Supplementary Information to

Pressure and Guest-Mediated Pore Shape Modification in a Small Pore MOF to 1200 bar

Charles J. McMonagle,[a] Gemma F. Turner,[b] Isabelle Jones,[b] David R. Allan,[c] Mark R. Warren,[c] Konstantin V. Kamenev,[e] Simon Parsons,[f*] Paul A. Wright[d*] and Stephen A. Moggach[b*]

[a.] SNBL at ESRF, Grenoble, France
[b.] School of Molecular Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, Perth, 6009, Western Australia, Australia
[c.] Diamond Light Source, Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Fermi Avenue, Didcot, OX11 0DE, United Kingdom
[d.] EastChem School of Chemistry, Purdie Building, The University of St Andrews, St Andrews, KY16 9ST, United Kingdom
[e.] Centre for Science at Extreme Conditions and School of Engineering, The University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, United Kingdom
[f.] EastChem School of Chemistry, Joseph Black Building, The University of Edinburgh, David Brewster Road, EH9 3FJ, Edinburgh, United Kingdom

Contents

S1. Synthesis of Sc_2BDC_3

$Sc(NO_3)_3$ $4H_2O$ (Alfa Aesar, 0.34 g, 99.9%, 1.1 mmol), 1,4-benzenedicarboxylate (Aldrich, 0.170 g, 99%, 1 mmol), H_2O_2 (Aldrich, 30 wt % in water, 0.25 mL), pyridine (Fisher, 0.5 mL, 99%), and dimethylformamide (DMF; Aldrich, 10 mL, 99.8%) were sealed in a Parr autoclave with a 23 mL Teflon liner. The mixture was subsequently heated to 493 K and allowed to react for 2 days. The autoclave was cooled, and the final product was filtered and washed with DMF. Large single crystals (~150 μm) were obtained.

S2. Moderate Pressure X-Ray Diffraction

A single of crystal of Sc_2BDC_3 was compressed in a hydrostatic medium of either *n*-pentane or isopentane using a sapphire capillary cell (SCC).[1] Diffraction data were collected on beamline I19, Experimental Hutch 2 (EH2) at Diamond Light Source, Rutherford Appleton Laboratory using synchrotron radiation (λ = 0.6889 Å). EH2 is equipped with a Newport 4-circle goniometer with a DECTRIS PILATUS 300 K hybrid-pixel detector. Data were collected using an exposure time of 0.2 s and a step size of 0.2°, using a refined strategy. CrysAlisPro (version 171.38.46)[2] was used for data integration, absorption correction and space group determination.

For compression in isopentane, a single crystal of Sc_2BDC_3 was mounted onto a carbon fibre and collected at ambient pressure. This was then placed into a 0.6 mm ID x 1 mm OD sapphire cell and the pressure was increased from 100 bar up to a maximum pressure of 1200 bar in 100 bar steps (ID = inner diameter, OD = outer diameter).

A resolution cut-off of 0.8 Å was used during data reduction for all datasets. Structures were refined against $|F^2|$ using the program CRYSTALS.[3] Up to 1100 bar, the structures were refined anisotropically and without restraints. Hydrogen atoms were placed geometrically and constrained to ride on their host atoms. At 1200 bar, it was necessary to model the phenyl ring of the Group 2 BDC linker as a 50:50 split over two positions. Bond distances and 1,3-angles, as well as vibrational and thermal similarity restraints were applied to the disordered BDC linker. Analysis of the solvent accessible volume and the residual electron density inside the pores were calculated and modelled, respectively, using the SQUEEZE algorithm within PLATON [4] with a probe radius of 1.2 Å. The results from the residual electron density calculations were used to determine the uptake of solvent at each pressure point.

For compression in *n*-pentane, a single crystal of Sc_2BDC_3 was similarly loaded into a larger 1 mm ID x 1.4 mm OD sapphire cell. Data were collected from 50 bar up to a maximum pressure of 900 bar. A resolution cut off of 0.7 Å was used for all data sets and refinements were carried out using CRYSTALS against $|F^2|$.[3] For the first two pressure points at 50 and 200 bar, the structures were freely refined without restraints. Hydrogen atoms were placed geometrically and constrained to ride. By 400 bar the phenyl ring of the Group 2 BDC linker became disordered and was modelled over two positions, and at 900 bar, the phenyl ring was modelled over four positions. Bond distances and 1,3-angles, as well as vibrational and thermal similarity restraints were applied to the disordered BDC linker. The solvent accessible volume and residual electron density were again analysed using SQUEEZE with the probe radius of 1.2 Å.[4] This was used to determine the uptake of solvent at each pressure point.

