

The synthesis, structures and reactions of zinc and cobalt metal-organic frameworks with an alkyne-based dicarboxylate linker

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Supplementary information

General information

All MOF synthesis reactions were carried out in Ace pressure tubes purchased from Sigma Aldrich, in a Sanyo MOV-112 oven. X-ray diffraction experiments were carried out on a Nonius Kappa CCD diffractometer using X-rays with molybdenum K_{α} radiation, wavelength 0.71073 Å. X-ray powder diffraction experiments were recorded on a Bruker AXS D8 Advance diffractometer with copper K_{α} radiation of wavelength 1.5406 Å at 298 K. Mass spectrometry (ESI) data were recorded on a Bruker MicroTOF spectrometer, NMR data on a Bruker Avance 250 MHz or Bruker Ultrashield 300 MHz spectrometer and infrared data on a Nicolet Nexus FT-IR spectrometer. Microanalytical data were recorded on a CE-440 Elemental Analyser by Alan Carver at the University of Bath and TGA experiments were performed on a Perkin Elmer TGA 4000 Thermogravimetric Analyser. N_2 adsorption data was recorded on a BELSORP Mini-II instrument.

Synthesis of 4,4'-ethynylenedibenzoic acid (H_2edb)

(i) Synthesis of methyl-4-ethynylbenzoate

Methyl-4-iodobenzoate (2.6 g, 10 mmol) and $PdCl_2(PPh_3)_2$ (0.14 g, 2 mol%) were placed in a two-necked flask and purged with N_2 . THF (20 cm³) was purged with N_2 and added via syringe. The reaction mixture was stirred until all solids had dissolved. Trimethylsilylacetylene (1.8 cm³, 12.5 mmol) and triethylamine (1.7 cm³, 12.5 mmol) were added, followed by copper(I) iodide (0.076 g, 4 mol%). The reaction mixture was stirred under N_2 for 4 h at room temperature, before being transferred to a round-bottomed flask. The THF was almost completely removed by rotary evaporation and hexane (50 cm³) was added to the remaining mixture. Solid $Et_3N \cdot HI$ was removed by filtration through Celite, which was washed with hexane (3 × 25 cm³). The filtrate and washings were then transferred to a separating funnel and washed with water (50 cm³). The hexane layer was collected, dried with sodium sulfate and decanted into a round-bottomed flask. The hexane was

removed by rotary evaporation and methanol (20 cm³) was added to re-dissolve the remaining solid. K₂CO₃ (0.15 g) was then added and the reaction mixture was stirred for 90 min at room temperature. The methanol was almost completely removed by rotary evaporation and water (50 cm³) was added to the remaining mixture. The product was extracted from this mixture with diethyl ether (3 × 30 cm³). The organic extracts were washed with water (3 × 30 cm³), followed by brine (20 cm³). The organic extracts were collected, dried with sodium sulfate and decanted into a round-bottomed flask. The diethyl ether was removed by rotary evaporation and the remaining solid was purified on a silica column, yielding methyl-4-ethynylbenzoate as a pale orange powder.

¹H NMR: δ(CDCl₃)/ppm: 7.92 (d, ³J_{HH} 8.7 Hz, 2H), 7.48 (d, ³J_{HH} 8.7 Hz, 2H), 3.85 (s, 3H), 3.16 (s, 1H).

(ii) Synthesis of 4-ethynylbenzoic acid

Methyl-4-ethynylbenzoate (1.43 g, 8.9 mmol), 1M aqueous sodium hydroxide (10.3 cm³, 10.3 mmol) and 1:1 methanol:THF (20 cm³) were added to a round bottomed flask and stirred for 2 h at room temperature. The solvents were removed by rotary evaporation and water (50 cm³) was added to the remaining solid. The mixture was filtered through celite and washed through with water. The filtrate was transferred to a conical flask and acidified with 1M HCl to precipitate the product, which was isolated by filtration and washed with water (3 × 30 cm³). The solid was dried, yielding 4-ethynylbenzoic acid as a pale orange powder.

¹H NMR: δ(d₆-DMSO)/ppm: 7.99 (d, ³J_{HH} 8.4 Hz, 2H), 7.65 (d, ³J_{HH} 8.4 Hz, 2H), 4.50 (s, 1H).

