Sterically Induced Distortions of Nickel(II) Porphyrins – Comprehensive Investigation by DFT Calculations and Resonance Raman Spectroscopy

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Supporting Information available.

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Abstract

A series of 5,15-disubstituted and 5,10,15,20-tetrasubstituted, and 5,10,15,20-tetrasubstituted-2,3,7,8,12,13,17,18-octaethyl nickel(II) porphyrins in dichloromethane is reported to comprehensively access their sterically induced distortions from planarity. Thus, the tutorial review focuses on both resonance Raman spectroscopic investigations and structural investigations based on DFT. We relate different theoretical and experimental methodologies to predict out-of-plane distortions of the porphyrin macrocycles which are quantified by normal-coordinate structural decomposition. This comprehensive compilation reveals shortcomings in the molecular mechanic calculations and illustrates the impact of crystal packing forces on crystal structures. Non-planar distortions shift the experimentally observed resonance Raman marker bands ν_2 , ν_3 and ν_4 to lower frequency. A revised correlation between this shift and the calculated structural parameter (ruffling angle) is presented and reveals deviations from reported correlations based on molecular mechanics.

Key words: porphyrins, resonance Raman, conformational analysis, density functional theory, molecular mechanics, out-of-plane distortions.

1. Introduction

Metalloporphyrins are a unique class of compounds with a wide variety of applications. They are utilized for light harvesting in, e.g., dye-sensitized solar cells [1] reaching efficiencies of up to 13 % [2] and thus, exceeding the efficiency obtained with ruthenium-complex based devices while avoiding the cost incurred using the expensive metal ruthenium [3]. Besides their light harvesting properties metalloporphyrins also attract attention due to their electrocatalytic activity [4]. Hydrogen and oxygen evolution reactions catalyzed by nickel porphyrins have been reported [5,6] as well as nickel porphyrin-based electrochemical sensors to detect nitric oxide release from a single cell [7,8]. Furthermore, the unique diagnostic and therapeutic potential of porphyrins, e.g., in tumor detection, tumor imaging and in the photodynamic treatment of malignancies are important motivations for porphyrin research [9–11]. Porphyrins are a ubiquitous class of compounds in nature. Classic examples are hemes, a group of iron porphyrins which serve as cofactor in proteins with multiple biological functions. Proteins such as myoglobin and hemoglobin are involved in reversible oxygen binding, while cytochromes function in reversible electron transfer processes. On the other hand, cytochromes P450 and peroxidases can perform oxidative transformations with a wide range of substrates [12]. The versatile biochemistry of cytochromes P450 has triggered the industrial applications of P450s for the production of fine chemicals [13,14]. P450s allow for a variety of regio- and enantioselective oxidation reactions, which are difficult to achieve by chemical synthesis [13,14].

The wide-range use of porphyrins is related to the unique properties of the porphyrins macrocycle: The large delocalized π -system leads to pronounced absorption in the visible range [15] and stabilizes various oxidation states of the central metal ions [16]. Additionally, the structural flexibility of the porphyrin macrocycle is remarkable and significantly impacts the optical, chemical and electronic properties of porphyrins [17,18]. Coordination of metal ions, which are small compared to the cavity size of the planar porphyrin, induces out-of-plane (*oop*) distortions [17,19,20], for example, nickel(II) ions. The optimal metal-nitrogen distance for a planar metalloporphyrin is about 2.01 Å [21,22], while Ni-N bonds prefer a shorter bond length of 1.85 Å [23]. As a result, the Ni-N bonds pull the pyrrole rings toward the center which induces *oop* deformations of the macrocycle. The actual degree of non-planarity is determined by the energetic trade-off between the energy gain from shorter Ni-N bonds within the contracted core of a non-planar porphyrin and the energy penalty arising from a decreased conjugation within the π -system of a non-planar porphyrin. The presence of substituents on the periphery of the macrocycle induces steric strain, which additionally contributes to non-planar distortions of nickel porphyrins. Thus, nickel porphyrins have been used to study the effect of non-planar distortions on the properties of porphyrins and to mimic conformationally distorted porphyrins found *in vivo* [18,24,25].

Distortion of the porphyrin macrocycle, in particular also the *oop* distortions of the macrocycle, have a significant impact on the chemical and photo-physical properties of nickel porphyrins [18], e.g., its affinity to axial ligation [26,27], redox potentials [28,29], optical absorption [30,31] and excited-state relaxation processes [25,32,33]. It can be demonstrated that the photo-physical properties of nickel porphyrins can be gradually altered by increasing the degree of non-planarity of the heterocycle, i.e.

by gradually increasing the steric demand of peripheral substituents [25,26,28]. This highlights the possibility to fine-tune the photo-physical parameters of nickel porphyrins for a given application by controlling the degree and type of *oop* distortion.

In order to understand the impact of *oop* distortions on the physical and chemical properties of metalloporphyrins, the type and degree of *oop* distortions have to be defined: Shelnutt and coworkers [34,35] introduced the concept of normal-coordinate structural decomposition (NSD), which represents a given macrocycle structure by displacements along the normal coordinates of a D_{4h} -symmetric reference macrocycle (see Figure 1 and for details Chapter 2). In most cases [34], the observed non-planarity can be adequately simulated by a linear combination of only the six lowest-frequency *oop* coordinates: *saddling* (B_{2u}), *ruffling* (B_{1u}), *doming* (A_{2u}), *waving(x)* ($E_{g(x)}$), *waving(y)* ($E_{g(y)}$) and *propellering* (A_{1u}) (minimal basis, see Figure 1B). For example, the structure of [5,15-bis(1-ethylpropyl)porphyrinato]nickel(II) (see Figure 1A) is essentially *ruffled*, i.e. strongly distorted along the lowest-frequency B_{1u} normal coordinate, while *sad*, *dom* and *wav(y)* distortions contribute only sparsely. Expressing the macrocycle distortion in terms of normal coordinates simplifies the description of non-planarity and provides an alternative to comparing frequently used structural parameters, e.g., Ni-N distance and ruffling dihedral angle $C_a-N-N-C_a$ (see Figure 1A). The simulation of a given, i.e. observed macrocycle distortion, can be improved by extending the minimal basis, i.e. by including both the lowest- and the second-lowest-frequency normal coordinate of all symmetries. Even if small, such higher order deformations contribute to the observed physical and chemical properties, as, e.g., to the red-shift of the Soret-band in non-planar nickel porphyrins [31].

While the biologically relevant hemes are planar without the apoprotein macrocycle, distortions are prevalent in heme proteins (i.e., the functional holoprotein) and induced by the protein scaffold in the vicinity of the binding pocket [35–37]. Usually, the interaction with the asymmetric protein environment leads to simultaneous and significant displacements along several lowest-frequency normal coordinates. Noteworthy, similar macrocycle distortions are found for specific functional class of heme proteins from different species, suggesting that the observed macrocycle distortion is functionally relevant [34,35]. For example, the distortion of heme in mitochondrial cytochrome c (from rice, horse and tuna) is dominated by the *ruf* distortion type with displacements of 0.7 to 1.0 Å [34]. On the other hand, the iron porphyrin cofactors in peroxidases are characterized by strong *sad* distortions of –0.6 to –0.9 Å and *ruf* distortions of –0.3 to –0.7 Å [34]. Likewise, the reversible oxygen binding proteins hemoglobin and myoglobin exhibit significant contributions of *doming* (0.3 Å in myoglobin, 0.4 to 0.5 Å for in hemoglobin) [34,35]. The total *oop* distortion of these oxygen binding cofactors (0.4 Å in myoglobin, 0.6 Å in hemoglobin) is similar to that in cytochromes P450 (0.4 to 0.5 Å), but small compared to other heme proteins such as peroxidases (0.7 to 1.2 Å) and mitochondrial cytochromes c (0.8 to 1.1 Å) [34]. Several investigation suggest that the protein-induced distortion of the heme prosthetic group is a critical factor for its biological function [18,20,35,38]. An established role of heme ruffling is the tuning of the reduction potential and electronic coupling in cytochrome c, which alters the electron transfer efficiency [39–42]. The distortion of the porphyrin macrocycle also impacts the affinity to axial ligand such as oxygen [27,43–45]. Non-planar distortions also affect the chlorophylls in

photosynthesis [38,46]. Nickel is found as the central metal in cofactor F430 in methyl-coenzyme M reductase and the importance of the nickel ion in regulating the macrocycle conformation has been clearly established [20,47–51].

In order to understand the impact of macrocycle distortions on the chemical and photo-physical properties of metalloporphyrins in solution and *in vivo*, nickel(II) porphyrins are an important and useful model system [20,52,53]. However, the NSD analysis of nickel(II) porphyrins and the resulting structural parameters are often based on crystallographic structures. Although several studies suggest a good agreement between the structure in the solid state and the actual structure in solution – and thus *in vivo* – [54,55], the molecular structure in the solid state may be altered as a result of packing forces in the crystal and π - π -interactions between neighboring porphyrins [26,56–59]. The impact of packing forces can be inferred from a comparison of the non-planar distortions for structurally similar porphyrins [26], multiple crystallographically independent molecules in the unit cell [60], and/or in crystal isomorphs [61]. For example, (5,10,15,20-tetrapentylporphyrinato)nickel(II) is strongly ruffled in the solid state, while the macrocycle with propyl instead of pentyl substituents is almost planar with only small contributions of a waving deformation [26]. Although small, these waving deformations correspond to a considerable deformation energy and arise from crystal packing forces [26]. Resonance Raman [26] and XAFS studies [57] confirm that the structure of the tetrapropyl substituted porphyrin is not planar in solution. The effects of crystal packing forces are also discussed for [2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II) (**NiOEP**), which is observed in both planar and non-planar crystalline forms [61].

To study the porphyrin structure without distortions arising from crystal packing forces, spectroscopic probes are needed to characterize the *oop* distortions of porphyrins in various environments, i.e. ideally ranging from crystals to biological *in vivo* settings. In this regard, resonance Raman spectroscopy [62] has been particularly useful. Several structure-sensitive resonance Raman bands in the high-frequency region between 1200 and 1700 cm^{-1} shift to a lower frequency with increasing non-planarity of the macrocycle. This frequency shift was investigated for a series of several nickel porphyrins with a gradual increasing steric demand of the substituents [24,26,31,63–67] and correlated to structural parameters, e.g., the Ni-N distance and the ruffling dihedral angle $\text{C}_a\text{-N-N-C}_a$. Both ruffling and saddling – which are frequently observed for metalloporphyrins – shift the structure-sensitive *ip* modes to lower frequencies [24,64,68]. As a consequence, the *ruf* and *sad* distorted conformers cannot be distinguished from the high-frequency region of the resonance Raman spectrum. However, indicators for the type of macrocycle deformation are *oop* modes in the low-frequency region of the resonance Raman spectrum, i.e. below 800 cm^{-1} . These modes become (resonance) Raman active if the *oop* mode and the distortion of the macrocycle have the same symmetry [69,70]. The coexistence of planar and non-planar conformations of **NiOEP** [71] and (5,10,15,20-tetraphenylporphyrinato)nickel(II) [72] in solution was proven by temperature-dependent resonance Raman measurements. Furthermore, resonance Raman spectroscopy was successfully applied to probe porphyrin-protein interactions and to monitor the ligation status of heme in heme proteins [73–76]. The resonance Raman spectra of porphyrins are also highly sensitive to chemical

alteration of the macrocycle. In this regard, we applied resonance Raman spectroscopy to probe the reactivity of singly-reduced nickel(II) porphyrins towards the formation of nickel(II) phlorin anions [77], which are discussed as a key intermediate in electrocatalytic hydrogen evolution reactions [5].

