

## Supporting Information

### Ligand Flexibility and Framework Rearrangement in a New Family of Porous Metal-Organic Frameworks

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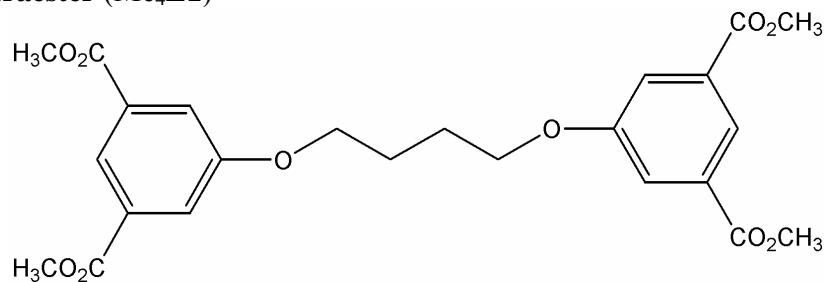
## Experimental

### 1. General

All chemicals were purchased from Aldrich or Lancaster and used as received. Infra-red spectra were recorded on a Perkin-Elmer Spectrum RX I FT-IR spectrometer equipped with a SensIR diamond attenuated total reflectance fitting. <sup>1</sup>H NMR spectra were recorded on a Bruker AC-250 (250 MHz) or AMX-400 (400 MHz) supported by an Aspect 3000 data system. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl<sub>3</sub>: δ 7.27 ppm and DMSO: δ 2.50 ppm). Data are reported as follows: chemical shift; multiplicity (s = singlet, d = doublet, t = triplet, br = broad, m = multiplet); integration. <sup>13</sup>C NMR spectra were recorded on a Bruker AC-250 (62.9 MHz) or AMX-400 (100.6 MHz) with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard (CHCl<sub>3</sub>: δ 77.00 ppm and DMSO: δ 39.50 ppm). The electron ionisation mass spectra were obtained on a VG Auto Spec Magnetic Sector machine working positive or negative ion mode. The elemental analyses were conducted by the Elemental Analysis service, Department of Chemistry, University of Sheffield. Powder diffraction data were obtained on a Bruker-AXS D8 Advance powder diffractometer at the Strathclyde Institute of Pharmacy and Biomedical Science, University of Strathclyde, using Cu K<sub>α1</sub> radiation (λ = 1.54056 Å).

### 2. Synthesis

#### 2.1 Butane Tetraester (Me<sub>4</sub>L1)



A mixture of dimethyl 5-hydroxyisophthalate (2.43 g, 11.6 mmol), 1,4-dibromobutane (1.08 g, 5.00 mmol) and  $K_2CO_3$  (2.50 g, 18.1 mmol) were stirred in DMF (40 ml) at room temperature for 48 hours. After this time, the reaction mixture was poured into water (~400 ml) and stirred for a further 15 minutes. The resulting white precipitate was collected and washed three times with water. The precipitate was dissolved in  $CH_2Cl_2$  (~150 ml) and then washed with a solution of 5 % aqueous NaOH solution (2 x 100 ml portions). The  $CH_2Cl_2$  solution was then dried over  $MgSO_4$ , filtered and reduced to give 1.79 g (75 %) of the butanetetraester  $Me_4L1$  as a white solid.

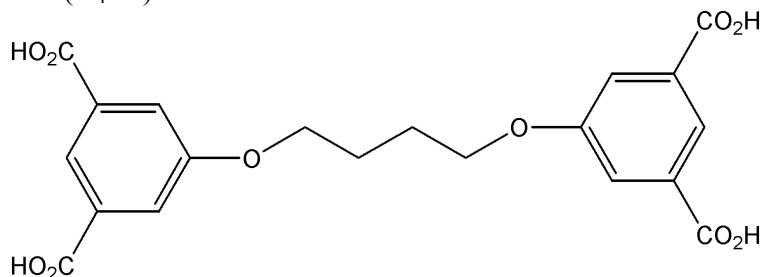
IR (ATR):  $\nu$  1723  $cm^{-1}$  (carbonyl)

$^1H$  NMR ( $CDCl_3$ ):  $\delta$  2.02 (m, 4H), 3.93 (s, 12H), 4.12 (m, 4H), 7.71 (d, 4H), 8.26 (t, 2H)

$^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  25.78, 52.44, 67.94, 119.79, 122.95, 131.73 (no  $4^o$  carbon signals observed)

MS (ESI+):  $m/z$  calcd for  $C_{24}H_{26}O_{10}$  474, found 474

## 2.2 Butane Tetraacid ( $H_4L1$ )



A mixture of butane tetraester  $Me_4L1$  (1.50 g, 3.16 mmol), KOH (0.710 g, 12.7 mmol), methanol (25 ml) and distilled water (25 ml) were stirred under  $N_2$  at 60  $^{\circ}C$  for 48 hours. After this time, the reaction mixture was filtered to remove any unreacted starting materials. HCl (6 M, 25 ml) was then added dropwise at 0  $^{\circ}C$ . The precipitate was collected, washed with water and dried under vacuum to give 1.04 g (79 %) of butanetetraacid  $H_4L1$  as a white solid.

