Supporting Information

Crystalline and permanently porous porphyrin-based metal

tetraphosphonates

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1 Materials and Characterization

1.1 Materials.

MnCl₂ · 4 H₂O (99 %, Merck), CoCl₂ · 6 H₂O (98 %, Fluka), NiCl₂ · 6 H₂O (97 %, Merck), CdCl₂ · H₂O (98 %, Merck), EtOH (99 % + 1 % MEK, Walther), dichloromethane (Walther), N,N-diemthylformamide (99 %, Grüssing), acetone (99 %, Walther), 100 % acetic acid (VWR chemicals), NaH₂PO₄ (99 %, Sigma-Aldrich) and Na₂HPO₄ (99 %, Sigma-Aldrich) were used without further purification. The linker Ni-4,4',4",4"'-(5,10,15,20-porphyrintetrayl)tetraphosphonobenzoic acid Ni-(4-tetraphosphonophenylporphyrin, Ni-H₈TPPP) was synthesized according to reported procedures¹⁻³ starting with 4-bromobenzaldehyd (98 %, ABCR) and pyrrole (98 %, ABCR) in propionic acid (99%, Grüssing) 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. HCl (35 %, VWR chemicals). Details are given in the Supporting Information.

1.2 Characterization.

Single crystal X-ray diffraction data for Ni-CAU-29 were acquired using a Bruker D8 Venture diffractometer equipped with a Photon 100 CMOS area detector and a Mo K α microsource ($\lambda = 0.71073$ Å). The reflections were indexed with the APEX3 suite, integrated with SAINT V9.32B,⁴ solved with the program SHELXT,⁵ and refined with the program SHELXL using Olex2 as GUI.⁶ The crystal was very small (5 x 20 µm) and poorly diffracting, limiting the resolution to a (sin θ)/ λ value of 0.36 which corresponds to a d spacing of 1.4 Å. The data also showed poor consistency (R_{int} = 0.186). The poor diffraction at higher angles resulted in a low number of unique reflections and thus limited accuracy of determined bond lengths. Geometric constraints were used on the 6-membered rings in the structure refinement to improve the data-to-parameter ratio, although the structure refines just as well without.

The structure contains sheets of stacked porphyrin rings, likely to cause stacking disorder in the crystals. This disorder is likely to have caused the poor diffraction quality, thus resulting in low precision on bond lengths and ADP values in the obtained crystal structures. Only Ni and P atoms were refined anisotropically to avoid overparametrization.

The crystal structure contains 1-dimensional channels along [1 0 0] that are partly filled with an unknown adsorbate. The data quality is not sufficient to use solvent masking. Instead, dummy atoms (C47, C48, O14) were used to emulate adsorbed species at the points of highest electron density in the pores (obtained from the Fourier difference map).

High resolution PXRD patterns were measured on a STOE Stadi-P combi powder diffractometer equipped with a Mythen detector (Cu K α_1 radiation). Rietveld-refinements and Pawley-fits (Fig. S8 – S11) were carried out for all M-CAU-29 (M= Mn, Co, Ni, Cd) derivatives to proof that they are phase pure and isostructural to Ni-CAU-29. Pawley-fits were performed with the program TOPAS academic V4.1.⁷ The results of the refinement and crystallographic data of M-CAU-29 is shown in Table S2. The diameters of all pores were determined using DIAMOND V.3⁸ taking the van-der-Waals radii of the atoms into account as well as Material Studio V5 ⁹ to determine the Connolly surface. The VT-PXRD measurements were recorded on a STOE Stadi-P combi powder diffractometer (Mo K α_1 radiation) equipped with a capillary furnace. For the measurements 0.5 mm quartz capillaries were used. The samples were heated up in steps of 5 K between 25 and 450 °C and measured for 10 minutes each.

