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$[Al_2(OH)_2(TCPB)]$ – An Al-MOF based on a tetratopic linker molecule

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ABSTRACT

High-throughput methods were employed in the discovery and synthesis optimization of the new microcrystalline metal-organic framework (MOF) $[Al_2(OH)_2(TCPB)] \cdot 2$ DMF (denoted CAU-9as), which contains the tetratopic linker ion 1,2,4,5-tetrakis-(4-carboxylatophenyl)-benzene ($TCPB^{4-}$). The compound is obtained under solvothermal reaction conditions and activation at 150 °C leads to the removal of the guest molecules (CAU-9act). Detailed characterization was carried out by FT-IR and NMR spectroscopy, thermogravimetric analysis, gas sorption measurements and X-ray powder diffraction. CAU-9act crystallizes in an orthorhombic unit cell (space group *Cmmm*) with the cell parameters: $a = 31.562(4)$, $b = 6.642(7)$, $c = 10.6612(7)$ Å. Modeling by force field calculations in combination with Rietveld refinement was used to determine the structure of CAU-9. The content of the asymmetric unit was corroborated based on NMR crystallographic strategies evaluating high-resolution ^{1}H, ^{13}C and ^{27}Al MAS NMR spectra. The structure of CAU-9 is isoreticular to the one of MIL-118B $[Al_2(OH)_2(BTEC)]$ (BTEC = 1,2,4,5-benzenetetracarboxylate) and Al-PMOF $[Al_2(OH)_2(TCPP)]$ (TCPP = *meso*-tetra(4-carboxylato-phenyl)porphyrin). According to the temperature dependent PXRD measurements and the thermogravimetric analysis, it is stable up to 480 °C in air. The nitrogen sorption measurement at 77 K has given a Brunauer–Emmett–Teller (BET) surface area of 1118 $m^2\ g^{-1}$ and a micropore volume of 0.45 $cm^3\ g^{-1}$. In contrast to MIL-118 no rearrangement of the carboxylate groups from a mono- to bidentate coordination mode was observed upon activation.

1. Introduction

In the past few years the development of new metal organic frameworks (MOFs) has been in the focus of many investigations [1]. Often new linker molecules are employed in the search of compounds with unprecedented topologies [2]. Alternatively, functionalized linker molecules are used in order to tune the pore size and the pore surface chemistry, for example, for applications in catalysis or gas separation or to be able to carry out post synthetic modification reactions [3–5]. An important aspect of MOF chemistry is the modular synthesis concept allowing for a straightforward access of isoreticular MOF structures [6–10]. Using existing, well-known topologies, the size of the linker molecule is varied while retaining its principal shape resulting in an adaption of pore sizes [10–15]. As a result of the large linker molecules often interpenetration is observed as shown for example in the IRMOF series [6]. This can be prevented through the choice of appropriate inorganic building units (IBUs) such as one-dimensional IBUs [9].

Carboxylate-based Al-MOFs have been of special interest due to their chemical and thermal stability, which is only surpassed by corresponding Cr- and Zr-MOFs [16,17]. An extraordinary advantage of aluminum is the fact that the salts are non-toxic and hence easy to handle and commercially available at low-cost. Therefore, aluminum based MOFs are of interest for industrial use [18]. A challenge in the investigation of Al-MOFs is the rich solution chemistry of Al^{3+} which can lead to a variety of IBUs ranging from isolated Al^{3+} ions, that are exclusively connected by carboxylate groups [16], to trimeric building units [19–21], rings of edge- and corner sharing AlO_6 polyhedra [11,12,22], chains of *trans*- or *cis*-corner sharing AlO_6 polyhedra [23–27], chains of edge sharing AlO_6 polyhedra [28] or very complex inorganic building units of corner-sharing Al_{13}-oxo clusters [29]. An in depth study on the use of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid, H_4BTEC) has been carried out by Loiseau et al. which lead to a variety of new Al-

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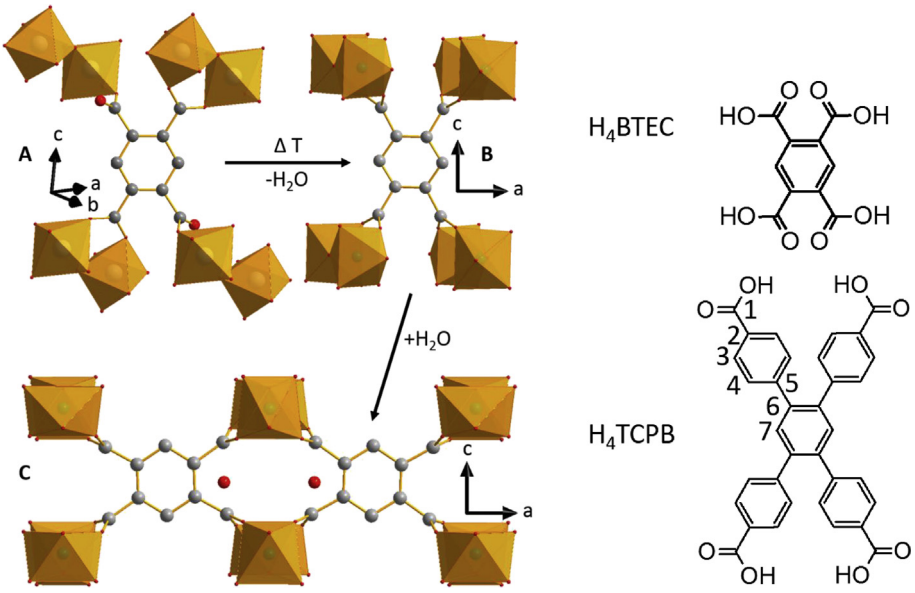

