Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

CAU-3: A new family of porous MOFs with a novel Al-based brick: $[Al_2(OCH_3)_4(O_2C\text{-}X\text{-}CO_2)]$ (X=aryl)

Helge Reinsch, Mark Feyand, Tim Ahnfeldt and Norbert Stock

Institute of Inorganic Chemistry, Christian-Albrechts-Universität, Max-Eyth-Straße 2, 24118 Kiel, Germany

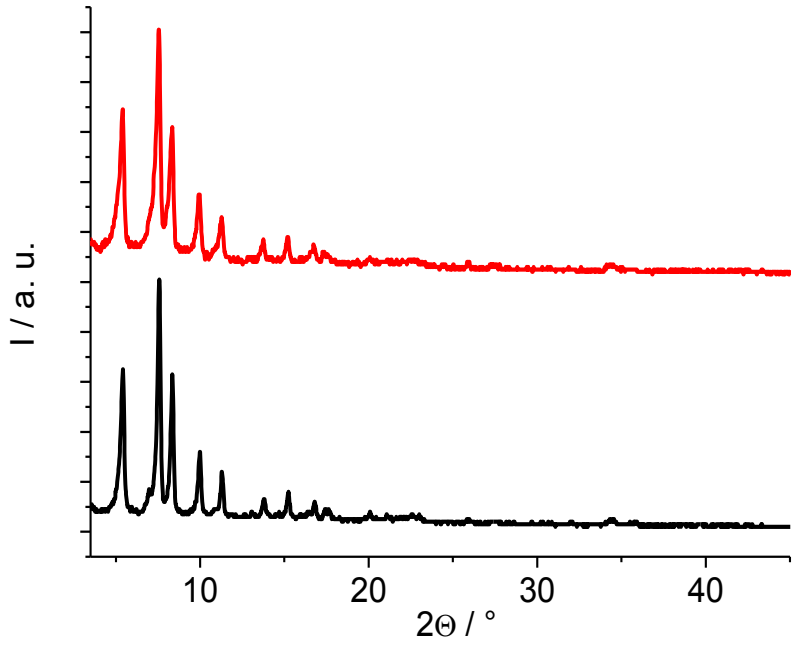

Figure S1: Powder pattern of an "as"-sample of CAU-3-BDC (black), and a sample after activation procedure and sorption measurement (red).

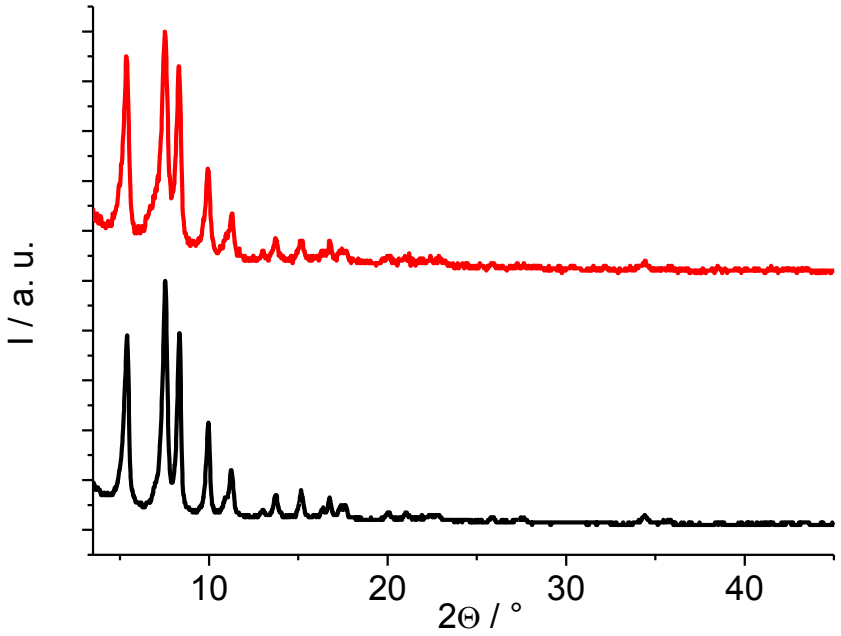

Figure S2: Powder pattern of an "as"-sample of CAU-3-BDC-NH_2 (black), and a sample after activation procedure and sorption measurement (red).