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (2202161-2202178). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; deposit@ccdc.cam.ac.uk).

Table S1. Single crystal X-ray crystallographic data for Sc_2BDC_3 during compression in a PTM of *n*-pentane in a sapphire capillary cell. Data were collected at Diamond Light Source, beamline I19, Experimental Hutch 2 (λ = 0.6889 Å, T = 298 K).

	50 bar	**200 bar**	**400 bar**	**600 bar**	**800 bar**	**900 bar**
Chemical formula	$C_{12}H_6O_6Sc{\cdot}0.436(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.414(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.438(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.478(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.530(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.500(C_5H_{12})$
M_r	291.13	291.13	291.13	291.13	291.13	29.13
Crystal system, space group	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*
***a*, *b*, *c* (Å)**	8.7483 (3), 20.7380 (4), 34.3334 (8)	8.7504 (2), 20.7378 (4), 34.3314 (8)	8.7547 (2), 20.7361 (4), 34.3257 (8)	8.7579 (3), 20.7370 (5), 34.3224 (9)	8.7604 (3), 20.7351 (5), 34.3174 (11)	8.7611 (3), 20.7372 (5), 34.314 (1)
***V* (Å^3)**	6228.8 (3)	6229.9 (2)	6231.4 (2)	6233.4(3)	6233.7 (3)	6234.2 (3)
Z	16	16	16	16	16	16
μ (mm^{-1})	0.45	0.45	0.45	0.45	0.45	0.45
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Diffractometer	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle
Absorption correction	Multi-scan *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997)	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*
T_{min}, T_{max}	0.61, 0.95	0.61, 0.95	0.61, 0.95	0.64, 0.95	0.60, 0.95	0.54, 0.95
No. of measured, independent and observed (?) reflections	14864, 2384, 2086	14673, 2384, 2111	14806, 2386, 2105	14843, 2386, 2078	14835, 2386, 2014	14877, 2385, 2007
R_{int}	0.055	0.054	0.058	0.065	0.069	0.069
(sin θ/λ)$_{max}$ (Å^{-1})	0.715	0.715	0.715	0.715	0.715	0.715
R*[$F^2 > 2\sigma(F^2)$], *wR*(F^2), *S	0.036, 0.102, 0.99	0.036, 0.102, 1.00	0.036, 0.102, 1.00	0.037, 0.108, 0.99	0.038, 0.107, 0.97	0.035, 0.099, 0.97
No. of reflections	2376	2376	2378	2378	2378	2377
No. of parameters	88	88	97	97	97	115
No. of restraints	0	0	61	61	61	311
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.34, -0.45	0.45, -0.45	0.42, -0.31	0.48, -0.53	0.47, -0.39	0.32, -0.44

Table S2. Single crystal X-ray crystallographic data for Sc_2BDC_3 during compression in a PTM of isopentane in a sapphire capillary cell. Data were collected at Diamond Light Source, beamline I19, Experimental Hutch 2 (λ = 0.6889 Å, T = 298 K), continued overleaf….

