

## A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability

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Porous crystals are strategic materials with industrial applications within petrochemistry, catalysis, and selective separation.<sup>1</sup> Their unique property is based on the molecular-scale porous character. However, a principal limitation of zeolites and similar oxide-based materials is the relatively small size of the pores. Metal organic frameworks (MOFs) provided a break-through in this respect;<sup>2</sup> however, MOFs have one major disadvantage, their weak stability.<sup>3</sup> New MOFs appear at a high pace, but the appearances of new, stable inorganic building bricks are rare. Here we present a new zirconium-based building brick that allows the synthesis of high surface area MOFs with unprecedented stability. In the synthesis of new MOFs, the structure of the organic linkers can be controlled, while the formation of the inorganic building brick and how the organic linkers will coordinate with this inorganic unit is still pure serendipity. However, once the synthesis of an inorganic brick has been established, is it possible to reproduce this unit, and also reproduce it when used in combination with new linkers. This has been demonstrated both by the elegant isorecticular synthesis of the IRMOF-1–16<sup>4</sup> and by the fact that an impressive number of new MOFs are based on surprisingly few highly symmetrical inorganic building units: the Cu<sub>2</sub>(OH)<sub>2</sub>(CO<sub>2</sub>)<sub>4</sub> brick from HKUST-1,<sup>5</sup> the Zn<sub>4</sub>O(CO<sub>2</sub>)<sub>6</sub> brick from MOF-5,<sup>6</sup> and the Cr<sub>3</sub>O(OH)<sub>3</sub>(CO<sub>2</sub>)<sub>6</sub> cornerstone from MIL-88.<sup>7</sup> The stability of the framework is mainly controlled by the inorganic brick and the strength of the chemical bonding between the inorganic brick and the linker. Identification of stable, flexible new inorganic building units is therefore of utmost importance for the development of new, usable, open hybrid structures. The thermal stability of MOFs is usually limited to 350–400 °C; there is only one example of a porous MOF structure that is stable above 500 °C, that is MIL-53.<sup>8</sup> The inorganic brick in this case chains of aluminum octahedra. Recent hybrid frameworks with metal–imidazole bonding (M = Zn and Co) CIFS<sup>9</sup> are claimed to have thermal and chemical stability similar to the new Zr–MOFs reported in this work. Nearly identical metal hydroxypyrimidine frameworks (M = Pd and Cu) are reported to have a stability like normal oxide linked MOFs.<sup>10</sup> Hybrid frameworks with metal–nitrogen bonding are therefore no general solution to improve stability.

Group four elements interact strongly with oxygen and are therefore obvious choices for stable inorganic cornerstones in combination with oxygen containing linkers. The new inorganic brick in the series of structures reported here, Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub>, is 12 coordinated, the highest coordination reported for a MOF. 12-coordination is the coordination of metal atoms in closed packed metal structures; the Zr–MOF structures formed with linear ligands