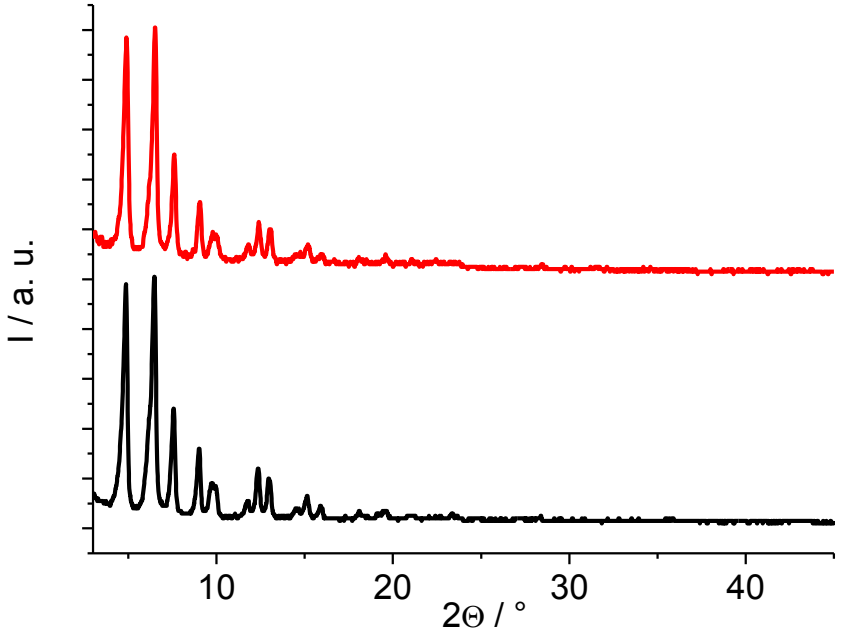

Figure S3: Powder pattern of an "as"-sample of CAU-3-NDC (black), and a sample after activation procedure and sorption measurement (red).

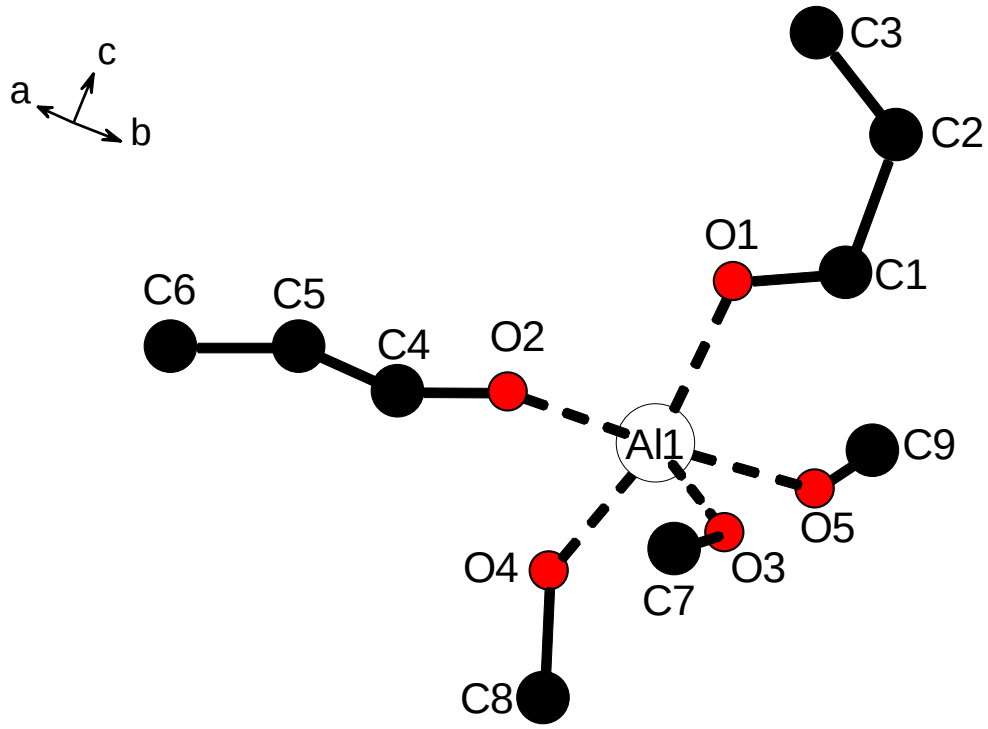

Figure S4: Asymmetric unit of CAU-3-BDC with numbering scheme.

