A new keto-functionalized microporous Al-based metal-organic framework: [Al(OH)(O_2C-C_6H_4-CO-C_6H_4-CO_2)]

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I: List of HT-reactions

II: Asymmetric unit of CAU-8

II: Topological analysis of MOFs based on infinite one-periodic building units

I: List of HT-reactions

Table S1: Exact compositions of the reaction mixtures in the HT-experiment.

number	n (Al^{3+}) [mmol]	n (linker) [mmol]	m (AlX) [mg]	m (linker) [mg]	Al-source	V H_2O [µL]	V DMF [µL]
1	0.11	0.11	111.1	30.0	$Al_2(SO_4)_3 \cdot 18H_2O$	400.0	100.0
2	0.11	0.11	111.1	30.0	$Al_2(SO_4)_3 \cdot 18H_2O$	300.0	200.0
3	0.11	0.11	111.1	30.0	$Al_2(SO_4)_3 \cdot 18H_2O$	200.0	300.0
4	0.15	0.15	148.1	40.0	$Al_2(SO_4)_3 \cdot 18H_2O$	400.0	100.0
5	0.15	0.15	148.1	40.0	$Al_2(SO_4)_3 \cdot 18H_2O$	300.0	200.0
6	0.15	0.15	148.1	40.0	$Al_2(SO_4)_3 \cdot 18H_2O$	200.0	300.0
7	0.19	0.19	185.2	50.0	$Al_2(SO_4)_3 \cdot 18H_2O$	400.0	100.0
8	0.19	0.19	185.2	50.0	$Al_2(SO_4)_3 \cdot 18H_2O$	300.0	200.0
9	0.19	0.19	185.2	50.0	$Al_2(SO_4)_3 \cdot 18H_2O$	200.0	300.0
10	0.22	0.22	222.2	60.0	$Al_2(SO_4)_3 \cdot 18H_2O$	400.0	100.0
11	0.22	0.22	222.2	60.0	$Al_2(SO_4)_3 \cdot 18H_2O$	300.0	200.0
12	0.22	0.22	222.2	60.0	$Al_2(SO_4)_3 \cdot 18H_2O$	200.0	300.0
13	0.11	0.11	55.6	30.0	$Al(NO_3)_3 \cdot 9H_2O$	400.0	100.0
14	0.11	0.11	55.6	30.0	$Al(NO_3)_3 \cdot 9H_2O$	300.0	200.0
15	0.11	0.11	55.6	30.0	$Al(NO_3)_3 \cdot 9H_2O$	200.0	300.0
16	0.15	0.15	74.1	40.0	$Al(NO_3)_3 \cdot 9H_2O$	400.0	100.0
17	0.15	0.15	74.1	40.0	$Al(NO_3)_3 \cdot 9H_2O$	300.0	200.0
18	0.15	0.15	74.1	40.0	$Al(NO_3)_3 \cdot 9H_2O$	200.0	300.0
19	0.19	0.19	92.6	50.0	$Al(NO_3)_3 \cdot 9H_2O$	400.0	100.0
20	0.19	0.19	92.6	50.0	$Al(NO_3)_3 \cdot 9H_2O$	300.0	200.0
21	0.19	0.19	92.6	50.0	$Al(NO_3)_3 \cdot 9H_2O$	200.0	300.0
22	0.22	0.22	111.1	60.0	$Al(NO_3)_3 \cdot 9H_2O$	400.0	100.0
23	0.22	0.22	111.1	60.0	$Al(NO_3)_3 \cdot 9H_2O$	300.0	200.0
24	0.22	0.22	111.1	60.0	$Al(NO_3)_3 \cdot 9H_2O$	200.0	300.0

