

Supporting Information

Multi-stimulus negative linear expansion of a breathing

M(O₂CR)₄-node MOF

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S1. General Methods and Techniques

Reagents and solvents were obtained from Sigma-Aldrich, Alfa Aesar, Acros Organics, Fisher Scientific, Fluorochem or Manchester Organics, and were used without additional purification.

Samples used for elemental analysis, thermogravimetric analysis, volumetric adsorption and in-house powder X-ray diffraction were ground into a powder using a mortar and pestle immediately prior to analysis, to ensure consistency of solvent content in the bulk material across different measurements. For solution-phase NMR spectroscopy, the sample (*ca.* 3 mg) was acid-digested in 50 μ L deuterium chloride (35 % in D₂O) in 1 mL DMSO-d₆.

Thermogravimetric analysis (Figure S4) was performed in air using a Perkin Elmer Pyris1 Thermogravimetric Analyser. Elemental analysis was performed by combustion in pure oxygen using a Perkin Elmer 24000 CHNS/O Series II Analyser or an Elementar Vario MICRO cube analyser. NMR spectroscopy (400 MHz) was performed using Bruker AVANCE III 400 HD or AVANCE 400 HD Spectrometers and analysed using MestReNova.

Laboratory single-crystal X-ray diffraction experiments (SCXRD) were performed using either a Bruker X8 APEX-II CCD diffractometer with SMART or KAPPA platform, with a Mo-K α sealed-

tube X-ray source, or a Bruker D8 Venture diffractometer with a PHOTON 100 dual-CMOS chip detector, operating a Cu-K α I μ S microfocus X-ray source. Data were processed using the APEX-3 suite of programs.^{S1} Sample temperature was maintained using an Oxford Cryosystems Cryostream 700 or CryostreamPlus 700 device. Samples were mounted directly from the mother liquor, unless stated otherwise. Absorption correction was performed using empirical methods (SADABS) based on symmetry-equivalent reflections combined with measurements at different azimuthal angles.^{S1,S2} Synchrotron single-crystal X-ray diffraction data were recorded at Beamline I19, Diamond Light Source. The crystal was carefully glued to a Mylar loop, ensuring minimum coverage of the crystal with glue, and loaded into a 0.7 mm quartz capillary built into a gas cell to allow CO $_2$ uptake. A minimum of one hemisphere of data was collected using three 132 $^\circ$ and one 180 $^\circ$ omega scans, with 0.4 $^\circ$ slicing, on a Newport diffractometer using a Pilatus 300K detector.^{S4} Data processing and absorption correction was performed using Rigaku Oxford Diffraction CrysAlis Pro.^{S5} Crystal structures were solved, and refined against F^2 values the program SHELX 2013^{S6} implemented via OLEX-2.^{S7} All non-hydrogen atoms were refined anisotropically except for some of the structures in which positional disorder of the cations or orientational disorder of the linker ligand was required. Crystallographic restraints and constraints were applied to some structures where necessary. Positions of hydrogen atoms were calculated with idealised geometries and refined using a riding model with isotropic displacement parameters. The *PLATON* function *SQUEEZE*^{S8} in some cases was applied to determine the contribution to the structure factors of the unmodelled electron density of solvent molecules and/or the cations in the MOF pores, where otherwise poor convergence of the least-squares refinement resulted. The equations below define the measures of agreement between calculated and observed structure factors:

$$R1(F) = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|} \quad wR2(F^2) = \sqrt{\frac{\sum(F_o^2 - F_c^2)^2}{\sum w F_o^4}} \quad S(F^2) = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{(n+r-p)}}$$

Laboratory powder X-ray diffraction (PXRD) experiments were performed using a Bruker D8 Advance, equipped with Göbel mirrors and recorded in the range 3 $^\circ$ < 2 θ < 60 $^\circ$ using Cu-K α radiation. Data collection was performed with Debye-Scherrer geometry, with a rotating capillary stage. Samples were loaded in 0.7 mm borosilicate capillaries. Temperature was either ambient (routine collections), or controlled using an Oxford Cryosystems Cryostream Plus device. Synchrotron powder X-ray diffraction data were collected at Beamline I11, Diamond Light Source using a wide-angle position sensitive detector comprising 18 Mythen-2 modules.^{S9,S10} Samples were packed into 0.7 mm quartz capillaries, built into a gas rig to allow sample evacuation and CO $_2$ uptake. A pair of scans was collected for each measurement, related by a 0.25 $^\circ$ detector offset, to account for gaps between modules. At each gas pressure four such pairs of patterns were summed to give the final pattern used for analysis. All powder diffraction data were analysed by Pawley refinement,^{S11} using TOPAS 4.1.^{S12-S14} The equations below define R_{wp} and R_{wp}' , the indices of agreement between calculated and experimental diffraction patterns:

$$R_{wp} = \sqrt{\frac{\sum[w(Y_{obs} - Y_{calc})^2]}{\sum[wY_{obs}^2]}} \quad R_{wp}' = \sqrt{\frac{\sum[w(Y_{obs} - Y_{calc})^2]}{\sum[w(Y_{obs} - bkg)^2]}}$$

S2. Synthesis and Characterisation

Cadmium nitrate hexahydrate (0.3072 g, 0.9926 mmol), 2-nitroterephthalic acid (0.4210 g, 1.994 mmol), dimethylamine hydrochloride (0.0080 g, 98 μ mol) and *N,N*-dimethylformamide (DMF) (10 mL) were stirred for *ca.* 5 mins (until dissolution of the solids) in a 23 mL Teflon vessel. The Teflon vessel was then sealed inside a stainless steel autoclave, heated to 130 $^\circ$ C at a rate of 1 $^\circ$ C min $^{-1}$ and held at 130 $^\circ$ C for 24 hours. The vessel was then cooled to room temperature at a rate of 0.1 $^\circ$ C min $^{-1}$

and the product (orange crystalline needles; 0.5621 g, 0.7381 mmol, 74 %) washed with DMF and stored under DMF. Expected: C, 40.16 %; H, 4.73 %; N, 10.75 %. Found: C, 40.16 %; H, 4.74 %; N, 10.74 %. Yield and expected elemental analysis results calculated using the formula:

[NMe₂H₂]₂[Cd(NO₂BDC)₂·2DMF·0.5H₂O (SHF-81-DMF). The product was characterised by PXRD, SCXRD, TGA and, after acid digestion, by solution-phase ¹H and ¹³C NMR spectroscopy.

