Supplementary Information

Post-synthetic pore-space expansion in a di-tagged Metal-Organic Framework

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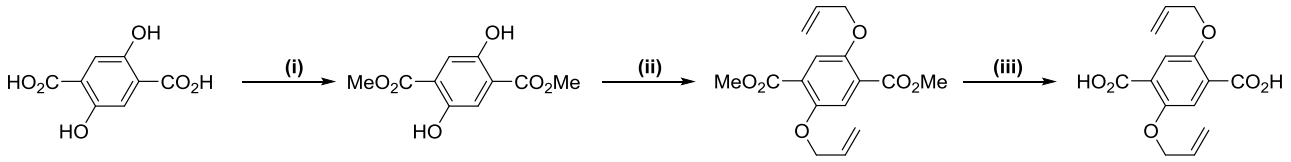
1 Synthesis of 2,5-bis(allyloxy)terephthalic acid, H_2L^1

The synthesis of this ligand has been reported in the literature.[1] The procedure below is what we used.



Scheme S1. (i) H_2SO_4, MeOH (ii) Allyl bromide, K_2CO_3, DMF (iii) $NaOH_{(aq)}$, MeOH/THF.

Dimethyl 2,5-dihydroxyterephthalate

Concentrated H_2SO_4 (1 cm^3) was added dropwise to 2,5-dihydroxyterephthalic acid (5.15 g, 26 mmol) in MeOH (40 cm^3) while stirring and then the mixture was heated at reflux for 2 days. After allowing to cool, a yellow solid was filtered and washed with fresh MeOH (3 × 5 cm^3). Yield 4.82 g (82 %). ^{1}H NMR δ_H (300 MHz, $CDCl_3$): 3.96 (6 H, s), 7.46 (2 H, s), 10.05 (2 H, s).

Dimethyl 2,5-bis(allyloxy)terephthalate

Allyl bromide (4.5 cm^3, 27 mmol) was added to dimethyl 2,5-bis(allyloxy)terephthalate (1.71 g, 7.5 mmol) in a mixture of DMF (12 cm^3), powdered K_2CO_3 (3.6 g, 26 mmol) and Me_4NI (0.1 g, 0.5 mmol) and the mixture stirred at room temperature over the weekend. The mixture was then diluted with H_2O (40-50 cm^3) and the precipitated solid collected by filtration and washed with water (2 × 10 cm^3). The solid was taken up in EtOAc and the solution washed with 10% Na_2CO_3 solution until the organic layer was colourless, then with H_2O, brine and dried over Na_2SO_4 and the solvent was removed by rotary evaporation. The resulting solid was taken up in CH_2Cl_2 and passed through a plug of silica gel then concentrated by rotary evaporation before crystallization from CH_2Cl_2/Pet. Ether. Yield 1.53 g (54 %). Found: C, 62.94; H, 5.92. $C_{16}H_{18}O_6$ requires C, 62.74; H, 5.92. ^{1}H NMR δ_H (300 MHz; $CDCl_3$) 3.94 (6 H, s), 4.60 (4 H, dt, *J* = 4.98, 1.46 Hz), 5.29 (2 H, m, *J* = 10.52, 1.47 Hz), 5.48 (2 H, m, *J* = 17.28, 1.76 Hz), 6.01 (2 H, m), 7.40 (2 H, s).

2,5-Bis(allyloxy)terephthalic acid, $H_2\mathbf{L^1}$

1 M NaOH (15 cm^3, 15 cm^3) was added to dimethyl 2,5-bis(allyloxy)terephthalate (1.75 g, 5.7 mmol) in a solvent mixture of MeOH–THF (1–1, 30 cm^3) and the mixture stirred overnight. The organic solvents were removed by rotary evaporation and the residue diluted with H_2O (20 cm^3) and filtered before acidification with 1 M HCl to precipitate a white solid and this was collected by filtration, washed with H_2O (3 × 5 cm^3) and oven dried (80 °C). Yield 1.44 g (91%). Found: C, 60.66; H, 5.04. $C_{14}H_{14}O_6$ requires C, 60.43; H, 5.07. ^{1}H NMR δ_H (300 MHz; DMSO-d_6) 4.59 (4 H, dt, *J* = 4.42, 1.71 Hz), 5.23 (2 H, m, *J* = 10.63, 1.74 Hz), 5.43 (2 H, m, *J* = 17.29, 1.62 Hz), 6.01 (2 H, m, *J* = 17.29, 10.63, 4.74 Hz), 7.30 (2 H, s); ^{13}C NMR δ_C (300 MHz; DMSO-d_6) 69.56, 116.01, 117.14, 125.52, 133.62, 150.24, 166.92.

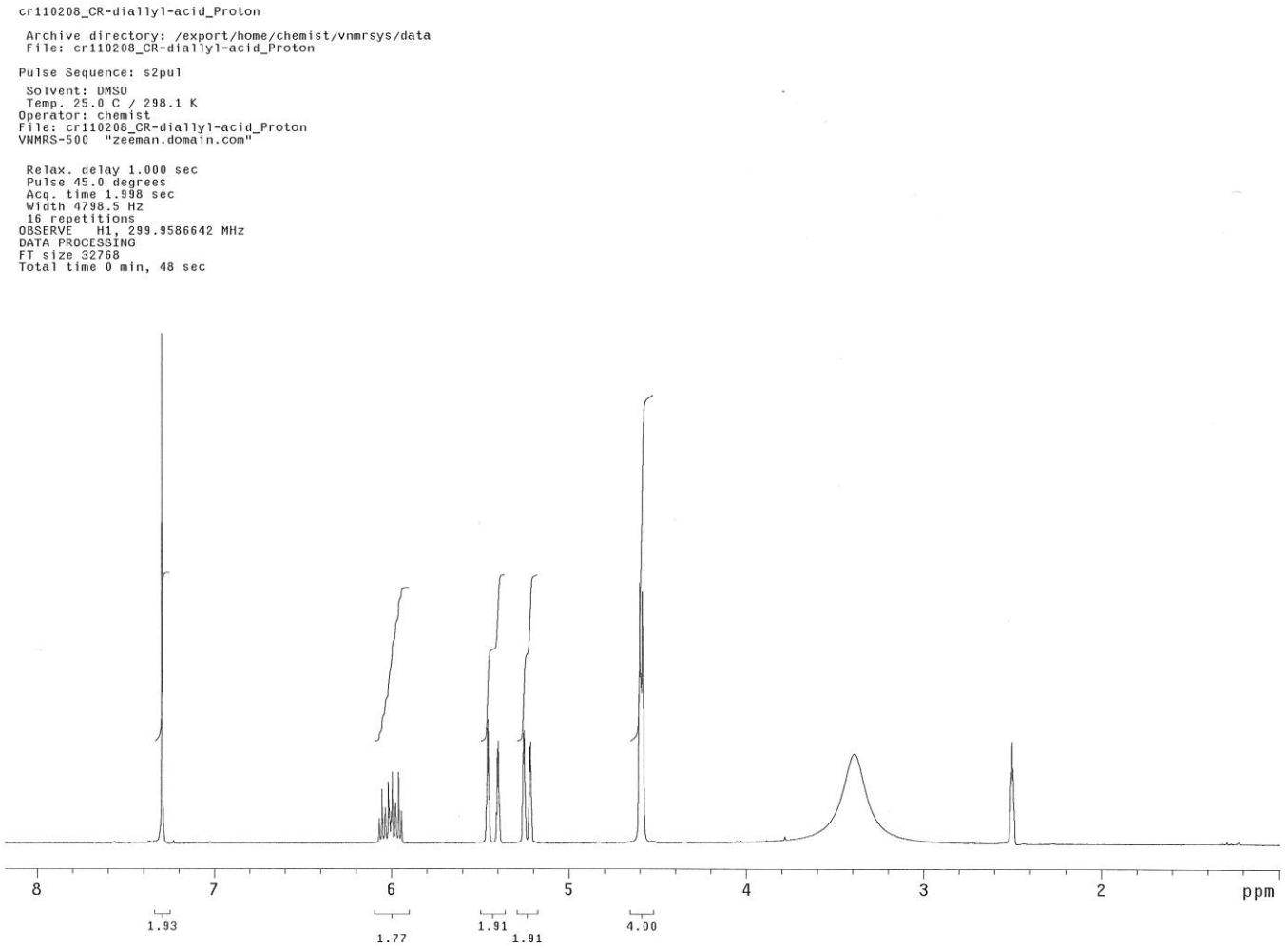


Figure S 1 ^{1}H NMR spectrum of $H_2\mathbf{L^1}$ in d_6-DMSO solution at 300 MHz.

