Spectroscopic interrogations of isostructural metalloporphyrin-based metal-organic frameworks with strongly and weakly coordinating guest molecules

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ABSTRACT
Two isostructural metal-organic frameworks based on cobalt(II) and nickel(II) metalloporphyrin linkers, Co-PCN222 and Ni-PCN222, are investigated using resonance Raman and X-ray absorption spectroscopy. The spectroscopic consequences of framework formation and host–guest interaction with weakly and strongly coordinating guest molecules (acetone and pyridine) are assessed. Structure sensitive vibrational modes of the resonance Raman spectra provide insights on the electronic and structural changes of the porphyrin linkers upon framework formation. XANES and EXAFS measurements reveal axial binding behavior of the metalloporphyrin units in Co-PCN222, but almost no axial interaction with guest molecules at the Ni porphyrin sites in Ni-PCN222.

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1. Introduction
Metalloporphyrins are commonly used as building blocks for self-assembled solid-state materials designed to harness their potential for small molecule binding and catalytic behavior in analogy to naturally occurring metalloporphyrin cofactors in protein environments. To promote the availability
of the metal axial binding sites through host–guest interactions, much effort has been dedicated to incorporation of these metal complexes in porous solid-state networks [1, 2]. Early strategies based on crystallization of various meso-substituted metalloporphyrin complexes produced cavities for small molecule access to the metal centers [3–6]. However, the relatively weak interactions that hold these porphyrin solids together often lead to porous structure instabilities, particularly after solvent removal.

A more promising approach involves incorporating porphyrins or metalloporphyrins as linkers in metal–organic frameworks (MOFs) [7–11]. MOFs are self-assembled 3-D networks of metal ions or clusters connected through coordination bonds with organic linker molecules. Upon solvent removal, these crystalline architectures retain their structures and exhibit microporosity, which makes them appealing for adsorption-based applications [12, 13]. Moreover, the tunability of the MOF structures affords potential reactivity controls through pore size and shape selectivity. In many porphyrin-based MOFs, high-valence metals that form stable metal-linker coordination bonds, such as Al(III) and Zr(IV), occupy the framework node positions with full coordination, while metals prone to accommodate coordination and oxidation state changes can be incorporated (pre- or post-synthetically) in the porphyrin linkers that connect these nodes [7, 8, 14]. With this motif, pore-wall accessible metals can be included for guest molecule binding or reaction without compromising the overall structural integrity or chemical/thermal stability of the framework. Many porphyrin-based MOFs have been reported using this strategy, yet despite progress in building these architectures and in showing their propensity for catalytic and small molecule binding behavior [7, 15–20], few studies have been carried out to probe the local interactions and structural consequences of the metalloporphyrin units within the framework. These molecular level insights, however, are important for understanding and ultimately controlling catalytic behavior in these materials.

In this article, we focus on molecular level host–guest interactions in the metalloporphyrin MOF structure shown in figure 1. The framework, reported as PCN222 [7], MOF-545 [8], or MMPF-6 [20], is comprised of Zr₆ nodes connected by carboxyphenyl meso-substituted metalloporphyrins to produce two types of 1-D channels along the c-axis (diameters of ~37 and ~10 Å). We recently investigated the iron porphyrin version of this MOF upon reaction with an axially coordinating reducing agent using several spectroscopic methods and determined how the framework dictated the reactivity and substrate binding patterns of the iron porphyrin linkers upon reduction [21]. Here, we present a systematic study

![Figure 1. PCn222 architecture, linker structure, and interaction of PCn222 with acetone and pyridine.](image-url)
of isostructural versions of this framework with different porphyrin linker metal centers (Co and Ni) in both weakly and strongly coordinating guest molecule environments using X-ray absorption (XAS) and vibrational spectroscopic methods, namely resonance Raman spectroscopy. These spectroscopy methods have been used to probe the electronic and geometric structures of metalloporphyrin complexes in various solutions, proteins, and other environments [22–38]. Moreover, having been well established in the study of other solid-state porous materials such as zeolites [39–44], XAS and Raman spectroscopy are increasingly being incorporated in the arsenal of characterization methods for MOF materials to provide new insights on potentially important metal electron distribution and framework and/or guest molecule structural changes that occur upon host–guest adsorption events [45–50]. In this study, these spectroscopic techniques are used to provide new insights on the metalloporphyrin local structure and coordination environment under the structural constraints of the framework and under coordinating and non-coordinating guest molecule conditions.

