Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

Green Synthesis of a New Layered Aluminium Citraconate: Crystal Structures, Intercalation Behavior towards H_2O and *in situ* PXRD Studies of its Crystallization

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1. IR spectroscopy

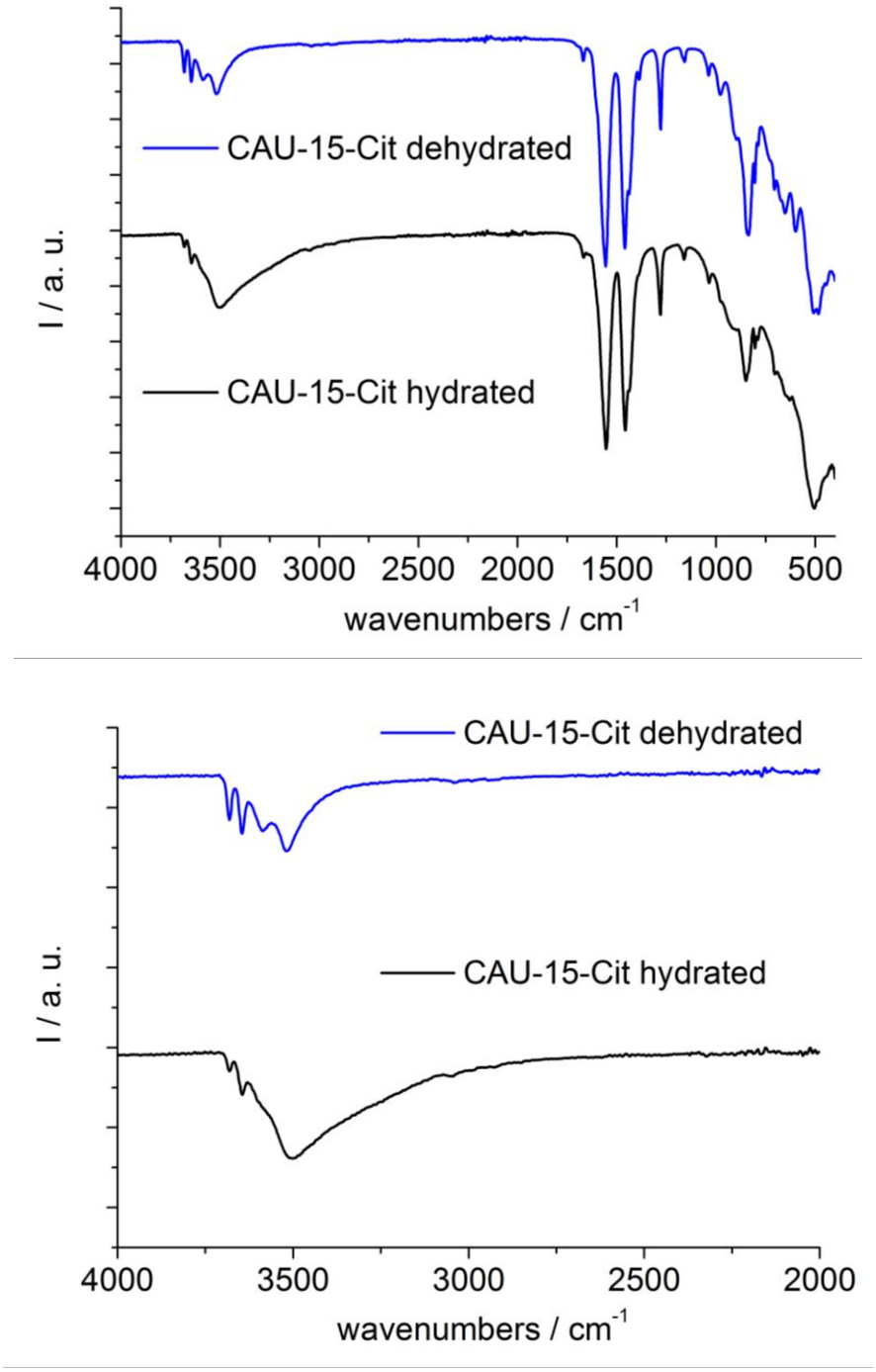

Figure S1. IR spectra (top: full range; bottom: focus on O-H region) of hydrated and dehydrated CAU-15-Cit.

Table S1: Observed IR bands and their assignment to the respective functional groups.

band for hydrated CAU-15-Cit	band for dry CAU-15-Cit	functional group
3683 cm^{-1}	3683 cm^{-1}	μ-O-H stretch
3645 cm^{-1}	3645 cm^{-1}	μ-O-H stretch
	3586 cm^{-1}	μ-O-H stretch
	3520 cm^{-1}	μ-O-H stretch
3500 cm^{-1} (broad)		μ-O-H hydrogen bonds
1665 cm^{-1}	1670 cm^{-1}	C=C stretch
1554 cm^{-1}	1554 cm^{-1}	asymmetric CO_2^- stretch
1458 cm^{-1}	1458 cm^{-1}	symmetric CO_2^- stretch (1)
1433 cm^{-1}	1433 cm^{-1}	symmetric CO_2^- stretch (2)
1281 cm^{-1}	1281 cm^{-1}	C-H alkene deformation
848 cm^{-1}	840 cm^{-1}	C-H out-of-plane deformation