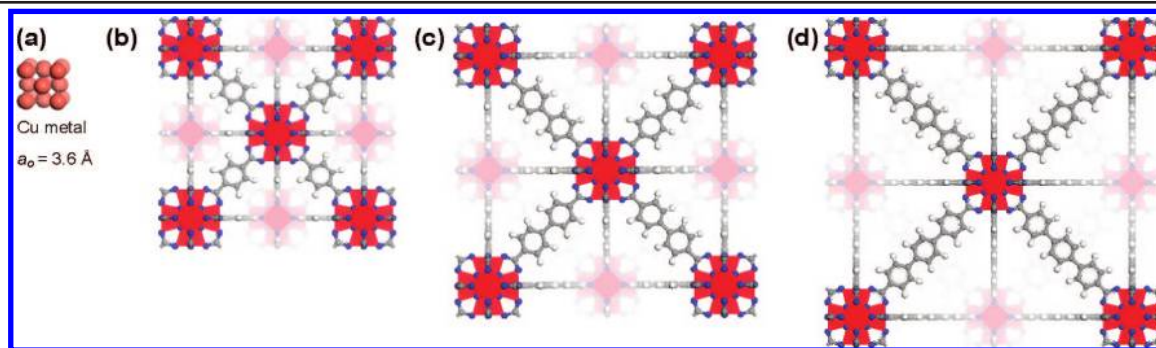
are therefore all expanded versions of the cubic close packed (CCP) structure (Figure 1). We demonstrate that the Zr–MOF structure can be made with increasing length of the linkers. Scale chemistry like this has been demonstrated before,<sup>4,9</sup> but the unique feature here is the possibility to increase the scale without compromising the stability of the material. The temperature of decomposition is exactly the same for Zr–MOF with BDC linkers, UiO-66, and with BPDC linkers, UiO-67. The decomposition during a TG experiment was followed by MS. At the temperature of breakdown of the lattice ( $T_{\text{decomp}} = 540$  °C), benzene is the fragment observed in the gas phase. **The weakest point in the structure is thus the bond between the benzene rings and the terminal carboxyl group and not the connection between the linker and the inorganic brick or the brick itself. Changing the ligand will therefore not alter the stability of the MOF.** These materials demonstrate the ultimate thermal stability obtainable for hybrid frameworks, with organic linkers. To increase the thermal stability further, the linker stability must be improved; an interesting approach is to use carborane-based linkers.<sup>11</sup>

**The inorganic brick is the key to the exceptional stability possessed by these structures.** It consists of an inner Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub> core in which the triangular faces of the Zr<sub>6</sub>-octahedron are alternatively capped by  $\mu_3$ -O and  $\mu_3$ -OH groups (Figure 2a). The same inner Zr<sub>6</sub>-cluster core has been reported by Puchberger et al.,<sup>12</sup> but only as isolated clusters. All of the polyhedron edges are bridged by carboxylates (–CO<sub>2</sub>) originating from the dicarboxylic acids forming a Zr<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(CO<sub>2</sub>)<sub>12</sub> cluster (Figure 2b). Each zirconium atom is eight-coordinated forming a square-antiprismatic coordination consisting of eight oxygen atoms. One square face is formed by oxygen atoms supplied by carboxylates while the second square face is formed by oxygen atoms coming from the  $\mu_3$ -O and  $\mu_3$ -OH groups. This results in a cluster shaped like a Maltese star (Figure 2c). The high symmetry and this famous graphical icon contribute to the exceptional beauty of these structures. Synthesis is described in Supporting Information. The materials crystallize as small (1–2  $\mu\text{m}$ ) intergrown cubic crystals which are too small for structure determination by single crystal diffraction. The crystal structure is therefore solved from powder X-ray data (see Supporting Information). Hydrogen atoms can not be located in the XRD-powder structure refinement, but charge balancing requires the presence of four OH groups, and the presence of OH groups is also evident from the IR data (see Supporting Information). Dehydroxylation of the cluster starts at 250 °C and is completed at 300 °C. Two of the 4  $\mu_3$ -OH groups leave together with the hydrogen from the remaining two  $\mu_3$ -OH groups, resulting in a Zr<sub>6</sub>O<sub>6</sub> inner cluster with seven-coordinated zirconium. The phenomenon is fully reversible. Figure 2d shows the new Zr<sub>6</sub>O<sub>6</sub> inner cluster while Figure 2e shows the full Zr<sub>6</sub>O<sub>6</sub>(CO<sub>2</sub>)<sub>12</sub> cluster. This rearrangement results in large changes in Zr–Zr distances within

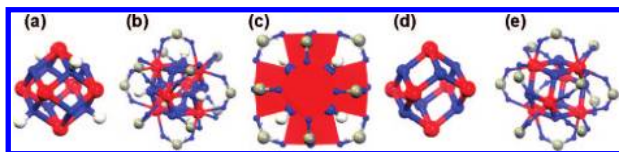
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**Figure 1.** (a) One unit cell of copper drawn to scale with: (b) Zr-MOF with 1,4-benzene-dicarboxylate (BDC) as linker, UiO-66, (c) Zr-MOF with 4,4'-biphenyl-dicarboxylate (BPDC) as linker, UiO-67, (d) Zr-MOF with terphenyl dicarboxylate (TPDC) as linker, UiO-68. Zirconium, oxygen, carbon, and hydrogen atoms are red, blue, gray, and white, respectively.