2. Experimental

2.1. Materials

Chemicals for synthesis were purchased from TCI America or Alfa Aesar. Reference porphyrin complexes CoTPP and NiTPP (TPP = tetraphenylporphyrin) were obtained from Frontier Scientific. All chemicals were used as received unless otherwise noted. Pyridine and acetone were dried over molecular sieves prior to use. The reference complexes, CoTPP(H2O)2ClO4 [51], CoTCPP [7], and NiTCPP [7] (where TCPP = tetakis(4-carboxyphenyl)porphyrin), were synthesized according to published procedures. The precursor MeTCPP and MOFs, M-PCN222 (where M = Co or Ni), were also made according to literature procedures [7]. [CoTCPP(H2O)2ClO4] was prepared by a modified procedure reported for CoTPP(H2O)2ClO4 [51]. The product was recrystallized from acetone–dichloromethane mixture. Yield: 52.7 mg, 90.8% Analysis: ESI-MS [M−2(H2O)] = 847.129, IR (figure S2): 3469 (w), 3073 (w), 3002 (w), 1682 (s), 1606 (s), 1566 (m), 1421 (sh), 1350 (m), 1313 (w), 1209 (m), 1178 (m), 1068 (s), 1004 (s), 865 (m), 786 (s), 765 (s), 727 (m) cm⁻¹. UV–vis (DMF): 430, 545, 592 nm.

2.1.1. Co-PCN222

A double scale reaction was carried out compared to the literature procedure [7]. Yield: 139 mg, 63%. Analysis: X-ray diffraction (XRD) (figure S1), IR (figure S2): 3353 (w), 2976 (w), 2924 (w), 1697 (w), 1604 (s), 1552 (s), 1415 (s), 1351 (m), 1305 (w), 1209 (m), 1178 (m), 1099 (m), 1007 (s), 866 (m), 793 (s), 765 (s), 725 (m) cm⁻¹. UV–vis diffuse reflectance (figure S3) λ, nm: 422, 542, 576 (sh).

2.1.2. Ni-PCN222

A double scale reaction was carried out compared to the literature procedure [7]. Yield: 39.2 mg, 18.9% Analysis: XRD (figure S1), IR (figure S2): 3342 (w), 2975 (w), 2927 (w), 1708 (m), 1604 (s), 1556 (s), 1415 (s), 1354 (m), 1305 (w), 1207 (m), 1180 (m), 1099 (m), 1002 (s), 869 (m), 800 (s), 775 (s), 715 (m) cm⁻¹. UV–vis diffuse reflectance (figure S3) λ, nm: 424, 542, 576 (sh).

2.1.3. M-PCN222-x (M = Co(II) or Ni(II) and x = acetone or pyridine)

The as-synthesized MOF samples were soaked for 3 days in acetone then activated for 12 h at 120 °C under vacuum prior to treatment with other guest molecules. 50 mg of each activated MOF sample were soaked in guest molecule solvent (acetone or pyridine) for 12 h. Each sample was again characterized by XRD to verify the preservation of the structure.

2.1.4. Co(III)-PCN222ClO4

The oxidized MOF was obtained by a modified procedure reported for the complex [51]. After soaking in acetone, Co-PCN222 (60 mg) was suspended in 60 mL methanol with addition of 1.2 mL of 5% HClO4. The mixture was left stirring overnight at room temperature. The solid was filtered out and washed with
150 mL (3 × 50 mL) of water. Yield: 61.2 mg. Analysis: IR (figure S2): 3338 (w), 3116 (w), 3062 (w), 1697 (m), 1606 (s), 1536 (sh), 1407 (s), 1347 (m), 1305 (w), 1205 (m), 1176 (m), 1070 (m), 1002 (s), 865 (m), 794 (s), 773 (s), 711 (m) cm⁻¹. UV–vis diffuse reflectance (figure S3) λ, nm: 424, 531.