Table S1: Selected bond lengths in CAU-3-BDC [Å].

Atom 1	***Atom 2***	***d / Å***
Al1	O1	1.96(1)
	O2	1.98(2)
	O3	1.92(1)
	O4	1.83(1)
	O5	1.89(2)
O1	C1	1.22(2)
C1	C2	1.54(1)
C2	C3	1.39(1)
O2	C4	1.23(1)
C5	C6	1.37(1)
O3	C7	1.47(3)
O4	C8	1.46(2)
O5	C9	1.51(3)
C9	O5	1.51(3)

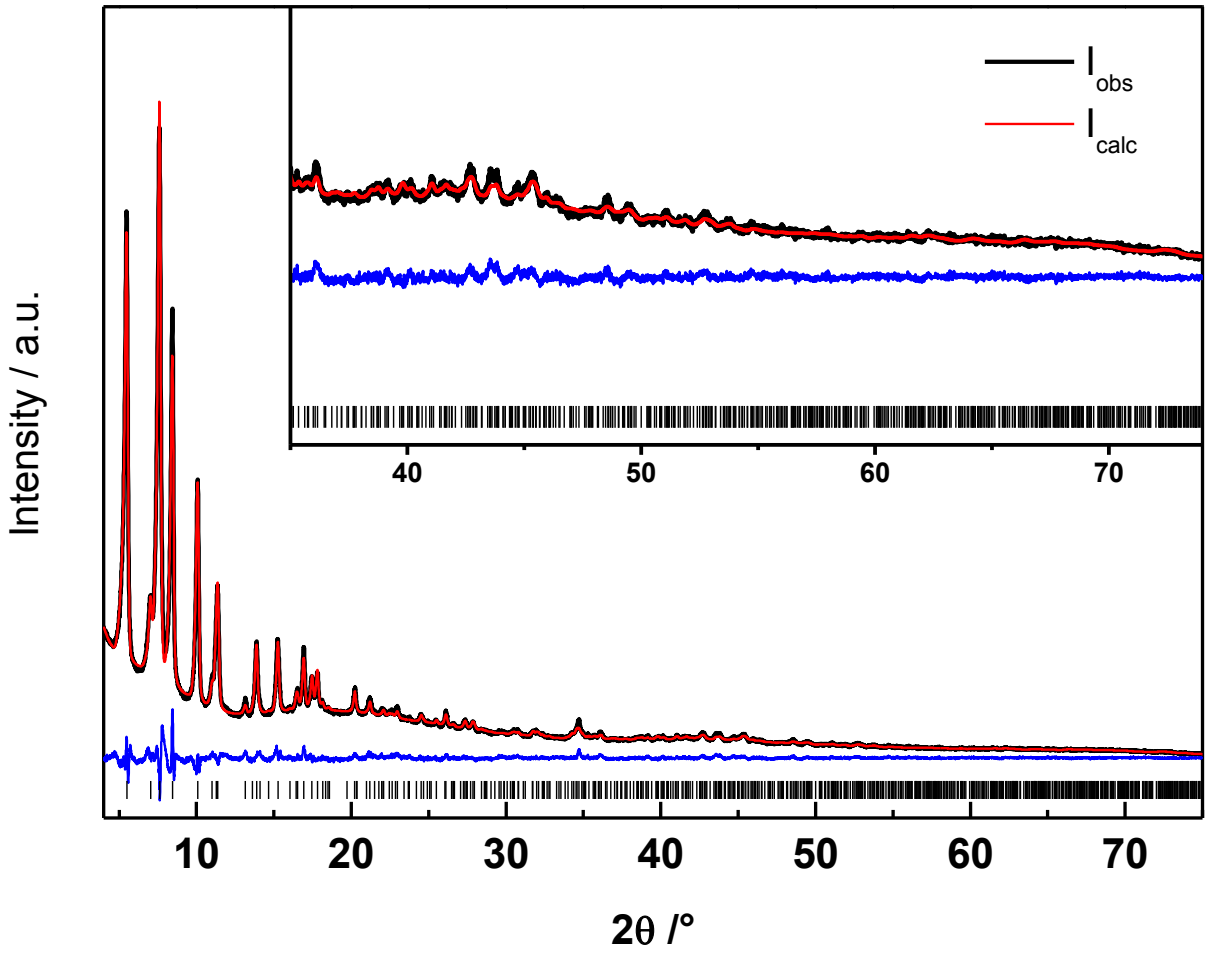

Figure S5: Final Rietveld plot of the refinement of CAU-3-BDC-NH_2. The observed intensities are shown in black, the calculated intensities are shown in red. The difference curve is shown below in blue, vertical bars mark the Bragg positions. The insert shows a plot enlargement from 35 -75 °2θ.

