the framework determined by Mowat *et. al.*[10] The pore content was calculated using the SQUEEZE algorithm within the program *PLATON*. Because of the low completeness of the data sets, all 1,2 and 1,3 distances on the BDC linkers were restrained to the values observed from our previous ambient temperature and pressure structure. Only the Sc atoms were refined anisotropically. All other non-hydrogen atoms were refined with isotropic thermal parameters. All metal-ligand distances and torsion angles were refined freely. Thermal and vibrational similarity restraints were applied to the organic linkers. H-atoms attached to carbon were placed geometrically and not refined.

References

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