Electronic Supplementary Information for:

Photolabile Protecting Groups Prevent Interpenetration and Mask Functionality in Metal-Organic Frameworks.

Rajesh K. Deshpande, Geoffrey I. N. Waterhouse, Geoffrey B. Jameson and Shane G. Telfer

[a] *MacDiarmid Institute for Advanced Materials and Nanotechnology, Institute of Fundamental Sciences, Palmerston North, New Zealand; E-mail: s.telfer@massey.ac.nz*

[b] *Department of Chemistry, University of Auckland, Auckland, New Zealand.*

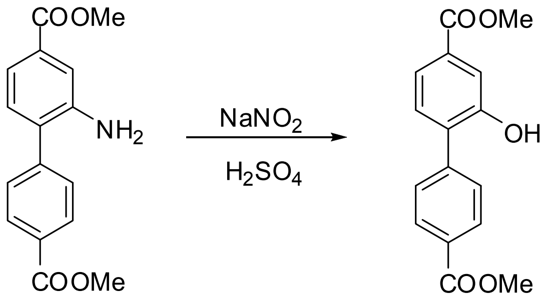
Contents

1. Ligand synthesis and characterization

General procedures

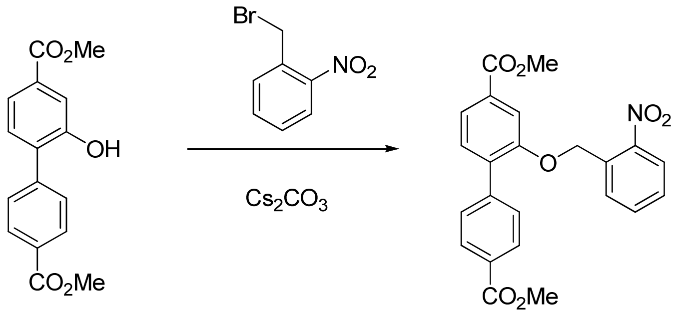
All starting compounds and solvents were used as received from commercial sources without further purification unless otherwise noted. Column chromatography was carried out on silica gel (grade 60, mesh size 230-400, Scharlau). NMR spectra were recorded at room temperature on Bruker-400 and Bruker-500 Avance instruments, with the use of the solvent proton as an internal standard. IR spectra were collected on a Thermo Scientific Nicolet 5700 FT-IR spectrophotometer equipped with an attenuated total reflection (ATR) module (Smart Omni sampler, Ge crystal). Spectra were measured at a resolution of 4 cm^{-1}. Elemental analyses were performed by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 instrument. All MOFs were stored in a desiccator and care was taken to limit their exposure to the atmosphere.

a) Dimethyl 2-hydroxybiphenyl-4,4'-dicarboxylate



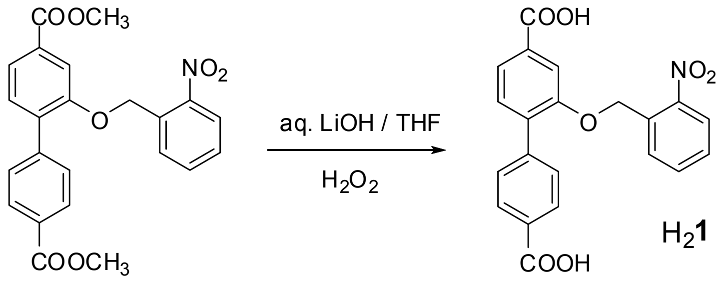
Dimethyl 2-aminobiphenyl-4,4'-dicarboxylate[1] (2.5 g, 8.76 mmol) was stirred in an ice-cold mixture of conc. H_2SO_4 (45 mL) and water (240 mL) for 5 minutes. An ice-cold solution of $NaNO_2$ (0.658 g, 9.54 mmol) in H_2O (80 mL) was then added dropwise over 40 minutes. The mixture was brought to 25 °C with vigorous stirring over 20 minutes. The reaction mixture was then heated to 110 °C for 5 minutes and then allowed to cool slowly to room temperature. An off-white solid was filtered off and washed with H_2O, which was purified by column chromatography using CH_2Cl_2/MeOH (97/3) as eluent. Yield: 1.32 g (4.61 mmol, 53%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 3.85 (s, 3H), 3.87 (s, 3H), 7.45 to 7.50 (m, 2H), 7.59 (d, J = 1.3 Hz, 1H), 7.75 (d, J = 8.5 Hz , 2H), 8.0 (d, J = 8.5 Hz, 2H), 10.23 (brs, 1H). ^{13}C NMR (125 MHz, DMSO-d_6): 52.17, 52.21, 116.60, 120.29, 128.31, 128.94, 129.42, 130.31, 130.75, 131.10, 142.23, 154.59, 165.95, 166.11 ppm. FT-IR: 681.1 (w), 700.0 (m), 733.0 (w), 756.0 (s), 776.3 (m), 796.1 (m), 831.3 (w), 857.3 (m), 888.6 (m), 963.0 (w), 991.7 (m), 1006.9 (w), 1114.2 (s), 1228.6 (s), 1296.2 (s), 1370.8 (w), 1398.6 (m), 1425.1 (sh), 1436.2 (m), 1587.5 (w), 1607.7 (w), 1701.4 (s), 1721.6 (s) cm^{-1}.