IR (ATR):  $\nu$  1671  $cm^{-1}$  (carbonyl)

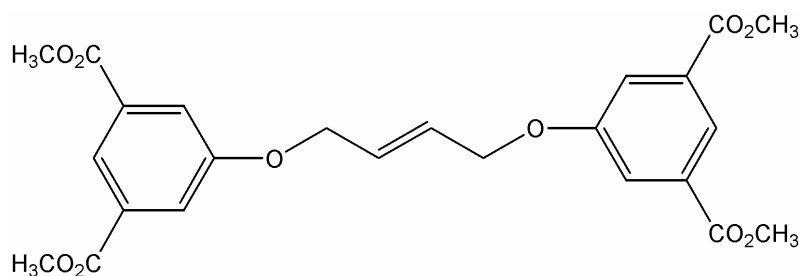
$^1H$  NMR ( $d_6$ -DMSO):  $\delta$  1.91 (s, 4H), 4.15 (s, 4H), 7.63 (d, 4H), 8.06 (t, 2H), 13.27 (br, 4H)

$^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  25.62, 68.17, 119.53, 122.62, 132.98, 159.22, 166.83

MS (ESI-):  $m/z$  calcd for  $C_{20}H_{18}O_{10}$  418, found 417  $[M - H]^+$

Elemental Analysis: calcd for  $C_{20}H_{18}O_{10}$  C 57.42 % H 4.54 % found C 56.75 % H 4.18 %

## 2.3 Butene Tetraester ( $Me_4L2$ )



A mixture of dimethyl 5-hydroxyisophthalate (2.10 g, 10.0 mmol), *trans*-1,4-dibromobut-2-ene (1.05 g, 4.90 mmol), K<sub>2</sub>CO<sub>3</sub> (2.21 g, 16.0 mmol) and dibenzo-18-crown-6 (0.10 g, 0.277 mmol) were stirred in dry THF (40 ml) under N<sub>2</sub> at 65 °C for 24 hours. After this time, a solution of 1 % aqueous Na<sub>2</sub>CO<sub>3</sub> (20 ml) was added at 0 °C. The resulting solid was collected, washed with water and ether and dried under vacuum to give 2.17 g (94 %) of the butenetetraester Me<sub>4</sub>L<sub>2</sub> as a white solid.

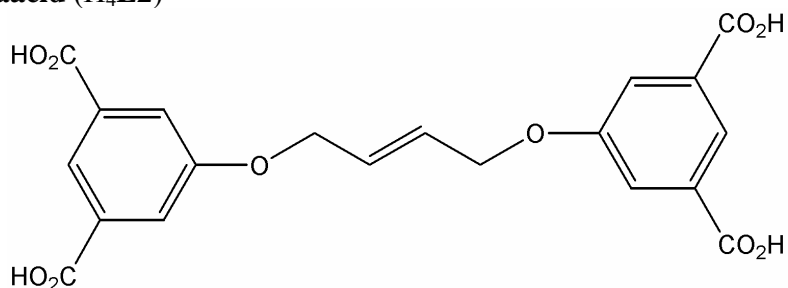
IR (ATR):  $\nu$  1719 cm<sup>-1</sup> (carbonyl)

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  3.92 (s, 12H), 4.68 (dd, 4H), 6.10 (dt, 2H), 7.75 (d, 4H), 8.26 (t, 2H)

<sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  52.48, 67.95, 120.00, 123.24, 128.00, 131.79 (no 4° carbon signals observed)

MS (ESI+): *m/z* calcd for C<sub>24</sub>H<sub>24</sub>O<sub>10</sub> 472, found 472

## 2.4 Butene Tetraacid (H<sub>4</sub>L<sub>2</sub>)



A mixture of butene tetraester Me<sub>4</sub>L<sub>2</sub> (1.00 g, 2.12 mmol), KOH (0.475 g, 8.46 mmol), methanol (15 ml) and distilled water (15 ml) were stirred under N<sub>2</sub> at 60 °C for 48 hours. After this time, the reaction mixture was filtered to remove any unreacted starting materials. HCl (6 M, 25 ml) was then added dropwise at 0 °C. The precipitate was collected, washed with water and dried under vacuum to give 0.556 g (63 %) of butenetetraacid H<sub>4</sub>L<sub>2</sub> as a white solid.

