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$_2$L$^1$

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

![Scheme S1](image)

**Scheme S1.** (i) H$_2$SO$_4$, MeOH (ii) Allyl bromide, K$_2$CO$_3$, DMF (iii) NaOH$_{aq}$, MeOH/THF.

*Dimethyl 2,5-dihydroxyterephthalate*

Concentrated H$_2$SO$_4$ (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 $\delta_H$ (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$_2$CO$_3$ (3.6 g, 26 mmol) and Me$_4$Ni (0.1 g, 0.5 mmol) and the mixture stirred at room temperature over the weekend. The mixture was then diluted with H$_2$O (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$_2$CO$_3$ solution until the organic layer was colourless, then with H$_2$O, brine and dried over Na$_2$SO$_4$ and the solvent was removed by rotary evaporation. The resulting solid was taken up in CH$_2$Cl$_2$ and passed through a plug of silica gel then concentrated by rotary evaporation before crystallization from CH$_2$Cl$_2$/Pet. 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 $\delta_H$ (300 MHz; CDCl$_3$) 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 $\delta_C$ (300 MHz; DMSO-d$_6$) 69.56, 116.01, 117.14, 125.52, 133.62, 150.24, 166.92.

2,5-Bis(allyloxy)terephthalic acid, H$_2$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$_2$O (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$_2$O (3 × 5 cm$^3$) and oven dried (80 ºC). 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 $\delta_H$ (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 $\delta_C$ (300 MHz; DMSO-d$_6$) 69.56, 116.01, 117.14, 125.52, 133.62, 150.24, 166.92.
Figure S1 $^1$H NMR spectrum of H$_2$L$^1$ in $d_6$-DMSO solution at 300 MHz.
Figure S2: $^{13}$C NMR spectrum of $\text{H}_2\text{L}^1$ 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.

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<th>2</th>
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<td>Empirical formula</td>
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<td>Largest diff. peak/hole / e Å⁻³</td>
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<td>0.66/-0.26</td>
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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 \textit{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. 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 Å³ with an electron count of 381 electrons. The atoms of the bridging ligand L¹ not accounted for in the formula per ligand of L¹ is C₆H₁₀O₂, which represents 62 electrons. This gives a total of 186 electrons for the number of L¹ ligands per unit cell (3), leaving 195 electrons per unit cell free for disordered solvate, which would account for ≈5 molecules of DMF.

![Figure S3](image)

\textit{Figure S3} Partial structure of 1 showing the disorder of the phenyl ring and Zn₈O 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 L² lying on three mirror planes and 1/24th of a Zn₄O subunit; the central μ₄-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 μ₄-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 R₁ was ≈11% and the highest peak in the difference map was 1.2 electrons/Å³ and afterward the R₁ lowered to 6.16% and the highest peak reduced to 0.7 electrons/Å³. The solvent accessible space is calculated to have a volume of 13280 Å³, which contains 1925 electrons. The formula of the missing atoms per molecule of L² is C₆H₁₀O₂, which accounts for 62 electrons. This gives a total of 1488 electrons for the number of molecules of L² per unit cell (24), leaving approximately 440 electrons per unit cell free for disordered solvate, likely taken up by ≈11 molecules of DMF.

![Figure S4](image.png)

*Figure S4 Partial structure expansion of 2 with thermal ellipsoids to show the small tilting of the phenyl rings.*
3 TG–DTA data

Figure S5. 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 S6. 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 S7 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 S8 $^1$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 Zn₄O(L¹)₃ 1 (black) and Zn₄O(L²)₃ 2 (red)

**Figure S 11** Infrared spectra of H₂L¹ (black) and H₂L² (red)
7 Mass Spectrometry

Figure S12 Negative mode ESI mass spectrum of $\text{H}_2\text{L}^1$

Figure S13 Negative mode ESI mass spectrum of $\text{H}_2\text{L}^2$
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 CO₂ isotherms at 196 K for Zn₄O(L¹)₃ (black) and Zn₄O(L²)₂ (red). Filled squares are adsorption, open squares are desorption.

Figure S 16 CO₂ adsorption data for Zn₄O(L¹)₃ 1 (solid squares) and Zn₄O(L²)₂ 2 (shaded triangles). Black, 273 K; blue, 288 K; orange, 298 K.
**Figure S 17** CO$_2$ and N$_2$ sorption data for Zn$_4$O(L$_1$)$_3$. 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$_4$O(L$_2$)$_2$. 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\textsubscript{2} was determined by comparing carbon dioxide isotherms at 288 and 298 K. Isosteric heat of adsorption calculations (\(-Q_{st}\)) for CO\textsubscript{2} at these temperatures were undertaken by virial fitting and the Clausius-Clapeyron equation:

\[
(ln P)_t = -\left(\frac{Q_{st}}{R}\right)\left(\frac{1}{T}\right) + C
\]

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 S19](image)

**Figure S19** 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, \(\sigma\), by \(2^{1/6}\).