2.2. Characterization methods
XRD patterns were recorded using a Bruker D8 ADVANCE ECO Diffractometer. Full metallation of the metalloporphyrin precursors was confirmed by high-resolution ESI-MS using a Bruker Daltonics Apex-ultra 70 hybrid Fourier transform mass spectrometer and UV–vis spectroscopy. Diffuse reflectance UV–vis spectra were collected using a Cary-Varian UV-visible-NIR spectrophotometer equipped with a diffuse reflectance accessory (Harrick Scientific). Samples were diluted and finely ground with KBr. Final spectra were plotted in Kubelka-Munk units and normalized to the Soret band peak maximum for better comparison. Attenuated total reflectance infrared spectra were collected for solid samples at room temperature using a Nicolette 6700 FT-IR spectrometer. Each IR spectrum was recorded as an average of 64 scans.

2.3. Resonance Raman spectroscopy
Raman spectra were collected using 420 nm laser excitation generated from the second harmonic of the fundamental output of a ps Ti: Sapphire laser oscillator (Tsunami, Spectra-Physics), which was pumped by a 532 nm diode-pumped solid-state laser (Millenia, Spectra-Physics). The Raman scattered light was collected and focused onto the slit (100 μm) of a triple monochromator and detected using a 1340 × 100 pixel liquid nitrogen-cooled CCD detector (Princeton Instruments). The power of the laser was attenuated to ~8 mW at the sample using neutral density filters. Samples were measured in pellet form by pressing a mixture of 20% complex or MoF with 20% of KNO₃ internal frequency standard and 60% of KBr. Samples were spun to minimize the residence time of the laser on one spot of the sample, thereby voiding heat- or photodamage of framework or complex.

2.4. XAS spectroscopy
XAS were collected at the Co and Ni K-edges (7709 and 8333 eV, respectively) in transmission mode at Beamline 2-2 at SSRL. The X-ray white beam was monochromatized by a Si(111) monochromator and detuned by 30% to minimize the harmonic content of the beam. Cobalt and nickel metal foils were used as references for energy calibration. The incident beam intensity (I₀) was measured by a 15 cm ionization chamber with 100% N₂ for both metal K-edges. The transmitted (Iₜ) and reference (Iₙ) beam intensities were both measured using 30-cm ionization chambers, each with a 75% N₂ and 25% Ar gas mixture. A mixture of approximately 20 mg of the reference complexes thoroughly ground with ~100 mg of boron nitride was packed into 3 mm sealed Kapton tubes to yield approximately one XAS length. MOF samples were ground and used in the same 3 mm sample tube format without additional dilution. Activated samples were packed and sealed inside a glovebox.

3. Results
3.1. Characterization
Crystal structures of the synthesized MOFs were verified using powder XRD. Peak patterns of the as-synthesized frameworks shown in figure S1 match those reported in the literature for this MOF series. Consistent patterns are obtained for these MOF samples after activation and post-synthetic guest molecule inclusion, indicating that the crystal structure is maintained in each case upon these treatments.

Diffuse reflectance UV–vis spectra of the reference TCPP metalloporphyrin complexes in the solid state were compared with the corresponding M-PCN222 MOF samples upon exposure to different
guest environments, as shown in figure S3. For the Co and Ni porphyrin MOF spectra, both Soret and Q bands appear at the same peak wavelengths with similar spectral shape as those of the corresponding MTCPP reference complexes.

Infrared spectra of the metalloporphyrin MOFs are presented and compared to the relevant reference complexes in figure S2. These data were used mainly to characterize the vibrational modes and to confirm the presence of the guest molecules inside the pores of the MOF. In CoTCPP and NiTCPP, the carboxylic acid stretching mode appears as a strong feature at 1685–1691 cm\(^{-1}\). In the MOF systems, the resulting asymmetric carboxylate modes appear at 1554–1556 cm\(^{-1}\) and a strong broad band around 1405 cm\(^{-1}\) is assigned to overlapping C–C aromatic stretch and symmetric –COO\(^{-}\) stretch peaks [52]. These carboxylate mode frequencies, which are consistent with the bridging-type coordination with Zr in the MOF [53], are observed at slightly higher frequencies for the MOFs treated with acetone compared to pyridine. These frequency differences, however, are nearly identical for both the Co and Ni versions of the MOF, which most likely reflects the different electrostatic environments created by the two solvents around the pore-exposed carboxylate bonds rather than indicating any differences in axial interaction of these guest molecules with the metalloporphyrin sites. Moreover, these carboxylate bands partially overlap with the porphyrin modes in this frequency range. The resulting congested fingerprint region prevents further analysis of the structure-sensitive porphyrin modes to establish the more subtle electronic and structural consequences of incorporating these metalloporphyrins in MOF structures and under guest molecule environments. Vibrational signatures of the guest species are clearly observed and confirm their presence in the treated MOF samples. For M-PCN222-ace, aliphatic \(\nu(C-H)\) appears at 2920–2927 cm\(^{-1}\) and \(\nu(C=O)\) at 1706–1710 cm\(^{-1}\). Pyridine has a strong band at 1438 cm\(^{-1}\) \(\nu(C=C)\) which is clearly seen in the spectra of the MOFs treated with this solvent.

