COMMUNICATION

Green synthesis of zirconium-MOFs†

Helge Reinsch,[a] Bart Bueken,[b] Frederik Vermoortele,[b] Ivo Stassen,[b] Alexandra Lieb,[c] Karl-Petter Lillerud[a] and Dirk De Vos*[b]

The synthesis of Zr-MOFs under green, industrially feasible conditions was investigated. Two new compounds with **bcu**-topology and the fluorinated analogue of UiO-66 exhibiting **fcu**-topology were obtained and characterised. All products exhibit permanent porosity. In the **bcu**-frameworks the interaction with sulfate anions apparently induces an unusual eightfold connectivity of the Zr cluster.

Metal–organic frameworks (MOFs) are one of the most intensely investigated classes of materials in fields like catalysis,[1] separation[2] or luminescence.[3] Among the thousands of different compounds, Zr^{4+}-based MOFs clearly occupy an outstanding position. These MOFs often exhibit an extremely high thermal and chemical stability[4] while having large specific surface areas and being excellent catalysts in various reactions.[5] Except the MIL-140 series of compounds,[6] most carboxylate-based Zr-MOFs are based on a hexanuclear Zr-oxo-cluster which coordinates up to twelve carboxylate moieties. This inorganic node is for example incorporated in the versatile series of compounds denoted as UiO-66-X (where UiO stands for University of Oslo and the X represents respective functional groups).[7] A great leap forward for the synthesis of Zr-MOFs was the utilization of modulating reagents during the synthesis.[8] This gave control over the crystal size[9] but resulted as well in a number of new compounds based on different linker molecules, which can be only obtained by adding such "modulators" like formic, acetic or benzoic acid.[10] These organic additives are not necessarily incorporated in the framework but can strongly affect the connectivity of the inorganic node.[11]

The synthesis of Zr-MOFs is commonly carried out in *N,N*-dimethylformamide or similar organic solvents. This represents a major drawback for the transfer of MOFs into applications since the employed amides are flammable, toxic and teratogenic. Recently, the synthesis of a functionalised Zr-MOF in water was reported.[12] This inspired us to further investigate the aqueous chemistry of Zr^{4+}-carboxylates. For two reasons we focussed on the use of zirconium sulphate. First of all, it is the only sufficiently water soluble Zr^{4+}-source that could be employed under large-scale industrial conditions.[13] In addition, it was already shown that SO_4^{2-}-anions can be utilised to guide the connectivity of MOFs[14] and therefore can be considered as potential inorganic modulators. This is supported by the structural diversity of sulphate based Zr-oxo-species.[15] Furthermore we limited the synthesis conditions to parameters which would be suitable for a straightforward transfer to industrial scale, as described recently by BASF (Fig. 1).[13] These parameters comprise the synthesis
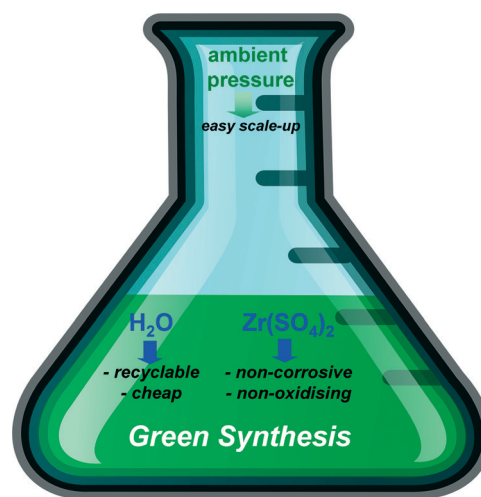
a Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, 0315 Oslo, Norway

b Centre for Surface Chemistry and Catalysis, University of Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium. E-mail: dirk.devos@biw.kuleuven.be; Fax: +32 16 3 21998; Tel: +32 16 32 16 39

c Institut für Chemie, Universitätsplatz 2, 39106 Magdeburg, Germany

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Fig. 1 Illustration for the green synthesis of zirconium MOFs based on the cornerstones defined by BASF.[13]

below the boiling point of the solvent or under reflux in an open system, in order to avoid autogenous pressure in the reactor. This enables the transfer to larger facilities, for example pilot plant stations, which are usually not compatible for high pressure syntheses. Moreover, the utilisation of nitrates or perchlorates is excluded due to their oxidising potential which impedes their use at larger scale. Chlorides should not be used either since such compounds can cause corrosion. In addition, water should be used as solvent since organic solvents are more expensive and in some cases very difficult to recycle.

