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## PAPER

## CAU-3: A new family of porous MOFs with a novel Al-based brick: $[Al_2(OCH_3)_4(O_2C-X-CO_2)]$ (X = aryl)<sup>†</sup>

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A new family of Al-based MOFs denoted as CAU-3 (CAU = Christian-Albrechts-Universität) was discovered in the solvothermal system  $Al^{3+}/aryldicarboxylic acid/NaOH/methanol by applying high-throughput-methods. The three compounds reported in this article [Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>BDC], [Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>BDC-NH<sub>2</sub>] and[Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>NDC] (BDC = 1,4-benzenedicarboxylate; NDC = 2,6-naphtalenedicarboxylate) are all based on the same unprecedented inorganic building unit [Al<sub>12</sub>(OCH<sub>3</sub>)<sub>24</sub>]<sup>12+</sup>, which is a dodecameric cyclic aluminium-methanolate-cluster. The material CAU-3-NDC was found to exhibit the highest surface area as well as the highest micropore volume of all Al-based MOFs reported until now.$ 

### Introduction

During the past few years, the research on highly porous MOFs with tailored properties has become a main objective for scientists in the field of porous materials.<sup>1-5</sup> This relatively new class of materials is built up from inorganic vertices, most often metal ions or cationic metal-oxo-clusters, which are connected to each other using polytopic organic linker-molecules. These organic parts of the network usually consist of organic anions often bearing carboxylate- or phosphonate-groups. To create pores by separating the inorganic vertices from each another, the linker molecule is often based on a rigid aromatic unit like benzene or naphthalene. Once the reaction conditions for the formation of such a hybrid compound are known, similar reaction parameters should in principle allow the incorporation of further functionalized and also larger organic molecules into the structure, while keeping the inorganic brick unchanged. This approach towards the synthesis of new compounds is commonly referred to as isoreticular synthesis.<sup>6</sup> There are only few examples for the synthesis of isoreticular families of MOFs, consisting of more than two materials based on the same inorganic building unit.<sup>7-12</sup> An example is the MIL-88-series, which is based on dicarboxylate ions but contains trimeric  $M(III)_3-\mu_3O^{7+}$ -clusters, where M(III)stands for a Cr<sup>3+</sup> or Fe<sup>3+</sup>. These compounds exhibit enormous changes in their lattice parameters, depending not only upon the metal ion ( $Fe^{3+}$ ,  $Cr^{3+}$ ) and the dicarboxylate-molecule, but also

on the presence and the nature of guest molecules inside the pores.<sup>9</sup> Another example was reported for the  $Zr^{4+}$ -based MOFs called UiO-66, -67, and 68.<sup>10,11</sup> In this case,  $Zr_6O_4(OH)_4^{12+}$ -clusters are twelvefold connected by linear dicarboxylate ions to form a **fcu**-net, which corresponds to a fcc-packing of inorganic building blocks. Due to their outstanding chemical stability, the functionalized analogues of the UiO-66 (based on 1,4-benzene-dicarboxylate) have shown to be ideal candidates for further post-synthetic modification reactions.<sup>12</sup>

One reason for this limited number of examples is due to the complexity of solvothermal reactions. Small changes of the organic linker molecule have often a strong influence on the solubility as well as the acid-base and the coordination properties. Thus, the reaction conditions have to be established and optimized for each organic linker molecule separately. In this context, high-throughput-methods have proven to be a highly valuable tool for the intentional synthesis of MOFs.<sup>13,14</sup> Applying this methodology, we were recently able to synthesize the amino-functionalized Al-MIL-53,<sup>15</sup> a MOF with lozenge-shaped channels bearing NH2-groups which can be further chemically modified, and Cr-MIL-101-NDC,<sup>16</sup> which exhibits giant pores with a diameter of 4.6 nm. The miniaturization of the reaction vessels, the parallelization of the synthesis and the automated characterization open the opportunity to screen even complex reaction systems with large parameter-spaces. Therefore, chemical trends can be easily identified, and synthesis parameters can be rapidly optimized with a rather low consumption of starting materials.