	100 bar	**200 bar**	**300 bar**	**400 bar**	**500 bar**	**600 bar**
Chemical formula	$C_{12}H_6O_6Sc{\cdot}0.329(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.249(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.438(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.293(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.359(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.356(C_5H_{12})$
M_r	291.13	291.13	291.13	291.13	291.13	291.13
Crystal system, space group	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*
***a*, *b*, *c* (Å)**	8.7455 (4), 20.7289 (10), 34.3277 (14)	8.7465 (4), 20.7246 (10), 34.3207 (14)	8.7486 (4), 20.7218 (10), 34.3093 (14)	8.7488 (4), 20.7196 (11), 34.2997 (16)	8.7508 (5), 20.7160 (11), 34.2933 (16)	8.7518 (5), 20.7136 (12), 34.2831 (17)
***V* (Å^3)**	6223.1 (5)	6221.2 (5)	6219.8 (5)	6217.6 (5)	6216.7 (6)	6214.9 (6)
Z	16	16	16	16	16	16
μ (mm^{-1})	0.45	0.45	0.45	0.45	0.45	0.45
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Diffractometer	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle
Absorption correction	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*	Multi-scan *DENZO*/*SCALEPACK*
T_{min}, T_{max}	0.72, 0.95	0.55, 0.95	0.53, 0.95	0.57, 0.95	0.65, 0.95	0.59, 0.95
No. of measured, independent and observed reflections	10697, 1567, 1371	1568, 1568, 1373	10946, 1567, 1350	10868, 1570, 1327	10752, 1568, 1320	10888, 1569, 1335
R_{int}	0.065	0.065	0.063	0.074	0.069	0.075
(sin θ/λ)$_{max}$ (Å^{-1})	0.625	0.625	0.625	0.625	0.625	0.625
R*[$F^2 > 2\sigma(F^2)$], *wR*(F^2), *S	0.033, 0.090, 1.00	0.032, 0.089, 1.01	0.033, 0.093, 1.00	0.033, 0.093, 1.00	0.035, 0.097, 0.99	0.036, 0.098, 1.00
No. of reflections	1559	1561	1559	1559	1560	1561
No. of parameters	88	88	88	88	88	88
No. of restraints	0	0	0	0	0	0
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.29, -0.30	0.27, −0.32	0.28, −0.40	0.32, -0.37	0.37, -0.31	0.33, −0.32

Table S2 continued. Single crystal X-ray crystallographic data for Sc_2BDC_3 during compression in a PTM of isopentane in a sapphire capillary cell. Data were collected at Diamond Light Source, beamline I19, Experimental Hutch 2 (λ = 0.6889 Å, T = 298 K).

	700 bar	**800 bar**	**900 bar**	**1000 bar**	**1100 bar**	**1200 bar**
Chemical formula	$C_{12}H_6O_6Sc{\cdot}0.405(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.397(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.405(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.372(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.374(C_5H_{12})$	$C_{12}H_6O_6Sc{\cdot}0.365(C_5H_{12})$
M_r	291.13	291.13	291.13	291.13	291.13	291.13
Crystal system, space group	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*	Orthorhombic, *Fddd*
***a*, *b*, *c* (Å)**	8.7541 (4), 20.7081 (12), 34.2740 (17)	8.7564 (5), 20.7042 (13), 34.2663 (19)	8.7577 (5), 20.7045 (12), 34.2603 (19)	8.7606 (5), 20.7017 (13), 34.245 (2)	8.7616 (5), 20.7028 (13), 34.237 (2)	8.7648 (6), 20.7017 (14), 34.221 (2)
***V* (Å^3)**	6213.2 (6)	6212.3 (6)	6212.2 (6)	6210.7 (6)	6210.2 (6)	6209.3 (7)
Z	16	16	16	16	16	16
μ (mm^{-1})	0.45	0.45	0.45	0.45	0.45	0.45
Crystal size (mm)	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Diffractometer	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle	Newport, 4-circle
Absorption correction	Multi-scan *DENZO/SCALEPACK*	Multi-scan *DENZO/SCALEPACK*	Multi-scan *DENZO/SCALEPACK*	Multi-scan *DENZO/SCALEPACK*	Multi-scan *DENZO/SCALEPACK*	Multi-scan *DENZO/SCALEPACK*
T_{min}, T_{max}	0.64, 0.95	0.70, 0.95	0.60, 0.95	0.53, 0.95	0.44, 0.95	0.38, 0.95
No. of measured, independent and observed reflections	10768, 1565, 1315	10882, 1564, 1327	10964, 1566, 1308	10779, 1559, 1274	10761, 1565, 1260	10718, 1565, 1255
R_{int}	0.073	0.076	0.077	0.084	0.086	0.083
(sin θ/λ)$_{max}$ (Å^{-1})	0.625	0.625	0.625	0.625	0.625	0.625
R*[F^2 > 2σ(F^2)], *wR*(F^2), *S	0.038, 0.104, 0.99	0.037, 0.104, 1.00	0.038, 0.106, 0.99	0.040, 0.115, 1.00	0.045, 0.135, 1.01	0.044, 0.135, 1.01
No. of reflections	1556	1556	1558	1552	1557	1557
No. of parameters	88	88	88	88	88	97
No. of restraints	0	0	0	0	0	61
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.37, -0.35	0.32, -0.36	0.40, -0.33	0.44, -0.41	0.42, -0.41	0.45, -0.49