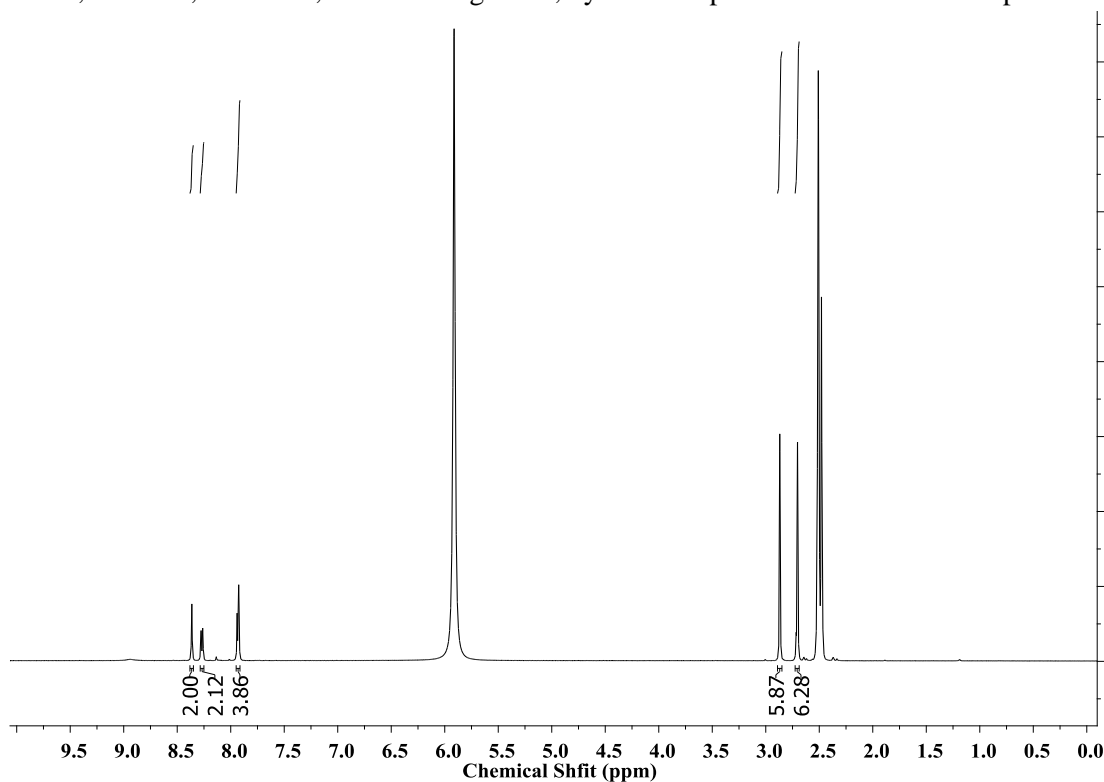


Figure S1. ¹H NMR spectrum of **SHF-81-DMF** following acid digestion. The aromatic region is expanded and assigned in Figure S2. The peak at 2.5 ppm is DMSO; the peak at *ca.* 2.45 ppm is (CH₃)₂NH₂⁺; the peak at *ca.* 5.8 ppm is H₂O/H₃O⁺. The DMF peaks can be seen at 7.5 ppm (formyl proton), 2.8 ppm (methyl) and 2.7 ppm (methyl).

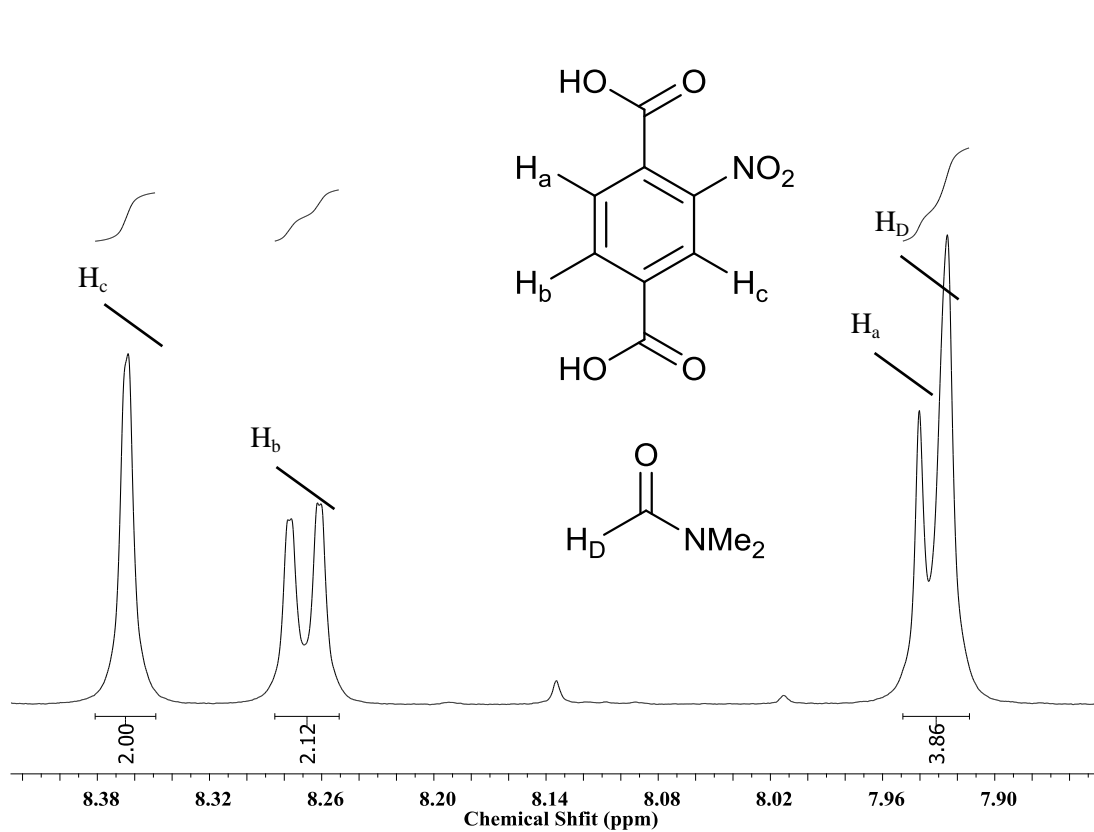


Figure S2. Expanded range of the aromatic region of the solution-phase ^1H NMR spectrum SHF-81-DMF following acid digestion.

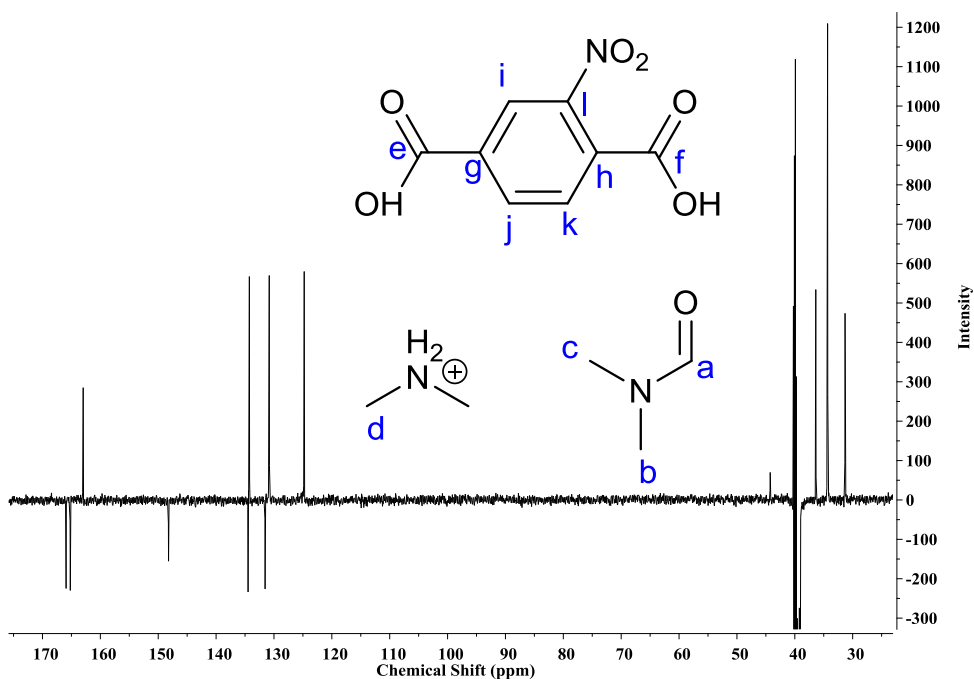


Figure S3. Solution-phase ^{13}C NMR DEPTQ-135 spectrum of acid-digested SHF-81-DMF. Assignment as follows: 166 ppm, f; 165.2 ppm, e; 163 ppm, a; 148.2 ppm, i; 134.5 ppm, h; 134.2 ppm, j; 131.5 ppm, g; 130.8 ppm, k; 124.7 ppm, b; 39.7 ppm, DMSO; 36.4 ppm, d; 34.3 ppm, c; 31.3 ppm, a.

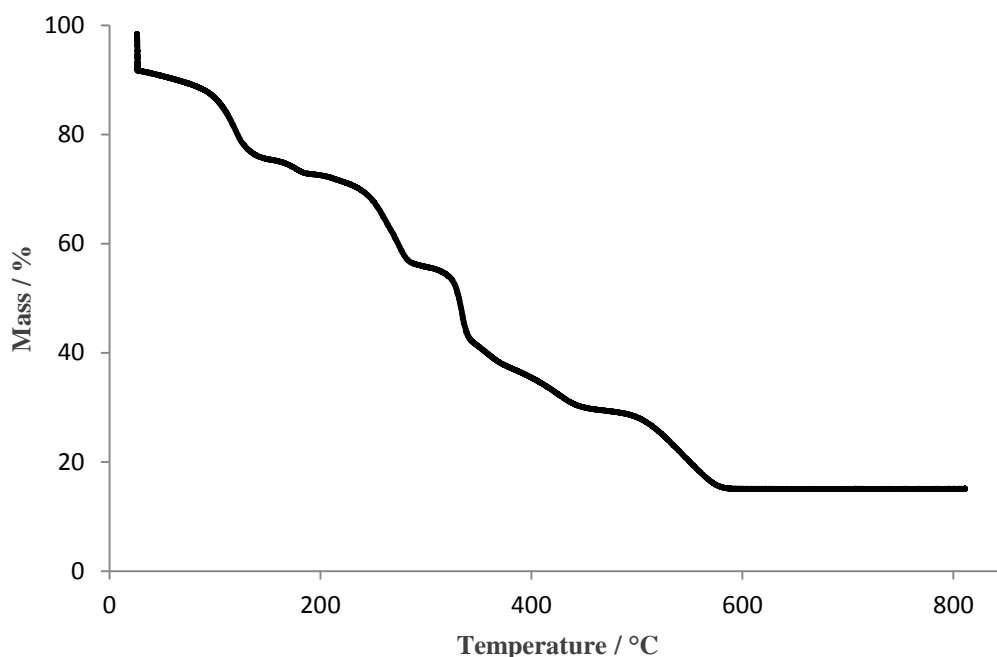


Figure S4. Thermogravimetric analysis of **SHF-81-DMF**. Sample (5 mg) was loaded into a pan, held at ambient temperature for 10 minutes prior to heating to allow the loss of surface-bound solvent, then heated in air from 25 °C to 800 °C at a rate of 3 °C min⁻¹.