IR (ATR):  $\nu$  1686 cm<sup>-1</sup> (carbonyl)

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta$  4.73 (s, 4H), 6.11 (s, 2H), 7.66 (s, 4H), 8.06 (s, 2H), 13.30 (br, 4H)

<sup>13</sup>C NMR (d<sub>6</sub>-DMSO):  $\delta$  67.67, 119.28, 122.38, 132.58, 158.27, 166.32

MS (ESI-): *m/z* calcd for C<sub>20</sub>H<sub>16</sub>O<sub>10</sub> 416, found 415 [M - H]<sup>+</sup>

Elemental Analysis: calcd for C<sub>20</sub>H<sub>18</sub>O<sub>11</sub> (H<sub>4</sub>·2H<sub>2</sub>O) C 55.30 % H 4.18 %, found C 55.49 % H 3.91 %

### 2.5 [Zn<sub>2</sub>(L1)(H<sub>2</sub>O)<sub>4</sub>]<sub>2</sub>·2H<sub>2</sub>O (1)

Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.112 g, 0.30 mmol) and butane tetraacid H<sub>4</sub>L2 (0.042 g, 0.10 mmol) were added to a Parr 23 ml pressure vessel with Teflon liner followed by DMF (3 ml), ethanol (3 ml) and distilled water (2 ml). The flask was sealed and heated at 95 °C for 48 hours before being cooled down to room temperature at 0.1 °C min<sup>-1</sup>. The colourless crystalline product was collected by filtration and included crystals suitable for single crystal diffraction study. Yield 0.039 g (59.7 %). Elemental analysis: calcd for Zn<sub>2</sub>C<sub>20</sub>H<sub>26</sub>O<sub>16</sub> C 36.78 % H 4.01 %; found C 36.72 % H 3.74 %.

### 2.6 [Zn<sub>4</sub>(L2)<sub>2</sub>(DMF)<sub>3</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>2</sub>·4H<sub>2</sub>O (2)

Zn(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.112 g, 0.30 mmol) and butene tetraacid H<sub>4</sub>L1 (0.042 g, 0.10 mmol) were added to a Parr 23 ml pressure vessel with Teflon liner followed by DMF (3 ml), ethanol (3 ml) and distilled water (2 ml). The flask was sealed and heated at 95 °C for 48 hours before being cooled down to room temperature at 0.1 °C min<sup>-1</sup>. The colourless crystalline product was collected by filtration and included crystals suitable for single crystal diffraction study. Yield 0.051 g (35.6 %). Elemental analysis: calcd for Zn<sub>4</sub>C<sub>49</sub>H<sub>59</sub>O<sub>30</sub>N<sub>3</sub> C 41.11 % H 4.15 % N 2.94 %; found C 40.64 % H 3.95 % N 2.56 %. The powder diffraction pattern of the bulk sample was consistent with that calculated from the single crystal diffraction data.

## 3. Crystallography

### 3.1 Single Crystal Diffraction

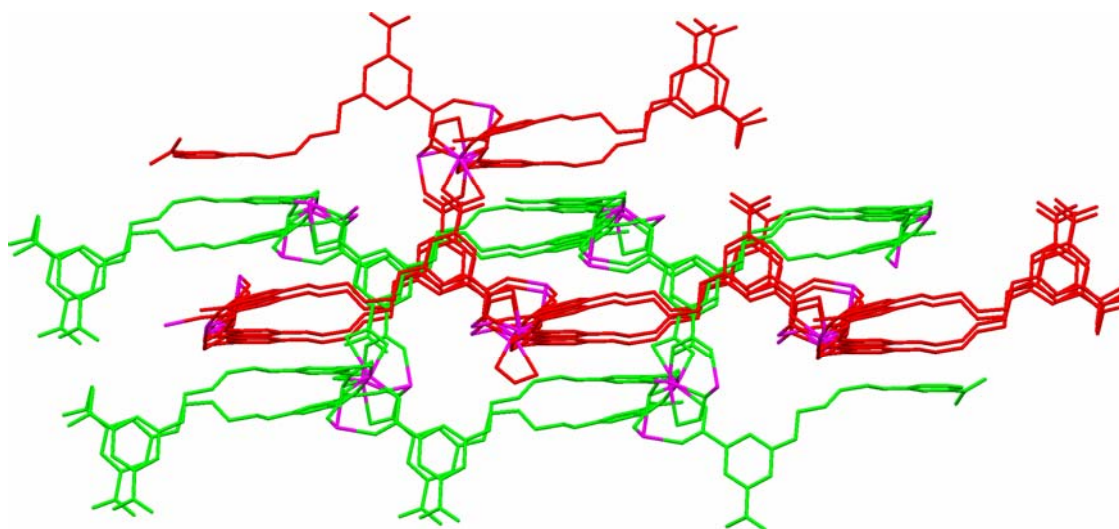
Crystals of **1** and **2** were mounted using a viscous hydrocarbon oil to coat the crystal on a thin carbon fibre attached to the end of a borosilicate glass capillary. X-ray data were collected on synchrotron beam line 16.2smx at the Synchrotron Radiation Source at the CCLRC Daresbury Laboratory at 100 K. For each compound, data were corrected for absorption using empirical methods (SADABS) based upon symmetry equivalent reflections combined with measurements at different azimuthal angles [1]. Crystal structures were solved and refined against all  $F^2$  values using the SHELXTL suite of programs [2]. Non-hydrogen atoms were refined anisotropically (when no disorder was present) and hydrogen atoms associated with oxygen atoms were located from the difference map and the O–H distance fixed at 0.96 Å. All other hydrogen atoms were placed in calculated positions with idealised geometries and refined using a riding model. In **2**, three of the four uncoordinated water molecules have the oxygen atom disordered over two sites and have been modelled with 59(1):41(1), 72(2):28(2) and 58(2):42(2) ratios respectively. Hydrogen atoms were not modelled on the disordered water molecules. Views of the two-fold interpenetrated diamondoid network adopted by **2** are shown in Figures S1 and S2.