S3. Unit Cell Parameters , Bulk Modulus and Uptake of Guest Species

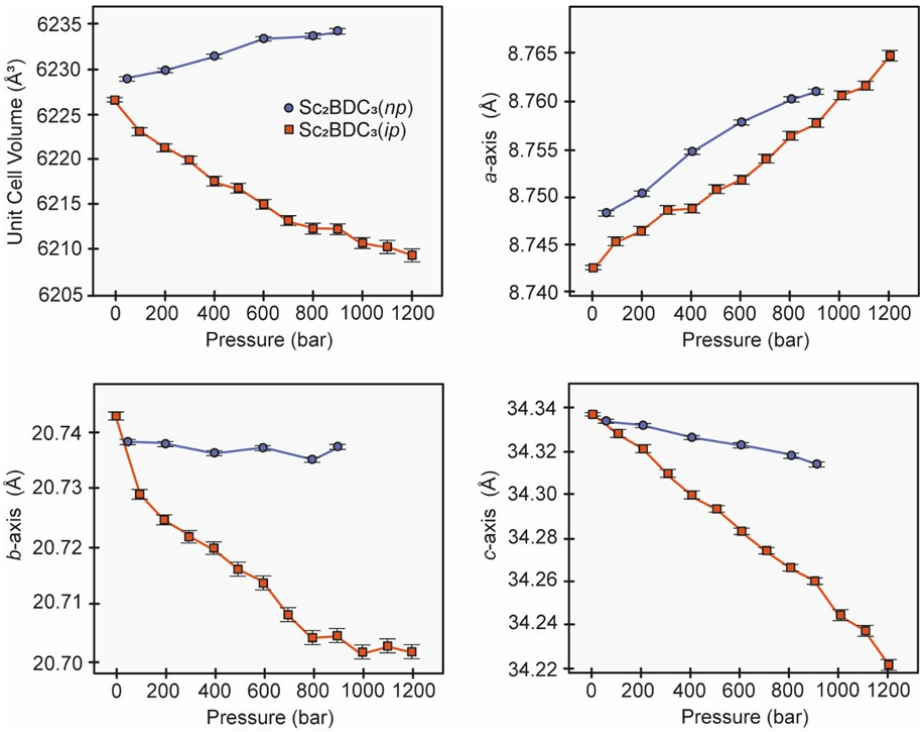


Figure S1. Unit cell volume and lattice parameters as a function of pressure for Sc_2BDC_3(*ip*) (blue circles), and Sc_2BDC_3(*np*) (red squares).

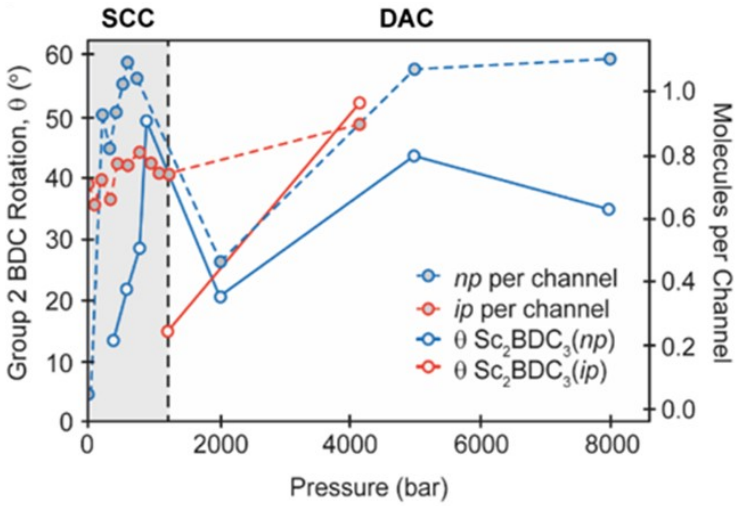


Figure S2. Rotation of BDC ligand and uptake of guest species of Sc_2BDC_3(*ip*) (red) and Sc_2BDC_3(*np*) (blue) as a function of pressure. The area marked in grey is this work, area in white is from McKellar *et al*.[8]

