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A Metal−Organic Framework with a Covalently Prefabricated Porous Organic Linker

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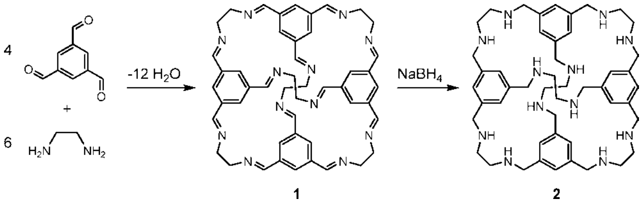
Abstract: We report here the synthesis of a metal−organic framework comprising an organic cage linker with covalently prefabricated, intrinsic porosity. The network can be compared to a porous rock salt structure where the pores are partially filled by charge-balancing cations.

Metal−organic frameworks (MOFs) are inorganic−organic hybrid materials comprising metals or metal clusters which are interconnected by organic linkers.[1] Porous MOFs have potential applications in gas storage,[2] molecular separation,[3] heterogeneous catalysis,[4] and drug delivery.[5] Commonly, rigid polydentate organic linkers based on carboxylate or pyridyl donors are used to coordinate metal ions or higher-nuclearity metal clusters, often referred to as ‘secondary building units’ (SBUs).[6] The ligands act as nodes to direct framework topology, and ligand geometries are typically linear, trigonal, or tetrahedral. To our knowledge, there are no examples of MOFs containing organic ligands which are themselves porous in nature as a result of their molecular structures. Here, we report the formation of a MOF utilizing a tetrahedral cage-like linker which itself contains a prefabricated covalent ‘pore’.

We recently reported the synthesis of imine-linked tetrahedral organic cages by [4 + 6] cycloimination condensation reactions between the *c*3-symmetric molecule 1,3,5-triformylbenzene (TFB) and various 1,2-ethylenediamines.[7] These crystallize to form porous solids that adsorb small gas molecules such as nitrogen, hydrogen, methane, and carbon dioxide. The porosity in these crystalline materials results from both the molecular voids in the cages and from inefficient packing of the tetrahedral molecules. Here, we show that one of these cages can be reduced to the corresponding dodecaamine and that this structurally complex, preporous ligand is suitable for the preparation of a ‘cage-MOF’ which shows gas uptake under certain conditions. Reduction of the 12 imine functions of cage **1** to secondary amino groups was carried out via addition of sodium borohydride in methanol to give cage **2** (see Supporting Information (SI) and Scheme 1). The saturated cage **2** is stable to >300 °C (see Figure S3, SI). Attempts to crystallize cage **2** only yielded amorphous solids.

Scheme 1. Preparation of Cage **2**



We investigated the use of **2** as a ‘preporous’ ligand by attempting to form a complex between **2** and zinc nitrate. Cage **2** (10 mg) was dissolved in 2 mL of methanol in a 8 mL vial. To this, a solution of $Zn(NO_3)_2 \cdot 6H_2O$ (17 mg, 4 equiv) in 2 mL of water was slowly added. After sealing the vial, the reaction mixture was heated to 80 °C at 5 °C/min in an oven for 24 h. After cooling at 5 °C/min, slow evaporation of solvent in an open vessel afforded air-stable colorless, cubic crystals of **3**.

Compound **3** crystallizes in space group *F*23. It contains hexanuclear zinc carbonate clusters $[Zn_6(\mu_3\text{-}CO_3)_4]^{4+}$ occupying Wyckoff sites 4a (0,0,0) and cage ligands **2** positioned on sites 4b (1/2,1/2,1/2) (Figure 1). The zinc carbonate cluster exhibits 23 symmetry. It comprises an octahedral arrangement of Zn(II) ions which are bridged by four carbonate ions in a μ_3-fashion.[8] The carbonate arises from the uptake of atmospheric CO_2, as described below. The cage ligands provide six bidentate chelates, which coordinate Zn(II) ions of the six neighboring clusters. The packing arrangement contrasts with other MOFs containing octahedral SBUs, such as MOF-5,[9] which are linked by more simple organic ligands which do not contain covalent cavities.

The zinc cluster measures 8.5 Å in diameter (Zn−Zn distance across the cluster), while the diameter of the organic cage is 10.4 Å, when based on the distance between the N...N centroids of two opposite chelates. The structure can be described by analogy as a ‘porous rock salt’ structure where the pores are filled by charge balancing anions within the cages described below. These anions and additional water molecules are highly disordered.

Charge balance requires additional carbonate or nitrate anions. These anions are isoelectronic and, as such, difficult to distinguish by means of X-rays. One such anion is located inside the cage where it is disordered across the 4b site. It forms CH...O interactions with the inward-facing ethylene groups. The remaining anions are located in the large voids that exist around half of the tetrahedral holes of the rocksalt structure (Wyckoff site 4c at 1/4,1/4,1/4). These spherical voids are bordered by four carbonate ions of adjacent $[Zn_6(\mu_3\text{-}CO_3)_4]^{4+}$ clusters and face into the windows of four cage molecules. The exact content of the 12 Å wide voids could not be determined from the X-ray data due to severe disorder. However, maxima appear in hydrogen bonding distances from each other, which indicates that the void contains two anions that are connected via a network of water molecules. The empirical formula $[(Zn_6(\mu_3\text{-}O_3C)_4(C_{48}H_{72}N_{12})](CO_3)(NO_3)_2(H_2O)_{19}$ best fitted the electron density. The elemental analysis data for the bulk material (C, 33.48%; H, 5.33%; N, 10.73%) is also broadly consistent with this composition (expected C, 32.22%; H, 5.61%; N, 9.92%) where 17.2% can be attributed to solvent.

