Supporting Information for:

A Tetratopic Phosphonic Acid for the Snythesis of Permanently Porous MOFs: Reactor Size-Dependent Product Formation and Crystal Structure Elucidation via Three-Dimensional Electron Diffraction

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Content

1	Table compounds containing linker molecules of similar geometry	2
2	Materials	5
3	High-Throughput Investigations	6
	3.1 Tables with exact amounts of starting materials employed in the high-throug studies	hput 6
	3.2 Graphical representation of the results of the high-throughput studies	13
	3.2.1 Discovery and synthesis optimisation of $[M(H_3DPBP)_2(H_2O)_4]$ (M ²⁺ =Ni, Co))13
;	3.3 Synthesis optimisation of $[Ni_2(H_4TPPE)(H_2O)_6] \cdot 4H_2O$ (CAU-46) $[Co_2(H_4TPPE)(H_2O)_4] \cdot 3H_2O$ (CAU-47)	and 17
4	NMR spectra and elemental analysis of H_8 TPPE and title compounds	19
5	Electron diffraction data and structure refinement	28
6	PXRD investigations	32
7	Structural details	37
8	Connolly surfaces	41
9	Topological analyses of CAU-46, CAU-47 and Co-CAU-48	43
10	Selected bond lengths and hydrogen bonds of the title compounds	45
11	1 Hydrogen bonding in CAU-46, CAU-47and M-CAU-48	49
12	2 Thermal properties	50
13	3 Sorption measurements	57
14	4 UV/Vis spectroscopy	59
15	5 IR spectroscopy	60
16	8 References	62

1 Table compounds containing linker molecules of similar geometry

Table S1: Overview of previously reported compounds obtained using tri- and tetratopic phosphonic acids as linker molecules. Compounds containing auxiliary ligands are excluded. The respective ligand for each number in column 1 is displayed in Fig. S1.

Linker	Compound	Porosity	Space group
Tritopic			
1	[Cu ₆ (L) ₂ (H ₂ O) ₈]·5.5H ₂ O ¹	Not measured	P1
1	$[Zn_3(L)(H_2O)_2] \cdot 2H_2O^2$	Not measured	Cmca
1	$[Zn_{2.5}(H)_{0.4-0.5}(L)(H_2O)_{1.9-2}(NH_4)_{0.5-0.6}]^3$	Not measured	lbam
1	[Zn _{2.5} (H) _{0.75} (L)(H ₂ O) ₂ (CH ₃ NH ₃) _{0.25}] ³	Not measured	lbam
1	$La(H_3L)(H_2O)_2]^4$	Not measured	P2 ₁ /c
2	[Cu ₃ (L)(H ₂ O) _{3.6}]·H ₂ O ⁵	Not measured	P2 ₁ /n
3	[Cu ₄ (H ₂ L) ₂ (H ₂ O) ₄] ⁵	Not measured	<i>P</i> 1
3	[Co ₆ (L) ₂ (H ₂ O) ₄] ⁵	Not measured	Pbca
3	[AI(H ₃ L)(H ₂ O)] ⁶	687 m ² g ⁻¹ (N ₂ , BET)	R3
4	[Sr ₂ (H ₂ L)(CH ₃ OH)(H ₂ O) ₄]	146 m ² g ⁻¹ (CO ₂)	P <u>1</u>
4	$[V_3O_3(OH)(H_3L)_2] \cdot 7.5H_2O^7$	Not measured	Pnma
4	$[Zr_3(H_3L)_4] \cdot 15H_2O^8$	Not porous	P <u>3</u> 1c
4	[M ₃ (H ₃ L) ₂ (H ₂ O) ₉ (C ₂ H ₆ SO) ₃] (M = Ni, Co) ⁹	Not measured	P6 ₃ /m
4	$[Zn_2(H_2L)(H_2O)_2] \cdot xH_2O^{10}$	0.4 mmol g ⁻¹ (CO ₂)	C2/c
5	[M ₄ (H ₂ L) ₂ (H ₂ O)]·H ₂ O (M=Ba, Sr) ¹¹	0.86 mmol g ⁻¹ (CO ₂)	
6	[Cu ₃ (L)(H ₂ O) ₃]·10H ₂ O ¹²	647 m²g⁻¹ (N₂, BET)	Ст
7	$[Zr(H_4L)_2] \cdot 10H_2O^{13}$	410 m ² g ⁻¹ (N ₂ , BET)	R3
Tetrahedral			
		100m ² m ⁻¹ (00.)	
ŏ	$[Uu_3(H_3L)(UH)(H_2U)_3] H_2U MeUH^4$	$198 \text{m}^2\text{g}^{-1}(\text{CO}_2)$	r2 ₁ /n

8	$[C_2py]_2[Zr_{3.5}(HL)F_9] \cdot 6.5H_2O^{15}$	572m ² g ⁻¹ (N ₂)	P2 ₁ /n
9	Zn ₂ (H ₄ L) ¹⁶	Not measured	C2/m
9	[C ₄ mpyr][Zr _{2.5} (H ₃ L)F ₆]·2.5H ₂ O ¹⁵	10m ² g ⁻¹ (N ₂)	Pbca
9	[C ₄ mpyr] ₂ [Zr _{1.5} (L) _{0.5} F ₄ ·6H ₂ O] ¹⁵	225m ² g ⁻¹ (N ₂)	I4/m
10	$Zn_2(H_4L)^{16}$	Not measured	<i>I</i> 2 ₁ 2 ₁ 2 ₁
10	[Cu ₂ (H ₄ L)]·2H ₂ O ¹⁶	Not measured	<i>P</i> 1
10	Zr(H ₄ L) ¹⁷	Not measured	P2 ₁ /c
Planar tetratopic			
11	[Y(H ₅ L)]·2.5H ₂ O ¹⁸	Not measured	P2 ₁ /c
11	[Ln(H ₅ L)]·2H ₂ O (Ln=Tb ³⁺ , Gd ³⁺) ¹⁹	Not measured	C2/c
11	$[La_4(H_6L)_2(H_4L)_2(H_8L)(H_2O)_{16}] \cdot 12H_2O^{21}$	Not measured	P4b2
12	$[Na_2Cu(H_4L)] \cdot (NH_2(CH_3)_2)_2^{20}$	Not measured	<i>P</i> 1
12	[M(Ni-H ₆ L)(H ₂ O)] (M=Ni, Mn, Co, Cd) ²²	0, 90, 145, 180 m²g ⁻¹ (N ₂ , BET)	PĪ
12	$[M_2(Ni-H_2L)(OH/F)_2] \cdot H_2O (M = Zr, Hf)^{21}$	970, 910 m ² g ⁻¹ (N ₂ , BET)	l4 ₁ /acd



Figure S1: Tri- and tetratopic phosphonic acid ligands employed for the synthesis of potentially porous MOFs.

2 Materials

 $Co(NO_3)_2 \cdot 6 H_2O$ (98 %, Merck), Ni(NO₃)₂ $\cdot 6 H_2O$ (97 %, Merck), MeOH (99 %, Walther), and dichloromethane (Walther) were used without further purification.

The linker 1,1,2,2-tetrakis[4-phosphonophenyl]ethylene (H_8 TPPE) was synthesized according to the procedure described in the manuscript. Starting with tetraphenylethylene (98 %, ABCR) and bromine (99 %, Merck) with following NiCl₂-catalyzed (97 %, Merck) phosphonylation in 1,3-Diisopropylbenzene (96 %, Sigma-Aldrich) using triethyl phosphite (98 %, Sigma-Aldrich) with following hydrolysis in conc. HCI (35 %, VWR chemicals).

3 High-Throughput Investigations

3.1 Tables with exact amounts of starting materials employed in the high-throughput studies

To investigate the influence of the counter ion the product formation, the following syntheses were carried out in high-throughput reactors with a maximum volume of 250 μ l and a filling volume of 200 μ l.

Table S2: High-throughput experiment, varying the concentrations and molar ratios using nickel nitrate (L = ligand). Results are shown in Figs. S2-S8.