**Table S1.** Data collection, Structure Solution and Refinement Parameters for **1** and **2**

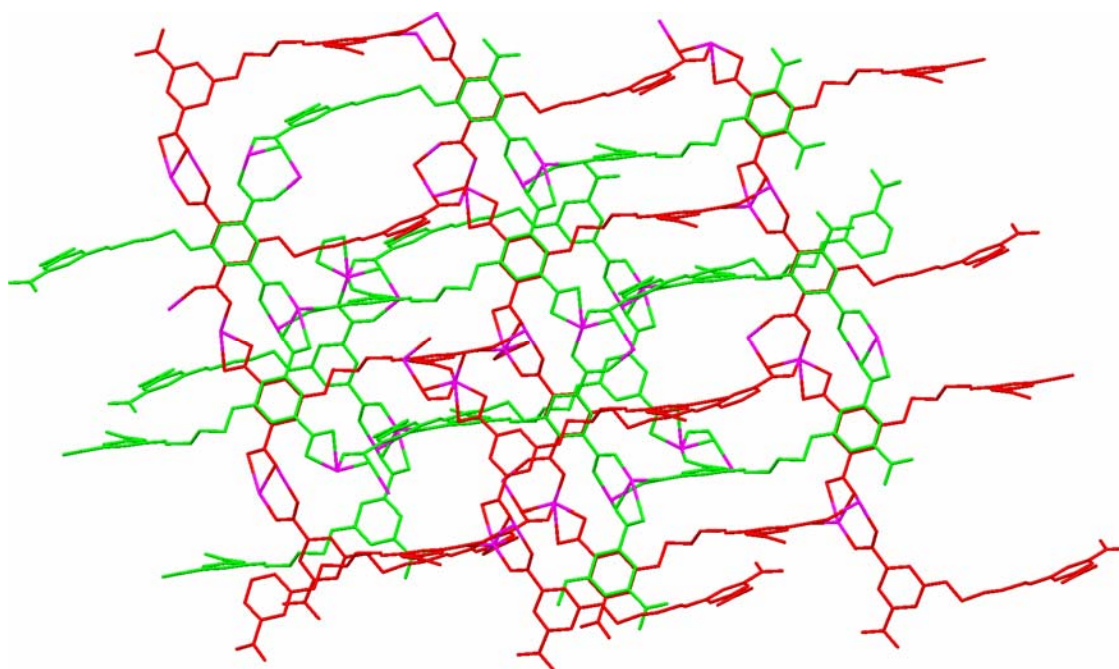
	<b>1</b>	<b>2</b>
Crystal colour	Colourless	Colourless
Formula	Zn <sub>2</sub> C <sub>20</sub> H <sub>26</sub> O <sub>16</sub>	Zn <sub>4</sub> C <sub>49</sub> H <sub>59</sub> O <sub>30</sub> N <sub>3</sub>
M <sub>r</sub>	326.57	1431.67
Crystal size (mm)	0.06 x 0.06 x 0.06	0.20 x 0.13 x 0.03
Crystal system	Triclinic	Triclinic
Space group, Z	<i>P</i> -1, 1	<i>P</i> -1, 2
<i>a</i> (Å)	7.6916(15)	13.0757(6)

<i>b</i> (Å)	8.5113(17)	14.1157(7)
<i>c</i> (Å)	9.827(2)	16.6631(8)
$\alpha$ (°)	68.56(3)	66.602(1)
$\beta$ (°)	79.47(3)	87.138(1)
$\gamma$ (°)	86.62(3)	89.757(1)
<i>V</i> (Å <sup>3</sup> )	588.7(2)	2818.7(2)
Calcd density (Mg/m <sup>3</sup> )	1.842	1.687
$\lambda$ (Å)	0.84600	0.84600
Temp (K)	100(2)	100(2)
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	2.121	1.779
$\theta$ range (deg)	3.81 to 32.87	3.74 to 31.00
Reflns collected	4270	19414
Independent reflns ( <i>R</i> <sub>int</sub> )	2358 (0.0357)	10334 (0.0403)
Reflns used in refinement, <i>n</i>	2358	10334
Restraints	0	0
L.S. parameters, <i>p</i>	172	811
<i>R</i> 1( <i>F</i> ) <sup>a</sup> , <i>I</i> > 2.0 $\sigma$ ( <i>I</i> )	0.0460	0.0487
<i>wR</i> 2( <i>F</i> <sup>2</sup> ) <sup>a</sup> , all data	0.1268	0.1341
<i>S</i> ( <i>F</i> <sup>2</sup> ) <sup>a</sup> , all data	1.059	1.088
Max final $\Delta\rho$ (e. Å <sup>-3</sup> )	1.081	1.306
Min final $\Delta\rho$ (e. Å <sup>-3</sup> )	-1.163	-1.053

$$^a R1(F) = \Sigma(|F_o| - |F_c|) / \Sigma|F_o| ; wR2(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{1/2} ; S(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$$



**Figure S1.** Two-fold interpenetrated diamondoid network exhibited by **2**. Separate networks shown in green and red, Zn atoms shown in purple. Hydrogen atom, water molecules and DMF molecules are not shown.