Table S2: Selected bond lengths in CAU-3-BDC-NH_2 [Å].

Atom 1	***Atom 2***	***d / Å***			
Al1	O1	1.99(2)	**C3**	C3	1.39(3)
	O2	1.80(2)	**O2**	C4	1.39(5)
	O3	1.74(2)	**C4**	O2	1.39(3)
	O4	1.87(3)		C5	1.53(9)
	O5	1.99(4)	**C5**	C6	1.33(5)
O1	C1	1.23(5)	**N1**	C3	1.5 (1)
C1	C2	1.60 (2)	**N2**	C6	1.5(1)
C2	C3	1.38 (6)			

Table S3: Atomic coordinates of CAU-3-NDC obtained from the force field calculations using Materials Studio 5.0.

Symbol	*x/a*	*y/b*	*z/c*
Fe1	0.25217	0.05104	0.51501
O2	0.27995	0.07593	0.55811
O3	0.32005	0.02894	0.51211
O4	0.21924	0.01434	0.47145
C5	0.26741	0.0306	0.44692
C6	0.24497	0.90175	0.2889
C7	0.24115	0.91213	0.32179
C8	0.19049	0.86321	0.34061
C9	0.14677	0.7935	0.29296
C10	0.19805	0.84234	0.27414
Fe11	0.0794	0.26015	0.48371
O12	0.11136	0.28559	0.44055
O13	0.06741	0.33477	0.4861
O14	0.04232	0.23563	0.52706
C15	0.05494	0.18882	0.54084
C16	0.5384	0.61932	0.48658
C17	0.47766	0.56072	0.48441
C18	0.47197	0.50052	0.49396
C19	0.58885	0.55858	0.50829
C20	0.59464	0.61894	0.49844
C21	0.29241	0.12878	0.57297
O22	0.31378	0.14379	0.50389
C23	0.34838	0.16804	0.47475
O24	0.18921	0.08691	0.51862
C25	0.15431	0.07905	0.54788
C26	0.31919	0.97871	0.49943
H27	0.31796	0.05445	0.456
H28	0.26201	0.06152	0.42827
H29	0.26215	0.9876	0.43382
H30	0.28504	0.94023	0.27504
H31	0.27804	0.9583	0.33253
H32	0.11043	0.7473	0.28205
H33	0.10738	0.20825	0.54132
H34	0.03412	0.14329	0.52646
H35	0.04152	0.18272	0.56665
H36	0.54135	0.665	0.47882
H37	0.43518	0.56247	0.47513
H38	0.63177	0.55735	0.51734
H39	0.31608	0.15723	0.45372
H40	0.3848	0.15121	0.47182
H41	0.3791	0.22248	0.47602
H42	0.1003	0.04938	0.54346
H43	0.16228	0.12602	0.55768
H44	0.16881	0.05767	0.56752