Recently we have started a systematic high-throughput investigation on the role of the solvent in the synthesis of Al-based MOFs. In contrast to MOFs based on divalent cations, only few Al-based MOFs have been reported in the literature since mostly very small  $\mu$ m-sized crystals have been obtained, which complicates the structure determination. The frameworks of these known porous Al-MOF structures contain only six different

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<sup>†</sup> Electronic supplementary information (ESI) available: Crystallographic data, details of the Rietveld refinements and further XRPD data, selected bond lengths, TG curves. CCDC reference numbers 799242–799244 for CAU-3-NDC, CAU-3-BDC, and CAU-3-BDC-NH<sub>2</sub>, respectively. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12005d

Al–O bricks.<sup>17–23</sup> This rather limited number of structures is in sharp contrast to the diversity of polynuclear species that are known from the solvolysis reactions of aluminium salts.<sup>24,25</sup> For this reason, the field of Al<sup>3+</sup>-based MOFs still is a promising chemical system for the discovery of new materials. Due to the high thermal and chemical stability of the known Al-based MOFs, as well as to the cost-effective availability of the usually nontoxic starting materials, these yet unknown compounds could be of high interest for commercial applications.

Especially linear dicarboxylic acids have shown to be useful for the synthesis of isoreticular compounds, not only but also due to the commercial availability of a variety of dicarboxylic acids with different size and functionalization. In combination with one-dimensional chains of corner-sharing AlO<sub>6</sub>-octahedra, several porous compounds based on the MIL-53 structure are known, showing interesting sorption behaviour as well as high thermal stabilities.<sup>26–30</sup> Another example for a dicarboxylatebased Al-MOF is CAU-1, which contains twelvefold connected octanuclear Al-oxo-clusters.<sup>23,31</sup> Herein we report the synthesis and characterization of a new family of porous MOFs based on linear aryldicarboxylate ions, which contain the novel dodecameric Al-based brick [Al<sub>12</sub>(OCH<sub>3</sub>)<sub>24</sub>]<sup>12+</sup>.

#### **Experimental**

#### Materials and methods

**Chemicals.** AlCl<sub>3</sub>·6H<sub>2</sub>O (Riedel-de Haen,  $\geq$ 99%), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Merck,  $\geq$ 99%), H<sub>2</sub>BDC (Aldrich,  $\geq$ 98%), H<sub>2</sub>BDC-NH<sub>2</sub> (Fluka,  $\geq$ 98%), NaOH (Baker,  $\geq$ 97%), methanol (BASF, purum), and *N*,*N*-dimethyl-formamide (BASF, tech.) were used as purchased. 2,6-Naphthalenedicarboxylic acid was synthesized by hydrolysis of dimethyl 2,6-naphthalenedicarboxylate (Aldrich, 98%).

Methods. Most reactions were carried out using our 24-highthroughput reactor system.32 The upscaled synthesis was performed in custom made Teflon inserts in steel autoclaves with a volume of 30 mL. The high-throughput X-ray analyses were performed in transmission geometry using a STOE HT powder diffractometer equipped with a xy-stage and an image plate detector (IPDS) system (Cu-Kal radiation). Temperature dependent X-ray powder diffraction (XRPD) data was measured on a STOE Stadi-P diffractometer in transmission geometry equipped with an image plate detector (IPDS) using Cu-Ka1 radiation. High-precision X-ray powder diffraction data for the structure solution was collected on a STOE Stadi-P powder diffractometer equipped with a linear position sensitive detector (PSD) system (monochromated Cu-Kαl radiation) in transmission geometry. XRPD data for the structure refinement was recorded on a Panalytical X-pert Highscore diffractometer in reflection-geometry. MIR spectra were recorded on an ATI Matheson Genesis spectrometer in the spectral range of 4000–400 cm<sup>-1</sup> using the KBr disk method. FT-Raman spectra were recorded on a Bruker IFS 66 FRA 106 in the range of  $0-3300 \text{ cm}^{-1}$  using a Nd/YAG-Laser (1064 nm). The thermogravimetric analyses were recorded using an NETZSCH STA 409 CD analyzer. The samples were heated in Al<sub>2</sub>O<sub>3</sub> crucibles at a rate of 4 K min<sup>-1</sup> under a flow of air (25 ml min<sup>-1</sup>). The TG data were corrected for buoyancy and current effects. The molecular modelling software used was Materials Studio 5.0.<sup>33</sup> Sorption experiments were performed using a BEL JAPAN INC. Belsorp<sub>max</sub>.