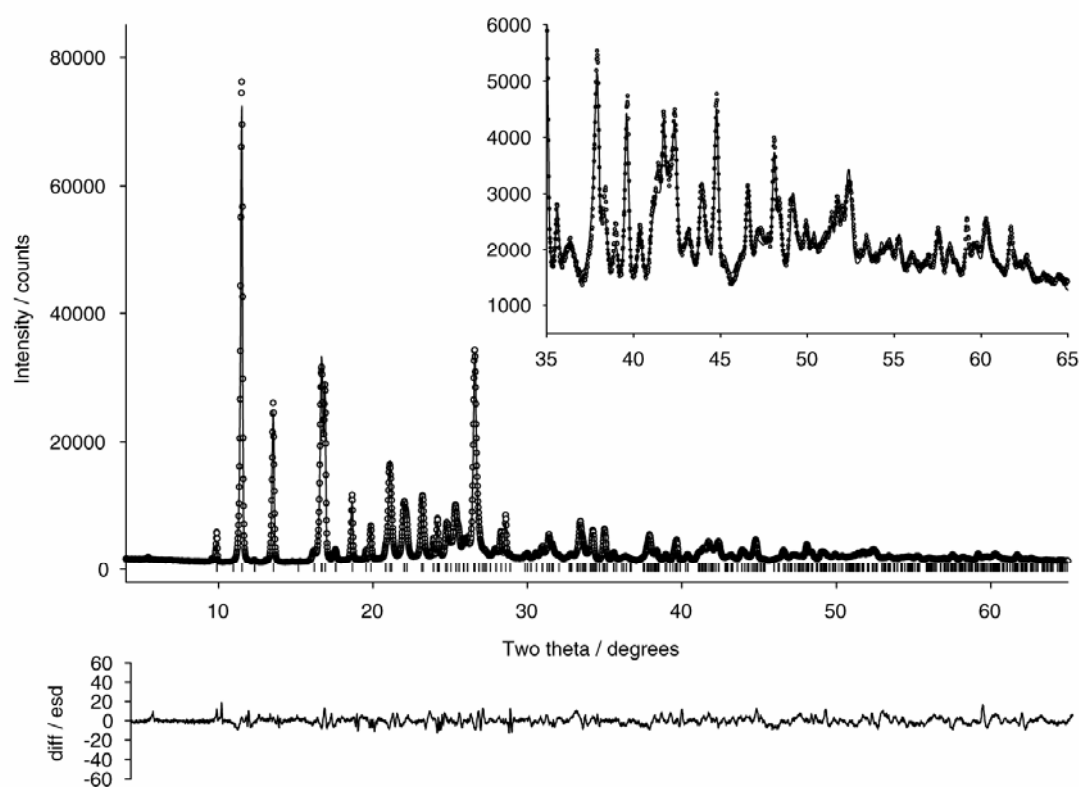
**Figure S2.** Alternative view of two-fold interpenetrated diamondoid network exhibited by **2**. Colours as in Figure S1. Hydrogen atom, water molecules and DMF molecules are not shown.

