Supporting Information

Controlled modification of the inorganic and organic brick in an Al-based MOF by direct and post-synthetic synthesis routes

Tim Ahnfeldt,[a] Daniel Gunzelmann,[b] Julia Wack,[b] Jürgen Senker[b,*] and Norbert Stock[a,*]

[a]Insitut für Anorganische Chemie, Christian-Albrechts-Universität, Max-Eyth Straße 2,
24118 Kiel, Germany
[b]Anorganische Chemie III, Universität Bayreuth, Universitätsstraße 30,
95447 Bayreuth, Germany

1. Proton-proton homonuclear spin diffusion spectra of CAU-1-NHCH$_3$, and CAU-1-NH$_2$

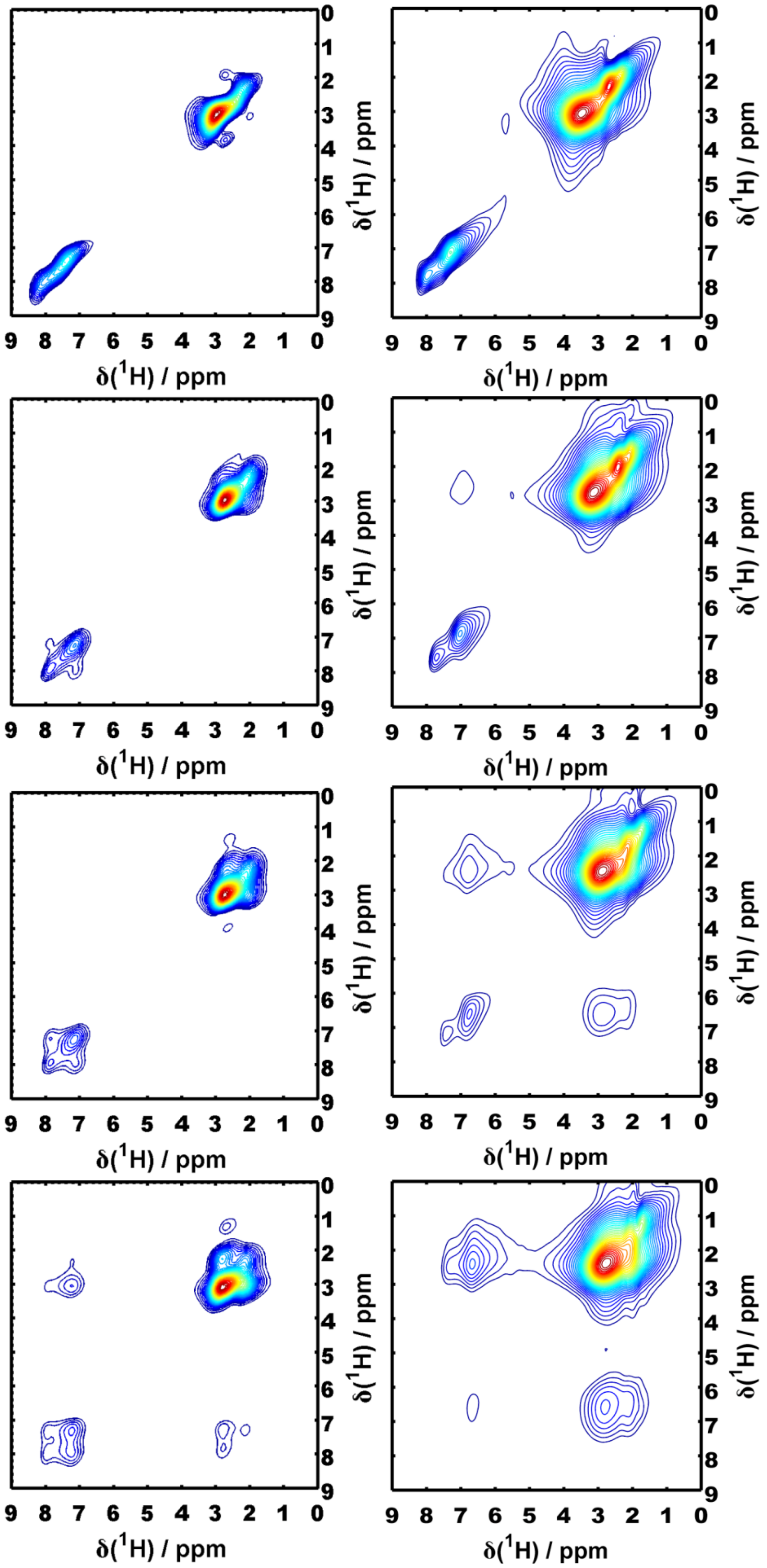


Fig. S1 Proton-Proton Spin-Diffusion Spectra of CAU-1-NHCH$_3$ (left), and CAU-1-NH$_2$ (right) at Spin Diffusion mixing times of 1 μs (top), 700 μs, 1500 μs and 4000 μs (from top to bottom).