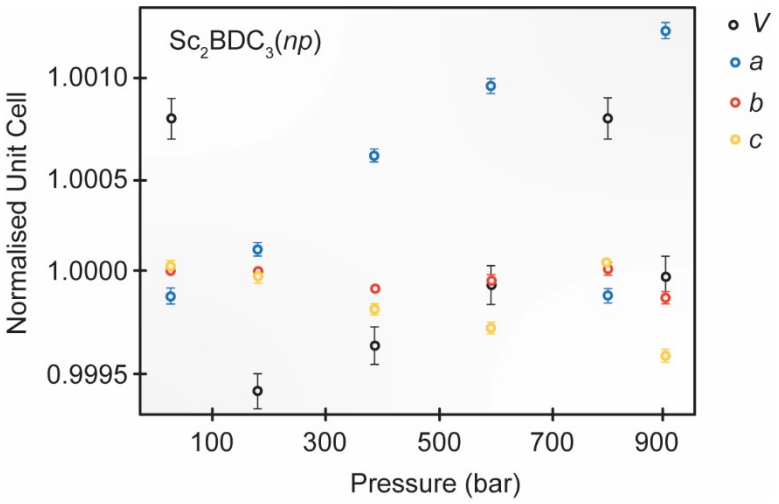


Figure S3. Normalised unit cell parameters of Sc_2BDC_3 during compression in a PTM of *n*-pentane.

Compression of the unit cell parameters of Sc_2BDC_3(*ip*) was fitted to a third-order Birch-Murnaghan equation of state in the program EoSFit7 (*Figure S2*).[5] For a third-order Birch-Murnaghan, pressure, *P*, is given by equation (1) below, where K_0 is the isothermal bulk modulus, *V* is the volume at a given pressure, V_0 is the volume at ambient pressure and K' is the pressure derivative of the isothermal bulk modulus at standard temperature. Linear bulk moduli are given by the same equation, in which *V* and V_0 replaced by a unit cell axis length. The linear compressibility, *k*, is the reciprocal of the linear bulk modulus.

$$P = \frac{3K_0}{2}\left[\left(\frac{V}{V_0}\right)^{\frac{7}{3}} - \left(\frac{V}{V_0}\right)^{\frac{5}{3}}\right] + \left[1 + \frac{1}{3}\left(K'_{T_0} - 4\right)\left\{\left(\frac{V}{V_0}\right)^{\frac{2}{3}} - 1\right\}\right] \quad (1)$$

Table S3. Experimentally determined bulk-moduli of various MOFs as reported in literature.

MOF	K (GPa)	Ref.
HKUST-1	29.5-30	6
UiO-66	35	7
UiO-67	21.1	7
Sc_2BDC_3	17[a] , 48^	[a]8, This study