IR-spectra were recorded using a Bruker ALPHA-FT-IR A220/D-01 spectrometer equipped with an ATR-unit. UV/vis spectra were recorded at a Spectroquant Pharo 300 M. Prior to the measurements all samples were dissolved in 2M NaOH and measured at once. The ¹H- and ³¹P-

NMR spectra of the Ni-H₈TPPP linker were recorded on a Bruker DRX 500 spectrometer. Sorption experiments were performed with a BEL Japan Inc. BELSORP-max. Before sorption measurements all samples were activated at 170 °C under reduced pressure (10^{-2} kPa) for 16 h. Thermogravimetric measurements were performed on a NETZSCH STA 409 CD analyzer under a flow of air (75 ml min⁻¹) with a heating rate of 4 °C min⁻¹ between 25 and 700 °C in Al₂O₃-crucibles. The data were corrected for buoyancy and current effects.

2. Synthesis of Ni-H₈TPPP and M-CAU-29 (M= Mn, Co, Ni, Cd).

The three step synthesis route of Ni-H₈TCPP (Fig. S1) was carried out employing in the first step the Adler method^{1, 2} in the synthesis of 4-Bromophenylporphyrin (H₂TBrPP). The second step, the phosphorylation of H₂TBrPP was achieved by using a Ni-catalyzed variation of the Arbuzov reaction,^{3, 10} with the following third step, the hydrolysis of the -PO(OEt)₂ groups in conc. HCl.



Figure S1. Schematic representation of the synthesis route of Ni-H₈TPPP.

H₂TBrPP: Pyrrole (7.47 mL, 108 mmol) and 4-brombenzaldehyde (20.0 g, 108 mmol) in 400 mL propionic acid were heated under reflux for 2 h. Afterwards the reaction mixture was cooled down to room temperature and poured into 500 mL of MeOH and stirred for 30 min in an ice bath. The resulting precipitate was filtered off and washed several times with MeOH until the filtrate was clear. Subsequently, the product was washed with 100 mL warm distilled water and dried at 70 °C in a drying oven over night. A blue powder of H₂TBrPP 7.63 g (8.2 mmol, 30.4 %) was obtained.

Elemental analysis of H₂TBrPP (Br₄C₄₄H₂₆N₄): calc (%): C 56.8, H 2.6, N 6.0, found (%): C 59.7, H 3.2, N 6.2. The small difference between the calculated and observed values is due to impurities caused by propionic acid used in the synthesis. Propionic acid was also observed in the ¹H-NMR measurements, but not in the ¹H-NMR spectra of the products in the next synthesis steps. The low intensity peaks between 8.5 and 8.0 ppm are due to interactions of the H₂TBrPP with propionic acid, indicated by the different chemical shift and have no influence on the purity of the products in the next synthesis steps.

¹H-NMR (Fig. S2), H₂TBrPP (500 MHz CDCl₃): δ = 8.76 (s, 8H, H-1); 7.99 (d, 8H, H-2); 7.82 (d, 8H, H-3); 7.18 (s, 1H, CDCl₃); 2.30 (q, 2H, propionic acid); 1.08 (t, 3H, propionic acid) ppm. Additional peaks between 7 and 9 ppm are due to low impurities with higher condensated porphyrines.



Figure S2. ¹H-NMR spectrum of H₂TBrPP digested in DMSO.

Ni-H₈**TPPP:** H₂TBrPP (3.42 g, 3.7 mmol) and anhydrous NiCl₂ (1.79 g, 13.8 mmol) in 70 mL 1,3-diisopropylbenzene (prior the reaction for 30 min with N₂ degassed) were heated up to exactly 170 °C under N₂ atmosphere. Afterwards triethylphosphite (7.05 mL, 43.7 mmol) as added slowly (30 min) and dropwise to the reaction mixture and heated for further 24 h at 170 °C. The reaction mixture was cooled down to room temperature and the resulting precipitate was filtered off and washed with 250 mL DCM. The resulting organic phase was washed 2 times each with 100 mL H₂O. The organic solvents were evaporated under reduced pressure and the resulting precipitate was filtered off, washed with 100 mL cooled water and afterwards stirred in 100 mL DCM for 24 h. The resulting clean product was filtered off and dried at 70 °C in a drying oven over night. A red powder of Ni-H₈TPPP 2.74 g (2.76 mmol, 75 %) was obtained.