L:M	M = Metal source L/µmol		1 mol/l metal $H_2O/\mu l$	
			salt solution/µl	
1:1	Ni(NO ₃) ₂ ·6H ₂ O	6	6	194
1:2	Ni(NO ₃) ₂ ·6H ₂ O	6	12	188
1:3	Ni(NO ₃) ₂ ·6H ₂ O	6	18	182
1:4	Ni(NO ₃) ₂ ·6H ₂ O	6	24	176
1:5	Ni(NO ₃) ₂ ·6H ₂ O	6	30	170
1:6	$Ni(NO_3)_2 \cdot 6H_2O$	6	36	164
2:2	$Ni(NO_3)_2 \cdot 6H_2O$	12	12	188
2:4	Ni(NO ₃) ₂ ·6H ₂ O	12	24	176
2:6	Ni(NO ₃) ₂ ·6H ₂ O	12	36	164
2:8	Ni(NO ₃) ₂ ·6H ₂ O	12	48	152
2:10	Ni(NO ₃) ₂ ·6H ₂ O	12	60	140
2:12	$Ni(NO_3)_2 \cdot 6H_2O$	12	72	128
3:3	$Ni(NO_3)_2 \cdot 6H_2O$	18	18	182
3:6	Ni(NO ₃) ₂ ·6H ₂ O	18	36	164
3:9	Ni(NO ₃) ₂ ·6H ₂ O	18	54	146
3:12	Ni(NO ₃) ₂ ·6H ₂ O	18	72	128
3:15	$Ni(NO_3)_2 \cdot 6H_2O$	18	90	110
3:18	Ni(NO ₃) ₂ ·6H ₂ O	18	108	92
2:1	Ni(NO ₃) ₂ ·6H ₂ O	12	6	194
3:1	Ni(NO ₃) ₂ ·6H ₂ O	18	6	194
4:1	Ni(NO ₃) ₂ ·6H ₂ O	24	6	194
4:2	Ni(NO ₃) ₂ ·6H ₂ O	24	12	188
6:2	Ni(NO ₃) ₂ ·6H ₂ O	36	12	188
8:2	Ni(NO ₃) ₂ ·6H ₂ O	42	12	188

Table S3: High-throughput experiment, varying the concentrations and molar ratios using nickel chloride (L = ligand). The formation of crystalline compounds was not observed.

L:M	M = Metal source	L/µmol	1 mol/l metal	H ₂ O/μl
1.1		6		10/
1.1		6	12	199
1.2		6	12	100
1.5		6	10	102
1.4 1.F		6	24	170
1.5		6	30	170
1:6		6	36	164
2:2	NICl ₂ ·6H ₂ O	12	12	188
2:4	NiCl₂·6H₂O	12	24	176
2:6	NiCl ₂ ·6H ₂ O	12	36	164
2:8	NiCl ₂ ·6H ₂ O	12	48	152
2:10	NiCl₂·6H₂O	12	60	140
2:12	NiCl ₂ ·6H ₂ O	12	72	128
3:3	NiCl ₂ ·6H ₂ O	18	18	182
3:6	NiCl ₂ ·6H ₂ O	18	36	164
3:9	NiCl₂·6H₂O	18	54	146
3:12	NiCl₂·6H₂O	18	72	128
3:15	NiCl ₂ ·6H ₂ O	18	90	110
3:18	NiCl ₂ ·6H ₂ O	18	108	92
2:1	NiCl ₂ ·6H ₂ O	12	6	194
3:1	NiCl ₂ ·6H ₂ O	18	6	194
4:1	NiCl ₂ ·6H ₂ O	24	6	194
4:2	NiCl ₂ ·6H ₂ O	24	12	188
6:2	NiCl ₂ ·6H ₂ O	36	12	188
8:2	NiCl ₂ ·6H ₂ O	42	12	188

L:M	M = Metal source	L/µmol	1 mol/l metal	H₂O/µl
1.1	$C_0(NO_2)_2 \cdot 6H_2O_2$	6		19/
1.1	$C_0(NO_3)_2 = 0 + 1_2 O$	6	12	194
1.2	$C_0(NO_3)_2 O I_2 O$	6	12	182
1.5	$C_0(NO_3)_2 O I_2 O$	6	24	176
1.4 1.F	$CO(NO_3)_2 \cdot OH_2O$	0	24	170
1:5	$CO(NO_3)_2 \cdot 6H_2O$	6	30	170
1:6	$CO(NO_3)_2 \cdot 6H_2O$	6	36	164
2:2	$Co(NO_3)_2 \cdot 6H_2O$	12	12	188
2:4	$Co(NO_3)_2 \cdot 6H_2O$	12	24	176
2:6	$Co(NO_3)_2 \cdot 6H_2O$	12	36	164
2:8	$Co(NO_3)_2 \cdot 6H_2O$	12	48	152
2:10	$Co(NO_3)_2 \cdot 6H_2O$	12	60	140
2:12	$Co(NO_3)_2 \cdot 6H_2O$	12	72	128
3:3	$Co(NO_3)_2 \cdot 6H_2O$	18	18	182
3:6	$Co(NO_3)_2 \cdot 6H_2O$	18	36	164
3:9	$Co(NO_3)_2 \cdot 6H_2O$	18	54	146
3:12	$Co(NO_3)_2 \cdot 6H_2O$	18	72	128
3:15	$Co(NO_3)_2 \cdot 6H_2O$	18	90	110
3:18	$Co(NO_3)_2 \cdot 6H_2O$	18	108	92
2:1	$Co(NO_3)_2 \cdot 6H_2O$	12	6	194
3:1	$Co(NO_3)_2 \cdot 6H_2O$	18	6	194
4:1	$Co(NO_3)_2 \cdot 6H_2O$	24	6	194
4:2	$Co(NO_3)_2 \cdot 6H_2O$	24	12	188
6:2	$Co(NO_3)_2 \cdot 6H_2O$	36	12	188
8:2	$Co(NO_3)_2 \cdot 6H_2O$	42	12	188

Table S4: High-throughput experiment, varying the concentrations and molar ratios using cobalt nitrate (L = ligand). Results are shown in Figs. S2-S8.

L:M	M = Metal source	L/µmol	1 mol/l metal salt solution/μl	H₂O/µI
1:1	CoCl ₂ ·6H ₂ O	6	6	194
1:2	CoCl ₂ ·6H ₂ O	6	12	188
1:3	CoCl ₂ ·6H ₂ O	6	18	182
1:4	CoCl ₂ ·6H ₂ O	6	24	176
1:5	CoCl ₂ ·6H ₂ O	6	30	170
1:6	CoCl ₂ ·6H ₂ O	6	36	164
2:2	CoCl ₂ ·6H ₂ O	12	12	188
2:4	CoCl ₂ ·6H ₂ O	12	24	176
2:6	CoCl ₂ ·6H ₂ O	12	36	164
2:8	CoCl ₂ ·6H ₂ O	12	48	152
2:10	CoCl ₂ ·6H ₂ O	12	60	140
2:12	CoCl ₂ ·6H ₂ O	12	72	128
3:3	CoCl ₂ ·6H ₂ O	18	18	182
3:6	CoCl ₂ ·6H ₂ O	18	36	164
3:9	CoCl ₂ ·6H ₂ O	18	54	146
3:12	CoCl ₂ ·6H ₂ O	18	72	128
3:15	CoCl ₂ ·6H ₂ O	18	90	110
3:18	CoCl ₂ ·6H ₂ O	18	108	92
2:1	CoCl ₂ ·6H ₂ O	12	6	194
3:1	CoCl ₂ ·6H ₂ O	18	6	194
4:1	CoCl ₂ ·6H ₂ O	24	6	194
4:2	CoCl ₂ ·6H ₂ O	24	12	188
6:2	CoCl ₂ ·6H ₂ O	36	12	188
8:2	CoCl ₂ ·6H ₂ O	42	12	188

Table S5: High-throughput experiment, varying the concentrations and molar ratios using cobalt chloride (L = ligand). The formation of crystalline compounds was not observed.

Table S6: High-throughput experiment, varying the concentrations and molar ratios using nickel and cobalt sulfate and cobalt acetate (L = ligand). The formation of crystalline compounds was not observed.

L:M	M = Metal source	L/µmol	1 mol/l metal salt solution/μl	H₂O/µl
2:2	NiSO ₄ ·6H ₂ O	12	12	188
2:4	NiSO ₄ ·6H ₂ O	12	24	176
2:6	NiSO ₄ ·6H ₂ O	12	36	164
2:8	NiSO ₄ ·6H ₂ O	12	48	152
2:10	NiSO ₄ ·6H ₂ O	12	60	140
2:12	NiSO ₄ ·6H ₂ O	12	72	128
3:3	NiSO ₄ ·6H ₂ O	18	18	182
3:6	NiSO ₄ ·6H ₂ O	18	36	164
3:9	NiSO ₄ ·6H ₂ O	18	54	146
3:12	NiSO ₄ ·6H ₂ O	18	72	128
3:15	NiSO ₄ ·6H ₂ O	18	90	110
3:18	NiSO ₄ ·6H ₂ O	18	108	92
2:2	CoSO ₄ ·7H ₂ O	12	12	188
2:4	CoSO ₄ ·7H ₂ O	12	24	176
2:6	CoSO ₄ ·7H ₂ O	12	36	164
2:8	CoSO ₄ ·7H ₂ O	12	48	152
2:10	CoSO ₄ ·7H ₂ O	12	60	140
2:12	CoSO ₄ ·7H ₂ O	12	72	128
3:3	CoSO ₄ ·7H ₂ O	18	18	182
3:6	CoSO ₄ ·7H ₂ O	18	36	164
3:9	CoSO ₄ ·7H ₂ O	18	54	146
3:12	CoSO ₄ ·7H ₂ O	18	72	128
3:15	CoSO ₄ ·7H ₂ O	18	90	110
3:18	CoSO ₄ ·7H ₂ O	18	108	92
2:2	Co(OAc) ₂ ·4H ₂ O	12	12	188
2:4	Co(OAc) ₂ ·4H ₂ O	12	24	176
2:6	Co(OAc) ₂ ·4H ₂ O	12	36	164
2:8	Co(OAc) ₂ ·4H ₂ O	12	48	152
2:10	Co(OAc) ₂ ·4H ₂ O	12	60	140
2:12	Co(OAc) ₂ ·4H ₂ O	12	72	128
3:3	Co(OAc) ₂ ·4H ₂ O	18	18	182
3:6	Co(OAc) ₂ ·4H ₂ O	18	36	164
3:9	Co(OAc) ₂ ·4H ₂ O	18	54	146
3:12	Co(OAc) ₂ ·4H ₂ O	18	72	128
3:15	Co(OAc) ₂ ·4H ₂ O	18	90	110
3:18	Co(OAc) ₂ ·4H ₂ O	18	108	92