(iii) Synthesis of 4,4'-ethynylenedibenzoic acid (H₂edb)

4-ethynylbenzoic acid (0.410 g, 2.8 mmol), 4-iodobenzoic acid (0.690 g, 2.8 mmol), K₂CO₃ (1.16 g, 8.4 mmol), Pd(OAc)₂ (0.032 g, 5mol%) and trisodium triphenylphosphine-3,3',3''-trisulfonate (0.350 g, 25 mol%) were placed in a two-necked flask and purged with N₂. A 1:1 mixture of acetonitrile and water (100 cm³) was purged with nitrogen and added via syringe. The reaction mixture was stirred until all solids had dissolved. The mixture was then heated to 50 °C in an oil bath. Copper(I) iodide (0.053 g, 10 mol%) was added and the mixture was stirred under N₂ for 24 h at 50 °C. The solvent was removed by rotary evaporation and water (100 cm³) added. The solution was filtered to remove any unwanted copper iodide or copper compounds that may have been formed. The filtrate was transferred to a conical flask and acidified with 1M HCl to precipitate the product. The solid was separated by filtration and the product washed with water (3 × 50 cm³).

The isolated solid was then re-dissolved in hot DMF and filtered hot, then washed with further DMF. The filtrate was allowed to cool and the product precipitated on cooling as a white powdery solid. Yield 0.396 g (53 %). This solid was found to be soluble in DMF and DMSO but insoluble in most other common solvents.

^1H NMR: $\delta(d_6\text{-DMSO})/\text{ppm}$: 8.00 (d (br), 4H), 7.72 (d (br), 4H).

MS: m/z (I %): (M – H) 265 (100 %); 248 (17.9 %), 221 (24.5 %), 220 (22.1 %), 176 (26.9 %).

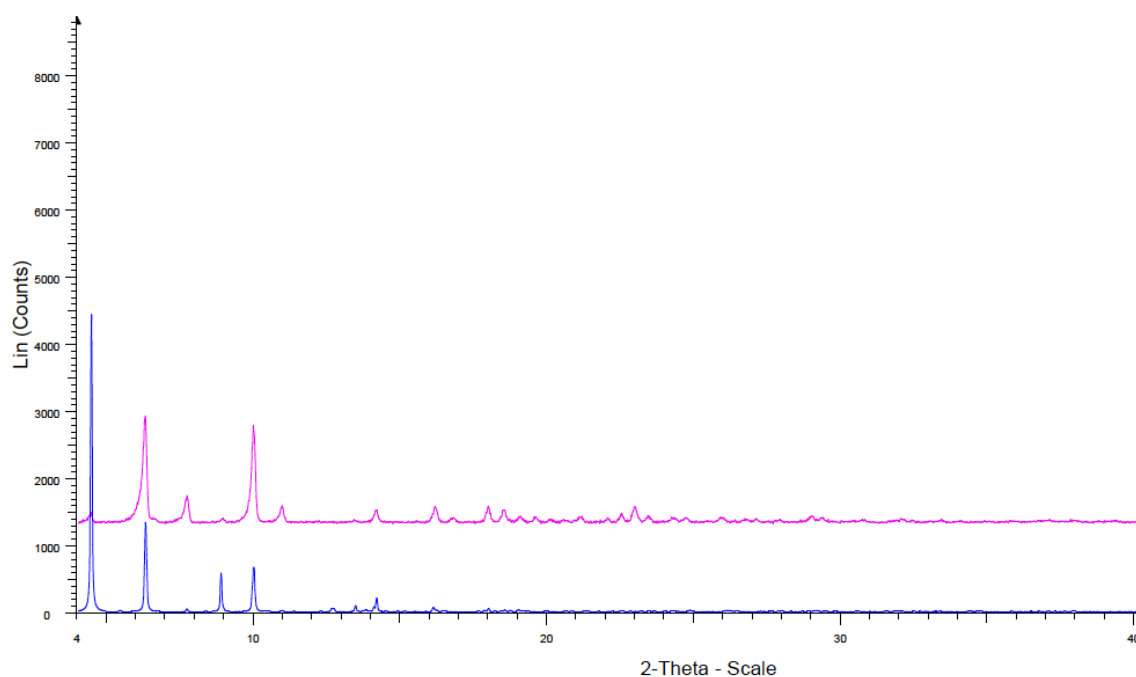


Fig. S1. Experimental X-ray powder diffraction pattern of $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2]\cdot 6\text{DMF}$ **1** (pink) compared to that simulated from the single crystal data (blue).