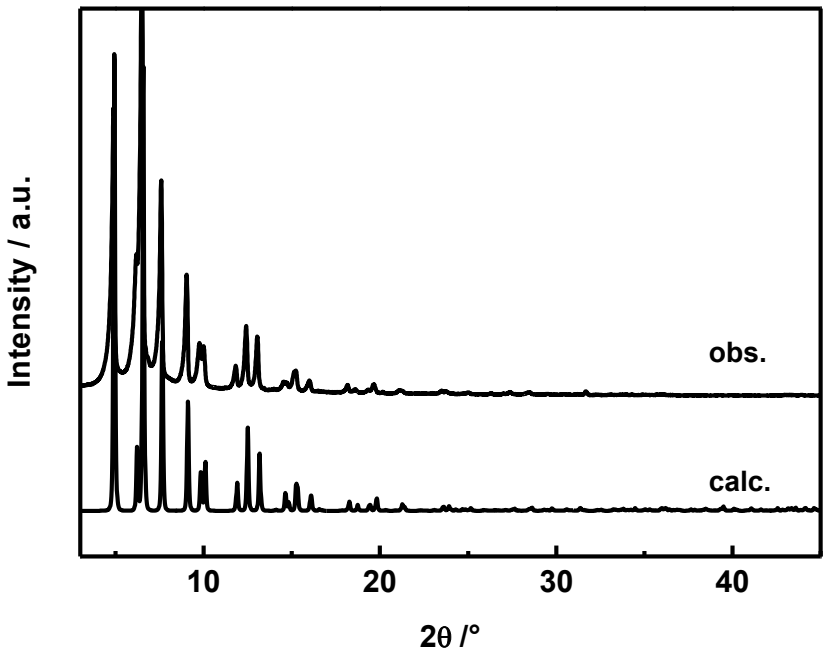

Figure S6: Calculated and observed powder pattern obtained from force field calculation.

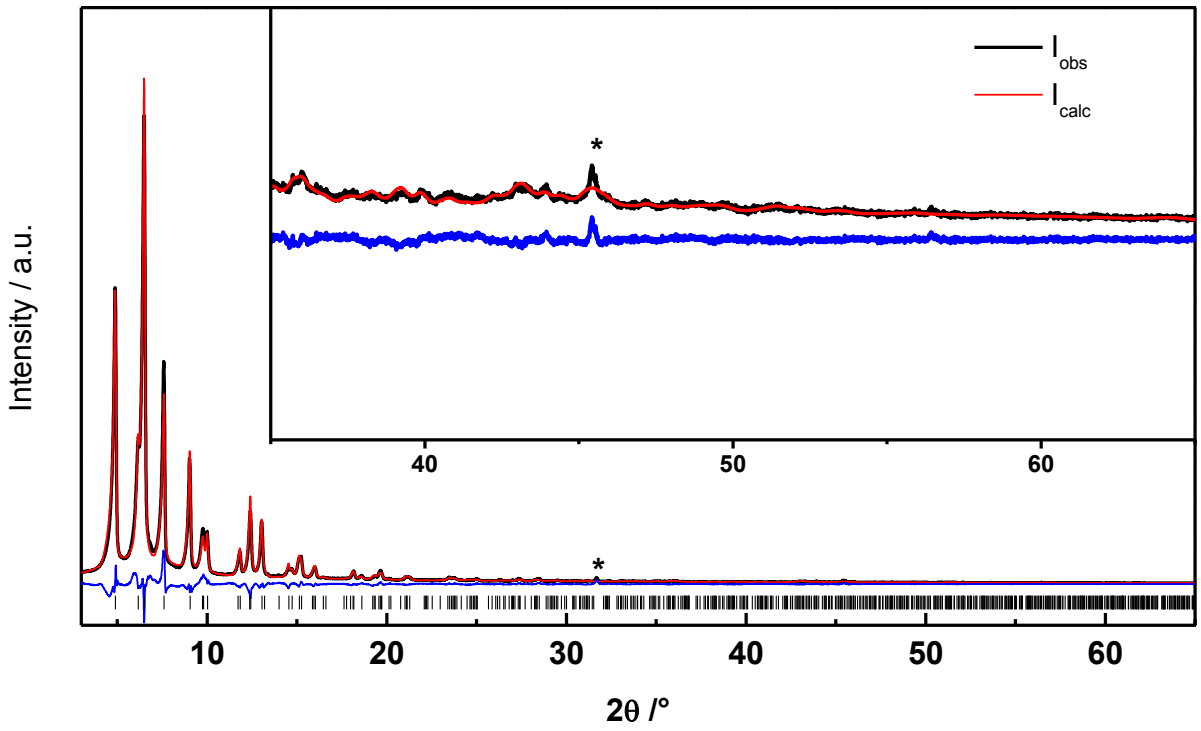

Figure S7: Final Rietveld plot of CAU-3-NDC. The asterisks correspond to NaCl as a by-product. The observed intensities are shown in black, the calculated intensities are shown in red. The difference curve is shown below in blue, vertical bars mark the Bragg positions. The insert shows a plot enlargement from 35 -65 °2θ.