L:M:Base	M = Metal source	L/µmol	1 mol/l metal salt	2 mol/l NaOH	H₂O/μl
			solution/µl	solution	
3:3:1	Ni(NO ₃) ₂ ·6H ₂ O	18	18	3	179
3:3:2	Ni(NO ₃) ₂ ·6H ₂ O	18	18	6	176
3:3:3	Ni(NO ₃) ₂ ·6H ₂ O	18	18	9	173
3:3:4	Ni(NO ₃) ₂ ·6H ₂ O	18	18	12	170
3:3:5	Ni(NO ₃) ₂ ·6H ₂ O	18	18	15	167
3:3:6	Ni(NO ₃) ₂ ·6H ₂ O	18	18	18	164
3:3:7	Ni(NO₃)₂·6H₂O	18	18	3	161
3:3:8	Ni(NO ₃) ₂ ·6H ₂ O	18	18	6	158
3:6:1	Ni(NO ₃) ₂ ·6H ₂ O	18	36	9	161
3:6:2	Ni(NO ₃) ₂ ·6H ₂ O	18	36	12	158
3:6:3	Ni(NO ₃) ₂ ·6H ₂ O	18	36	15	155
3:6:4	Ni(NO ₃) ₂ ·6H ₂ O	18	36	18	152
3:6:5	Ni(NO ₃) ₂ ·6H ₂ O	18	36	3	149
3:6:6	Ni(NO ₃) ₂ ·6H ₂ O	18	36	6	146
3:6:7	Ni(NO ₃) ₂ ·6H ₂ O	18	36	9	143
3:6:8	Ni(NO ₃) ₂ ·6H ₂ O	18	36	12	140
3:9:1	Ni(NO ₃) ₂ ·6H ₂ O	18	54	15	143
3:9:2	Ni(NO ₃) ₂ ·6H ₂ O	18	54	18	140
3:9:3	Ni(NO ₃) ₂ ·6H ₂ O	18	54	3	137
3:9:4	Ni(NO ₃) ₂ ·6H ₂ O	18	54	6	134
3:9:5	Ni(NO ₃) ₂ ·6H ₂ O	18	54	9	131
3:9:6	Ni(NO ₃) ₂ ·6H ₂ O	18	54	12	128
3:9:7	Ni(NO ₃) ₂ ·6H ₂ O	18	54	15	125
3:9:8	Ni(NO ₃) ₂ ·6H ₂ O	18	54	18	122

Table S7: High-throughput experiment, varying molar ratios and amount of base using nickel nitrate (L = ligand). Results are shown in Fig. S9.

L:M:Base	M = Metal source	L/µmol	1 mol/l metal salt	2 mol/l NaOH	H₂O/µl
			solution/µl	solution	
3:3:1	$Co(NO_3)_2 \cdot 6H_2O$	18	18	3	179
3:3:2	Co(NO ₃) ₂ ·6H ₂ O	18	18	6	176
3:3:3	$Co(NO_3)_2 \cdot 6H_2O$	18	18	9	173
3:3:4	$Co(NO_3)_2 \cdot 6H_2O$	18	18	12	170
3:3:5	Co(NO ₃) ₂ ·6H ₂ O	18	18	15	167
3:3:6	Co(NO ₃) ₂ ·6H ₂ O	18	18	18	164
3:3:7	$Co(NO_3)_2 \cdot 6H_2O$	18	18	3	161
3:3:8	$Co(NO_3)_2 \cdot 6H_2O$	18	18	6	158
3:6:1	$Co(NO_3)_2 \cdot 6H_2O$	18	36	9	161
3:6:2	$Co(NO_3)_2 \cdot 6H_2O$	18	36	12	158
3:6:3	$Co(NO_3)_2 \cdot 6H_2O$	18	36	15	155
3:6:4	$Co(NO_3)_2 \cdot 6H_2O$	18	36	18	152
3:6:5	$Co(NO_3)_2 \cdot 6H_2O$	18	36	3	149
3:6:6	$Co(NO_3)_2 \cdot 6H_2O$	18	36	6	146
3:6:7	$Co(NO_3)_2 \cdot 6H_2O$	18	36	9	143
3:6:8	Co(NO ₃) ₂ ·6H ₂ O	18	36	12	140
3:9:1	Co(NO ₃) ₂ ·6H ₂ O	18	54	15	143
3:9:2	$Co(NO_3)_2 \cdot 6H_2O$	18	54	18	140
3:9:3	$Co(NO_3)_2 \cdot 6H_2O$	18	54	3	137
3:9:4	$Co(NO_3)_2 \cdot 6H_2O$	18	54	6	134
3:9:5	$Co(NO_3)_2 \cdot 6H_2O$	18	54	9	131
3:9:6	Co(NO ₃) ₂ ·6H ₂ O	18	54	12	128
3:9:7	Co(NO ₃) ₂ ·6H ₂ O	18	54	15	125
3:9:8	$Co(NO_3)_2 \cdot 6H_2O$	18	54	18	122

Table S8: High-throughput experiment, varying molar ratios and amount of base using cobalt nitrate (L = ligand). Results are shown in Fig. S10.

3.2 Graphical representation of the results of the high-throughput studies In the following figures the variation of reaction parameters in the high-throughput studies

and the data evaluation are presented. The results are based on the PXRD measurements. The varied parameters are given in the respecting figure caption.



Figure S2: Discovery of [M(H₃DPBP)₂(H₂O)₄] (M²⁺=Ni, Co). Reaction trends discovered via HT methods using a 1 mol/l solution of M(NO₃)₂·6H₂O (M=Ni, Co) as metal source. Exact amounts of starting materials are given in Table S2 and S4.

 $[Ni(H_3DPBP)_2(H_2O)_4]$



Figure S3: SEM micrographs of the single crystals of $[Ni(H_3DPBP)_2(H_2O)_4]$ (1, left) and $[Co(H_3DPBP)_2(H_2O)_4]$ (**2**, right).

200 µm

After the discovery of $[Ni(H_3DPBP)_2(H_2O)_4]$ (1) and $[Co(H_3DPBP)_2(H_2O)_4]$ (2) additional experiments were carried out to optimize the reaction conditions. Thus reaction time and temperature as well as the metal salt source (counter ions as well as the use of solids or solutions) was investigated. Some of the results are summarized in the following figures.



Figure S4: Influence of shortened reaction time (48 to 12 hours) and lowered reaction temperature (180 to 140°C) on the product formation. Exact amounts of starting materials are given in Tables S2 and S4. The formation of title compounds could not be observed.



Figure S5: Influence of shortened reaction time (48 to 24 hours) and lowered reaction temperature (180 to 160 °C) on the product formation. Only reactions at higher concentrations were carried out. Exact amounts of starting materials are given in Tables S2 and S4. These reaction conditions lead to less crystalline reaction products of **1** and **2**.



Figure S6: Influence of metal salt source (solution or solid) on the product formation of **1** and **2**. Exact amounts of starting materials are given in Table S2 and S4.



Figure S7: Influence of the temperature program (extended heating and cooling from 6 to 48 hours) on the product formation of **1** and **2**. Exact amounts of starting materials are given in Table S2 and S4.

The reaction conditions leading to the formation of $[M(H_3DPBP)_2(H_2O)_4]$ with $M^{2+}=Ni$, Co seems to depend on various parameters. Therefore, the reproducibility of the synthesis was tested using the previously optimized molar ratios (linker : metal = 3 : 9).



Figure S8: Results of two sets of identical reactions carried out in 250 μ l reactors. The major reaction product is indicated by the larger section of the circle.

The results of these syntheses demonstrate that the reactions are not fully reproducible. In addition to compounds **1** and **2**, two additional reaction products are observed, which are described in the following section. The reactions seem to be highly sensible to small changes in the reaction parameters. Since Teflon reactors were used, these could be the critical factor. Teflon is known to be microporous and the reactors could contain irremovable trace contamination that could influence the product formation.