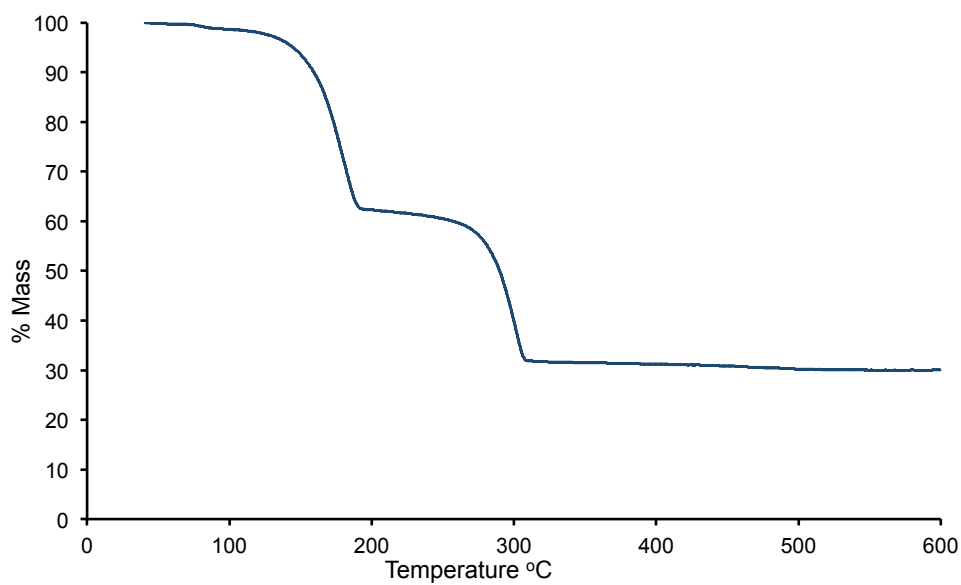


Fig. S2. Thermogravimetric analysis for $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2]\cdot 6\text{DMF}$ **1**.

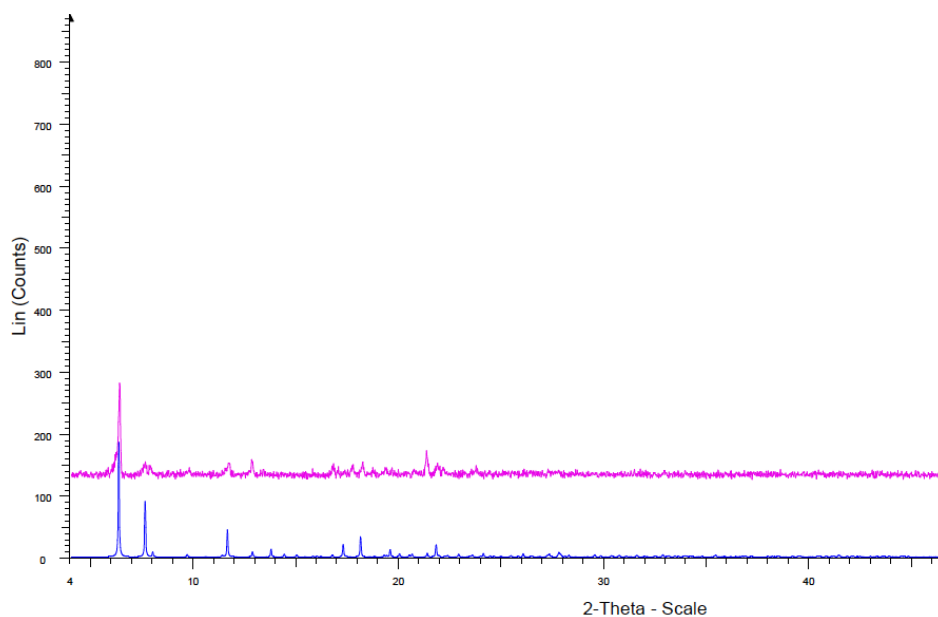


Fig. S3. Experimental X-ray powder diffraction pattern for $[\text{Co}_3(\text{edb})_3(\text{DMF})_4] \cdot 2.6\text{DMF}$ **2** (pink) compared to that simulated from the single crystal data (blue).