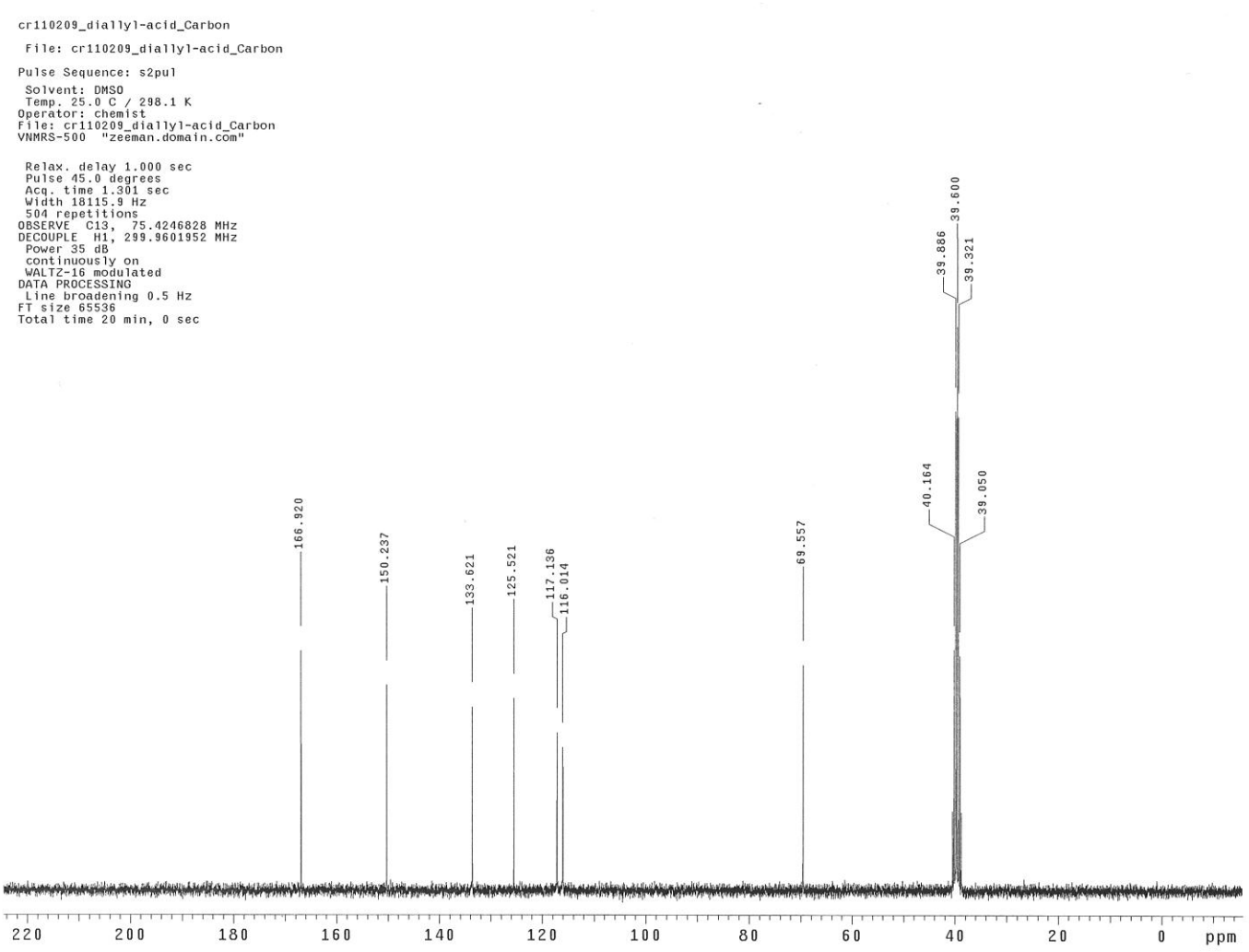


Figure S 2 ^{13}C NMR spectrum of $H_2\mathbf{L^1}$ in d_6-DMSO solution at 75.5 MHz.

2 Single Crystal X-ray Crystallography

Table S1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$C_{24}O_{13}Zn_4$	$C_{24}O_{13}Zn_4$
Formula weight	757.71	757.73
Temperature/K	120.0(1)	120.0(1)
Crystal system	cubic	cubic
Space group	Pm-3m	Fm-3m
a/Å	12.7953(10)	25.7643(3)
b/Å	12.7953(10)	25.7643(3)
c/Å	12.7953(10)	25.7643(3)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/Å^3	2094.8(5)	17102.3(7)
Z	1	8
ρ_{calc}mg/mm^3	0.601	0.589
m/mm^{-1}	1.493	1.129
F(000)	368.0	2944.0
Crystal size/mm^3	0.16 × 0.14 × 0.10	0.15 × 0.14 × 0.11
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection	6.908 to 146.806°	5.244 to 59.24°
Index ranges	-15 ≤ h ≤ 14, -15 ≤ k ≤ 7, -8 ≤ l ≤ 10	-26 ≤ h ≤ 35, -35 ≤ k ≤ 35, -32 ≤ l ≤ 32
Reflections collected	1977	21972
Independent reflections	476	1224
Data/restraints/parameters	476/0/23	1224/0/25
Goodness-of-fit on F^2	2.242	1.067
Final R indexes [I>=2σ (I)]	0.1982	0.0616
Final R indexes [all data]	0.5309	0.2249
Largest diff. peak/hole / e Å^{-3}	1.19/-0.84	0.66/-0.26

NOTES

The data for **1** was collected at low temperature using CuKα (λ = 1.54184) radiation. The structure of **1** was solved and refined in the cubic space group *Pm-3m* (a = 12.7953(1)Å). This is the same space group and unit cell parameter as the MOF reported by Fischer et al. (CSD code AJOQEW) using a ligand that differs only in the identity of the pendant tag groups.[2] The data collected for **1** was of poor quality, and the structure is considerably disordered. The asymmetric unit consists of a Zn atom coordinated to an oxo-atom of the SBU with a bond length of 1.919(5) Å and a carboxylate atom of the bridging ligand at a distance of 1.884(17) Å, and is completed by 3 carbons belonging to the phenyl ring of the ligand. The asymmetric unit described is disordered over two sites, each with 50% occupancy (Figure S3). Pendant tag groups on the phenyl ring and solvate molecules were not able to be located and the SQUEEZE algorithm as implemented in the Platon program suite was used. This showed a solvent accessible void space of 1497 $Å^3$ with an electron count of 381 electrons. The atoms of the bridging ligand $\mathbf{L^1}$ not accounted for in the formula per ligand of $\mathbf{L^1}$ is $C_6H_{10}O_2$, which represents 62 electrons. This gives a total of 186 electrons for the number of $\mathbf{L^1}$ ligands per unit cell (3), leaving 195 electrons per unit cell free for disordered solvate, which would account for ≈5 molecules of DMF.

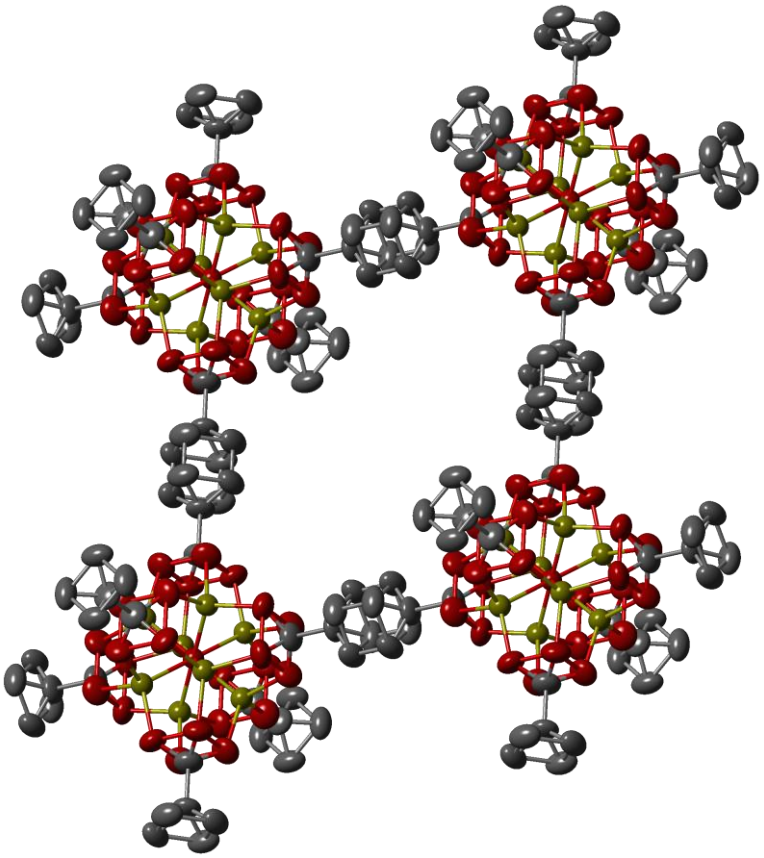


Figure S 3 Partial structure of **1** showing the disorder of the phenyl ring and Zn_4O SBU.