2. Thermogravimetry

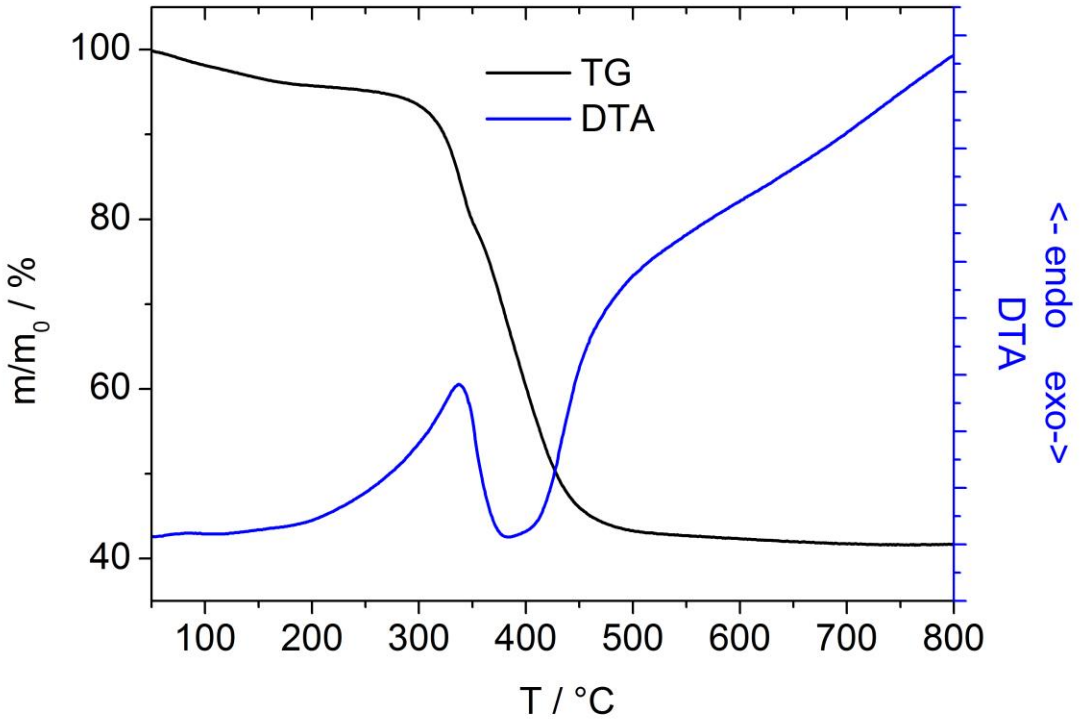

Fig. S2. Thermogravimetric curve for anhydrous CAU-15-Cit. Up to 300 °C a mass loss of 6.7 wt % could correspond to the loss of one water molecule per formula sum while above this temperature the compound decomposes. The total mass loss (58.4 wt%) corresponds well with the expected value (59.2 wt%)

3. Additional PXRD data

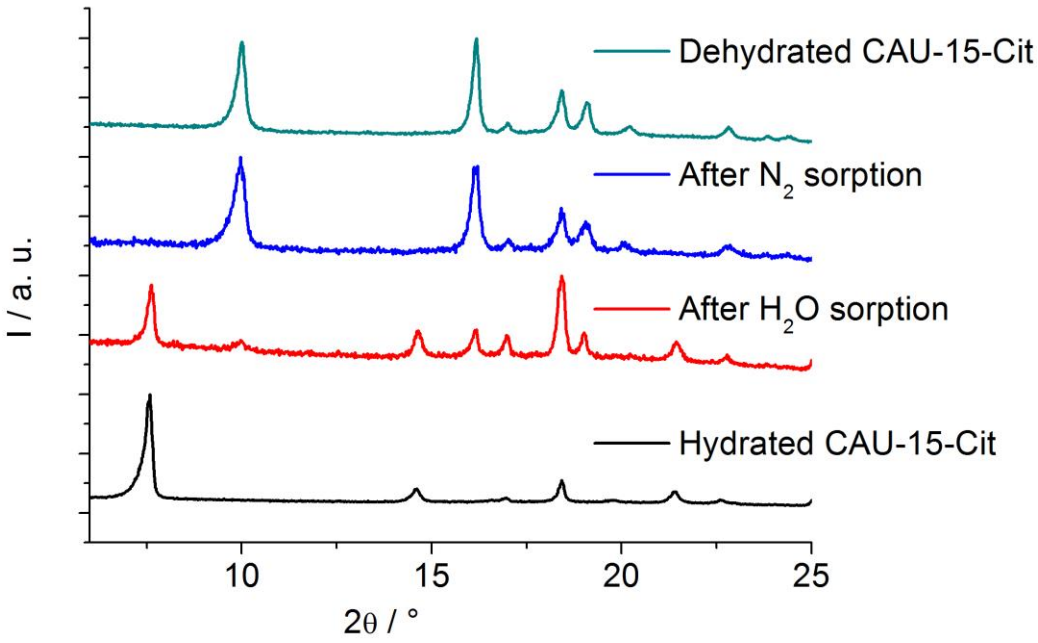

Fig. S3. PXRD patterns of hydrated CAU-15-Cit (black line) and dehydrated CAU-15-Cit (green line) in comparison with data for the MOF after H_2O adsorption measurement (red line) indicating mostly hydrated CAU-15-Cit and of the still dehydrated MOF after N_2 sorption measurement (blue line).