### 3.2 Powder diffraction

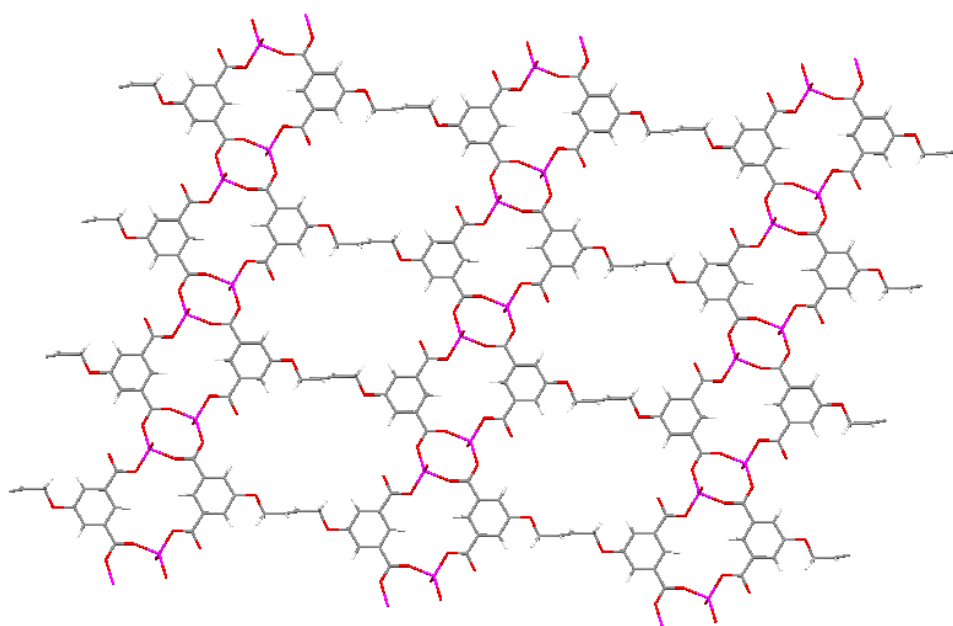
The polycrystalline sample **3** was lightly ground in an agate mortar and pestle and filled into 1.0 mm borosilicate glass capillary prior to being mounted and aligned on a Bruker-AXS D8 Advance powder diffractometer, using Cu  $K_{\alpha 1}$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). One dataset ( $2\theta = 3 - 65^\circ$ ) was collected at room temperature using variable a count time (VCT) [3] scheme ( $3.00 - 43.00^\circ = 5 \text{ s/step}$ ;  $43.00 - 65.00^\circ = 20 \text{ s/step}$ ) for  $0.017^\circ$  steps. The diffraction pattern was indexed using DICVOL91 [4] to a triclinic cell [ $F(18) = 54.5$ ,  $M(18) = 24.1$ ] and space group P-1 was assigned from volume considerations [5]. The presence of two, weak peaks at low angle which were not accounted for by the indexed cell and space group indicate the presence of a small amount of polycrystalline impurity in the sample. The dataset was background-subtracted for Pawley refinement [6] and structure solution was performed using the simulated annealing (SA) global optimization procedure, described previously [7], as implemented in the DASH computer program [8]. Z-matrices describing the molecular topology of the fragments were generated within DASH using analogous moieties taken from the CSD [9] and manually modified using standard bond lengths and angles.

Global optimization of external (rotational for the half-ligand; translational for Zn and both water oxygens) degrees of freedom against the extracted intensities was carried out with cooling rate set to 0.01 and all other DASH SA control parameters set to default values. One hundred SA runs with  $2.5 \times 10^7$  SA moves per run were implemented for the structure determination. The SA structure solution involved the optimisation of four independent fragments in the asymmetric unit (one  $\text{Zn}^{2+}$  ion, one half-ligand and two water molecules), totalling 17 degrees of freedom. The position of the half ligand was constrained to rotate around the origin using a dummy atom in the z-matrix (reducing the external (rotational) degrees of freedom by 3). All degrees of freedom were assigned random values at the start of the simulated annealing. The best SA solutions had  $\chi^2(\text{profile})/\chi^2(\text{Pawley})$  ratio of 4.77 and a chemically reasonable packing arrangement. The solved

structure was then refined against the data in the range 4 - 65 ° 2 $\theta$  using a restrained Rietveld method as implemented in TOPAS v3.1 [10], where only the scale factor, background, zero error, axial model, peak shape and unit cell parameters were refined. The  $R_{wp}$  fell to 0.06027 during the refinement. All atomic positions (including H-atoms) for the structure of were refined, subject to a series of restraints on bond lengths, bond angles and planarity. A spherical harmonics correction of intensities for preferred orientation was applied in the final refinement [11]. The observed and calculated diffraction patterns for the refined crystal structures are shown in Figure S3. The crystal structure of **3** is shown in Figure S4.



**Figure S3.** Final observed (points), calculated (line) and difference plot  $[(I_{obs} - I_{calc})/\sigma(I_{obs})]$  from the Rietveld refinement for **3** (2 $\theta$  range 4.0 – 65.0 °).



**Figure S4.** Crystal structure of **3** shown without water molecules in channels. Hydrogen atoms on coordinated water molecules are omitted (and were not used in the model).