Elemental analysis of Ni-H₈TPPP ($C_{44}H_{32}N_4NiO_{12}$) · 4H₂O: calc (%): C 49.8, H 3.6, N 5.3, found (%): C 49.1, H 3.6, N 5.1.

¹H-NMR (Abb. S3), Ni-H₈TPPP (500 MHz DMSO-d₆): δ = 8.74 (s, 8H, H-1); 8.11 (dd, 8H, H-2); 8.06 (dd, 8H, H-3); 2.50 (s, 6H, DMSO-d₆); 2.09 (s, 6H, acetone) ppm.



Figure S3. ¹H-NMR spectrum of Ni-H₈TPPP digested in DMSO.





Figure S4. ³¹P-NMR spectrum of Ni-H₈TPPP digested in DMSO.

Synthesis of M-CAU-29.

High-throughput methods (2 mL teflon inserts) were employed in the screening of synthesis parameters such as molar ratio of metal to linker, pH and reaction temperature. The usage of molar linker to metal ratios of 1 : 1 resulted in CAU-29 with low crystallinity, while higher ratios up to a five times excess of metal (1 : 1 in the structure) and the 3-fold concentration of the reactants led to highly crystalline CAU-29 (Fig. S5). Furthermore an upscaling in 30 mL teflon inserts of CAU-29 was possible using the 12 fold amount of all reactants. In the following the optimized and upscaled synthesis parameters of M-CAU-29 (M= Mn, Co, Ni, Cd) are given.

The usage of other divalent cations like Mg^{2+} , Ca^{2+} , Fe^{2+} , Cu^{2+} and Zn^{2+} under this synthesis conditions led in most cases either to X-ray amorphous or products of low crystallinity.

Synthesis of Mn-CAU-29: Ni-H₈TPPP (180 mg, 18.3 x 10^{-5} mmol), MnCl₂ · 4 H₂O (190.5 mg, 91.5 x 10^{-5} mmol) and H₂O (12 mL) were added to a 30 mL Teflon insert and placed in a steel reactor. The reactor was heated for 48 h at 180 °C and cooled down to room temperature in 6 h. The resulting product was filtered off and washed with H₂O and acetone. A yield of 162 mg, (84 % based on Ni-H₈TPPP) was obtained for Mn-CAU-29, [Mn(Ni-H₆TPPP)(H₂O)] · 7 H₂O. Elemental analysis of Mn-CAU-29: calc (%): C 50.4, H 4.2, N 5.4, found (%): C 50.1, H 3.4, N 5.2.

Synthesis of Co-CAU-29: Ni-H₈TPPP (180 mg, 18.3 x 10^{-5} mmol), CoCl₂ · 6 H₂O (229.2 mg, 91.5 x 10^{-5} mmol) and H₂O (12 mL) were added to a 30 mL Teflon insert and placed in a steel reactor. The reactor was heated for 48 h at 180 °C and cooled down to room temperature in 6 h. The resulting product was filtered off and washed with H₂O and acetone. A yield of 156 mg, (81 % based on Ni-H₈TPPP) was obtained for Co-CAU-29, [Co(Ni- H₆TPPP)(H₂O)] · 5 H₂O. Elemental analysis of Co-CAU-29: calc (%): C 49.2, H 3.8, N 5.2, found (%): C 49.3, H 3.3, N 5.1.

Synthesis of Ni-CAU-29: Ni-H₈TPPP (180 mg, 18.3 x 10^{-5} mmol), NiCl₂ · 6 H₂O (228.9 mg, 91.5 x 10^{-5} mmol) and H₂O (12 mL) were added to a 30 mL Teflon insert and placed in a steel reactor. The reactor was heated for 48 h at 180 °C and cooled down to room temperature in 6 h. The resulting product was filtered off and washed with H₂O and acetone. A yield of 165 mg, (86 % based on Ni-H₈TPPP) was obtained for Ni-CAU-29, [Ni(Ni- H₆TPPP)(H₂O)] · 5 H₂O. Elemental analysis of Ni-CAU-29: calc (%): C 49.2, H 3.8, N 5.2, found (%): C 49.3, H 3.4, N 5.1.