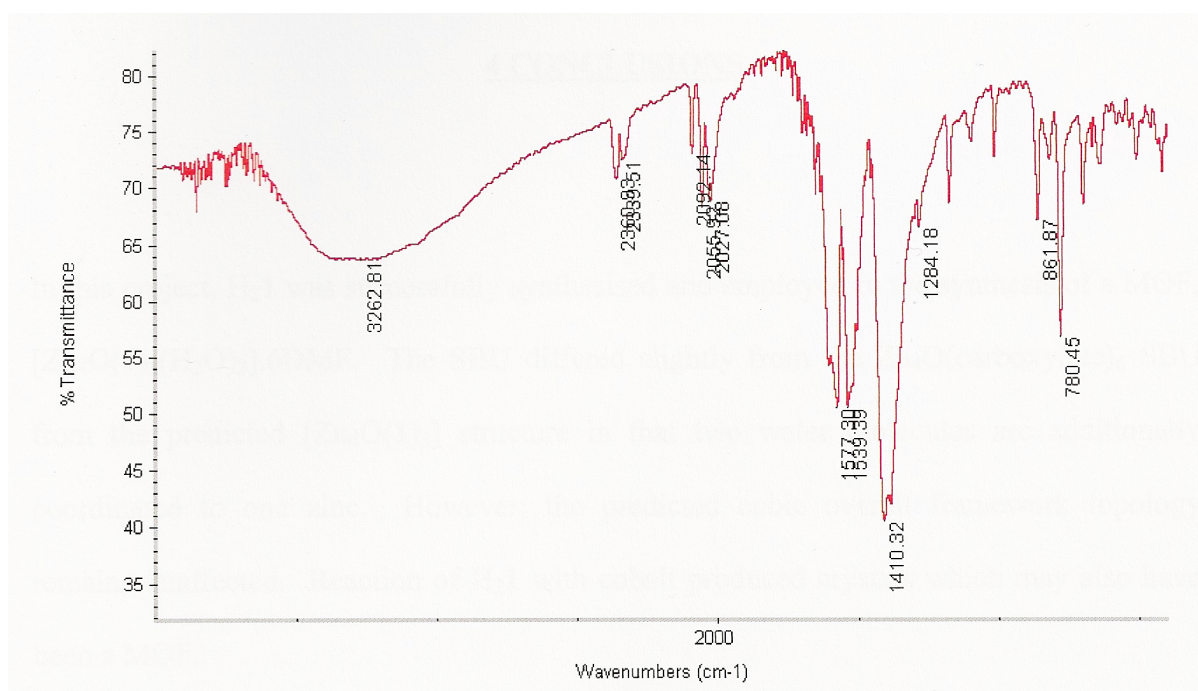


Fig. S4. IR spectrum of $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2] \cdot 6\text{DMF}$ **1** following treatment with $[\text{Co}_2(\text{CO})_8]$.

X-ray crystallographic analysis of $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2] \cdot 6\text{DMF}$ **1**

The structure were solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97.^{S1} The asymmetric unit in this structure, shown in Figure S5, consists of one full zinc atom, one full dicarboxylate ligand, two half-occupancy zinc atoms (located at special positions coincident with a crystallographic mirror plane in the space group symmetry), one half of a dicarboxylate ligand (wherein O6, O7, O8, C18-26, C29, C30, O8 and associated hydrogen atoms where relevant also lie on the mirror plane), two half water molecules (O9, O10, also on the mirror symmetry element), and approximately three DMF molecules.

The water hydrogen atoms could not be located reliably, and hence were omitted from the final least squares refinement. The DMF was very diffuse / disordered, hence the data were subjected to the PLATON SQUEEZE routine, from which the estimate of three molecules per asymmetric unit arose. This solvent was accounted for in the unit cell contents during the final least squares cycles. Details of the crystal data and structural refinement for **1** are given in Table S1.