#### Synthesis and high-throughput-investigations

Discovery and synthesis optimisation of CAU-3-BDC, [Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>BDC]. The compound CAU-3-BDC (1) was discovered in a high throughput-experiment using AlCl<sub>3</sub>·6H<sub>2</sub>O, terephthalic acid (H<sub>2</sub>BDC), methanol and 2  $\mbox{M}$  methanolic NaOH as starting materials. After the reaction at 125 °C for 5 h, the tendencies in the product formation shown in Fig. 1 could be observed. Exact amounts of starting materials can be found in Table S5.† The molar ratio Al<sup>3+</sup>:H<sub>2</sub>BDC was kept constant at 4, the absolute amount of starting material was increased from row to row and from column to column, the amount of base was raised.

The compound was obtained from a highly diluted basic solution. Under more acidic and more concentrated conditions the well known compounds CAU-1 and MIL-53 are formed. Furthermore an unknown product of very low crystallinity was observed. Although the material obtained under these conditions already exhibited a remarkable porosity (apparent specific surface area of  $A_{BET} \sim 1200 \text{ m}^2 \text{ g}^{-1}$ ), the crystallinity of the sample was rather low. A detailed high-throughput-investigation (~200 reactions) led to an improved synthesis procedure for CAU-3-BDC and the crystallinity was improved substantially. Therefore, the Al<sup>3+</sup>-source was varied (nitrate, chloride and perchlorate), as well as the molar ratios and the absolute amounts of starting materials. We also investigated the influence of H<sub>2</sub>O on the product formation. While the use of  $Al(ClO_4)_3$ .9H<sub>2</sub>O or the addition of small amounts of water led to the formation of X-ray amorphous products or Al<sub>2</sub>O<sub>3</sub>, we observed highest crystallinity only for very small concentrations of H<sub>2</sub>BDC and large excess of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and NaOH. To achieve an optimum of crystallinity we also varied the heating program. The progress during this synthesis optimization is visualized in Fig. 2.

The optimized synthesis procedure of **1** in the 24 reactor system is as follows: a mixture of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (45.2 mg, 0.120 mmol), terephthalic acid (H<sub>2</sub>BDC; 2.5 mg, 0.015 mmol) and a solution of NaOH in methanol (2 M, 60  $\mu$ L, 0.120 mmol) was suspended in methanol (1.340 mL). The reactor was heated up to 125 °C in 12 h. The temperature was held for 5 h and the reactor was allowed to cool down to room temperature in 4 h.



**Fig. 1** Results of the high-throughput investigation for the discovery of CAU-3-BDC.



Fig. 2 Improvement of the crystallinity of the products during the HT-assisted synthesis optimization.

Scale-up of the reaction was performed in a 30 mL custommade autoclave with Teflon insert. For this synthesis, the reaction parameters were stepwise adjusted to the larger reactor.

Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (540 mg, 1.44 mmol), H<sub>2</sub>BDC (40 mg, 0.240 mmol) and a solution of NaOH in methanol (2 M, 720  $\mu$ L, 1.44 mmol) were suspended in methanol (16.0 mL). The reactor was heated up to 125 °C in 12 h. The temperature was held for 3 h and the reactor was allowed to cool down to room temperature in 1 h.

After the filtration, a white microcrystalline powder was Thermogravimetric analysis and TEM-images obtained. revealed, that a large amount of an X-ray amorphous byproduct was formed. To remove this byproduct, 100 mg of the reaction product were treated with 10 mL of DMF in a microwave oven (Biotage Initiator) at 150 °C for 1 h under stirring. To remove the DMF, the filtrated solid was treated with 10 mL methanol and heated up in the microwave oven to 100 °C for 1 h. The product was dried at room temperature in air, and further activated under vacuum for the sorption experiments (160 °C/12 h/0.1 mbar). Since the crystallinity slightly decreases during this process (Fig. S1), the structure solution and refinement were performed using the XRPD measurements of the "as synthesized" compound. All other analytical data was measured for the activated product stored under ambient conditions prior to the measurements.

Elemental analysis on an activated sample: found: C: 35.43%, H: 4.07%. Calculated values, based on the deduced formula  $[Al_2(OCH_3)_4(O_2CC_6H_4CO_2)]$ · $3.6H_2O$ : C: 35.4%, H: 5.7%.