Fig. 1. Representation of the different forms of MIL-118 (left). Thermal treatment of as synthesized MIL-118A (A) leads to MIL-118B (B), which adsorbs water under ambient conditions forming MIL-118C (C) [30]. Carbon atoms are colored grey, oxygen red and the AlO_6 polyhedra are orange. On the right side the extension of the H_4BTEC linker as it is used in the synthesis of MIL-118 to H_4TCPB which served as linker molecule in this investigation is shown. In addition labeling of the magnetically inequivalent carbon atoms is presented for a molecule with *mmm* symmetry. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

MOFs [28,30,31]. In particular a high-throughput investigation was carried out and the exact fields of formation were established. The pH of the reaction mixture was found to be the main variable on the product formation [31].

One Al-MOF obtained using H_4BTEC and undergoing irreversible structural changes upon heating is the MIL-118 series $[Al_2(OH)_2(BTEC)]$ [30]. The structure of the as synthesized compound MIL-118A $[Al_2(OH)_2(H_2O)_2(BTEC)]$ exhibits a distinct structural feature, i.e. the carboxylate ions coordinate in a bidentate and a monodentate mode. Upon thermal treatment coordinated water molecules are removed and the free coordination site is occupied by the previously monodentate carboxylate group (MIL-118B $[Al_2(OH)_2(BTEC)]$). Upon rehydration of MIL-118B under ambient conditions only water molecules are adsorbed in the pores and MIL-118C $[Al_2(OH)_2(BTEC)] \cdot 3H_2O$ is formed (Fig. 1).

Here we present the results of our work on using an extended version of the H_4BTEC linker molecule, i.e. H_4TCPB (Fig. 1) in the synthesis of Al-MOFs, which was envisioned to lead to a structure isoreticular to MIL-118.

2. Experimental section

2.1. General

The chemicals used for the synthesis of CAU-9 are commercially available and were used without further purification. Discovery and synthesis optimization of this compound were carried out employing our 48-high-throughput reactor system for solvothermal high-throughput reactions [32–34]. The high-throughput PXRD measurements were performed in transmission geometry using a STOE HT diffractometer equipped with a *xy*-stage and an IPDS system (Cu $K_{\alpha 1}$ radiation). Collection of high-resolution powder diffraction data was possible on a STOE Stadi-P powder diffractometer equipped with a MYTHEN1K detector system (Cu $K_{\alpha 1}$ radiation). Temperature dependent high-resolution powder diffraction data was recorded on a STOE StadiP-Combi diffractometer using Cu $K_{\alpha 1}$ radiation and equipped with a MYTHEN1K detector. These measurements were carried out under air in a 0.5 mm quartz capillary in a range of 3–45° 2Θ with a measuring time of 85 min for each temperature step. MIR spectra were recorded on an ATI Matheson Genesis spectrometer equipped with an ATR unit in the spectral range of 400–4000 cm^{-1}. The thermogravimetric analyses were performed using a NETSCH STA 409 CD analyzer. The samples were heated in Al_2O_3 crucibles at a rate of 4 K min^{-1} under a flow of air (75 mL min^{-1}). The TG data were corrected for buoyancy and current effects. Sorption experiments were carried out using a Belsorp-max instrument (BEL JAPAN INC.). Before the sorption experiments, the samples were activated at 150 °C under vacuum (10^{-2} kPa) over night. For setting up a structural model Accelrys Materials Studio 4.1 was used [35]. Rietveld refinement of this structural model was carried out with TOPAS Academic v4.1 [36]. Theoretical micropore volumes were calculated using the calc solv feature implemented in PLATON [37]. A probe molecule with a diameter of 2.6 Å was used. Parametric Pawley refinements were performed using Powder3D Parametric [38].

2.2. Solid-state nuclear magnetic resonance

All solid-state NMR experiments were acquired on a Bruker Avance-III HD operating at a B_0 field of 14.1 T. ^1H (600.15 MHz) high-resolution spectra were acquired after a 90° pulse of 1.4 μs with a spinning speed of 62.5 kHz using a commercial 1.3 mm MAS double resonance probe (Bruker). ^{13}C (150.9 MHz) MAS spectra were obtained with a ramped cross-polarization (CP) experiment where the nutation frequency ν_{nut} on the proton channel was varied linearly by 30%. The samples were spun at 20 kHz in 3.2 mm MAS triple resonance probe (Bruker). The corresponding ν_{nut} on the ^{13}C channel and the contact time were adjusted to 70 kHz and 3.0 ms, respectively. Proton broadband decoupling with spinal-64 was applied during acquisition. Both the ^1H and ^{13}C spectra are referenced with respect to TMS (tetramethylsilane) using the secondary standard adamantane. Finally, the ^{27}Al (156.4 MHz) 1D experiments were acquired after a 3° flip angle of 0.5 μs with a spinning speed of 40 kHz (1.9 mm probe). The reference was set using a solution of $AlCl_3$ adjusted to pH of one with hydrochloric acid. The ^1H–^{27}Al 2D spectrum was acquired at a spinning rate of