To corroborate such spectroscopic methods for the examination of macrocycle non-planarity, theoretical chemistry has become increasingly valuable. Molecular mechanics (MM) calculations [78] – based on an empirical determined porphyrin force field [64,79] – enable the prediction of different conformers, their energies [26,64,66,67] and vibrational frequencies [80]. Particular shortcomings of the MM approach using empirical force fields can be overcome with quantum mechanics. Contrary to calculations with the empirical force field, density functional theory (DFT) calculations predict a (slightly) non-planar structure for (porphyrinato)nickel(II), which was indeed spectroscopically proven [58,66,81,82]. The normal modes of nickel porphyrins are better reproduced by DFT than by the empirical force field [58,83]. DFT calculations and their time-dependent counterparts allow for the simulation of resonance Raman spectra for a particular molecular equilibrium geometry [70,84]. These calculations can verify the calculated molecular geometry by comparing the simulated spectra with experimental ones [74]. With molecular dynamics [78,83], structural fluctuations within an ensemble of energetically close conformational states can be simulated yielding a time-averaged structure, rather than a particular minimum energy geometry [31,85]. Systematic resonance Raman studies of various nickel porphyrin with gradually increasing non-planarity (*vide supra*) – published in the 1990's and 2000's – had to rely on crystal structures and molecular calculation based on the then state-of-the-art MM with empirical force fields [24,26,63–67,69]. However, today ground-state geometry optimizations by DFT are feasible and might give additional insights.

This review gives an overview of the sterically induced distortions and resonance Raman spectroscopic features of metalloporphyrins using a series of nickel(II) porphyrins, i.e., 5,15-disubstituted and 5,10,15,20-tetrasubstituted, and 5,10,15,20-tetrasubstituted-2,3,7,8,12,13,17,18-octaethyl nickel(II) porphyrins (see Figure 2 for structures). The first part of the review describes the NSD method used to analyze the macrocycle distortions of the nickel(II) porphyrins. Subsequently, X-ray crystal structures of nickel(II) porphyrins are compared to reported structures calculated by MM. To provide a statistically significant basis for investigations and to identify general trends, the structures of 18 nickel(II) porphyrins were obtained here by DFT calculations. This second part of the review points out the effects of crystal packing forces on the structure of nickel(II) porphyrins as well as shortcomings in the MM calculations compared to DFT calculations. Finally, the third part gives an overview of resonance Raman spectroscopy as an experimentally technique to determine the degree of macrocycle ruffling in solution. The correlations between structure-sensitive Raman frequencies and the porphyrin macrocycle distortion are summarized, which includes an updated correlation based on the DFT calculations performed here. The review includes six previously unreported nickel(II) porphyrins. To link literature data with the current state-of-the-art in the field, resonance Raman spectra of 18 nickel(II) porphyrins are discussed, including 11 previously unreported ones.

Figure 1: Structure of **NiD(1-Et-Pr)P** – calculated at the DFT level of theory – reveals the out-of-plane distortion of the porphyrin macrocycle (A). Displacements d (in Å) along the lowest-frequency out-of-plane normal coordinates are determined by normal-coordinate structural decomposition (NSD, results in bar chart). The effect of a 1 Å deformation is illustrated for each of these normal-coordinates (B, adopted from reference [66]). Figure A highlights one of the ruffling dihedral angles $\text{cis-C}_a\text{-N-N-C}_a$ (red line), the mean-square plane – determined by the 24 macrocycle atoms – (grey plane) and the position of meso (C_m), α (C_a) and β (C_b) carbon atoms.

NiD(alkyl)P and NiD(aryl)P

NiT(alkyl)P and NiT(aryl)P

NiOET(aryl)P

Figure 2: Structures and acronyms of the nickel porphyrins investigated.

2. Normal-Coordinate Structural Decomposition (NSD)

NSD is a structural decomposition method for classifying and quantifying the *oop* and *ip* distortions of a porphyrin macrocycle [35]. As reference structure for the NSD procedure serves a planar D_{4h} -symmetric copper porphyrin [(porphyrinato)copper(II), copper “porphine”]. The energy-minimized structure and normal modes of this reference structure were determined by MM calculations [35,64,67]. The displacements along the normal modes obtained are denoted as normal deformations $\widehat{\mathbf{D}}_k$. These normal deformations are normalized displacements, which is, the square root of the sum of the squares of the displacements of the 24 macrocycle atoms is 1 Å. The D_{4h} -symmetric porphyrin macrocycle with its 24 atoms has 66 normal modes (3N-6), i.e., 66 normal deformations $\widehat{\mathbf{D}}_m$, consisting of 21 *oop* and 45 *ip* (in-plane) normal deformations. Any distorted macrocycle can exactly be represented by this full basis set.

It was shown, that the crystal structures of many synthetic and protein-bound metalloporphyrins can be adequately simulated by a linear combination of only the lowest-frequency *ip* and *oop* normal deformations (minimal basis) [35]. The lowest-frequency *oop* normal deformations are displayed in Figure 1B and are denoted as: *saddling* (B_{2u}), *ruffling* (B_{1u}), *doming* (A_{2u}), *waving(x)* ($E_{g(x)}$), *waving(y)* ($E_{g(y)}$) and *propellering* (A_{1u}) (see Figure 1B). The symmetry of these normal deformations is classified according to the D_{4h} point group and given in brackets.

The following procedure describes the decomposition of the *oop* distortion into the lowest frequency normal deformations. The *oop* distortion of a macrocycle is represented by a linear combination of the lowest-frequency normal deformations $\widehat{\mathbf{D}}_k$,

$$\Delta \mathbf{z}_{\text{sim}} = d_{\text{sad}} \widehat{\mathbf{D}}_{\text{sad}} + d_{\text{ruf}} \widehat{\mathbf{D}}_{\text{ruf}} + d_{\text{dom}} \widehat{\mathbf{D}}_{\text{dom}} + d_{\text{wav(x)}} \widehat{\mathbf{D}}_{\text{wav(x)}} + d_{\text{wav(y)}} \widehat{\mathbf{D}}_{\text{wav(y)}} + d_{\text{pro}} \widehat{\mathbf{D}}_{\text{pro}} = \sum_{k=1}^6 d_k \widehat{\mathbf{D}}_k$$

where $\Delta \mathbf{z}_{\text{sim}}$ is a 24-dimensional vector representing the displacement of each atom with respect to the least-squares mean plane of the 24 macrocycle atoms. The coefficient d_k gives the displacements (in Å) along the normal deformation $\widehat{\mathbf{D}}_k$ and is obtained by solving the least square problem,

$$f(d_k) = |\Delta \mathbf{z}_{\text{sim}} - \Delta \mathbf{z}_{\text{obs}}|^2 = \left| \sum_{k=1}^6 d_k \widehat{\mathbf{D}}_k - \Delta \mathbf{z}_{\text{obs}} \right|^2 = \text{minimum}$$

$$\frac{\partial f(d_k)}{\partial d_k} = 0$$

which requires that the square of $|\Delta \mathbf{z}_{\text{sim}} - \Delta \mathbf{z}_{\text{obs}}|$, i.e. the difference between the simulated *oop* deformation $\Delta \mathbf{z}_{\text{sim}}$ and the observed *oop* deformation $\Delta \mathbf{z}_{\text{obs}}$, becomes minimal. For the decomposition of the *ip* distortion, the *ip* displacements, Δx and Δy , are given with respect to the mentioned copper porphyrin reference structure. The NSD analysis using all *oop* and *ip* normal deformations is described in detail by Jentzen *et al.* [35].

The results of the NSD analysis can be summarized in a graph as, for example, depicted in the inset of Figure 1A. This graph shows that the macrocycle of [5,15-bis(1-ethylpropyl)porphyrinato]nickel(II) is with $d_{\text{ruf}} = 1.58$ Å strongly displaced along the *ruf* mode, while *sad*, *dom*, *wav(x)*, *wav(y)* and *pro*

displacements are smaller than $d < 0.1 \text{ \AA}$ and thus contribute only sparsely to the observed macrocycle distortion.

Due to the fact, that the lowest-frequency *oop* normal deformations only span a 6-dimensional and not the full 21-dimensional coordinate space, the simulated macrocycle deformation ($\Delta\mathbf{z}_{\text{sim}}$) does not exactly represent the observed one ($\Delta\mathbf{z}_{\text{obs}}$). To evaluate the goodness of fit, the mean deviation $\bar{\delta}_{\text{oop}}$ between the simulated and the observed out-of-plane displacements is considered [35], which is given by

$$\bar{\delta}_{\text{oop}} = \frac{1}{24} \sum_{n=1}^{24} |(\Delta\mathbf{z}_{\text{sim}})_n - (\Delta\mathbf{z}_{\text{obs}})_n|$$

For reference, in x-ray crystallography, the mean positional error for a single atom is about 0.006 Å in three dimensions (and 0.003 Å in one dimension) (assuming a refinement factor, R-value, of 0.07) [34].

The vibrational frequency for the copper porphyrin reference macrocycle, obtained from the normal mode calculations by MM calculations, are 65 (*sad*), 88 (*ruf*), 135 (*dom*), 65 (*sad*), 176 (*wav(x)*, *wav(y)*) and 335 cm^{-1} (*pro*) [35]. Thus, a porphyrin macrocycle is easier to distort along, *e.g.*, the *sad* and the *ruf* mode than along the *pro* mode. As will be shown in the next chapter, the actual distortion of the macrocycle depends on the peripheral substituents and the substitution pattern of the macrocycle. Due to the small amount of energy necessary to deform the porphyrin macrocycle, packing forces can affect the macrocycle distortion and thus lead to a difference between the structure in the solid state (x-ray crystallography) and the structure in solution.

The NSD analysis can be performed using a program available online [86].