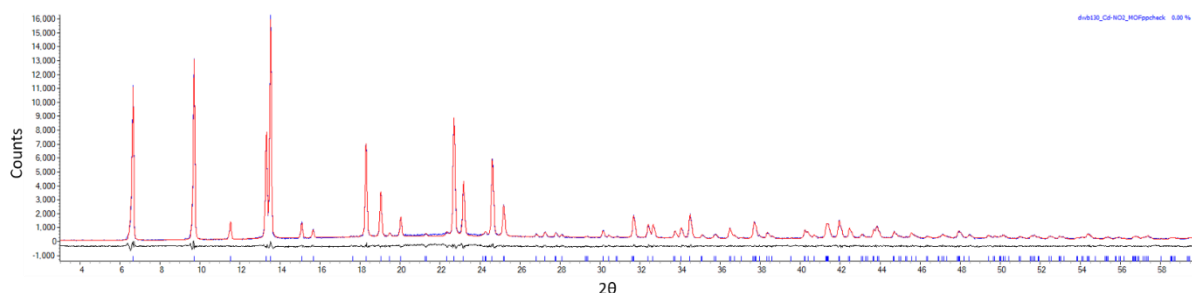


Figure S5. Observed (blue) and calculated (red) profiles and difference plot [$I_{\text{obs}} - I_{\text{calc}}$] (grey) for Pawley^{S11} refinement of PXRD data for **SHF-81-DMF** at room temperature (2θ range 3.0 – 60.0 °, $d_{\text{min}} = 1.54\text{\AA}$). Pawley fit: trigonal, $P3_121$; $a = 15.2736(2)\text{\AA}$; $c = 12.5538(3)\text{\AA}$; $V = 2536.23(10)\text{\AA}^3$; $R_{\text{wp}} = 0.0502$; $R_{\text{wp}}^2 = 0.0836$; 191 parameters used in refinement (8 background, 1 zero error, 5 profile, 2 cell and 175 reflections).

Table S1. Crystal structure data for solvated **SHF-81-DMF** at 100 K (A_1 = trigonal solution; A_2 = hexagonal solution), and at 195 K (B).

	A_1	A_2	B
Crystal Size / mm	0.5 x 0.2 x 0.2	0.5 x 0.2 x 0.2	0.5 x 0.3 x 0.3
Crystal System	Trigonal	Hexagonal	Trigonal
Space Group	$P3_221$	$P6_222$	$P3_221$
$a / \text{\AA}$	14.8922(7)	14.8917(7)	15.0467(5)
$b / \text{\AA}$	14.8922(7)	14.8917(7)	15.0467(5)
$c / \text{\AA}$	12.7663(6)	12.7663(6)	12.6619(4)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
$V / \text{\AA}^3$	2452.0(3)	2451.8(3)	2482.63(18)
Z	3	3	3

Radiation	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)	Mo-K α ($\lambda = 0.71073 \text{ \AA}$)	Cu- K α ($\lambda = 1.54178 \text{ \AA}$)
Density / g cm $^{-3}$	1.265	1.078	1.250
Temperature /K	100	100	195
μ / mm $^{-1}$	0.721	0.709	5.758
2 θ range ($^\circ$)	3.158 – 50.028	5.472 – 55.794	6.784 – 133.384
Reflns collected	18166	22642	41893
Independent reflns	2896	1965	2919
Reflns used in refinement, n	2896	1965	2919
L.S. parameters, p	157	55	157
No. of restraints, r	275	11	162
Flack parameter	0.005(18)	0.05(2)	0.028(6)
R_{int}	0.0514	0.0642	0.0384
R_{sigma}	0.0339	0.0318	0.0184
$R1(F)^a$ $I > 2\sigma(I)$	0.0449	0.0574	0.0345
$wR2(F^2)^a$, all data	0.1389	0.1847	0.1054
$S(F^2)^a$, all data	1.168	1.089	1.176

^a $R1(F)$, $wR2(F^2)$ and $S(F^2)$ defined in section S1.

S3. Activation/Desolvation

Solvent removal was performed on bulk-phase **SHF-81-DMF** by vacuum filtering the crystals from the mother liquor, grinding to a fine powder, and subsequently heating the powdered sample at 80 °C under vacuum for ≥ 16 hours using standard Schlenk techniques to generate activated/desolvated **SHF-81**. The desolvated material was characterised by PXRD, SCXRD and, after acid digestion, by solution-phase ^1H NMR spectroscopy.

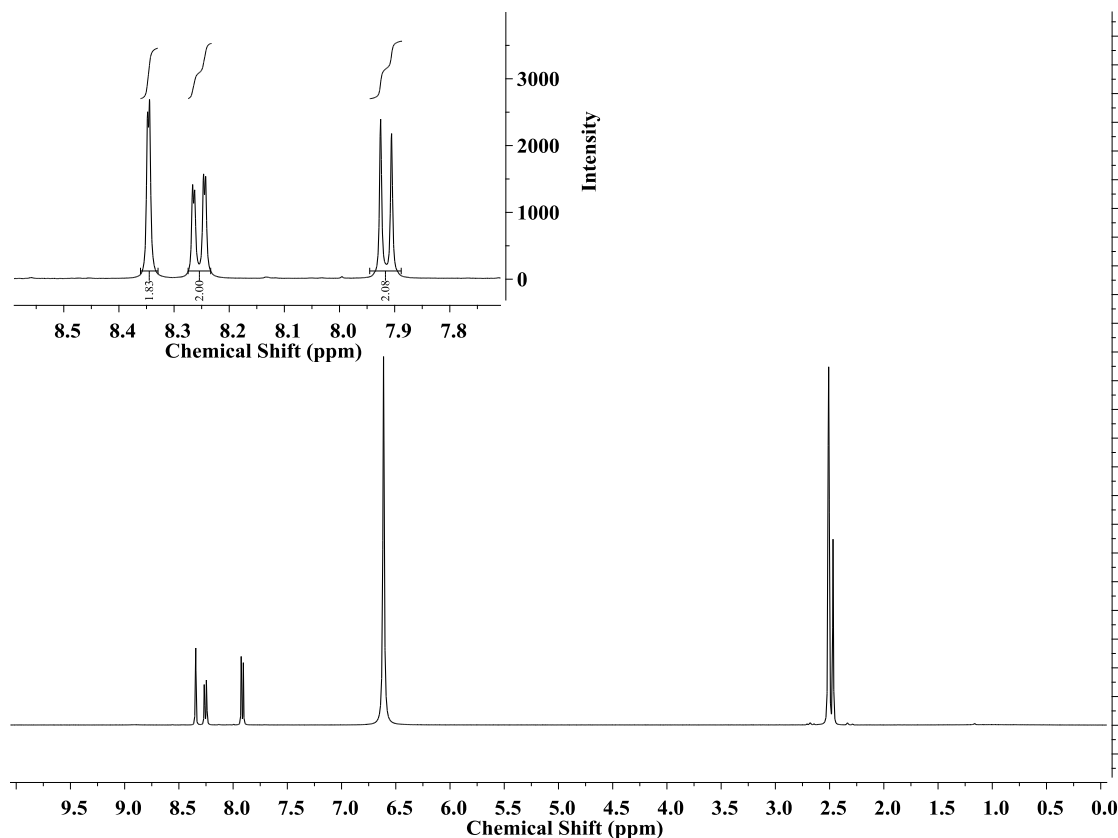


Figure S6. ^1H NMR of desolvated **SHF-81** after acid-digestion. The aromatic region is expanded in the inset. The peak at 2.5 ppm is DMSO; the peak at *ca.* 2.45 ppm is Me_2NH_2^+ ; and the peak at *ca.* 6.6 ppm $\text{H}_2\text{O}/\text{H}_3\text{O}^+$.

