DOI: 10.1002/ange.201204963

Metal–Organic Frameworks

Automated Diffraction Tomography for the Structure Elucidation of Twinned, Sub-micrometer Crystals of a Highly Porous, Catalytically Active Bismuth Metal–Organic Framework[**]

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The number of metal–organic framework (MOF) compounds has increased almost exponentially over the last decade as a consequence of their fascinating structures and potential applications.[1] They are composed of inorganic building units, such as metal ions or clusters, which are connected through organic linker molecules to form a porous three-dimensional network. Most of the MOFs are based on rigid polycarboxylate linker molecules,[2] but a large variety of metal ions, mainly transition-metal ions, have also been incorporated.[2c,3] The chemical and thermal stability of metal carboxylate based MOFs is crucial for potential applications and depends on the metal ions incorporated.[4] In general, metal ions in higher oxidation states lead to more stable structures.

While the use of divalent metal ions often results in the formation of single crystals, whose structures can be routinely determined by single-crystal X-ray diffraction,[2c,3c] tri- and tetravalent metal carboxylates are mostly obtained as microcrystalline powders and the determination of their structures poses immense challenges.[2a,3a,4c,5] Direct methods have been successfully employed, but complicated structures with large unit cells necessitate the use of nonstandard approaches. Thus, computational assisted structure determination, namely, the AASBU[4c] approach (assembling of secondary building units), the ligand-replacement strategy,[2a,6] and DFT[7] calculations have been applied. Recently automated diffraction tomography (ADT) has been introduced as a new method for collecting three-dimensional electron diffraction data from single nanosized crystals,[8] thus allowing single-crystal analysis even for porous and organic sub-microcrystalline samples.

A trivalent metal that exhibits interesting catalytic properties is bismuth. It is nontoxic, noncarcinogenic, and for a rare metal relatively inexpensive, and thus bismuth compounds are used as green catalysts.[9] Despite these characteristics, the number of bismuth-based MOFs is rather limited and only a few compounds with limited porosity have been described.[10] This is in contrast to the many known bismuth-oxo clusters, which could possibly be used for the construction of new MOFs.[11]

Here, we present the synthesis of the first highly crystalline, porous, and catalytically active bismuth-based MOF Bi(BTB) (BTB = 1,3,5-benzenetrisbenzoate), whose structure was elucidated by a combination of electron diffraction, Rietveld refinement, and DFT calculations.

Bi(BTB), denoted as CAU-7 (CAU = Christian-Albrechts-Universität) was synthesized by using conventional as well as microwave (MW) assisted heating. The reaction of $Bi(NO_3)_3{\cdot}5\,H_2O$ with H_3BTB in methanol at 120 °C led to phase-pure CAU-7 (for a detailed synthesis procedure see the Supporting Information). The reaction time can be reduced from 12 h to 20 min by using MW-assisted instead of conventional heating, but this leads to the formation of 10–20 μm large agglomerates of strongly intergrown elongated crystals of about 100 nm (see Figures S2–S4 in the Supporting Information). The addition of DMF in the conventional synthesis results in the formation of larger rodlike crystals ranging from 200 to 300 nm in length. Transmission electron microscopy confirmed that isolated CAU-7 crystals have a typical rodlike shape with different length/diameter ratios (see Figure S5 in the Supporting Information). Such isolated rods were used to collect electron diffraction data by automated diffraction tomography (ATD).

Single-crystal ADT electron diffraction datasets were collected using a cryo holder cooled to 120 K and mild illumination conditions. To prevent beam damage and improve the signal intensity, the diffraction data were acquired in the precession mode.[12] The three-dimensional diffraction space reconstruction leads to lattice parameters $a = 32$ Å, $b = 28$ Å, $c = 4$ Å, $\alpha = \beta = \gamma = 90°$, and extinction group *Pb-a*. The reconstructed reciprocal space is shown in Figure 1.

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[**] We thank Steffen Schmidt (LMU München) for the SEM micrographs, Michael T. Wharmby for his assistance in preparing the graphics, and the DFG for financial support (SPP 1362, grant agreement no. STO 643/5-2). This work has also been supported by the Stiftung Rheinland-Pfalz für Innovation and the state Schleswig Holstein.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201204963.