### 3.2. Resonance Raman spectroscopy

Full Raman spectra for the isostructural MOF series and corresponding metalloporphyrin reference complexes are presented in figures S4–S6. Selected spectral regions highlighting the structure sensitive modes of the metalloporphyrin complexes and MOFs are presented in figures 2 and 3. A summary of these vibrational mode frequencies is provided in table 1. Laser excitation at 420 nm is resonant with the Soret band region of the porphyrin electronic absorption spectra and leads to significant enhancement of the porphyrin skeletal vibrational modes. This selective enhancement allows assessment of the porphyrin localized modes, providing a distinct advantage over IR spectroscopy, which frequently yields poorly resolved congested fingerprint regions. Raman spectra of model complexes are consistent with those reported in the literature [25, 26, 54–57]. Most modes are assigned as in-plane skeletal modes that involve either a combination of C–C stretches, for example, \(\nu_2\) and \(\nu_3\), or pyrrole ring deformation: \(\nu_1\) and \(\nu_4\). These modes appear in the region of the spectrum from around 1000 to 1600 cm\(^{-1}\). C–C stretch modes localized on the peripheral phenyl groups, labeled \(\phi_4\) and \(\phi_5\), are also observed in this fingerprint region. Another important mode is \(\nu_8\) which is assigned to M–N breathing with porphyrin ring deformation. This low frequency mode is at ~380–400 cm\(^{-1}\) for the porphyrin systems measured in this study. (Mode assignment and notation follows that of the normal coordinate analysis reported [56].)

### 3.3. XAS spectroscopy

The XAS data for the metalloporphyrin complexes and MOFs are presented in figures 4 and 5. The XANES spectra for the Co-porphyrin systems contain both pre-edge and edge features at 7709 and 7715 eV, respectively, which are consistent with the values reported for Co(II) porphyrin XANES spectra [58]. The intensity of the edge feature varies significantly among the set, with the square planar CoTPP and (guest free) activated Co-PCN222 spectra having the highest intensity and Co-PCN222-py spectrum having minimal intensity for this edge feature. The spectra are overlaid with those of the oxidized Co-PCN222 MOF and Co(III) reference complex, CoTPP(H\(_2\)O)\(_2\)ClO\(_4\) for comparison. NiTCPP, Ni-PCN222-ace, and Ni-PCN222-py produce nearly the same XANES spectra consisting of a very weak pre-edge
feature at 8333 eV and a more intense edge feature at 8337.5 eV. These results are consistent with the reported XANES spectrum of NiTPP [59].

