Metal–Organic Frameworks

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Thermolabile Groups in Metal–Organic Frameworks: Suppression of Network Interpenetration, Post-Synthetic Cavity Expansion, and Protection of Reactive Functional Groups**

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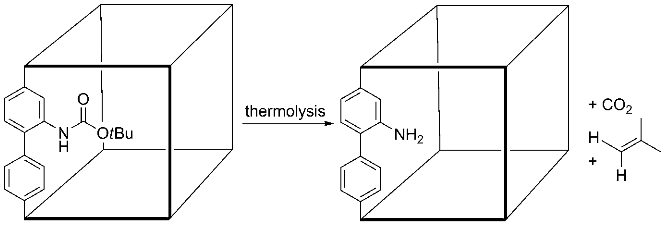
Metal–organic frameworks (MOFs) are often sufficiently porous and robust that the initially occluded solvent can be exchanged or removed without the loss of crystallinity. This property has been exploited for the post-synthetic modification of MOFs, wherein functional groups that line the framework channels react with incoming molecules.[1,2] We are interested in the reverse of this process, in particular, the post-synthetic expulsion of functional groups from MOFs whilst conserving framework crystallinity and porosity. Herein we show that a specifically designed ligand enables 1) the suppression of network interpenetration (catenation), 2) the post-synthetic expansion of cavities and apertures within the framework, 3) the unmasking of reactive amino functional groups that are located on the surface of this void space, and 4) the preparation of MOFs that cannot be synthesized directly.

Our approach to these goals relies on the thermolytic cleavage of the *tert*-butylcarbamate (NHBoc) group of a functionalized biphenyldicarboxylate ligand after its incorporation into a MOF (Scheme 1).[3] The NHBoc moiety is a protected amino group, which can be deprotected by a thermolytic reaction involving no external reagents and resulting in no non-volatile debris.[4] We envisaged that simple heating after MOF synthesis may unmask an amino functional group without further perturbing the framework structure. Gaseous CO_2 and isobutylene are expected as byproducts, however these are anticipated to freely diffuse out of the framework if there is a contiguous network of pores.

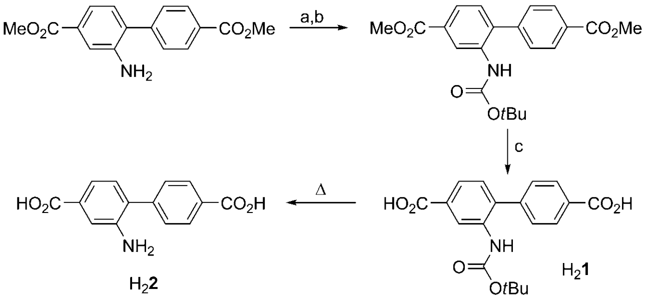


Scheme 1. The incorporation of a bulky NHBoc group is anticipated to preclude the catenation of MOF networks. The post-synthetic cleavage of the Boc group by thermolysis is designed to expand the void space within the framework and to unmask a reactive amino functional group.

The post-synthetic thermolysis of *tert*-butoxycarbonyl (Boc) groups is a clean and effective, yet underutilized, technique for increasing the porosity of solid-state materials. The reaction has been exploited to generate amine-lined cavities in silica-based materials,[5] to induce porosity in poly(phenylquinoxaline) polymers,[6] and to trigger decomposition of the "porogen" component of porous membranes.[7] However, to our knowledge, the thermolysis of Boc groups in single crystals has not been reported.

The choice of the biphenyl-4,4′-dicarboxylate skeleton of ligand **1** was informed by the pioneering work of Yaghi and co-workers, who have demonstrated that this family of ligands reliably furnishes networks with a cubic topology upon reaction with $Zn(NO_3)_2$.[8] Subsequent reports from Burrows et al. confirm that MOF formation proceeds smoothly and predictably even with small functional groups in the 2 and 2′ positions to give isoreticular cubic networks.[2b,f] The compound H_2**1** was synthesized starting from known[9] dimethyl 2-aminobiphenyl-4,4′-dicarboxylate (Scheme 2).