II: Asymmetric unit of CAU-8

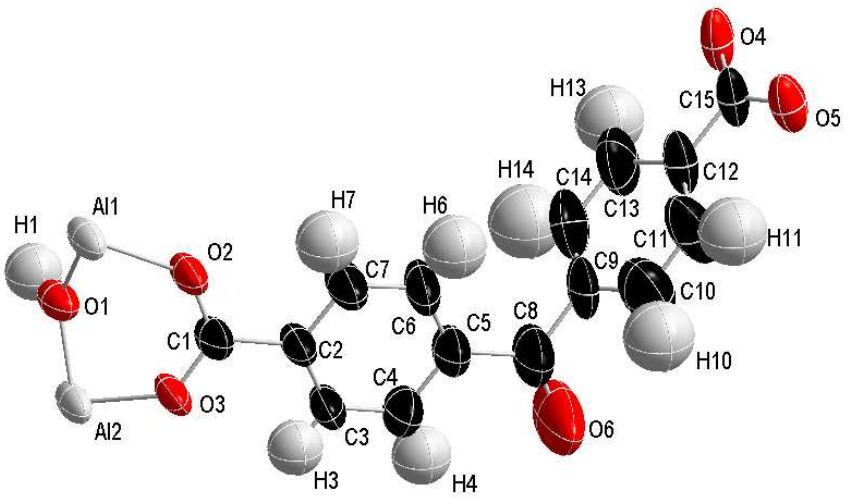

Fig. S1: Asymmetric unit of CAU-8 with numbering scheme as use in Tab. S2.

Tab. S2: Bond lengths in CAU-8 in Angstrom.

Al1	O1	1.8431(11)	C5	C6	1.3712(29)
	O2	1.9029(11)		C8	1.4924(27)
	O5	1.9034(11)	C6	H6	0.9319(19)
Al2	O1	1.8216(11)		C5	1.3712(29)
	O4	1.9079(12)		C7	1.3719(27)
	O3	1.9217(13)	C7	H7	0.9308(20)
O1	H1	0.9526(83)	C8	C9	1.4809(32)
O2	C1	1.2713(20)	C9	C14	1.3338(37)
O3	C1	1.2480(19)		C10	1.3739(35)
O4	C15	1.2458(20)	C10	H10	0.9304(26)
O5	C15	1.2508(19)		C11	1.3575(36)
O6	C8	1.2378(35)	C11	H11	0.9314(23)
C1	C2	1.4960(23)		C12	1.3931(31)
C2	C3	1.3564(24)	C12	C13	1.4069(31)
	C7	1.3758(26)		C15	1.4780(27)
C3	H3	0.9305(17)	C13	H13	0.9297(26)
	C4	1.3620(23)		C14	1.3872(34)
C4	H4	0.9292(20)	C14	H14	0.9292(24)
	C5	1.3892(27)			

III: Topological analysis of MOFs based on infinite one-periodic building units

For the following topological analysis the complexity of the infinite inorganic building unit was reduced to a minimum of complexity. Thus for the inorganic buidling unit zig-zag chains instead of ladder-like fragments are obtained as previously described.[1]

Tab. S3. MOFs based on infinite inorganic building units and their topologies as observed in this study.

compound	MIL-53	MIL-68	MIL-120	CAU-4	CAU-6	CAU-10
building unit	chain	chain	helices	bridged ions	columns	helices
connectivity	uninodal 4	binodal 4,4	bimodal 3,4	bimodal 3,5	uninodal 8	uninodal 4
name	dia	bik	nor-3,4-C2/m	hms	ecf	gis
SG (MOF)	Pnma	Cmcm	C2/m	P312	$P6_3/mmc$	I41/amd
SG (net)	Fd-3m	Cmcm	C2/m	P-6m2	$P6_3/mmc$	I41/amd
point symbol	(6^6)	$(5.6^5)(5^4.6^8)_2$	$(6.8^2)_4(6^2.8^2.10^2)$	$(6^3)(6.9^8)$	$(3^8.4^{10}.5^8.6^2)$	$4^3.6^2.8$

In MIL-53 (Fig. S2) and MIL-68 (Fig. S3), the inorganic units are identical to the ones observed in CAU-8. Thus the infinite chains were considered in the same way as for CAU-8.