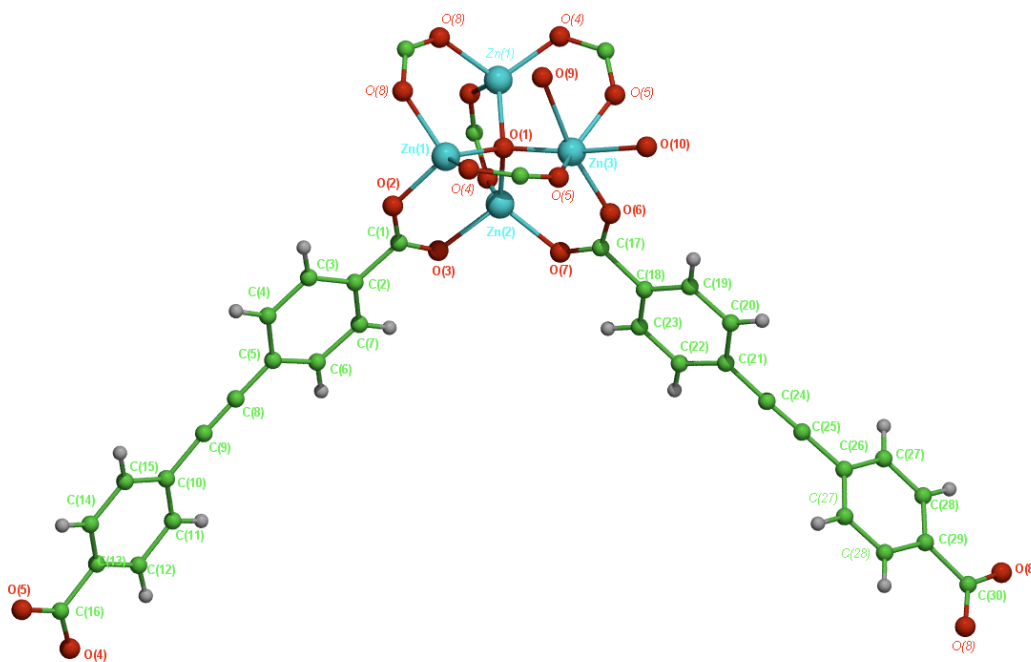


Fig. S5 The asymmetric unit for $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2] \cdot 6\text{DMF}$ **1**. The atoms labelled in italics are related to those in the asymmetric unit by symmetry.

Table S1. Crystal data and structure refinement for $[\text{Zn}_4\text{O}(\text{edb})_3(\text{H}_2\text{O})_2]\cdot 6\text{DMF}$ **1**.

Empirical formula	$\text{C}_{33}\text{H}_{35}\text{N}_3\text{O}_{10.5}\text{Zn}_2$
Formula weight	772.38
Temperature / K	200(2)
Crystal system	Orthorhombic
Space group	$Pn\bar{m}n$
Unit cell dimensions	$a = 19.8070(3) \text{ \AA}, \alpha = 90^\circ$
	$b = 27.7140(5) \text{ \AA}, \beta = 90^\circ$
	$c = 27.8470(5) \text{ \AA}, \gamma = 90^\circ$
Volume / \AA^3	15286.1(5)
Z	8
Absorption coefficient / mm^{-1}	0.655
Reflections collected	117607
Independent reflections	9432 [$R(\text{int}) = 0.1865$]
Reflections observed ($>2\sigma$)	5767
Data Completeness	0.991
Data / restraints / parameters	9432 / 0 / 331
Goodness-of-fit on F^2	0.985
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0602$ $wR2 = 0.1523$
R indices (all data)	$R1 = 0.1209$ $wR2 = 0.1769$
Largest diff. peak and hole / e \AA^{-3}	0.549 and -0.481

X-ray crystallographic analysis of $[\text{Co}_3(\text{edb})_3(\text{DMF})_4] \cdot 2.6\text{DMF}$ **2**

The structure were solved using SHELXS-97 and refined using full-matrix least squares in SHELXL-97.^{S1} The asymmetric unit, shown in Figure S6, consists of one and a half cobalt centres, one full edb ligand, one half of an edb ligand, one DMF ligand and two areas of free solvent. The latter comprises of one DMF fragment with 50% occupancy plus one DMF fragment with 80% occupancy. The partial solvent was refined subject to similarity restraints for the bond distances and ADPs therein. There was clearly some disorder in these two areas, which is not unsurprising, but this could not be readily modelled. The largest difference peak in the electron density map is associated with the free solvent. Details of the crystal data and structural refinement for **2** are given in Table S2.