The reaction of H_2**1** with $Zn(NO_3)_2{\cdot}4\,H_2O$ under standard conditions—in dry *N*,*N*′-diethylformamide (DEF) at 85 °C—produces well faceted, colorless, transparent crystals (see Supporting Information). Solvent exchange with CH_2Cl_2 followed by activation in vacuo produced a material that was formulated by elemental analysis as $[Zn_4O(\mathbf{1})_3]{\cdot}5\,H_2O$. A



Scheme 2. Synthesis of *tert*-butylcarbamate-containing ligand H_2**1**, amino ligand H_2**2**, and the conversion of H_1**1** into H_2**2** by thermolysis: a) Boc_2O/DMAP/THF; b) $LiBr/CH_3CN$; c) aq. KOH/THF. DMAP = 4-dimethylaminopyridine.

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^{1}H NMR spectrum of crystals dissolved in [D$_6$]DMSO/DCl confirmed that the Boc group was incorporated fully intact into the MOF (Supporting Information, Figure S2).

[Zn$_4$O(**1**)$_3$] belongs to the space group $P\bar{4}3m$.[10] A non-interpenetrated cubic network is generated by the linking of octahedral Zn$_4$O nodes by **1** ligands (Figure 1 a and b). The length of the unit cell axes (17.173 Å) corresponds to the distance between Zn$_4$O clusters. The phenyl rings of each biphenyl motif are orthogonal to one another and co-planar with their appended carboxylate groups. The phenyl rings of the ligands are oriented orthogonal to the (011) and (0$\bar{1}$1) lattice planes, which makes all the framework pores identical. This feature distinguishes [Zn$_4$O(**1**)$_3$] from other related non-interpenetrated MOFs, such as MOF-5 and IRMOF-12,[8] in which two different types of pores exists as a consequence of the rotational orientation of the ligand phenyl rings.[11]

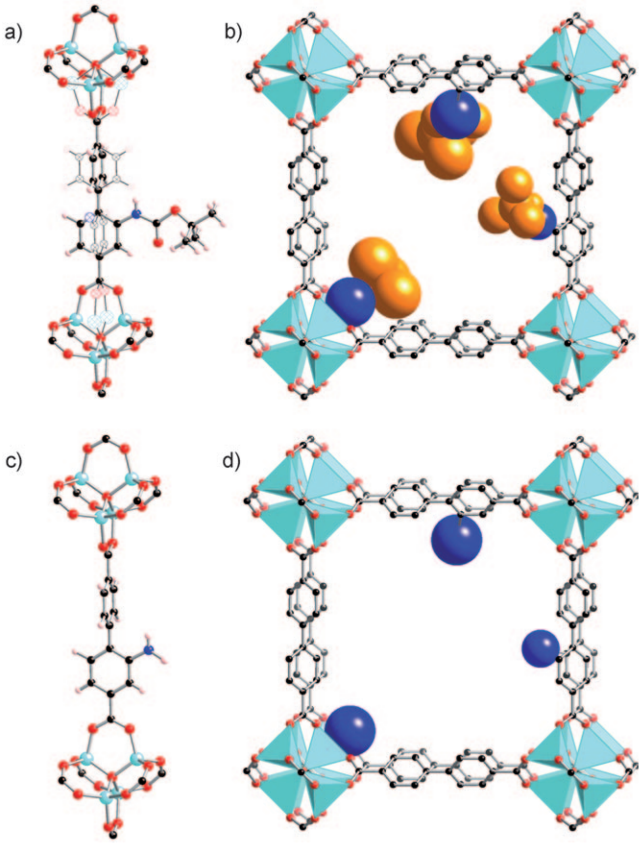

Figure 1. The structures of a),b) [Zn$_4$O(**1**)$_3$] and c),d) [Zn$_4$O(**2**)$_3$] as determined by X-ray crystallography (C black, H pink, O red, N blue, Zn turquoise (spheres/tetrahedra)). The disordered component of [Zn$_4$O(**1**)$_3$] is shown using hatched spheres. In (b) and (d), respectively, the statistically disordered NHBoc (blue/orange) and NH$_2$ (blue) groups are shown in representative locations. Some NHBoc groups and all hydrogen atoms have been omitted for clarity in (b) and (d), and the Boc group has been omitted from the disordered component in (a).