^Solvent stabilised K_0

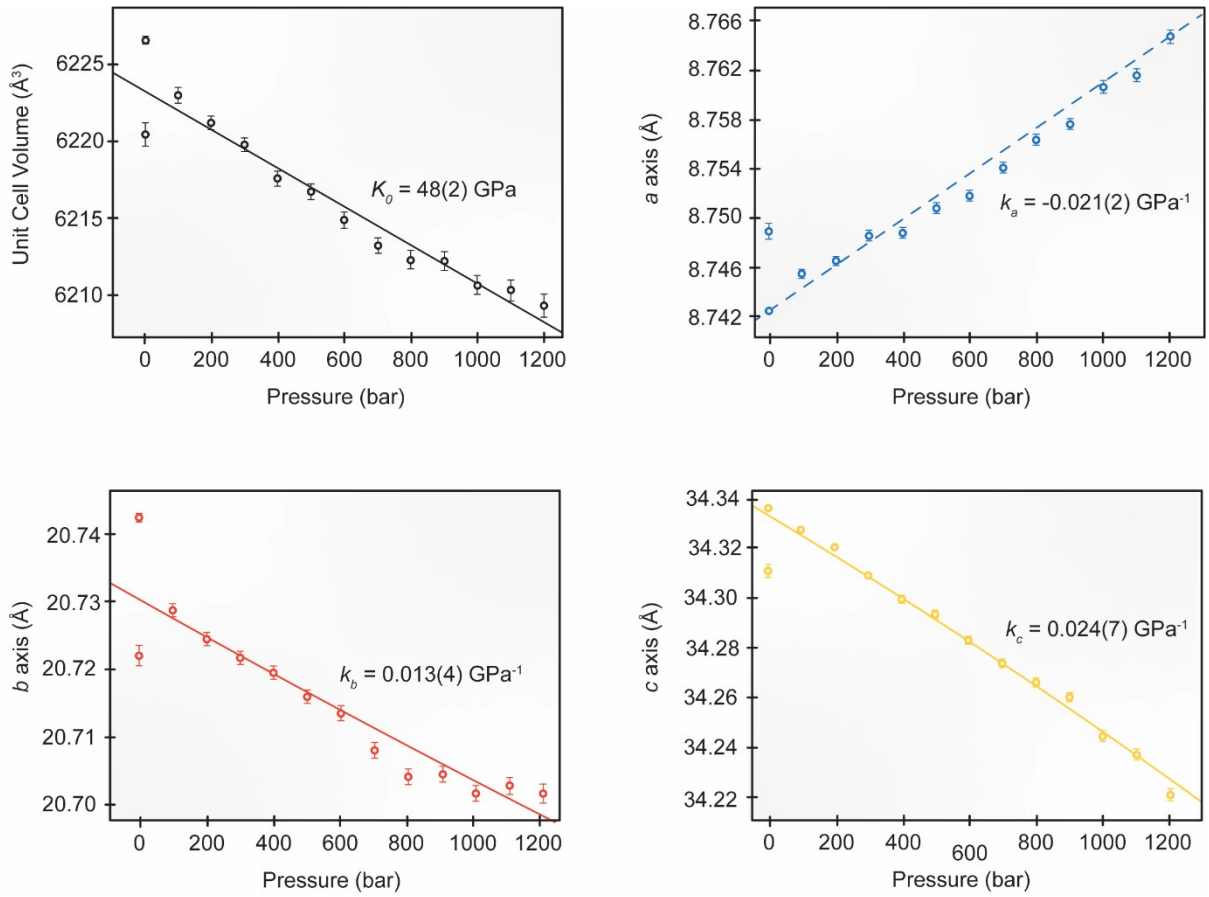


Figure S4. Unit cell parameters of Sc_2BDC_3 during compression in a PTM of isopentane. Third-order Birch-Murnaghan fits from EoSFit7[5] are shown as solid lines, and the bulk modulus, K_0, and linear compressibility, k_0, is overlaid. The compressibility of the *a*-axis was derived from a linear fit (dashed line).

S4. Pore Contents Calculated using PLATON SQUEEZE

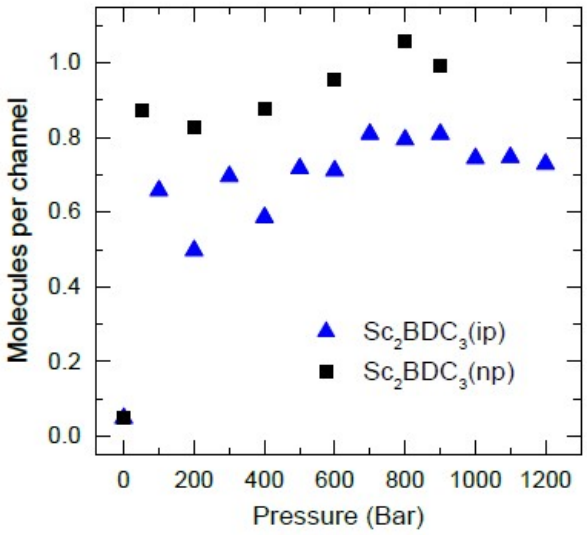
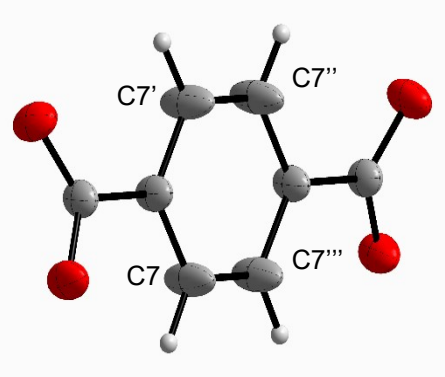


Figure S5. Quantity of *n*-pentane (black squares) or isopentane (blue triangles) per channel of Sc_2BDC_3 during compression in a PTM of *n*-pentane or isopentane.