b) Dimethyl 2-nitrobenzyloxybiphenyl-4,4’-dicarboxylate



Dimethyl 2-hydroxybiphenyl-4,4’-dicarboxylate (0.700 g, 2.44 mmol), Cs_2CO_3 (0.812 g, 2.5 mmol), and 2-nitrobenzyl bromide (0.793 g, 3.67 mmol) were combined and stirred under argon in dry THF (15 mL) for 9 h at 50 °C. The solvents were evaporated and the yellow-colored product then isolated by column chromatography, eluting with hexane/CH_2Cl_2 (2/3) then CH_2Cl_2. Yield: 1.011 g (2.40 mmol, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.95 (s, 3H), 3.96 (s, 3H), 5.55 (s, 2H), 7.44 - 7.65 (m, 6H), 7.75 (d, *J* = 1.6 Hz, 1H), 7.80 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 8.11 (d, *J* = 8.5 Hz, 2H), 8.15 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-*d*$_6$): δ 52.35, 52.53, 67.86, 113.81, 123.35, 125.22, 128.63, 128.65, 129.50, 129.54, 129.72, 131.12, 131.44, 133.22, 134.22, 134.95, 142.34, 146.94, 155.10, 166.63, 167.09 ppm. FT-IR: 706.3 (m), 728.7 (s), 764.3 (s), 780.3 (s),790.9 (m), 824.6 (w), 852.8 (w), 862.5 (w), 873.9 (w), 978.5 (w), 1005.6 (w), 1037.1 (m), 1049.2 (m), 1105.9 (s), 1136.3 (w), 1182.6 (w), 1193.3 (m), 1219.0 (s), 1257.7 (m), 1280.8 (s), 1304.7 (m), 1339.9 (s), 1380.8 (w), 1397.7 (w), 1417.2 (w), 1436.9 (m), 1493.9 (w), 1525.7 (s), 1576.3 (w), 1609.6 (w), 1713.3 (s) cm^{-1}.

c) 2-Nitrobenzyloxybiphenyl-4, 4’-dicarboxylic acid ($H_2$1)

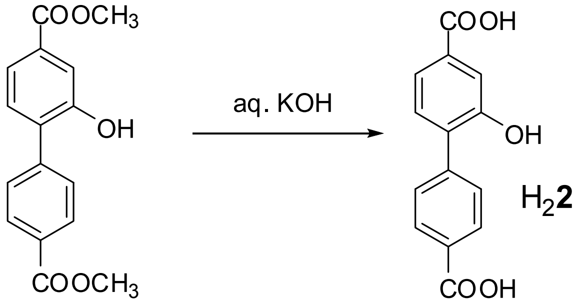


H_2**1**

A mixture of dimethyl 2-nitrobenzyloxybiphenyl-4,4’-dicarboxylate (500 mg, 1.18 mmol), LiOH (1.3 g in 10 mL water), 30% aq. H_2O_2 (10 mL) and THF (10 mL) was stirred for 48 hours at 25 °C. The THF was then removed under reduced pressure then the reaction mixture chilled to ~3 °C and acidified to pH 2.5 with aq. HCl. The resulting white solid was filtered off and washed copiously with H_2O. It was then dissolved in CH_3OH, reprecipitated by the addition of H_2O, filtered off and dried.

Yield: 447 mg (1.11 mmol, 94 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.56 (s, 2H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.59 - 7.76 (m, 7H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.12 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 13.09 (br s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 67.21, 113.35, 122.63, 124.96, 129.08, 129.24, 129.43, 129.87, 130.94, 130.98, 131.98, 132.02, 133.51, 134.09, 141.40, 147.25, 154.71, 166.84, 167.09 ppm. ES-MS (negative mode): *m/z* = 392.54 ($[C_{21}H_{14}NO_7]^-$). FT-IR: 700.5 (w), 724.6 (s), 742.6 (w), 760.1 (s), 789.0 (w), 808.3 (w), 833.9 (w), 865.0 (m), 1006.2 (w), 1034.7 (m), 1121.1 (m), 1231.1 (m), 1290.7 (s), 1341.4 (m), 1425.2 (s), 1528.7 (s), 1578.5 (w), 1605.4 (m), 1648.8 (s) cm^{-1}. Anal. calcd. for $(C_{21}H_{15}NO_7)\ 0.5H_2O$: C, 62.69; H, 4.01; N, 3.48; Found: C, 62.97; H, 3.97; N, 3.45.

d) 2-Hydroxybiphenyl-4,4’-dicarboxylic acid ($H_2$2)



H_2**2**

A mixture of dimethyl 2-hydroxybiphenyl-4,4’-dicarboxylate (286 mg, 1 mmol) in THF (5 mL) and aq. 1 M KOH (5 mL) was refluxed for 20 h. All volatiles were then removed and crude product precipitated by the addition of 1 M HCl. This solid was filtered off and washed with water before being dissolved in CH_3OH and re-precipitated with H_2O. The grayish white product was filtered off, washed with water, and dried. Yield: 256 mg (0.99 mmol, 99 %). ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.42-7.48 (m, 2H), 7.56 (d, *J* = 1.5Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 10.13 (s, 1H), 12.97 (br s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 116.88, 120.64, 129.21, 129.39, 129.47, 130.70, 131.05, 131.55, 142.16, 154.55, 167.19, 167.36 ppm. ES-MS (negative mode): *m/z* = 257.19 ($[C_{14}H_9O_5]^-$). All other data matched those previously reported for this compound.[2]

2. MOF synthesis and photolysis

The following protocol was used for digestion of the MOFs for ^1H NMR spectroscopy[3]: 23 µL of 35% DCl solution in D_2O was mixed with 1 mL of DMSO-*d₆* to give a DCl/DMSO-*d₆* stock solution. Around 5 mg of MOF was digested in 71 µL of this stock solution and 0.45 mL of DMSO-d_6. Spectra were acquired immediately following dissolution of the framework.