Discovery and synthesis optimisation of CAU-3-BDC-NH<sub>2</sub>, [Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>BDC-NH<sub>2</sub>]. Starting from the optimized reaction conditions for 1, the synthesis of the amino-functionalized analogue CAU-3-BDC-NH<sub>2</sub> (2) was attempted. Surprisingly, the reaction conditions are very similar. For the optimized synthesis of 2 in the multiclave, a mixture of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (52 mg, 0.139 mmol), 2-aminoterephthalic acid (H<sub>2</sub>BDC-NH<sub>2</sub>, 2.5 mg, 0.014 mmol) and a 2 M solution of NaOH in methanol (69 µL, 0.138 mmol) were suspended in methanol (1.330 mL). The reactor was heated up to 125 °C in 8 h. The temperature was held for 6 h and the reactor was allowed to cool down to room temperature in 1 h. For the up-scaling of the reaction we used again our 30 mL custom-made autoclave with a Teflon insert. For this synthesis, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (540 mg, 1.44 mmol), H<sub>2</sub>BDC-NH<sub>2</sub> (40 mg, 0.220 mmol) and a solution of NaOH in methanol (2 M, 720  $\mu$ L, 1.44 mmol) were suspended in methanol (16.0 mL). The reactor was heated up to 125 °C in 12 h. The temperature was held for 3 h and the reactor was allowed to cool down to room temperature in 1 h.

After the filtration, a yellow microcrystalline product was obtained. Thermogravimetric measurements revealed the presence of an X-ray amorphous byproduct, which was removed by applying the same procedure as for CAU-3-BDC. The crystallinity of CAU-3-BDC-NH2 decreased slightly during this treatment (Fig. S2<sup>†</sup>). Therefore, XRPD data of the as-synthesized product was used for the structure refinement while all other analytical data was measured for the activated material. Elemental analysis on an activated sample (160 °C/12 h/0.1 mbar) stored under ambient conditions: found: C: 31.02%, H: 3.81%, N: 1.96%; These values differ from the assumed formula [Al<sub>2</sub> (OCH<sub>3</sub>)<sub>4</sub>(O<sub>2</sub>C-C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>-CO<sub>2</sub>)]·3.6H<sub>2</sub>O which are calculated to be: C: 34.1%, H: 5.7%, N: 3.3%. After dissolution in D<sub>2</sub>O/NaOD we observed in the NMR-spectrum, that CAU-3-NH<sub>2</sub> not only contains aminoterephthalate ions, but also terephthalate anions and N-methylated aminoterephthalate ions. We attribute the discrepancy between the experimental values and the ideal formula to this in situ conversion of the linker and to small amounts of X-ray amorphous Al-species (see also TG-measurement). Further investigations of this phenomenon are in progress.

Discovery and synthesis optimisation of CAU-3-NDC, [Al<sub>2</sub>(OCH<sub>3</sub>)<sub>4</sub>NDC]. The synthesis of CAU-3-NDC (3) needed much more effort, since it is highly sensitive to every single parameter during the synthesis, and every small change leads to the formation of crystalline byproducts, whose structures and compositions are a subject of current research. Without the use of high-throughput-methods, optimization of the synthesis conditions (~800 reactions) would have been hardly possible. Due to the large number of reactions that were performed, a detailed description of the HT-investigations is not given. The varied parameters comprise the Al<sup>3+</sup>-source (nitrate, chloride and perchlorate) and the molar ratios and absolute amounts of starting materials. Due to the sensitivity of the reaction towards the thermal process, the chemical composition of the starting mixture had to be screened using different heating programs. This finally led to the optimized synthesis of 3 in the 24 reactor system, which is as follows: a mixture of AlCl<sub>3</sub>·6H<sub>2</sub>O (29.3 mg, 0.12 mmol), 2,6-naphtalenedicarboxylic acid (H<sub>2</sub>NDC; 7.5 mg, 0.03 mmol) and a 2 M solution of NaOH (52 µL, 0.1 mmol) in methanol was suspended in methanol (448 µL) and heated to 130 °C in 1 h. The temperature was kept for 4 h and the reactor was allowed to cool down in 1 h. The white, as-synthesized product contains traces of sodium chloride (see also structure refinement) and X-ray amorphous byproducts like residual linker molecules in the pores. EDX measurements showed molar ratios of Al: Cl ranging from 2.5 to 3. IR-spectroscopy proved the presence of residual naphthalene dicarboxylic acid. Elemental analysis on a thermally activated sample (160 °C/12 h/0.1 mbar) stored under ambient conditions prior to the measurement:

found: C: 47.97%, H: 3.81%. Calculated values, based on the ideal formula  $[Al_2(OCH_3)_4(O_2CC_{10}H_6CO_2)]$ : C: 48.9%, H: 4.6%. Although these values are in quite good agreement, the described material still contains the mentioned byproducts.