The data of **2** was collected at low temperature using MoKα (λ = 0.71073) radiation. The structure of **2** solved and refined in the F-centered cubic space group *Fm-3m* (a = 25.7643(3)Å). The data for **2** is of higher quality than **1** and examination of the systematic absences confirmed this space group assignment. The asymmetric unit comprises one-quarter of a bridging ligand of $\mathbf{L^2}$ lying on three mirror planes and $^1/_{24}{}^{th}$ of a Zn_4O subunit; the central μ_4-oxo atom (O1) of the SBU is located on a special position (¼, ¾, ¼). The independent zinc atom has Zn-O bond lengths of 1.9366(9)Å to the central μ_4-oxo atom and 1.922(4)Å to the carboxylate. The asymmetric unit is completed by the carbon belonging to the carboxylate (C1) and by two carbons from the phenyl ring (C2 and C3). The thermal ellipsoids of C2 and C3 are elongated perpendicular to the plane of the ring, indicating some small tilting, as shown in Figure S4. This contributes to 'smearing out' the electron density of the attached tag groups. To account for the electron density of these groups and to attempt to reconcile the electron density of solvate molecules in the pores, the data was treated with the SQUEEZE algorithm as implemented in the Platon program suite (as above). Prior to treatment with SQUEEZE, the R_1 was ≈11% and the highest peak in the difference map was 1.2 electrons/Å^3 and afterward the R_1 lowered to 6.16% and the highest peak reduced to 0.7 electrons/Å^3. The solvent accessible space is calculated to have a volume of 13280 Å^3, which contains 1925 electrons. The formula of the missing atoms per molecule of $\mathbf{L^2}$ is $C_6H_{10}O_2$, which accounts for 62 electrons. This gives a total of 1488 electrons for the number of molecules of $\mathbf{L^2}$ per unit cell (24), leaving approximately 440 electrons per unit cell free for disordered solvate, likely taken up by ≈11 molecules of DMF.

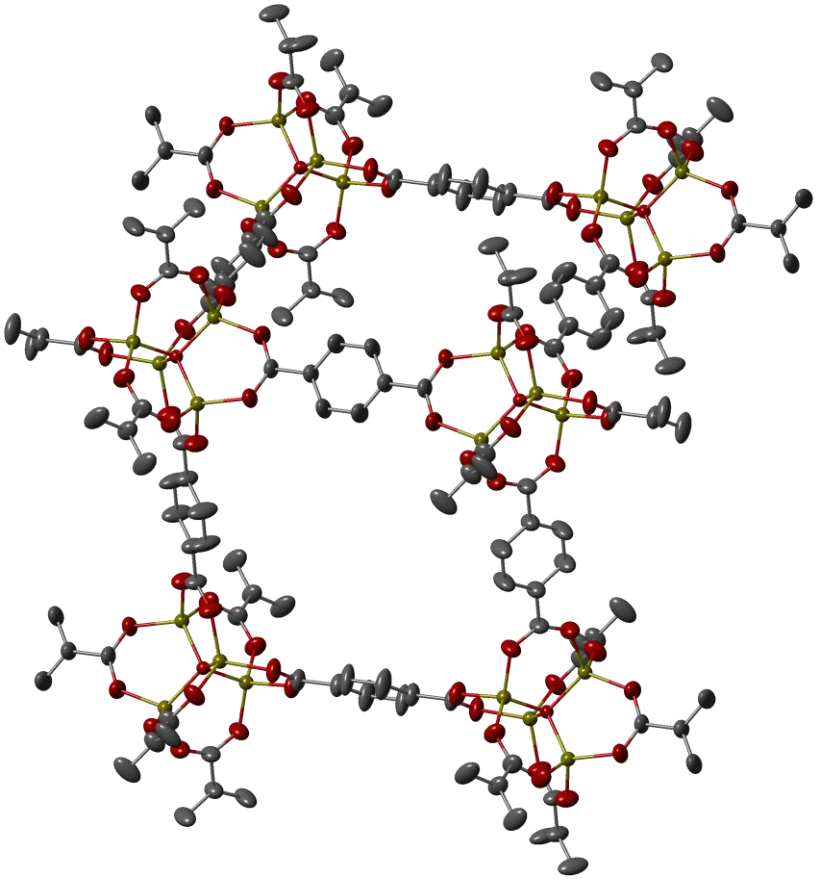


Figure S 4 Partial structure expansion of **2** with thermal ellipsoids to show the small tilting of the phenyl rings.

3 TG—DTA data

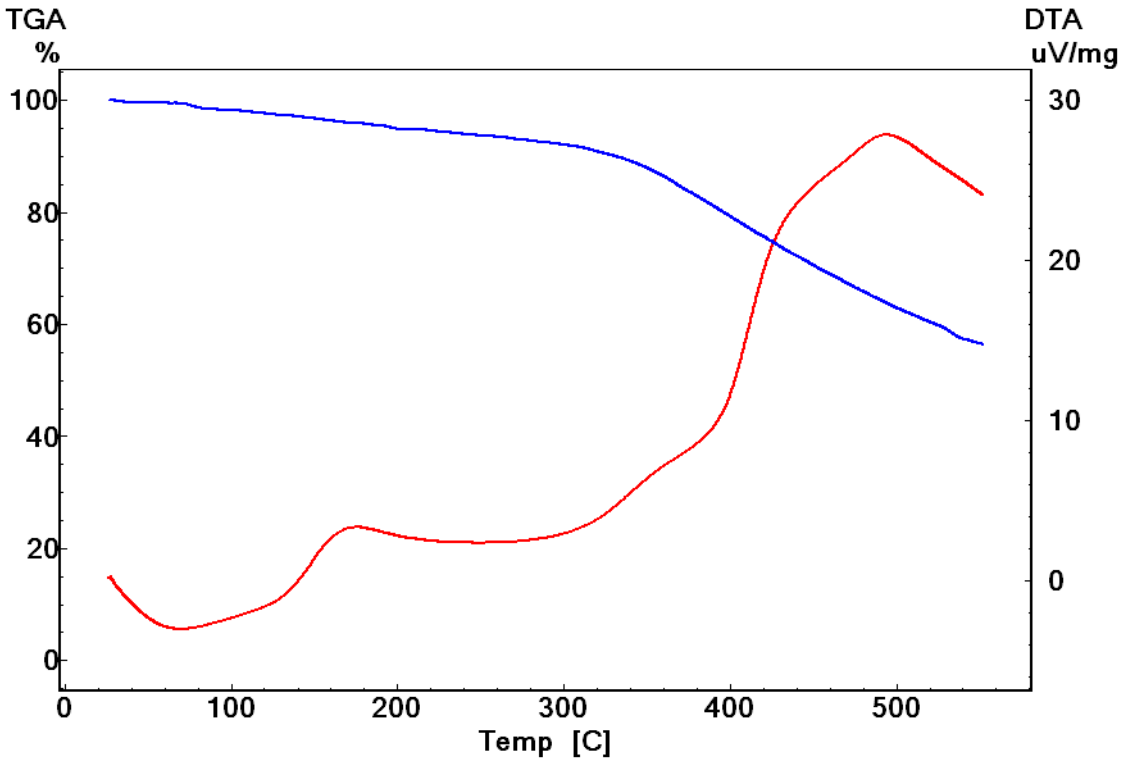


Figure S 5. TG—DTA traces for dried **1**; the exotherm centred about 160 °C is evident. The blue curve represents the TGA; the red curve represents the DTA.