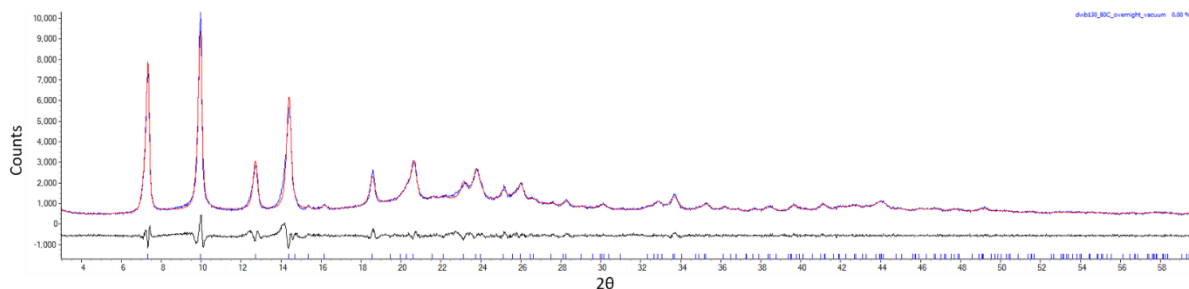


Figure S7. Observed (blue) and calculated (red) profiles and difference plot [$I_{\text{obs}} - I_{\text{calc}}$] (grey) for Pawley^{S10} refinement of PXRD data for **SHF-81** at room temperature (2θ range $3.0 - 60.0^\circ$, $d_{\text{min}} = 1.54\text{\AA}$). Pawley fit: trigonal, $P3_121$; $a = 13.931(2)\text{\AA}$; $c = 13.148(3)\text{\AA}$; $V = 2209.6(9)\text{\AA}^3$; $R_{\text{wp}} = 0.0592$; $R_{\text{wp}}' = 0.1298$; 191 parameters used in refinement (16 background, 1 zero error, 5 profile, 2 unit cell and 167 reflections).

Two single crystals of **SHF-81-DMF** were desolvated by heating at 100°C for 1 hour, in a temperature-controlled oven and the crystal structure of the resulting **SHF-81** was determined by single-crystal X-ray diffraction at 100 K and 195 K (Table S2).

Table S2. Crystal Structure Data Table for desolvated **SHF-81** at 100 K (**C**) and 195 K (**D**).

	C	D
Crystal Size / mm	0.36 x 0.18 x 0.18	0.1 x 0.1 x 0.1
Crystal System	Trigonal	Trigonal
Space Group	$P3_121$	$P3_121$
$a / \text{\AA}$	13.619(1)	13.7702(3)
$b / \text{\AA}$	13.619(1)	13.7702(3)
$c / \text{\AA}$	13.229(1)	13.2048(3)
$\alpha (^\circ)$	90	90
$\beta (^\circ)$	90	90
$\gamma (^\circ)$	120	120
$V / \text{\AA}^3$	2124.9(5)	2168.4(1)
Z	3	3
Radiation	Cu-K α ($\lambda = 1.54178\text{\AA}$)	Mo-K α ($\lambda = 0.71073\text{\AA}$)
Density / g cm $^{-3}$	1.460	1.431
Temperature /K	100	195
μ / mm^{-1}	6.728	0.815
2θ range ($^\circ$)	6.682 – 133.35	3.084 – 54.212
Reflns collected	71934	24159
Independent reflns	2516	3203
Reflns used in refinement, n	2516	3203
L.S. parameters, p	132	157
No. of restraints, r	50	125
Flack parameter	0.031(5)	0.05(2)
R_{int}	0.0511	0.1104
R_{sigma}	0.0125	0.0725
$R1(F)^a$ $I > 2\sigma(I)$	0.0483	0.0630
$wR2(F^2)^a$, all data	0.1374	0.1716
$S(F^2)^a$, all data	1.172	1.046

^a $R1(F)$, $wR2(F^2)$ and $S(F^2)$ defined in section S1.

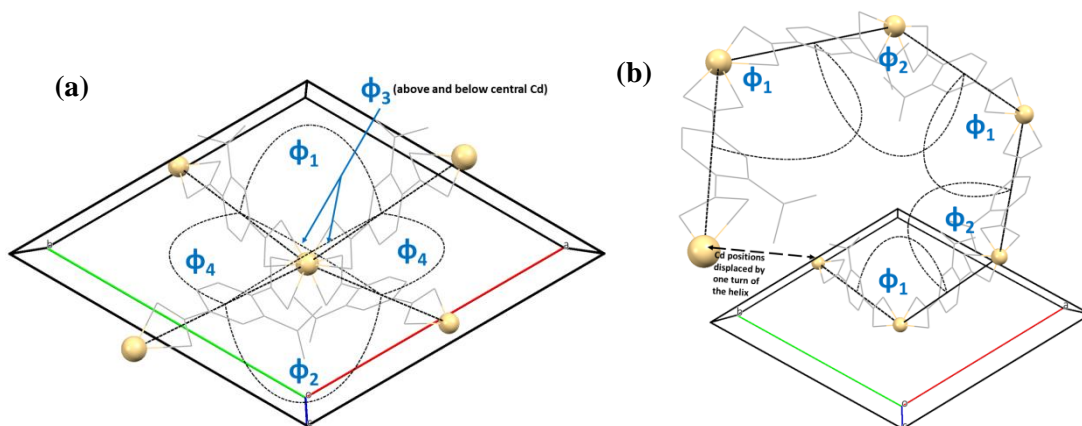


Figure S8. (a) The six Cd...Cd...Cd angles (ϕ_1 , ϕ_2 , $\phi_3(x2)$, $\phi_4(x2)$) subtended at each tetrahedral network node (Cd); (b) angles ϕ_1 and ϕ_2 , and their relation to the pore shape. Upon activation/desolvation of **SHF-81-DMF** to give **SHF-81**, angle ϕ_1 decreases and the Cd atom at its apex moves away from the channel centre; the Cd atom at the apex of angle ϕ_2 moves towards to the channel centre as angle ϕ_2 increases.

In situ Desolvation

An *in situ* single-crystal X-ray diffraction desolvation study was carried out using a laboratory diffractometer with the following procedure. A single crystal was allowed to dry (in air, from mother liquor) on a glass slide, and subsequently attached with two-part epoxy resin to a glass fibre, viewed using a light microscope. The crystal was then mounted on the diffractometer in a temperature-controlled nitrogen stream at 298 K. A short sequence of scans, sufficient for accurate determination of the orientation matrix and unit cell parameters (such scans subsequently referred to as “matrix scans”) were recorded, and the temperature increased to 313 K and held for 30 minutes. The temperature was then reduced to 298 K, and a set of matrix scans recorded after a 5-minute equilibration time. This cycle was repeated for the temperatures 333 K, 353 K, 373 K, 393 K, 413 K and 433 K.

Table S3. Unit cell parameters obtained from *in situ* desolvation study with single-crystal X-ray diffraction.

Temperature ^a / K	a / Å	c / Å	V / Å ³
298	15.144(3)	12.638(3)	2510.0(6)
313	15.069(3)	12.682(3)	2494.0(6)
333	14.932(17)	12.762(12)	2464(4)
353	14.232(18)	13.051(15)	2289(4)
373	14.202(10)	13.076(7)	2284(2)
393	14.122(6)	13.105(4)	2264(1)
413	14.058(8)	13.102(6)	2242(2)

^a All data were collected at 298 K. The temperature listed refers that to which the material was heated to prior to data collection. Equilibration at 298 K for 5 mins preceded all data collections.