Synthesis of Cd-CAU-29: Ni-H₈TPPP (180 mg, 18.3 x 10⁻⁵ mmol), CdCl₂ · H₂O (193.8 mg, 91.5 x 10⁻⁵ mmol) and H₂O (12 mL) were added to a 30 mL Teflon insert and placed in a steel reactor. The reactor was heated for 48 h at 180 °C and cooled down to room temperature in 6 h. The resulting product was filtered off and washed with H₂O and acetone. A yield of 180 mg, (89 % based on Ni-H₈TPPP) was obtained for Cd-CAU-29, [Cd(Ni- H₆TPPP)(H₂O)] · 7 H₂O. Elemental analysis of Ni-CAU-29: calc (%): C 47.8, H 4.0, N 5.1, found (%): C 47.7, H 3.2, N 4.9.



Figure S5. Results of the high-throughput investigation of CAU-29.

3. SEM image of Ni-CAU-29, coordination mode, crystallographic parameters, bond distances and results of the Rietveld- and Pawley-refinement of M-CAU-29

The SEM image of Ni-CAU-29 reveals small needles and block shaped crystals in a range of $10-50 \ \mu m$.

The coordination mode of the (di)hydrogen phosphonate groups (P003-P006) in Ni-CAU-29 is given in Figure S7 using the Harris notation. The Harris-notation has the format [A,XYZ], the value A is the number of metal ions coordinated by the (di)hydrogen phosphonate group and X, Y, Z is the number of bonds every oxygen shares with a metal ion.¹¹

The crystallographic data and results of the single crystal X-ray diffraction analysis of Ni-CAU-29 (Tab. S1, selected bond lengths Tab. S1a) and all M-CAU-29 derivatives (Tab. S2) reveal very similar cell parameters and the resulting Rietveld- and Pawley-refinements prove all M-CAU-29 (M=Mn, Co, Ni, Cd) derivatives are isostructural and show no further impurities in the samples (Fig. S8 – S11).



Figure S6. SEM image of Ni-CAU-29. The SEM measurements reveal crystal sizes between 10 and 50 μ m.



Figure S7. Graphical representation of the coordination mode of the (di)hydrogen phosphonate groups (P003-P006) in Ni-CAU-29. Numbers in brackets represent the Harris notation.

	Ni-CAU-29
Crystal system	triclinic
<i>a</i> [Å]	9.561(5)
<i>b</i> [Å]	15.086(9)
<i>c</i> [Å]	16.722(9)
α [°]	94.723(9)
β [°]	97.602(9)
γ [°]	97.880(9)
V [Å ³]	2356(2)
Ζ	2
space group	<i>P</i> 1
total data	6040
unique data	1832
R _{int}	0.118
Observed data [I>2 σ (I)]	1180
$\mathbf{R}_{1}\left[\mathbf{I} > 2\sigma(\mathbf{I})\right] \left[\%\right]$	9.97
$wR_2 [I > 2\sigma(I)] [\%]$	a23.46
GOF	1.13

Table S1. Results of the single crystal X-ray diffraction analysis of Ni-CAU-29.

	bond distance [Å]		bond distance [Å]
Ni01—O007	2.11 (2)	P003—C00P	1.794 (18)
Ni01—O007	2.14 (2)	P004—O009	1.50 (2)
Ni01—O008	2.05 (2)	P004—O00A	1.57 (2)
Ni01—O009	2.13 (2)	P004—O00B	1.52 (2)
Ni01—O00E	2.10 (2)	P004—C01B	1.86 (2)
Ni01—O00F	2.04 (2)	P005—O008	1.48 (2)
Ni02—N00H	1.90 (2)	P005—O00G	1.57 (2)
Ni02—N00L	1.95 (3)	P005—O00J	1.54 (2)
Ni02—N00M	1.94 (3)	P005—C01E	1.78 (2)
Ni02—N00N	1.93 (3)	P006—O00F	1.51 (2)
P003—O007	1.50 (2)	P006—O00I	1.56 (3)
P003—O00C	1.55 (2)	P006—O00K	1.56 (2)
P003—O00D	1.57 (2)	P006—C01G	1.83 (2)

Table S1a. Selected bond lenghts in Ni-CAU-29.