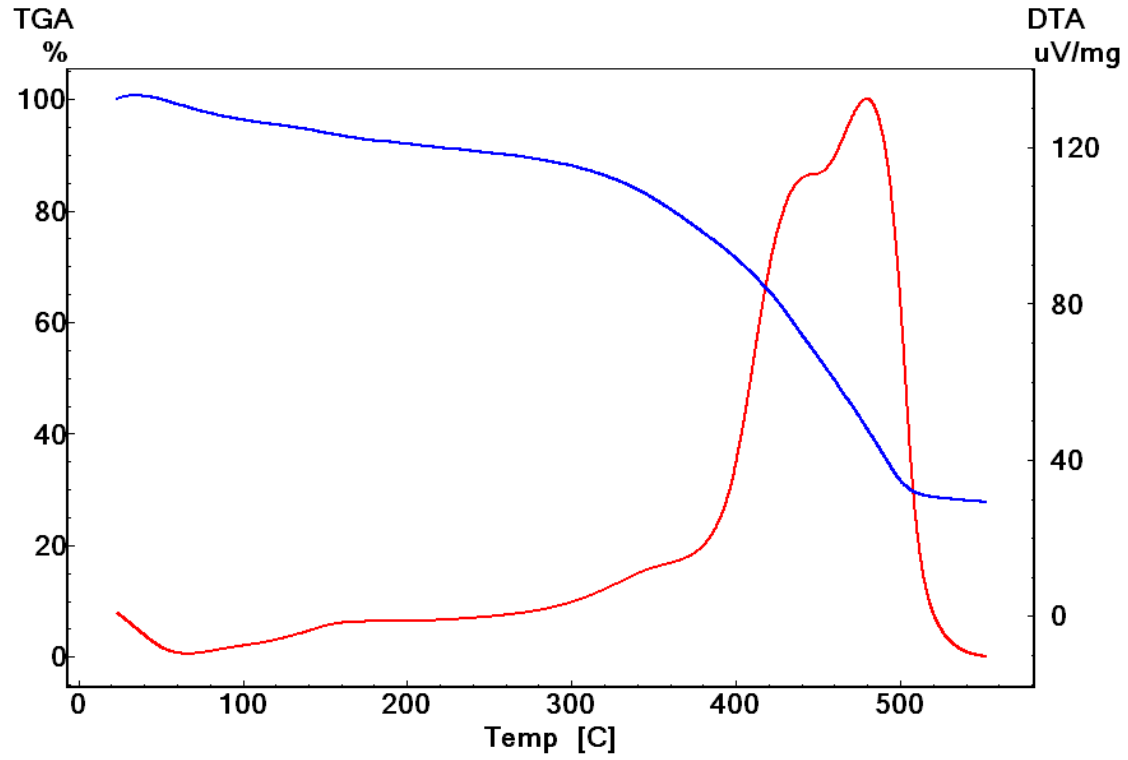


Figure S 6. TG—DTA traces for dried **2**; there is no exotherm around 160 °C. The blue curve represents the TGA; the red curve represents the DTA.

4 Images of modified crystals

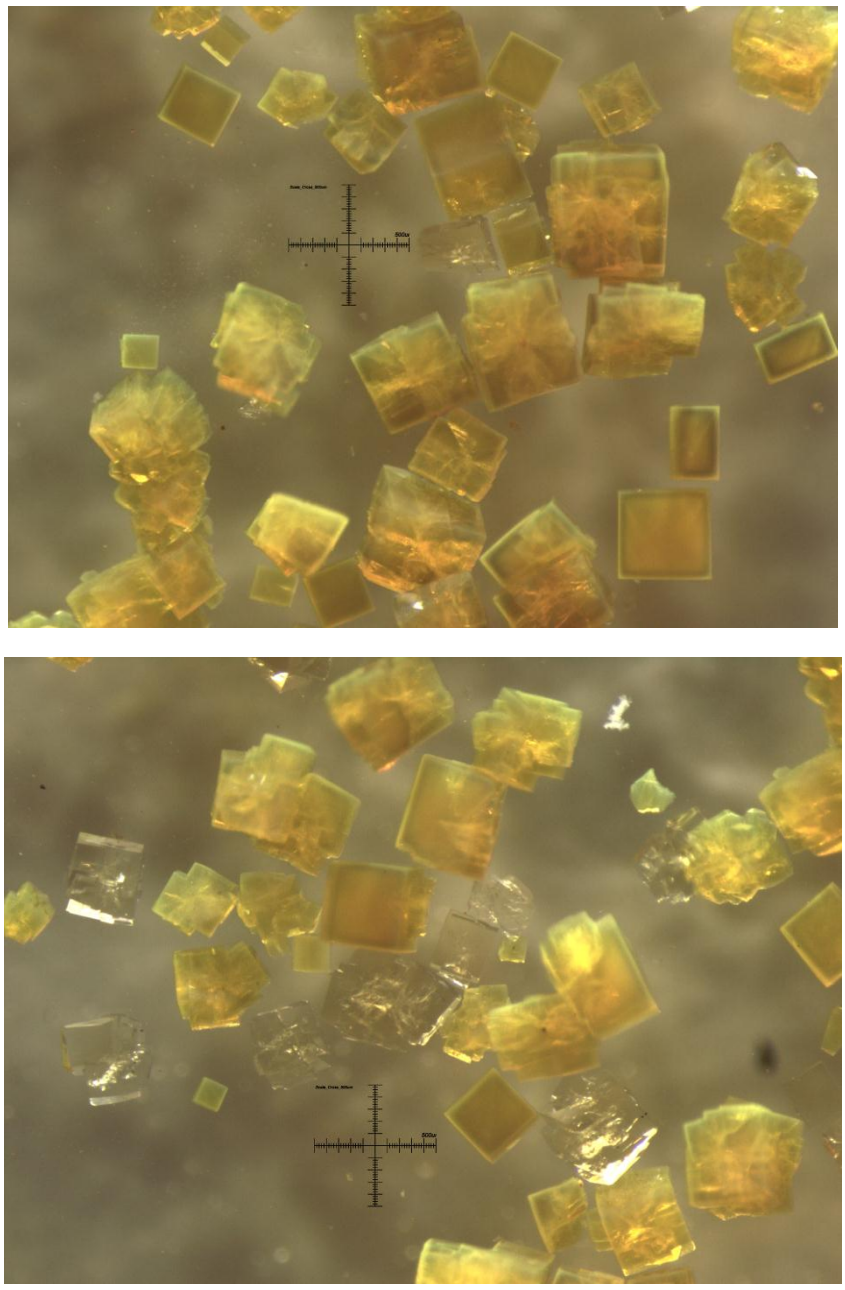


Figure S 7 Image of modified crystals (top) and image of modified crystals **2** deliberately spiked with some near colourless starting crystals of **1** (bottom). The scale bar in each image is 500 µm.

