Amati, Mario; Baerends, Evert Jan; Ricciardi, Giampaolo; Rosa, Angela

published in
Inorganic Chemistry
2020

DOI (link to publisher)
10.1021/acs.inorgchem.0c01327

document version
Publisher's PDF, also known as Version of record
document license
Article 25fa Dutch Copyright Act

Link to publication in VU Research Portal

citation for published version (APA)

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

E-mail address:
vuresearchportal.ub@vu.nl
ABSTRACT: Axial coordination to metalloporphyrins is important in many biological and catalytic processes. Experiments found the axial coordination of nitrogenous bases to nickel(II) porphyrins to be strongly favored by electron-withdrawing substituents such as perfluorophenyls at the meso carbon positions. Careful analysis of the electronic structure reveals that the natural explanation in terms of density change of the nickel(II) porphyrin system (in particular the metal), does not apply. Electron density changes, by the assumed inductive or polarizing effects on the metal or on the porphyrin ring system, are slight. The effect is caused by a remarkable through-space electric field effect on the metalloporphyrin system, originating from the charge distribution inside the perfluorophenyl groups (mostly the C–F dipoles).

INTRODUCTION

The coordination of axial ligands to metalloporphyrins influences their electronic and structural properties with relevant implications on their physicochemical and catalytic behavior.1 Nature utilizes coordination processes for optimizing biological functions, as exemplified by the binding of O2 to the heme group in hemoglobin and myoglobin.2 The elucidation of the axial coordination mechanism in metalloporphyrins has been regarded as an important task, primarily in connection with the understanding of naturally occurring catalytic processes.1b,3 Synthetic nickel porphyrins have been widely used to model axial-ligand binding/releasing processes in nickel-containing biomolecules4 such as tunichlorins,5 and F430, a cofactor incorporated in the active site of S-methyl-coenzyme M reductase.6

The axial binding of nitrogenous bases such as pyridine or piperidine to nickel(II) porphyrins consists primarily of a σ interaction between the nitrogen lone pair of the ligand and the 3d\(^{z^2}\) orbital of the metal. The four-coordinate nickel(II) porphyrin complexes are diamagnetic (S = 0) in their ground state with the metal in a d\(^8\) configuration in which the 3d\(^{z^2}\) orbital is doubly occupied and the 3d\(^{x^2−y^2}\) orbital is empty (Scheme 1).

As first recognized by Caughey et al.,^3a when the nitrogen lone pair (N\(_{lp}\)) of the ligand(s) and the nickel 3d\(^{z^2}\) orbitals interact, the resulting “antibonding” combination rises in energy and it becomes easier for one of its electrons to be promoted to the 3d\(^{x^2−y^2}\) orbital (Scheme 1), leading to paramagnetic (S = 1) five- or six-coordinate nickel(II) porphyrin complexes.
Formation of complexes with stoichiometries of 1:1 (five-coordinate), 1:2 (six-coordinate), or both, according to the equilibrium shown in eqs 1–3:

\[
\text{NiPor} + \text{L} \rightleftharpoons \text{NiPor(L)} \quad (1)
\]

\[
\text{NiPor(L)} + \text{L} \rightleftharpoons \text{NiPor(L)_2} \quad (2)
\]

\[
\text{NiPor} + 2\text{L} \rightleftharpoons \text{NiPor(L)_2} \quad (3)
\]

The equilibrium constants, \(K_1\) (eq 1), \(K_2\) (eq 2) and \(K_3\) (eq 3) have been determined for a number of Ni(II) porphyrins and nitrogenous bases using UV–visible and/or \(^1\)H NMR spectroscopic titrations. In some cases the thermodynamic parameters \(\Delta H\) and \(\Delta S\) have also been obtained from temperature-dependent measurements of \(K_1\), \(K_2\), and \(K_3\). According to the experimental data, the presence of electron-withdrawing substituents at the meso or \(\beta\) positions of the porphyrin ring greatly favors the association process. This has been interpreted in terms of an enhancement of the electron deficit on the metal by the electron-withdrawing peripheral substituents. Nevertheless, the X-ray structures available for these systems show that the electronic communication (π induction and/or π conjugation) between the peripheral substituents and the porphyrin macrocycle is very modest, if any, which would prevent an effective electron density displacement from the metal to the periphery. Therefore, the enhanced binding capability to nitrogenous bases of porphyrins bearing electron-withdrawing substituents should have a different electronic origin.

The aim of this work is to identify the electronic factors governing the axial coordination process of nitrogenous bases to Ni(II) porphyrins and to shed light on the mechanism underlying the enhanced reactivity of the latter in the presence of electron-withdrawing peripheral substituents. To this end we have performed a density functional theory (DFT) analysis of the electronic and energetic aspects of the axial coordination of pyridine (py) to nickel(II) porphyrins bearing substituents with different electron-withdrawing capabilities at the meso positions, NiTTP (TPP = tetraphenylporphyrin) and NiTPPF\(_{20}\) (TPPF\(_{20}\) = pentafluorophenylporphyrin) (Chart 1).

