Understanding and Controlling Molecular Compositions and Properties in Mixed-linker Porphyrin Metal-Organic Frameworks

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Porphyrin-based metal-organic frameworks (MOFs) are attractive materials for photo- and thermally activated catalysis due to their unique structural features related to the porphyrin moiety, guest accessible porosity and high chemical tunability. In this study, we present a synthetic approach for the integration of nonplanar β-ethyl-functionalized porphyrin linkers into the framework structure of PCN-222, resulting in a solid solution series of materials with different functionalized linker contents. Comprehensive analysis by a combination of characterization techniques such as NMR, UV-vis and IR spectroscopy, powder X-ray diffraction and N_2 sorption analysis allows for the confirmation of linker incorporation. A detailed structural analysis of intrinsic material properties such as the thermal response of the different materials underlines the complexity of synthesizing and understanding such materials. This study presents a blueprint for synthesizing and analyzing porphyrin-based mixed-linker MOF systems and highlights the hurdles of characterizing such materials.

Introduction

In catalysis, the concept of multifunctionality is prominent to exploit synergistic effects or for tandem catalysis where more than one catalytic transformation is performed within one system.[1] Due to their enormous design flexibility and tunability, metal-organic frameworks (MOFs) have emerged as a promising material platform for the realization of multifunctional synthetic systems.[2] MOFs are built from metal nodes and linkers, and either of these components can be varied to obtain a multifunctional porous system or several functionalities can be integrated either *in situ* or post-synthetically, which in principle provides a platform for material design towards tailored properties.[3] This allows for the synthesis of different catalytically active MOFs and the study of their specific properties *via* advanced/*in situ* characterization techniques, ideally revealing structure-property relations or catalysis insights. Exemplarily, molecular catalysts are frequently incorporated into established MOF scaffolds to introduce further reactivities.[4]

Zr-based MOFs with porphyrins as linkers are predestined for the design of multifunctional catalysis due to: (1) the capability of porphyrin core metalation with a large variety of transition metals allowing for several catalytic applications, and (2) the large pore volumes where even sterically demanding guests can be incorporated without significantly preventing molecule diffusion within the pores.[5,6,7] In parallel, significant synthetic challenges have to be faced when working with Zr-based frameworks since different framework topologies are accessible based on the combination of the same building units such as Zr-oxo-clusters and porphyrin linkers. Therefore, precise tuning of reaction conditions is important for phase-pure synthesis as was recently shown for PCN-222 and PCN-224 as model systems.[8,9,10,11] Changing any synthetic parameters. Including subtle changes in the chemistry of linker molecules, might therefore result in altered synthetic outcomes.

One prominent strategy for the implementation of new functionalities based on a Zr-based framework is a mixed-linker approach.[12] This renders pore blockage unlikely since the functionality is part of the linker leaving free pore space. Therefore, a rational choice are β—functionalized porphyrins, e.g., with halides or alkyl chains attached to the macrocycle, with a similar structure motif as conventionally used porphyrin linkers. Previous reports have shown that the chemical functionalization of the porphyrin with ethyl groups results in a conformational flexibility from planar to non-planar[12A] where the nitrogen atoms are located out-of-plane.[13,14] This results in a high basicity enabling metal-free catalysis and preferrable kinetics for metal incorporation into the porphyrin core which usually has to change its conformation for metalation (especially for metals of larger size like Ru, Rh, etc.).[14A] Therefore, adding non-planar porphyrins such as 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin (**Et-TCPPH$_2$**) as a linker in MOF synthesis is anticipated to add a further functionality to the parent porphyrin-based material while keeping the underlying network topology.

By varying (and controlling) one crucial structural parameter – i.e., the porphyrin functionalization – we here provide a systematic study of the impact of linker functionalization and its framework amount on the MOF properties. Following this purpose, we used the mixed-