Crystals of [Zn$_4$O(**1**)$_3$] contain a minor disordered component in which the ligands are rotated 90° about their long axes (Figure 1 a). The Zn atom, the carboxylate O atom, and two of the C atoms of each phenyl ring of the disordered component occupy unique sites, while the other atoms are coincident with the major component. The ratio of the two components was observed to vary from crystal to crystal from 85/15 to 96/4.

The NHBoc group is statistically disordered over the four symmetry-equivalent 2 positions of the biphenyl skeleton in [Zn$_4$O(**1**)$_3$]. Locating these groups on a Fourier difference map during refinement of the structure was hampered by this disorder coupled with the large amplitude of their thermal motion. Analysis of the electron-density present in the void spaces within the cubic framework was consistent with the presence of the expected three NHBoc groups per unit cell along with included solvent.[12] To complete the refinement, the atoms of the NHBoc groups were placed in calculated positions with chemically reasonable bond lengths and angles and their positional and thermal parameters were held fixed.

[Zn$_4$O(**1**)$_3$] could be converted into [Zn$_4$O(**2**)$_3$] in a single-crystal-to-single-crystal (SCSC) fashion by heating at temperatures above 150 °C. To maintain crystallinity, the crystals were suspended in DMF. The macroscopic form of the crystals was preserved upon heating, although some crystals became opaque (see Supporting Information). ^{1}H NMR spectroscopy after dissolution in DCl/[D$_6$]DMSO showed a set of signals corresponding to 2-aminobiphenyl-4,4′-dicarboxylic acid (H$_2$**2**), confirming the complete cleavage of the Boc group (Supporting Information, Figure S3). IR spectroscopy (Supporting Information, Figure S4) revealed that peaks assignable to the carbamate moiety[13] in [Zn$_4$O(**1**)$_3$] (at 1245, 1156, and 1053 cm^{-1}) disappear upon heating, while prominent vibrational modes of the MOF skeleton[8] are present both before and after thermolysis (around 1600, 1540, 1400, 1005 and 775 cm^{-1}).

Single-crystal X-ray diffraction indicated that the structural integrity of the framework was maintained during thermolysis, with [Zn$_4$O(**2**)$_3$] (Figure 1 c and d) adopting the same space group ($P\bar{4}3m$) and a similar unit cell length (17.218 Å) to [Zn$_4$O(**1**)$_3$].[14] The amino group of the ligand is statistically disordered over four symmetry-equivalent sites. In contrast to [Zn$_4$O(**2**)$_3$], no disorder of the framework is apparent in the individual crystal of [Zn$_4$O(**2**)$_3$] selected for analysis. As the two components can be interconverted without bond cleavage, this may be a result of the thermal treatment of the crystals. Powder X-ray diffraction confirmed the phase purity of the bulk material (see below).

It is noteworthy that [Zn$_4$O(**2**)$_3$] does not form directly from H$_2$**2** under standard conditions. Despite varying several parameters (Zn^{II}/H$_2$**2** ratio, concentration, temperature), at best only a trace of solid material could be produced.

As anticipated, the calculated void volume[12] of [Zn$_4$O(**2**)$_3$] (4200 Å^3) is significantly larger than that of [Zn$_4$O(**1**)$_3$] (3900 Å^3). Around 83 % of the unit cell volume of [Zn$_4$O(**2**)$_3$] is accessible to solvent, which compares with 77 % for [Zn$_4$O(**1**)$_3$]. The fixed pore diameters[15] of [Zn$_4$O(**1**)$_3$] and [Zn$_4$O(**2**)$_3$] will vary from cell to cell depending on the exact location of the statistically disordered NHBoc and amino groups. The largest possible pore diameter for both structures is 17.8 Å, for those pores into which no substituents penetrate (Supporting Information, Figure S5).