Rietveld refinements of Co- and Ni-CAU-29.

To further confirm the crystal structures of Ni- and Co-CAU-29, structure refinements by the Rietveld method were carried out using TOPAS academics V4.1.⁷ The structure as determined from single crystal X-ray diffraction was used as a starting point. The hydrogen atoms, guest atoms and atoms resulting from disorder were removed from the structure after inserting cobalt atoms into the inorganic building unit. The Ni-tetra(4-phosphonophenyl)porphyrin moiety was refined as rigid body while the positions of all other atoms were freely refined. Residual electron density was identified by Fourier synthesis and considered as two independent oxygen atoms, representing any kind of guest molecules, although the interatomic distances are in a reasonable range for strong hydrogen bonding. The temperature factors of the rigid body and all other atoms, respectively, were refined as general coefficients. In addition preferred orientation along the *c* axis was also taken into account. The structure obtained after convergence was further used as starting point for the Rietveld refinement of Ni-CAU-29 which was refined in the same manner. The final plots are shown below in Figure S9 and S10 and some relevant parameters are summarized in Table S2.

		• •	· ·	
	Mn	Co	Ni	Cd
SG	P^1	PĪ	PĪ	РĪ
a [Å] b [Å] c [Å]	9.761(2) 15.055(5) 17.022(6)	9.6860(7) 15.1223(18) 16.7747(22)	9.6473(6) 15.1046(15) 16.7115(19)	9.691(3) 15.067(7) 16.722(9)
α [°] β [°] γ [°]	94.168(7) 96.809(20) 97.057(17)	94.751(3) 97.412(8) 97.288(8)	94.662(4) 97.263(8) 97.309(7)	94.638(10) 97.158(35) 97.489(29)
V [Å ³]	2455(1)	2404.5(5)	2384.3(4)	2390(2)
GoF <i>R_{wp}</i> [%] R _{Bragg} [%]	1.65 3.51	1.1 3.1 0.7	1.5 6.7 2.5	1.75 3.42

Table S2. Results of the Rietveld refinements of Co- and Ni-CAU-29 and Pawley refinements of Mn- and Cd-CAU-29 of the crystallographic data of M-CAU-29 (M= Mn, Co, Ni, Cd).



Figure S8. Result of the Pawley fit of Mn-CAU-29 (as-synthesized). Measured data are shown as a black line, calculated data as a red line and the blue line gives the difference plot. Predicted peak positions are marked as vertical bars.



Figure 9: Result of the Rietveld refinement of Co-CAU-29. The black line gives the measured data, the red line gives the fit and the blue line is the difference curve. Black vertical bars indicate allowed peak positions.



Figure 10: Result of the Rietveld refinement of Ni-CAU-29. The black line gives the measured data, the red line gives the fit and the blue line is the difference curve. Black vertical bars indicate allowed peak positions.



Figure S11. Result of the Pawley fit of Cd-CAU-29 (as-synthesized). Measured data are shown as a black line, calculated data as a red line and the blue line gives the difference plot. Predicted peak positions are marked as vertical bars.

4. H₂O Sorption properties and PXRD patterns of the activated samples

 H_2O -sorpton isotherms of M-CAU-29 (M= Mn, Co, Ni, Cd) (Figure S12) and PXRD patterns of the samples after the sorption experiment compared with the PXRD pattern before the measurement (Figure S13).



Figure S12. Results of the H₂O sorption experiments at 298 K (activated prior measurement at 170 °C, overnight under reduced pressure of 10^{-2} kPa). The uptake corresponds to the amount of physisorbed water in the pores (Mn- : 9 H₂O, Co- : 11 H₂O, Ni- : 11 H₂O, Cd- : 8 H₂O).