We ascribe the presence of carbonate to the uptake and fixation of atmospheric CO_2 which is well documented for alcoholic aqueous

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solutions of zinc complexes[10] and also confirmed by infrared and solid state NMR spectroscopy. Strong carbonate vibrations were observed at 1491 cm^{-1} as well as nitrate vibrations at 1384 cm^{-1} (Figure S6). A peak at 170.8 ppm in the $^{13}C\{^1H\}$solid-state NMR spectrum can be assigned to the coordinated carbonate ligands (Figure S10). **3** was not formed when the reaction was carried out under a nitrogen atmosphere. However, the reaction time could be decreased when the reaction was carried out under a CO_2 atmosphere (see SI). Thermogravimetric analysis demonstrated that the complex is stable up to 330 °C under N_2, with a loss of 14.4 wt % by 120 °C, consistent with significant solvent incorporation in the structure.

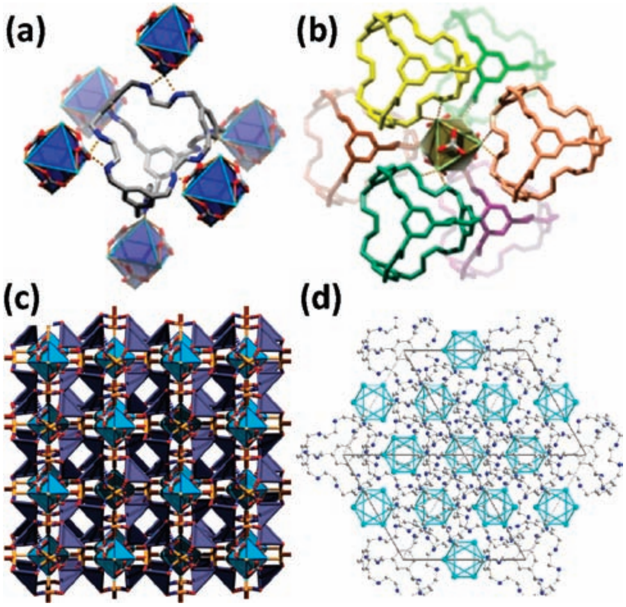

Figure 1. (a) A single cage **2** is linked to six octahedral $(Zn_6(\mu_3\text{-}CO_3)_4)^{4+}$ clusters in **3**, nitrogen shown in blue, oxygen in red, carbon in gray. (b) Each zinc cluster is linked to six cage **2** molecules. (c) The 3-D extended network structure of **3** with cubic symmetry. (d) 111 view of rock salt packing via alignment of 3-fold axes of the cage and cluster units, metal clusters shown in light blue.

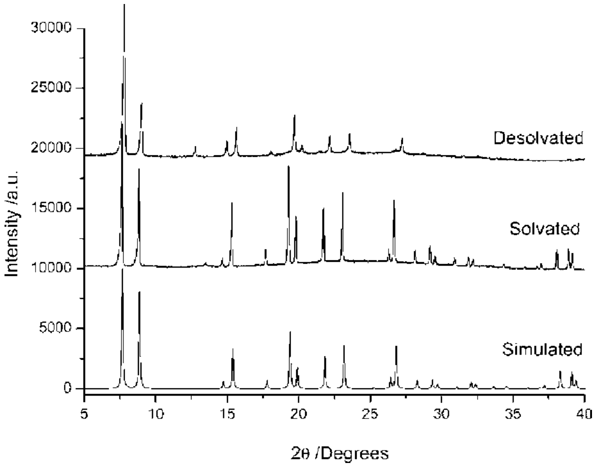

Figure 2. Powder X-ray diffraction patterns for **3** recorded for a desolvated sample (top), a solvated sample (middle), and simulated from single crystal data (bottom) obtained for a solvated sample.

On heating to 100 °C under dynamic vacuum, **3** maintains its crystallinity with a contraction of the unit cell due to the loss of water (Figure 2; Le Bail fit shown in Figures S8, S9). Calculation of the total available pore volume from the crystal structure (minus the disordered anion volume) suggests a significant pore volume in the desolvated structure but does not indicate whether this volume is interconnected or accessible because of the disorder in the counteranions. Gas sorption analysis using both N_2 and H_2 at 77 K indicated that the desolvated material was nonporous to these gases at this temperature. We ascribe this to pore blocking by the counteranions (**3** is still nonporous to these gases after anion exchange with chloride (Figure S22)). By contrast, **3** adsorbed 0.899 mmol g^{-1} (3.96 wt %) CO_2 at 298 K and 1 bar (Figure S15), suggesting a dynamic, cooperative diffusion process which does not operate at lower temperatures.[11]

The preparation of **3** is unique because it exploits two sequential equilibrium self-assembly reactions: the first to produce the porous cage **1**, prior to reduction, via a reversible 10-component imine condensation (Scheme 1)[7] and the second to form the extended network in **3** via solvothermal synthesis where a metal cluster of similar size to the preassembled porous cage forms. This two-step preorganization strategy presents opportunities to produce new MOF materials with functionalities that might be difficult to obtain in one-pot syntheses.

In conclusion, we have prepared a ‘cage-MOF’ using a dodecaamine cage as the organic linker. This linker is unique among MOFs as it represents a preformed covalent organic ‘pore’. This strategy exploits covalent molecular preassembly in the formation of the organic linker, building in a degree of structure and complexity prior to the solvothermal network assembly step. Our findings demonstrate a design principle for using ‘preporous’ covalent organic linkers in the preparation of extended ‘cage-MOFs’, suggesting future materials which are intermediate between MOFs and covalent organic frameworks.[12,13]

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Supporting Information Available: Full synthetic and experimental details, gas sorption data, Le Bail fitting. This material is available free of charge via the Internet at http://pubs.acs.org.

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