2. Carbon-proton HETCOR spectra of CAU-1-NHCH$_3$ and CAU-1-NHCOCH$_3$

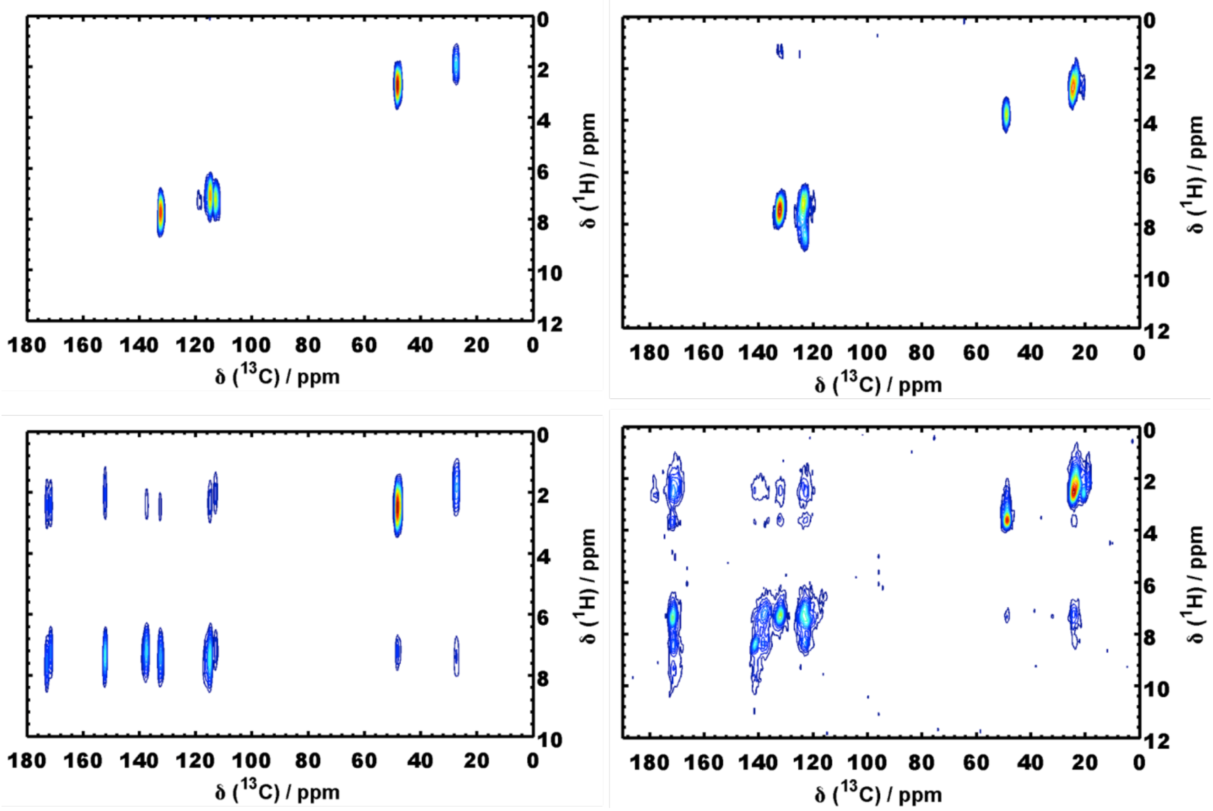


Fig. S2 Carbon-proton HETCOR spectra of CAU-1-NHCH$_3$ (left) and CAU-1-NHCOCH$_3$ (right) at contact times of 75 μs (top) and 1000 μs (bottom) showing short and long distance correlations, respectively.