3. Classification of Nickel(II) Porphyrins Structures

To illustrate the sterically induced distortions of the nickel(II) porphyrins investigated (Figure 2), structures from X-ray crystallography, MM calculations [78] and DFT calculations are considered. For this comparison, the structures are analyzed by NSD and the displacements along the lowest-frequency *oop* normal modes are summarized in Figure 3-6. All nickel(II) porphyrins exhibit strong *oop* distortions with displacements of at least 0.9 Å along the *ruf* or 4.0 Å along the *sad* mode. First, the structures of nickel(II) porphyrins derived from our DFT calculations will be briefly described, while a comprehensive analysis and comparison with MM and crystal structures follows subsequently. The series of nickel(II) porphyrins is divided into three groups: (i) **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins, (ii) **NiD(aryl)P** and **NiT(aryl)P** porphyrins, and (iii) **NiOET(aryl)P** porphyrins (see Figure 2).

The calculated structures of the di- and tetraalkyl substituted porphyrins are essentially ruffled (see Figure 3 and 4). Increased steric strain induced by spatially more demanding substituents or by a higher number of meso-substituents is relieved by an increased *ruf* distortion. However, **NiT(2-Me-Pr)P** exhibits significant contributions of saddling (0.26 Å) and waving(y) (0.13 Å) in addition to the *ruf*

distortion (2.20 Å). Distortions along these higher frequency normal modes of the minimal basis are associated with (asymmetric) alkyl chains bearing two γ -carbon atoms.

In contrast to the essentially ruffled alkyl-substituted porphyrins, the macrocycle of the di- and tetraaryl-substituted porphyrins is distorted by a mixture of ruffling and saddling (see Figure 5). Saddling sterically enables the rotation of the aryl-substituents into the porphyrin plane and thus increases the energetically favorable overlap for the π -system of the peripheral aryl-substituents and the macrocycle [87]. A larger number of meso-substituents increases the driving force associated with saddling, thus causing a strong increase of saddling upon increasing the number of meso-aryl-substituents from two (**NiD(aryl)P**) to four (**NiT(aryl)P**).

NiOET(aryl)P porphyrins are essentially saddled (see Figure 6). The sterically crowded **NiOET(aryl)P** shows large saddle distortions and almost no contribution from ruffling. Apparently, the steric repulsion between neighboring peripheral substituents is most effectively minimized by distortion along the saddling mode.

The DFT calculations assign different types and degrees of *oop* deformations to specific porphyrins compared to the results of MM calculations (Figure 3-6). In particular: (i) Based on MM, a gabled distortion was previously assumed for **NiD(alkyl)P** porphyrins, i.e. a contribution of both *ruf* and *dom* distortion [65,67], while DFT predicts an essentially *ruf* conformation (see Figure 3). (ii) Compared to DFT, MM slightly overestimates the *ruf* distortion of **NiT(alkyl)P** porphyrins with primary alkyl substituents, while for the corresponding porphyrins with tertiary alkyl substituents an overestimation was found (see Figure 4) [26]. (iii) A mixture of *ruf* and *sad* distortion is predicted for **NiD(aryl)P** and **NiT(aryl)P** porphyrins by DFT, which is experimentally supported [88]. In contrast, MM gives purely *ruf* distorted conformers for these porphyrins (see Figure 5) [26,67,72]. A comparison of the nickel(II) porphyrin structures calculated by DFT and MM to their reported crystal structures (Figure 3-6) leads to the conclusion, that in some cases crystal packing forces strongly impacts the porphyrin macrocycle distortion.

Normal-Coordinate Structural Decomposition

The calculated structures are analyzed using only the minimal basis, i.e. the lowest-frequency *oop* and *ip* normal modes. To quantify the goodness of fit the mean deviation $\bar{\delta}_{oop}$ between the simulated and observed *oop* displacement of the 24 macrocycle atoms is considered [35]. This value is 0.01 Å or less for the investigated series of **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins. In the case of the strongly distorted **NiT(tBu)P** the mean deviation for the *oop* distortions is 0.03 Å, i.e. larger compared to porphyrins with less sterically demanding alkyl-substituents. The aryl-substituted porphyrins exhibit slightly higher mean deviation in comparison to their alkyl-substituted counterparts. For the series of **NiD(aryl)P**, **NiT(aryl)P** and **NiOET(aryl)P** the mean deviations are 0.01, 0.02 and 0.04 Å, respectively. For each of the porphyrins investigated the mean deviation for the *oop* distortions is small compared to the total *oop* distortion of 0.95 – 4.05 Å. Thus, the minimal basis is considered as appropriate to simulate the observed structures and to compare the *oop* distortion of the investigated

porphyrins. The agreement between observed and simulated structure can be improved by decomposing the observed structure with an extended basis, which includes both the lowest and the second lowest-frequency normal coordinates of each symmetry type. The complete results of the NSD including the mean deviations and total distortion for the *oop* and *ip* displacements using the minimal basis are tabulated in the Supporting Information (see Table S1-3 and Figure S8).

NiD(alkyl)P and NiT(alkyl)P Porphyrins

The series of **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins are essentially ruffled (see Figure 3 - 4). The distortion along normal modes other than *ruf* reaches maximal values of 0.14 Å, which is small compared to observed *ruf* displacements of 1.10 to 2.91 Å. This is not the case for **NiT(2-Me-Pr)P**, which exhibits contributions of saddling (0.26 Å) and waving(y) (0.13 Å) besides the *ruf* distortion (2.20 Å).

For the series of **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins the simulated *ruf* displacement (d_{ruf}) as well as the observed total *oop* displacement increases in the following order: **NiD(2-Me-Pr)P** (1.10 Å) << **NiD(1-Et-Pr)P** (1.59 Å) < **NiT(2-Me-Pr)P** (1.62 Å) < **NiT(Bu)P** (1.92 Å), **NiT(He)P** (1.93 Å) << **NiT(1-Et-Pr)P** (2.12 Å) < **NiT(iPr)P** (2.19 Å) < **NiT(1-Me-Pr)P** (2.20 Å) << **NiT(tBu)P** (2.90 Å). The sequence observed illustrates the following: (i) Increasing the number of meso-substituents significantly increases the degree of ruffling. The tetrasubstituted **NiT(2-Me-Pr)P** and **NiT(1-Et-Pr)P** are stronger displaced along *ruf* than the corresponding disubstituted porphyrins, **NiD(2-Me-Pr)P** and **NiD(1-Et-Pr)P**. (ii) The degree of ruffling increases with the steric demand of the meso-alkyl-substituents, which is the highest for substituents with tertiary α -carbon atoms, considerably lower for secondary and lowest for primary α -carbon atoms. The *ruf* displacement for the **NiT(alkyl)P** porphyrins, which amounts to 1.62-1.74 Å for primary substituents, 2.12-2.20 Å for secondary substituents and 2.90 Å for tertiary substituents, clearly illustrates this trend. Despite its larger secondary alkyl-substituent, both the *ruf* displacement (d_{ruf}) and the observed total *oop* displacement (D_{oop}) is smaller for **NiT(1-Et-Pr)P** (d_{ruf} = 2.12 Å, D_{oop} = 2.12 Å) than for **NiT(iPr)P** (d_{ruf} = 2.19 Å, D_{oop} 2.20 Å). Rather than an increase in *ruf* displacement, the larger 1-ethylpropyl substituent of **NiT(1-Et-Pr)P** with the presence of its two γ -carbon atoms induces additional displacements along higher frequency normal modes of the minimal basis: *dom* (0.04 Å), *wav(x)* (0.02 Å) and *wav(y)* (0.04 Å). For **NiT(iPr)P** these *oop* displacements are essentially nonexistent, i.e. smaller than 0.01 Å.

As mentioned above, small contributions of distortions other than *ruf* are observed for the **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins. The degree and type of these additional distortions strongly depend on the type of substituents: A small contribution of saddling is observed for all alkyl-substituted porphyrins (0.01 – 0.14 Å), except for the porphyrins with *n*-alkyl chains, which exhibit a small *dom* distortion (0.04 Å), i.e. a deformation along the third highest frequency normal coordinate of the minimal basis. Waving, i.e. a deformation along one of the two second highest frequency normal modes, is only observed for the porphyrins with two γ -carbon atoms, e.g., **NiD(2-Me-Pr)P** (d_{dom} = 0.02 Å, $d_{wav(x)}$ = 0.05 Å, $d_{wav(y)}$ = 0.03 Å), **NiD(1-Et-Pr)P** (d_{dom} = 0.05 Å, $d_{wav(x)}$ = 0.01 Å, $d_{wav(y)}$ = 0.04 Å), **NiT(2-Me-Pr)P** (d_{dom} = 0.00 Å, $d_{wav(x)}$ = 0.02 Å, $d_{wav(y)}$ = 0.13 Å), **NiT(1-Et-Pr)P** (d_{dom} = 0.04 Å, $d_{wav(x)}$ = 0.02 Å, $d_{wav(y)}$ =

0.04 Å). Propelling distortions, i.e. displacements along the highest frequency normal coordinate of the minimal bases, are not observed.

The macrocycle of the investigated dialkyl- and tetraalkyl-meso-substituted nickel porphyrins is essentially ruffled, although distortion along the *ruf* normal mode is energetically slightly more demanding (88 cm⁻¹, calculated based on an atomic force field approach) [35] than along the softer *sad* normal mode (65 cm⁻¹). Small metal ions such as nickel(II) favor ruffling over saddling as ruffling contracts the porphyrin core more than saddling and thus provides a shortened and more favorable Ni–N bond distance [65]. Additionally, the distortion along the ruffling normal mode effectively decreases the steric repulsion between the peripheral substituents and the porphyrin macrocycle. The *ruf* distortion places the meso-carbon atoms alternately above and below the macrocycle mean plane. This motion tilts the peripheral substituents away from the porphyrin macrocycle and thus reduces the steric repulsion between these substituents and the porphyrin macrocycle – in particular to the closest β-carbon atoms of the porphyrin macrocycle (see Figure 1A for illustration of the **NiD(1-Et-Pr)P** structure). Thus, ruffling is observed for the dialkyl- and tetraalkyl-meso-substituted nickel porphyrins. As noted for **NiD(alkyl)P** and **NiT(alkyl)P** porphyrins, increased steric strain induced by spatially-demanding substituents or by a higher number of meso-substituents is relieved by increasing the *ruf* distortion.