**METHODS**

The calculations were performed with ADF (Amsterdam Density Functional), using the hybrid B3LYP functional. The calculations included relativistic effects through the zero-order regular approximation (ZORA) and made use of the all-electron ZORA TZP basis set that is an uncontracted triple-ζ STO basis with one polarization function. To evaluate the influence of the chosen exchange-correlation functional on the optimized geometries and the energetics of the formation processes of the five- and six-coordinate complexes, the ADF calculations were also performed using the pure GGA (generalized gradient approximation) functional BP86 in combination with the same basis set used for the B3LYP calculations. To evaluate the influence of the basis set on the optimized geometries and the energetics of the formation processes of the five- and six-coordinate complexes, B3LYP calculations were also performed using TURBOMOLE using the triple-ζ-quality de2-TZVP basis sets. The results of the ADF/BP86 and TURBOMOLE/B3LYP calculations are reported in Tables S1–S3 in the Supporting Information and will be discussed in the following when relevant differences with the ADF/B3LYP calculations occur. For the open-shell five- and six-coordinate complexes of NiTTP and NiTPPF\(_{20}\) with pyridine as well as for the excited triplet state of the prepared NiTTP(py), NiTPPF\(_{20}\)(py), NiTTP, and NiTPPF\(_{20}\) fragments (side infra) the spin-unrestricted formalism was employed. Geometry optimizations of all complexes were performed in the gas phase under a C\(_2\) symmetry constraint and verified to be local minima by subsequent frequency calculations. The zero-point energies (ZPE) and thermal corrections used to compute the formation enthalpies, \(\Delta H_0\), \(\Delta S\), and \(\Delta E\) were obtained from these frequency calculations. The effects of the solvent on the frontier orbitals of NiTTP, NiTPPF\(_{20}\), and pyridine ligand as well as on the formation energies (\(\Delta E_{\text{f}}\), \(\Delta E_{\text{f}}^0\), \(\Delta E_{\text{f}}^0\)) were modeled through the conductor-like continuum model (COSMO), using toluene as solvent, which is the solvent employed in most of the experiments.

To analyze and quantify the electronic factors governing the formation of the five- and six-coordinate complexes of NiTTP and NiTPPF\(_{20}\) with pyridine, we made use of the energy-partitioning scheme implemented in ADF, which was originally developed for Hartree–Fock wave functions by Morokuma and modified for the relaxation energy (or orbital interaction term) by Ziegler and Rauk. The energy decomposition analysis (EDA) is for the bonding between the nickel(II) porphyrins and pyridine to form five- and six-coordinate complexes, as well as for the bonding between the five-coordinate complexes and pyridine to form the six-coordinate complexes. According to the energy-partitioning scheme, the overall bond energy \(\Delta E\) is made up of two major components, \(\Delta E_{\text{prep}}\) and \(\Delta E_{\text{int}}\),

\[
\Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}}
\]

The preparation energy term, \(\Delta E_{\text{prep}}\), comprises two components: (i) the energy needed to deform the separate molecular fragments from their equilibrium structure to the geometry they attain in the overall molecular system, \(\Delta E_{\text{prep}}\), and (ii) the energy required to excite the interacting fragments from their ground-state electronic structure to a proper “valence state”, \(\Delta E_{\text{val}}\). In the present case \(\Delta E_{\text{prep}}\) is the energy required to excite the deformed nickel(II) porphyrins from the closed-shell ground state to the excited triplet state where the 3d\(_{z^2}\) and 3d\(_{x^2-y^2}\) orbitals are singly occupied. The interaction energy term, \(\Delta E_{\text{int}}\), accounts for the energy released when the prepared fragments are brought together into the position they have in the overall molecule. It is analyzed in the framework of the Kohn–Sham (KS) MO model, using a Morokuma-type decomposition into the steric interaction term, \(\Delta E_{\text{st}}\), and the (attractive) orbital interaction term, \(\Delta E_{\text{orb}}\),

\[
\Delta E_{\text{int}} = \Delta E_{\text{st}} + \Delta E_{\text{orb}}
\]

In turn, the \(\Delta E_{\text{st}}\) term comprises the electrostatic interaction, \(\Delta V_{\text{elstat}}\), and the Pauli repulsion (or exchange repulsion), \(\Delta E_{\text{Pauli}}\).

\[
\Delta E_{\text{st}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}}
\]

The term \(\Delta V_{\text{elstat}}\) corresponds to the classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments and is usually attractive. The second term in eq 6, \(\Delta E_{\text{Pauli}}\), refers to the repulsive interactions between the fragments,
which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. \( \Delta E_{\text{Pauli}} \) is calculated by enforcing the KS determinant of the superimposed fragments to obey the Pauli principle by antisymmetrization and renormalization. The \( \Delta E_{\text{Pauli}} \) term comprises the three- and four-electron destabilizing interactions between occupied orbitals and unoccupied orbitals on the other, and polarization (empty/occupied orbital mixing on one fragment). In the case of two open-shell fragments \( \Delta E_{\text{Pauli}} \) also contains the energy lowering connected to the formation of an electron-pair bond: viz., the pairing of the two unpaired electrons of the original fragments in the bonding combination of the orbitals. If only one fragment has an unpaired electron, which interacts with an electron pair of a closed shell on the other fragment, we are dealing with a two-orbital—three-electron (2o-3e) bond. Herein it is shown that the bonding interaction between the nickel(II) porphyrins in their excited triplet state and the pyridine ligand(s) mainly consists of a 2o-3e bond.