5 [1]H NMR Digestion Spectra

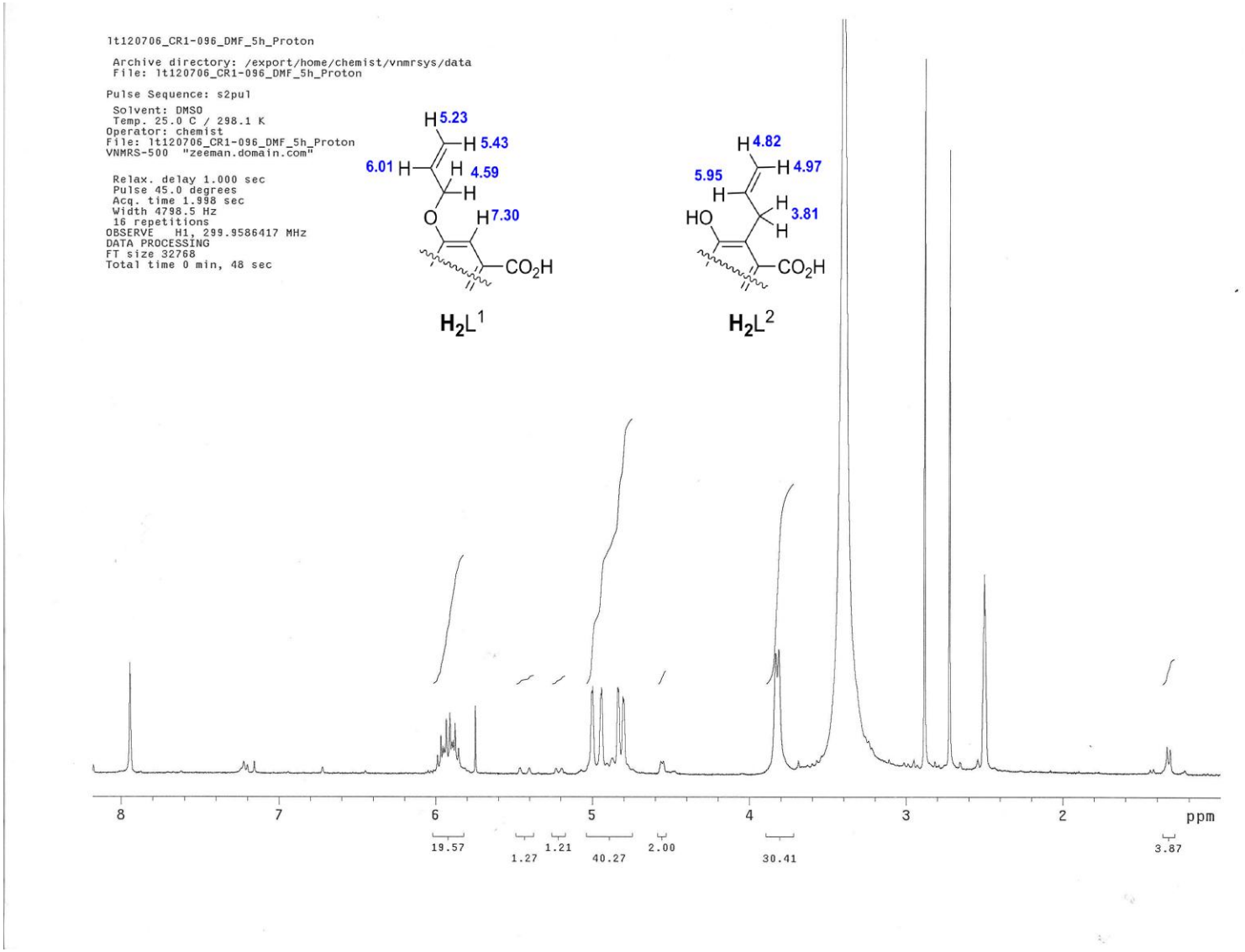


Figure S 8 [1]H NMR spectrum in d_6-DMSO solution of **2** from the PSR in DMF.

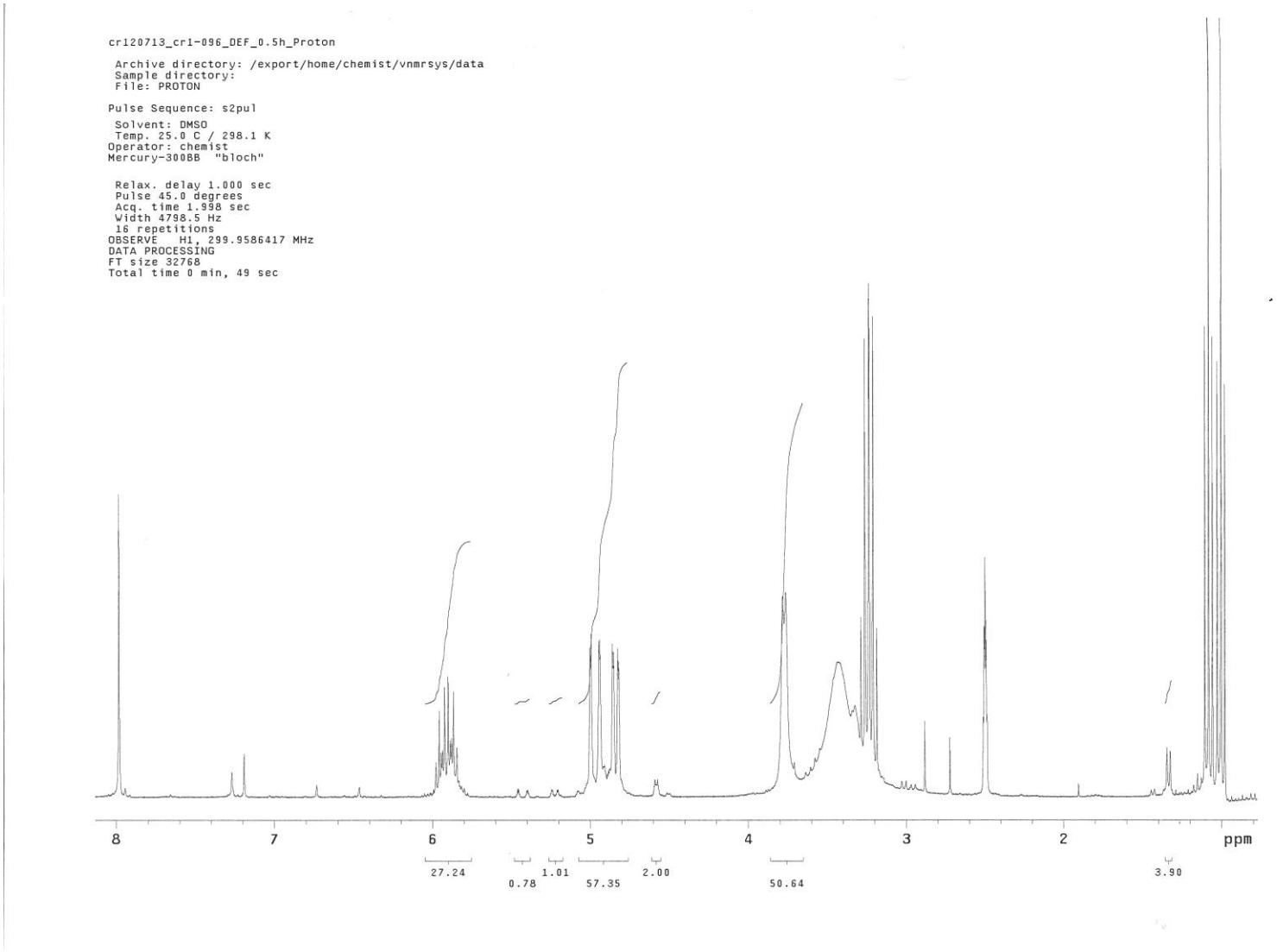


Figure S 9 ^{1}H NMR spectrum in d_6-DMSO solution of **2** from the PSR in DEF.

6 Infrared Spectroscopy

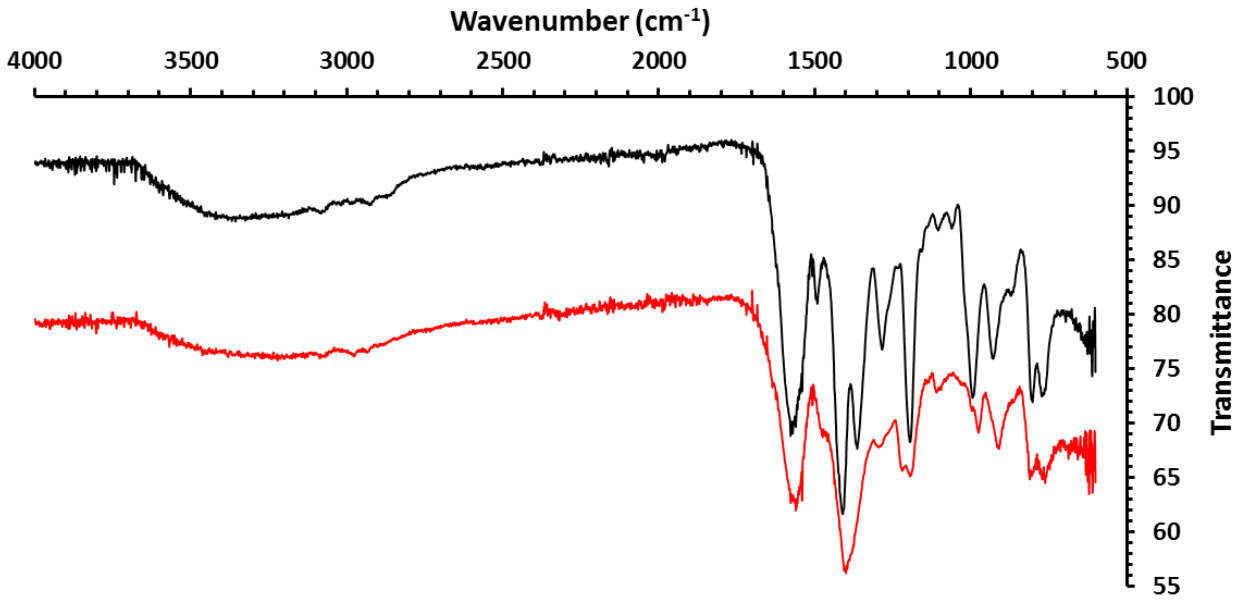


Figure S 10 Infrared spectra of $Zn_4O(\mathbf{L^1})_3$ **1** (black) and $Zn_4O(\mathbf{L^2})_3$ **2** (red)