All measurements were performed with the as-synthesized microcrystalline product. The only activation step for the sorption measurements was heating under vacuum, which hardly influences the crystallinity (Fig. S3†). Several attempts were made, to perform a scale-up of the synthesis and to further activate the as-synthesized compound. The products of the synthesis in larger reactors exhibit a much lower specific surface area, although, based on the XRPD measurements, no differences were observed. Further activation steps were attempted in several solvents, but the raw material decomposes in water, DMF and even ethanol. The solvent treatment in methanol led only to a reduction of the amount of chloride ions.

The absolute amounts synthesized are in all three cases quite low. In the case of CAU-3-BDC and CAU-3-BDC-NH<sub>2</sub>, we usually obtain ~25 mg of fully activated sample from one upscaled reaction. One reason is the low overall concentration of the linker molecule that is necessary to obtain the title compounds. The other reason is the elaborate activation procedure to remove the X-ray amorphous byproducts. In the case of CAU-3-NDC, around 8 mg are obtained from one HT-reaction.

#### Structure determination and refinement

The experimental XRPD pattern of CAU-3-BDC was successfully indexed with Topas Academics<sup>34</sup> as a hexagonal crystal system with the lattice parameters a = 21.0480(4) Å and c =34.8305(7) Å with a goodness of fit of 23. Based on the extinction conditions, the rhombohedral space group  $R\bar{3}m$  was suggested by the program. The structure solution was carried out successfully with the Expo2004<sup>35</sup> software package using Direct Methods. Starting from the space group  $R\bar{3}m$ , the positions of the aluminum based brick were determined. By recycling these fragments in a new intensity extraction, in addition parts of the BDC<sup>2-</sup> ion were localized. This starting model was completed by force field calculations with the software package Forcite implemented in Materials Studio 5.0.33 For the calculations, the universal force field was used without an optimization of the cell parameters. The completed model was refined with Rietveld techniques using Topas Academics.<sup>34</sup> The final Rietveld refinement involved 15 background parameters, 15 atomic parameters, 4 temperature factors, 1 scale factor and 2 cell parameters. The peak shape was modeled using a pearson VII function and anisotropic peak broadening effects were taken into account using a spherical harmonics series. The C-C distances and the C-O distances of the methoxy groups were restrained. The final Rietveld plot shown in Fig. 3 led to satisfying structural model indicators  $(R_{\text{Bragg}} = 0.4\%, R_{\text{wp}} = 4.76\% \text{ and GoF} = 1.64)$ . Selected bond lengths and the asymmetric unit can be found in the supporting informations in Fig. S4 and Table S1,† respectively.

The structural model of CAU-3-BDC was used for the Rietveld refinement of CAU-3-BDC-NH<sub>2</sub>. The difference Fourier calculations showed electron densities at a distance of 1.5 Å from the lateral carbon atoms of the phenyl ring. Assigning these electron densities to a nitrogen atom with a site occupation of 0.25 led to a significant lowering of the *R*-values  $R_{\text{bragg}}$  and  $R_{\text{wp}}$  by 1 and 0.5%. The results of the final Rietveld refinement are shown in Fig. S5.† The C–C distances, C–O distances of the methoxy groups as well as the C–N distances were restrained and an overall temperature factor was used. The refinement led to good structure indicators of  $R_{\text{Bragg}} = 0.59\%$ ,  $R_{\text{wp}} = 4.17\%$  and GoF = 1.71. Selected bond lengths are given in Table S2.†