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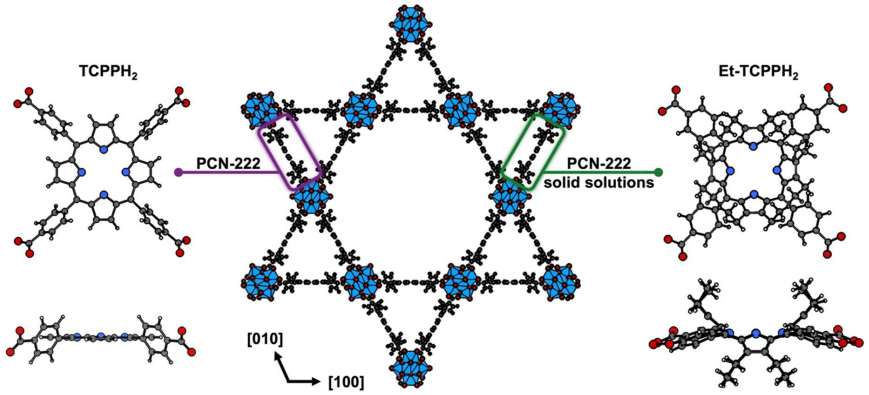

Figure 1. Structure of PCN-222 (middle, CCDC deposition code 893545) and schematics of porphyrin linkers $TCPPH_2$ (left; top and side-view) and the functionalized bulkier linker **Et-TCPPH₂** (right; top and side-view) that are used in this work in a mixed-linker solid-solution approach (color code: C, N, O and H are shown in dark grey, blue, red, and light grey).

linker strategy to incorporate the non-planar porphyrin (**Et-TCPPH₂**) in PCN-222, a Zr-porphyrin-based 3D network architecture with an underlying Kagomé-like topology (Figure 1). We prepared a series of mixed-linker solid solution PCN-222 analogues with different contents of non-planar porphyrin and thoroughly analyzed the resulting materials by ^{1}H NMR, infrared (IR) and UV-vis spectroscopy, powder X-ray diffraction (PXRD), N_2 sorption measurements, inductively coupled plasma mass spectrometry (ICP-MS), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). Moreover, we performed variable-temperature PXRD (VTPXRD) experiments to investigate the structural consequences of the integrated bulkier linker **Et-TCPPH₂** in this series of functionalized PCN-222 derivatives as a function of temperature. Additionally, material properties such as pH stability, fluorescence and metalation capability are examined. Thus, the detailed investigation of structural and chemical properties of functionalized MOFs accessible *via* a mixed-linker approach – realized by a combination of different characterization techniques – presents an important step towards understanding and controlling multifunctional MOF synthesis and highlights the synthetic and subsequent analytical challenges in obtaining such multifunctional materials.

Results and Discussion

Synthesis and Characterization. The porphyrin linker 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin (**TCPPH₂**) was prepared according to a literature procedure,[14a] while 2,3,7,8,12,13,17,18-octaethyl-5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin (**Et-TCPPH₂**) (Figure S1-S2) was prepared via saponification of the ester precursors[16].. Both were analyzed

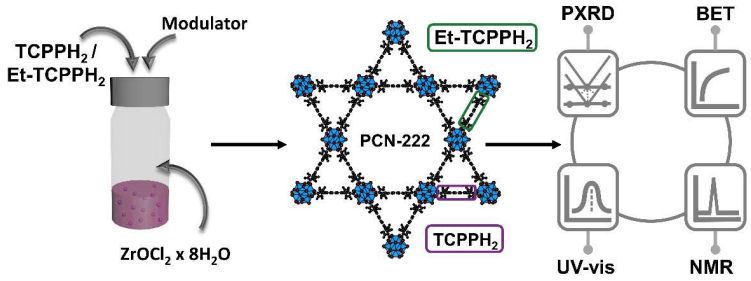

Figure 2. Schematic of the approach to synthesize and characterize a series of mixed-linker PCN-222 type MOFs. After MOF synthesis a combination of analytical techniques (PXRD, N_2 sorption analysis (BET), solid state UV-vis and ^{1}H NMR spectroscopy) was applied to determine the underlying structure and composition.

with ^{1}H NMR and UV-vis spectroscopy (Figure S3). The **Et-TCPPH2** and its ester analogue could be crystallized as dication salts in the orthorhombic space-group *Pnna* (for details of SCXRD data collection and details for crystal structure solution see SI and Figures S4-S5, Table S1). PCN-222 was synthesized with **TCPPH2** as the organic linker by following a published procedure.[7] The incorporation of **Et-TCPPH2** into the MOF framework, i.e., applying **Et-TCPPH2** as a linker, was achieved *via* a mixed linker approach (Figure 2). Different molar ratios of Et-TCPPH$_2$ and TCPPH$_2$ were used in the synthesis of PCN-222 where both linkers were added simultaneously (see SI for detailed synthesis protocols S-9).