Most pores will be more constricted than this, and up to twelve substituents will occupy the most congested cavities.[16] In [$Zn_4O(\mathbf{1})_3$], the bulkiness of the NHBoc groups results in a minimum fixed pore diameter of 6.4 Å (Supporting Information, Figure S6). Expulsion of the Boc groups results in a significant increase of the minimum fixed pore diameter to 15.7 Å in [$Zn_4O(\mathbf{2})_3$] (Supporting Information, Figure S7).

The apertures between pores (the free pore diameter) also vary widely. The upper limit is 11.9 Å for both structures (Supporting Information, Figure S8), though most apertures will actually be more constricted than this. Where several NHBoc groups come into close proximity in [$Zn_4O(\mathbf{1})_3$], it will narrow to 3.1 Å (Supporting Information, Figure S9). As a result of the smaller size of the amino group, the apertures in [$Zn_4O(\mathbf{2})_3$] will on average be larger and exhibit less variation than those in [$Zn_4O(\mathbf{1})_3$]. The minimum aperture in [$Zn_4O(\mathbf{2})_3$] is 10.5 Å (Supporting Information; Figure S10).

The crystal structures of [$Zn_4O(\mathbf{1})_3$] and [$Zn_4O(\mathbf{2})_3$] indicate significant potential microporosity in both frameworks. The thermolysis step increases the void volume and allows the admission of much larger guests. Attempts to provide experimental verification of permanent porosity in these materials by gas sorption measurements met with limited success. This problem is presumably related to the loss of crystallinity upon removal of the occluded solvent by solvent exchange or evaporation (Supporting Information; Figures S11 and S12). Loss of porosity in this manner has previously been ascribed to detrimental shear forces, although it has also been shown that crystallinity is not a prerequisite for high porosity in related MOFs.[17]

The loss of the Boc group from [$Zn_4O(\mathbf{1})_3$] could be directly monitored by thermogravimetric analysis (TGA) after solvent exchange with CH_2Cl_2 and drying in vacuo (Figure 2). After the loss of residual solvent up to 120 °C, weight loss of 22 % is observed in the region 120–240 °C owing to expulsion of CO_2 and isobutylene. The TGA curve plateaus in the region 240–380 °C prior to the onset of framework decomposition above 400 °C. TGA analysis of [$Zn_4O(\mathbf{2})_3$], prepared by thermolysis of a bulk sample of [$Zn_4O(\mathbf{1})_3$] crystals, indicated that this material loses only 5.4 % of its weight up to 260 °C. This change can be attributed to small amounts of residual CH_2Cl_2 and H_2O, which resisted removal in vacuo. Framework decomposition commences above 400 °C, paralleling [$Zn_4O(\mathbf{1})_3$] and related MOF materials.[8]

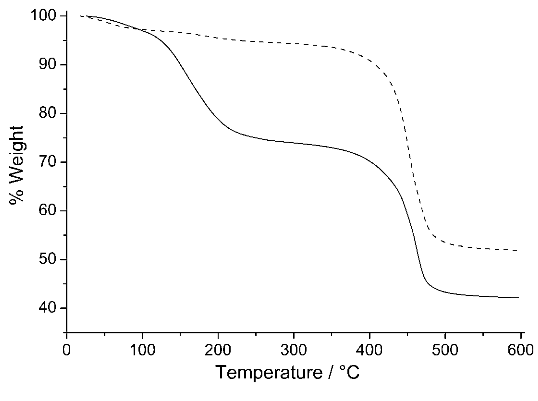

Figure 2. Thermogravimetrograms of [$Zn_4O(\mathbf{1})_3$] (solid line) and [$Zn_4O(\mathbf{2})_3$] (dashed line) recorded under a N_2 atmosphere with a heating rate of 5 °C min^{-1}.