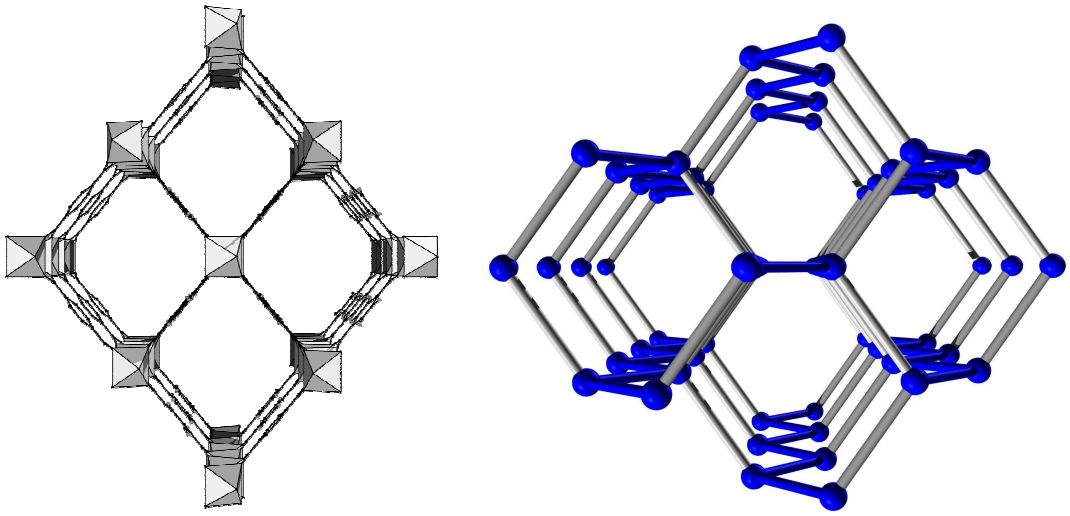

Fig. S2: Left: Framework structure of MIL-53. Right: Representation of the underlying **dia**-net with the fragments corresponding to the Al-oxo-chains emphasized in blue. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

1 O'Keeffe, M.; Yaghi, O. M.; *Chem. Rev.* **2012**, *112*, 675-702.

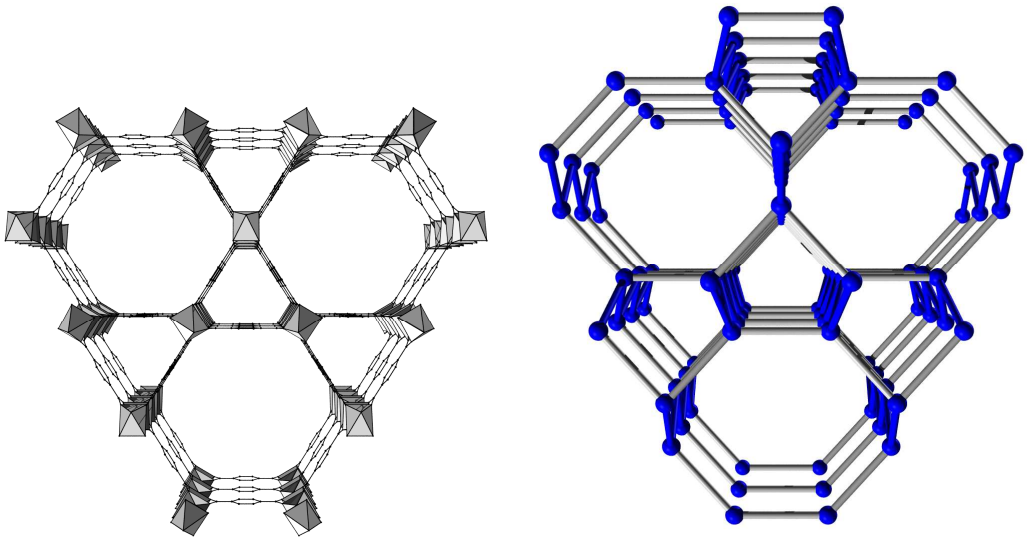

Fig. S3: Left: Framework structure of MIL-68. Right: Representation of the underlying **bik**-net with the fragments corresponding to the Al-oxo-chains emphasized in blue. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

In both cases, the chain-like character is retained in a similar way as observed for CAU-8 and the pore system is accurately represented by the respective topology.