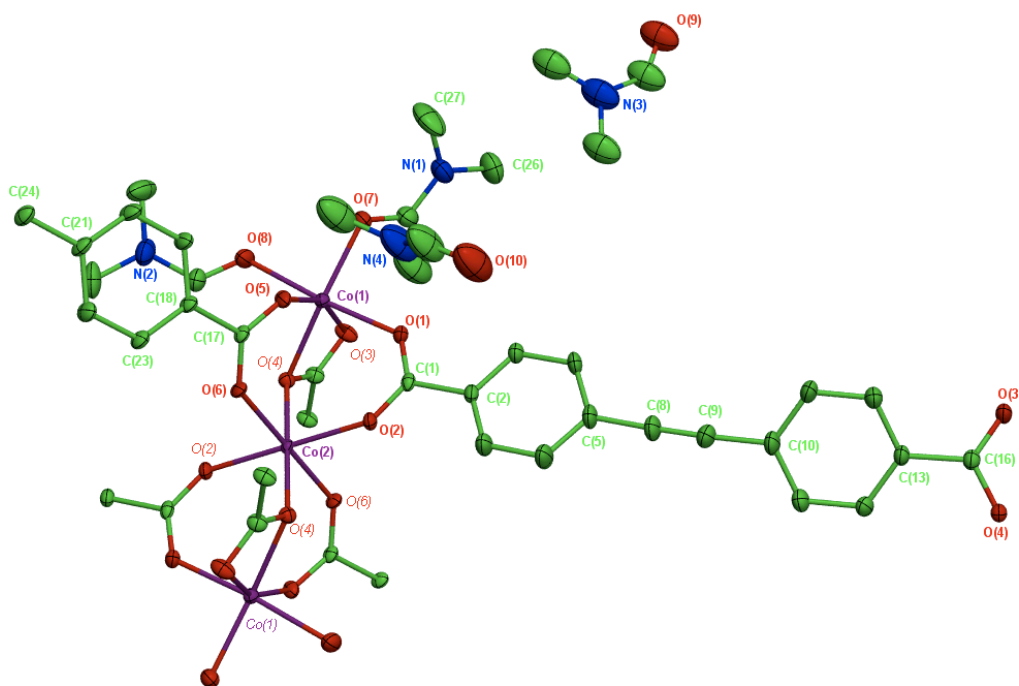


Fig. S6. The asymmetric unit for $[\text{Co}_3(\text{edb})_3(\text{DMF})_4] \cdot 2.6\text{DMF}$ **2**. The atoms labelled in *italics* are related to those in the asymmetric unit by symmetry.

Table S2. Crystal data and structure refinement for $[\text{Co}_3(\text{edb})_3(\text{DMF})_4] \cdot 2.6\text{DMF}$ **2**.

Empirical formula	$\text{C}_{33.9}\text{H}_{35.1}\text{Co}_{1.5}\text{N}_{3.3}\text{O}_{9.3}$
Formula weight	725.95
Temperature / K	150(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 15.3310(2) \text{ \AA}, \alpha = 90^\circ$
	$b = 17.9570(3) \text{ \AA}, \beta = 117.704(1)^\circ$
	$c = 16.5330(3) \text{ \AA}, \gamma = 90^\circ$
Volume / \AA^3	4029.73(11)
Z	4
Absorption coefficient / mm^{-1}	0.674
Reflections collected	76129
Independent reflections	9233 [R(int) = 0.1353]
Reflections observed ($>2\sigma$)	5204
Data Completeness	0.988
Data / restraints / parameters	9233 / 53 / 451
Goodness-of-fit on F^2	1.033
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0775 \quad wR2 = 0.2087$
R indices (all data)	$R1 = 0.1507 \quad wR2 = 0.2547$
Largest diff. peak and hole / e \AA^{-3}	1.566 and -1.049