3. Reaction times to reach full crystallisation ($\alpha = 1$) determined from the EDXRD studies for MW-assisted reactions

CAU-1 was synthesized by MW-assisted heating in the temperature range 115 - 145 °C. The reaction time for each temperature was determined from EDXRD studies on the product formation of CAU-1-NH_2 and corresponds to the time required to reach full crystallisation, i.e. extent of crystallisation, $\alpha = 1$ (Table S1).[1]

Tab. S1 Reaction times to reach full crystallisation ($\alpha = 1$) determined from the EDXRD studies for MW-reactions carried out in the temperature range between 115-145 °C. Values taken form reference [1].

reaction temperature / °C	reaction time / min
115	105
120	65-70
125	42
130	25
135	16
140	10
145	7-9

4. X-ray powder diffraction (XRPD) patterns of CAU-1 obtained by MW-assisted heating at different temperatures

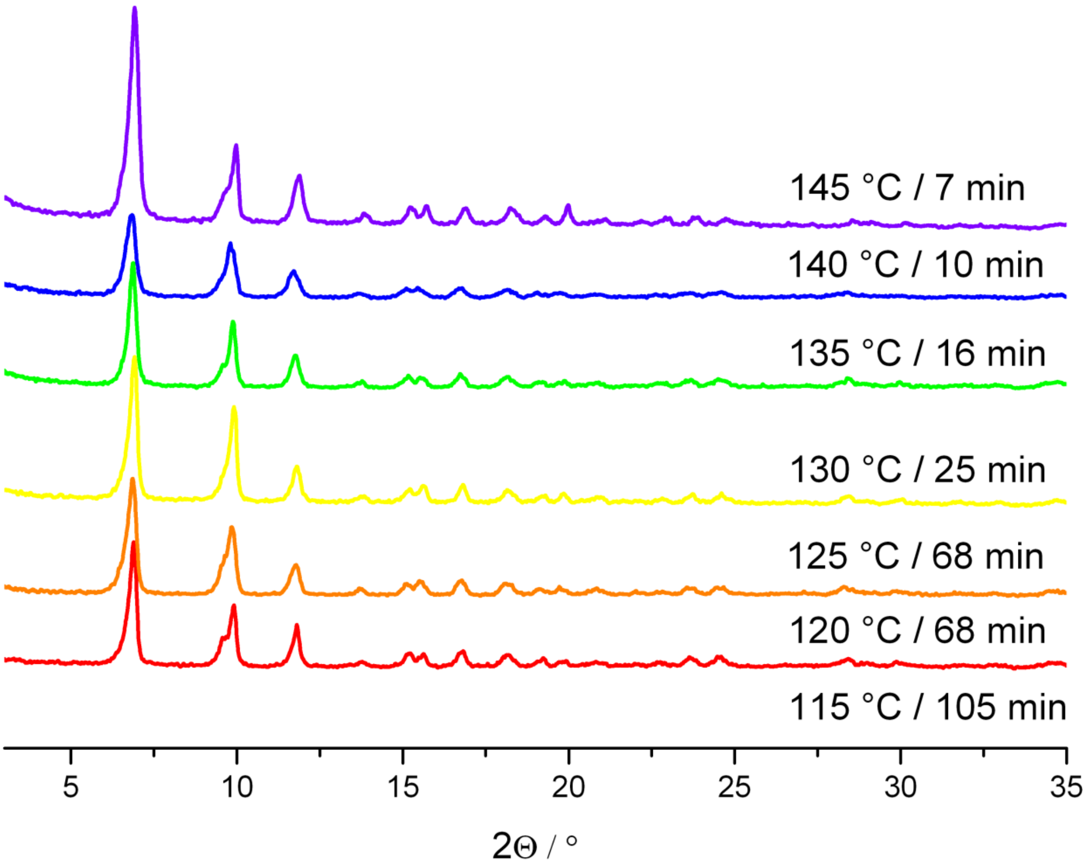


Fig. S3 X-ray powder diffraction (XRPD) patterns for CAU-1 obtained by MW-assisted heating carried out in the temperature range between 115 °C – 145 °C.