[$Zn_4O(\mathbf{1})_3$] could be conveniently synthesized on a large (ca. 0.5 g) scale by the reaction of $H_2\mathbf{1}$ and $Zn(OAc)_2$ in DMF at room temperature.[18] This method produced a white solid with a small crystallite particle size. The constitution of this material is identical to that obtained by solvothermal methods, as shown by IR spectroscopy and elemental analysis. Furthermore, the powder X-ray diffractograms presented in Figure 3 A and C indicate that the two synthetic routes both produce a single phase with the same non-interpenetrated cubic topology.

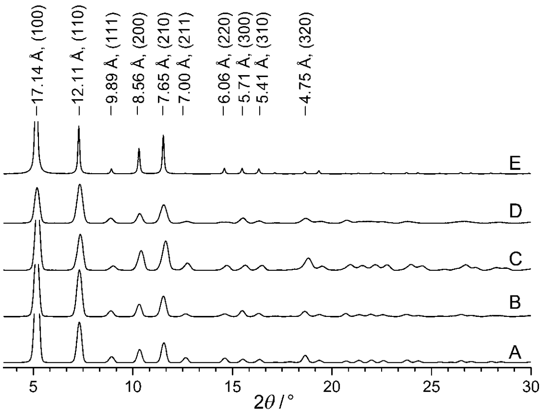

Figure 3. Powder X-ray diffractograms (Cu_α radiation) of [$Zn_4O(\mathbf{1})_3$] prepared at 85 °C before (A) and after (B) thermolysis, and [$Zn_4O(\mathbf{1})_3$] prepared at room temperature before (C) and after (D) thermolysis. The powder pattern predicted from the single-crystal structure of [$Zn_4O(\mathbf{1})_3$] is shown for comparison (E). The d spacings and corresponding Miller indices are given for the major peaks observed at low Bragg angles.

The thermolysis of room temperature-synthesized [$Zn_4O(\mathbf{1})_3$] also proceeded smoothly to yield [$Zn_4O(\mathbf{2})_3$] (Figure 3 D). It was found that this conversion could be effected in quantitative yield by direct heating of the material using microwave irradiation. As expected, the crystal structure of this material is virtually identical to that produced by the thermolysis of solvothermally synthesized [$Zn_4O(\mathbf{1})_3$] (Figure 3 B).

Several MOFs feature biphenyl-4,4′-dicarboxylate ligands that have various small functional groups at either their 2-position or their 2- and 2′-positions.[2b,f,8] In parallel with the parent framework, [Zn_4O(biphenyl-4,4′-dicarboxylate)$_3$], two-fold interpenetration of cubic networks is observed in most cases. The exceptions are IRMOF-10 and IRMOF-12, which are synthesized at high dilution.[19] Other methods have been employed to suppress interpenetration in related structures. For example, acetyl groups appended to 2,5-dihydroxyterephthalic acid (H_2dhybdc), which were lost during formation of the MOF, produce an open network of [Zn(dhybdc)(bpy)] (bpy = 4,4′-bipyridine).[20] Also, a non-catenated form of MOF-508 ([Zn(1,4-benzenedicarboxylate)-

(bpy)]) bound to a functionalized gold surface was fabricated by liquid-phase epitaxy.[21]

In contrast, we have shown in this case that $[Zn_4O(\mathbf{1})_3]$ forms a non-catenated structure under standard synthesis conditions. We attribute this to the bulkiness of the NHBoc substituent of ligand **1**; interpenetration is suppressed to avoid steric clashes between NHBoc groups of neighboring ligands. This is a unique approach to curbing framework catenation, and one which produces free-standing MOFs in gram-scale quantities.

Our method has additional advantages in that the thermolabile Boc group serves to mask an amino functional group that is found to otherwise preclude MOF growth.[22] Deprotection to reveal the amino moiety can be triggered in a controlled fashion, without the use of external chemical agents. This approach allows for complete removal of the protective group, including those groups buried deep inside the crystal,[23] and precludes any pore blockage by chemical detritus.