An *in situ* laboratory powder X-ray diffraction desolvation study was performed using the following method. The powdered sample was packed into a 0.7 mm borosilicate capillary and a diffraction pattern recorded at 298 K. The temperature was then raised to 313 K and held for 30 minutes, before being lowered to 298 K. A second diffraction pattern was then recorded at 298 K after a 5-minute equilibration time. Subsequent cycles were performed at temperatures of 333 K, 353 K, 373 K, 393 K, 413 K and 433 K. A heating/cooling rate of 4 K min⁻¹ was used throughout. A 5-minute equilibration time preceded all measurements.

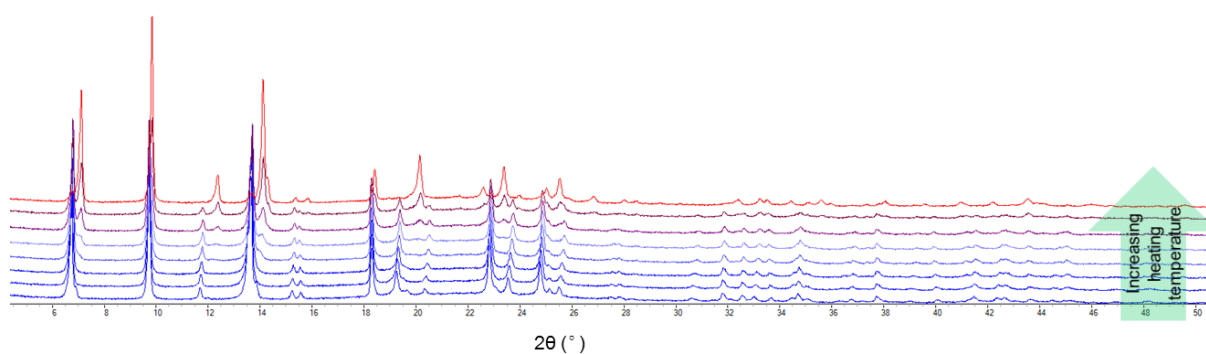


Figure S9. Powder X-ray diffraction patterns obtained during *in situ* desolvation study of **SHF-81-DMF** ($\lambda = 1.54178 \text{ \AA}$), presented in ascending order; *i.e.* bottom pattern is first measurement (298 K, no heating, top pattern is final measurement (298 K, after heating to 433 K). Details of Pawley refinements are provided in Tables S4 and S5.

Table S4. Unit cell parameters from Pawley refinement to fit the data from *in situ* powder diffraction desolvation experiment.

Temp. ^a / K	R_{wp}	R_{wp}'		$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
298	0.0650	0.1632		15.1241(8)	12.6216(8)	2500.3(3)
313	0.0566	0.1401		15.0963(7)	12.6371(7)	2494.1(3)
333	0.0539	0.1351		15.0606(5)	12.6589(6)	2486.6(2)
353	0.0438	0.1009	Phase 1	15.0235(6)	12.6846(6)	2479.4(2)
			Phase 2	14.511(6)	12.996(7)	2370(2)
373	0.0459	0.1045	Phase 1	14.9980(7)	12.7000(6)	2474.0(3)
			Phase 2	14.429(3)	12.997(6)	2343(1)
393	0.0458	0.0767	Phase 1	14.9890(8)	12.7046(7)	2471.9(3)

			Phase 2	14.327(2)	13.039(4)	2318(1)
413	0.0593	0.1232	Phase 1	14.978(1)	12.692(1)	2465.9(5)
			Phase 2	14.279(2)	13.031(2)	2300.9(7)
433	0.0776	0.1892		14.306(1)	13.026(1)	2309.0(4)

^a All data were collected at 298 K. The temperature listed refers that to which the material was heated to prior to data collection. Equilibration at 298 K for 5 mins preceded all data collections.

Table S5. Pawley refinement parameters^a for patterns in *in situ* activation/desolvation study presented in Figure S9 and Table S4.

Temp. ^b / K	R_{wp}	R_{wp}'	No. of parameters			
			Background	Profile	Unit Cell	Reflections
298	0.0650	0.1632	14	5	2	174
313	0.0566	0.1401	14	5	2	174
333	0.0539	0.1351	13	5	2	173
353 ^c	0.0438	0.1009	12	9	4	342
373 ^c	0.0459	0.1045	14	9	4	339
393 ^c	0.0458	0.0767	14	9	4	339
413 ^c	0.0593	0.1232	11	9	4	279
433	0.0776	0.01892	14	5	2	169

^a All patterns fitted to a hexagonal lattice (trigonal $P3_121$) and used 1 zero-point-error parameter. ^b All data were collected at 298 K. The temperature listed refers that to which the material was heated to prior to data collection. ^c Two-phase Pawley fit.

S4. Gas Adsorption

Volumetric gas adsorption was performed on a Micromeritics ASAP 2020Plus Analyser. The bulk-phase sample (*ca.* 100 mg) was desolvated at 80 °C under vacuum overnight (*ca.* 16 hours) using standard Schlenk techniques, transferred to the analyser and degassed for a further 16 hours under vacuum at 80 °C prior to analysis. Nitrogen uptake was performed at 77 K using a liquid N₂ bath for temperature control.

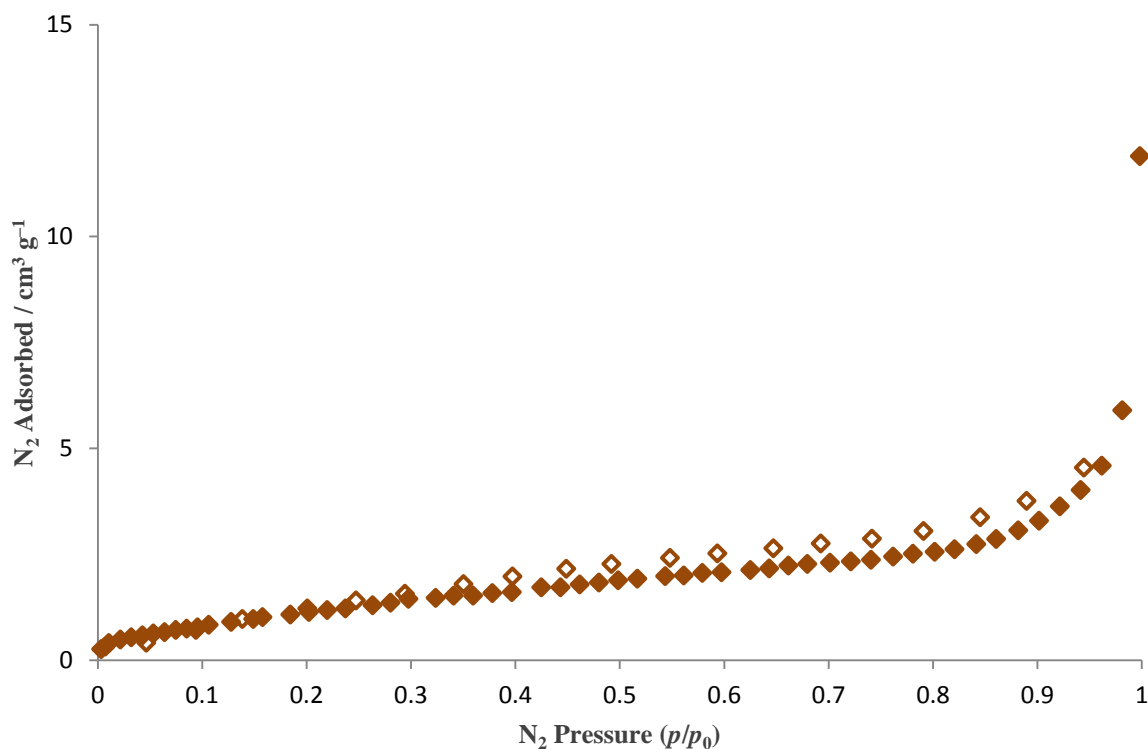


Figure S10. Volumetric N₂ adsorption (filled markers) and desorption (hollow markers) isotherms for **SHF-81** at 77 K.

Gravimetric CO₂ adsorption measurements were made using an Intelligent Gravimetric Analyser (*IGA-300*) supplied by Hiden Isochema Ltd, which was thermally regulated via active computer control. A computer algorithm was applied to monitor the approach to equilibrium at each pressure step. Prior to measurements, the sample was activated at room temperature under ultra-high vacuum (10⁻⁸ bar) until constant mass was attained. Adsorption isotherms for CO₂ were measured at 273, 288 and 298 K (Figure S11) and used to determine the isosteric enthalpy of adsorption (Figure S12).