**Figure 2.** Structures a and d show the inner core  $Zr_6$ -cluster drawn alone for clarity, in hydroxylated and dehydroxylated form, and the symmetry change from  $T_d$  ( $-43\text{ m}$ ) to  $D_{3d}$  ( $-3\text{ m}$ ) when the two  $\mu_3$ -OH groups are removed. Structures b and e show the full cluster to illustrate the change in zirconium coordination from 8 to 7 upon dehydration. Zirconium, oxygen, carbon and hydrogen atoms are red, blue, gray, and white, respectively.

the cluster; the structural transformation can be followed by EXAFS (see Supporting Information). However, the overall framework structure is virtually unchanged, as seen by powder XRD. This ability to maintain the network structure upon dehydroxylation and change in coordination around zirconium is the key to understanding the extension in structural stability from the typical value of  $350\text{ }^\circ\text{C}$  observed for other MOFs with inorganic cornerstones containing hydroxyl groups; example structures are MIL-88,<sup>7</sup> MIL-100,<sup>13</sup> and MIL-110.<sup>14</sup> The  $Zr_6$ -cluster rearranges reversibly upon removal or addition of  $\mu_3$ -OH groups, without any changes in the connecting carboxylates. Puchberger et al.<sup>12</sup> have observed that the carboxylate groups can change their coordination mode from edge-bridging to monodentate and that the  $Zr_6O_6$  core is only slightly affected by these changes. This is a further illustration of the flexibility of the  $Zr_6$ -cluster, which gives potential for forming a large variety of MOF frameworks.

The Langmuir surface area of UiO-66 is  $1187\text{ m}^2/\text{g}$ . Calculation<sup>15</sup> of solvent surface area for UiO-66 is in perfect agreement with measured surface area. Increasing the length of the linkers is a route to create high surface area materials. The high density of linkers in this structure makes this approach particularly advantageous, extending the linkers to two and three benzene ring dicarboxylic acids, increases the surface area of the material to 3000 and  $4170\text{ m}^2/\text{g}$ , respectively. Increasing the length of the linker does not reduce the stability of these structures; ultrastable materials with surface areas in the range of the highest reported can therefore be reached. Access to the internal surface of Zr-MOFs is restricted by triangular windows. The window opening is estimated from the largest sphere which may fit the window. Linkers with one, two, and three benzene rings, give openings corresponding to 6, 8, and  $10\text{ }\text{\AA}$ , respectively. A molecule with the size of a fully methylated benzene may enter even the most restricted structure, UiO-66.

Structural resistance toward solvents and mechanical pressure is critical for the application of MOFs. The resistance of Zr-BDC MOF toward solvents like water, DMF, benzene, and acetone was investigated by stirring the desolvated sample in the solvent for 24 h. The UiO-66 material has further been exposed to increasing pressure up to  $10.000\text{ kg/cm}^2$ . Evidently, the powder XRD pattern remains virtually unaltered by the applied treatment (see Supporting Information).

**Acknowledgment.** The authors thank Ch. Baerlocher and P. D. C. Dietzel for measuring X-ray powder-patterns at BM1, C. Prestipino for EXAFS beamtime at BM29, ESRF Grenoble, France, and M. H. Nilsen for performing stress tests and the Norwegian Research Council for economical support.

**Supporting Information Available:** Description of the structures, synthesis, SEM photo of the crystals, TG-data, structure solution, tables of crystal data, EXAFS data and analysis, IR characterization, diffraction patterns after chemical and mechanical stress. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA8057953