5. Time dependence of the methylation of the MW-assisted synthesis at 145 °C

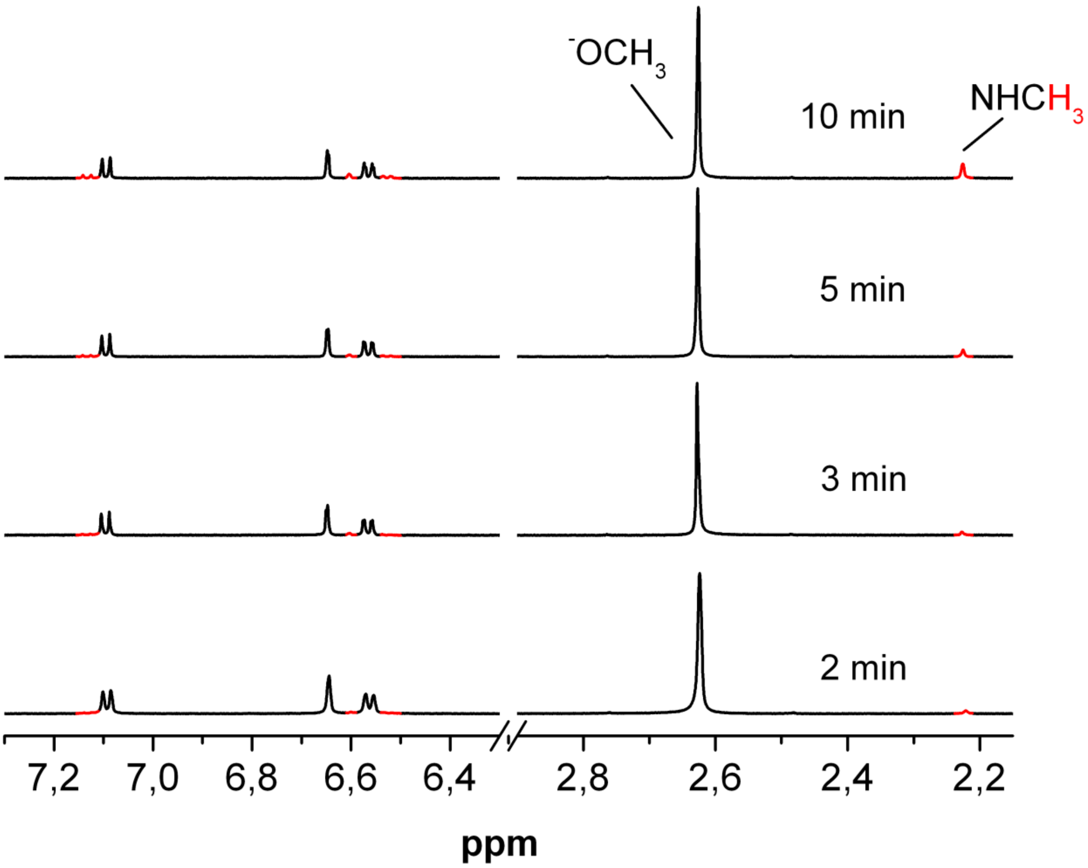


Fig. S4 ^{1}H NMR spectra of the dissolved CAU-1 samples collected from MW-assisted syntheses at 145 °C using reaction times between 2 and 15 min. Each spectrum is normalized to the sum of the aromatic H signals (methylated and non-methylated). Signals due to methylated CAU-1 are highlighted red.

6. Accuracy of ^{1}H NMR spectra and reproducibility of the MW-assisted synthesis of CAU-1-NH_2

In three repeated reactions under identical condition (3min a-c) all directly dissolved products exhibit the identical degree of methylation in the ^{1}H NMR spectra, which clearly shows the good reproducibility of the synthesis and the measurements.

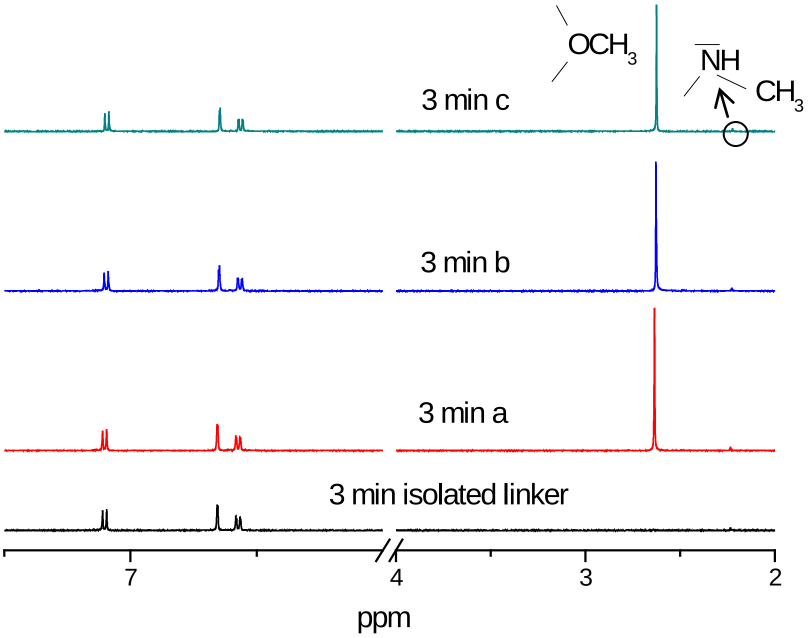
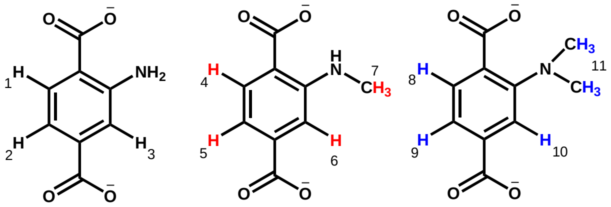