4. Additional crystallographic infomation

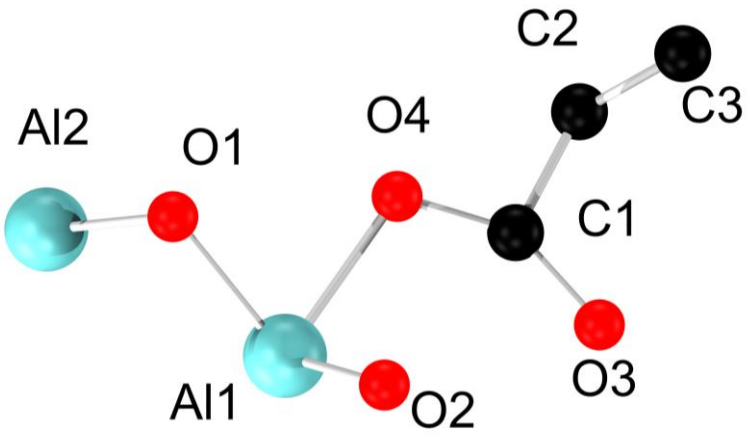

Figure S4. Asymmetric unit of hydrated CAU-15-Cit with numbering scheme used in Table S2. Guest molecules are omitted for clarity.

Table S2. Relevant bond distances for hydrated CAU-15-Cit.

Al1	O1	1.943(12)	O3	C1	1.253(12)
	O2	1.946(13)	O4	C1	1.249(12)
	O4	1.954(9)	C1	C2	1.457(14)
Al2	O3	1.909(11)	C2	C2	1.326(12)
	O1	1.940(14)		C3	1.504(20)
	O2	1.944(8)			

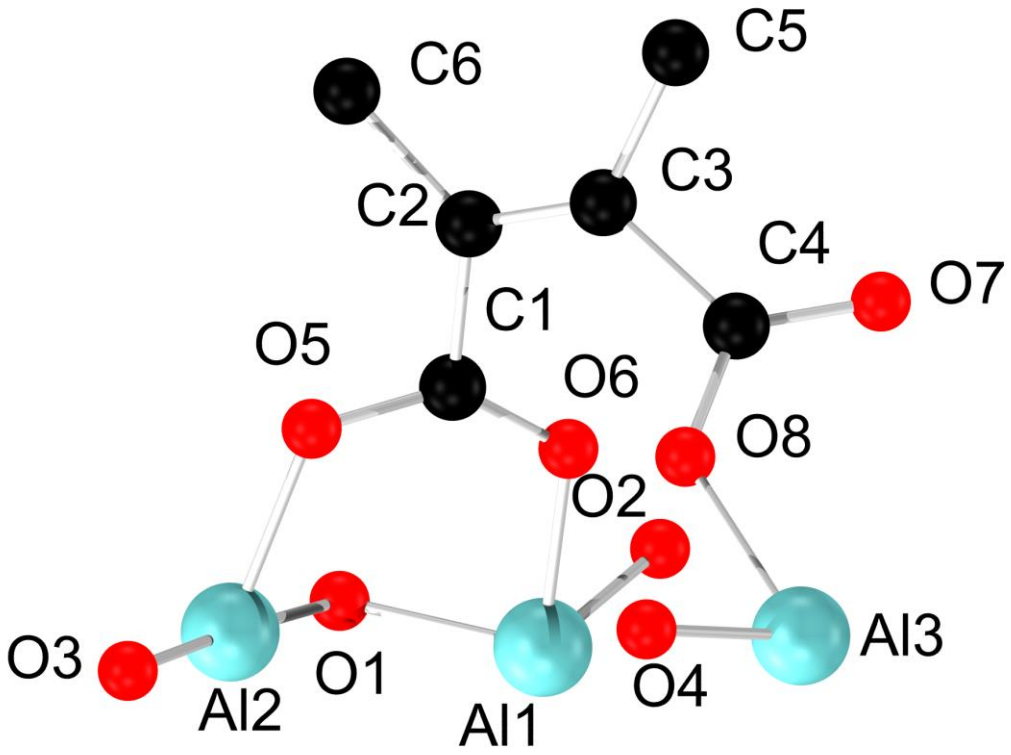

Figure S5. Asymmetric unit of dehydrated CAU-15-Cit with numbering scheme used in Table S3.

Table S3. Relevant bond distances for dehydrated CAU-15-Cit.