Table S4: Selected bond lengths of CAU-3-NDC [Å]

Atom 1	Atom 2	d /
Al1	O1	1.8(2)
	O4	1.8(2)
	O5	1.9(2)
	O6	1.9(2)
	O7	1.8(1)
	O8	2.0(3)
Al2	O2	1.8(2)
	O3	1.8(1)
	O5	2.0(3)
	O6	1.9(3)
	O7	1.9(2)
	O8	2.0(2)
O1	C1	1.2(4)
O2	C1	1.2(4)
C1	C2	1.4(3)
C2	C3	1.4(1)
	C6	1.4(4)
C3	C4	1.4(3)
C4	C5	1.3(3)
C5	C5	1.3(4)
	C6	1.5(6)
O3	C7	1.2(3)
O4	C7	1.2(2)
C7	C8	1.5(2)
C8	C9	1.3(6)
	C12	1.4(6)
	C7	1.5(2)
C9	C10	1.3(4)
C10	C11	1.3(7)
C11	C12	1.3(4)
O5	C13	1.4(2)
O6	C16	1.3(4)
O7	C14	1.3(2)
O8	C15	1.4(2)

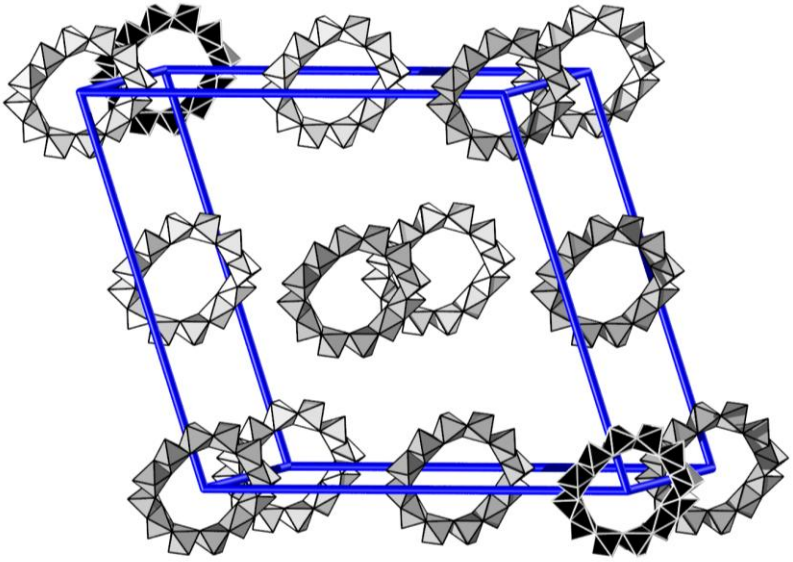

Figure S8: Pseudo-fcc-arrangement of the inorganic units. The colours emphasize the ABC-stacking,