Fig. S5 ^{1}H NMR spectra of the isolated aminoterephthalic acid linker (black) and directly dissolved CAU-1 (red, blue and green) prepared by MW-assisted synthesis at 145 °C using a reaction time of 3 min. Each spectrum is normalized to the sum of aromatic H signals (methylated and unmethylated).

The integral ratios methoxy H-atoms : aromatic H-atoms of the products (3 min a-c) are between 1.14 and 1.21 (1.33 calc.). Thus, approximately 88% of the methoxy groups are incorporated in the framework after this reaction time according to the formula sum. We presume that syntheses at very short reaction times may lead to CAU-1-NH_2 for which a small fraction (12%) of the methoxy groups is replaced by OH-groups. Nevertheless, the product is still very crystalline and exhibits high thermal and chemical stability, such as CAU-1-CH_3 and CAU-1-$CHCOCH_3$.

7. Labelling of the set of ^{1}H signals of the reaction product carrying out under conventional heating method using a glass reactor



Scheme S1 Labelling of the ^{1}H signals in dimethylated, methylated and non-methylated CAU-1. ^{1}H NMR 500 MHz, (NaOD/D_2O) δ: **BDC-NH$_2^{2-}$:** 7.23 (d, 1H, H_1 $^3J_{H\text{-}H}$ = 8.2Hz); 6.79 (s, 1H, H_3); 6.71 (d, 1H, H_2 $^3J_{H\text{-}H}$ = 8.1Hz); **BDC-NHCH$_3^{2-}$:** 7.27 (d, 1H, H_5 $^3J_{H\text{-}H}$ = 8.0Hz); 6.76 (s, 1H, H_6); 6.52 (d, 1H, H_5 $^3J_{H\text{-}H}$ = 8.0Hz); 2.37 (s,3H,H_7); **BDC-N(CH$_3$)$_2^{2-}$:** 7.04 (s, 1H, H_{10}); 6.94 (d, 1H, H_9 $^3J_{H\text{-}H}$ = 8.0Hz); 6.87 (d, 1H, H_8 $^3J_{H\text{-}H}$ = 7.9Hz); 2.28 (s, 6H, H_{11})