Al1	O1	1.871(16)			
	O2	1.883(17)	O5	C1	1.278(18)
	O6	1.893(17)	O6	C1	1.284(17)
Al2	O7	1.931(12)	O7	C4	1.272(17)
	O4	1.938(18)	O8	C4	1.290(19)
	O2	1.939(16)	C1	C2	1.564(18)
	O3	1.943(15)	C2	C3	1.397(17)
	O1	1.948(15)		C6	1.534(29)
	O5	1.970(16)	C3	C5	1.528(31)
Al3	O4	1.945(16)		C4	1.557(15)
	O8	1.948(11)			
	O3	1.959(21)			

4. Sharp-Hancock plots and in-situ PXRD data

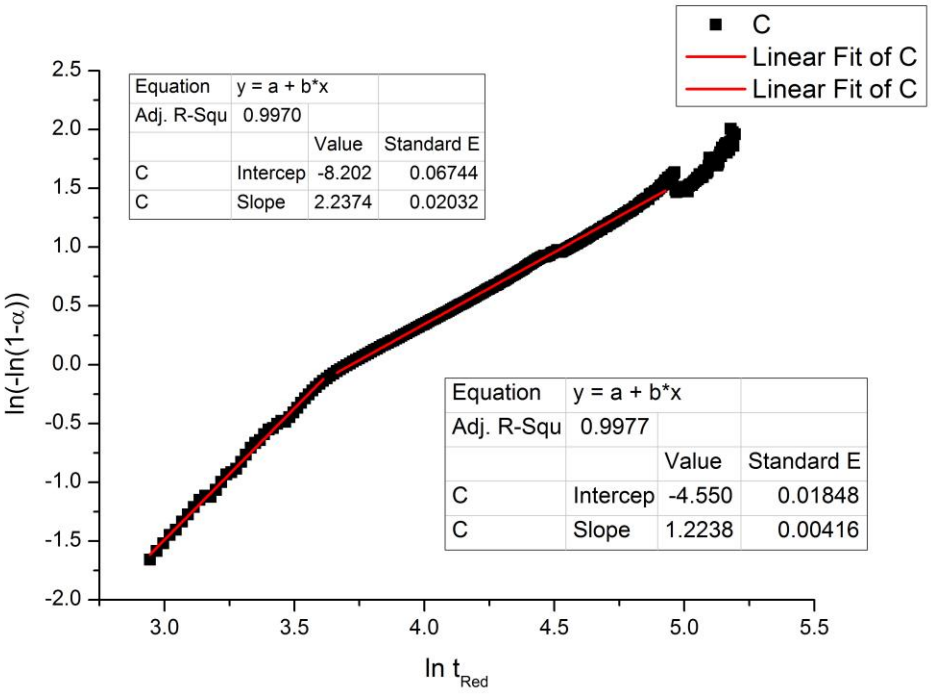

Fig. S6. Sharp-Hancock plot for the reaction at 90 °C.

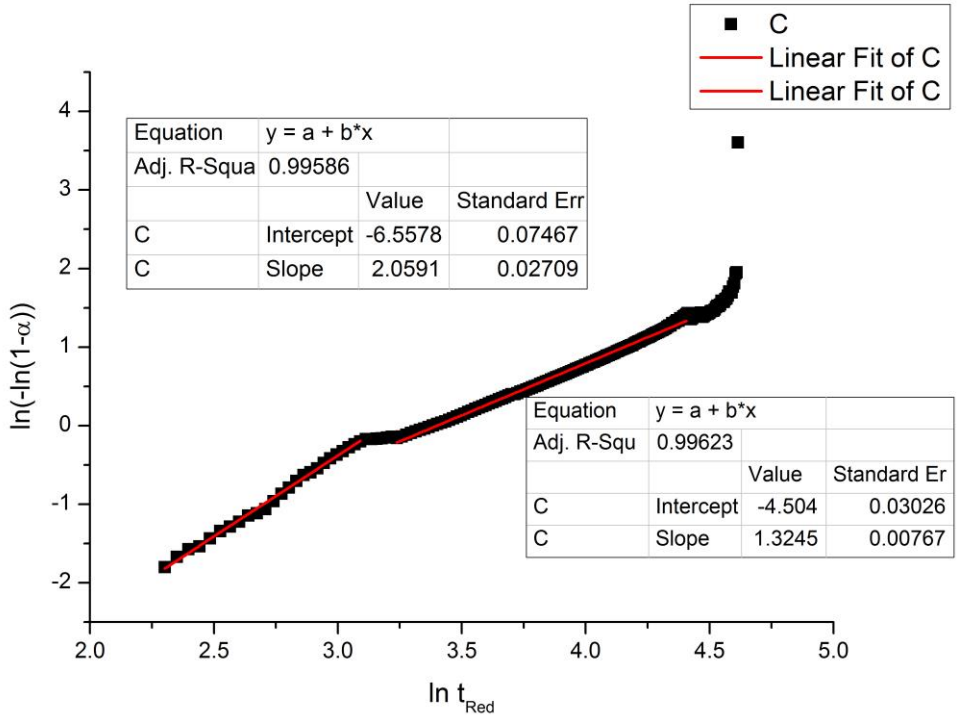

Fig. S7. Sharp-Hancock plot for the reaction at 100 °C.