The indexing and lattice parameter refinement of the experimental powder pattern of 3 was carried out with the Stoe WinxPow software package.<sup>36</sup> The hexagonal cell parameters a= 23.1533(5) Å and c = 40.4120(9) Å were obtained. For the construction of a model of CAU-3-NDC, we started from the structure of CAU-3-BDC. The space group was converted to P1 and the terephthalate ions were replaced by naphthalene dicarboxylate ions after adjusting the cell parameters to the ones obtained from the indexing process, using Materials Studio 5.0. The model was submitted to a full energy minimization without an optimization of the unit cell constants with the universal force field (UFF) implemented in the software. For this simulation, the aluminum atoms were replaced by iron due to their very similar ionic radii (0.67 vs. 0.69) and the missing parameters for octahedrally coordinated aluminum in the parameter set. Van der Waals interactions were represented by a classical 12-6 Lennard Jones potential. The convergence criteria were set to  $1.0 \times 10^{-4}$ kcal mol<sup>-1</sup> and 0.005 kcal mol<sup>-1</sup> Å<sup>-1</sup> and  $5.0 \times 10^{-5}$  Å (displacement) respectively. The obtained structural model possesses lower symmetry than the parent-structure CAU-3-BDC and exhibits the space group  $R\bar{3}$ , due to the break of the symmetry caused by the naphthalene dicarboxylate ions (atomic coordinates and a simulated powder pattern of this model can be found in Table S3 and Fig. S6<sup>†</sup>). This structural model was used to carry out the Rietveld refinement. Due to the lower crystallinity and the two-fold number of atomic parameters caused by the lower symmetry, the atomic positions of the  $NDC^{2-}$  ions were restrained and an overall temperature factor was used. The final refinement leads to satisfying structure indicators ( $R_{\text{Bragg}}$  = 4.47%,  $R_{wp} = 9.41\%$  and GoF = 4.80). The final Rietveld plot is shown in Figure S7<sup>†</sup> and selected bond lengths are given in Table S4.<sup>†</sup> Two reflections at 32.62° and 45.42° are observed which are due to NaCl as an impurity. The final parameters of all three refinements are summarized in Table 1.



**Fig. 3** Final Rietveld-plot for **1**. Measured intensities are in black, calculated intensities are in red, the difference plot is blue. The vertical bars mark the Bragg-positions.

Table 1 Final parameters obtained from the Rietveld-refinements

	CAU-3-BDC	CAU-3- BDC-NH <sub>2</sub>	CAU-3-NDC
Empirical formula M g mol <sup>-1</sup> Crystal system Space group a/pm c/pm $V/10^6$ pm <sup>3</sup> Z $R_{wp}/\%$ $R_{Bragg}/\%$ GoF weighted Durbin- Watson statistic	$\begin{array}{c} Al_2O_8C_{12}H_{16}\\ 342.21\\ Rhombohedral\\ R\bar{3}m\\ 2110.51(5)\\ 3488.8(1)\\ 13458.1(8)\\ 18\\ 4.76\\ 0.4\\ 1.64\\ 0.594 \end{array}$	Al <sub>2</sub> O <sub>8</sub> C <sub>12</sub> N <sub>1</sub> H <sub>17</sub> 357.23 Rhombohedral <i>R</i> 3 <i>m</i> 2093.5(1) 3481.3(2) 13214(1) 18 4.17 0.59 1.71 0.312	$\begin{array}{c} Al_2O_8C_{16}H_{18}\\ 368.25\\ Rhombohedral\\ R\bar{3}\\ 2320.56(2)\\ 4063.51(4)\\ 18950.(3)\\ 18\\ 9.41\\ 4.47\\ 4.8\\ 0.120\\ \end{array}$



**Fig. 4** Dodecameric building unit and its connectivity mode in the framework of CAU-3-BDC. Methyl-groups are omitted for clarity.

### **Results and discussion**

#### Structural description

The structure of CAU-3-BDC is based on dodecameric  $[Al_{12}(OCH_3)_{24}]^{12+}$  cations, to which twelve carboxylate moieties are coordinated, each one bridging two Al-ions (Fig. 4).

Thus, the inorganic units are composed of twelve edgesharing AlO<sub>6</sub>-polyhedra. The edge-sharing oxygen atoms are part of methanolate ions, while the other oxygen-atoms result from the coordination of the bridging carboxylate-groups. Similar dodecameric clusters have been only observed twice in molecular complexes containing the transition metals  $Fe^{3+}$  and  $Mn^{3+}/Cr^{3+}$  ions.<sup>37,38</sup> To the best of our knowledge this is the first time, that this cluster has been observed in Al chemistry as well as in the chemistry of MOFs. Recently, the  $Mn^{3+}/Cr^{3+}$  building block was proposed as a possible brick for the formation of new metal–organic frameworks.<sup>39</sup> Besides the octanuclear cyclic cluster incorporated in the framework of CAU-1,<sup>23</sup> this building unit is the second example of an wheel-shaped aluminium carboxylate, whose occurrence is again strictly limited to the incorporation into a metal–organic framework.