Adsorption simulations

Grand Canonical Monte Carlo^{S2} (GCMC) simulations were used to calculate nitrogen adsorption isotherms. Nitrogen molecules were modelled as diatomic rigid molecules with the nitrogen atoms separated by the experimental bond length of 1.10 Å. The Lennard-Jones potential parameters for the atoms in the nitrogen molecule were taken from the TraPPE force field developed by Potoff and Siepmann.^{S3} The intrinsic quadrupole of the molecule was described using partial charges with a partial charge on each nitrogen atom of -0.482 and, to maintain electro-neutrality, a further partial charge of $+0.964$ positioned at the centre of mass of the molecule. The MOF framework was represented in atomistic detail with the atoms kept fixed at the crystallographic positions.

For the nitrogen-nitrogen interactions, both dispersive and electrostatic interactions were taken into account using the Lennard Jones potential and the Ewald summation method,^{S2,S4} respectively. The Dreiding force field^{S5} was used to describe the dispersive nitrogen-framework interactions. The electrostatic nitrogen-framework interactions were neglected following the work of Walton and Snurr,^{S6} who showed that their influence on the amount of nitrogen adsorbed in IRMOF materials is negligible.

The pore size distribution (Figure S7) was calculated using the method of Gelb and Gubbins,^{S7} which determines the diameter of the largest sphere that can fit into the cavity without overlapping the framework atoms. The geometric accessible surface area was determined using the methodology described by Düren *et al.* using a nitrogen-sized, spherical probe molecule. This approach has shown to give good agreement with the BET surface area determined using the Rouquerol method for good quality, highly activated MOF samples.^{S8}

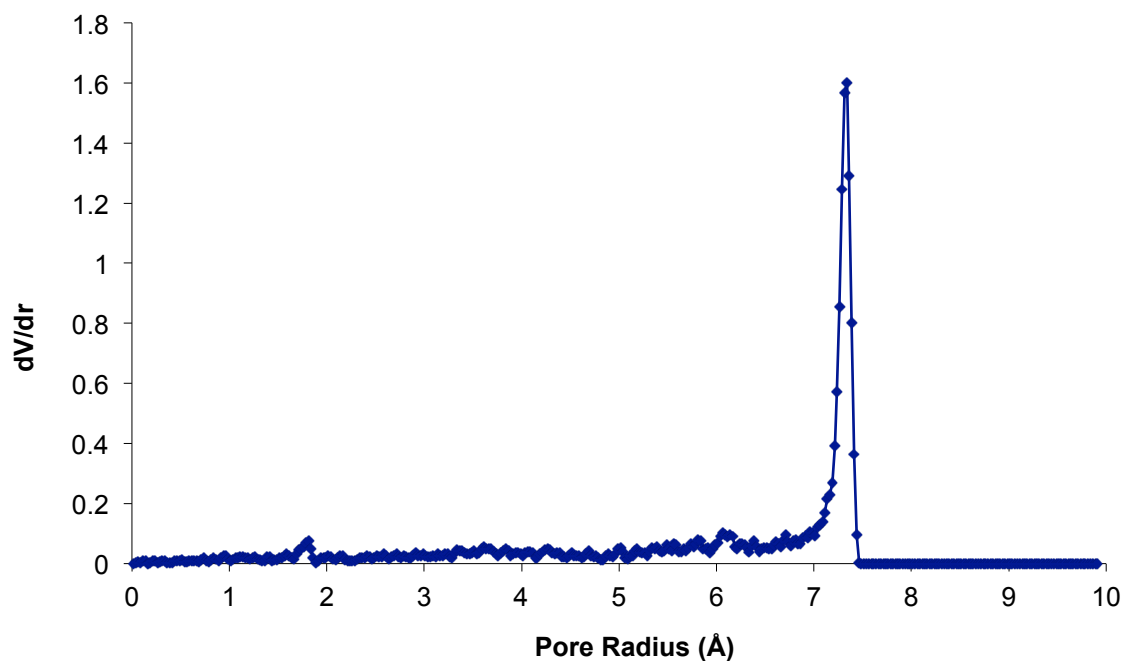


Fig. S7. Pore size distribution calculated from the crystal structure of **1**.

References

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