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Ref 16 also refers to ref 6 and thus should be removed.

After solvothermal synthesis, the MOF powders were isolated by centrifugation and washed and characterized by ^{1}H NMR spectroscopy to determine the varying molar ratios of **TCPPH2** and **Et-TCPPH2** (Figure 3a, Figure S6-S7). For ^{1}H NMR spectroscopy, the MOFs are digested in a DCl/DMSO-d_6 solution (0.1 mL/0.3 mL). The molar ratio of both linkers is calculated by comparison of the phenyl signal integrals of **TCPPH2** (8.55 ppm, 8.62 ppm, 8.75 ppm) and Et-TCPPH$_2$ (8.38 ppm, 8.64 ppm), respectively (Table S2, for details see SI S-14). Note that the signals in the ^{1}H NMR spectrum of **TCPPH2** and **Et-TCPPH2** are slightly shifted in the spectrum of the dissolved MOF (8.49, 8.55 and 8.69 ppm for **TCPPH2** and 8.35 and 8.61 ppm for **Et-TCPPH2**) as a result of an acid-based concentration dependent proton shift. For an accurate determination of the **Et-TCPPH2** content in the MOFs, three different spectra of the same acid-digested MOF were recorded to obtain a weighted average and a standard deviation.

Three **Et-TCPPH2** functionalized PCN-222 materials with different Et-TCPPH$_2$ content were synthesized: 20EtP-PCN-222 (20 mol% Et-TCPPH$_2$, 80 mol% TCPPH$_2$ in PCN-222), 59EtP-PCN-222 (59 mol% Et-TCPPH$_2$, 41 mol% TCPPH$_2$ in PCN-222) and 72EtP-PCN-222 (72 mol% Et-TCPPH$_2$, 28 mol% TCPPH$_2$ in PCN-222). Interestingly, both 20EtP-PCN-222 and 72EtP-PCN-222 were obtained by weighing in 20 mol% Et-TCPPH$_2$ and 80 mol% TCPPH$_2$ for the mixed linker synthesis; the difference between both synthetic approaches was a different batch of Et-

$TCPPH_2$ linker, which differed in size of single crystals, i.e., single crystals compared to a more powdered sample. It is likely that the solubility of Et-$TCPPH_2$ determines the amount that is incorporated into the MOF. Thus, with the same amount of linker used for synthesis the more powdered Et-$TCPPH_2$ batch – and therefore more soluble one – resulted in 72EtP-PCN-222 while with the more crystal-like batch 20EtP-PCN-222 was obtained.

The IR spectra of the four materials did not show significant variations (Figure S11), while changes of the porphyrin's Soret and Q bands are discernible in the solid-state UV-vis spectra (Figure 3b, Figure S12). Here, with increasing amount of integrated Et-$TCPPH_2$ in the MOF, the development of Et-$TCPPH_2$ bands in the ranges 450-530 nm (Soret & Q bands) and 680-720 nm (Q bands) is prominent, confirming the incorporation of **Et-$TCPPH_2$** into the material network. Additionally, analysis of the different materials with confocal microscopy allowed for the evaluation of their optical properties. Here, the fluorescence of the samples decreased upon non-planar porphyrin incorporation (Figure S21) which is in accordance to the reported lower fluorescence properties of Et-$TCPPH_2$ compared to $TCPPH_2$.[17] It has to be noted that this method only allows for qualitative discussions of the fluorescence. Additionally, no general trend in fluorescence properties depending on the non-planar porphyrin content was observable.

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PXRD of the synthesized materials revealed phase purity and clear Bragg reflections for **Et-$TCPPH_2$** functionalized PCN-222 derivatives with up to a stoichiometry of approximately 80 mol% **Et-$TCPPH_2$**. The PXRD pattern of all materials are similar to that of PCN-222 (Figure S8). PCN-222 itself was reported to crystallize in a hexagonal crystal system (space-group $P6/mmm$) with a *csq* topology and the Zr_6 oxo cluster with an 8-fold connectivity.[6,18] Based on the PXRD pattern, where no changes in peak number and peak intensities wers observed, we conclude that the mixed-linker solid solution series of EtP-PCN-222 forms isostructural single-phase solid solutions. Raising the **Et-$TCPPH_2$** content in the MOF (above 72%) resulted in a significant increase of peak width of Bragg reflections, which we ascribe to a decreasing size of diffraction domains (Figure S8). For instance, the PXRD pattern of synthesized PCN-222 with 100 mol% Et-$TCPPH_2$ still features the main Bragg reflections of PCN-222; however, with significantly increased full width at half maximum. In turn, the hypothetical material 100EtP-PCN-222 is not used for further studies. Therefore, based on PXRD analysis, the isostructural series of PCN-222, 20EtP-PCN-222, 59EtP-PCN-222 and 72EtP-PCN-222 is suitable for studying properties as a function of compositional changes.