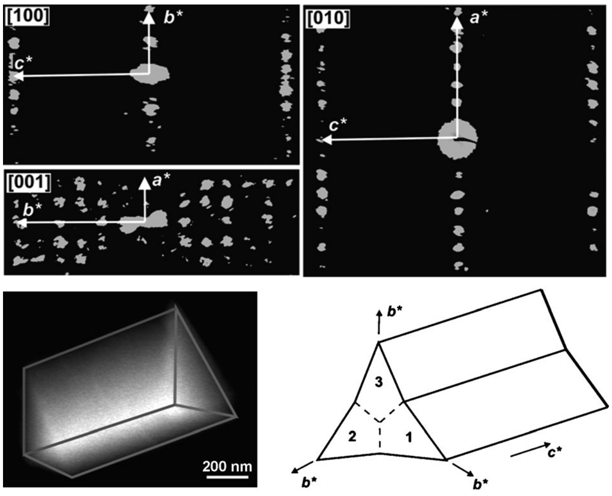

Figure 1. Reconstructed three-dimensional diffraction space of CAU-7 projected along the main directions (top), a rod tilted to expose the triangular base (bottom left), and a sketch of the trilling arrangement (bottom right).

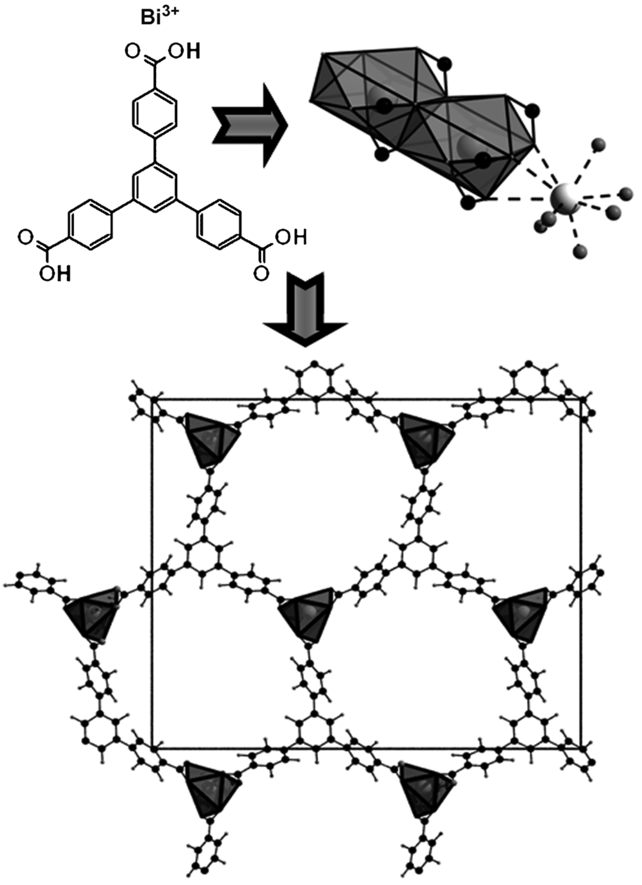

Figure 2. Crystal structure of CAU-7. The connection of 1,3,5-benzenetrisbenzoate (BTB^{3-}) and Bi^{3+} ions (top left) leads to face-sharing BiO$_9$ polyhedra which form chains along the [001] direction (top right). These chains are interconnected into a honeycomb network (bottom).

The ADT data also showed that each rod is in fact a twin aggregate composed of three individuals that grow following the pseudohexagonal symmetry of the structure (Figure 1), and thus a trilling is formed (see Figures S6 and S7 in the Supporting Information). The three individuals share the same [001] direction, which is also the main growth direction of the rod. The [010] directions are rotated by 120°, and are parallel to the "almost" equivalent [2−10] and [−2−10] directions of the other domains.

The structure of CAU-7 was determined on the basis of electron diffraction data collected on two single domains. Simulated annealing (SA) routines were used as implemented in SIR2011.[13] The structure was finally solved in the space group $Pb2_1a$ with one independent bismuth atom and one independent BTB^{3-} molecule in the unit cell. All six torsion angles of the BTB^{3-} molecule were kept free to rotate during the solving process. The crystal structure was refined from X-ray powder diffraction data using Topas Academics 4.1.[14] More details are given in the Supporting Information.

DFT-based calculations on the CAU-7 crystal structure were carried out to further support the experimental observations. A plane-wave approach, as implemented in the CPMD program package was employed, using the PBE functional together with Goedecker–Teter–Hutter pseudopotentials and a final wavefunction cutoff of 100 Rydberg (density cutoff: 400 Ry) and the experimental lattice parameters.[15] The calculated Bi-O distances are between 2.336 and 3.221 Å for the optimized structure, which is in good agreement with the experimentally obtained values (2.16(1)–3.38(1) Å). More details of the DFT calculations are given in the Supporting Information.