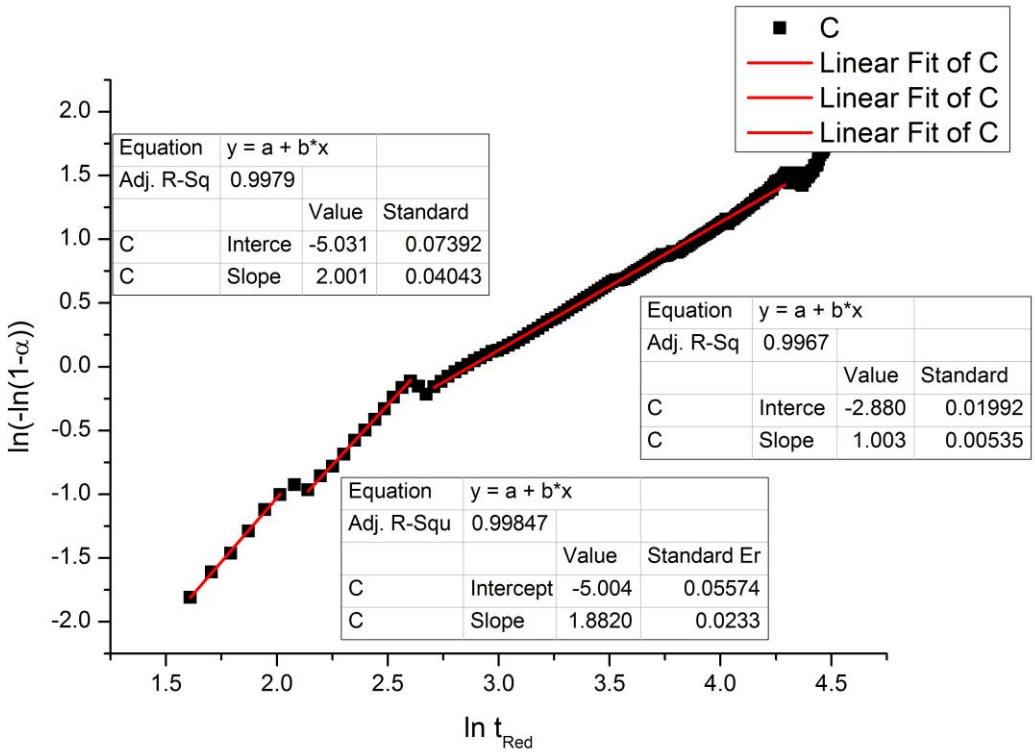

Fig. S8. Sharp-Hancock plot for the reaction at 110 °C.

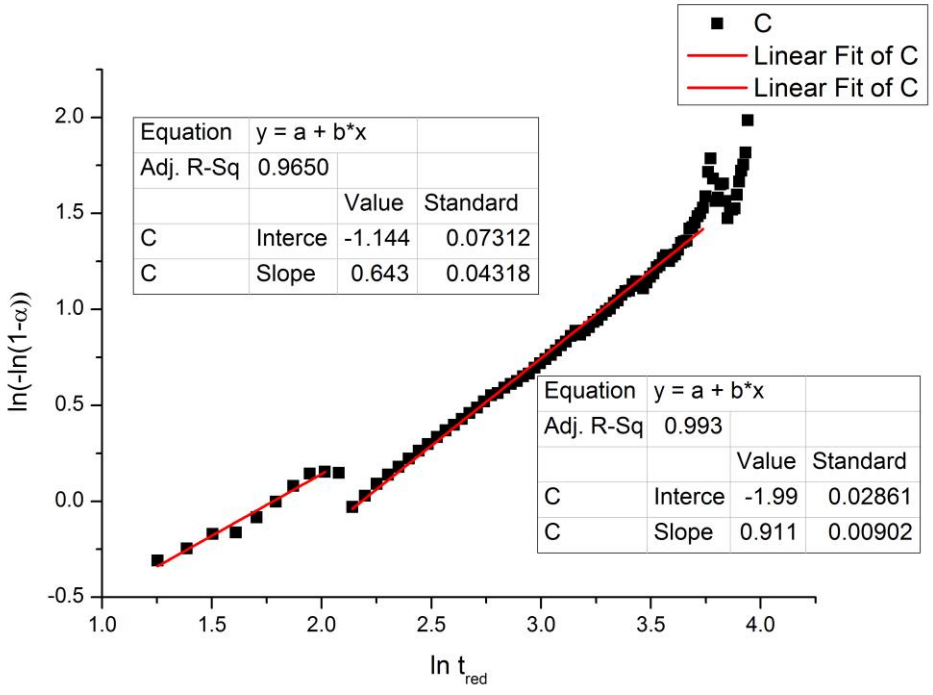

Fig. S9. Sharp-Hancock plot for the reaction at 120 °C.