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SEM of the powdered samples is in good agreement with published shapes and morphologies of PCN-222 from the literature.[7,15,19] The images show that the rod shape and morphology of the crystals was maintained upon porphyrin functionalization – excluding a change in topology (Figures S17-S20). Simultaneously, no particle agglomeration of the rods – which show a flat surface – was observable. The size of the crystals was in the same order of magnitude independent of the degree of functionalization.

After establishing the composition and structure of the mixed-linker series, we would like to note that other approaches were demonstrated in the literature to incorporate (linker) molecules into MOFs post-synthetically, such as solvent-assisted ligand incorporation (SALI) or solvent-assisted linker exchange (SALE).[20] The latter could be applied in our case to further increase the content of **Et-TCPPH$_2$** in the synthesized MOFs, since the content of **Et-TCPPH$_2$** in PCN-222 accessible *via* the here presented mixed-linker approach is limited to a certain amount (here up to 72%). The reaction conditions for SALI and SALE are rather similar, soaking the synthesized MOF in a linker solution at elevated temperature. Therefore, the coordination of the linker cannot be controlled, i.e., linker exchange and coordination to the unsaturated Zr-node into the pores are possible – comparable to the MOF synthesis itself. Thus, due to the entailing characterization challenges (and likely no benefits toward understanding resulting material properties), this approach was not further followed.

N_2 sorption properties of PCN-222 and its **Et-TCPPH₂** functionalized analogues were investigated, encompassing the evaluation of N_2 adsorption quantities, and BET surface areas. The

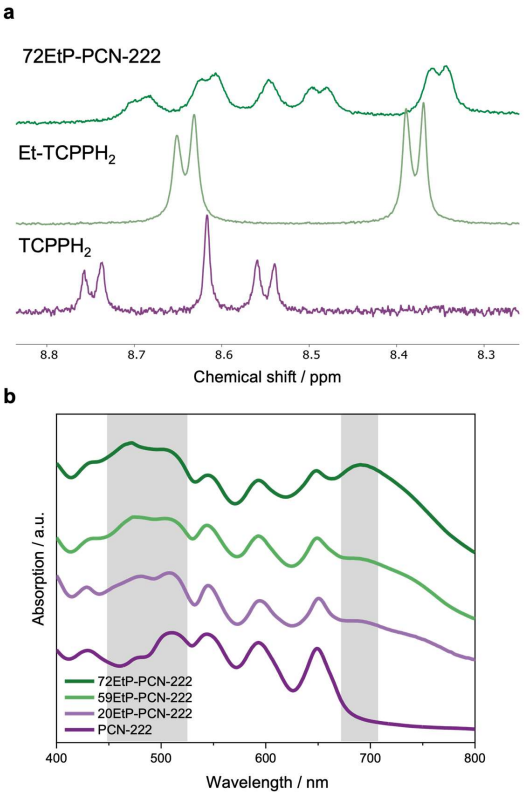

Figure 3. (a). Solution based ^{1}H NMR spectra of digested 72EtP-PCN-222 compared to the linkers **Et-TCPPH₂** and **TCPPH₂** in the range of the porphyrin signals (measured in DCl/DMSO-d_6). (b). Normalized solid-state UV-vis spectra of 72EtP-PCN-222, 59EtP-PCN-222 and 20EtP-PCN-222 compared to PCN-222

isotherms observed in sorption analysis suggest the presence of both micro- and mesopores which is comparable to N_2 sorption properties reported for PCN-222 materials (type IV isotherms).[6,15,19] With increasing amount of **Et-TCPPH₂** a decrease in the adsorbed N_2 quantity and BET surface area was observed (Figure S9). For instance, for PCN-222 we obtained a BET surface area of 2079 ± 6.9 $m^2 \cdot g^{-1}$, while the surface area decreased to 1744 ± 15 $m^2 \cdot g^{-1}$ for 20EtP-PCN-222, 1594 ± 12 $m^2 \cdot g^{-1}$ for 59EtP-PCN-222 and 1512 ± 10 $m^2 \cdot g^{-1}$ for 72EtP-PCN-222, i.e., a monotonic decrease