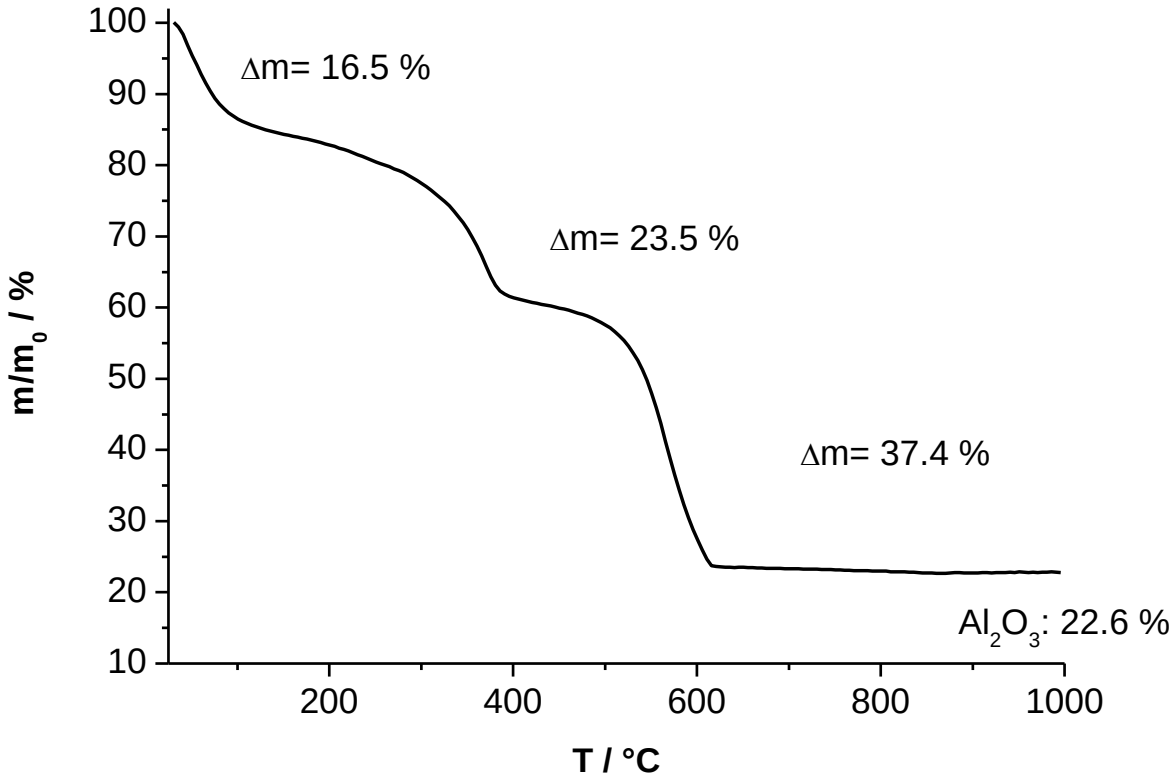

Fig. S9: TG-curve for CAU-3-BDC (**1**).

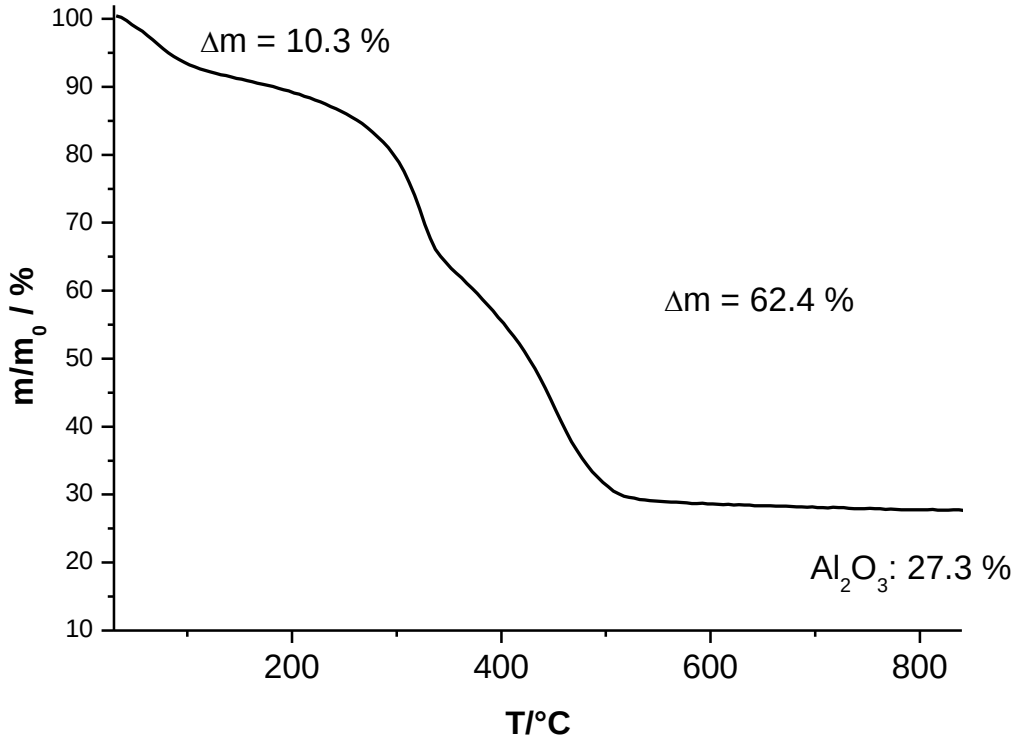

Figure S10. TG-diagram of the decomposition of CAU-3-BDC-NH_2 **(2)**.