4. Discussion

4.1. Electronic and structural changes upon porphyrin carboxylate functionalization and framework integration

Several metalloporphyrin ring vibrational modes observed in the resonance Raman spectra (figure 2) can provide useful insights on the electronic and structural consequences of framework integration of this macrocycle due to their sensitivity to porphyrin ring functionalization and distortion. For example, the frequency of the mode containing prominent M–N stretching displacement, $v_8$, is shown to be quite sensitive to the TPP ring phenyl group functionalization and incorporation in the MOF environment. For
the CoTPP complex, $v_8$ occurs at 393 cm$^{-1}$, yet is shifted 17 cm$^{-1}$ to lower energy in CoTCP. A similar frequency trend is also observed for the Ni complexes when comparing the TPP and TCPP versions. The drastic change in the frequency for $v_8$ in these systems is attributed to the addition of the electron-withdrawing carboxylic acid groups to the TPP ring, which weakens the metal porphyrin coordination bonds and decreases the force constant of the M–N stretch. Placing the carboxylate functionalized complexes in the MoF environment has the opposite effect on this mode which also includes a substantial ring distortion component. The increased rigidity of the framework yields upshifted frequencies of $v_8$ for both M-PCN222 MOFs by +6 to +9 cm$^{-1}$ depending on the metal, compared to that of the corresponding TCPP complexes. In most other metalloporphyrin systems, this mode exhibits primary sensitivity to the metal oxidation state since the metal ion size and charge strongly affect the porphyrin core size and therefore the force constant of this mode [25]. To evaluate the relative influence of the peripheral functionality and framework incorporation on this mode frequency compared to the influence of the metal oxidation state, Raman spectra of the oxidized Co(III) porphyrin complexes and MoF were compared with those of the Co(II) analogs. Only different oxidation states of the Co systems were investigated due to the instability of other Ni-porphyrin oxidation states besides Ni(II). The oxidation state for all systems was first confirmed by XAS. The XANES edge energies for the Co reference complexes match

Figure 3. Resonance Raman spectral region highlighting $v_8$ mode: comparison of Co(II) and Co(III) complexes and MOFs.

Table 1. Structure sensitive Raman modes for reference M-TPP complexes, their TCPP analogs, and M-PCN222 MOFs in the presence of acetone or pyridine.

| Porphyrin system | $v_8$ | $v_1$ | $v_4$ | $v_3$ | $v_4$ | $v_2$ | $v_4$ |
|-----------------|------|------|------|------|------|------|------|
| CoTPP           | 393  | 1237 | 1371 | –    | 1504 | 1565 | 1600 |
| CoTCP           | 378  | 1239 | 1370 | 1486 | 1511 | 1569 | 1608 |
| CoPCN222ace     | 384  | 1238 | 1371 | 1486 | 1510 | 1570 | 1607 |
| CoPCN222py      | 385  | 1239 | 1372 | 1485 | 1510 | 1570 | 1608 |
| NITPP           | 402  | 1234 | 1374 | 1470 | 1502 | 1572 | 1595 |
| NITCPP          | 383  | 1238 | 1373 | 1472 | 1511 | 1573 | 1608 |
| NiPCN222ace     | 389  | 1236 | 1373 | 1473 | 1509 | 1573 | 1608 |
| NiPCN222py      | 389  | 1237 | 1373 | 1473 | 1509 | 1573 | 1608 |
those found in the literature for similar compounds [58]. The edge energy of the as-synthesized Co MOF sample is nearly identical to those of the corresponding Co(II) metalloporphyrin reference complexes as shown in figure 5, and are unaltered by inclusion of the weakly and strongly coordinating solvent.

**Figure 4.** XANES spectra of CoTPP, Co-PCN222-act, CoTPP(\(\text{H}_2\text{O}\))\(_2\)Cl\(_4\) and Co-PCN222-Cl\(_4\).

**Figure 5.** XANES and EXAFS spectra of: (top) CoTPP and Co-PCN-222 activated and in the presence of acetone or pyridine guest molecules; (bottom) NiTPP and Ni-PCN222 in the presence of acetone or pyridine.
molecules. This observation confirms that no change in oxidation state of the metal sites occurs under these guest environment conditions as expected. Only the inclusion of the oxidizing agent in the case of Co-PCN222 induces and edge shifts of +5 eV (figure 4) indicate the change to the Co(III) valence. With oxidation states confirmed, comparison of the Raman spectra of the Co-porphyrin systems (as illustrated in figure 3) reveals that with the presence of the carboxylate functionality, in either the complex or MOF, the frequency of \( v_8 \) becomes much less sensitive to oxidation state of the metal. The dominance of this factor on dictating the frequency of this traditional “oxidation state marker” mode is important to note given the prevalence of carboxylate functionalized porphyrins used in MOF architectures.