3.3 Synthesis optimisation of $[Ni_2(H_4TPPE)(H_2O)_6] \cdot 4H_2O$ (CAU-46) and $[Co_2(H_4TPPE)(H_2O)_4] \cdot 3H_2O$ (CAU-47)

The metal nitrates and a linker : metal ratio of 3 : 9 were chosen as optimal synthesis parameters for upscaling reactions in 2ml autoclaves, which resulted in the discovery of CAU-46 and CAU-47. Using the respective metal nitrates as metal source, the following reaction trends could be discovered: To prevent in situ oxidation of the ligand the pH of the reaction mixture was varied. Thus aqueous NaOH (2 mol/l) was added in different amounts. First reactions were carried out in the smallest reactors.



Figure S9: Influence of the addition of NaOH on the product formation of CAU-46. Exact amounts of starting materials are given in Table S7.



Figure S10: Influence of the addition of NaOH on the product formation of Co-CAU-48. Exact amounts of starting materials are given in Table S8.



Figure S11: Final reproduction experiments for CAU-46 and CAU-47. All samples contain minor amount of **1** and **2**. Phase purity was achieved via stirring in water, as described in the experimental section. Exact amounts of starting materials are given in the experimental section of the manuscript.

Table S9: High-throughput experiment, varying the metal source using the optimized reaction parameters (6-48-6, T=180 $^{\circ}$ C). For each reaction product, the formation of crystalline compounds was observed. The PXRD pattern of each product is shown in Fig. S12.

L:M	M = Metal source	L/µmol	1 mol/l metal salt solution/μl	H₂O/µl
3:9	Ca(NO ₃) ₂ ·4H ₂ O	18	54	146
3:9	Mg(NO ₃) ₂ ·6H ₂ O	18	54	146
3:9	Sr(NO ₃) ₂	18	54	146
3:9	Ba(NO ₃) ₂	18	54	146
3:9	Fe(II)Cl ₂ ·4H ₂ O	18	54	146
3:9	Zn(NO ₃) ₂ ·6H ₂ O	18	54	146
3:9	Cu(NO ₃) ₂ ·3H ₂ O	18	54	146
3:9	SnSO ₄	18	54	146

Table S10: High-throughput experiment, varying the amount of base and NaF using the optimized reaction parameters (6-48-6, T=180 °C) and $ZrOCI_2 \cdot 6H_2O$ as metal source. For each reaction product, the formation of crystalline compounds was observed. Reaction parameters highlighted in yellow led to crystalline products shown in Fig. S12.

L:M:NaF:Base	M = Metal	L/µmol	1 mol/l metal salt	2 mol/l NaOH	NaF/mg	H₂O/µl
	source		solution/µl	solution		
1:1:4:20	ZrOCl ₂ ·6H ₂ O	6	6	12	5	182
<mark>1:2:4:20</mark>	<mark>ZrOCl₂·6H₂O</mark>	<mark>6</mark>	<mark>12</mark>	<mark>12</mark>	<mark>5</mark>	<mark>176</mark>
1:3:4:20	ZrOCl ₂ ·6H ₂ O	6	18	12	5	170
1:4:4:20	ZrOCl ₂ ·6H ₂ O	6	24	12	5	164
1:5:4:20	ZrOCl ₂ ·6H ₂ O	6	30	12	5	258
1:6:4:20	ZrOCl ₂ ·6H ₂ O	6	36	12	5	152
1:1:8:20	ZrOCl ₂ ·6H ₂ O	6	6	24	5	170
1:2:8:20	ZrOCl ₂ ·6H ₂ O	6	12	24	5	164
1:3:8:20	ZrOCl ₂ ·6H ₂ O	6	18	24	5	158
1:4:8:20	ZrOCl ₂ ·6H ₂ O	6	24	24	5	152
1:5:8:20	ZrOCl ₂ ·6H ₂ O	6	30	24	5	146
1:6:8:20	ZrOCl ₂ ·6H ₂ O	6	36	24	5	140
1:1:4:40	ZrOCl ₂ ·6H ₂ O	6	6	12	10	182
1:2:4:40	ZrOCl ₂ ·6H ₂ O	6	12	12	10	176
1:3:4:40	ZrOCl ₂ ·6H ₂ O	6	18	12	10	170
1:4:4:40	ZrOCl ₂ ·6H ₂ O	6	24	12	10	164
<mark>1:5:4:40</mark>	ZrOCl ₂ ·6H ₂ O	<mark>6</mark>	<mark>30</mark>	<mark>12</mark>	<mark>10</mark>	<mark>258</mark>
1:6:4:40	ZrOCl ₂ ·6H ₂ O	6	36	12	10	152
1:1:8:40	ZrOCl ₂ ·6H ₂ O	6	6	24	10	170
1:2:8:40	ZrOCl ₂ ·6H ₂ O	6	12	24	10	164
1:3:8:40	ZrOCl ₂ ·6H ₂ O	6	18	24	10	158
1:4:8:40	ZrOCl ₂ ·6H ₂ O	6	24	24	10	152
1:5:8:40	ZrOCl ₂ ·6H ₂ O	6	30	24	10	146
1:6:8:40	ZrOCl ₂ ·6H ₂ O	6	36	24	10	140
1:1:4:60	ZrOCl ₂ ·6H ₂ O	6	6	12	15	182
1:2:4:60	ZrOCl ₂ ·6H ₂ O	6	12	12	15	176
1:3:4:60	ZrOCl ₂ ·6H ₂ O	6	18	12	15	170
1:4:4:60	ZrOCl ₂ ·6H ₂ O	6	24	12	15	164
1:5:4:60	ZrOCl ₂ ·6H ₂ O	6	30	12	15	258
1:6:4:60	ZrOCl ₂ ·6H ₂ O	6	36	12	15	152
1:1:8:60	ZrOCl ₂ ·6H ₂ O	6	6	24	15	170
1:2:8:60	ZrOCl ₂ ·6H ₂ O	6	12	24	15	164
1:3:8:60	ZrOCl ₂ ·6H ₂ O	6	18	24	15	158
1:4:8:60	ZrOCl ₂ ·6H ₂ O	6	24	24	15	152
1:5:8:60	ZrOCl ₂ ·6H ₂ O	6	30	24	15	146
1:6:8:60	ZrOCl ₂ ·6H ₂ O	6	36	24	15	140
1:1:4:80	ZrOCl ₂ ·6H ₂ O	6	6	12	20	182
1:2:4:80	ZrOCl ₂ ·6H ₂ O	6	12	12	20	176
1:3:4:80	ZrOCl ₂ ·6H ₂ O	6	18	12	20	170
1:4:4:80	ZrOCl ₂ ·6H ₂ O	6	24	12	20	164
1:5:4:80	ZrOCl ₂ ·6H ₂ O	6	30	12	20	258
1:6:4:80	ZrOCl ₂ ·6H ₂ O	6	36	12	20	152
1:1:8:80	ZrOCl ₂ ·6H ₂ O	6	6	24	20	170
1:2:8:80	ZrOCl ₂ ·6H ₂ O	6	12	24	20	164

1:3:8:80	ZrOCl ₂ ·6H ₂ O	6	18	24	20	158
1:4:8:80	ZrOCl ₂ ·6H ₂ O	6	24	24	20	152
1:5:8:80	ZrOCl ₂ ·6H ₂ O	6	30	24	20	146
1:6:8:80	ZrOCl ₂ ·6H ₂ O	6	36	24	20	140



Figure S12: PXRD patterns of the reaction products obtained by using other divalent metal ions as well as Zr^{4+} salts. Synthetic parameters are given in Tables S9 and S10.

Table S11: High-throughput experiment, varying the filling level while keeping the concentration constant and using the optimized reaction parameters (6-48-6, T=180 °C). Teflon inserts with a total volume of 2 ml were used to screen for influences of the autogenous pressure. To minimize influences of trace impurities in the Teflon walls, completely new Teflon inserts were used. Possible evaporation of solvent from the reactor was controlled via measuring the filling level with a slide gauge before and after the reaction.