According to MM, **NiD(alkyl)P** porphyrins exhibit a mixture of *ruf* and *dom* distortion (see Figure 3) [67]. In contrast, DFT calculations predict an essentially ruffled macrocycle with minor contributions of *sad*, *dom*, *wav(x)* and *wav(y)*. This is apparent by comparing the MM structure for **NiD(iPr)P** [65] (*d_{ruf}* = 1.47 Å, *d_{dom}* = 0.23 Å) and **NiD(tBu)P** [67] (*d_{ruf}* = 2.01 Å, *d_{dom}* = 0.54 Å) with the DFT structure of the structurally similar **NiD(1-Et-Pr)P** (*d_{ruf}* = 1.59 Å, *d_{dom}* = 0.05 Å). The results of the MM calculations are supported by the crystal structures of **NiD(iPr)P** and **NiD(tBu)P**, which exhibit similar degrees of *ruf* and *dom* distortions (see Figure 3). However, nickel porphyrins are prone to deformation in the solid state due to packing forces and non-planar deformation of the porphyrin ring. It should be noted that the empirical force field used for the MM calculations is derived from and refined for nickel porphyrin crystal structures (*vide supra*) [67]. Thus, the predicted mixture of *ruf* and *dom* distortions for **NiD(alkyl)P** might originate from a shortcoming of MM calculations. For the series of **NiD(alkyl)P** porphyrins investigated only the crystal structure of **NiD(2-Me-Pr)P** has been reported [89]. However, this compound forms π-π-dimers, which leads to an almost planar macrocycle. Thus, this situation cannot be considered for a comparison to the DFT structure.

For **NiT(alkyl)P** porphyrins DFT calculations predicts an essentially *ruf* distortion of the macrocycle which is in line with MM calculations [26] (see Figure 4). However, compared to DFT, MM slightly underestimates the degree of ruffling upon increasing the steric demand of the substituents: **NiT(Bu)P** (DFT: 1.92 Å), **NiT(Pr)P** (MM: 1.80 Å), **NiT(iPr)P** (DFT: 2.19 Å, MM: 2.23 Å), **NiT(tBu)P** (DFT: 2.90 Å, MM: 2.74 Å) [26]. According to DFT and MM calculations, the crystal structures for **NiT(alkyl)P** porphyrins exhibit strong contributions of *ruf* distortion (see Figure 4). Additional *sad* distortions are observed in the crystal structure of **NiT(Pe)P** [26] (*d_{sad}* = 0.46 Å, *d_{ruf}* = 1.57 Å) and

NiT(iPr)P [90] ($d_{\text{sad}} = 0.46 \text{ \AA}$, $d_{\text{ruf}} = 2.03 \text{ \AA}$). Although *sad* distortions are observed for **NiT(iPr)P**, it is not observed in the crystal structure of structurally similar **NiT(1-Et-Pr)P** [91] ($d_{\text{sad}} = 0.00 \text{ \AA}$, $d_{\text{ruf}} = 2.25 \text{ \AA}$). DFT and MM calculations predict much smaller *sad* distortions for **NiT(Pe)P** and **NiT(iPr)P** with displacements of less than $0.10 \text{ \AA}$. Thus, the strong *sad* distortion observed in crystals of these porphyrins might originate from crystal packing forces. The impact of crystal packing forces on the conformation of the macrocycle is also apparent for **NiT(Pr)P** which is almost planar in the solid state [26], while the crystal structure of the structurally similar **NiT(Pe)P** and the DFT structure of **NiT(Bu)P** show strong non-planar distortions. The calculated Ni–N distance for **NiT(Bu)P** is $1.93 \text{ \AA}$ according to DFT calculations, which is consistent with the $1.90(2) \text{ \AA}$ Ni–N distance for **NiT(Pr)P** in solution determined by extended X-ray absorption fine structure spectroscopy [57]. DFT calculations predicted small *wav* distortions, i.e. displacements along a higher frequency normal coordinate of the minimal basis. However, such *wav* displacements are only found for porphyrins with substituents bearing two γ -carbon atoms, e.g., for **NiT(2-Me-Pr)P** and **NiT(1-Et-Pr)P**. The crystal structures of **NiT(2-Me-Pr)P** [91] and **NiT(1-Et-Pr)P** [91] exhibit small contributions of *wav*, too. However, in the crystal almost all **NiT(alkyl)P** porphyrins exhibit *wav* deformation (see Figure 4), which is likely to arise from crystal packing forces in many cases. Thus, the crystal structures are not reliable to address the question if *wav* deformations occur for porphyrins with substituents bearing two γ -carbon atoms.

Figure 3: Displacements along the lowest-frequency *oop* normal coordinates for **NiD(alkyl)P** porphyrins: *sad* (black), *ruf* (red), *dom* (blue), *wav(x)* (magenta), *wav(y)* (olive) and *pro* (navy). Structures are calculated with DFT (this study) and compared to reported MM calculations (values taken from literature) [67] and to crystal structures (X-ray): **NiD(2-Me-Pr)P** (two conformers in unit cell) [89], **NiD(iPr)P** [65], **NiD(tBu)P** [67].

Figure 4: Displacements along the lowest-frequency *oop* normal coordinates for **NiT(alkyl)P** porphyrins: *sad* (black), *ruf* (red), *dom* (blue), *wav(x)* (magenta), *wav(y)* (olive) and *pro* (navy). Structures are calculated with DFT (this study) and compared to reported MM calculations (values taken from literature, [26]) and to crystal structures (X-Ray): **NiT(2-Me-Pr)P** [91], **NiT(iPr)P** [90], **NiT(1-Et-Pr)P** [91] and **NiT(Pe)P** (four independent porphyrins per unit cell with similar *oop* distortions, parameters for porphyrin containing nickel atom number 4, [26]). *oop* displacements in the crystal structure of **NiT(Pr)P** are taken from the literature [26].

NiD(aryl)P and NiT(aryl)P Porphyrins

In contrast to the essentially ruffled alkyl-substituted porphyrins, the macrocycle of the aryl-substituted porphyrins is displaced along both the *sad* and the *ruf* normal mode (see Figure 5). Displacements along higher frequency normal modes occur only for the diaryl-derivatives, particularly with a very small contribution of doming (0.01 Å). In the diaryl-substituted series, i.e. **NiD(3-MeOPh)P**, **NiD(Ph)P** and **NiD(4-MePh)P**, the displacement along *ruf* is 0.93 – 0.97 Å and along *sad* 0.19 – 0.26 Å. For the tetraaryl substituted porphyrins, i.e. **NiT(Ph)P** and **NiT(4-MeOPh)P**, larger *ruf* displacements of 1.28 – 1.35 Å and much larger *sad* displacements of 0.75 – 1.08 Å are observed. The increase of ruffling upon raising the number of meso-aryl substituents from two to four is similar to the above described meso-alkyl substituted counterparts, but the increased saddling is unprecedented, compared to, e.g., **NiD(1-Et-Pr)P** ($d_{\text{ruf}} = 1.59$ Å, $d_{\text{sad}} = 0.09$ Å) and **NiT(1-Et-Pr)P** ($d_{\text{ruf}} = 2.12$ Å, $d_{\text{sad}} = 0.09$ Å). The specific type of aryl-substituent significantly impacts *oop* distortions in tetraaryl substituted porphyrins. For example, the saddling in **NiT(4-MeOPh)P** ($d_{\text{ruf}} = 1.28$ Å, $d_{\text{sad}} = 1.08$ Å) is much stronger than for **NiT(Ph)P** ($d_{\text{ruf}} = 1.35$ Å, $d_{\text{sad}} = 0.75$ Å), while ruffling is slightly decreased.

In contrast to the dialkyl- and tetraalkyl-substituted porphyrins, the macrocycle of diaryl- and tetraaryl-substituted porphyrins is not only ruffled but shows additional contributions of saddling. The dihedral angle between the aryl-substituents and the porphyrin mean plane decreases with the number of aryl-

substituents from 66° for **NiD(Ph)P** to 61° for **NiT(Ph)P**. The stronger tilting of the substituents in the diaryl-substituted porphyrins is related to the extent of saddling, which increases from $d_{\text{sad}} = 0.23 \text{ \AA}$ for **NiD(Ph)P** ($d_{\text{ruf}} = 0.96 \text{ \AA}$) to $d_{\text{sad}} = 0.75 \text{ \AA}$ for **NiT(Ph)P** ($d_{\text{ruf}} = 1.35 \text{ \AA}$). Saddling sterically enables the rotation of the aryl-substituents into the porphyrin plane and thus increases the energetically favorable overlap for the π -system of the peripheral aryl-substituents and the macrocycle [87]. This fact can be understood by comparing pure *ruf* and *sad* distortions: Upon saddling the two β -carbon atoms which are closest to the meso-carbon atom are displaced to opposite sides of the porphyrin mean plane while the meso-carbon atom stays in the porphyrin mean plane. Thus, the steric repulsion between the meso-aryl group and the closest β -carbon atoms is reduced. This, in turn, enables tilting of the originally perpendicular meso-aryl substituent into the porphyrin mean plane. On the other hand, the *ruf* distortion displaces the meso-substituents and both closest α - and β -carbon atoms to one side of the porphyrin mean plane. Tilting of the meso-aryl group into the porphyrin plane is inhibited by the steric repulsion between the meso-aryl groups and the closest β -carbon atoms of the porphyrins. To graphically illustrate ruffling and saddling and the consequences for the orientation of the peripheral substituents Figure S1-2 in the Supporting Information compares the structures of **NiD(Ph)P** and **NiT(Ph)P**. A correlation between the degree of saddling and the dihedral angle between the aryl-substituents and the porphyrin mean plane was observed in X-ray crystallographic studies [92] and MM calculations [21]. It was concluded that a small dihedral angle requires a saddled conformer. Increasing the number of meso-aryl substituents raises the energy gain from π -conjugation, which allows to overcome the energy cost for a stronger saddling distortion, as observed for **NiD(Ph)P** ($d_{\text{sad}} = 0.23 \text{ \AA}$) and **NiT(Ph)P** ($d_{\text{sad}} = 0.75 \text{ \AA}$).

DFT calculations predict a mixture of *ruf* and *sad* distortion for **NiT(Ph)P** ($d_{\text{ruf}} = 1.35 \text{ \AA}$, $d_{\text{sad}} = 0.75 \text{ \AA}$). This is also observed in the crystal structure ($d_{\text{ruf}} = 1.27 \text{ \AA}$, $d_{\text{sad}} = 0.26 \text{ \AA}$, see Figure 5) [93]. According to DFT, *sad* distortions are further increased for **NiT(4-MeOPh)P** to $d_{\text{sad}} = 1.08 \text{ \AA}$, while the *ruf* distortion is slightly decreased, which illustrates exemplarily how the substitution of the aryl-group influences the π -conjugation and can increase the driving force for saddling. The predicted increase (decrease) of saddling (ruffling) is also supported by the crystal structure of **NiT(4-MeOPh)P** ($d_{\text{ruf}} = 0.97 \text{ \AA}$, $d_{\text{sad}} = 2.11 \text{ \AA}$) [94]. The correlation of porphyrin-core saddling and twisting of meso-aryl substituents was studied in detail for free-base porphyrins by DFT [87], where a similar effect was found, which is that substituents on the aryl groups tend to increase *sad* distortions.