The thermolysis step leads to an increased guest-accessible volume and significantly widened pore diameters. This work can thus be viewed in the broader context of post-synthetic pore expansion in solid-state materials. In addition to other methods involving Boc groups in amorphous materials,[5–7] this has previously been achieved in single crystals by reactions with external reagents for example, the hydrolysis of acetyl groups in crystals of molecular tectons.[24] We anticipate that the method presented herein will be quite general given the variety of known thermolabile protective groups.[25]

We are currently focusing on expanding the scope of this approach to incorporate traceless protective groups that leave behind no functional group remnants, and to introduce catalytically active functional groups that otherwise hinder MOF formation. In addition, the crystal structure of $[Zn_4O(\mathbf{2})_3]$ indicates that this framework contains a contiguous network of fairly wide pores. We therefore anticipate that the amino groups that line these channels should be available for reaction with incoming reactants that are larger than have previously been employed in post-synthetic modification reactions.[1]

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[1] For a recent Review, see: Z. Wang, S. M. Cohen, *Chem. Soc. Rev.* **2009**, *38*, 1315.

[2] For recent examples, see: a) K. K. Tanabe, Z. Wang, S. M. Cohen, *J. Am. Chem. Soc.* **2008**, *130*, 8508; b) A. D. Burrows, C. G. Frost, M. F. Mahon, C. Richardson, *Angew. Chem.* **2008**, *120*, 8610; *Angew. Chem. Int. Ed.* **2008**, *47*, 8482; c) W. Morris, C. J. Doonan, H. Furukawa, R. Banerjee, O. M. Yaghi, *J. Am. Chem. Soc.* **2008**, *130*, 12626; d) T. Kawamichi, T. Kodama, M. Kawano, M. Fujita, *Angew. Chem.* **2008**, *120*, 8150; *Angew. Chem. Int. Ed.* **2008**, *47*, 8030; e) T. Gadzikwa, G. Lu, C. L. Stern, S. R. Wilson, J. T. Hupp, S. T. Nguyen, *Chem. Commun.* **2008**, 5493; f) A. D. Burrows, C. G. Frost, M. F. Mahon, C. Richardson, *Chem. Commun.* **2009**, 4218; g) Z. Wang, K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* **2009**, *48*, 296; h) C. J. Doonan, W. Morris, H. Furukawa, O. M. Yaghi, *J. Am. Chem. Soc.* **2009**, *131*, 9492; i) T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, N. Stock, *Inorg. Chem.* **2009**, *48*, 3057; j) K. K. Tanabe, S. M. Cohen, *Angew. Chem.* **2009**, *121*, 7560; *Angew. Chem. Int. Ed.* **2009**, *48*, 7424.

[3] A NHBoc group has been incorporated in IRMOF-3 by post-synthetic modification, though no thermolysis reactions were reported. See: S. J. Garibay, Z. Wang, K. K. Tanabe, S. M. Cohen, *Inorg. Chem.* **2009**, *48*, 7341.

[4] a) V. H. Rawal, M. P. Cava, *Tetrahedron Lett.* **1985**, *26*, 6141; b) The thermolysis of $H_2\mathbf{1}$ proceeds smoothly at elevated temperatures to give $H_2\mathbf{2}$ in quantitative yield.

[5] J. D. Bass, A. Solovyov, A. J. Pascall, A. Katz, *J. Am. Chem. Soc.* **2006**, *128*, 3737.

[6] a) S. Merlet, C. Marestin, O. Romeyer, R. Mercier, *Macromolecules* **2008**, *41*, 4205; b) S. Merlet, C. Marestin, F. Schiets, O. Romeyer, R. Mercier, *Macromolecules* **2007**, *40*, 2070.

[7] A. M. Eyal, B. Hazan, K. Hajdu, D. Edlestein, *J. Appl. Polym. Sci.* **1992**, *45*, 1065.

[8] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.

[9] V. K. Olkhovik, D. A. Vasilevskii, A. A. Pap, G. V. Kalechyts, Y. V. Matveienko, A. G. Baran, N. A. Halinouski, V. G. Petushok, *ARKIVOC* **2008**, *9*, 69.