In the framework of MIL-120 which is based on chains of edge-sharing AlO_6-polyhedra 1,2,4,5-benzenetetracarboxylate, the infinite inorganic building unit exhibits a helical shape and the linker molecule is represented by a 4-connected node (Fig. S4). No merging of the points of extension seems possible.

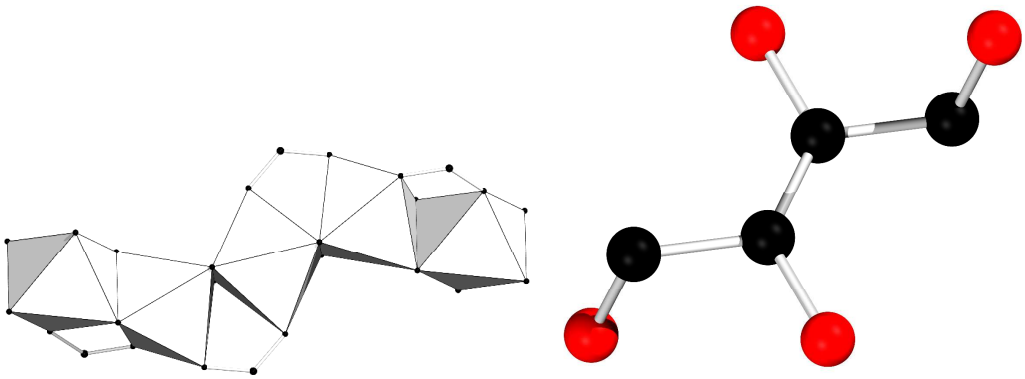

Fig. S4: Left: A fragment of the inorganic unit in MIL-120. Right: Corresponding helical representation of this infinite building unit. The red spheres represent the four-connected organic linker molecules.

Although the infinite unit has a different shape, our analysis resulted in a suitable, accurate topology (Fig. S5).

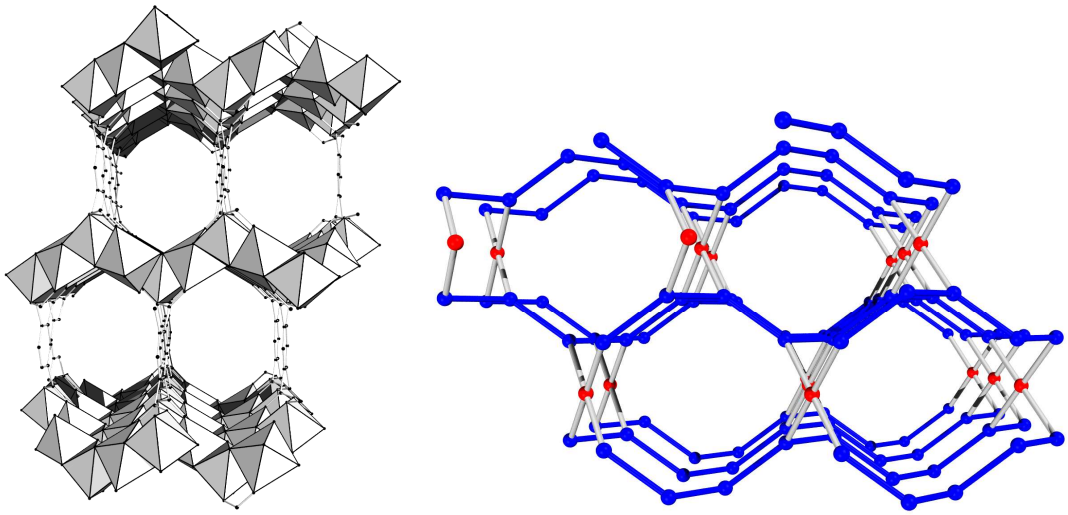

Fig. S5: Left: Framework structure of MIL-120. Right: Representation of the underlying **nor**-net with the fragments corresponding to the Al-oxo-chains emphasized in blue and the nodes corresponding to the linker molecules represented in red. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

Another MOF based on infinite helical building units is CAU-10. This compound is based on chains of *cis*-connected corner-sharing AlO_6-polyhedra bridged by 1,3-benzenedicarboxylate. Two polyhedra are bridged by two carboxylate groups and thus these points of extension were merged into one point (Fig. S6).