L:M	M = Metal source	L/µmol	1 mol/l metal	H₂O/µl	Reaction	Initial	Filing level
			sait solution/µi		ρισααεί	level/mm	reaction/mm
3:9	Co(NO ₃) ₂ ·6H ₂ O	18	51	146	Co-CAU-48	3	2ª
3:9	$Co(NO_3)_2 \cdot 6H_2O$	27	87	219	Co-CAU-48	3	2 ª
3:9	$Co(NO_3)_2 \cdot 6H_2O$	36	108	292	2	2.5	3ª
3:9	$Co(NO_3)_2 \cdot 6H_2O$	45	135	365	CAU-47	4	4
3:9	$Co(NO_3)_2 \cdot 6H_2O$	54	162	438	CAU-47	5	5
3:9	$Co(NO_3)_2 \cdot 6H_2O$	63	189	511	CAU-47	6	5.5
3:9	$Co(NO_3)_2 \cdot 6H_2O$	72	216	584	CAU-47	6.5	6
3:9	$Co(NO_3)_2 \cdot 6H_2O$	81	243	657	CAU-47	7	7
3:9	$Co(NO_3)_2 \cdot 6H_2O$	90	270	730	CAU-47	8	8
3:9	$Co(NO_3)_2 \cdot 6H_2O$	99	297	803	CAU-47	9	9
3:9	$Co(NO_3)_2 \cdot 6H_2O$	108	324	876	CAU-47	10	9.5
3:9	$Co(NO_3)_2 \cdot 6H_2O$	117	351	949	CAU-47	10.5	10
3:9	$Co(NO_3)_2 \cdot 6H_2O$	126	378	1022	CAU-47	11	11
3:9	$Co(NO_3)_2 \cdot 6H_2O$	135	405	1095	CAU-47	12	12
3:9	$Co(NO_3)_2 \cdot 6H_2O$	144	432	1168	CAU-47	12.5	13.5
3:9	$Co(NO_3)_2 \cdot 6H_2O$	153	459	1241	CAU-47	13.5	13
3:9	$Co(NO_3)_2 \cdot 6H_2O$	162	486	1314	CAU-47	14	14
3:9	$Co(NO_3)_2 \cdot 6H_2O$	171	513	1387	CAU-47	15	15

^aDue to the small amount of solvent, the bottom of the Teflon inlet was not completely covered.

4 NMR spectra and elemental analysis of H₈TPPE and title compounds

In the following sections, the NMR spectra for the linker molecule and its precursor as well as the spectra of dissolved title compounds are presented. All samples were dissolved in 10%NaOD/H₂O under ultrasonication (except for TBPE, which was dissolved in CDCl₃).

4.1 NMR spectrum of TBPE (brominated precursor of H₈TPPE)



Figure S13: ¹H-NMR-spectrum of tetrabromophenylethylene.

 $^1\text{H-NMR}$ (400 MHz, 300 K, CDCl_3): $\delta\text{=}7.27$ (m, 8H), 6.87 (m, 7.74 H), 5.32 (s, 0. H) ppm. 1.57 (s, 0.49, H_2O).

4.2 NMR spectra of the linker molecule H₈L



Figure S14: ¹H-NMR-spectrum of the linker molecule H₈L.

¹H-NMR (400 MHz, 300 K, NaOD/D₂O): δ=7.12 (dd, J=11.4/8.0 Hz, 8H, 2), 6.85 (m, 0.54 H), 6.78 (dd, J=8.2 Hz, 8H, 3), 3.40 (m, 0.14 H), 0.77 (m, 0.25 H), 4.80 (H₂O) ppm.



Figure S15: ¹³C-NMR-spectrum of the linker molecule H₈L.

¹³C-NMR (101 MHz, 300 K, NaOD/D₂O): δ=143.73 (d, 4J=2.9 Hz, C4), 140.67 (s, C5), 139.18 (d, 1J=167 Hz, C1), 130.13 (d, 2J=12.9 Hz, C2), 129.43 (d, 3J=8.1 Hz, C3), 127.82, 61.16, 15.64 ppm.



Figure S16: ³¹P-NMR-spectrum of the linker molecule H_8L .

³¹P-NMR (162 MHz, 300 K, NaOD/D₂O): δ=15.92, 11.80, 12.31/11.28 (1 J=167 Hz) ppm.

4.3 NMR spectra of $[Ni(H_3DPBP)_2(H_2O)_4]$ (1).



Figure S17: ¹H-NMR-spectrum of **1** ([Ni(H₃DPBP)₂(H₂O)₄]) dissolved in NaOD/D₂O. ¹H-NMR (400 MHz, 300 K, NaOD/D₂O): δ = 7.46-7.34 (m, 8H, C2,3), 4.84 (H₂O) ppm.



Figure S18: ¹³C-NMR-spectrum of **1** ([Ni(H₃DPBP)₂(H₂O)₄]) dissolved in NaOD/D₂O.

¹³C-NMR (101 MHz, 300 K, NaOD/D₂O): δ = 200.47 (s, C5), 146.04(d, C1), 136.58 (s, C4), 129.74 (m, C2,3) ppm.



Figure S19: ³¹P-NMR-spectrum of **1** ([Ni(H₃DPBP)₂(H₂O)₄]) dissolved in NaOD/D₂O.

 $^{31}\text{P-NMR}$ (162 MHz, 300 K, NaOD/D2O): δ = 13.55, 12.14 (4 P, PO_3H2), 12.64/11.63 (PO_3H2) ppm.

4.4 NMR-spectra of CAU-46 ([Ni₂(H₄TPPE)(H₂O)₆]·4H₂O).



Figure S20: ¹H-NMR-spectrum of CAU-46 dissolved in NaOD/D₂O.

¹H-NMR (400 MHz, 300 K, NaOD/D₂O): δ = 7.03 (dd, J=11.5/8.2 Hz, 8H, 2), 6.69 (dd, J = 8.2 Hz, 8H, 3) ppm. 4.83 (H₂O)



Figure S21: ¹³C-NMR-spectrum of CAU-46 dissolved in NaOD/D₂O.

¹³C-NMR (101 MHz, 300 K, NaOD/D₂O): δ=143.63 (d, 4J=2.8 Hz, C4), 140.60 (s, C5), 138.63 (d, 1J=167 Hz, C1), 130.06 (t, 2J=12.2 Hz, C2), 129.35 (t, 3J=9.3 Hz, C3), 127.82, 61.16, 15.64 ppm.



Figure S22: ³¹P-NMR-spectrum of CAU-46 dissolved in NaOD/D₂O.

 $^{31}\text{P-NMR}$ (162 MHz, 300 K, NaOD/D_2O): $\delta\text{=}11.72,\ 12.33/11.20$ (1J=167 Hz), 11.56, 10.31 ppm.

4.5 NMR-spectra of CAU-47 ([$Co_2(H_4TPPE)(H_2O)_4$]·3H₂O).



Figure S23: ¹H-NMR-spectrum of CAU-47 dissolved in NaOD/D₂O.

¹H-NMR (400 MHz, 300 K, NaOD/D₂O): δ =7.47 (m), 7.12 (d), 7.08 (dd, J=11.2/8.0 Hz 8H, 2), 6.99 (m), 6.73 (dd, J = 2.6/8.2 Hz, 8H, 3) ppm. 4.82 (H₂O)



Figure S24: ¹³C-NMR-spectrum of CAU-47 dissolved in NaOD/D₂O.

¹³C-NMR (101 MHz, 300 K, NaOD/D₂O): δ=143.67 (d, 4J=2.9 Hz, C4), 140.63 (s, C5), 139.14 (d, 1J=167 Hz, C1), 130.12 (m, C2), 129.42 (m, C3), 126.86, 74.30 ppm.



Figure S25: ³¹P-NMR-spectrum of CAU-47 dissolved in NaOD/D₂O.

5 Electron diffraction data and structure refinement

Specimens for TEM studies were prepared by suspending a small amount of each respective compound in ethanol, which was then drop-cast onto a copper grid covered with a holey carbon film. Each prepared grid was then put into a Gatan 914 cryo-transfer holder and cooled down to approximately 170 K before being introduced into the ultra-high vacuum of the TEM. Once inside the TEM column, a temperature of 96 K was maintained for each sample. Three-dimensional electron diffraction data were collected using a JEOL JEM-2100 TEM operating at 200 kV, equipped with a Timepix detector from Amsterdam Scientific Instruments, while continuously rotating the crystal at 0.45° s⁻¹. The experiments were carried out using Instamatic,²³ with data reduction being done in XDS.²⁴ The acquired intensities were then used to solve the structure of each compound with SHELXT,²⁵ with a subsequent least-squares refinement in SHELXL,²⁶ using electron scattering factors extracted from SIR2014.²⁷

Prior to Rietveld refinement, the tilted phenyl rings were constrained to ideal geometry via AFIX commands.

The thus acquired structural model for **CAU-46** was further refined against PXRD data using TOPAS academics.²⁸ The phenyl rings of the linker molecule were refined as rigid bodies while all other atoms were freely refined using element-specific temperature factors and distance restraints. Furthermore, a preferred orientation along the *a*-axis had to be taken into account until the refinement converged. The most important crystallographic parameters are shown in Table 2 in the manuscript while the final Rietveld plot is shown in Figure 6, also in the manuscript.

The structure of **CAU-47** was also refined against PXRD data using a model obtained from TEM experiments. Again, the phenyl rings were treated as rigid bodies while all other atoms were freely refined using one general temperature factor and only distance restraints. As in the case of CAU-46, a preferred orientation along the *a*-axis also had to be taken into account for CAU-47 until the refinement converged. The most important crystallographic parameters are shown in Table 2 in the manuscript while the final Rietveld plot is shown in Figure 6, also in the manuscript.