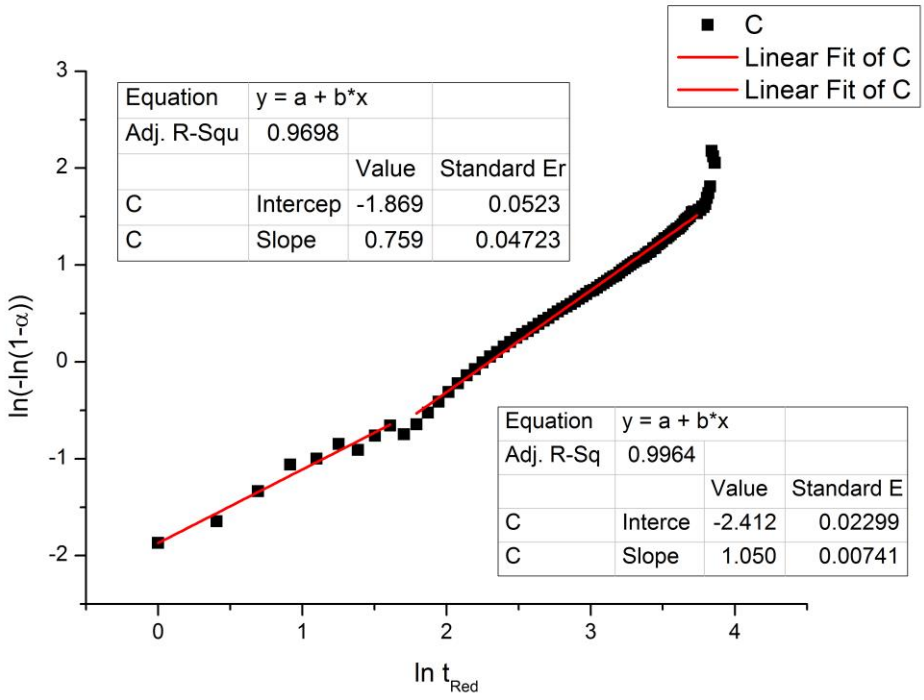

Fig. S10. Sharp-Hancock plot for the reaction at 130 °C.

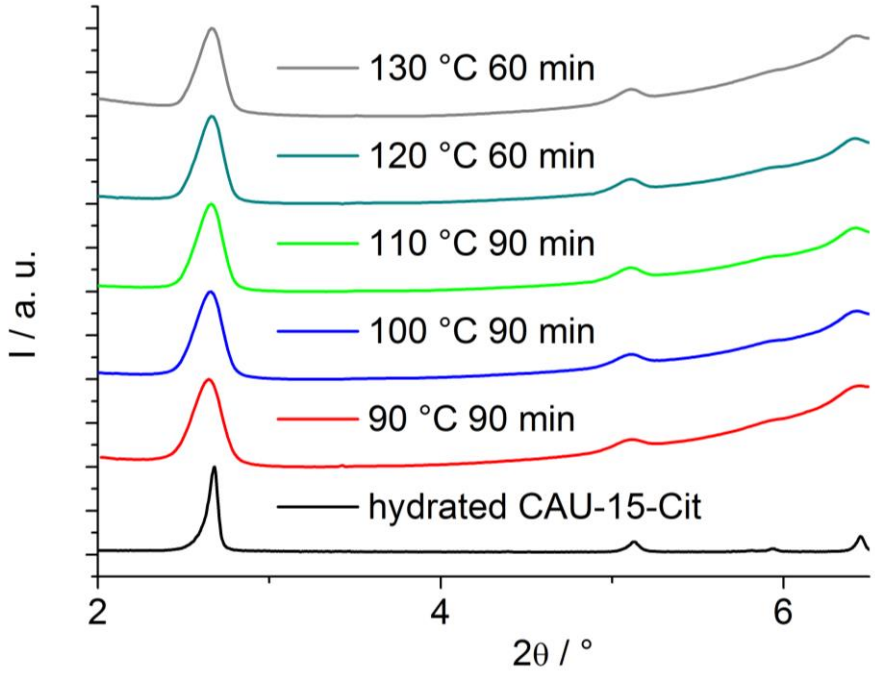

Fig. S11. PXRD patterns measured *in-situ* during the crystallization at the respective temperature and after the respective reaction time in comparison with the pattern for hydrated CAU-15-Cit as calculated for the experimental wavelength of 0.53906 Å. No by-products are visible.

5. Additional data on CAU-15

The originally reported structure was revised since CAU-15 did not show any signal in a second harmonics generation experiment, which made us doubt the correctness of the originally attributed non-centrosymmetric space group *P*2. After removing guest water molecules and structural optimization of CAU-15 by force-field methods, indeed the centrosymmetric space group *P*2/*c* was indicated. This higher symmetry structure was converted to the conventional setting and used for a revising Rietveld refinement. Residual electron density determined by Fourier synthesis was attributed to oxygen atoms representing water molecules. All atoms were freely refined using only distance restraints and element specific temperature factors. Relevant data is summarized in Table S4. This new, revised structure also matches very well with the originally reported TG and IR data of CAU-15.[1] The observed mass loss for dehydration (6.8 wt%) is in reasonable agreement with the expected value for 0.7 water molecules per formula sum (4.2 wt%) and in even better agreement with a fully hydrated structure with one water molecule per formula sum (5.9 wt %) In the original report only 0.5 molecules per $[Al_2(OH)_4(O_2C\text{-}C_6H_4\text{-}CO_2)]$ were crystallographically determined.