Not surprisingly, the modes in the high frequency region highlighted in figure 2 and table 1 that undergo the biggest frequency change upon the addition of the carboxylate functionality are those localized on the phenyl groups. These modes, \( \phi_4 \) and \( \phi_5 \), exhibit a large increase in frequency between the TPP and TCPP versions of these complexes owing to the resonance effect of the –COOH groups. The porphyrin-localized modes in this fingerprint region traditionally demonstrate some correlation with porphyrin core size, which can be influenced by the metal ion size and strongly coupled peripheral ring functionality. The pyrrole deformation mode, \( \nu_1 \), demonstrates modest sensitivity to the phenyl functionalization of both the Co and Ni porphyrin complexes, with +2 and +4 cm\(^{-1}\) frequency shift in each case, upon the inclusion of the –COOH groups. This is most likely attributed to the substantial phenyl ring vibration component of this mode. Incorporation in the MOF environment, however, does not appear to further influence its frequency. The other pyrrole deformation mode \( \nu_{4'} \), which is considered a spin state marker band, does not appear to be sensitive to either the peripheral carboxylate functionalization or framework formation. While the structure sensitive mode, \( \nu_2 \), is not affected by the presence of the carboxylate in NiTCPP, this mode does exhibit increased frequency between CoTPP and CoTCPP. The reason for this shift is not entirely clear. The mode frequency, however, is not further altered for either of the metalloporphyrin systems upon framework formation.

4.2. Guest molecule interaction in metalloporphyrin MOF environments

Analysis of the XAS results for the MOFs in comparison with those of the corresponding complexes reveals the influence of the framework on the axial interaction of the metalloporphyrin metal sites with guest species contained within the pores. With particular sensitivity to the presence and nature of axial metal ligation, the pre-edge and edge features in the XANES spectra (figure 5) provide useful insights regarding the axial interaction in the metalloporphyrin MOFs compared to their respective reference complexes. For the Co porphyrin systems, XANES spectra contain weak pre-edge features at approximately 7709 eV, attributed to the 1s → 3d quadrupole allowed transitions. The relative intensity of this feature indicates the degree of centrosymmetry of the absorbing metal, with higher intensities indicating lower symmetry coordination environments of the absorbing metal. The CoTPP reference complex and activated Co-PCN222 MOF produce poorly resolved low intensity pre-edge features, reflecting their four-coordinate metalloporphyrin environments with relatively high symmetry. Both the pyridine and acetone-treated MOFs, Co-PCN222-py, and Co-PCN222-ace yield substantially more resolved pre-edge features. This may reflect the less centrosymmetric environments of the Co sites due to mono axial ligation of the guest species (a mixture of five and six coordinate species is likely due to the pore size restrictions of the MOF) however, intensity differences are difficult to extract accurately since the pre-edge bands are partially obscured by the more intense edge feature at slightly higher energy (~7715 eV). This feature on the rising absorption edge is assigned to a metal localized 1s to 4p transition with “shakedown” contribution arising from a coupled LMCT transition [60, 61]. It is commonly observed in the K-edge XANES spectra of square planar first row transition metal complexes. The feature arises from transitions with metal 4p<sub>f</sub> final-state character [62]. In the absence of axial coordination, the metal 4p<sub>f</sub> orbital has primarily \( \sigma \)-nonbonding character and therefore is highly localized. Axial ligation delocalizes the orbital and the resulting changes in the valence electron shielding lead to decreased intensity of this edge feature. The square planar environments in the CoTPP reference complex and in the activated form of the Co-PCN222 MOF therefore yield prominent 1s → 4p edge features. The
presence of both weakly and strongly coordinating solvent guest molecules in the MOF, however, significantly reduces the intensity. The edge feature in the XANES spectrum of the acetone treated MOF is still resolved, but the band is almost completely absent from the pyridine-treated MOF spectrum. These intensities correlate with the relative strength of the axial binding interactions with these guest molecules in the Co-porphyrin MOF environment.

The Ni porphyrin MOF does not yield lower shakedown feature intensities (nor changes in the pre-edge) upon exposure to either acetone or pyridine. The unchanged edge feature intensity under these conditions indicates that, in the MOF environment, these Ni-porphyrin sites are not undergoing any substantial axial interaction with weakly or strongly coordinating guests. Instead, the Ni sites retain a similar four-coordinate geometry as the NiTPP reference molecule. This conclusion is further supported by analysis of the EXAFS spectra for the Ni porphyrin complexes and MOFs compared to those of the Co porphyrin systems (figure 5). Significantly higher amplitude of the first shell peak is observed for the guest-treated Co-PCN222 MOFs compared to the CoTPP reference. The analogous comparison among the Ni porphyrin MOFs and complex on the other hand does not reveal substantial amplitude differences. While a direct correlation with coordination number is complicated by the fact that other factors such as \( \sigma^2 \), the mean squared disorder term, influence scattering amplitude, these results indicate that the Co porphyrin MOF under coordinating solvent environments has a higher first shell coordination number (i.e. axially interacting with guest species) than the CoTPP reference but the same axial interaction is not occurring in the Ni-PCN222 MOF.