Figure S26: Crystal of CAU-46, studied using three-dimensional electron diffraction (top left) as well as reciprocal space projections along a*, b* and c*.



Figure S27: Crystal of CAU-47, studied using three-dimensional electron diffraction (top left) as well as reciprocal space projections along a*, b* and c*.



Figure S28: One of the three Co-CAU-48 crystals which were studied using threedimensional electron diffraction (top left) as well as reciprocal space projections along a*, b* and c*. For the subsequent refinement, all three datasets were merged.

ED Deremeter			
ED Parameter	CAU-46	CAU-4/	CO-CAU-48
Empirical formula	C ₂₆ Ni ₂ O ₁₈ P ₄	$C_{26}Co_2O_{15}P_4$	$C_{26}Co_2O_{12}P_4$
Wavelength	0.0251 Å	0.0251 Å	0.0251 Å
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c (No. 15)	C2/c (No. 15)	<i>P</i> 1(No. 2)
Unit cell dimensions	<i>a</i> = 29.26 Å	<i>a</i> = 30.42 Å	<i>a</i> = 10.43 Å
	<i>b</i> = 12.03 Å	<i>b</i> = 10.47 Å	<i>b</i> = 12.13 Å
	<i>c</i> = 9.98 Å,	c = 11.036 Å,	c = 14.28 Å,
	β = 96.90	β = 90.59	<i>α</i> = 99.33°
			β = 92.56°
			γ = 95.53°
Volume	3489 Å ³	3515 Å ³	1772 Å ³
Z	4	4	2
Index ranges	$-33 \le h \le 34$	$-32 \leq h \leq 30$	-12 ≤ <i>h</i> ≤ 12
	-15 ≤ <i>k</i> ≤ 14	-13 ≤ <i>k</i> ≤ 12	-15 ≤ <i>k</i> ≤ 15
	-12 ≤ <i>I</i> ≤ 12	-13 ≤ / ≤ 13	-16 ≤ <i>l</i> ≤ 16
Reflections collected	7138	5879	6603
Independent reflections	2476	2088	3797
	[R(int) = 0.2018]	[R(int) = 0.2089]	[R(int) = 0.1921]
Completeness (to 0.8 Å resolution)	70 %	59 %	82 %
R_1 (ED model) [I > 2 σ (I)]	0.2398	0.3049	0.1929

Table S12: Crystal parameters, as determined by electron diffraction.

6 PXRD investigations

To confirm phase purity PXRD measurements were carried out. First, PXRD patterns of CAU-46 and -47 before and after the washing procedure are compared to the calculated patterns of **1** and **2**. Second, Pawley refinements are shown to demonstrate phase purity for the final products. Third, the experimental PXRD patterns of **1**, **2** and M-CAU-48 are compared to their theoretical patterns.



Figure S29: PXRD patterns of as synthesized (black) and washed (blue) CAU-46 as well as compound **1** (red).



Figure S30: PXRD patterns of as synthesized (black) and washed (blue) CAU-47 as well as compound **2** (red).



Figure S31: Pawley-Fit of Ni-CAU-48. The observed PXRD pattern (λ = 1.5405 Å) (black), the calculated curve (red), and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks.



Figure S32: Pawley-Fit of Co-CAU-48. The observed PXRD pattern (λ = 1.5405 Å) (black), the calculated curve (red), and the difference plot (blue) are shown. The allowed peak positions are marked as black ticks.



Figure S33: Measured and calculated PXRD pattern of **1** [Ni(H₃DPBP)₂(H₂O)₄].



Figure S34: Measured and calculated PXRD pattern of **2** [Co(H₃DPBP)₂(H₂O)₄].



Figure S35: Measured and calculated PXRD pattern of Ni-CAU-48. The theoretical pattern was calculated using the model obtained by electron diffraction and using the cell parameters from a Pawley-refinement (Fig. S31) and a subsequent force-field optimization.



Figure S36: Measured and calculated PXRD pattern of Co-CAU-48. The theoretical pattern was calculated using the model obtained by electron diffraction and using the cell parameters from a Pawley-refinement (Fig. S32) and a subsequent force-field optimization.

7 Structural details

In the following section, structural details of the title compounds are given in order to provide a better understanding of the structures.



Figure S37: Asymmetric unit of **1** [Ni(H₃DPBP)₂(H₂O)₄]. Ellipsoids are drawn at the 50% probability level. Bond lengths are provided in Table S13.



Figure S38: Asymmetric unit of **2** $[Co(H_3DPBP)_2(H_2O)_4]$. Ellipsoids are drawn at the 50% probability level. Bond lengths are provided in Table S15.



Figure S39: Asymmetric unit of CAU-46. Bond lengths are provided in Table S17.



Figure S40: Asymmetric unit of CAU-47. Bond lengths are provided in Table S19.



Figure S41: Asymmetric unit of Co-CAU-48. Bond lengths are provided in Table S21.



Figure S42: Crystal structure of a) CAU-46, a) coordination environment of Ni^{2+} , b) edgesharing dimer Ni_2O_{10} , surrounded by phosphonate groups, and c) 3D porous network of CAU-46, view along [001]. General colour scheme: C (black), O (red), P and P-O- tetrahedra (violet), Ni and Ni-O-polyhedra (green).



Figure S43: Crystal structure of CAU-47, a) coordination environment of Co^{2+} , b) chain of edge- and corner-sharing CoO_6 octahedra, coordinated by phosphonate groups, and c) 3D porous network of CAU-47, view along [001]. General colour scheme: C (black), O (red), P and P-O-tetrahedra (violet), Co and Co-O-polyhedra (light blue).



Figure S44: Crystal structure of Co-CAU-48, a) repeating unit of the inorganic layer, b) inorganic layer of Co-CAU-48, c) 3D porous network of Co-CAU-48, view along [100], and d) 3D porous network of Co-CAU-48, view along [010]. General colour scheme: C (black), O(red), P and P-O-tetrahedra (violet), Co and Co-O-polyhedra (light blue).



Figure S45: Comparison of ligand shape, inorganic building unit and overall structure of the herein presented CAU-46 vs. the previously reported Ni-CAU-29.²⁰

8 Connolly surfaces

For a better understanding of the pore geometry, Connolly surfaces were calculated using the program Materials Studio.²⁹



Figure S46: Connolly surface of CAU-46. For the generation of the surface, a water molecule (diameter: 2.6 Å) was employed as a probe molecule.



Figure S47: Connolly surface of CAU-47. For the generation of the surface, a water molecule (diameter: 2.6 Å) was employed as a probe molecule.



Figure S48: Connolly surface of Co-CAU-48. For the generation of the surface, a water molecule (diameter: 2.6 Å) was employed as a probe molecule.

9 Topological analyses of CAU-46, CAU-47 and Co-CAU-48

To better understand the framework structures the underlying nets were determined.

For all of the structures, the phosphorous atoms of the TPPE ligands were chosen as points of extensions, which were then used for deconstructing the frameworks into their underlying nets. For CAU-46, the nickel dimer can be represented as a single 4-coordinated node, owing to the two coordinating phosphonate groups for each Ni²⁺ ion. The TPPE ligand can be described as a single 4-c node as well, giving the binodal 4,4-c net **pts** (where the high-symmetry form has a space-group symmetry of *P*4₂/*mmc*). A similar deconstruction was performed for CAU-47, which contains an infinite rod-shaped IBU. By linking up the coordinating phosphonate groups for each cation, the IBU can be treated as a rod made up of edge-sharing tetrahedra. The representation of the TPPE ligand will however be different in this case, as to stay consistent with previous topological analyses of MOFs with infinite IBUs, leading to the treatment of the TPPE ligand as four 3-c nodes. The rod-shaped IBU of the second cobalt-based MOF, M-CAU-48 can also be deconstructed into tetrahedra, specifically as alternating pairs of corner-/edge-sharing tetrahedra. As in CAU-47, the TPPE ligand is designated as four 3-c nodes, giving an octanodal net.



Figure S49: Tiling of CAU-46, exhibiting the pts net.



Figure S50: Tiling of CAU-47. The topological analysis of this representation gives a point symbol of $\{3^3.8^2.9\}\{3^9.4^8.5^4.8^2.9^5\}\{4.8^2\}_2$. The net seems to be previously undescribed and shows a natural tiling with a transitivity of 4(10)(10)4, i.e. 4 vertices, 10 edges, 10 faces, and 4 tiles.



Figure S51: Tiling of Co-CAU-48. The point symbol for this previously undescribed net is $\{3^3.8^2.9\}\{3^6.4^4.5^4.6.8^5.9\}\{3^6.4^4.8^3.9^2\}\{3^9.4^8.5^4.8^4.9^3\}\{4.8^2\}_4$. Three different tilings can be found for the net, where that of lowest complexity has a transitivity of 8(19)(16)6.