of BET surface area with increasing amount of **Et-TCPPH$_2$** (SI, Figure S10). This is ascribed to reduced pore space due to the incorporation of the bulkier porphyrin linker with ethyl groups and is in a similar range to porphyrin metalation[6,15,21]. We would like to note, however, that remaining porphyrin linkers in the pore space after washing cannot be fully excluded. For literature reported Et-TCPPH$_2$ functionalized PCN-224 (which crystallizes in $Im\bar{3}m$ space group with a *she* topology) the decrease upon ethyl porphyrin incorporation is smaller;[16] however, this phenomenon is also observed upon metal incorporation.[15,22]

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The thermal stability of the materials was analyzed by TGA, where all four materials showed similar thermal stabilities up to approximately 405-415 °C (Figure S13-S16). These decomposition temperatures are comparable to previously published temperatures of PCN-222.[6,22,23] Furthermore, the amount of point defects, i.e., linker defects and/or missing node defects, was determined based on the TGA traces since Zr-MOFs are prone for defect formation.[7–9,22,24,25] In general, the amount of **TCPPH$_2$** linkers derived from the ideal sum formula is two. Based on our analysis which follows an established protocol from the literature,[26] the real linker quantity was calculated to 2.53 for PCN-222, 2.08 for 20EtP-PCN-222, 2.20 for 59EtP-PCN-222 and 2.27 for 72EtP-PCN-222 which is in the typical range for PCN-222 materials (Table S3).[22,25]

In summary, the characterizations presented show that a combination of different analytical techniques is necessary to evaluate the incorporation of functionalized linkers into the desired MOF. While PXRD gives insights into the MOF structure, phase purity and crystallinity, the degree of functionalization can be followed by ^{1}H NMR and solid-state UV-vis spectroscopy, supported by N_2 sorption measurements and TGA.

Material Properties. In addition to the detailed characterization of the newly synthesized materials, their thermal, chemical and catalytical properties and metalation capability (compared to PCN-222) were studied.

Given the conformational change from planar to non-planar porphyrin linkers (Figure 1), the degree of framework flexibility in chemically functionalized isostructural PCN-222 derivatives is anticipated to change across the mixed linker solid solution series. To test for this network flexibility, we investigated the thermal expansion as a proxy.[27] For this, we performed variable temperature PXRD (VTPXRD) experiments of PCN-222, 20EtP-PCN-222, 59EtP-PCN-222 and 72EtP-PCN-222 in the temperature range $150 \leq T \leq 400$ K (for experimental details see SI and Figure S27-S30). To study the compositional dependence of PCN-222's hexagonal lattice parameters (*a, c*) and volume (V) as a function of increasing **Et-TCPPH$_2$** content, profile fitting based on the Pawley method was performed for the series of PCN-222 derivatives at each temperature point (Table S4-S7). Representative Pawley refinements of PCN-222, 20EtP-PCN-222, 59EtP-PCN-222 and 72EtP-PCN-222 at 310 K given (Figure S23-S26) showing a good fit by using a single-phase model with a hexagonal space-group $P6/mmm$ symmetry.

Recently, a study on the thermal response of PCN-222 as a function of water content inside the pore space revealed a rather complex case of the underlying expansion behavior of PCN-222. The study showed an unusual switching of the thermal expansion when water is present as guest species.[28] Such an influence is not expected here, as PCN-222 and its chemically functionalized analogues are all identically dehydrated, but a similar unusual response can be expected due to the modulator remaining in the pores. This suggests that our case is even more complex, as differences in the thermal behavior are assumed to originate from the varying $TCPPH_2$/Et-$TCPPH_2$ composition and the pore content, i.e., modulator itself.