Figure S13. PXRD patterns of M-CAU-29 (M= Mn, Co, Ni, Cd) after the sorption experiments (activation 170 °C, 10^{-2} kPa). For comparison the patterns of M-CAU-29 before the sorption experiment are also presented below the ones after the sorption experiments each.

5. TG investigations, PXRD patterns of the decomposition products, VT-PXRD studies and chemical stability.

The results of all TG measurements are shown in Fig. S14-S18 and Tab. S3. The decomposition products of M-CAU-29 (M= Mn, Co, Ni, Cd) are Ni-M-pyro- and metaphosphates (M= Mn, Co, Cd) which was shown by PXRD measurements (Fig. S19). The results of VT-PXRD studies (Fig. S20- S23) confirm the results obtained from the TG measurements. Complete collapse of the frameworks takes place above ca. 350 °C.

The results of the chemical stability test in different solvents as well as in a pH range between 0 and 14 and phosphate buffer (pH 7) are shown for Ni-CAU-29 in Fig. S24.

Table S3. Results of the TG measurements of M-CAU-29 (M=Mn, Co, Ni, Cd). Number in brackets represents the amount of H_2O taken up during H_2O sorption experiments.

sum formula	residual mass	dual mass mass loss linker decomposition	
	meas. [%]	meas. [%]	meas. [%]
	calc. [%]	calc. [%]	calc. [%]
[Mn(Ni-H ₆ TPPP)(H ₂ O)] ·	31.1	58.9	8.8
6.7 H ₂ O (9.0 H ₂ O)	31.8	59.4	8.8
[Co(Ni-H ₆ TPPP)(H ₂ O)] ·	35.5	55.5	8.0
6.4 H ₂ O (11.2 H ₂ O)	32.1	59.4	8.0
[Ni(Ni-H ₆ TPPP)(H ₂ O)] ·	34.8	56.0	11.3
9.0 H ₂ O (10.8 H ₂ O)	31.0	57.4	11.3
[Cd(Ni-H ₆ TPPP)(H ₂ O)] ·	34.4	58.2	8.2
8.2 H ₂ O (7.9 H ₂ O)	34.7	57.2	8.2



Figure S14. Thermogravimetric curve of Mn-CAU-29 (under air). Evaluation of the data reveals a molar ratio of metal : linker : H_2O of 1 : 2.0 : 6.7 (Tab. S3). The weight gain before

the collapse of the framework indicates a reaction for example between the Ni^{2+} ions with oxygen, since it was not observed in the TG measurement under N_2 atmosphere.



Figure S15. Thermogravimetric curve of Co-CAU-29 (under air). Evaluation of the data reveals a molar ratio of metal : linker : H_2O of 1 : 2.4 : 6.4 (Tab. S3). The weight gain before the collapse of the framework indicates a reaction for example between the Ni²⁺ ions with oxygen, since it was not observed in the TG measurement under N₂ atmosphere.



Figure S16. Thermogravimetric curve of Ni-CAU-29 (under air). Evaluation of the data reveals a molar ratio of metal : linker : H_2O of 1 : 2.3 : 9.0 (Tab. S3). The weight gain before the collapse of the framework indicates a reaction for example between the Ni²⁺ ions with oxygen, since it was not observed in the TG measurement under N₂ atmosphere.



Figure S17. Thermogravimetric curve of Ni-CAU-29 (under N_2). Measurement under N_2 could only be carried out up to a temperature of 800 °C. The whole curve is shifted to higher temperatures compared to the measurement under air, though the observed weight gain before the collapse of the framework is not observed anymore.



Figure S18. Thermogravimetric curve of Cd-CAU-29 (under air). Evaluation of the data reveals a molar ratio of metal : linker : H_2O of 1.9 : 1 : 6.3 (Tab. S3). The weight gain before the collapse of the framework indicates a reaction for example between the Ni²⁺ ions with oxygen, since it was not observed in the TG measurement under N₂ atmosphere.