10 Selected bond lengths and hydrogen bonds of the title compounds

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Ni1	O2	2.005(1)	P1	01	1.525(2)
	08	2.082(2)		O2	1.488(2)
	O9	2.066(2)		O3	1.561(2)
				C1	1.791(2)
			P2	O5	1.525(2)
				O6	1.558(2)
				07	1.493(2)
				C11	1.791(2)

Table S13: Selected bond lengths [Å] in **1** ($[Ni(H_3DPBP)_2(H_2O)_4]$).

Table S14: Hydrogen bonds in 1 ([Ni(H₃DPBP)₂(H₂O)₄]).

Donor	Acceptor	D-H [Å]	D…A [Å]	D-H…A [°]
O3	07	0.74(3)	2.608(3)	164(4)
O5	01	0.93(3)	2.501(3)	169(3)
O6	01	0.88(4)	2.602(3)	176(3)
O9	07	0.81(4)	2.836(3)	167(4)
O8	07	0.80(4)	2.781(3)	155(4)

Table S15: Selected bond lengths [Å] in 2 ([Co(H₃DPBP)₂(H₂O)₄]).

Atom 1	Atom 2	d [Å]	Atom 1 A	tom 2	d [Å]
Co1	01	2.023(3)	P1	01	1.477(4)
	07	2.115(4)		O2	1.546(4)
	O8	2.121(4)		O3	1.523(4)
				C1	1.787(6)
			P2	O4	1.525(4)
				O5	1.544(4)
				O6	1.487(4)
				C11	1.788(6)

Donor	Acceptor	D-H [Å]	D…A [Å]	D-H…A [°]
02	O6	0.82	2.604(5)	157.1
O5	O3	0.82	2.599(5)	172.6
O4	O3	0.82	2.499(5)	147.5
O8	O6	0.88	2.760(6)	125.9
07	O5	0.85	2.900(6)	139.1

Table S16: Hydrogen bonds in **2** ($[Co(H_3DPBP)_2(H_2O)_4]$).

Table S17: Selected bond lengths [Å] in CAU-46.

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Ni1	OW1	2.116(18)	P1	011	1.55(2)
	OW2	2.128(17)		012	1.52(2)
	OW3	2.173(18)		O13	1.563(19)
	O11	2.05(2)		C11	1.812(11)
	O23	2.02(2)	P2	O21	1.579(19)
	O23	2.116(18)		O22	1.507(18)
				O23	1.53(2)
				C24	1.833(10)

Table S18: Possible hydrogen bonds based on donor-acceptor distances in CAU-46.

Donor	Acceptor	D…A [Å]
OW1	O12	2.70(2)
	O23	2.90(2)
	O23	2.94(3)
OW2	O11	2.96(3)
	O12	2.72(3)
	O21	2.76(3)
	O22	2.82(3)
OW3	O11	2.86(3)
	O12	2.88(2)
	O13	2.94(2)
	O23	2.89(2)

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Co1	OW1	2.24(6)	P1	01	1.53(8)
	OW2	2.20(3)		02	1.54(7)
	01	2.13(8)		O3	1.47(7)
	O1	2.18(6)		C11	1.80(4)
	O3	1.98(6)	P2	O4	1.50(6)
	O4	2.17(6)		O5	1.47(6)
				O6	1.57(5)
				C21	1.82(4)

Table S19: Selected bond lengths [Å] in CAU-47.

Table S20: Possible hydrogen bonds based on donor-acceptor distances in CAU-47.

Donor	Acceptor	D…A [Å]
OW1	O1	2.99(8)
	O2	2.98(8)
	O5	2.63(8)
OW2	O3	2.79(7)
	O6	2.50(7)

Table S21: Selected bond lengths [Å] for Co-CAU-48. Distances were calculated from the initial electron diffraction data.

Atom 1	Atom 2	d [Å]	Atom 1	Atom 2	d [Å]
Co1	01	1.965(16)	P1	01	1.540(15)
	O5	2.012(8)		02	1.613(13)
	08	2.046(10)		O3	1.568(11)
	O11	1.969(9)		C1	1.854(11)
Co2	O3	1.934(12)	P2	O4	1.551(11)
	O4	1.966(10)		O5	1.545(9)
	O9	2.020(13)		O6	1.578(11)
	O9	2.075(8)		C12	1.819(16)
			P3	07	1.611(13)
				08	1.522(11)
				O9	1.608(13)
				C18	1.854(12)
			P4	O10	1.581(10)
				011	1.538(97)
				012	1.625(9)
				C24	1.796(17)

Table S22: Possible hydrogen bonds based on donor-acceptor distances for Co-CAU-48. Distances were calculated from the initial electron diffraction data.

Donor	Acceptor	D…A [Å]
O5	O2	2.77(13)
07	012	2.75(1)
O6	O10	2.67(1)

11 Hydrogen bonding in CAU-46, CAU-47and M-CAU-48

Due to the small number of coordinated metal ions per phosphonate group, many hydrogen bonds (Fig. S52) are observed. In the crystal structures of CAU-46 and CAU-47, they are mainly established between coordinating water molecules and phosphonate groups, but also hydrogen bridges between two $-PO_3H^-$ groups are formed. Due to the absence of coordinating water molecules in M-CAU-48, only hydrogen bonds between $-PO_3H^-$ groups can be found.



Figure S52: Hydrogen bonds (dashed orange lines) in a) CAU-46, b) CAU-47 and c) M-CAU-48. The shown hydrogen bonds range from 2.50(7) Å to 2.99(8) Å.

12 Thermal properties

Thermal properties were determined by thermogravimetric and variable-temperature PXRD measurements. The TG measurements resulted in the formation of highly crystalline residues, which were characterised by PXRD.

The following equations correspond to the full oxidation of the title compounds:

 $\begin{array}{l} \mathsf{CAU-46:} \\ [\mathsf{Ni}_2(\mathsf{C}_{26}\mathsf{H}_{20}\mathsf{P}_4\mathsf{O}_{12})(\mathsf{H}_2\mathsf{O})_6]\cdot 4\mathsf{H}_2\mathsf{O} + 36\ \mathsf{O}_2 \to \mathsf{Ni}_2\mathsf{P}_4\mathsf{O}_{12} + 26\ \mathsf{CO}_2 + 20\ \mathsf{H}_2\mathsf{O} \\ \\ \mathsf{CAU-47:} \\ [\mathsf{CO}_2(\mathsf{C}_{26}\mathsf{H}_{20}\mathsf{P}_4\mathsf{O}_{12})(\mathsf{H}_2\mathsf{O})_4]\cdot 3\mathsf{H}_2\mathsf{O} + 36\ \mathsf{O}_2 \to \mathsf{Co}_2\mathsf{P}_4\mathsf{O}_{12} + 26\ \mathsf{CO}_2 + 17\ \mathsf{H}_2\mathsf{O} \\ \\ \\ \mathsf{Ni-CAU-48:} \\ [\mathsf{Ni}_2(\mathsf{C}_{26}\mathsf{H}_{20}\mathsf{P}_4\mathsf{O}_{12})]\cdot 9\mathsf{H}_2\mathsf{O} + 36\ \mathsf{O}_2 \to \mathsf{Ni}_2\mathsf{P}_4\mathsf{O}_{12} + 26\ \mathsf{CO}_2 + 19\ \mathsf{H}_2\mathsf{O} \\ \\ \\ \mathsf{Co-CAU-48:} \\ [\mathsf{Co}_2(\mathsf{C}_{26}\mathsf{H}_{20}\mathsf{P}_4\mathsf{O}_{12})]\cdot 6\mathsf{H}_2\mathsf{O} + 36\ \mathsf{O}_2 \to \mathsf{Co}_2\mathsf{P}_4\mathsf{O}_{12} + 26\ \mathsf{CO}_2 + 16\ \mathsf{H}_2\mathsf{O} \end{array}$



Figure S53: PXRD pattern of the thermal decomposition product of CAU-46 after the TG experiment (black) and calculated PXRD pattern of $Ni_2P_4O_{12}$ (red, CCDC: 1607767).



Figure S54: PXRD pattern of the thermal decomposition product of CAU-47 after the TG experiment (black) and calculated PXRD pattern of $Co_2P_4O_{12}$ (red, CCDC 1723731).



Figure S55: PXRD pattern of the thermal decomposition product of Ni-CAU-48 after the TG experiment (black) and calculated PXRD pattern of $Ni_2P_4O_{12}$ (red, CCDC: 1607767).



Figure S56: PXRD pattern of the thermal decomposition product of Co-CAU-48 after the TG experiment (black) and calculated PXRD pattern of $Co_2P_4O_{12}$ (red, CCDC 1723731).

In the following section, the results of the VT-PXRD measurements are shown and compared to the ones of the TG experiments. Differences in the phase transition temperature between the TG and the VT-PXRD studies are due to the experimental set ups: While the samples for VT-PXRD are packed within open quartz capillaries (0.5 mm), the samples for TG experiments are placed in open Al_2O_3 -crucibles under a constant flow of air (75 ml/min.)