**Fig. 5** Schematic representation of a part of the distorted **fcu**-net. The white bonds represent the connectivity in the *xy*-plane of the inorganic brick, the black ones the connectivity along the *z*-axis.



Fig. 6 The two different types of cavities in the **fcu**-framework. Different colours emphasize the ABC stacking of the of the Al-based bricks  $[Al_{12}(OCH_3)_{24}]^{12+}$ .

The twelvefold connectivity by dicarboxylate units leads to the formation of a **fcu**-net (Fig. 5).

This high connectivity is remarkable, since only few examples of such MOFs have been reported. Besides the well known UiO-66,<sup>10</sup> for example the frameworks of CAU-1<sup>23</sup> and its Ti-analogue MIL-125<sup>40</sup> exhibit this connectivity mode. While the latter two MOFs show a distorted pseudo-bcc packing of clusters, the assembly in CAU-3 leads to a fcc-packing like in UiO-66. Due to the anisotropic shape of the cluster a strongly distorted packing is observed (Fig. S7<sup>†</sup>).

Accordingly, the  $[Al_{12}(OCH_3)_{24}]^{12+}$  clusters are connected sixfold in their *xy*-plane and sixfold alternating in both directions along the *z*-axis of the cyclic cluster. The resulting network contains tetrahedral and octahedral cavities which are strongly distorted due to the anisotropic shape of the Al-containing brick (Fig. 6).

Assuming a spherical shape, the diameters of the tetrahedral and octahedral cavities are approximately 10 and 11 Å (calculated based on van-der-Waals radii), respectively. In reality larger molecules could be accommodated and based on the estimated available free space, the incorporation of rod-shaped guests with maximum length of 27 Å should be possible. The triangular apertures of these cavities differ only slightly in size and should be accessible for molecules up to a diameter of 7 Å. The dimensionality and shape of the pores differ only slightly for compound **2**, since the amino-group is statistically distributed over the four possible positions of the aromatic ring. The larger linker molecule in **3** leads to an extended, non-interpenetrating framework containing distorted tetrahedral and octahedral cavities of ~14 Å and ~15 Å in diameter, assuming a spherical guest. Based on the structure, rod-shaped guests with maximum length of 38 Å should fit into the octahedral cavities.

#### Spectroscopic and thermal properties

The vibrational spectra (Fig. 7) of the three title compounds are very similar. The characteristic bands for the carboxylate vibrations around 1580 cm<sup>-1</sup> and 1420 cm<sup>-1</sup> clearly show the presence of the dicarboxylate ions coordinating to the  $AI^{3+}$ -ions. The aliphatic C–H vibrations at 2950 cm<sup>-1</sup> and 2840 cm<sup>-1</sup> are due to the bridging methanolate ions in the Al-based brick. In the case of as synthesized CAU-3-NDC, the absorption band around 1700 cm<sup>-1</sup> is attributed to residual naphthalene dicarboxylic acid molecules occluded in the pores.

The band at 1250 cm<sup>-1</sup> (C–N-vibration) in the spectrum of CAU-3-BDC-NH<sub>2</sub> proves the incorporation of aminoterephtalic acid, although the characteristic NH<sub>2</sub>-bands around 3450 cm<sup>-1</sup> are not observed, probably due to the presence of hydrogenbonded water inside the pores. In the Raman-spectra, especially the aromatic C–C-vibrations between 1640 cm<sup>-1</sup> and 1380 cm<sup>-1</sup> are well resolved.

The thermal stability of all three MOFs was investigated in air atmosphere up to at least 800  $^\circ$ C with a heating rate of 4 K



Fig. 7 IR- (top) and Raman-spectra (bottom) of the different CAU-3 MOFs.

min<sup>-1</sup> (Fig. S9, S10 and S11<sup>†</sup>). For **1**, the first weight loss of -16.5% corresponds to the removal of incorporated solvent molecules. At higher temperatures (~200 °C), the decomposition of the frameworks and thus the structural collapse proceeds in two steps (calc.: 58.7%, obs.: 60.9%). The product formed in the end is weakly crystalline Al<sub>2</sub>O<sub>3</sub>. In the case of CAU-3-BDC, we were also able to prove the structural rigidity of the framework during the activation process. Temperature-dependent XRPD data (Fig. 8) demonstrates, that no uncommon cell parameter shifts can be observed.