(a) Synthesis of [$Zn_4O(1)_3$]

Ligand H_2**1** (200 mg, 0.5 mmol) was combined with $Zn(NO_3)_2{\cdot}4H_2O$ (390 mg, 1.5 mmol) in dry DEF (18 mL) and placed in an oven preheated to 87 °C for 10 h. The resulting transparent dark yellow cubical crystals were washed with dry DMF then THF and dried *in vacuo*. Yield: 400 mg. Anal. calcd. for $(C_{63}H_{39}N_3O_{22}Zn_4){\cdot}5H_2O{\cdot}0.2$ DMF·0.2THF: C, 49.24; H, 3.34; N, 2.85; Found: C, 49.26; H, 3.27; N, 2.63. Analysis of digested samples by ^1H NMR spectroscopy showed that some DMF and THF always remained trapped in the material. FT-IR: 685.7 (w), 709.6 (m), 729.0 (m), 737.4 (w), 753.2 (w), 776.3 (m), 833.1 (w), 845.0 (w), 873.9 (w), 858.5 (w), 964.1 (w), 1006.4 (w), 1031.1 (w), 1124.3 (w), 1184.4 (w), 1231.5 (w), 1305.6 (w), 1341.8 (m), 1400.4 (br s), 1420.3 (sh), 1525.6 (br s), 1602.3 (br m) cm^{-1}. ES-MS of digested crystals (negative mode): *m/z* = 392.50 ($[C_{21}H_{14}NO_7]^-$).

Crystals could also be obtained if DEF was replaced by DMF; however, the yield was reduced.

(b) Photochemical conversion of [$Zn_4O(1)_3$] to [$Zn_4O(2)_3$]

Crystals of [$Zn_4O(\mathbf{1})_3$] were suspended in THF or DMF and irradiated at 355 nm using a Quantel Brilliant B pulsed laser with the power adjusted to 250 mW. The progress of the photochemical reaction was monitored by ^1H NMR spectroscopy following digestion of the samples in DMSO-d_6/DCl. The reaction was generally complete in around 2 − 6 hours.

For experiments targetting samples for X-ray crystallography experiments, the reaction mixture was not stirred during irradiation. The exterior form of the large single crystals of [$Zn_4O(\mathbf{1})_3$] was preserved, though the crystals lost some degree of transparency. These crystals were used directly for X-ray crystallography without any solvent exchange or activation steps.

In other experiments, a magnetic stirbar was employed to agitate the reaction mixture. In this case, the crystals were crushed and [$Zn_4O(\mathbf{2})_3$] was obtained as a microcrystalline solid. The product was activated by suspending in THF then drying *in vacuo*. Anal. calcd. for $(C_{42}H_{24}O_{16}Zn_4){\cdot}1.5DMF{\cdot}2H_2O{\cdot}THF$: C, 48.60; H, 3.76; N, 1.68; Found: C, 48.47; H, 4.01; N, 1.82. FT-IR: 709.3 (w), 736.7 (m), 776.1 (s), 795.5 (w), 808.4 (w), 840.8 (w), 866.3 (w), 954.9 (w), 1007.3 (w), 1042.3 (w), 1106.7 (w), 1185.7 (w), 1405.3 (br, s), 1535.1 (br, m), 1586.8 (br, m), 1605.5 (m) cm^{-1}. ES-MS (negative mode): *m/z* = 257.39 ($[C_{14}H_9O_5]^-$). For the characterization of [$Zn_4O(\mathbf{2})_3$] by NMR spectroscopy, see the main text, and for characterization by TGA, see below.