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Looking at the evolution of the relative volume change, normalized to the unit cell volume at 150 K, as a function of temperature across the series, the expected complex trend is already apparent (Figure 4 and S33). First, when looking at the parent PCN-222 (Figure 4), almost no changes in volume were observed. This is slightly different compared to recent results, where a strong sensitivity of dehydrated PCN-222 in the temperature range between 100 and 200 K, and 350 and 450 K was observed. Apart from the temperature range, heat treatment of the samples has been found to increase the framework flexibility as the pore content is reduced compared to the as-synthesized (hydrated) sample.[28] Beyond that, we assume that the different thermal response observed in our studied PCN-222 could be related to the presence of the modulator in the pores, limiting the flexibility of the network. Looking at the complete set of temperature-dependent PXRD data of the PCN-222 series (Figure 4, Figure S27-S30), no clear trends within the individual data sets were visible (Figure 4, Figure S29-S30). This makes a reliable calculation of thermal expansion coefficients impossible, and therefore, the evolution of unit cell parameters can only be discussed qualitatively. Increasing the amount of **Et-$TCPPH_2$**, i.e., for 20EtP-PCN-222 and 59EtP-PCN-222, a stronger sensitivity towards temperature was observed compared to PCN-222 and 72-EtP-PCN-222. Their volume reduction is predominantly related to the decrease of the hexagonal lattice parameter *a* upon heating (Figure S31a-33a). Moreover, Figure 4 illustrates that the thermal responsiveness decreases for the maximum amount of the integrated bulkier linker in 72EtP-PCN-222, which is closer to the behavior observed in pure PCN-222. The defect-poor 20EtP-PCN-222 sample shows the largest volume change and variation of the *c/a* ratio with increasing the temperature. This is in line with the trend observed in the calculated linker defects for the series of PCN-222 and its solid solutions (Table S3). Note that the defectiveness refers to the deviation of real linker content to the ideal linker content and thus can also indicate that in a defect rich sample more linkers are present. For PCN-222 and 72EtP-PCN-222 more linkers are integrated in the framework compared to 20EtP-PCN-222 and 59EtP-PCN-222 which probably limits the flexibility of the material – in accordance with the hypothesis of a decreased thermal

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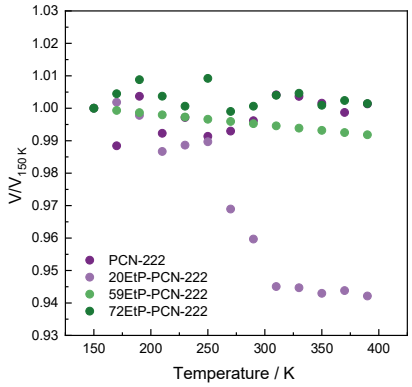

Figure 4. The evolution of the volume as determined by Pawley refinement against variable-temperature PXRD data as a function of temperature along the series of PCN-222 solid solutions with increasing Et-TCPPH$_2$ amount.

responsiveness with increasing guest content.[28] This working hypothesis is supported by a study on a series of UiO-66(Hf) where negative thermal expansion is reduced for higher defect concentration in the framework.[29] This is a rather counterintuitive phenomenon, since the framework flexibility and hence the thermomechanical response is expected to be greater in a defect-rich framework, i.e., in a less rigid network. Therefore, the inclusion of **Et-TCPPH$_2$** influences the thermomechanical response, but the interplay between modulator in the pores, defects and the integrated non-planar linker represents a more complex case that remains almost untouched (also throughout literature).

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In addition to the thermal stability and their thermal response, the chemical stability of PCN-222 and its **Et-TCPPH$_2$** functionalized analogues was evaluated with 59EtP-PCN-222 as a representative example for the series with >50% functionalized linker. The stability of **TCPPH$_2$**-based Zr-MOFs has previously been confirmed in aqueous media within a broad pH range (0-11).[30] Testing the stability of the here synthesized materials in basic solutions was necessary to avoid protonation of the porphyrin core of **Et-TCPPH$_2$** for potential applications such as metal-free catalysis. Both MOFs were soaked in different aqueous sodium hydroxide solutions at room temperature for 24 h with specific pH values: 8.0, 8.5, 10.3, 11.0, 12.3. In the NaOH/H$_2$O solution with pH = 12.3, both MOF samples rapidly decomposed. For all other solutions, no change compared to pure H$_2$O was apparent. After washing the MOF with water and subsequent drying, the powder was analyzed by PXRD. The patterns of each sample showed the typical Bragg reflections for PCN-222 and crystallinity is maintained up to pH = 11 for both base-treated PCN-222 and 59EtP-PCN-222 (Figures S34-S35). The increased background for the latter soaked in pH = 11 solution results from sample preparation and the decreased amount of solid material (a

certain loss of very fine powdered MOF upon washing and centrifugation needs to be taken into account).