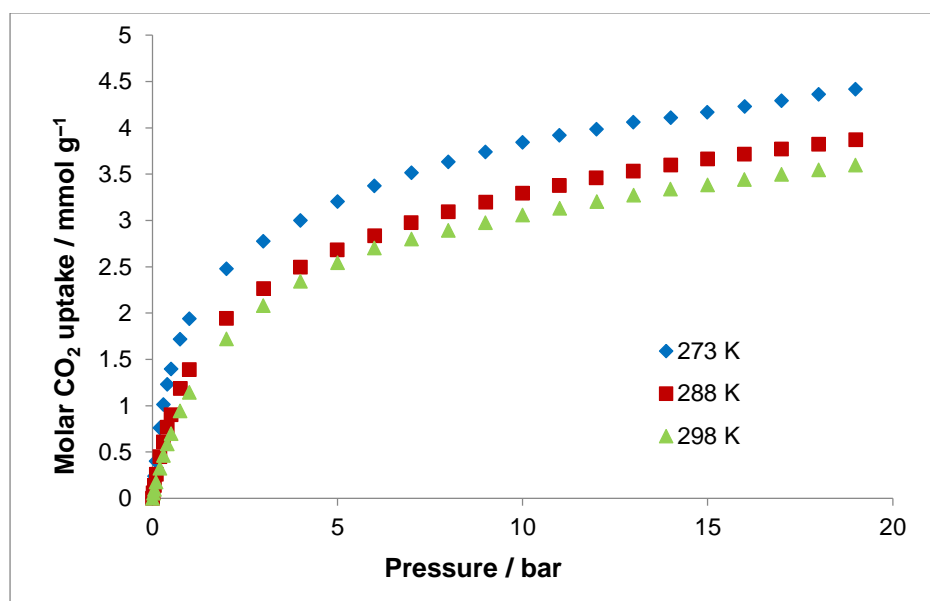


Figure S11. Gravimetric CO₂ adsorption isotherms at 273, 288 and 298 K for **SHF-81** (activated from **SHF-81-DMF**). See also Figure 6 for analogous plot showing adsorption as a function of p/p_0 .

Calculation of enthalpies of adsorption for CO₂ uptake by SHF-81

Enthalpies of adsorption were determined using the van't Hoff isochore, which is found from the Clapeyron equation:

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T\Delta V_{vap}}$$

together with the fact that $V_{(g)} \gg V_{(l)}$ at STP, then from gas ideality, ΔV_{vap} can be replaced by RT/p . Rearranging the equation and assuming that ΔH is temperature independent it follows that:

$$\ln p = \frac{-\Delta H_{vap}}{RT} + \frac{\Delta S}{R}.$$

A plot of $\ln(p)$ against $1/T$ at fixed surface coverage should give a straight line with a gradient that yields the isosteric enthalpy of adsorption ($-\Delta H_{vap}/R$) and an intercept equal to the entropy of adsorption ($\Delta S/R$).

Analysis of data obtained for CO₂ adsorption at four temperatures (273 K, 288 K and 298 K) by **SHF-81**, activated from **SHF-81-DMF**, was performed. The data were interpolated between adsorption points and isochores taken at pre-selected molar uptakes. The isotherm (273 K) was chosen for analysis. A maximum of 9 enthalpies of adsorption could be determined. The trend of enthalpies is shown in Figure S12. The data obtained for the enthalpies of adsorption show a small amount of variation (-22.7 to -28.1 kJ/mol), and the trend for the early points allows extrapolation to an isosteric enthalpy of adsorption (i.e. adsorption at zero surface coverage) of -27.4 kJ/mol. It is noted that the heat of adsorption, $Q_{st} = -\Delta H_{vap}$ (or $-\Delta H_{ads}$).^{S15}

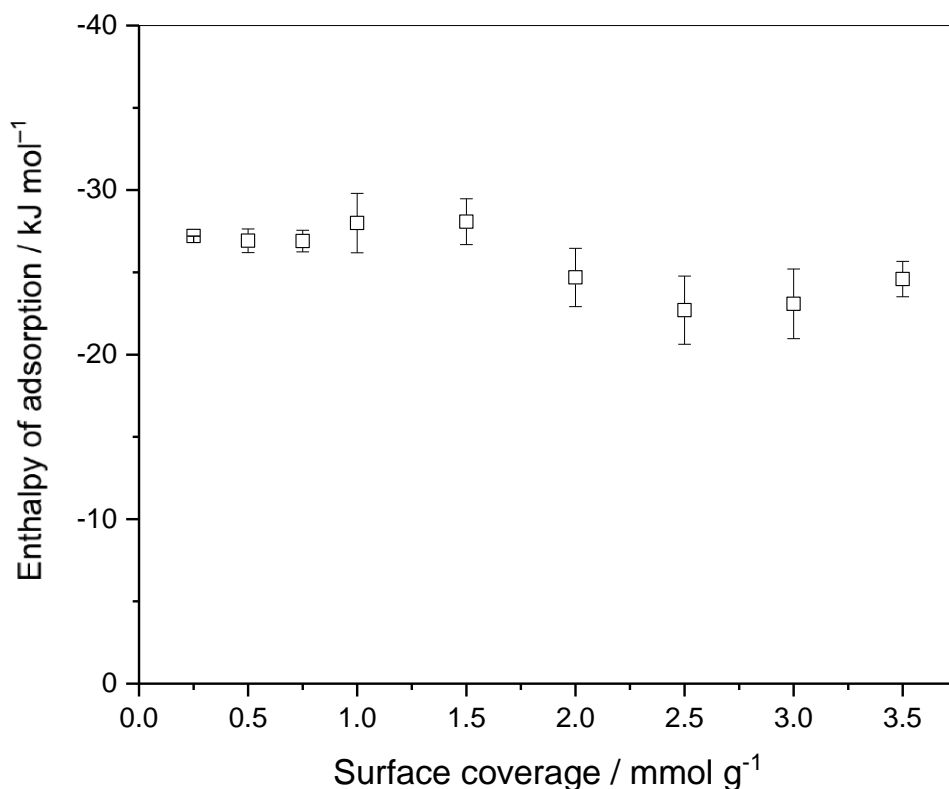


Figure S12. Calculated Enthalpies of CO₂ Adsorption for **SHF-81** (activated from **SHF-81-DMF**).

S5. Crystallographic Studies of Gas Sorption

For the *in situ* powder X-ray diffraction study during CO₂ uptake at 298 K, the sample was activated according to the procedure outlined in Section S3 for bulk-phase material. Afterwards, the material was removed from the Schlenk tube carefully under an argon atmosphere (generated by dynamic argon flow through an upturned funnel over the working area) and packed into a 0.7 mm quartz capillary, which was sealed with wax. The sample was stored in this manner during transport to Diamond Light Source, and the capillary loaded into a gas cell before the experiment.

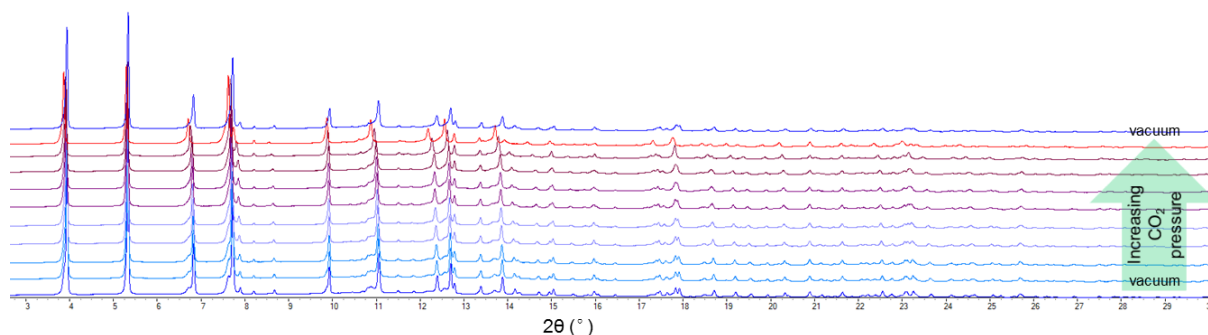


Figure S13. Powder patterns for the *in situ* PXRD study during CO₂ adsorption by **SHF-81** at 298 K, presented in ascending order; *i.e.* bottom pattern is first measurement (vacuum), top pattern is final measurement (vacuum, after CO₂ uptake and subsequent removal). Details of Pawley refinements are provided in Table S6.