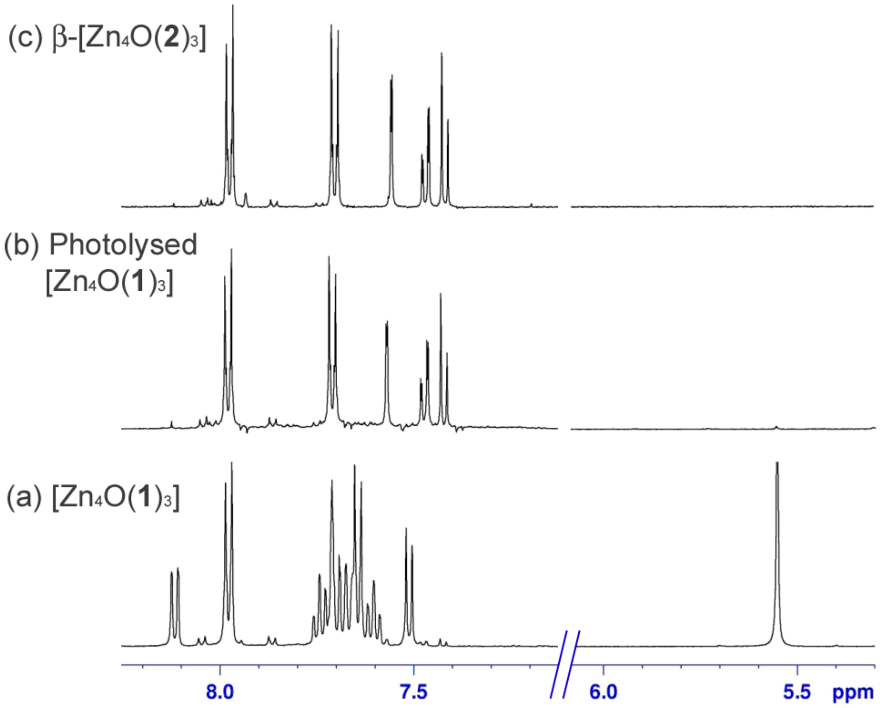


Figure S1. ^{1}H NMR spectra of MOFs digested in DMSO-d$_6$/DCl. (a) [Zn$_4$O(**1**)$_3$], (b) [Zn$_4$O(**2**)$_3$] produced by the photolysis of [Zn$_4$O(**1**)$_3$], and (c) β-[Zn$_4$O(**2**)$_3$].

(d) Synthesis of β-[Zn$_4$O(2)$_3$]

Ligand H$_2$**2** (207 mg, 0.8 mmol) was combined with Zn(NO$_3$)$_2$·4H$_2$O (627 mg, 2.4 mmol) in dry DEF (18.5 mL) and placed in an oven that was then heated to 90°C for 15 h. The resulting pale yellow cubic crystals were washed with dry DMF then THF and dried *in vacuo*. Yield: 80 mg. Anal. calcd. for ($C_{42}H_{24}O_{16}Zn_4$)·3H$_2$O·0.5DMF: C, 45.96; H, 2.97; N, 0.62; Found: C, 46.07; H, 3.48; N, 0.72. FT-IR: 638.6 (w), 707.6 (m), 738.4 (w), 773.9 (s), 791.9 (m), 804.7 (w), 839.5 (w), 866.6 (w), 951.8 (w), 1006.7 (w), 1048.9 (w), 1110.3 (w), 1181.8 (w), 1252.6 (w), 1399.5 (br, s), 1533.5 (br, m), 1584.8 (br, m), 1654.5 (w) cm^{-1}. ES-MS (negative mode): *m/z* = 257.19 ([$C_{14}H_9O_5$]$^-$). Crystals could also be obtained if DEF was replaced by DMF; however, the reaction time had to be extended to 40 h.

(d) Synthesis of β-[Zn$_4$O(3)$_3$] [4]

Ligand H$_2$**3** was prepared according to a literature procedure.[2] H$_2$**3** (40.0 mg, 0.15 mmol) was combined with Zn(NO$_3$)$_2$·4H$_2$O (118 mg, 0.45 mmol) in dry DMF (3 mL) and heated to 100 °C for 17 h in a closed vial. Transparent block shaped crystals were obtained, which were washed with dry DMF then dry THF, and dried *in vacuo.* Yield: 51 mg. IR: 679.9 (w), 699.5 (m), 708.4 (m), 721.7 (m), 728.6 (m), 738.1 (w), 776.3 (s), 802.0 (w), 839.0 (w), 866.9 (w), 912.3 (w), 1005.9 (w), 1033 (w), 1120.0 (w), 1182.1 (w), 1257.1 (m), 1396.3 (s, br), 1537.9 (s, br), 1595 (m, br), 1656.8 (m, br).

3. Thermogravimetric analysis (TGA)

Sample preparation

[$Zn_4O(\mathbf{1})_3$], [$Zn_4O(\mathbf{2})_3$], and β-[$Zn_4O(\mathbf{3})_4$]: These samples were prepared by first exchanging the DMF with acetone over a period of 3 days (solvent replenished daily) then removing the solvent using supercritical CO_2 according to a published method.[5]

β-[$Zn_4O(\mathbf{2})_3$]: This sample was prepared by soaking in DMF overnight, repeated washing with dry THF and drying under vacuum.