Reacting 2-aminoterephthalic acid ($H_2BDC-NH_2$) and $Zr(SO_4)_2 \cdot 4H_2O$ in water at 98 °C, a highly crystalline compound could be obtained under mild synthesis conditions. The PXRD data showed strong similarities to the pattern of UiO-66 but indexing indicated a lower symmetry with different unit cell parameters (extinction conditions corresponding to $I\bar{4}$, $a = b = 14.2302(25)$ Å, $c = 21.4142(22)$ Å; for UiO-66: space group $Fm\bar{3}m$, $a = b = c = 20.7004(2)$ Å). The observed space group is related to the one of UiO-66 by a supergroup-subgroup relationship. Utilising this relationship, a structural model and a chemical formula in agreement with further analytical results (EDX and IR spectroscopy, thermogravimetry) could be established; it was confirmed by Rietveld refinement (for details about deduction of the formula see ESI†). The crystal structure of $[Zr_6(OH)_{10.8}(SO_4)_{3.6}(BDC-NH_2)_3(H_2O)_{7.4}] \cdot nH_2O$ (1) exhibits the same spatial arrangement of inorganic building units as UiO-66. However, due to the reduced connectivity (idealised eightfold instead of idealised twelvefold like in UiO-66) a **bcu**-topology is observed (Fig. 2 left). The inorganic nodes are interconnected via linker molecules only along the crystallographic c-axis while they are not interconnected but decorated with sulphate anions around the equatorial plane of the Zr_6-cluster (Fig. 3). A fraction of the anions is directly coordinated to the inorganic node in a monodentate η^1 fashion while another fraction is interacting via hydrogen bonds with μ_3-OH-groups of the inorganic building unit (Fig. 2 right).

Fig. 3 Framework structure of **1** showing the sulphate-decoration of the **bcu**-framework. ZrO-polyhedra in grey, linker molecules in black, sulphate ions as yellow tetrahedra and hydrogen bonds as dashed blue lines.

The positions of the sulphate anions as well as those of the linker molecules are only partially occupied which is a common phenomenon in Zr-MOFs. Thus a sulphate-decorated open framework with **bcu**-topology is obtained (Fig. 3) in which intersecting rhombic channels can be observed.

Employing pyromellitic acid (1,2,4,5-benzenetetra-carboxylic acid or H_4BTEC) under similar reaction conditions, a new compound with the approximate composition $[Zr_6(OH)_{14}(BDC(CO_2H)_2)_4(H_2O)_2(SO_4)] \cdot nH_2O$ (2) could be obtained (for details see ESI†). The framework of **2** represents an isoreticular analogue of **1** bearing functional CO_2H-groups instead of NH_2-groups. Thus the use of sulfate in the synthesis induces again the formation of an eightfold connected **bcu**-framework. A similar structure directing effect was already observed for the synthesis of zirconium adipates.[16] However, the amount of inorganic anions in **2** is much lower than in **1** (about one SO_4^{2-} per inorganic node) and therefore the anions could not be located inside the framework by XRD methods. In this context it should be also mentioned that we assume that the intracluster oxygen atoms are solely part of OH^- ions, which was previously reported for a molecular compound exhibiting similar hexanuclear cluster geometry obtained under similar conditions.[17] Nevertheless, these intracluster atoms can be also part of O^{2-} ions and thus the number of water molecules bound to the Zr^{4+} ions might be higher.

Employing tetrafluoroterephthalic acid (H_2BDC-F_4), we obtained UiO-66-F_4 (3) with the approximate formula $[Zr_6O_2(OH)_6(BDC-F_4)_6(SO_4)] \cdot nH_2O \cdot 1.2H_2BDC-F_4$, the perfluorinated analogue of UiO-66. The framework of this compound exhibits the **fcu**-topology. Due to the F-functionalization, the aromatic rings are not arranged in plane with the carboxylate groups but disordered over two possible orientations (Fig. 4). The framework contains cavities of tetrahedral and octahedral shape with reduced size compared to UiO-66 (diameters
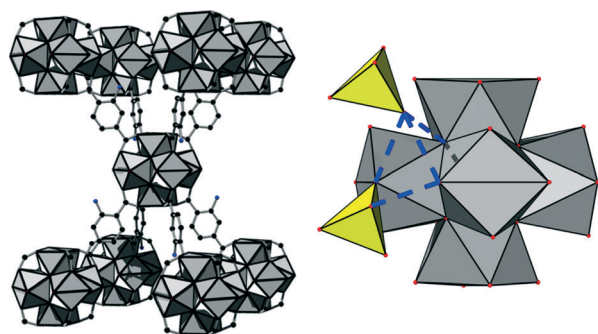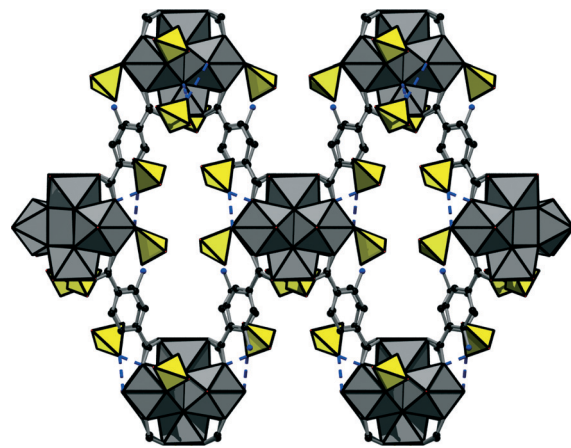