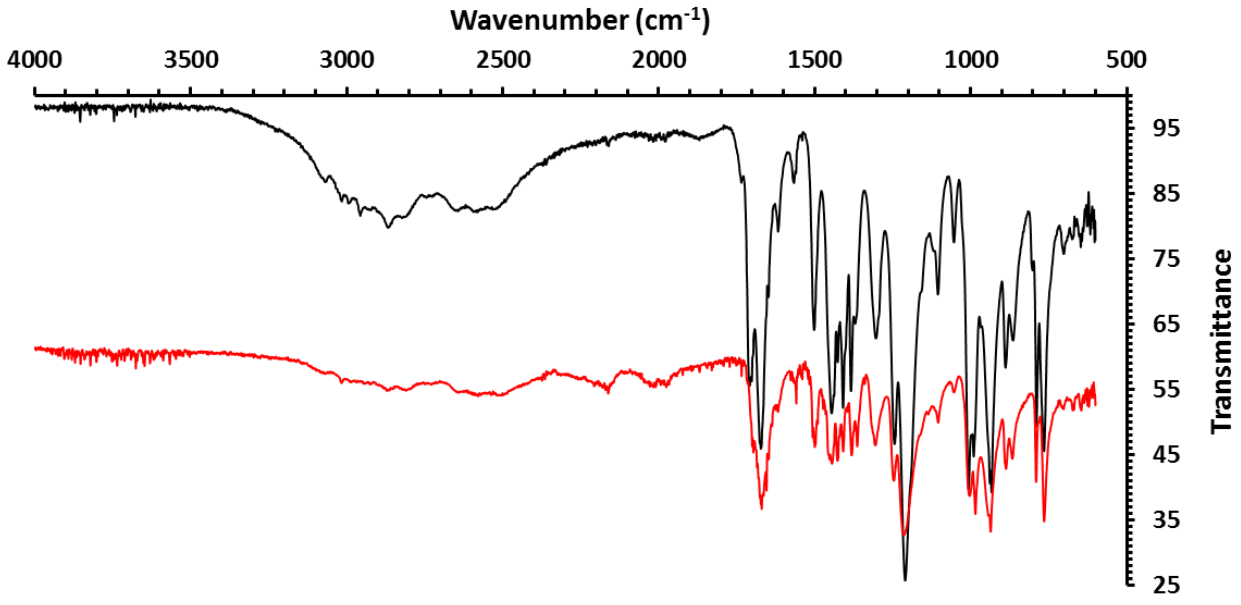


Figure S 11 Infrared spectra of $H_2\mathbf{L^1}$ (black) and $H_2\mathbf{L^2}$ (red)

7 Mass Spectrometry

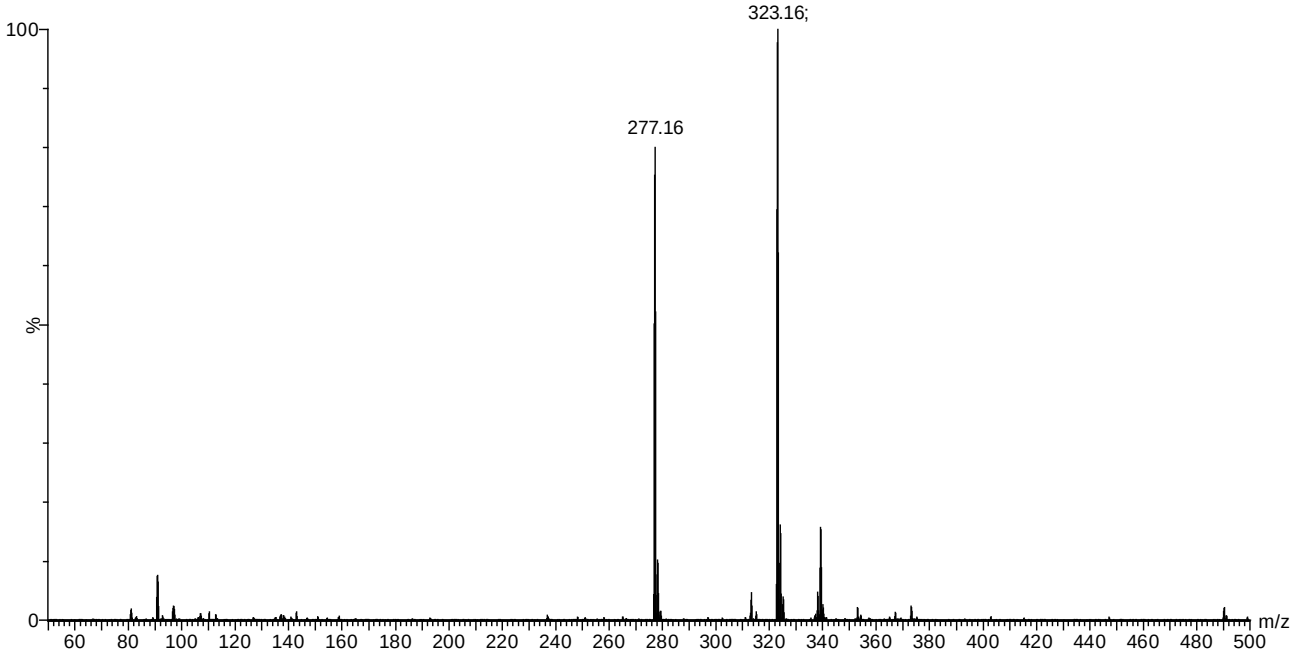


Figure S 12 Negative mode ESI mass spectrum of H_2**L**[1]

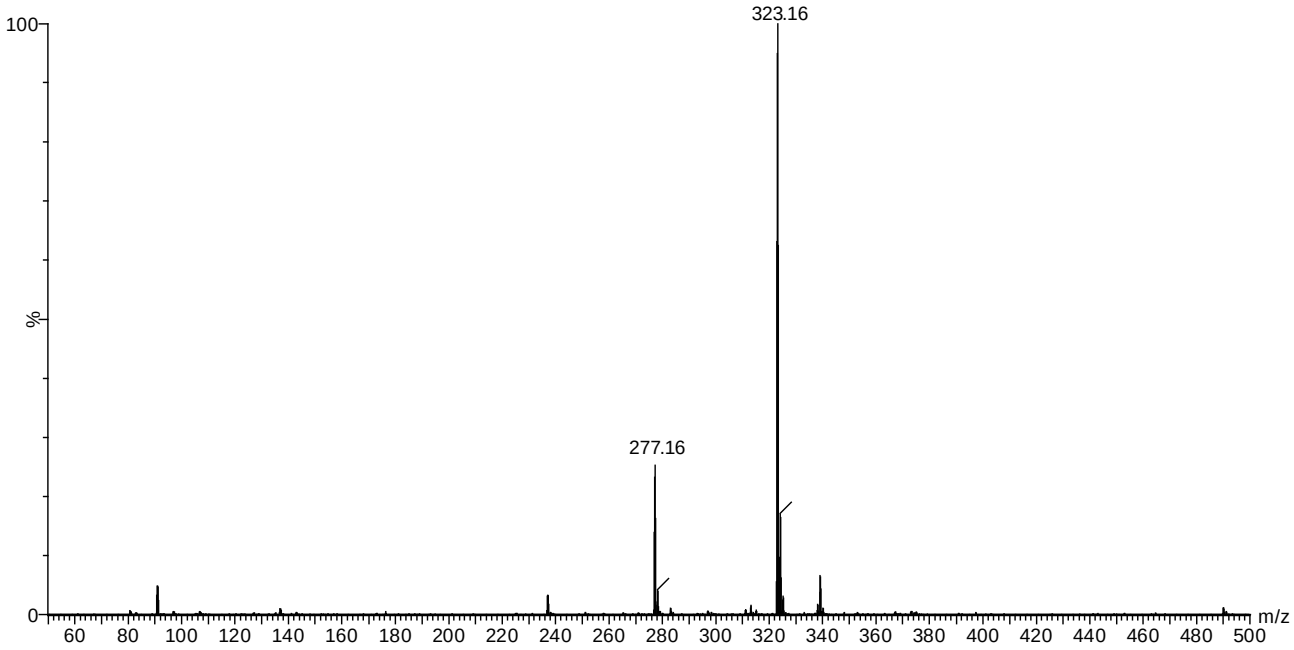


Figure S 13 Negative mode ESI mass spectrum of H_2**L**[2]