Table S4. Some relevant crystallographic parameters for CAU-15.

Compound	CAU-15	Originally reported parameters
Formula sum	$[Al_2(OH)_4(O_2C\text{-}C_6H_4\text{-}CO_2)]\cdot 0.7H_2O$	$[Al_4(OH)_8(O_2C\text{-}C_6H_4\text{-}CO_2)_2]\cdot H_2O$
Space group	*P*2/*c*	*P*2
Crystal system	monoclinic	monoclinic
Cell parameters	*a* = 6.8720(1) Å	*a* = 6.8729(3)Å
	b = 10.2460(3) Å	*b* = 10.2449(6)Å
	c = 9.7389(2) Å	*c* = 7.6152(4) Å
	α = 90°	*α* = 90°
	β = 128.918(2)°	*β* = 95.6701(35)°
	γ = 90°	*γ* = 90°
R_{WP}	4.9 %	8.6 %
GoF	1.59	1.09
R_{Bragg}	1.3 %	1.3 %

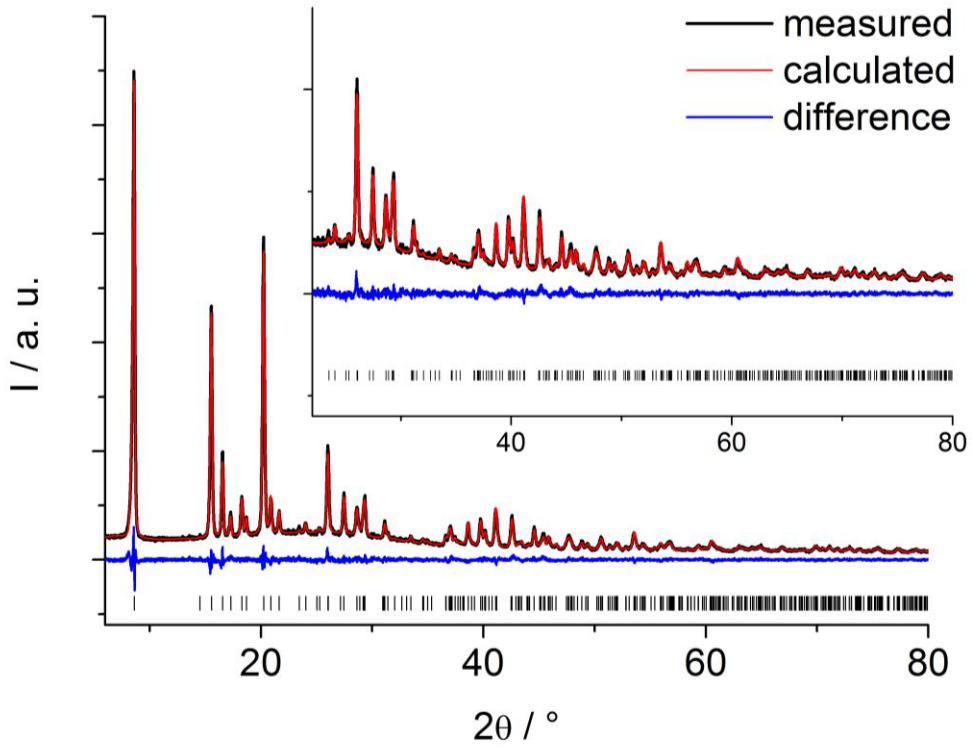

Fig. S12. Rietveld plot for the revised CAU-15. Black line is the experimental data, red line give the fit and blue line is the difference curve. Vertical bars mark the allowed Bragg peak positions.