Fig. 2 Left: The eight-connected inorganic node shown with its neighbouring Zr-clusters; sulphate ions are omitted for clarity. Right: Inorganic Zr-cluster and the interacting sulphate ions. ZrO-polyhedra in grey with oxygen atoms in red, linker molecules with NH_2-groups in black, sulphate ions as yellow tetrahedra and hydrogen bonds as dashed blue lines.
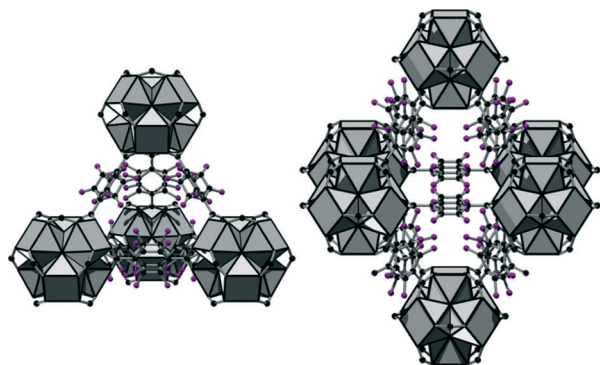
Fig. 4 Tetrahedral (left) and octahedral (right) cavities observed in the framework of UiO-66-F_4 (**3**), showing the non-planarity of the linker molecules. ZrO-polyhedra in grey, carbon atoms in black and fluorine atoms in purple.

Fig. 5 Type-I-isotherms for **1**–**3** measured with N_2 at 77 K after activation at 150 °C under vacuum.

of ≈3.6 and 6 Å in **3**, respectively) which are interconnected by trigonal windows (diameter between 2.4 and 4.6 Å). Thus the employed green synthesis conditions do not only lead to the formation of compounds with **bcu**-topology but allow as well the formation of **fcu**-frameworks with UiO-66-structure.

EDX spectroscopy indicates the presence of sulphate in all three compounds. The sulphate ions in **1** could be localised by crystallographic methods and can only partially be removed by treatment in water at elevated temperature (≈3 SO_4^{2-}-ions per Zr_6-cluster after washing instead of 3.6 in the *as-synthesized* form), indicating a strong interaction between anions and framework. In the isoreticular framework **2**, the sulphate ions are only present in very small amount and could therefore not be localised crystallographically. Moreover the sulphate ions can be completely removed by aqueous treatment, indicating only weak interaction with the framework. Thus the functional groups of the linker molecules clearly affect the binding strength of the anions to the **bcu**-framework, possibly due to the larger amount of missing linker molecules in **1** compared to **2**. Another reason could be the fact that SO_4^{2-} ions can only leave as uncharged moieties, *i.e.* H_2SO_4 molecules, which might be deprotonated by the weakly basic NH_2-groups and therefore retained in the framework. In **3**, sulphate ions are found as well. It can be conjectured that these ions could occupy positions resulting from the existence of missing-linker defects. This is supported by a recent report on the coordination of sulphate ions to the inorganic unit in a zirconium MOF with sixfold connecting inorganic building units.[18] As in **2**, the anions could not be localised due to the lower sulphate content (≈1 SO_4^{2-}-ion per Zr_6-cluster).

Upon thermal activation (150 °C under vacuum), all three compounds exhibit permanent porosity towards N_2 at 77 K (Fig. 5) with isotherms characteristic for microporous materials. The apparent specific surface areas are $S_{BET} ≈ 420$ $m^2 g^{-1}$ for **1**, 250 $m^2 g^{-1}$ for **2** and 640 $m^2 g^{-1}$ for **3**. The corresponding micropore volumes are $V_{MIC} = 0.15$ $cm^3 g^{-1}$ for **1**, 0.08 $cm^3 g^{-1}$ for **2** and 0.24 $cm^3 g^{-1}$ for **3**, respectively, as calculated from the amount adsorbed at $p/p_0 = 0.5$.