Table S6. Pawley refinements^a and lattice parameters for *in situ* PXRD study during CO₂ adsorption by **SHF-81** at 298 K (patterns shown in Figure S13).

Pressure / bar	R_{wp}	R_{wp}'	Lattice Parameters		
			$a / \text{Å}$	$c / \text{Å}$	$V / \text{Å}^3$
0 (vacuum)	0.0994	0.2266	13.8276(4)	13.1535(6)	2178.0(2)
0.52	0.0962	0.2195	13.8407(6)	13.1501(9)	2181.6(2)
1.01	0.0926	0.2134	13.8536(4)	13.1465(5)	2185.1(2)
2.09	0.0884	0.2064	13.8683(4)	13.1426(6)	2189.0(2)
5.42	0.0847	0.1996	13.8854(4)	13.1382(6)	2193.7(2)
10.14	0.0815	0.1965	13.8995(5)	13.1340(6)	2197.5(2)
15.01	0.0790	0.1936	13.9092(5)	13.1308(6)	2200.0(2)
20.02	0.0751	0.1901	13.9201(5)	13.1260(6)	2202.7(2)
40.45	0.0701	0.1865	13.9843(5)	13.1073(6)	2219.9(2)

49.84	0.0721	0.2026	14.1024(6)	13.0718(7)	2251.4(2)
0 (vacuum)	0.0771	0.2046	13.8500(6)	13.1276(7)	2180.8(2)

^a For all Pawley fits: $\lambda = 0.824528 \text{ \AA}$; trigonal, $P3_121$; 14 background parameters; *ca.* 150 reflections; 1 zero-point-error parameter; 5 profile parameters; 2 unit cell parameters refined.

The *in situ* single-crystal X-ray diffraction study during CO₂ uptake was performed at beamline I19 at Diamond Light Source. A crystal was selected from the mother liquor, allowed to dry in air, and mounted using 2-part epoxy resin to a Mylar loop, which was then threaded into a quartz capillary fashioned into a gas cell. The gas cell was evacuated and the atmosphere replaced with pure nitrogen using standard Schlenk techniques. The cell was heated to 100 °C for two hours; during which time the atmosphere was evacuated and replaced with fresh pure nitrogen (3 purges) after one hour. At the end of the study, the atmosphere was again replaced with nitrogen and then subsequently removed by vacuum, before mounting the cell onto the diffractometer at the start of the experiment. A full set of diffraction data was then collected with the cell (and crystal) under vacuum. CO₂ gas was then introduced into the cell and the sample allowed to equilibrate at that pressure for 30 mins prior to collection of a full set of diffraction intensities. After each data collection the CO₂ pressure was increased, the sample equilibrated for 30 mins and a full set of diffraction intensities collected. Table S7 lists the crystal data tables for the final crystal structures at each pressure of CO₂.

Table S7. Crystal data for *in situ* SCXRD study during CO₂ uptake by **SHF-81** at 298 K. (E0 = vacuum; E1 = 1 bar CO₂; E2 = 5 bar CO₂; E3 = 10 bar CO₂; E4 = 20 bar CO₂; E5 = 40 bar CO₂).

	E0	E1	E2
Crystal Size / mm ³	0.20 x 0.13 x 0.13	0.20 x 0.13 x 0.13	0.20 x 0.13 x 0.13
Crystal System	Trigonal	Trigonal	Trigonal
Space Group	$P3_121$	$P3_121$	$P3_121$
$a / \text{\AA}$	13.9484(7)	13.9775(9)	14.0982(10)
$b / \text{\AA}$	13.9484(7)	13.9775(9)	14.0982(10)
$c / \text{\AA}$	13.1157(4)	13.0994(5)	13.0538(6)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
$V / \text{\AA}^3$	2209.9(2)	2216.4(3)	2247.0(3)
Z	3	3	3
Radiation	$\lambda = 0.6889 \text{ \AA}$	$\lambda = 0.6889 \text{ \AA}$	$\lambda = 0.6889 \text{ \AA}$
Density / g cm ⁻³	1.404	1.400	1.381
Temperature /K	298	298	298
μ / mm^{-1}	0.741	0.739	0.729
2 θ range (°)	3.01 – 59.88	3.014 – 59.892	3.024 – 59.884
Reflns collected	31932	31828	32158
Independent reflns	4705	4713	4766
Reflns used in refinement, n	4705	4713	4766
L.S. parameters, p	157	157	157
No. of restraints, r	129	129	129
Flack Parameter	-0.011(19)	0.00(2)	0.01(2)
R_{int}	0.0613	0.0668	0.0729
R_{sigma}	0.0375	0.0423	0.0483
$R1(F)^a \text{ } I > 2\sigma(I)$	0.0542	0.0661	0.0748

$wR2(F^2)^a$, all data	0.1676	0.2159	0.2451
$S(F^2)^a$, all data	1.007	1.031	1.031

^a $R1(F)$, $wR2(F^2)$ and $S(F^2)$ defined in section S1.

	E3	E4	E5
Crystal Size / mm ³	0.20 x 0.13 x 0.13	0.20 x 0.13 x 0.13	0.20 x 0.13 x 0.13
Crystal System	Trigonal	Trigonal	Trigonal
Space Group	$P3_121$	$P3_121$	$P3_121$
$a / \text{\AA}$	14.2180(12)	14.366(3)	14.515(3)
$b / \text{\AA}$	14.2180(12)	14.366(3)	14.515(3)
$c / \text{\AA}$	13.0014(6)	12.8607(10)	12.8247(10)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
$V / \text{\AA}^3$	2276.1(4)	2298.5(8)	2340.0(9)
Z	3	3	3
Radiation	$\lambda = 0.6889 \text{ \AA}$	$\lambda = 0.6889 \text{ \AA}$	$\lambda = 0.6889 \text{ \AA}$
Density / g cm ⁻³	1.363	1.350	1.130
Temperature /K	298	298	298
μ / mm^{-1}	0.720	0.713	0.689
2 θ range (°)	3.206 – 59.884	4.416 – 40.292	4.398 – 40.29
Reflns collected	32634	14756	15010
Independent reflns	4844	1607	1645
Reflns used in refinement, n	4844	1607	1645
L.S. parameters, p	157	157	130
No. of restraints, r	129	179	289
Flack Parameter	0.02(3)	0.05(6)	0.04(4)
R_{int}	0.0830	0.1260	0.1075
R_{sigma}	0.0580	0.0506	0.0438
$R1(F)^a$ $I > 2\sigma(I)$	0.0851	0.1232	0.1069
$wR2(F^2)^a$, all data	0.2857	0.3602	0.3258
$S(F^2)^a$, all data	1.024	1.198	1.102

^a $R1(F)$, $wR2(F^2)$ and $S(F^2)$ defined in section S1.

S6. Variable-Temperature Crystallographic Studies (VT1 – VT5)

Study VT1: A single-crystal structure of **SHF-81-DMF** was determined at 170 K (**VT1-1**).

Additional data sets were collected on the same crystal, immediately afterwards, at 140 K (**VT1-2**) and 100 K (**VT1-3**).

Table S8. Crystal data for study **VT1**.

	VT1-1	VT1-2	VT1-3
Crystal Size / mm ³	0.2 x 0.15 x 0.15	0.2 x 0.15 x 0.15	0.2 x 0.15 x 0.15
Crystal System	Trigonal	Trigonal	Trigonal
Space Group	$P3_121$	$P3_121$	$P3_121$
$a / \text{\AA}$	14.9689(4)	14.9210(5)	14.8744(10)
$b / \text{\AA}$	14.9689(4)	14.9210(5)	14.8744(10)
$c / \text{\AA}$	12.6934(4)	12.7118(5)	12.7248(9)
α (°)	90	90	90
β (°)	90	90	90

γ (°)	120	120	120
$V / \text{\AA}^3$	2463.14(15)	2450.94(19)	2438.1(4)
Z	3	3	3
Radiation	Cu-K α ($\lambda = 1.54178 \text{ \AA}$)	Cu-K α ($\lambda = 1.54178 \text{ \AA}$)	Cu-K α ($\lambda = 1.54178 \text{ \AA}$)
Density / g cm $^{-3}$	1.073	1.079	1.084
Temperature /K	170	140	100
μ / mm^{-1}	5.717	5.745	5.775
2 θ range (°)	6.818 – 133.314	6.84 – 133.41	6.862 – 133.32
Reflns collected	33600	30993	32861
Independent reflns	2915	2901	2877
Reflns used in refinement, n	2915	2901	2877
L.S. parameters, p	130	130	130
No. of restraints, r	134	122	120
Flack Parameter	0.053(9)	0.066(8)	0.074(9)
R_{int}	0.0555	0.0574	0.0587
R_{sigma}	0.0240	0.0251	0.0247
$R1(F)^a$ $I > 2\sigma(I)$	0.0338	0.0336	0.0335
$wR2(F^2)^a$, all data	0.1096	0.1063	0.1047
$S(F^2)^a$, all data	1.062	1.075	1.069

^a $R1(F)$, $wR2(F^2)$ and $S(F^2)$ defined in section S1.