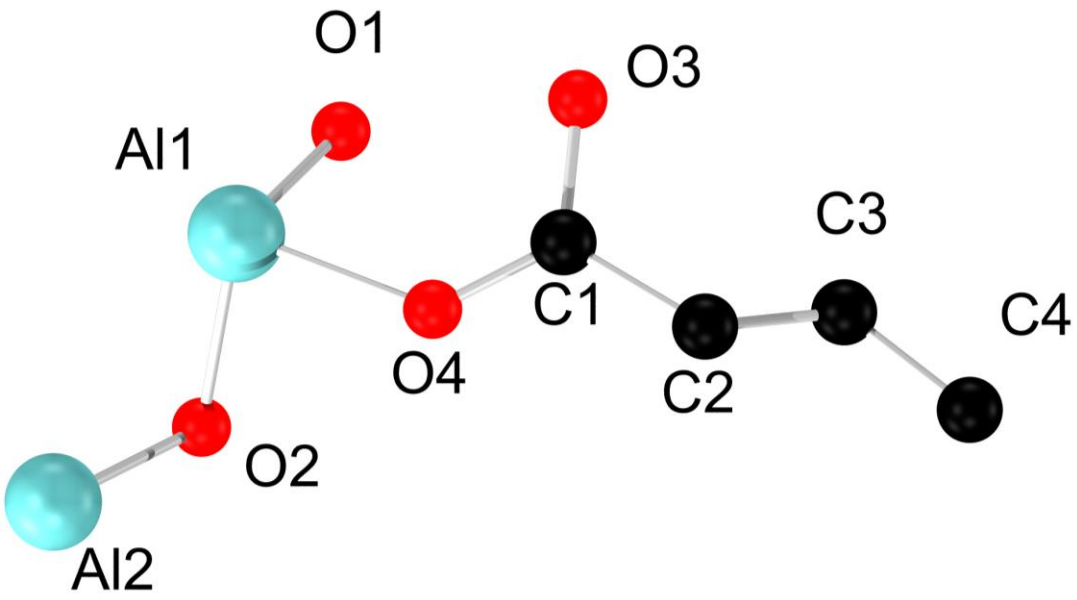

Figure S13. Asymmetric unit of CAU-15 with numbering scheme used in Table S5. Guest molecules omitted for clarity.

Table S5. Relevant bond distances for CAU-15.

Al1	O2	1.880(4)	O4	C1	1.269(6)
	O1	1.908(4)	C1	C2	1.498(6)
	O4	1.915(4)	C2	C3	1.381(4)
Al2	O2	1.876(4)		C2	1.392(3)
	O1	1.890(4)	C3	C4	1.391(5)
	O3	1.954(5)	C4	C4	1.371(3)
O3	C1	1.277(4)			

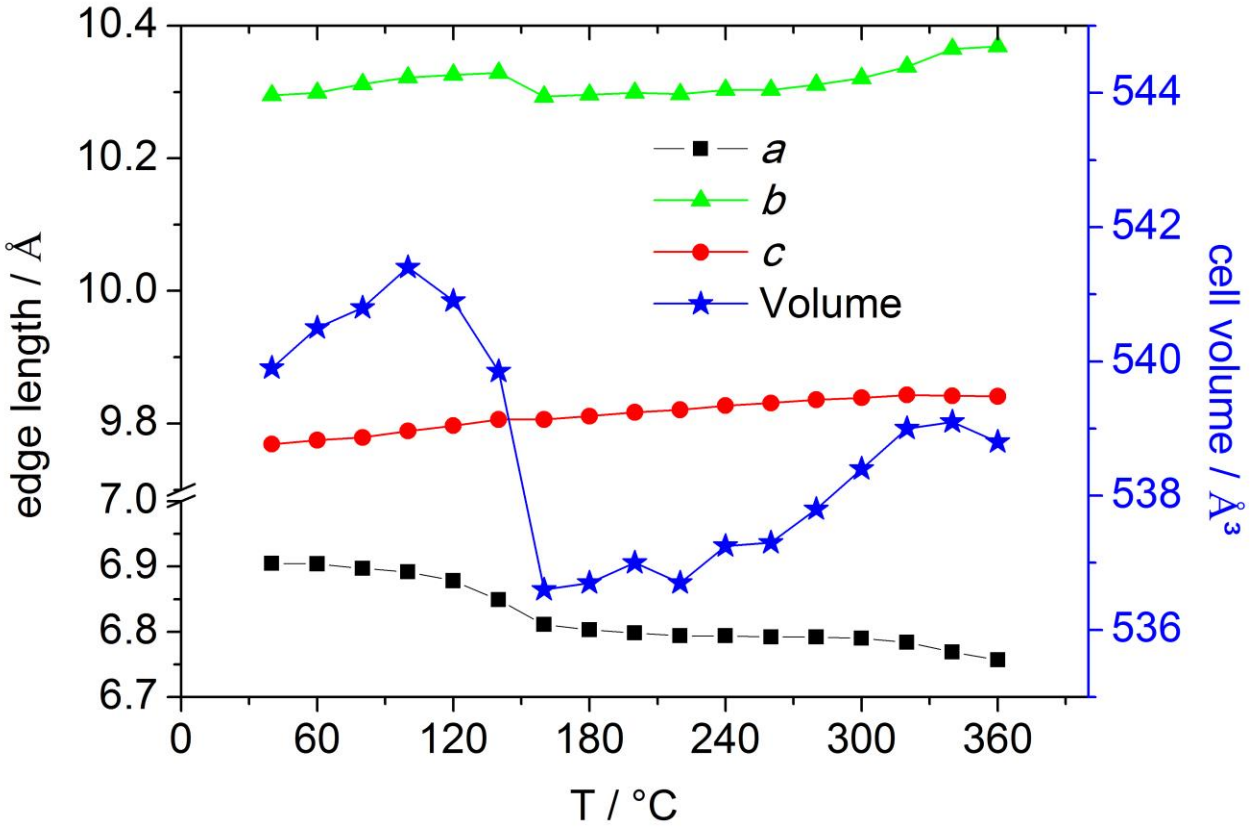

Fig. S14. Cell parameters and volumes of CAU-15 as obtained by Pawley refinement of the temperature dependent PXRD data. While the *a* axis constantly decreases and the *c* axis increases, the *b* axis and cell volume first increase upon heating, decrease upon full dehydration and finally increase till decomposition.

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[1] H. Reinsch, D. De Vos, N. Stock, *Z. anorg. allg. Chem.* 2013, *639*, 2785-2789.