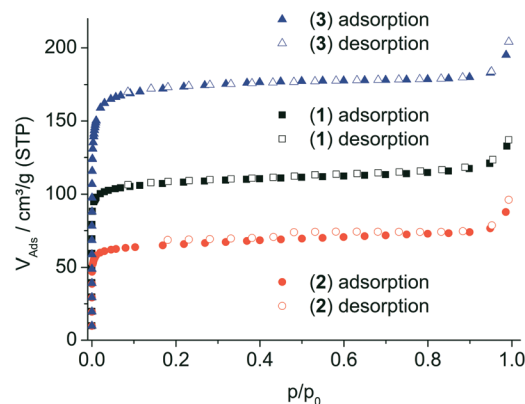While compound **3** exhibits a rigid framework upon thermal activation and does not show any structural changes according to PXRD data, the frameworks of **1** and **2** exhibit a strong structural change upon removal of the occluded solvent molecules. The PXRD data (Fig. 6) after activation indicate a drastic decrease in long-range order. This amorphisation is fully reversible and a treatment in diluted sulphuric acid leads to a complete recovery of the compound's crystallinity already at a comparably low temperature (60 °C). Instead of sulphuric acid, diluted formic acid can be utilized as well. Thus the regeneration of the framework is in general induced by acids. We assume that this remarkable behaviour originates mostly from the partial occupancy of the positions of the organic building units and the presence of sulphate anions. A perfect **bcu**-framework could show structural changes as well, but in this case transitions between different crystalline framework conformations would be expected. The relatively high degree of structural imperfection, especially in the framework of **1**, implies that the coordination environments of different inorganic nodes are rather heterogeneous and therefore the structural changes due to dehydration should be diverse across the framework
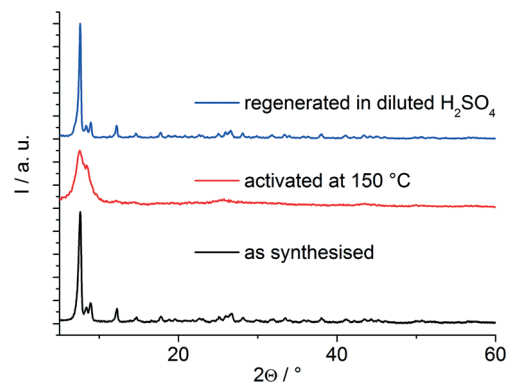

Fig. 6 PXRD patterns of the *as synthesised* (black line), thermally activated (red line) and regenerated (blue line) compound **2**. The patterns for **1** look very similar while **3** does not show any structural changes.

structure. In addition to this effect, we also observed the formation of anhydrides in the structure of **2** which form upon condensation of two functional carboxylic acid groups (see ESI†). This was reported previously for other MOFs with free CO_2H-groups,[19] and might in this case also affect the crystallinity of the compound.

Since MOFs of the UiO-66-series are versatile Lewis-acidic catalysts,[5] we examined also the presence of acid sites by IR-spectroscopy *via* adsorption of deuterated acetonitrile for **3**. MOFs with UiO-66-structure are well known to possess active Lewis acid sites upon dehydration of the inorganic node at temperatures above 200 °C.[20] In the new framework of UiO-66-F$_4$ we observed Brønsted- as well as Lewis-acid sites after evacuation at 220 °C (ESI,† Fig. S7). We attribute the Brønsted sites to the inclusion of unreacted linker molecules in the pores of the framework. The inorganic cluster itself is dehydrated at high temperatures, resulting in sevenfold coordinated Zr-ions with Lewis acid sites. However, these sites could exist as well due to the presence of defects in the framework structure.[21] The position of the signal for the CN-vibration at 2305 cm^{-1} indicated a much stronger Lewis acidity compared to the unfunctionalised parent framework UiO-66 as it was reported in ref. 5, further confirming the inductive effect of functional groups on the Lewis acidity of the Zr-cluster.[5]

Summarising our findings, three different new Zr-MOFs could be synthesised under green, industrially feasible synthesis conditions. The **bcu**-framework compounds show a reversible structural disarrangement which can be attributed to the high density of defects in the structures. Such findings could not only enable the synthesis of Zr-MOFs at large scale but moreover might also result in an extension of modulator-based MOF chemistry to inorganic modulating anions.

Acknowledgements

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