Figure S19. PXRD pattern of M-Ni-phosphates (M=Mn, Co, Ni, Cd) (ICSD-79015, 3000027, 27424, 35730, 81575) compared with the remaining products of the thermogravimetric experiments of M-CAU-29 (M=Mn, Co, Ni, Cd).



Figure 20. Results of the VT-PXRD studies of Mn-CAU-29 measured in open quartz capillaries (0.5 mm) under atmospheric conditions.



Figure 21. Results of the VT-PXRD studies of Co-CAU-29 measured in open quartz capillaries (0.5 mm) under atmospheric conditions.



Figure 22. Results of the VT-PXRD studies of Ni-CAU-29 measured in open quartz capillaries (0.5 mm) under atmospheric conditions.



Figure 23. Results of the VT-PXRD studies of Cd-CAU-29 measured in open quartz capillaries (0.5 mm) under atmospheric conditions.



Figure S24. Chemical stability of Ni-CAU-29 in different solvents (24 h, stirring at room temperature).

6. Proton conductivity

The proton conductivity of Ni-CAU-29 was determined by electrochemical impedance spectroscopy (EIS). Powder samples were compressed between two porous stainless steel electrodes by a torque of 40 cN·m to purchase pellets of 82 mm in diameter and approx. 0.53 mm thickness. GDL 25 BC (SGL) graphite felt ensures the connection of the pellet and the electrode surface. The Teflon sample holder was placed in a previously described custommade measuring cell which was connected to a ZahnerZennium electrochemical workstation.¹² In the EIS measurements an alternating voltage of 10 mV was employed in the frequency range from 1 Hz to 1 MHz. The relative humidity was adjusted by means of the temperature difference between sample chamber and water reservoir.



Figure S25a. Bode plots, top left: 50 % relative humidity, top right: 75 % relative humidity, bottom: 90 % relative humidity. Square symbols: ionic resistance, triangle symbols: phase shift.



Figure S25b. Nyquist plots and equivalent circuit, top: equivalent circuit; bottom left: 50 % relative humidity, bottom right: 75 % relative humidity. *Black*: 80 °C, *red*: 100 °C, *blue*: 120 °C, *green*: 140 °C; *square symbols:* measured data, *straight line:* fits for the depicted equivalent circuit. The fits were computed with the program EIS Analyser 1.0.¹³



Figure S25c. Representative Nyquist plots for measurements at 90 %RH; *square symbols:* measured data, *straight lines:* fitted data. Clockwise: 80 °C, 100 °C, 120 °C, 140 °C.



Figure S26. Comparison of the PXRD pattern of Ni-CAU-29 before and after the EIS measurements. Furthermore the PXRD pattern of the graphite felt in which the sample was embedded for the measurement is shown.

Table S4. Fit parameter.

relative humidity [%RH]	temperature [°C]	Parameters	Values of the Parameters	Errors [%]	
relative humidity [%RH]	•	R1	3.76E+05	0.16777	
		P1	2.96E-10	0.84572	
	80	n1	0.89067	0.10521	
		P2	1.31E-05	2.4697	
		n2	0.202	6.1721	
		R1	2.67E+05	0.8445	
		P1	2.62E-10	2.0489	
	100	n1	0.90695	0.21599	
		P2	1.14E-05	1.6027	
50		n2	0.20381	1.7565	
30		R1	1.39E+05	0.55092	
		P1	1.99E-10	5.6562	
	120	n1	0.94104	0.52788	
		P2	8.29E-06	5.9269	
		n2	0.22955	4.8118	
		R1	84191	0.41542	
		P1	1.87E-10	2.797	
	140	n1	0.94889	0.24101	
		P2	8.67E-06	3.5874	
		n2	0.27614	1.7075	