Contrary to the DFT calculations, MM predict a purely *ruf* distortion for **NiD(Ph)P** ($d_{\text{ruf}} = 0.61 \text{ \AA}$) [67] and **NiT(Ph)P** ($d_{\text{ruf}} = 1.48 \text{ \AA}$) (see Figure 5) [26,72]. In previous X-ray crystallographic studies [92] and MM calculations [21] it was assumed that the tilting of the aryl groups in metalloporphyrins, and thus saddling, is induced by crystal packing forces. According to the DFT calculation described here and prior DFT studies on **NiT(Ph)P** [83] both saddling and ruffling contribute to the non-planar distortion of **NiD(aryl)P** and **NiT(aryl)P**. This is also supported by Raman dispersion spectroscopy showing that **NiT(Ph)P** exhibits both *sad* and *ruf* distortions [88]. Thus, DFT structures for the **NiD(aryl)P** and **NiT(aryl)P** porphyrins revealing a mixture of *ruf* and *sad* distortion seem reasonable,

while the force field used for MM calculations is not able to accurately describe the electronic effects of aryl-substituents on the conformation of the macrocycle.

Figure 5: Displacements along the lowest-frequency *oop* normal coordinates for **NiD(aryl)P** and **NiT(aryl)P** porphyrins: *sad* (black), *ruf* (red), *dom* (blue), *wav(x)* (magenta), *wav(y)* (olive) and *pro* (navy). Structures are calculated with DFT (this study) and compared to reported MM calculations (values taken from literature, [26,67]) and to reported crystal structures (X-ray): **NiT(Ph)P** [93] and **NiT(4-MeOPh)P** [94]. The *oop* displacements for the crystal structure of **NiD(Ph)P** are taken from the literature [35].

NiOET(aryl)P Porphyrins

For the series of **NiOET(aryl)P**, i.e. **NiOET(3-MeOPh)P**, **NiOET(Ph)P**, **NiOET(4-MeOPh)P** and **NiOET(4-Br-Ph)P**, strong saddling distortions of 4.02 – 4.04 Å are predicted by DFT (see Figure 6). Displacements of another type of symmetry are only observed along *ruf*. Ruffling is very small and decreases in the following order: **NiOET(3-MeOPh)P** (0.06 Å), **NiOET(Ph)P** (0.03 Å), **NiOET(4-Br-Ph)P** (0.01 Å) and **NiOET(4-MeOPh)P** (0.00 Å).

The **NiOET(aryl)P** investigated show large saddle distortions and exhibit almost no contribution of ruffling distortion. These sterically crowded porphyrins have peripheral substituents in all meso- and β -positions and thus, steric repulsion between neighboring peripheral substitutions contributes additionally to the ones between the substituents and the porphyrin macrocycle. Apparently, this steric strain is most effectively minimized with a distortion along the saddling mode. The torsion angle between the phenyl-substituent and the porphyrin mean plane is 40° for **NiOET(Ph)P**, i.e. much smaller compared to the 61° for **NiT(Ph)P**. This smaller torsion angle is possible due to the strong *sad* displacement of 4.03 Å as discussed for the **NiD(aryl)P** and **NiT(aryl)P** porphyrins in the previous section. DFT gives a Ni–N distance of 1.92 Å in dichloromethane solution, which agrees with the value of 1.91 ± 0.02 Å [54] in tetrahydrofuran solution determined by extended X-ray absorption fine structure measurements. The calculated saddling distortion for **NiOET(Ph)P** ($d_{\text{sad}} = 4.03$ Å) is consistent with the one from the crystal structure [54] ($d_{\text{sad}} = 3.81$ Å, see Figure 6) and with MM calculations [54,64,95].

Figure 6: Displacements along the lowest-frequency *oop* normal coordinates for **NiOE(aryl)P** porphyrins: *sad* (black), *ruf* (red), *dom* (blue), *wav(x)* (magenta), *wav(y)* (olive) and *pro* (navy). Structures are calculated with DFT (this study) and compared to the reported crystal structure (X-ray) of **NiOET(Ph)P** [54].

4. Resonance Raman Spectroscopy

This section introduces resonance Raman spectroscopy as a spectroscopic technique to gain insight into the structure of the porphyrins in solution. As will be explained subsequently, the resonance Raman spectra of nickel(II) porphyrins contain structure-sensitive resonance Raman bands which shift to lower frequency upon an increase in the ruffling angle. Correlation of the frequency of these structure-sensitive resonance Raman bands and structural parameters have been reported in the literature [24,26,31,63–65]. These correlations are based purely on molecular mechanic calculations and crystal structures. Crucially, as discussed, *oop* deformations of nickel(II) porphyrins can be affected by crystal packing forces limiting the relevance of the crystal data for solution samples. Furthermore, the structural parameters calculated by MM may be affected by shortcomings of the MM calculations. Thus, the review will present updated correlations based on the structural parameters calculated at the DFT level of theory and will compare the derived correlation to reported ones based on MM calculations. DFT calculations are considered more reliable than MM calculations. Structures calculated by DFT are generally in better agreement with experimental results [58,66,82] and experimental normal modes of nickel(II) porphyrins are more reliably reproduced reproduced by DFT than by MM [58,83].

Description of Resonance Raman Spectra

The resonance Raman spectra of **NiD(alkyl)P**, **NiT(alkyl)P**, **NiD(aryl)P** and **NiT(aryl)P** porphyrins upon excitation at 413 nm show overall similarities in the high-frequency region between 1300 – 1700 cm^{-1} (see Figures 7 and 8, for UV-vis absorption spectra see Figure S3). Two intense resonance Raman bands appear at approximately 1370 (ν_4) and 1570 cm^{-1} (ν_2) and weaker bands at approximately 1460 (ν_3) and 1500 cm^{-1} (ν_{28}). Additionally, a weak and broad resonance Raman band occurs at 1640 cm^{-1} (ν_{10}) for the disubstituted porphyrins (see Figure 7). Bands ν_4 , ν_3 , and ν_2 shift to lower frequencies upon increasing the sterically demand of the peripheral substituents, i.e. upon increasing the degree of non-planarity (see Figures 7 and 8). For this reason, the bands mentioned have been identified as structure-sensitive resonance Raman modes [24,26,31,63–65]. The resonance Raman bands of nickel(II) porphyrins can be assigned by analogy with, e.g., **NiD(Ph)P** [67]

and **NiT(Ph)P** [72,88] using the notation from the normal coordinate analysis as derived by Li *et al.* [96]. For the aryl-substituted porphyrins an aryl *ip* mode ν_ϕ contributes to the resonance Raman spectrum of **NiD(aryl)P** and **NiT(aryl)P** porphyrins in the region between 1600-1620 cm^{-1} [88,96]. This mode can be distinguished from the porphyrin macrocycle *ip* mode ν_{10} by the quite different half-width and intensity: for Soret excitation ν_{10} is weak and very broad (see Figure 7) [88,96].

Figure 7: Resonance Raman spectra of **NiD(aryl)P** and **NiD(alkyl)P** porphyrins in dichloromethane obtained upon 413 nm laser excitation. Structure-sensitive marker bands are indicated by grey bars. Solvent bands are marked by asterisks.

Figure 8: Resonance Raman spectra of **NiT(alkyl)P** and **NiT(aryl)P** porphyrins in dichloromethane obtained upon 413 nm laser excitation. Structure-sensitive marker bands are indicated by grey bars. Solvent bands are marked by asterisks.

The resonance Raman spectra of the **NiOET(aryl)P** porphyrins (see Figure 9) are characterized by two intense structure-sensitive Raman marker bands ν_4 and ν_2 at approximately 1360 and 1560 cm^{-1} , respectively [64] and additional strong bands in the 1400-1550 cm^{-1} region. The latter region is similar to that of **NiOEP** [64,97] and contains the intense mode ν_3 [64]. The aryl group mode ν_ϕ appears at approximately 1600 cm^{-1} [64].

Figure 9: Resonance Raman spectra of **NiOET(aryl)P** porphyrins in dichloromethane obtained upon 413 nm laser excitation. Structure-sensitive marker bands are indicated by grey bars. Solvent bands are marked by asterisks.

The resonance Raman bands of nickel(II) porphyrins in the region below 1300 cm^{-1} strongly depend on the type of peripheral substituents (see Figure 10) and thus can serve as fingerprint to identify and distinguish porphyrins [24,67]. Furthermore, this region contains *oop* modes, which can be used to distinguish between different types of *oop* distortions [69,70].

Figure 10: Resonance Raman spectra of the nickel(II) porphyrins investigated in dichloromethane obtained upon 413 nm laser excitation. The low-frequency region is presented. No solvent bands were observed within the presented frequency region.

Shift of Resonance Raman Frequencies

For the ruffled porphyrins, i.e. **NiD(alkyl)P**, **NiT(alkyl)P**, **NiD(aryl)P** and **NiT(aryl)P**, a shift of the resonance Raman bands to lower frequencies is observed for increasing degrees of ruffling [24,26,63–65]. For illustration, Figure 11A presents a plot of the frequency of the structure-sensitive resonance Raman bands ν_4 , ν_3 , and ν_2 as a function of the calculated ruffling dihedral angle τ_{ruf} (torsion angle cis- $\text{C}_a\text{-N-N-C}_a$, see Figure 1). Notably, **NiOET(aryl)P** porphyrins do not follow the trend of the ruffled nickel(II) porphyrins, due to the fact that **NiOET(aryl)P** porphyrins are essentially saddled [54,64,95]. However, the resonance Raman bands are also shifted to lower frequencies by saddling [64], e.g., as shown in Figure 11A, the ν_2 mode for **NiOET(aryl)P** porphyrins (ruffling angles of less than 1.2°) is at approximately 1564 cm^{-1} , which is the same as for the ruffled **NiT(Bu)P** (ruffling angle of 41°).

Figure 11: (A) Experimental (black) and calculated (blue) frequency of ν_2 , ν_3 and ν_4 for the **NiD(alkyl)P** (filled circles), **NiD(aryl)P** (open circles), **NiT(alkyl)P** (filled squares), **NiT(aryl)P** (open squares) and **NiOET(aryl)P** porphyrins (filled triangles) as a function of the calculated ruffling angle τ_{ruf} (Table 1 lists τ_{ruf} and experimental ν_2 , ν_3 and ν_4). Geometry and frequency calculations at the DFT level of theory. Fit of data using the functional form $\nu = A + B \cos(\tau_{ruf})$ (solid lines, see text for details). Graph (B) compares the correlation of the experimental frequencies obtained and DFT calculated τ_{ruf} (black symbols and line, same as A) to correlations based on reported ruffling angles derived from MM calculations: experimental frequencies for a series of tetra-alkyl porphyrins (for details see text) [24] as function of τ_{ruf} calculated by MM using an empirical force (cyan symbols, values taken from Jentzen *et al.*, [24]) and an improved empirical force field (red symbols, values taken from Song *et al.*, [26]). Arrows indicate the deviation between the respective ruffling angles calculated by DFT and by the two force fields. (C) The displacement vectors of the respective normal modes are shown exemplarily for **NiD(1-Et-Pr)P** as derived from DFT calculations.