8. TG-curve of CAU-1-NH_2

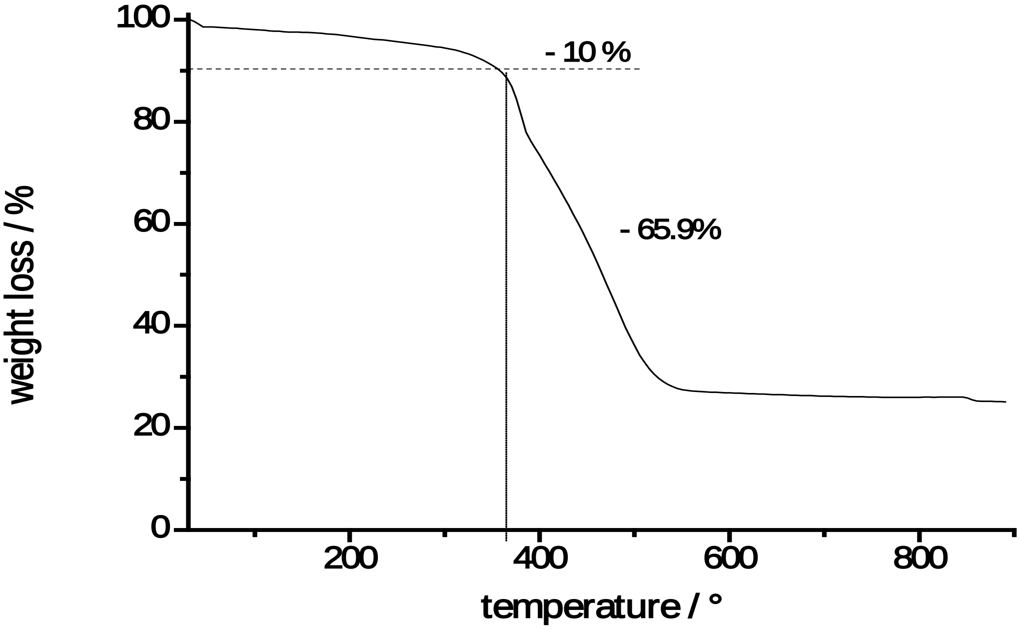


Fig. S6 TG-curve of CAU-1-NH_2 synthesized via MW-heating (3min / 145°C). The sample was measured in air with a heating rate of 4K / min and was degassed (30 min / 130 °C) before the measurement.

9. Activation process screened by ^{1}H NMR

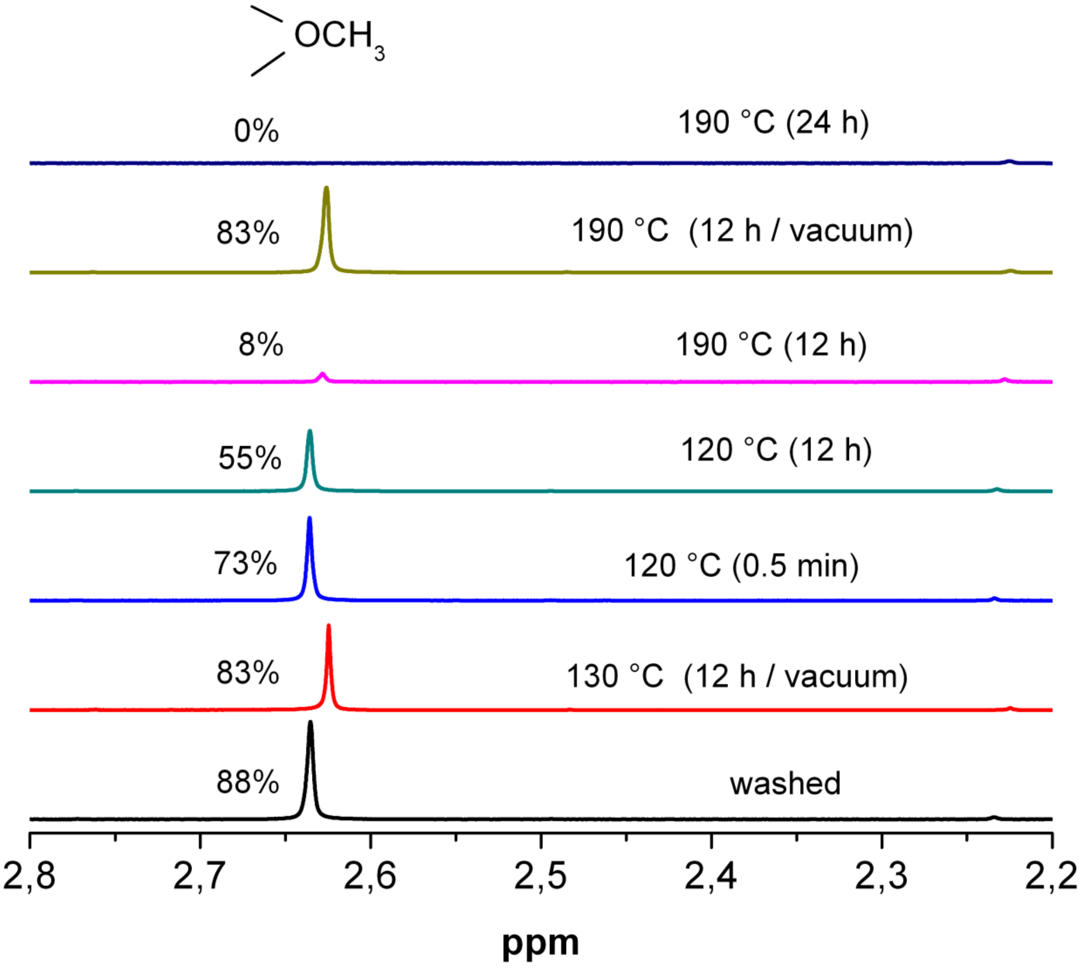


Fig. S7 ^{1}H NMR spectra of differently activated CAU-1-NH_2 compounds prepared by MW-synthesis. After the washing process the compounds were treated using different activation procedures. Each spectrum is normalized to the sum of aromatic H signals (methylated and non-methylated, not shown).