**Table S2.** Data collection, Structure Solution and Refinement Parameters for **3**

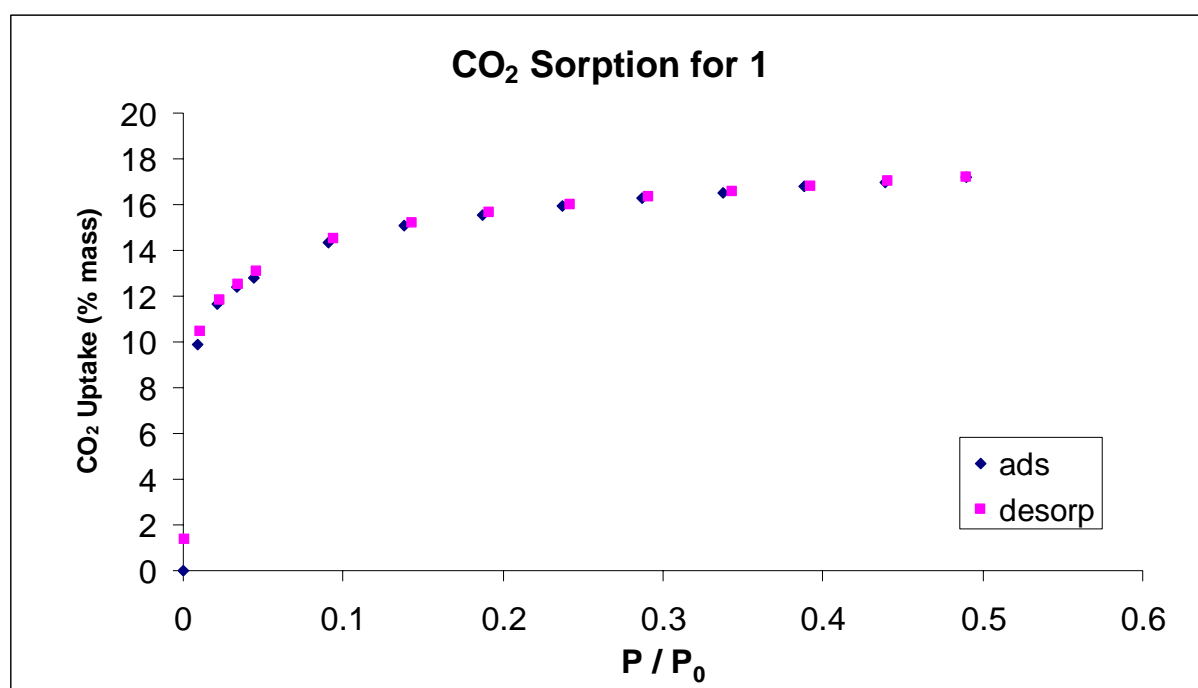
<b>3</b>	
Specimen colour	White
Specimen shape (mm)	Cylinder 12 × 1.0 × 1.0 mm
Crystal system	Triclinic
Space group, Z	<i>P</i> -1, 1
<i>a</i> (Å)	9.5471(7)
<i>b</i> (Å)	7.8520(7)
<i>c</i> (Å)	8.4756(6)
$\alpha$ (°)	91.891(4)
$\beta$ (°)	107.086(3)
$\gamma$ (°)	100.815(4)
<i>V</i> (Å <sup>3</sup> )	593.90(8)
Density (Mg/m <sup>3</sup> )	1.695
Temperature (K)	298
$\mu$ (mm <sup>-1</sup> )	3.139
2 $\theta$ range (deg)	3.0 to 65.0
Increment in 2 $\theta$ (deg)	0.0172
reflns measured	429
Specimen mounting	1.0 mm borosilicate capillary
Mode	Transmission
Scan method	Step
Parameters refined	95
No. of Restraints	57
<i>R</i> <sub>p</sub>	0.0478
<i>R</i> <sub>wp</sub>	0.0630
<i>R</i> <sub>exp</sub>	0.0164

#### 4. CO<sub>2</sub> Sorption Measurements

Sorption studies were carried out using a Hiden Isochema (Warrington, U. K.) Intelligent Gravimetric Analyser (IGA) equipped with a micro-gram balance and 2, 100 and 20000 mbar baratron pressure transducers. Temperature control was via a furnace for desolvation of the as-



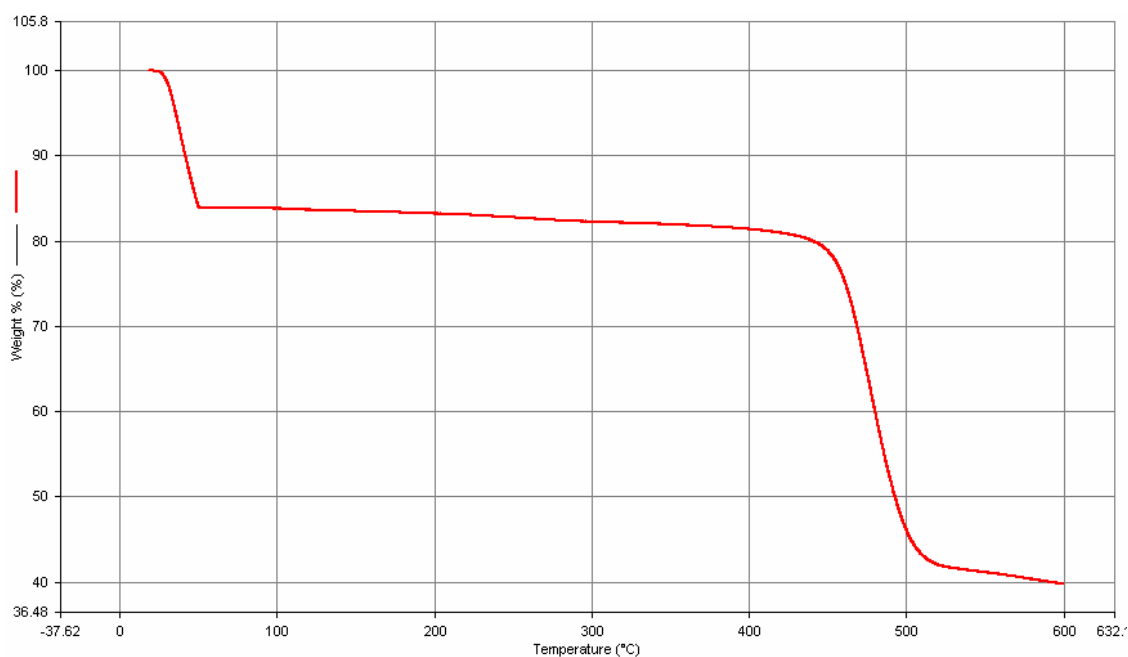
made phases, and by immersion of the reaction chamber into solid carbon dioxide contained in a cryogenic vessel (at 198 K) during isotherm measurement. Samples were desolvated at 150°C under high dynamic vacuum ( $10^{-7}$  mbar) until a constant mass had been reached; typically overnight. The carbon-dioxide (SFC grade) used for this study was supplied by BOC gases. All admittance pipe work was thoroughly decontaminated under high vacuum prior to the admission of any gas, and an activated carbon standard of known surface area was used to validate all measurement protocols. All isotherm data points were fitted by the IGASwin systems software v.1.03.84 (Hidden Isochema 2002) using a linear driving force model, and all data were corrected for buoyancy effects. The CO<sub>2</sub> sorption and desorption isotherms for **1** are shown in Figure S5. The corresponding isotherms for **2** can be found in Figure 3.