The structure-sensitive resonance Raman bands ν_4 , ν_3 , and ν_2 result from macrocycle *ip* vibrations [96]. The displacement vectors of ν_4 , ν_3 , and ν_2 – derived from our DFT calculations – are exemplarily shown for **NiD(1-Et-Pr)P** in Figure 11C. Table S4 in the Supporting Information lists the displacement vectors of all investigated porphyrins. The frequency downshift of the *ip* vibrations ν_4 , ν_3 , and ν_2 observed upon an increase in the ruffling angle (Figure 11A) is caused by a decreased π -conjugation within the porphyrin macrocycle [98]. *ruf* Distortions twist p_z orbitals relative to each other and thus reduce the mutual orbital overlap. The orbital overlap has a cosine dependence on the dihedral angle between the individual p_z orbitals. Consequently, a cosine dependence of the vibrational frequencies on the ruffling angle is expected [98].

Indeed, for the ruffled porphyrins, i.e. **NiD(alkyl)P**, **NiT(alkyl)P**, **NiD(aryl)P** and **NiT(aryl)P** (black symbols, Figure 11A), the vibrational frequency ν_4 and ν_2 exhibit a $\cos(\tau_{\text{ruf}})$ dependence: the fit of the data using the equation $\nu = A + B \cos(\tau_{\text{ruf}})$ yields good results for ν_2 ($A=1497(5)\text{cm}^{-1}$, $B=82(6)\text{cm}^{-1}$, $r^2 = 0.93$, the number given in brackets refers to the uncertainty of the fit) and reasonable results for ν_4 ($A=1338(3)\text{cm}^{-1}$, $B=42(4)\text{cm}^{-1}$, $r^2=0.90$) (black lines, Figure 11A). An analogous fit to ν_4 and ν_2 cannot be successfully applied for ν_3 due to the fact that the corresponding frequency is smaller for the disubstituted porphyrins than for the tetrasubstituted porphyrins with similar ruffling angles. The latter is apparent, e.g., for **NiD(1-Et-Pr)P** (1459cm^{-1} , $\tau_{\text{ruf}}=34.0^\circ$) and **NiT(2-Me-Pr)P** (1468cm^{-1} , $\tau_{\text{ruf}}=34.6^\circ$). Therefore, the obtained frequencies of ν_3 are fitted separately for the series of disubstituted ($A=1374(6)\text{cm}^{-1}$, $B=102(7)\text{cm}^{-1}$, $r^2=0.98$, grey line, Figure 11A) and tetrasubstituted porphyrins ($A=1390(8)\text{cm}^{-1}$, $B=97(11)\text{cm}^{-1}$, $r^2=0.92$, black line, Figure 11A). The value for B, which describes the sensitivity of ν_3 to an increasing ruffling angle, is similar for both series of porphyrins (disubstituted: $B=102(7)\text{cm}^{-1}$, tetrasubstituted $B=97(11)\text{cm}^{-1}$). Table 1 lists the experimentally obtained resonance Raman frequencies for ν_4 , ν_3 , and ν_2 , as well as the ruffling angles obtained from the calculated nickel(II) porphyrin structures.

Notably, the cosine dependence for ν_4 , ν_3 , and ν_2 includes the values for the aryl-substituted porphyrins, which, contrary to the alkyl-substituted porphyrins, have geometries distorted by both *ruf* and *sad*. The strongest contributions of saddling to the overall distortion were predicted by DFT calculations to occur for **NiT(Ph)P** ($d_{\text{ruf}} = 1.35\text{ \AA}$, $d_{\text{sad}} = 0.75\text{ \AA}$) and **NiT(4-MeOPh)P** ($d_{\text{ruf}} = 1.08\text{ \AA}$, $d_{\text{sad}} = 1.28\text{ \AA}$). Despite the additional contribution of saddling, these porphyrins do not significantly deviate from the cosine correlation (see black squares, Figure 11A); due to the fact that ν_4 , ν_3 , and ν_2 are much less sensitive to saddling than to ruffling [64,68].

The fact that ν_2 is well described by the cosine function shows that the mode is solely determined by the ruffling angle and is independent of the number and type of meso-substituents. According to DFT calculations, the mode ν_3 and ν_4 are – contrary to ν_2 – not pure macrocycle *ip* modes, but also involve the substituents (see Figure 11C and Table S4 in the Supporting Information). Thus, the frequencies of ν_3 and ν_4 are not solely determined by the macrocycle non-planarity but additionally by number and

specific chemical nature of the substituent. This might explain the deviations from the expected cosine correlation.

Table 1: Selected structural parameters for the calculated structures: *sad* and *ruf* displacements as determined from normal-coordinate structural decomposition and ruffling angle τ_{ruf} . The experimental frequencies of selected resonance Raman bands were determined for the porphyrins in dichloromethane solution upon excitation at 413 nm.

	$d_{\text{sad}} / \text{\AA}$	$d_{\text{ruf}} / \text{\AA}$	$\tau_{\text{ruf}} / ^\circ$	ν_2 / cm^{-1}	ν_3 / cm^{-1}	ν_4 / cm^{-1}
NiD(3-MeOPh)P	0.19	0.93	19.9	1574	1470	1376
NiD(Ph)P	0.23	0.96	20.6	1572	1470	1376
NiD(4-MePh)P	0.26	0.97	20.9	1572	1470	1376
NiD(2-Me-Pr)P	0.05	1.10	23.7	1570	1462	1375
NiD(1-Et-Pr)P	0.09	1.58	34.0	1563	1459	1376
NiT(Ph)P	0.75	1.35	28.9	1573	1473	1374
NiT(4-MeOPh)P	1.08	1.28	27.4	1573	1473	1374
NiT(2-Me-Pr)P	0.26	1.62	34.7	1563		1372
NiT(Bu)P	0.00	1.74	41.1	1564	1471	1372
NiT(He)P	0.00	1.74	41.3	1564	1472	1372
NiT(1-Et-Pr)P	0.09	2.12	45.4	1554	1457	1367
NiT(iPr)P	0.06	2.19	47.0	1553		1367
NiT(1-Me-Pr)P	0.12	2.20	47.1	1554		1367
NiT(tBu)P	0.14	2.90	62.1	1533	1432	1355
NiOET(3-MeOPh)P	4.02	0.06	1.2	1564		1362
NiOET(Ph)P	4.03	0.03	0.5	1564		1361
NiOET(4-MeOPh)P	4.03	0.00	0.0	1564		1362
NiOET(4-Br-Ph)P	4.04	0.01	0.2	1564		1363

Verification of Structures Calculated by DFT

The correlation of vibrational frequencies frequency and ruffling angle described above depends on experimentally observed resonance Raman frequencies and the calculated ruffling angles. However, the structures predicted by DFT might be erroneous and, consequently, the thus determined correlations. In order to address the accuracy of the DFT structures, a subsequent vibrational analysis can be performed for each fully optimized porphyrin structure and the calculated frequencies can be compared to the experimentally observed frequencies. Figure 11A shows that the calculated frequencies for ν_2 , ν_3 , and ν_4 are in good agreement with the experimental ones.

Analogous to the experimentally obtained frequencies, the calculated frequencies of ν_2 are fitted using the cosine function, which yields $A=1505(4) \text{ cm}^{-1}$ and $B=78(5) \text{ cm}^{-1}$ ($r^2=0.95$) (blue line, Figure 11A). The value for B is in good agreement with the value determined from the experimental data ($B=83(6) \text{ cm}^{-1}$). Thus, the structures in solution calculated by DFT and, more precisely, the increase in ruffling angle seem to be accurate. The value for A derived from the DFT calculations ($A=1505(4) \text{ cm}^{-1}$)

deviates from the value determined using the experimentally observed frequencies ($1496(4) \text{ cm}^{-1}$). However, A represents a constant offset of the resonance Raman frequencies with respect to structurally induced shifts of the Raman bands, which is apparently not exactly covered by the scaling factor of 0.98 applied for the DFT calculations [77,99]. The overall good agreement, which also holds true for the joint DFT-experimental analysis of ν_3 ($A=1394(8) \text{ cm}^{-1}$, $B=95(11) \text{ cm}^{-1}$, $r^2=0.90$, fits only for tetrasubstituted porphyrins) and ν_4 ($A=1327(5) \text{ cm}^{-1}$, $B=42(6) \text{ cm}^{-1}$, $r^2=0.79$, values of **NiT(4-MeOPh)P** and **NiT(Ph)P** excluded for fit; see Figure 11A), indicates that the calculated structures and the calculated ruffling angle are overall correctly predicted by DFT. Minor deviations for the aryl tetrasubstituted porphyrins **NiT(4-MeOPh)P** and **NiT(Ph)P** might be associated with the geometry of these porphyrins, which is distorted by both *ruf* and *sad*.

Comparison to Molecular Mechanics

In this section, the correlation between the experimental resonance Raman frequency of ν_2 , ν_3 , and ν_4 and the DFT calculated ruffling angle is compared to the MM calculations reported in the literature. Jentzen *et al.* [24] (cyan symbols, Figure 11B) reported the experimental resonance Raman spectra for a series of tetraalkyl-meso-substituted nickel porphyrins **NiT(alkyl)P** and determined the porphyrin structures and ruffling angles by MM using an empirical force field [24]. The series of porphyrins studied by Jentzen *et al.* included **NiT(iPr)P**, **NiT(tBu)P** and **NiT(Ph)P**, i.e. porphyrins which are also investigated here by DFT, as well as **NiT(alkyl)P** porphyrins with the following alkyl substituents: methyl, ethyl, propyl, pentyl, cyclopropyl, cyclohexyl. They measured the degree of non-planarity using the torsion angle ϕ of the N-C_a-C_m-C_a bond, which is about one half of the ruffling angle [24], and applied a quadratic equation for fitting (Raman frequency ν in cm^{-1} , $\nu = A + B \phi^2$). This quadratic equation represents a truncated Taylor polynomial approximating the cosine function at zero angle. Thus – for the observed ruffling angles smaller than 70° – the proposed analysis is similar to the one applied here. Here, for sake of comparison, the calculated ruffling τ_{ruf} is considered and fits were obtained using the cosine-dependence ($\nu = A + B \cos(\tau_{\text{ruf}})$), which yields a reasonable fit for ν_2 ($A=1475(10) \text{ cm}^{-1}$, $B=100(11) \text{ cm}^{-1}$, $r^2 = 0.90$) (cyan line Figure 11B). Figure 11B also compares the resulting correlation for ν_3 and ν_4 . Subsequently, solely ν_2 , which, as discussed, is less dependent on the specific nature of the substituents, is considered for the comparison of correlations based on DFT and MM.