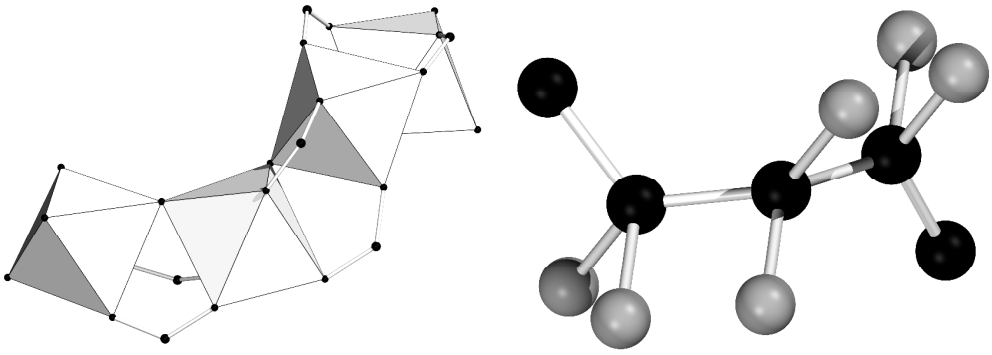

Fig. S6: Left: A fragment of the inorganic unit in CAU-10. Right: Corresponding helical representation of this infinite building unit. The helical chain is emphasized in black while the nodes of the adjacent chains are emphasized in grey.

The underlying topology of CAU-10 is the **gis**-network (Fig. S6).

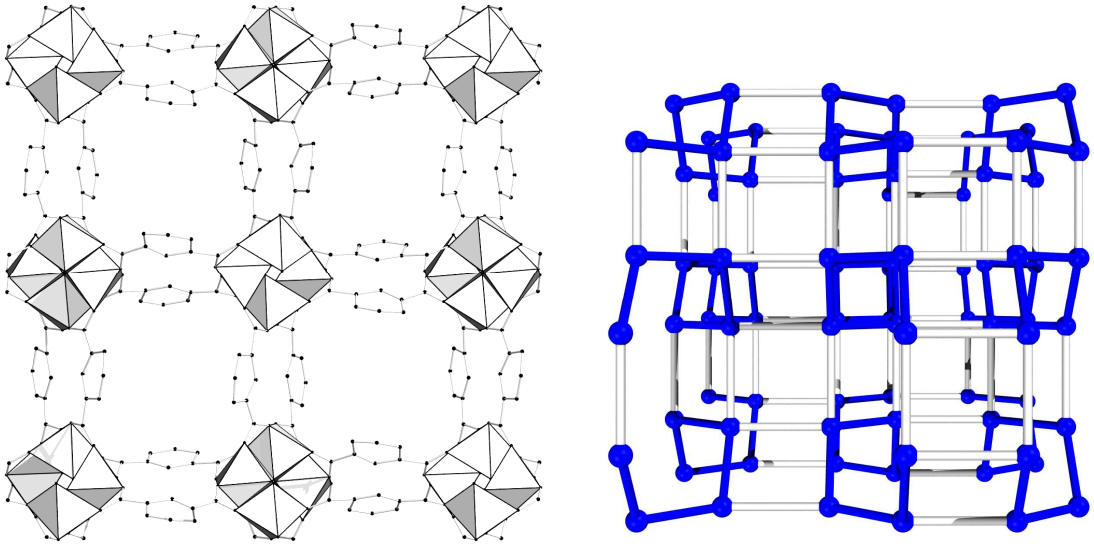

Fig. S7: Left: Framework structure of CAU-10. Right: Representation of the underlying **gis**-net with the helical fragments corresponding to the Al-oxo-chains emphasized in blue. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

Another MOF which is based on infinte building units is CAU-4, in which the inorganic unit consists of carboxylate-bridged Al^{3+}-ions (Fig. S7) which are connected via tritopic 1,3,5-benzenetrisbenzoate linker molecules. Thus three points of extension are merged into one point.