10. Temperature-dependent X-ray powder diffraction measurements (TD-XRPD)

The TD-XRPD measurements of CAU-1-NH_2(OH), CAU-1-$NHCH_3$ and CAU-1-$NHCOCH_3$ are shown in Figure S8-S10. The data were obtained under air with a STOE STADI P diffractometer equipped with an image plate detector and a STOE capillary furnace (version 0.65.1) using monochromated Cu-$K_{\alpha 1}$ radiation. Each powder pattern was recorded in the 4-35° range (2θ) at intervals of 10 °C up to 350 °C, and interval of 25 °C from 350-400 °C with duration of 15 min per scan. The temperature ramp between two patterns was set to 2 °C min^{-1}.

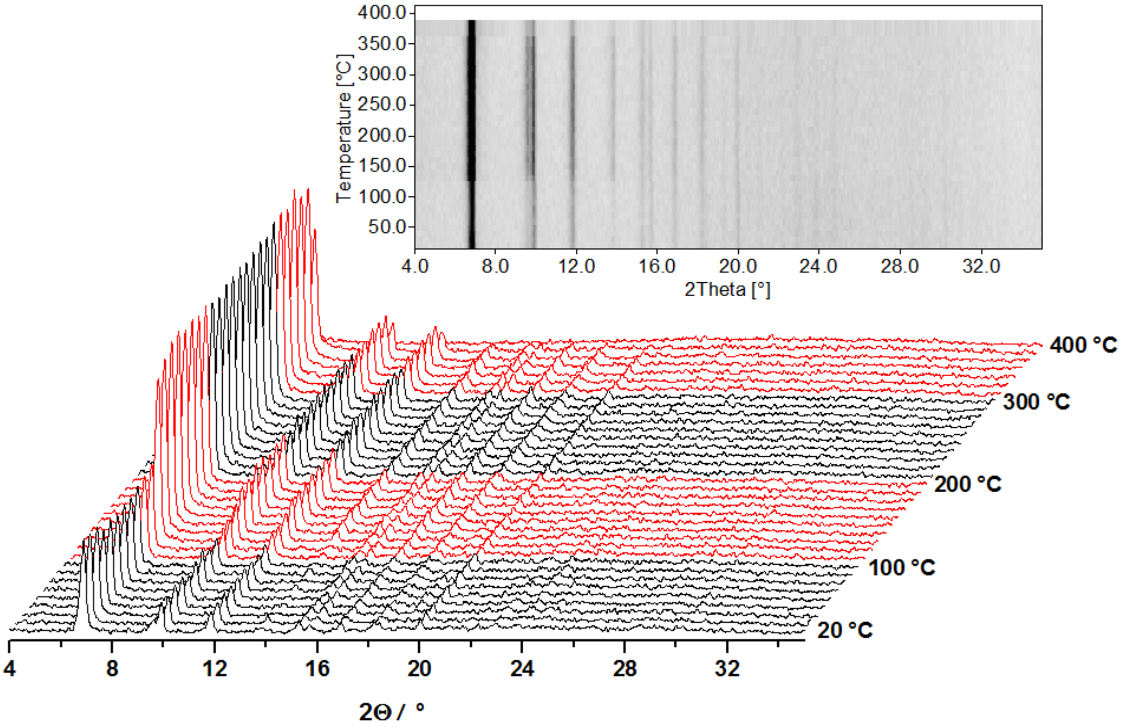


Fig. S8 Temperature-dependent X-ray powder diffraction patterns of CAU-1-NH_2(OH), $[Al_4(OH)_6((BDC\text{-}NH_2)_3]\cdot xH_2O$, in air (20 - 400 °C).