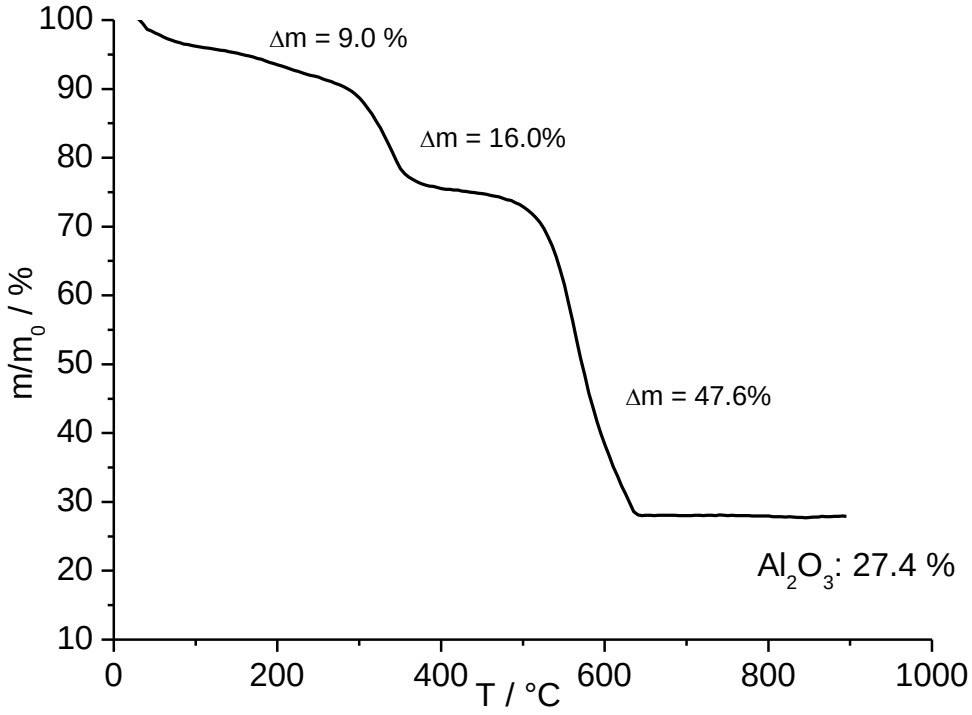

Figure S11. TG-diagram of the decomposition of CAU-3-NDC **(3)**.

Table S5: Exact amounts of starting materials used in the discovery of CAU-3-BDC.

Reaktor No.	molar ratio H_2BDC	molar ratio $AlCl_3*6H_2O$	molar ratio NaOH	amount H_2BDC [µmol]	amount $AlCl_3*6H_2O$ [µmol]	amount NaOH [µmol]	mass H_2BDC [mg]	mass $AlCl_3*6H_2O$ [mg]	volume NaOH [µL]	volume MeOH [µL]
1	0,25	1	0,5	32	128	64	5	31	32	1368
2	0,25	1	0,75	32	128	96	5	31	48	1352
3	0,25	1	1,25	32	128	160	5	31	80	1320
4	0,25	1	1,5	32	128	192	5	31	96	1304
5	0,25	1	1,75	32	128	224	5	31	112	1288
6	0,25	1	2	32	128	256	5	31	128	1272
7	0,25	1	1	32	128	130	5	31	65	935
8	0,25	1	1	32	128	130	5	31	65	1185
9	0,25	1	1	32	128	130	5	31	65	1435
10	0,50	2	2	64	256	260	11	62	130	870
11	0,50	2	2	64	256	260	11	62	130	1120
12	0,50	2	2	64	256	260	11	62	130	1370
13	0,50	2	1	64	256	128	11	62	64	1336
14	0,50	2	1,25	64	256	160	11	62	80	1320
15	0,50	2	1,50	64	256	192	11	62	96	1304
16	0,50	2	1,75	64	256	224	11	62	112	1288
17	0,50	2	2	64	256	256	11	62	128	1272
18	0,50	2	2,5	64	256	320	11	62	160	1240
19	1	4	1,55	128	512	198	21	124	99	1301
20	1	4	2,18	128	512	279	21	124	140	1260
21	1	4	2,81	128	512	360	21	124	180	1220
22	1	4	3,43	128	512	439	21	124	220	1180
23	1	4	4,06	128	512	520	21	124	260	1140
24	1	4	4,68	128	512	599	21	124	300	1100