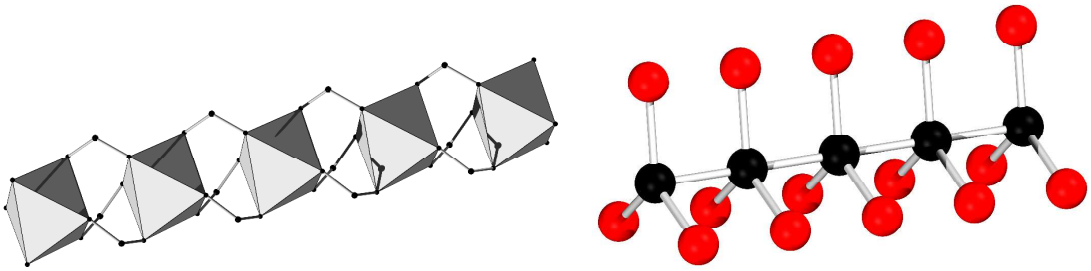

Fig. S8: Left: A fragment of the inorganic unit in CAU-4. Right: Corresponding representation of this infinite building unit. The red spheres represent the three-connected organic linker molecules.

This framework exhibits the binodal **hms**-topology (Fig. S9).

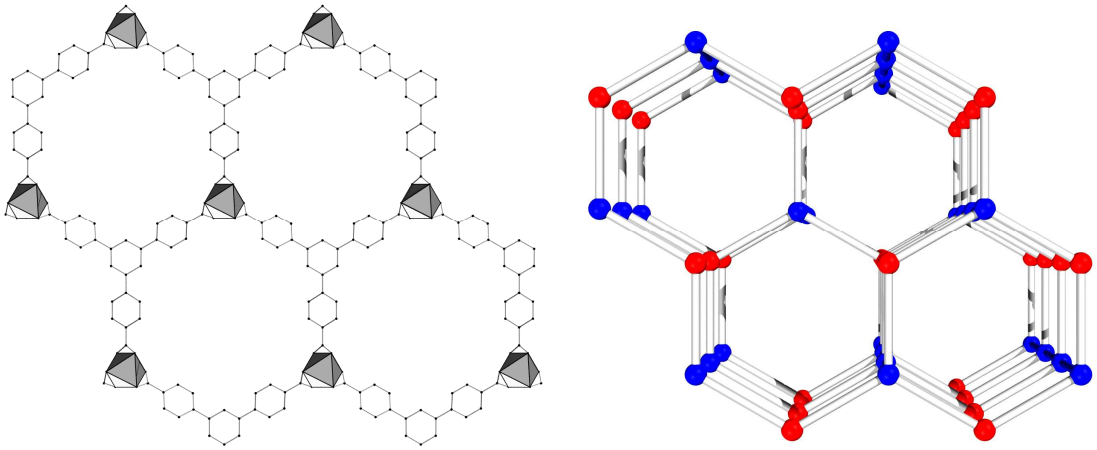

Fig. S9: Left: Framework structure of CAU-4. Right: Representation of the underlying **hms**-net with the linear fragments corresponding to the Al-oxo-chains emphasized in blue and the three-connected organic nodes emphasized in red. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

A very special framework is observed in the MOF CAU-6, which is based on column-like infinite inorganic units which are connected via 2-amino-1,4-benzenedicraboxylate molecules. The points of extension for this column-like unit were generated as shown in Fig. S10. Thus two carboxylate groups were merged into one point of extension.