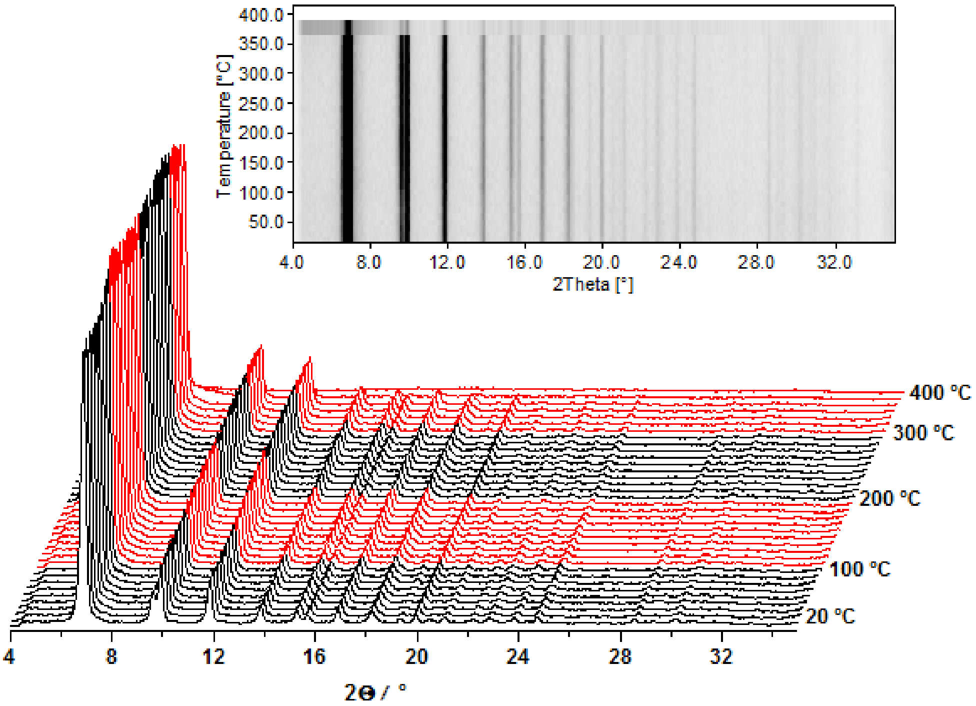


Fig. S9 Temperature-dependent X-ray powder diffraction patterns of CAU-1-NHCH$_3$, $[Al_4(OH)_2(OCH_3)_4(BDC\text{-}NHCH_3)_3]\cdot xH_2O$, in air (20 - 400 °C).

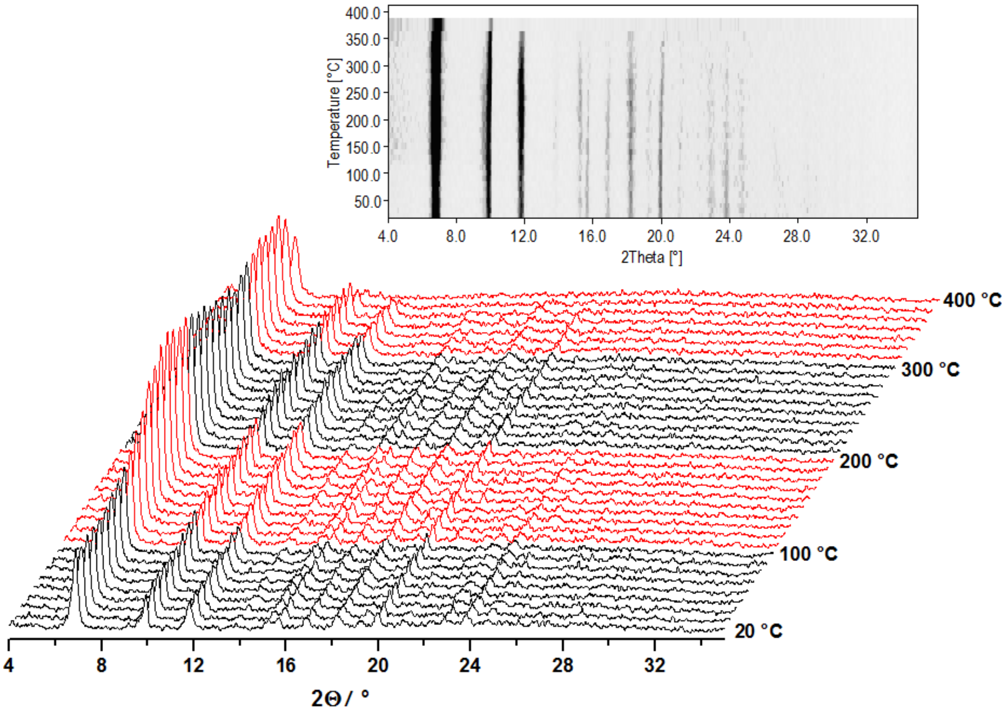


Fig. S10 Temperature-dependent X-ray powder diffraction patterns of CAU-1-NHCOCH$_3$, $[Al_4(OH)_2(OCH_3)_4(BDC\text{-}NHCOCH_3)_3]\cdot xH_2O$, in air (20 - 400 °C).

Literature

[1] T. Ahnfeldt, N. Stock, *CrystEngComm*, **2011**, doi:110.1039/c1ce05956d