The observed evidence for axial interaction in Co-PCN222 is consistent with the known ligation behavior of CoTPP complexes in coordinating solvent solutions [63]. The lack of axial interaction in Ni-PCN222, however, is in stark contrast with the established behavior of most Ni porphyrin complexes in solution [64, 65]. Double axial ligation of NiTPP occurs in strongly coordinating solvents such as pyridine [66]. Upon consideration of the lower axial binding affinity and the \( d \) electron reorganization required to accommodate the axial ligands in Ni versus Co porphyrins, however, this contrasting behavior in the MOF environments is not that surprising. In solution, the overall binding constants of six-coordinate Ni(II)TPP complexes with pyridine are two orders of magnitude lower than those for the analogous Co(II)TPP species [63, 66]. Moreover, axial ligation with diamagnetic \( d^8 \) Ni(II) porphyrin systems requires electron promotion from the filled \( d_{z^2} \) to the \( d_{x^2-y^2} \) orbital, which is accompanied by increased Ni–N bond lengths of the porphyrin core [67–69]. In solution, this can occur readily but when the Ni-porphyrin linkers are incorporated within a MOF structure, the rigidity of the framework may severely restrict this core expansion and discourage axial ligation. The partially filled \( d_{z^2} \) orbital of Co(II) low spin \( d^7 \) configurations can accommodate one or two axial ligands without any \( d \) electron rearrangement (and therefore porphyrin core expansion) [69], so the rigidity imposed by the MOF structure in this case would not hinder this ligation. A substantial distortion from planarity of the Ni-porphyrin ring when in the framework structure may also be involved in preventing axial interaction behavior in Ni-PCN222. Previous studies on substituted Ni-porphyrin complexes that remain non-planar in solution have shown extremely low-axial binding affinity for bases such as pyridine or piperidine [70]. The contracted core of the ruffled porphyrin is thought to destabilize the \( d_{x^2-y^2} \) orbital, making the electron promotion to this orbital needed for the \( \sigma \)-donating axial bond energetically unfavorable. Combined with the small triangular pore size dimension in the PCN222 structure, a rigid non-planar porphyrin geometry in the MOF structure may create a framework environment that severely hinders axial interaction with guest molecules.

Although limited in scope, some further insights on the guest molecule axial interaction (or lack thereof) in these MOF systems are afforded through analysis of the resonance Raman spectra. While direct observation of metal-axial ligand or internal axial ligand modes is precluded by lack of resonant enhancement, some structure sensitive modes of the porphyrin macrocycle can be altered by the presence of axial ligands, particularly when this is accompanied by a metal spin state change. For example, axial ligation of Ni-porphyrin complexes with nitrogenous bases is known to alter the vibrational frequency of the spin-state marker bands, \( v_4 \) and \( v_2' \), due to the accompanying low to high spin-state change of the metal center [64]. Raman spectra of the Ni-PCN222 systems under coordinating guest
environment, however, show no frequency differences in these modes. This observation, while not definitive on its own, further supports the conclusion that the Ni-porphyrin sites in the MOF are not participating in axial coordination under the guest environment conditions tested. The Co-PCN222 also shows no changes in these spin-state sensitive vibrational modes upon inclusion of pyridine (or acetone) but this is not surprising, however, since a metal spin state change is not anticipated for these metalloporphyrid complexes upon axial ligation.

In conclusion, this combined resonance Raman and XAS spectroscopy study serves to illustrate how metalloporphyrid electronic and geometric structures can be altered by incorporation as linkers in metal-organic framework architectures. The investigation of strongly and weakly coordinating guest molecule environments revealed changes in axial binding behavior imposed by the structural constraints of the framework compared to the known behavior of similar metalloporphyrid complexes in solution.

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