While the chemical decomposition of **1** shows a stepwise mechanism in the TG curve, the structure of the framework collapses directly during the second weight loss. The increased stability during the TDXRPD experiment compared to the TG-data is attributed to the different experimental set ups.

The decomposition of CAU-3-BDC-NH<sub>2</sub> (2) is similar to that of 1. Like for CAU-3-BDC, the decomposition starts after the removal of adsorbed solvent (10.3%) at a temperature of ~180 °C. The two last weight losses correspond quite well to the decomposition of 2 (calc.: 66.4%, obs.: 62.4%), although the difference could be attributed to a small amount of X-ray-amorphous Al-oxo-species.

The decomposition of **3** during the TG-experiment shows a similar stability ( $\sim$ 180 °C), but due to the observed byproducts, we did not attribute the weight losses to defined steps of decomposition.

#### Sorption properties

For the sorption measurements, the samples were activated in vacuum  $(10^{-2} \text{ mbar})$  at 160 °C for 12 h. The XRPD patterns of the samples after the sorption experiments can be found in the supporting information (Fig. S1–S3). The nitrogen isotherms (Fig. 9) were measured at 77 K. The BET-method was applied to calculate the apparent surface area and the micropore volumes were calculated from the amount adsorbed at  $p/p_0 = 0.5$ .

The sorption experiments confirm the tendencies that we expected. The incorporation of the amino-group leads to a decrease of micropore volume as well as apparent surface area,



Fig. 8 Temperature-dependent XRPD patterns of CAU-3-BDC (1), measured under air.





Fig. 9 N<sub>2</sub>-Sorption isotherms for 1, 2 and 3 measured at 77 K.

Table 2 Apparent specific surface areas and  $V_{\rm mic}$  values of the CAU-3-MOFs

Compound	$A_{\rm BET} \mathrm{m}^2 \mathrm{g}^{-1}$	$A_{\rm Langmuir} {\rm m}^2 {\rm g}^{-1}$	$V_{\rm mic}~{ m cm}^3~{ m g}^{-1}$
CAU-3-BDC	1550	1920	0.64
CAU-3-BDC-NH <sub>2</sub>	1250	1520	0.53
CAU-3-NDC	2320	2750	0.95

while the enlargement of the linker molecule results in a drastically increased uptake. The BET-surfaces as well as the micropore volumes are summarized in Table 2.

The apparent specific surface areas and the micropore volume measured for CAU-3-NDC **3** are to the best of our knowledge the highest reported so far for any literature known Al-MOF. Changing the adsorbate from  $N_2$  to  $H_2O$ , the influence of the functional group is clearly visible (Fig. 10). The use of  $H_2O$  vapour leads to strong hysteresis. The absolute amount of adsorbed water is similar for both CAU-3-BDC and CAU-3-BDC-NH<sub>2</sub>, but due to the presence of the polar amino group, the adsorbed amount of water vapour at lower partial pressures is higher in CAU-3-NH<sub>2</sub>.

Although this is a purely qualitative sorption study, the influence of the amino group with its ability for hydrogen bonding is obvious.

### Conclusion

Summarizing our results, we have synthesized three new Alcontaining MOFs by applying our high-throughput-methods and characterized them in detail. This new family of MOFs contains an unprecedented brick,  $[Al_{12}(OCH_3)_{24}]^{12+}$ , which is twelvefold connected by dicarboxylate molecules to form a **fcu**-net. This inorganic unit is the second example for the occurrence of a wheel-shaped aluminium cluster in a metal–organic framework. All three compounds of the CAU-3-family are highly porous and exhibit BET-surface areas larger than 1200 m<sup>2</sup> g<sup>-1</sup> and micropore volumes higher than 0.5 cm<sup>3</sup> g<sup>-1</sup>. They are thermally stable up to at least 180 °C in air. The sorption properties are altered upon incorporation of a functional group or a larger linker molecule, respectively.



Fig. 10 Water vapour isotherms for 1 and 2 measured at 25 °C. Blue triangles for the  $NH_2$ -functionalized compound 2, red squares for 1. Empty symbols represent the desorption-, filled symbols represent the adsorption-branch.

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