The horizontal arrows in Figure 11B indicate that the ruffling angles for **NiT(iPr)P**, **NiT(tBu)P**, and **NiT(Ph)P** calculated with the original force field used by Jentzen *et al.* [24] strongly deviate from the angle predicted the DFT calculations. This deviation becomes apparent for, e.g., **NiT(Ph)P** for which a planar structure was predicted by the original force field. However, these predictions are in contrast to both the experiments and the DFT calculations, according to which this porphyrin exists as a non-planar structure in solution. Overall, the ruffling angle calculated with the original force field strongly underestimates the ruffling angle. Although the absolute ruffling angle is not predicted correctly, the B value derived from the cosine fit for ν_2 ($B=100(11) \text{ cm}^{-1}$) is roughly similar to the DFT calculations ($B=82(6) \text{ cm}^{-1}$), thus highlighting that the relative impact of an increasing sterically demand of

substituents on the macrocycle non-planarity seems to be adequately covered irrespective of the method employed.

An improved empirical force field was applied by Song *et al.* [26] which gives significantly different ruffling angles compared to the work by Jentzen [24] (red symbols, Figure 11B). The improved force field predicts for **NiT(Ph)P** and for **NiT(iPr)P** ruffling angles, which are in good agreement with the DFT calculations. However, compared to DFT calculations, the ruffling angle for **NiT(tBu)P** is underestimated (see red arrows in Figure 11B). As a consequence, the cosine-dependence for ν_2 ($A=1459(5) \text{ cm}^{-1}$, $B=135(7) \text{ cm}^{-1}$, $r^2 = 0.98$) gives a significantly higher value for B than the DFT calculations ($B=82(6)$). To cross-validate the correlations, the specified cosine-dependence and fit parameters are used to predict the frequency of ν_2 for a planar nickel porphyrin ($\tau_{\text{ruf}} = 0^\circ$), which yields 1594 cm^{-1} (improved force field) and 1579 cm^{-1} (DFT). By comparison of these values to the reported frequency for a planar **NiT(Ph)P** (1578 cm^{-1}) [72], it appears that the cosine-dependence derived from the ruffling angles calculated by DFT is more accurate than the one derived from the improved force field (see Figure 11).

5. Conclusion

This tutorial review exemplarily summarizes various experimental and theoretical approaches to predict and correlate the structural distortions of nickel(II) porphyrins. Therefore, the structures for a series of 5,15-disubstituted and 5,10,15,20-tetrasubstituted, and 5,10,15,20-tetrasubstituted-2,3,7,8,12,13,17,18-octaethyl nickel(II) porphyrins in dichloromethane were considered and evaluated by comparing the results from DFT and force-field calculations, resonance Raman spectroscopy as well as crystallographic studies. The systematic comparison of the various analytical methods highlights both the impact of crystal packing forces on the macrocycle distortions observed in crystal structures and the deviations between DFT and MM. For example, contrary to MM, DFT is able to correctly predict the mixed *ruf* and *sad* distortion of the di- or tetraaryl-substituted porphyrins, **NiD(aryl)P** and **NiT(aryl)P**.

For the meso-substituted porphyrins, a $\cos(\tau_{\text{ruf}})$ correlation between the experimental frequency of the structure-sensitive resonance Raman modes ν_2 , ν_3 , and ν_4 and the calculated ruffling angle τ_{ruf} is established, supporting that the origin of the frequency shift is a decreased π -overlap of the macrocycle. The most robust resonance Raman band to probe the ruffling angle of meso-substituted porphyrins is mode ν_2 . This vibrational mode is a pure macrocycle *ip* mode, which is almost not affected by the meso-substituents, while the *ip* modes ν_3 and ν_4 involve vibrations of the substituents and thus depend on the number and chemical nature of the substituent. The review demonstrates that the DFT calculated structures can be supported by the fact, that (i) the calculated vibrational frequencies for ν_2 , ν_3 and ν_4 are in good agreement with the experimentally observed resonance Raman frequencies and (ii) that the calculated vibrational frequencies resemble the experimentally obtained cosine correlation. Thus, this paper serves as a comparative and tutorial approach to access the structural distortions of metal porphyrins, which are ubiquitous molecular building blocks in biology, artificial photosynthesis and molecular electronics.

6. Materials and Methods

6.1. Synthesis

Nickel(II) porphyrins were prepared *via* standard metallation of the respective free base porphyrins with nickel(II) acetylacetonate ($\text{Ni}(\text{acac})_2$) and general experimental techniques were as reported before [100]. The following compounds were reported in the literature and gave satisfactory analytical data: **NiD(Ph)P** [67], **NiD(3-MeOPh)P** [101], **NiD(4-MePh)P** [102], **NiD(2Me-Pr)P** [101], **NiD(1-Et-Pr)P** [103], **NiT(Ph)P** [104], **NiT(4-MeOPh)P** [105], **NiT(Bu)P** [91], **NiT(2-Me-Pr)P** [91], **NiT(iPr)P** [24,91], **NiT(1-Et-Pr)P** [91], **NiT(tBu)P** [24,91], **NiOET(Ph)P** [64,95].

[5,10,15,20-Tetrakis(*n*-hexyl)porphyrinato]nickel(II) NiT(He)P: 5,10,15,20-Tetrakis(*n*-hexyl)porphyrin (200 mg, 0.309 mmol) was dissolved in toluene (30 mL) in a 100 mL RBF. The solution was heated to 120 °C before $\text{Ni}(\text{acac})_2$ (318 mg, 1.236 mmol) was added. The reaction was stirred at this temperature 3 h, monitoring *via* TLC control. The reaction was then cooled to rt and solvents were removed *in vacuo*. The crude residue was redissolved in CH_2Cl_2 and filtered through a short plug of silica gel using CH_2Cl_2 as eluent. The solvent was removed *in vacuo* and the residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give fine purple/red crystals (210 mg, 0.298 mmol, 97 %). Mp = 112–114 °C; R_f (CH_2Cl_2 :hexane = 2:3, v/v): 0.85; ^1H NMR (400 MHz, CDCl_3): δ = 0.88 (t, J = 7.2 Hz, 12H, CH_3), 1.26–1.43 (m, 16H, CH_2), 1.51–1.58 (m, 8H, CH_2), 2.18–2.26 (m, 8H, CH_2), 4.47 (t, J = 8.1 Hz, 8H, CH_2), 9.23 ppm (s, 8H, β -H); ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 22.6, 30.0, 31.8, 33.9, 37.2, 116.8, 129.6, 141.1 ppm; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) = 419 (5.37), 538 nm (4.17); HRMS (MALDI): m/z = calcd. for $\text{C}_{44}\text{H}_{60}\text{N}_4\text{Ni}$: 702.4171, found 702.4203.

[5,10,15,20-Tetrakis(1-methylpropyl)porphyrinato]nickel(II) NiT(1-Me-Pr)P: 5,10,15,20-Tetrakis(1-methylpropyl)porphyrin (150 mg, 0.280 mmol) was dissolved in toluene (20 mL) in a 100 mL RBF. The solution was heated to 120 °C before $\text{Ni}(\text{acac})_2$ (360 mg, 1.402 mmol) was added. The reaction was stirred at this temperature 3 h, monitoring *via* TLC control. The reaction was then cooled to rt and solvents were removed *in vacuo*. The crude residue was redissolved in CH_2Cl_2 and filtered through a short plug of silica gel using CH_2Cl_2 as eluent. The solvent was removed *in vacuo* and the residue was recrystallized from $\text{CH}_2\text{Cl}_2/\text{MeOH}$ to give fine purple/red crystals (144 mg, 0.243 mmol, 87 %). Mp = 283–285 °C; R_f (CH_2Cl_2 :hexane = 2:3, v/v): 0.75; ^1H NMR (400 MHz, CDCl_3): δ = 0.91 (t, J = 7.4 Hz, 12H, CH_3), 2.18 (d, J = 7.3 Hz, 12H, CH_3), 2.45–2.56 (m, 8H, CH_2), 4.36–4.45 (m, 4H, CH), 9.19 ppm (s, 8H, β -H); ^{13}C NMR (100 MHz, CDCl_3): δ = 13.9, 26.3, 34.4, 41.6, 121.4, 130.6, 139.4 ppm; UV-vis (CH_2Cl_2): λ_{max} (log ϵ) = 423 (5.16), 548 (4.03), 585 nm (3.41); HRMS (MALDI): m/z = calcd. for $\text{C}_{36}\text{H}_{44}\text{N}_4\text{Ni}$: 590.2919, found 590.2947.

5,10,15,20-Tetrakis(4-bromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin H₂OET(4-Br-Ph)P: Dry CH_2Cl_2 (1L), 3,4-diethylproline (1.23 g, 7 mmol, 1 eq.) and 4-bromobenzaldehyde (1.3 g, 7 mmol, 1 eq.) were placed in a 2 L RBF and stirred for 10 minutes. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.08 mL, 0.7 mmol, 0.1 eq.) was added and left to stir for 18 h at room temperature. 4,5-Dichloro-3,6-dioxocyclohexa-1,4-diene-1,2-dicarbonitrile (DDQ) (1.589 g, 7 mmol, 1 eq.) was added and the solution was stirred for 1 h. The reaction was quenched with triethylamine (0.1 mL, 0.7 mmol, 0.1 eq.). The solvent was removed *in*

vacuo and the residue taken up in CH₂Cl₂. The mixture was ultra-sonicated for 2 min and then filtered through a plug of silica, washing with 1 % MeOH in CH₂Cl₂. The eluted porphyrin fractions were evaporated to dryness and purified with silica gel chromatography using hexane:EtOAc (4:6) and dried *in vacuo* to give green flakes (664 mg, 0.57 mmol, 33 %). Mp = 278–280 °C; *R_f* (CH₂Cl₂:hexane = 2:3, v/v): 0.77; ¹H NMR (400.2 MHz, CDCl₃): δ = -2.1 (s, 2H, NH), 0.5 (br s, 24H, CH₂CH₃), 1.8–2.6 (m, 16H, CH₂CH₃), 7.8 (d, 8H, *J* = 8.4 Hz, Ar-*H*), 8.2 ppm (d, 8H, *J* = 8.4 Hz, Ar-*H*); ¹³C NMR (100.6 MHz, CDCl₃): δ = 16.8, 19.4, 116.8, 123.0, 130.3, 139.4 ppm; HRMS (MALDI) *m/z* [M + H]⁺ calcd. for [C₆₀H₅₉Br₄N₄]: 1151.1473, found 1151.1525.