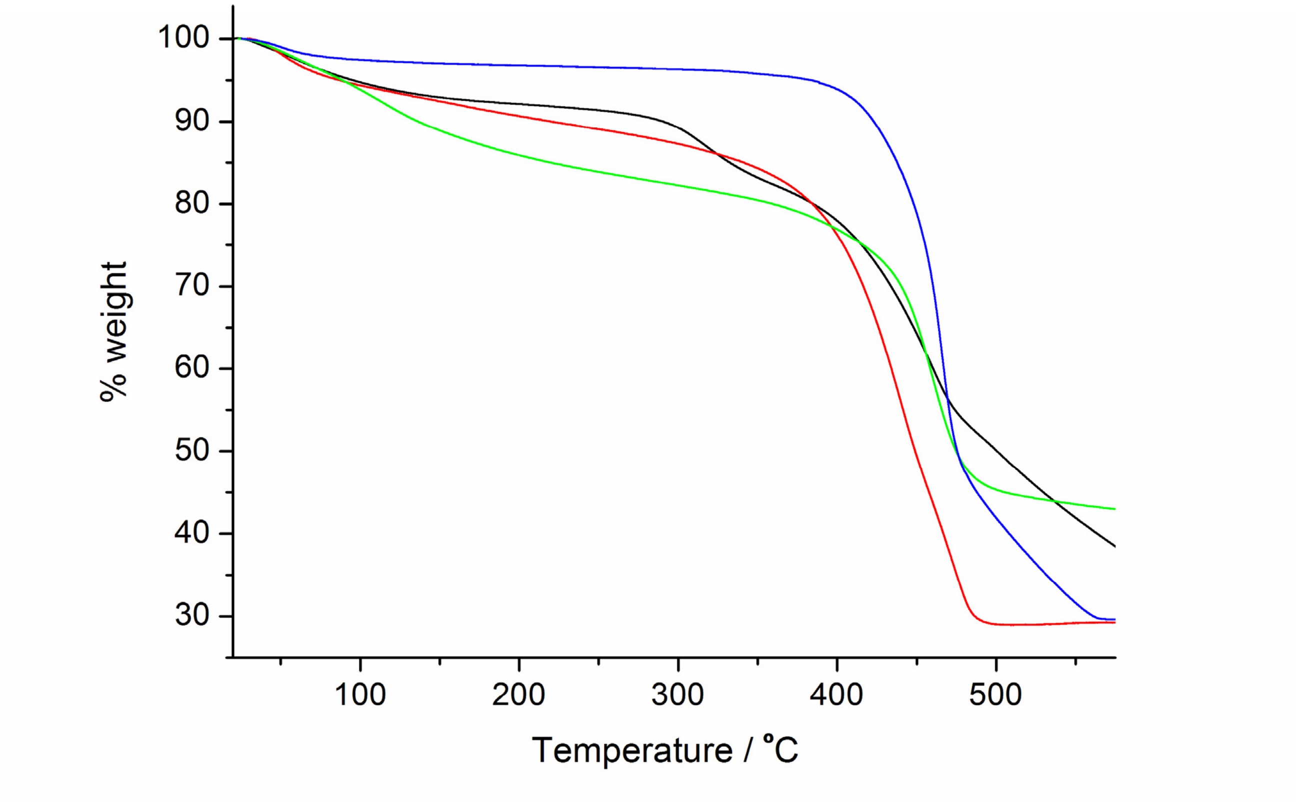


Figure S2. Thermogravimetrograms of [$Zn_4O(\mathbf{1})_3$] (black line), [$Zn_4O(\mathbf{2})_3$] (red line), β-[$Zn_4O(\mathbf{2})_3$] (green line), and β-[$Zn_4O(\mathbf{3})_4$] (blue line) recorded under N_2 with a heating rate of 5 °C min^{-1}.

4. X-ray crystallography

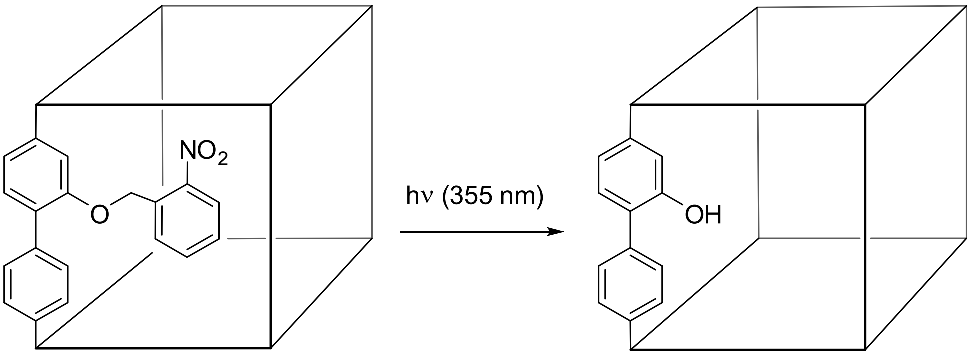
(a) Single-crystal XRD of [$Zn_4O(\mathbf{1})_3$]

A pale yellow crystal of [$Zn_4O(\mathbf{1})_3$] was mounted with some mother liquor in a polymer capillary sleeve. Data were collected on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating-anode generator (Cu Kα radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image-plate detector at 292 K. Data collected at lower temperatures were of lesser quality. The data were integrated and scaled and averaged with FS Process. Good diffraction out to high Bragg angles was observed (beyond 0.85 Å). A total of 21493 reflections were found, of which 1535 were unique. Analysis of the data with XPREP[6] indicated that the space group was $P\bar{4}3m$ (R_{int} = 0.044). This cubic space group is consistent with the observation that the crystals extinguished at all rotational positions when viewed with crossed polarizers. The structure was solved using SIR-92.[7] All non-hydrogen atoms of the Zn_4O cluster and the skeleton of biphenyl-4,4'-dicarboxylate ligand (comprising Zn1, O1, O2, C1, C2, C3, C4 and C5) were refined anisotropically. Analysis with Platon indicated that there were 495 electrons per unit cell in addition to the Zn_4O cluster and the biphenyl-4,4'-dicarboxylate ligand skeleton, which is consistent with the requirement for three nitrobenzyloxy side chains (231 electrons), along with additional disordered DEF. As the atoms of the side chains could not be located from the difference Fourier map, they were placed in calculated positions with chemically reasonable bond lengths and angles and conformation. The atomic positions and thermal parameters of this side chain were held fixed during the refinement (U_{eq} = 0.20, based on the thermal parameters of C2 − C5). Restraints were placed upon certain bond distances and angles within the biphenyl skeleton to keep them within chemically sensible values. The SQUEEZE routine in Platon[8] was used to estimate the amount of residual electron density − 305 electrons per unit cell − which corresponds to around five highly disordered DEF solvate molecules. Accounting for this solvent, final full-matrix least-squares refinement on F^2 converged to R_1 = 0.117 and wR_2 = 0.330 (all data).