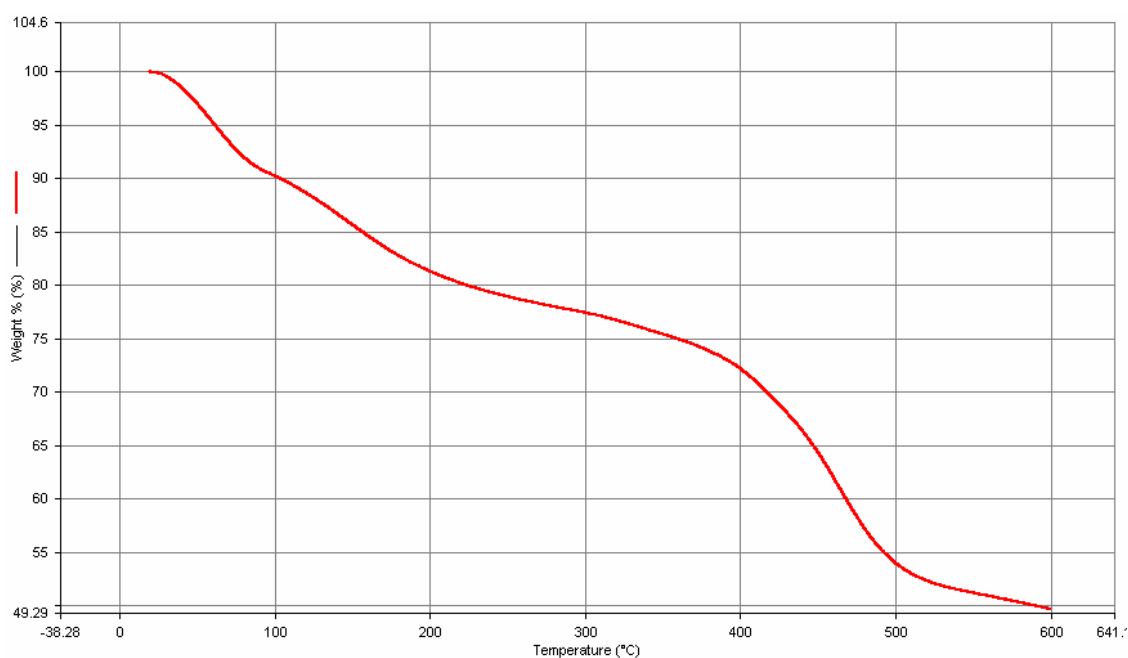
**Figure S5.** Sorption-desorption isotherm of **1** at 198 K obtained with CO<sub>2</sub> gas over the pressure range 2-1000 mbar (relative pressure range from  $6 \times 10^{-5}$  to 0.5)

## 5. TGA Measurements

Thermogravimetric analysis (TGA) was conducted using a Perkin-Elmer Pyris 1 TGA instrument with heating under N<sub>2</sub> at 5 °C min<sup>-1</sup> from room temperature to 600 °C for **1** and **2**. The TGA traces for **1** and **2** are shown in Figures S6 and S7, respectively.



**Figure S6.** TGA trace for **1** (heating under N<sub>2</sub> at 5 °C min<sup>-1</sup> from room temperature to 600 °C)



**Figure S7.** TGA trace for **2** (heating under N<sub>2</sub> at 5 °C min<sup>-1</sup> from room temperature to 600 °C)

## 5. References

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