[10] Crystal data for $[Zn_4O(\mathbf{1})_3]$ (see Supporting Information for details): $C_{57}H_{51}N_3O_{19}Zn_4$ ($M_w = 1343.57$), $T = 292(1)$ K, cubic, space group $P\bar{4}3m$ (No. 215), $a = 17.1728(3)$ Å, $V = 5064.35(15)$ Å^3, $Z = 1$, $\rho_{calcd} = 0.440\ g\,cm^{-3}$, $\mu = 0.723\ mm^{-1}$, 5777 measured reflections, 1195 unique reflections ($R_{int} = 0.0197$), $R_1 = 0.116$ for 1011 observed reflections ($I > 2\sigma(I)$) and 44 parameters (after accounting for disordered solvent with SQUEEZE[12]). CCDC 756192 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] S. Amirjalayer, R. Schmid, *J. Phys. Chem. C* **2008**, *112*, 14980.

[12] All calculations were carried out using Platon. A. L. Spek, *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2007**; P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194. PLATON calculates the volume accessible to guests by allowing a spherical probe of radius 1.20 Å to roll over the van der Waals surface of the network. The van der Waals radii used to define surfaces for these calculations are [Å]: C 1.70, H 1.20, Zn 2.25, N 1.55, and O 1.52. The percentage of accessible volume is given by $100\ V_g/V$, where V is the volume of the unit cell and V_g is the guest-accessible volume as calculated by PLATON.

[13] G. Socrates, *Infrared Characteristic Group Frequencies*, 2nd ed., Wiley, Weinheim, **1994**.

[14] Structure data for $[Zn_4O(\mathbf{2})_3]$ (see Supporting Information for details): $C_{42}H_{27}N_3O_{13}Zn_4$ ($M_w = 1043.32$), $T = 173(1)$ K, cubic, space group $P\bar{4}3m$ (No. 215), $a = 17.2184(6)$ Å, $V = 5104.8(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 0.339\ g\,cm^{-3}$, $\mu = 0.655\ mm^{-1}$, 5033 measured reflections, 1227 unique reflections ($R_{int} = 0.036$), $R_1 = 0.096$ for 919 observed reflections ($I > 2\sigma(I)$) and 42 parameters (after accounting for disordered solvent with SQUEEZE[12]). CCDC 756193 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] The fixed pore diameter is defined by a sphere that would fit inside the pores without overlapping with the framework atoms.

[16] Statistically, one in every 4^{12} (1.68×10^7) unit cells will accommodate twelve substituents in this way. There will be on average about 75 such cells per crystal.

[17] a) J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.* **2006**, *128*, 1304; b) M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376.

[18] D. J. Tranchemontagne, J. R. Hunt, O. M. Yaghi, *Tetrahedron* **2008**, *64*, 8553.

[19] O. M. Yaghi, M. Eddaoudi, H. Li, J. Kim, N. Rosi, US Patent 6930193B2, **2005**.

[20] T. Yamada, H. Kitagawa, *J. Am. Chem. Soc.* **2009**, *131*, 6312.

[21] O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer, C. Wöll, *Nat. Mater.* **2009**, *8*, 481.

[22] Even if suitable reaction conditions can be found, the direct synthesis of $[Zn_4O(\mathbf{2})_3]$ will likely produce a catenated framework, hence this stands as reliable route to non-catenated $[Zn_4O(\mathbf{2})_3]$.

[23] The deprotection of an acetylene group by an external reagent on the surface of MOF crystals has been reported: O. K. Farha, K. L. Mulfort, A. M. Thorsness, J. T. Hupp, *J. Am. Chem. Soc.* **2008**, *130*, 8598.

[24] E. Le Fur, E. Demers, T. Maris, J. D. Wuest, *Chem. Commun.* **2003**, 2966.

[25] P. G. M. Wuts, T. W. Greene, *Greene's Protective Groups in Organic Synthesis*, 4th ed., Wiley, Hoboken, **2007**.