8 PXRD

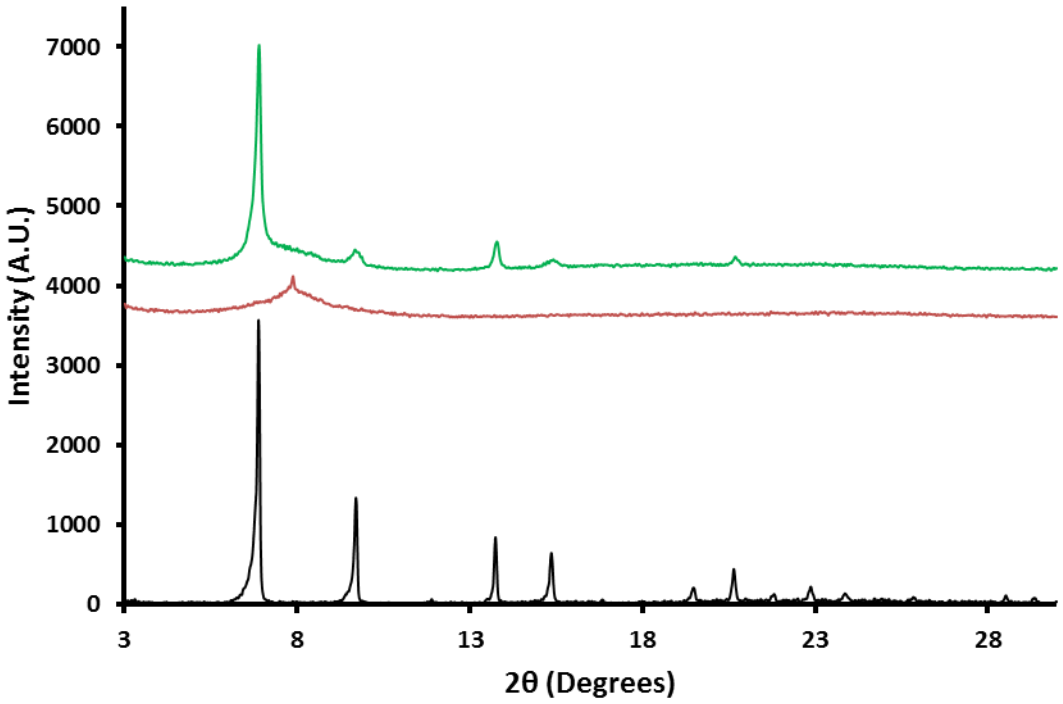


Figure S 14 PXRD patterns for 'as synthesised' **1** (black; bottom); activated **1** (red; centre); resolvated **1** (top; green).

9 Gas Sorption Data

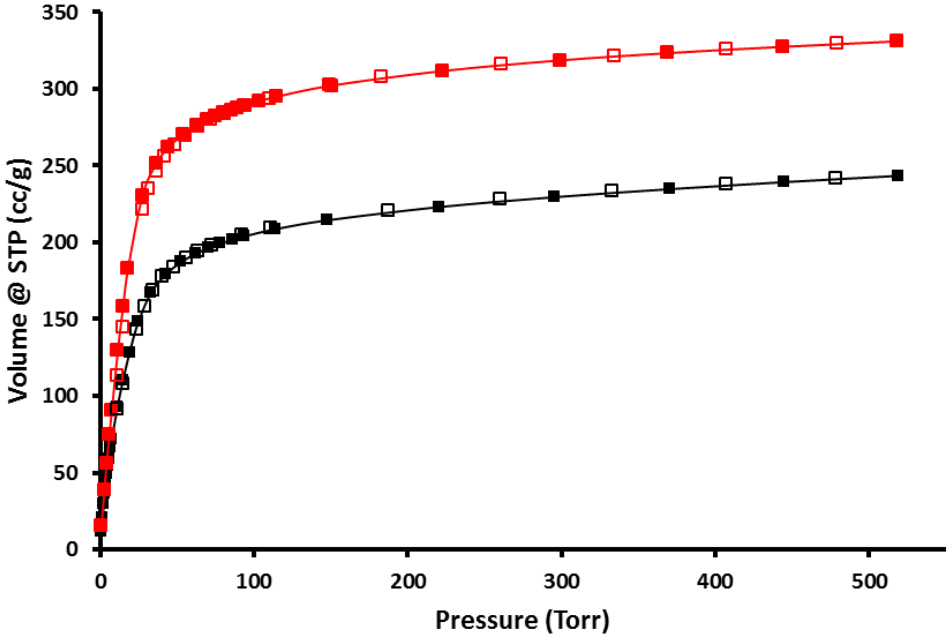


Figure S 15 CO_2 isotherms at 196 K for $Zn_4O(\mathbf{L}^1)_3$ **1** (black) and $Zn_4O(\mathbf{L}^2)_3$ **2** (red). Filled squares are adsorption, open squares are desorption.

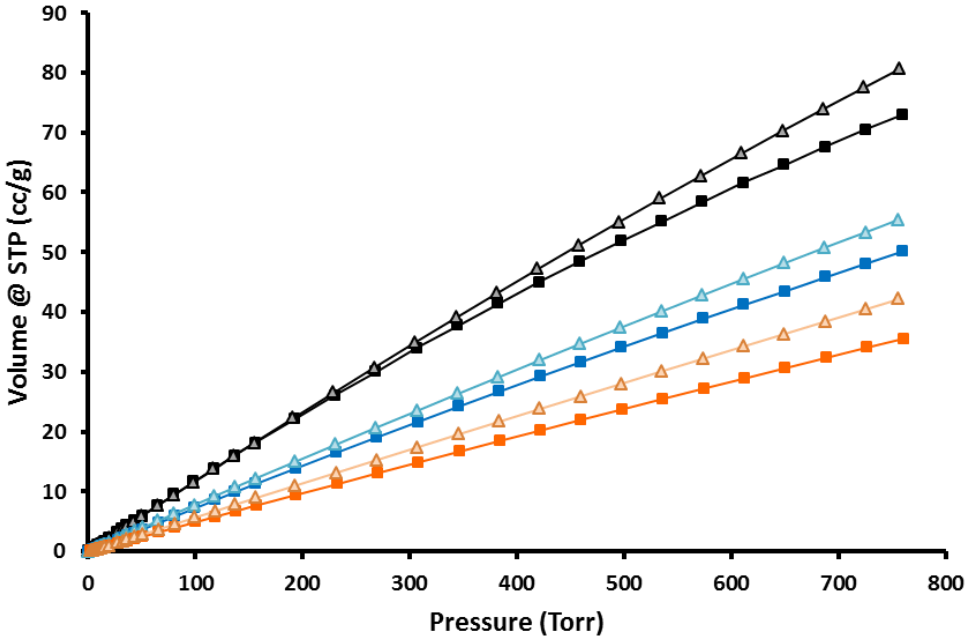


Figure S 16 CO_2 adsorption data for $Zn_4O(\mathbf{L}^1)_3$ **1** (solid squares) and $Zn_4O(\mathbf{L}^2)_3$ **2** (shaded triangles). Black, 273 K; blue, 288 K; orange, 298 K.