After successful stability tests, the **Et-TCPPH$_2$** functionalized PCN-222 was applied in the thia-Michael addition where organocatalytic activity was previously shown for Et-TCPPH$_2$ in a homogeneous system.[13] Thus, the experiment aimed to investigate the performance of the non-planar porphyrin after MOF incorporation and simultaneously potential matrix integration effects. However, under the applied reaction conditions (see supporting information S-26, comparable to homogeneous conditions) no conversion was detected. Therefore, this approach was not further studied.

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One promising feature of porphyrin-based MOFs is the capability of introducing several transition metals in the porphyrin core which allows for various applications especially in catalysis. Therefore, the metalation ability of **Et-TCPPH$_2$** functionalized PCN-222 *via* a post-synthetic approach was explored. Rhodium was selected since its integration is in general more challenging due to the metal's size compared to the space in the porphyrin core. The saddle conformation of **Et-TCPPH$_2$** is beneficial since the four N atoms are already located out of plane facilitating metal incorporation (Figure 1). In a typical reaction setup, the MOF was suspended in *N,N*-dimethylformamide (DMF) with addition of the metal precursor ($RhCl_3 \bullet \times H_2O$) and different setups were tested such as heating to reflux *versus* heating in an oven without stirring (for details see the SI). After washing and drying, the MOF was analyzed by PXRD and ICP-MS to determine the metal content. The results were compared to unfunctionalized PCN-222. Confirmed by the PXRD pattern the structure and crystallinity of EtP-PCN-222 was retained upon Rh incorporation with both methods while the crystallinity of PCN-222 decreased after Rh metalation under reflux conditions (indicated by the decreased signal-to-noise ratio and broadening of Bragg reflections, Figure S36 – S37). ICP-MS analysis revealed comparable Zr:Rh ratios for both MOFs with significantly higher values for the metalation method using an oven instead of refluxing (Table S8). For complete metalation (100% of porphyrins in the MOF metalated with Rh), an Zr:Rh ratio of 3 is expected (note that this is calculated from the ideal sum formula and does not take defects into account). Thus, less than approximately 30% of the porphyrins are metalated in both MOFs (Table S7). However, the results show that the **Et-TCPPH$_2$** functionalized PCN-222 can still be metalated and that the metalation capability of PCN-222 is not changed upon **Et-TCPPH$_2$** functionalization and allows for the application of EtP-PCN-222, e.g., in metal catalysis.

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Conclusion

In summary, we report the preparation of a series of mixed-linker solid solution PCN-222 analogues with β-ethyl-functionalized porphyrin linkers *via* a mixed-linker approach, showing synthetic control over ethyl-porphyrin content over a large range of 0 – 72 mol%. The successful incorporation of this nonplanar linker into the framework was confirmed by a combination of analytical techniques such as ^{1}H NMR, solid-state UV-vis and IR spectroscopy, PXRD, SEM, N_2

sorption measurements, and thermogravimetric analysis. We find that the material properties, e.g., the BET surface area or the linker's fluorescence, change as the amount of functionalized linker increases. Thus, our work presents an appealing strategy for the design of, in principle, multifunctional systems with controllable modified material properties and their detailed characterization. Additionally, this PCN-222 case study highlights the need to thoroughly characterize such mixed-component materials with several complementary analytical techniques – currently often a caveat in MOF literature.

In theory, a straightforward characterization was expected since only one parameter was altered in the synthesis, i.e., the linker functionalization. However, our results highlight the complexity arising from a subtle linker variation such as different crystallinity, defect concentration changes, as well as altered thermal and optical properties. Likewise, this showcased increasing complexity upon subtle changes reinforces the importance of fundamental studies with model systems and their precise/detailed characterization. While the complexity of porphyrinic MOF systems – starting with their synthetic challenges – is already reported in literature,[8,9,11] further investigations are required to understand these MOF structures. This is particularly desirable as their showcased multifunctionality makes them interesting candidates to mimic certain enzyme properties, i.e., the arrangement of different functionalities in a confined environment. This would allow for tailored molecular evel structure – property relationship control and will be subject of future studies.

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Acknowledgements

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