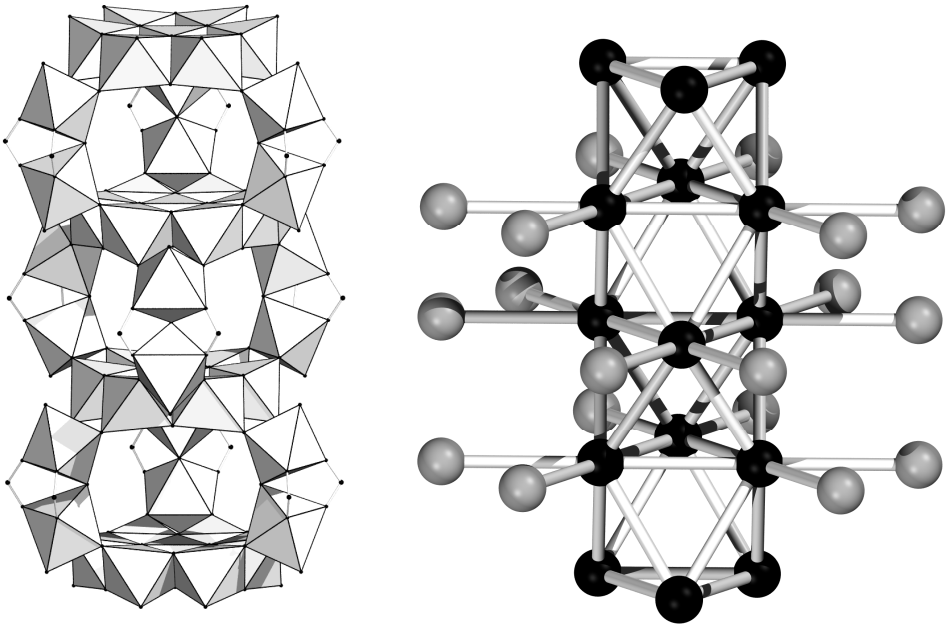

Fig. S10: Left: A fragment of the inorganic unit in CAU-6. Right: Corresponding representation of this infinite building unit. The central chain is emphasized in black while the nodes of the adjacent chains are emphasized in grey.

On every “level”, six linker molecules are coordinating pair wise and thus after merging these pairs into three distinct points, triangles are obtained which are alternating oriented at each level. The observed topology is the **ecf**-net (Fig. S11).

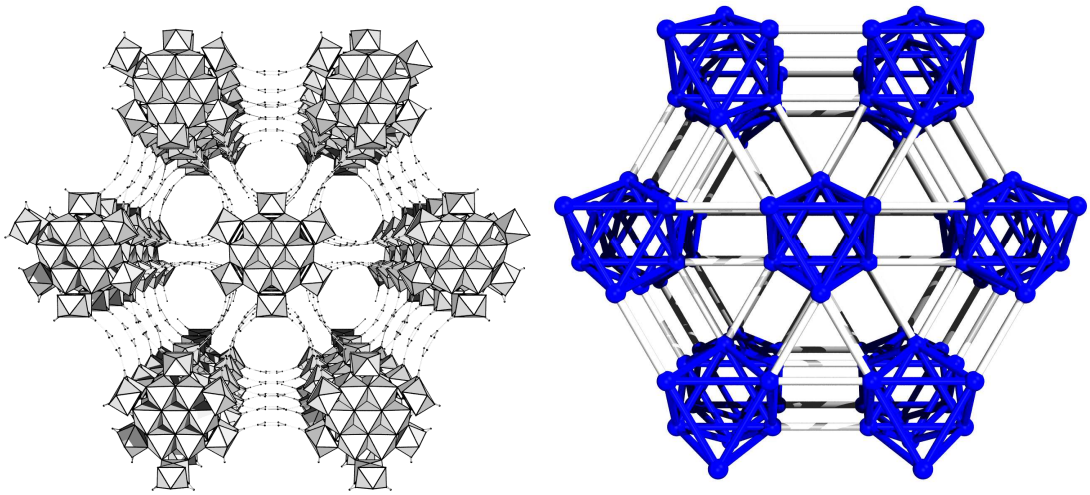

Fig. S11: Left: Framework structure of CAU-6. Right: Representation of the underlying **ecf**-net with the “linear” fragments corresponding to the Al-oxo-columns emphasized in blue. Intra-chain bonds are colored in blue, bonds representing the organic linker molecules are colored in grey.

Thus in all structures discussed herein, the approach presented in the paper resulted in accurate topological representations of the corresponding frameworks.