Study VT2: Sets of matrix scans were performed on a single crystal of **SHF-81-DMF** at successively lower temperatures between 160 K and 85 K. The unit cell parameters determined from these matrix scans are detailed in Table S9.

Table S9. Lattice parameters for study VT2.

Temperature / K	Lattice Parameters		
	$a / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
160	14.976(3)	12.6880(11)	2464.5(5)
130	14.927(3)	12.7089(14)	2452.5(6)
120	14.915(3)	12.7149(18)	2449.4(6)
110	14.903(3)	12.7193(16)	2446.4(6)
100	14.889(3)	12.7246(15)	2443.0(6)
90	14.881(3)	12.7273(15)	2441.0(6)
85	14.859(4)	12.7234(19)	2432.7(8)

Study VT3: Sets of matrix scans were performed on a single crystal of **SHF-81-DMF** at successively lower temperatures between 300 K and 90 K. The unit cell parameters determined from these matrix scans are detailed in Table S10.

Table S10. Lattice parameters for study **VT3**.

Temperature / K	Lattice Parameters		
	$a / \text{Å}$	$c / \text{Å}$	$V / \text{Å}^3$
300	15.166(4)	12.592(7)	2508.1(15)
280	15.041(3)	12.676(4)	2483.5(9)
260	14.988(2)	12.697(4)	2470.0(9)
240	14.935(2)	12.725(4)	2458.0(9)
220	14.883(2)	12.754(4)	2446.7(9)
200	14.836(2)	12.778(4)	2435.7(9)
180	14.787(2)	12.793(4)	2422.4(9)
160	14.750(2)	12.816(4)	2414.7(9)
140	14.716(2)	12.829(5)	2406.1(10)
120	14.686(3)	12.837(5)	2397.7(10)
100	14.666(3)	12.834(5)	2390.7(11)
90	14.650(3)	12.843(5)	2387.3(11)

Study VT4: Sets of matrix scans were performed on a single crystal of **SHF-81** (desolvated from **SHF-81-DMF** as described in section S3) at 100 K. The temperature was then lowered to 85 K and sets of matrix scans performed at successively higher temperatures up to 300 K. A final set of matrix scans was performed at 298 K. The unit cell parameters determined from these matrix scans are detailed in Table S11.

Table S11. Lattice parameters for study *VT4*.

Temperature / K	Lattice Parameters		
	$a / \text{Å}$	$c / \text{Å}$	$V / \text{Å}^3$
100	13.645(5)	13.211(4)	2130.1(9)
85	13.623(4)	13.212(3)	2123.5(7)
90	13.643(4)	13.211(4)	2129.7(9)
100	13.647(5)	13.210(4)	2130.6(10)
120	13.678(4)	13.202(3)	2138.8(7)
140	13.709(3)	13.203(3)	2149.0(6)
160	13.738(3)	13.193(3)	2156.4(7)
180	13.776(4)	13.181(3)	2166.1(7)
200	13.809(4)	13.172(3)	2175.3(7)
220	13.833(4)	13.162(3)	2181.3(8)
240	13.879(4)	13.149(3)	2193.6(8)
260	13.908(4)	13.149(3)	2202.9(7)
280	13.945(4)	13.143(3)	2213.5(8)
300	13.986(6)	13.128(5)	2224.0(13)
298	13.984(7)	13.123(6)	2222.4(15)

Study VT5: Powder diffraction was performed on a sample of **SHF-81-DMF** at temperatures between 300 K and 90 K at Beamline I11, Diamond Light Source. After the 90 K measurement, the temperature was then raised to 300 K, with measurements performed at the same temperatures for comparison. The results are presented in Figure S14 and Table S12.

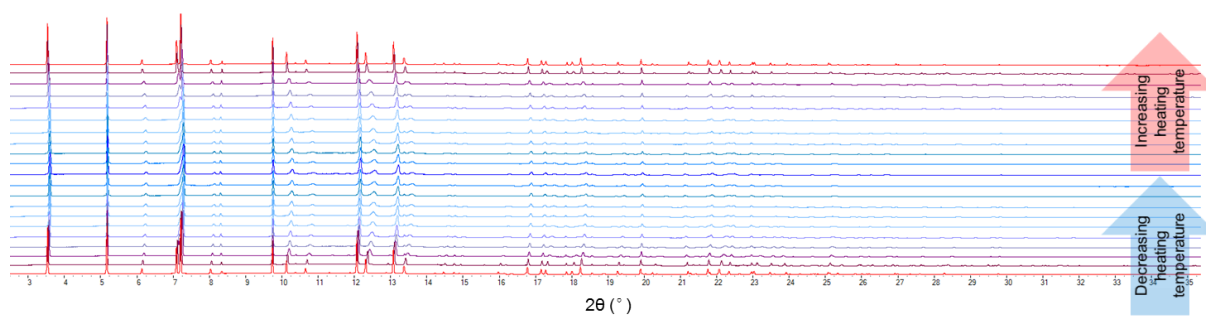


Figure S14. Powder patterns obtained in the *in situ* variable-temperature study **VT5**, in ascending order; *i.e.* bottom pattern is the top row of Table S12 (300 K); top pattern is bottom row of Table S12 (also 300 K). Details of Pawley refinements are provided in Table S12.

Table S12. Pawley refinements^a and lattice parameters for variable-temperature PXRD study **VT5**.

Temp. / K	R_{wp}	R_{wp}'	Lattice Parameters		
			$a / \text{Å}$	$c / \text{Å}$	$V / \text{Å}^3$
300	0.0416	0.0955	15.35834(7)	12.50260(7)	2553.99(3)
250	0.0494	0.1138	15.29143(8)	12.53023(9)	2537.38(3)
200	0.0917	0.2234	15.2189(3)	12.5590(3)	2519.1(1)
180	0.0966	0.2412	15.1807(4)	12.5755(4)	2509.8(1)
160	0.0963	0.2441	15.1479(4)	12.5887(4)	2501.6(2)
140	0.0953	0.2441	15.1199(4)	12.5994(5)	2494.5(2)
130	0.0936	0.2413	15.1078(4)	12.6048(5)	2491.6(2)
120	0.0914	0.2386	15.0963(5)	12.6090(5)	2488.6(2)
110	0.0892	0.2345	15.0858(5)	12.6129(5)	2485.9(2)
100	0.0865	0.2291	15.0763(5)	12.6167(5)	2483.5(2)
90	0.0855	0.2255	15.0658(5)	12.6205(5)	2480.8(2)
100	0.0865	0.2314	15.0763(5)	12.6163(5)	2483.4(2)
110	0.0882	0.2348	15.0866(5)	12.6123(5)	2486.0(2)

120	0.0890	0.2364	15.0970(5)	12.6078(5)	2488.6(2)
130	0.0904	0.2404	15.1075(5)	12.6030(5)	2491.1(2)
140	0.0915	0.2444	15.1184(5)	12.5975(5)	2493.6(2)
160	0.0949	0.2509	15.1448(4)	12.5842(4)	2499.7(2)
180	0.1048	0.2740	15.1786(5)	12.5662(5)	2507.2(2)
200	0.1145	0.2989	15.2293(5)	12.5386(5)	2518.5(2)
250	0.0811	0.1968	15.3188(2)	12.4920(2)	2538.70(8)
300	0.0548	0.1323	15.3554(1)	12.4897(1)	2550.38(4)

^a For all Pawley fits: $\lambda = 0.82471\text{\AA}$; trigonal, $P3_121$; 14 background parameters; ca. 150 reflections; 1 zero error; 5 profile parameters; 2 lattice parameters refined.

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