[5,10,15,20-Tetrakis(4-bromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrinato]nickel(II)

NiOET(4-Br-Ph)P: 5,10,15,20-Tetrakis(4-bromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (100 mg, 0.09 mmol, 1 eq.) and Ni(acac)₂ (111 mg, 0.43 mmol, 5 eq.) were placed in a 25 mL Schleck tube and dissolved in toluene (5 mL). The solution was stirred at 120 °C for 18 hours. The reaction was then cooled to rt and solvent was removed *in vacuo*. The crude residue was redissolved in CH₂Cl₂ and filtered through a short plug of silica gel using CH₂Cl₂ as eluent. The solvent was removed *in vacuo* and the residue was recrystallized from CH₂Cl₂/MeOH to give fine purple/red crystals (84 mg, 0.07 mmol, 77 %). Mp = >300 °C; *R_f* (EtOAc:hexane = 1:1, v/v): 0.77; ¹H NMR (400.2 MHz, CDCl₃): δ = 0.5 (t, 24H, *J* = 7.5 Hz, CH₂CH₃), 2.0 (br s, 8H, CH₂CH₃), 2.5 (br s, 8H, CH₂CH₃), 7.8 (d, 8H, *J* = 8.3 Hz, Ar-*H*), 7.9 ppm (d, 8H, *J* = 8.3 Hz, Ar-*H*); ¹³C NMR (100.6 MHz, CDCl₃): δ = 17.0, 19.7, 116.0, 122.8, 130.3, 135.7, 138.8, 144.6, 145.5 ppm; UV-vis (CH₂Cl₂): λ_{max} (log ε): 435 (5.18), 555 (4.01), 591 nm (3.94); HRMS (MALDI) *m/z* [M]⁺ calcd. for [C₆₀H₅₆Br₄N₄Ni]: 1206.0592, found 1206.0629.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato]nickel(II)

NiOET(4-MeO-Ph)P: Prepared following the procedure given for **NiOET(4-Br-Ph)P**. 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(4-methoxyphenyl)porphyrin (100 mg, 0.1 mmol) and Ni(acac)₂ (77 mg, 0.3 mmol) were placed in a 100 mL RBF and dissolved in toluene (40 mL). The solution was stirred at 120 °C for 3 hours. The reaction was then cooled to rt and solvent was removed *in vacuo*. The crude residue was redissolved in CH₂Cl₂ and filtered through a short plug of silica gel using CH₂Cl₂ as eluent. The solvent was removed *in vacuo* and the residue was recrystallized from CH₂Cl₂/MeOH to give fine purple/red crystals (52 mg, 51 μmol, 51 %). Mp = >300 °C; *R_f* (CH₂Cl₂:hexane = 2:3, v/v): 0.41; ¹H NMR (400 MHz, CDCl₃): δ = 0.5 (t, 24H, *J* = 7.3 Hz, CH₂CH₃), 2.0–2.4 (m, 16H, CH₂CH₃), 4.0 (s, 12H, OCH₃), 7.1 (d, 8H, *J* = 8.6 Hz, Ar-*H*), 8.0 ppm (d, 8H, *J* = 8.6 Hz, Ar-*H*); ¹³C NMR (100 MHz, CDCl₃): δ = 17.1, 19.6, 55.5, 112.4, 116.5, 133.0, 135.2, 145.0, 145.3, 159.7 ppm; UV-vis (CH₂Cl₂): λ_{max} (log ε): 436 (5.00), 554 (3.85), 588 nm (3.67); HRMS (MALDI) *m/z* [M]⁺ calcd. for [C₆₄H₆₈N₄NiO₄]: 1014.4594, found 1014.4615.

2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin H₂OET(3-MeO-Ph)P: Dry CH₂Cl₂ (1L), 3,4-diethylpyrrole (1.23 mg, 0.1 mmol) and 3-methoxybenzaldehyde (1.49 g, 0.1 mmol) were placed in a 2 L RBF and stirred for 10 minutes. BF₃•Et₂O (0.3 mL, 0.3 mmol) was added and left to stir for 18 h at room temperature. DDQ (4.54 g, 0.2 mmol) was added and the solution was stirred for 1 h. The reaction was quenched with triethylamine (6.7 mL, 0.3 mmol). The solvent was

removed *in vacuo* and the residue taken up in CH₂Cl₂. The mixture was ultra-sonicated for 2 min and then filtered through a plug of silica, washing with 1 % MeOH in CH₂Cl₂. The eluted porphyrin fractions were evaporated to dryness and purified with silica gel chromatography using *hexane*:EtOAc (4:6) and dried *in vacuo* to give green flakes (620 mg, 0.6 mmol, 25 %). Mp = 273–274 °C; *R_f* (CH₂Cl₂:EtOAc = 20:1, v/v): 0.25; ¹H NMR (600.1 MHz, CDCl₃:TFA-*d*): δ = -(0.3–0.2) (m, 4H, *NH*), 0.2 (br s, 24H, CH₂CH₃), 2.2 (br s, 8H, CH₂CH₃), 2.4 (br s, 8H, CH₂CH₃), 4.1 (s, 12H, OCH₃), 7.5 (d, 4H, *J* = 7.2 Hz, *Ar-H*), 7.8 ppm (t, 4H, *J* = 7.2 Hz, *Ar-H*), 7.9–8.0 (m, 4H, *Ar-H*), 8.1 ppm (m, 4H, *Ar-H*); ¹³C NMR (150.9 MHz, CDCl₃:TFA-*d*): δ = 15.0, 18.4, 55.9, 111.5, 113.3, 115.2, 116.6, 117.1, 121.7, 129.6, 137.7, 139.7, 143.1 ppm; HRMS (MALDI) *m/z* [M + H]⁺ calcd. for [C₆₄H₇₁N₄O₄]: 959.5475, found 959.5453.

[2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrinato]nickel(II)

NiOET(3-MeO-Ph)P: 2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(3-methoxyphenyl)porphyrin (100 mg, 0.1 mmol) and Ni(acac)₂ (77 mg, 0.3 mmol) were placed in a 100 mL RBF and dissolved in toluene (40 mL). The solution was stirred at 120 °C for 1.5 hours. The reaction was then cooled to rt and solvent was removed *in vacuo*. The residue was dissolved in CH₂Cl₂ and the mixture filtered through a plug of silica gel, eluting with CH₂Cl₂. The solvent was removed *in vacuo* and the residue was recrystallized from CH₂Cl₂/MeOH to give fine purple/red crystals (94 mg, 0.1 mmol, 92 %). Mp = >300 °C; *R_f* (CH₂Cl₂:hexane = 2:3, v/v): 0.32; ¹H NMR (400.2 MHz, CDCl₃): δ = 0.6 (t, 24H, *J* = 7.2 Hz, CH₂CH₃), 2.3 (bs, 16H, CH₂CH₃), 3.9–4.0 (m, 12H, OCH₃), 7.2 (m, 4H, *Ar-H*), 7.5 (bs, 4H, *Ar-H*), 7.6–7.7 ppm (m, 8H, *Ar-H*); ¹³C NMR (100.6 MHz, CDCl₃): δ = 17.1, 19.7, 55.6, 114.1, 116.8, 119.8, 127.2, 127.9, 141.5, 144.3, 145.6, 158.3 ppm; UV-vis (CH₂Cl₂): λ_{max} (log ε): 433 (5.15), 552 (3.96), 589 nm (3.88) HRMS (MALDI) *m/z* [M]⁺ calcd. for [C₆₄H₆₈N₄NiO₄]: 1014.4594, found 1014.4577.

6.2. Sample Preparation

For the resonance Raman measurements, the samples were dissolved in dichloromethane and the concentration was adjusted to an absorbance of 0.3 at the excitation wavelength, i.e. 413 nm, using a cuvette with 1 mm path length.

6.3. Resonance Raman Spectroscopy

Resonance Raman spectra were measured with a micro-Raman set-up (LabRam HR800, Horiba Jobin Yvon), consisting of an inverted microscope (Olympus IX71), a 600 lines per millimeter grating and a liquid-nitrogen-cooled CCD detector. The excitation light – delivered by a krypton ion laser (Coherent Innova 300C, λ = 413 nm) – was focused by a microscope objective (Olympus 10×/NA 0.25, RMS10X) into a cuvette containing the sample solution. The backscattered resonance Raman signals were collected by the same objective and detected without polarization filters. A rotating quartz cell was utilized as cuvette to prevent heating of the solution. UV/Vis-spectra were collected on Jasco V-670 spectrophotometer prior to and after each measurement to check the sample integrity. The Resonance Raman spectra presented here are baseline corrected with the software R [106] using the package baseline wavelet [107] (parameter lambda = 500 and signal-to-noise = 3). Figure S7 in the Supporting Information gives an example for the original and baseline-corrected spectrum.

6.4. X-ray Crystallographic Data

The structures of the nickel porphyrins investigated – derived from our DFT calculations – are compared to reported crystal structures which are taken from the Cambridge Structural Database (respective CSD entry given in parenthesis) [108] and analyzed by NSD: **NiD(2-Me-Pr)P** (QEBXUS) [89], **NiTPP** (ZZZUUC01) [93], **NiT(4-MeOPh)P** (OROJUB) [94], **NiT(2-Me-Pr)P** (DOWCAT) [91], **NiT(1-Et-Pr)P** (DOWDUO) [91], **NiT(iPr)P** (HETDAL) [90] and **NiOETPP** (SULCUX) [54]. Additionally, crystal structures of structurally similar nickel porphyrins were considered: [5,15-bis(1,1-dimethylethyl)porphyrinato]nickel(II) (**NiD(tBu)P**, REFPOH) [67], [5,15-bis(1-methylethyl)porphyrinato]nickel(II) (**NiD(iPr)P**, VAFQEY) [65], (5,10,15,20-tetrapentylporphyrinato)nickel(II) (**NiT(Pe)P**, FEZJOK01) [26]. *Oop* displacements for the crystal structure of **NiT(Pr)P** were taken from the literature [26].

6.5. Computational Details

All quantum chemical calculations have been performed using the Gaussian 09 program. Equilibrium structures and electronic structures of all 18 porphyrins were obtained at the DFT level of theory by means of a functional based on B3LYP [109,110], comprising 15 % of exact-exchange, 58.5 % of non-local B88 exchange and the LYP correlation, which is denoted B3LYP(15) [77,111–113]. The 10-electron non-relativistic effective core potential MDF-10 [114] was used with its basis set for the nickel atom, that is, 3s, 3p, 3d and 4s electrons are treated explicitly, whereas the two first inner shells are described by the core potential. For the ligand, the 6-31G(d) double- ζ basis set [115] was employed. To correct for the lack of anharmonicity and for the approximate description of electron correlation, the harmonic frequencies were scaled by a factor of 0.98 [77,99]. Solvent effects (dichloromethane: $\epsilon = 8.93$) with respect to equilibrium structures and vibrational frequencies were taken into account by means of the integral equation formalism of the polarizable continuum model [116].

6.6. Normal-Coordinate Structural Decomposition

The *oop* and *ip* deformation present in the calculated, as well as the reported crystallographic structures were quantified by using the normal-coordinate structural decomposition (NSD) method by Shelnutt and coworkers [35]. The porphyrin structures were analyzed using the NSD program available online (Version 3.0) [86].

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