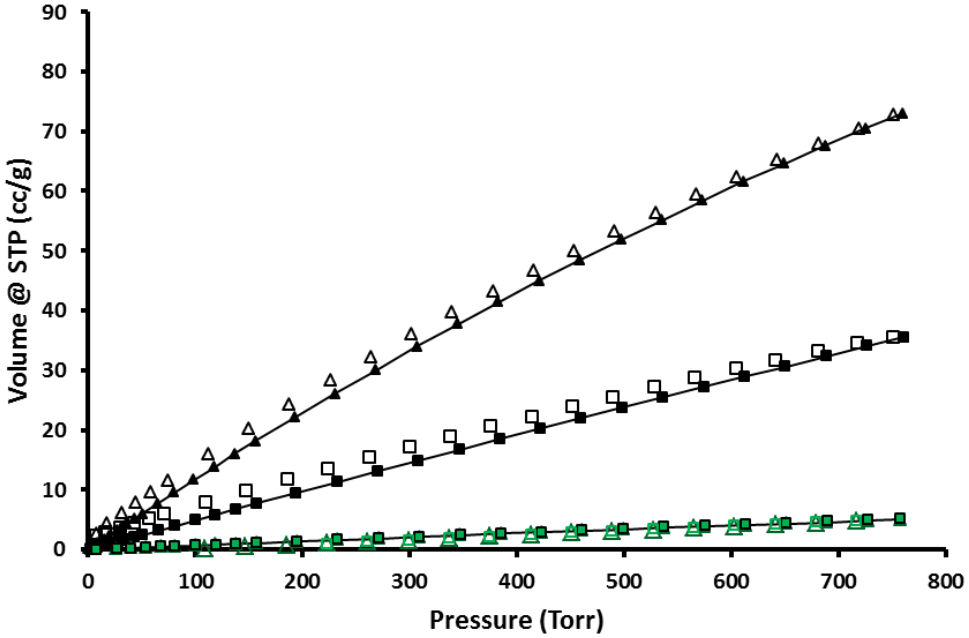


Figure S 17 CO_2 and N_2 sorption data for $Zn_4O(\mathbf{L}^1)_3$ **1**. Black triangles are CO_2 at 273 K; light green triangles are N_2 at 273 K; black squares are CO_2 at 298 K; green squares are N_2 at 298 K. Filled squares/triangles are adsorption, open squares/triangles are desorption.

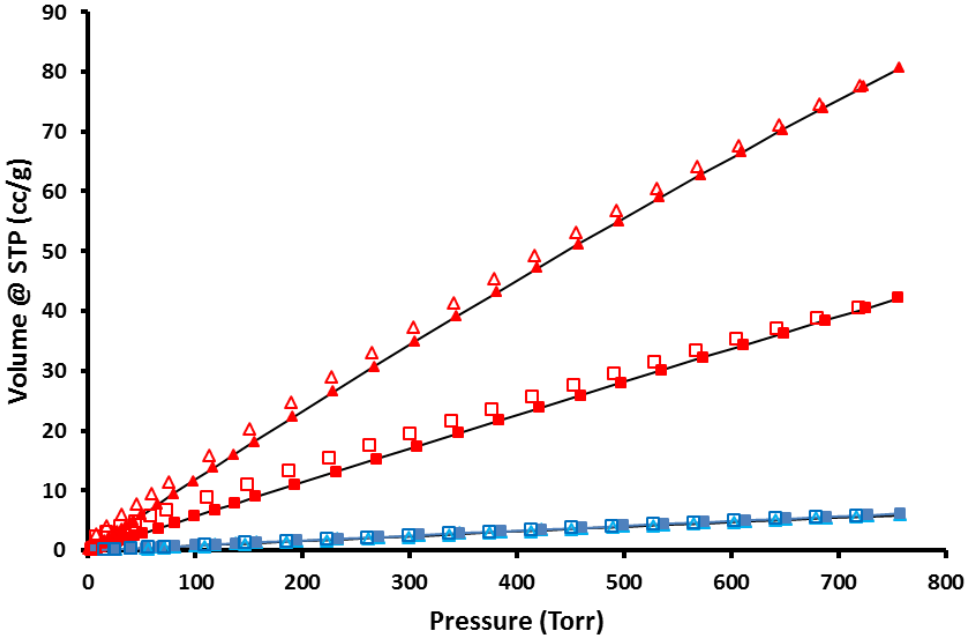


Figure S 18 CO_2 and N_2 sorption data for $Zn_4O(\mathbf{L}^2)_3$ **2**. Red triangles are CO_2 at 273 K; light blue triangles are N_2 at 273 K; red squares are CO_2 at 298 K; blue squares are N_2 at 298 K. Filled squares/triangles are adsorption, open squares/triangles are desorption.

10 Heat of Adsorption Calculations

The heat of adsorption for CO_2 was determined by comparing carbon dioxide isotherms at 288 and 298 K. Isosteric heat of adsorption calculations ($-Q_{st}$) for CO_2 at these temperatures were undertaken by virial fitting and the Clausius-Clapeyron equation:

$$(ln\, P)_n = -\left(\frac{Q_{st}}{\mathrm{R}}\right)\left(\frac{1}{T}\right) + \mathrm{C}$$

where P is the pressure, n is the amount adsorbed, T is the temperature, R is the universal gas constant and C is a constant.

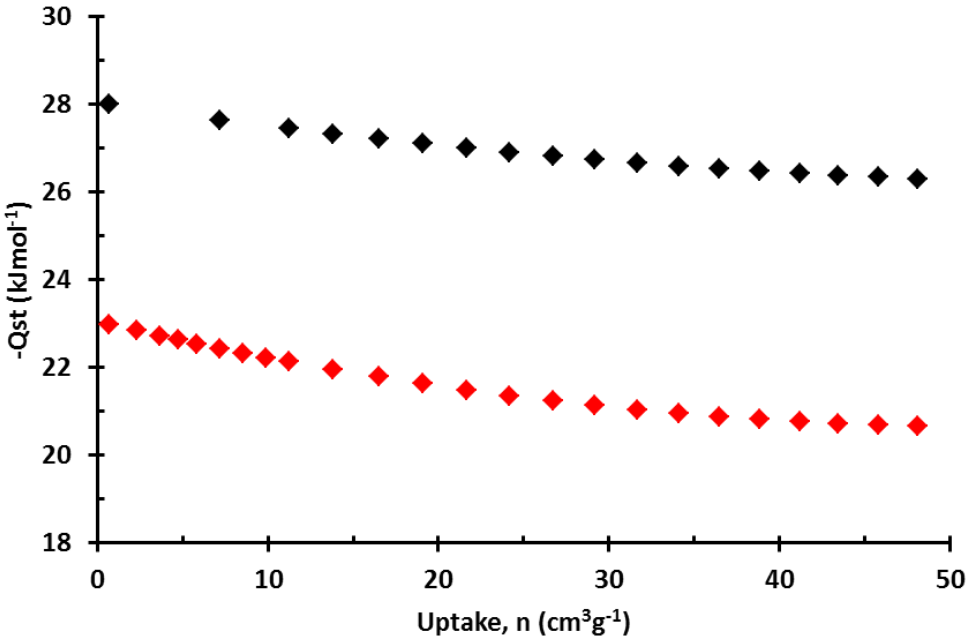


Figure S 19 Isosteric heat of adsorption profiles (obtained by Virial fitting) of the adsorption data at 288 and 298 K for **1** (black) and **2** (red).

11 Surface Area Calculations

The geometric surface areas of MOF **2** was calculated following the method of Duren et. al.[3] with a probe diameter set to 3.72 Å to match nitrogen.[4] The diameters of framework atoms were taken from the DREIDING force field and set to their van der Waals diameters by multiplying their Lennard-Jones well-depth diameters, σ, by $2^{1/6}$.

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[1] S. Henke, A. Schneemann, A. Wüscher and R. A. Fischer, *J. Am. Chem. Soc.*, 2012, **134**, 9464.

[2] S. Henke, R. Schmid, J.-D. Grunwaldt and R. A. Fisher, *Chem. Eur. J.*, 2010, **16**, 14296.

[3] (a) H. Frost, T. Düren and R.Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565; (b) T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C* 2007, **111**, 15350.

[4] Y.-S. Bae, A. O. Yazaydın, R. Q. Snurr, *Langmuir* 2010, **26**, 5475.