In the crystal structure of CAU-7, the Bi^{3+} ions are ninefold coordinated by oxygen atoms of the BTB^{3-} ions, thereby forming threefold capped trigonal prisms. Face sharing of the BiO$_9$ polyhedra leads to chains along the *c*-axis (Figure 2). Such polyhedra are already known for the bismuth benzoate Bi(O$_2$C$_6$H$_5$)$_3$, which shows very similar bond lengths that range from 2.250(6) to 3.110(6) Å.[16] The BTB^{3-} linkers connect the chains into a slightly distorted honeycomb network with approximately 1 nm wide, one-dimensional channels, as determined with PLATON.[15b,17] Each carboxylate group of the linker molecule contains one μ- and one end-on-linked oxygen atom.

The thermal stability of CAU-7 was investigated by thermogravimetric (TG) analysis and temperature-dependent X-ray powder diffraction (TD-XRPD) measurements. The as-synthesized product, which contains noncoordinating H$_3$BTB molecules (see Figure S17 in the Supporting Information for the IR spectra), was treated with DMF and methanol. This was followed by ultrasonication in methanol for 30 min. The TG curve (see Figure S15 in the Supporting Information) shows a weight loss of 14.2 % as a result of the loss of solvent molecules from the pores between 25 and 80 °C. Above 350 °C, the loss of one BTB molecule is observed, which results at 1000 °C in Bi$_2$O$_3$ (found: 52.1 %, calcd: 51.1 %). The TD-XRPD measurements (see Figure S16 in the Supporting Information) confirm the stability of the crystalline framework up to 380 °C. Above this temperature, decomposition takes place and results in an X-ray amorphous phase at 400 °C.

Prior to the sorption experiments CAU-7 was thermally activated at 160 °C for 12 h under vacuum. The elemental analysis of the activated sample confirms the complete removal of the H_3BTB and DMF molecules.[15c] The BET evaluation of the type 1 N_2 sorption curve of CAU-7 results in a specific surface of $A_{(\mathrm{BET})} = 1150\ \mathrm{m^2\,g^{-1}}$ and a micropore volume of $V_\mathrm{m} = 0.43\ \mathrm{cm^3\,g^{-1}}$ ($V_\mathrm{m}(\mathrm{calcd}) = 0.43\ \mathrm{cm^3\,g^{-1}}$[17]). These values are comparable to other BTB-based MOFs with honeycomb networks, such as CAU-4 (Al(BTB): $A_{(\mathrm{BET})} = 1520\ \mathrm{m^2\,g^{-1}}$, $V_\mathrm{m} = 0.61\ \mathrm{cm^3\,g^{-1}}$[18] and MIL-103 (Tb-$(H_2O)$(BTB): $A_\mathrm{BET} = 700\ \mathrm{m^2\,g^{-1}}$).[19] Isolated AlO_6 and edge-sharing TbO_9 polyhedra are observed in these structurally related compounds. The sorption behavior towards H_2, H_2O, and CO_2 shows the expected results for a hydrophobic MOF (see Figures S11–S14 in the Supporting Information). Thus, an uptake of 1.07, 2.62, and 4.31 wt % is observed for H_2 (77 K), H_2O (298 K), and CO_2 (298 K), respectively, at 1 bar.

The catalytic activity of CAU-7 was demonstrated in the solvent-free hydroxymethylation of hemicellulose-derived 2-methylfuran to 5-methylfurfuryl alcohol (see the Supporting Information).

This reaction requires Lewis or Brønsted acid sites of well-defined strength.[20] If the acidity is too strong, consecutive condensations and polymerization result; the optimum catalyst should give high yields at high conversions. CAU-7 was compared to other MOFs with reported Lewis or Brønsted acidity, such as the Zr-terephthalate UiO-66[21] and the Ga-terephthalate MIL-53(Ga).[22] In contrast with these, CAU-7 gives high yields at high conversions, thus avoiding consecutive condensation reactions. CAU-7 possesses mild Lewis acid sites, as demonstrated by the chemisorption of acetonitrile (see Figure S4 in the Supporting Information). The hydrophobic nature of the material facilitates fast desorption of the alcohol reaction product. The heterogeneity of the catalyst was confirmed.

In conclusion, we have discovered the first permanently porous, highly crystalline bismuth-based MOF that also exhibits catalytic activity. The incorporation of other potentially interesting metals into MOF structures should also be possible. Moreover, the potential of the ADT method for the investigation of crystalline features and structure–property relationships of nanosized crystals has been shown. ADT revealed the twinning law and the orientation of CAU-7 crystals in the rodlike aggregates, and, coupled with the SA method, resulted in an efficient method for the structure determination of beam-sensitive materials.

Received: June 25, 2012

Keywords: bismuth · heterogeneous catalysis · metal–organic frameworks · structure elucidation

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