Table S1. Details of the data collection and refinement of the X-ray crystal structure of $[Zn_4O(\mathbf{1})_3]\cdot5(DEF)$.

CCDC deposition number	826054
Formula	$C_{63}H_{39}N_3O_{22}Zn_4$ ($C_{88}H_{94}N_8O_{27}Zn_4$)
Formula weight	1451.63 (1957.37 including DEF)
Crystal size	0.15 × 0.15 × 0.10 mm
Temperature	292(1) K
Wavelength	1.54180 Å
Crystal system	cubic
Space group	$P\bar{4}3m$ (No. 215)
Unit cell dimensions	$a = b = c = 17.2108(17)$ Å; $\alpha = \beta = \gamma = 90$ °
Volume	5098.0(9) $Å^3$
Z	1
D_{calc}	0.473 g cm^{-3}
μ	0.776 mm^{-1}
F(000)	734 (1014 including DEF)
Reflections collected/unique, R_{int}	21493/1535, 0.054
Resolution range for data	8.0 − 0.85 Å
Index ranges	$-10 \le h \le 17$, $-19 \le k \le 13$, $-18 \le l \le 11$
Completeness to $d = 0.85$ Å	90%
Max. and min. transmission factors	1.0, 0.59
R indices for 1332 data with $[I>2\sigma(I)]$	$R_1 = 0.1138$, $wR_2 = 0.3214$
R indices for all data	$R_1 = 0.1172$, $wR_2 = 0.3304$

(b) Single-crystal XRD of partially photolyzed [$Zn_4O(\mathbf{1})_3$]



[$Zn_4O(\mathbf{1})_3$]

[$Zn_4O(\mathbf{2})_3$]

A batch of crystals of [$Zn_4O(\mathbf{1})_3$] was suspended in DMF and photolyzed using 355 nm laser light. Digestion in DCl/DMSO-d_6 indicated that the photochemical reaction was 50% complete. Several of the yellow-brown crystals were mounted individually in polymer capillaries together with some mother liquor. Data were collected on these crystals at 292 K on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating-anode generator (Cu Kα radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image-plate detector.

In all cases, clean diffraction patterns were obtained to a resolution of greater than 0.90 Å. This indicated that the crystallinity had been well maintained. Inspection of the diffraction images indicated that the primary cubic lattice had been maintained, though there were indications of a doubling of some (or all) of the cell axes. However, further analysis was complicated by the likelihood that the crystal has become a composite; the two ligands − **1** and **2** − may not be distributed isotropically within the crystal (the photolyzed strut, **2**, is expected to dominate the outer shell of the crystal).

(c) Single crystal XRD of β-[$Zn_4O(\mathbf{2})_3$]

A pale yellow crystal β-[$Zn_4O(\mathbf{2})_3$] was mounted with some mother liquor in a −50 °C cold stream. Data were on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating anode generator (Cuα radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image-plate detector. Diffraction spots out to a resolution of about 1.30 Å were observed.

The diffraction spots could not satisfactorily be indexed to a reasonable unit cell. Close inspection of the diffraction images revealed a primary reciprocal lattice corresponding to a cubic unit cell with dimensions of approximately 17.2 Å. Secondary diffraction spots were observed along the reciprocal lattice vectors of the primary lattice, but at positions that were not integral fractions of the primary lattice (Fig. S3). These spots can be attributed to another lattice, in this case a second interpenetrating framework, that is non-commensurate with the first. Although interpenetrated frameworks are difficult to distinguish from their non-catenated counterparts by PXRD, the additional peaks in the PXRD pattern of β-[$Zn_4O(\mathbf{2})_3$] (Fig. 2d), are consistent with deviations from a simple cubic structure.

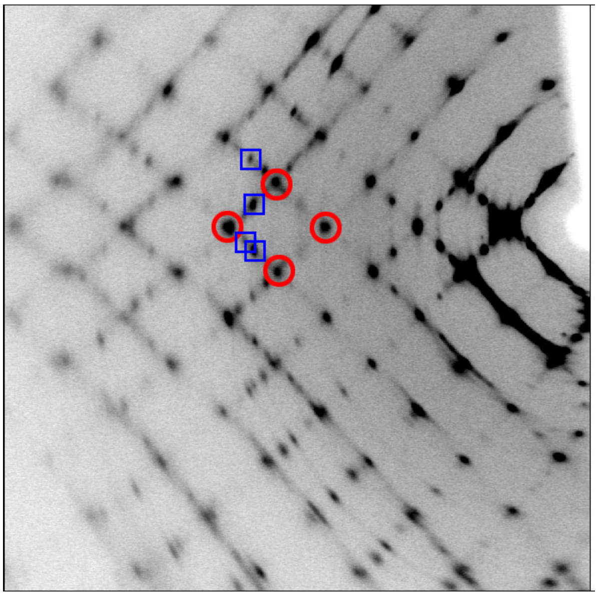


Figure S3. Single crystal X-ray diffraction pattern of β-[$Zn_4O(\mathbf{2})_3$] highlighting the primary reciprocal lattice (red circles), corresponding to a 17.2 Å cubic cell, and the secondary diffraction spots (blue boxes), which appear along the primary lattice vectors but at non-integral fractional distances.