Figure S57: Results of the VT-PXRD study of CAU-46 measured in an open quartz capillary (0.5 mm) under atmospheric conditions. No defined weight-loss steps can be observed in the TG measurement, making correlations ambiguous.



Figure S58: Results of the VT-PXRD study of CAU-47 measured in an open quartz capillary (0.5 mm) under atmospheric conditions. CAU-47 exhibits a step at 150°C, which is correlated to the phase transition at 170 °C observed in the VT-PXRD measurement.



Figure S59: Results of the VT-PXRD study of Co-CAU-48 measured in an open quartz capillary (0.5 mm) under atmospheric conditions. The phase transitions of Co-CAU-48 occur at 110, 180 and 270 °C, which correspond to steps located at 100, 160 and 270 °C in the TG curve.

Since the TG curves of CAU-47 and Co-CAU-48 exhibit well-defined weight-loss steps a more detailed evaluation of the data was carried out.

While the overall weight-loss between room temperature and 400 °C fits well to the results of the elemental analysis, the step wise loss cannot be unambiguously assigned to coordinating and adsorbed water molecules.



Figure S60: TG curve of CAU-47 with weight loss steps assigned to the removal of water molecules.

Table S23: Possible assignments of the steps observed in the TG curve of $[Co_2(H_4TPPE)(H_2O)_4]$ ·3H₂O (CAU-47). In the first row, a non-stoichiometric assignment is given according to the observed weight loss steps.

Assumed		ss loss I	H ₂ O	Mass loss linker decomposition
Composition	calc. [%]	calc. [%]	calc. [%]	calc. [%]
$[Co_2(H_4TPPE)] \cdot 3.3H_2O \cdot 1.7H_2O \cdot 2.1H_2O$	6.7	3.6	4.3	38.6
$[Co_2(H_4TPPE)] \cdot 3H_2O \cdot 2H_2O \cdot 2H_2O$	6	4	4	37.8
$[Co_2(H_4TPPE)] \cdot 3H_2O \cdot 1H_2O \cdot 2H_2O$	6.13	2.04	4.08	38.6
$[Co_2(H_4TPPE)] \cdot 4H_2O \cdot 2H_2O \cdot 2H_2O$	7.85	3.92	3.92	37.08



Figure S61: TG curve of Co-CAU-48 with weight loss steps assigned to the removal of water molecules.

Table S24: Possible assignments of the steps observed in the TG curve of $[Co_2(H_4TPPE)] \cdot 6H_2O$ (Co-CAU-48). In the first row, a non-stoichiometric assignment is given according to the observed weight loss steps.

Assumed		mass lo	oss H₂O	Mass loss linker decomposition	
Composition	calc. [%]	calc. [%]	calc. [%]	calc. [%]	calc. [%]
$[Co_{2}(H_{4}TPPE)] \cdot 1.4H_{2}O \cdot 2.2H_{2}O \cdot 1.5H_{2}O \cdot 1.$ 2H ₂ O	3.4	4.6	3.1	2.4	38.48
$[Co_2(H_4TPPE)] \cdot 1H_2O \cdot 2H_2O \cdot 2H_2O \cdot 1H_2O$	2.05	4.1	4.1	2.05	38.3
$[Co_2(H_4TPPE)] \cdot 2H_2O \cdot 2H_2O \cdot 1H_2O \cdot 1H_2O$	4.1	4.1	2.05	2.05	38.3
$[Co_2(H_4TPPE)] \cdot 2H_2O \cdot 2H_2O \cdot 2H_2O \cdot 1H_2O$	4.1	4.1	4.1	2.05	37.5

13 Sorption measurements

Sorption and PXRD experiments were carried out to investigate for porosity and structural integrity during sorption.



Figure S62: Water sorption isotherms for a) CAU-46 ($[Ni_2(H_4TPPE)(H_2O)_6] \cdot 4H_2O$) and b) Ni-CAU-48 (($[Ni_2(H_4TPPE)] \cdot 9H_2O$). Activation of CAU-46 was carried out for 16 hours at elevated temperatures at 80 °C under reduced pressure (10⁻² kPa), while Ni-CAU-48 was activated for 16h at 120 °C (10⁻² kPa).

For CAU-46, the uptake of water is observed with no distinct steps. Thus, the uptake is heavily effected by kinetic effects as discussed in the manuscript, making a detailed evaluation difficult.

The same is observed for Ni-CAU-48. The unusual high uptake of water can be explained through additional chemisorption of water, changing the tetrahedral coordination of Ni²⁺ to a square-pyramidal coordination environment. The difference to the isotherm of Co-CAU-48 is apparent, however, different sorption behaviour of isostructural phosphonates containing different metal ions have been reported (STA-12³⁰, CAU-29²²) and can be traced back to a small pore diameter and different, metal-dependent coordination sites and responses to thermal activation.



Figure S63: PXRD patterns of a) CAU-46 and b) CAU-47 before and after the H_2O sorption experiment.



Figure S64: PXRD patterns of a) Ni-CAU-48 and b) Co-CAU-48 before and after the H_2O sorption experiment.



Figure S65: Nitrogen sorption isotherms for CAU-46 ($[Ni_2(H_4TPPE)(H_2O)_6] \cdot 4H_2O$), CAU-47 ($[Co_2(H_4TPPE)(H_2O)_4] \cdot 3H_2O$), Ni-CAU-48 (($[Ni_2(H_4TPPE)] \cdot 9H_2O$) and Co-CAU-48 (($[Co_2(H_4TPPE)] \cdot 6H_2O$). Activation of CAU-46 and CAU-47 was carried out for 16 hours at elevated temperatures at 80 °C under reduced pressure (10^{-2} kPa), while Ni-CAU-48 and Co-CAU-48 were activated for 16h at 120 °C (10^{-2} kPa).



Figure S66: PXRD patterns of a) CAU-46, b) CAU-47, c) Ni-CAU-48 and d) Co-CAU-48 before and after the N_2 sorption experiment.

14 UV/Vis spectroscopy



Figure S67: UV/Vis spectra of the title compounds and the linker molecule.

15 IR spectroscopy

In order to confirm the structural features of the MOFs, FT-IR-spectra were recorded (Fig. S68). The assignment of the bands is summarized in Table S25.

Table S25: Assignment of the bands occurring in the IR spectra of the title compounds and comparison to the ones observed in the linker molecule.

Vibration $\tilde{\vartheta}$ IR [cm ⁻¹]	H ₈ TPPE	CAU-46	CAU-47	Ni-CAU-48	Co-CAU-48	
<i>v</i> (OH)	-	3438	3537	-	3465	
δ (OH)	-	1665	1665	1647	1647	
<i>v</i> (PO-H)	3600-2000	3600-2000	3600-2000	3600-2000	3600-2000	
v (P=O)	1137	1111	1137	1138	1138	
<i>v</i> (P-OH)	918	918	918	918	918	
<i>v</i> (P-C)	997	997	997	997	997	
v (C=C)	1600/1395	1600/1550/	1600/1550/	1600/1550/	1600/1550/	
		1500/1395	1500/1395	1500/1395	1500/1395	
v (C-H)	3100-3000	3050	3062	3033	3033	
δ (C-H)	996	1008	1014	1017	1015	
Co-CAU-48						



Figure S68: IR spectra of CAU-46 (green), CAU-47 (blue), Ni-CAU-48 (dark green) and Co-CAU-48 (dark blue) in comparison to the linker molecule H_8 TPPE (black).

The spectra of the title compounds strongly resemble each other. For CAU-46, the band in the region of 3438 cm⁻¹ can be attributed to coordinated and incorporated water molecules. For CAU-47, this band appears at 3537 cm⁻¹, while for Ni-CAU-48 no well defined band due to water molecules and for Co-CAU-48 a small band at 3465 cm⁻¹ due to physisorbed water is observed. The linker does not contain water molecules and thus exhibits a broad band from 3600-2000 cm⁻¹, which is due to the O-H stretching vibration of the phosphonic acid groups. This band also appears for CAU-46, CAU-47 and M-CAU-48, but weaker due to -PO₃H⁻ groups involved in hydrogen bonds between each other or with water molecules. At 1600-1395 cm⁻¹, a region with two (H₈TPPE) or four bands (CAU-46, CAU-47 and M-CAU-48) can be observed and is due to the C=C-ethylene group and the aromatic C=C stretching vibration. Both occur in this region, making a separate assignment ambiguous.³¹ The broad band around 1650 cm⁻¹ is due to bending vibrations of the water molecules. Furthermore, the broad band from 1111-1138 cm⁻¹ can be assigned to the P=O vibration, whereas the P-O-vibration is found at 918 cm⁻¹. The band for the aromatic P-Cbond is observed at 997 cm⁻¹.³¹ Several other bands with strong intensities can be observed in the fingerprint region, which are mainly due to C-H in-plane and out-of-plane deformation vibrations. All assignments were made in comparison with the IR spectra of the unsubstituted and brominated precursors of H₈TPPE.

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