S5. Libration of the Group 2 BDC Phenyl Ligand



Atom	Symmetry
C7	x, y, z
C7'	0.25-x, y, 1.25-z
C7''	0.25-x, 1.25-y, z
C7'''	x, 1.25-y, 1.25-z

Figure S6. Group-2 BDC linker with C7 and its symmetry equivalents.

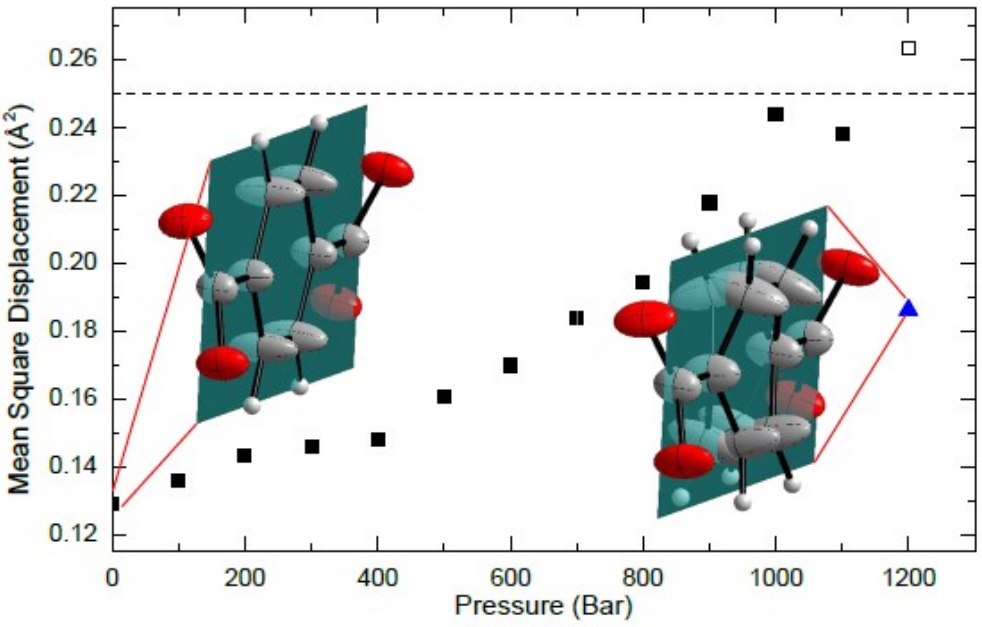


Figure S7. Magnitude of the principle ADP axis length of the carbon atom C7 as a function of pressure for Sc_2BDC_3(*ip*) as an un-split model (black squares), and as a 50:50 split model (blue triangles). Open square at 1200 bar exceeds 0.25 Å^3, and so a split model is used. Inserts of the Group 2 BDC linker at ambient pressure (left) and as a split model at 1200 bar (right) are overlaid. Both inserts show non-hydrogen atoms with 50 % probability ellipsoids and the (001) plane is shown in green.

References

1 C. J. McMonagle, D. R. Allan, M. R. Warren, K. V. Kamenev, G. F. Turner and S. A. Moggach, *J. Appl. Cryst.*, 2020, **53**, 1519-1523 (reference 22 in main text)
2 CrysAlis Pro, Agilent Technologies Ltd., Yarton, England, 2017
3 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Cryst.*, 2003, **36**, 1487 (reference 23 in main text)
4 A. L. Spek, *Acta Cryst*, 2015, **C71**, 9-18 (reference 24 in main text)
5 J. Gonzalez-Platas, M. Alvaro, F. Nestola and R. Angel., *J. Appl. Cryst.*, 2016, **49**, 1377-1382 (reference 26 in main text)
6 K. W. Chapman, G. J. Halder, and P. J. Chupas., *J. Am. Chem. Soc.,* 2008, **130**, 10524–10526.
7 L. R. Redfern, L. Robison, M. C. Wasson, S. Goswami, J. Lyu, T. Islamoglu, K. Chapman and O. K. Farha., *J. Am. Chem. Soc.,* 2019, **141**, 4365-4371.
8 J. Sotelo, PhD thesis, University of Edinburgh, 2016. (reference 27 in main text)