(d) Single crystal XRD of β-[$Zn_4O(3)_3$]

A pale yellow crystal of β-[$Zn_4O(\mathbf{3})_3$] was mounted with some mother liquor in a polymer capillary sleeve. Data were collected on a Rigaku Spider diffractometer equipped with a MicroMax MM007 rotating-anode generator (Cu Kα radiation, 1.54180 Å), high-flux Osmic multilayer mirror optics, and a curved image-plate detector at 292 K. Data collected at lower temperatures were of lesser quality. The data were integrated and scaled and averaged with FS Process. Good diffraction out to high Bragg angles was observed (to around 0.87 Å). A total of 38669 reflections were found, of which 4241 were unique. Analysis of the data with XPREP[6] indicated that the space group was $P\bar{4}2_1m$ (R_{int} = 0.044). The structure was solved using SIR-92[7] and refined as a racemic twin. All non-hydrogen atoms of the Zn_4O cluster and the skeleton of ligand **3** were refined anisotropically. A difference Fourier electron density map indicated the approximate positions of the methoxy groups, which were subsequently placed in calculated positions with chemically reasonable bond lengths and angles and fixed isotropic thermal parameters (U_{eq} = 0.20). The SQUEEZE routine in Platon[8] estimated the presence of 413 electrons per unit cell, which corresponds to around seven highly disordered DEF solvate molecules. Following treatment of the data with SQUEEZE to account for this solvent, a final full matrix least squares refinement on F^2 converged to R_1 = 0.069 and wR_2 = 0.220 (all data).

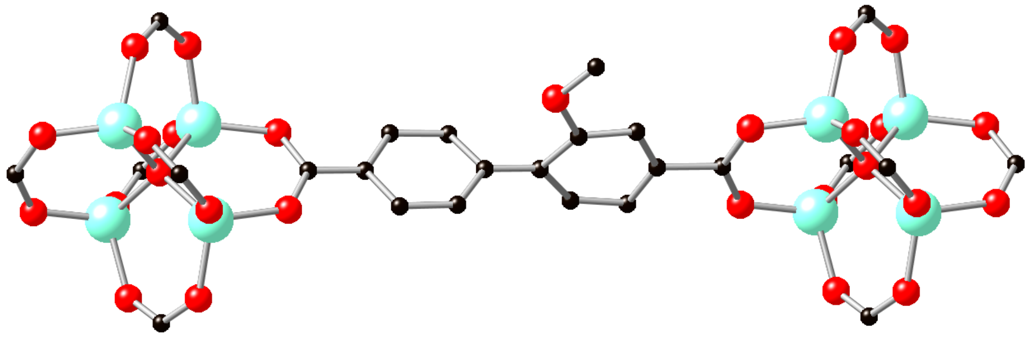


Table S2. Details of the data collection and refinement of the X-ray crystal structure of β-[$Zn_4O(\mathbf{3})_3$]·7(DEF).

CCDC deposition number	826055
Formula	$C_{45}H_{30}O_{16}Zn_4$ ($C_{80}H_{107}N_7O_{23}Zn_4$ including DEF)
Formula weight	1088.17 (1796.38 including DEF)
Crystal size	0.20 × 0.10 × 0.10 mm
Temperature	292(1) K
Wavelength	1.54180 Å
Crystal system	tetragonal
Space group	$P\bar{4}2_1m$ (No. 113)
Unit cell dimensions	$a = b = 17.2215(4)$, $c = 17.1168(12)$ Å
	$\alpha = \beta = \gamma = 90$ °
Volume	5076.5(4) $Å^3$
Z	2
D_{calc}	0.712 g cm^{-3}
μ	1.34 mm^{-1}
$F(000)$	1096 (1488 including DEF)
Reflections collected/unique, R_{int}	38669/4241, 0.044
Resolution range for data	8.0 − 0.87 Å
Index ranges	$-16 \leq h \leq 19$, $-19 \leq k \leq 19$, $-19 \leq l \leq 19$
Completeness to d = 0.87 Å	99.5%
Max. and min. transmission factors	1.0, 0.55
R indices for 3747 data with [I>2$\sigma(I)$]	$R_1 = 0.066$, w$R_2 = 0.213$
R indices for all data	$R_1 = 0.069$ w$R_2 = 0.220$

5. Surface area and porosity analysis

A bulk sample of [$Zn_4O(\mathbf{2})_3$] in the form of a microcrystalline powder was prepared by photolysis of [$Zn_4O(\mathbf{1})_3$] in dry DMF with stirring. The sample was activated by first exchanging the DMF with acetone over a period of 3 days (solvent replenished daily) then removing the solvent using supercritical CO_2 according to a published method.[5] The activated compound was stored in a dessicator.