Relative humidity [%RH]	temperature [°C]	Parameters	Values of the Parameters	Errors [%]
		R1	70073	1.7805
		P1	2.46E-10	2.6283
	80	n1	0.92295	0.18929
		P2	2.45E-05	2.886
		n2	0.32653	2.6006
		R1	53828	0.28282
		P1	2.99E-10	1.4666
	100	n1	0.90685	0.13069
		P2	3.36E-05	1.1611
75 —		n2	0.28825	1.5418
15		R1	36602	0.30357
		P1	3.25E-10	1.6097
	120	n1	0.90064	0.13954
		P2	4.54E-05	1.1269
_		n2	0.26445	1.5289
		R1	26467	0.4174
		P1	3.07E-10	2.2488
	140	nl	0.90746	0.18776
		P2	5.86E-05	1.4152
		n2	0.23732	1.9669
		R1	13661	3.0103
		P1	3.14E-10	1.2919
		nl	0.91296	0.10124
	80	P2	2.93E-05	1.1463
_		n2	0.42224	1.5035
		R1	13359	0.19722
		P1	3.09E-10	3.377
		n1	0.90613	0.28191
	100	P2	4.35E-05	0.83672
90 —		n2	0.40667	0.44136
		R1	11512	1.2678
		P1	2.88E-10	4.8049
		nl	0.91297	0.36949
	120	P2	6.26E-05	1.2923
_		<u>n2</u>	0.39673	0.69649
		R1	10246	0.33638
	140	P1	2.31E-10	3.4176
	140	nl	0.93387	0.24437
		P2	8.25E-05	1.3766
		n2	0.39097	0.87166



Figure S26. Comparison of the PXRD pattern of Ni-CAU-29 before and after the EIS measurements. Furthermore the PXRD pattern of the graphite felt in which the sample was embedded for the measurement is shown.

7. IR and UV/vis spectroscopy

IR spectra of M-CAU-29 (M= Mn, Co, Ni, Cd) and the Ni-H₈TPPP linker are shown in Figures S27. The assignment of the bands are given in Table S4.



Figure S27. IR-spectra of M-CAU-29 (M= Mn, Co, Ni, Cd). For comparison the IR-spectrum of the linker Ni-H₈TPPP (purple) is also presented.

Table S5. Assignment of the vibrations in the IR-spectra of M-CAU-29 (M= Mn, Co, Ni, Cd) and the free linker Ni-H₈TPPP.^{14, 15}

					Ni-
Vibration ^v IR [cm ⁻¹]	Mn	Со	Ni	Cd	H ₈ TPPP
ν CH (phenyl, pyrrole)	2970	2970	2970	2970	2970
ν P-OH	1606	1606	1606	1606	1606
ν C=C (arom.)	1549	1549	1549	1549	1519
ν P-C (phenyl)	1480	1480	1480	1480	1480
δ C=C, N=C (in plane)	1389	1389	1389	1389	1389
ν C-N (pyrrole)	1352	1352	1352	1352	1352
ν P=O (stretching)	1223	1223	1223	1223	1223
ν P-O (stretching)	1136	1136	1136	1136	1136
δ C-H, N-H (pyrrole)	1100	1100	1100	1100	1100
δ C-H (in plane)	1005	1005	1005	1005	1005
ν P=O (stretching)	944	944	944	944	921
<i>γ</i> C-H (1,4-subst.)	793	793	793	793	793
δ C-H, N-H (pyrrole)	730	730	730	730	730
<i>γ</i> P-C	704	704	704	704	704
$\delta P(OR)_3$	578	578	578	578	567
δ C=C (skeleton)	499	499	499	499	484

UV/vis spectra were recorded to prove the metalation of the porphyrin after the synthesis of the MOF (Fig. 28). For the measurement 0.1 mg sample was dissolved in 1 mL 2 M aqueous NaOH solution and filled up with water to a total volume of 5 mL. Afterwards a 4 mL cuvette was filled with 3 mL water and 5 drops of the porphyrin containing solution was added to the cuvette and subsequently measured.



Figure S28. UV/vis spectra between 380 and 800 nm of M-CAU-29 (M= Mn, Co, Ni, Cd) compared with the spectrum of the free linker Ni-H₈TPPP (for comparison all intensities were normalized). All spectra show the absorption maximum (Soret-band) of the Nickel complexed porphyrin at 412/413 nm. Furthermore the Q_1 band of the Ni complexed porphyrin is observed at 526/527 nm.

8. References

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