Samples were activated immediately prior to N_2 physisorption measurements at 70 °C for 6 h under vacuum in a Hereaus vacuum oven (Thermo Scientific). Isotherms were determined at liquid nitrogen temperature (77 K) using a Micromeritics Tristar 3000 instrument. Specific surfaces areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/Po values in the range 0.06 – 0.22. [$Zn_4O(\mathbf{2})_3$] gave a linear fit in this pressure region as well as a positive C constant, leading to a reproducible estimate of the accessible surface area of 132 $m^2\ g^{-1}$ (Fig. S3).

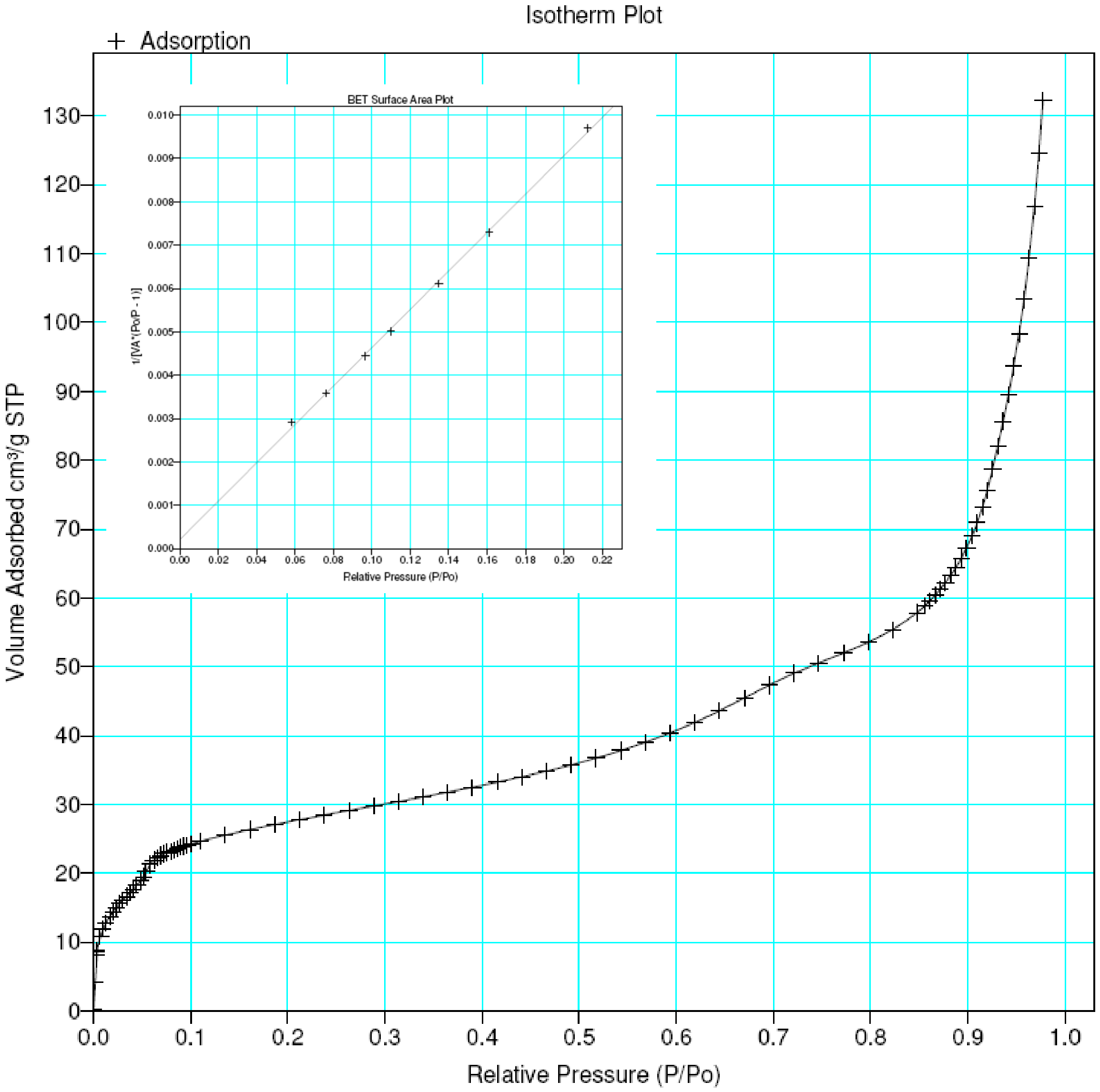


Figure S4. N_2 sorption isotherm of [$Zn_4O(\mathbf{2})_3$] at 77 K. The inset shows the BET surface area plot.

References

1. Deshpande, R. K.; Minnaar, J. L.; Telfer, S. G. *Angew. Chem. Int. Ed.* **2010**, *47*, 4598.
2. Ol'khovik, V. K.; Matveenko, Y. V.; Kalechits, G. V.; Pap, A. A.; Zenyuk, A. A. *Russ. J. Org. Chem.* **2006**, *42*, 1164.
3. Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 12368.
4. Burrows, A. D.; Frost, C.; Mahon, M. F.; Richardson, C. *Angew. Chem., Int. Ed.* **2008**, *47*, 8482.
5. Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. *J. Am. Chem. Soc.* **2009**, *131*, 458.
6. Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112.
7. Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.
8. Spek, A. L. *J. Appl. Cryst.* **2003**, *36*, 7.