The \( \Delta E_{\text{Pauli}} \) term can be decomposed, using the extended transition state (ETS) method developed by Ziegler and Rauk, into the contributions from each irreducible representation \( \Gamma \) of the overall symmetry group of the system:

\[
\Delta E_{\text{Pauli}} = \sum_{\Gamma} \Delta E_{\text{Pauli}}(\Gamma)
\]

To evaluate the solvent (toluene) effects on the energy terms and the additional terms related to the solvation/desorvation of the interacting fragments and the final complexes, the EDA was also performed in toluene with COSMO in the case of the formation of an electron-pair bond: viz., the pairing of the two unpaired electrons of the original fragments in the bonding combination of the orbitals. If only one fragment has an unpaired electron, which interacts with an electron pair of a closed shell on the other fragment, we are dealing with a two-orbital—three-electron (2o-3e) bond. Herein it is shown that the bonding interaction between the nickel(II) porphyrins in their excited triplet state and the pyridine ligand(s) mainly consists of a 2o-3e bond.

The \( \Delta E_{\text{Pauli}} \) term can be decomposed, using the extended transition state (ETS) method developed by Ziegler and Rauk, into the contributions from each irreducible representation \( \Gamma \) of the overall symmetry group of the system:

\[
\Delta E_{\text{Pauli}} = \sum_{\Gamma} \Delta E_{\text{Pauli}}(\Gamma)
\]

To evaluate the solvent (toluene) effects on the energy terms and the additional terms related to the solvation/desorvation of the interacting fragments and the final complexes, the EDA was also performed in toluene with COSMO in the case of the formation of the five-coordinate complexes NiTPP(py) and NiTPPF20(py).

## RESULTS AND DISCUSSION

**Molecular Structures of the Ni(II) Porphyrin Complexes.** 
**NiTPP and NiTPPF20.** The key bond parameters determined experimentally and computed at different levels of theory are reported in Figure 1 and Table S1 in the Supporting Information.

According to the X-ray data, replacement of the phenyl hydrogen by fluorine atoms has a very modest effect on the key structural parameters, especially on the Ni—Np distances which are nearly identical in the two complexes. In NiTPP and in its fluorinated derivative, the porphyrin macrocycle deviates substantially from planarity, showing a significant degree of ruffling. According to the \( \theta \) values and in line with the modest degree of saddling of the macrocycles, the tilting of the meso aryl groups toward the porphyrin mean plane is quite small. This prevents conjugation between the \( \pi \) system of the meso aryl groups and the porphyrin \( \pi \) system to the effect that the electron distribution of the metal core is not influenced by the nature of the meso aryl groups. Geometry optimization of NiTPP and NiTPPF20 under a C2-symmetry constraint yielded molecular structures of \( S_4 \) symmetry (Figure 1).

There is generally a satisfactory agreement between the calculated and experimental bond parameters, irrespective of the basis set and functional used. The only significant difference between BP86 and B3LYP results concerns the Ni—Np bond lengths, which are predicted at the BP86 level nearly coincident with the experimental values, while they are slightly overestimated (by ~0.02 Å) at the B3LYP level, in line with what is found in similar metalloretaporphyrines. As inferred from the calculated \( \omega \) and \( \varphi \) values, the macrocycle distortions (ruffling and saddling) are theoretically well reproduced, indicating that these features are mainly dictated by intrinsic electronic reasons, packing effects playing only a minor role.

**NiTPP(py) and NiTPPF20(py).** The five-coordinate complexes have never been isolated, and hence, there are no structural data available. Optimization under a C2-symmetry constraint in their triplet \( (S = 1) \) ground states yielded the structures of \( C_2 \) symmetry shown in Figure 2. Occupation of the strongly Ni—Np \( \sigma \) antibonding \( \alpha \)-spin 3d\( ^{x^2-y^2} \) orbital results in a lengthening (by ~0.1 Å) of the Ni—Np bond relative to the unligated parent complex. The structural parameters (Figure 2 and Table S2 in Supporting Information) indicate that in NiTPP(py) and NiTPPF20(py) the porphyrin macrocycle is appreciably domed (\( \Delta \approx 0.3 \) Å).

The central metal protrudes from the pyrrolic nitrogen mean plane by 0.23–0.25 Å to minimize the repulsion between the porphyrin \( \pi \) system and the occupied orbitals of the pyridine ligand (the \( \pi \) system and the \( C_2-H \) \( \sigma \) bonds) while preserving an efficient Ni—Np interaction. Actually, the calculated Ni—Np bond is quite short in both complexes, especially at the BP86 level.

The pyridine ligand is orthogonal to the porphyrin mean plane and rotated by ~45° with respect to the vertical plane through the Np—Ni—Np atoms, i.e., toward the meso carbons, as indicated by the \( \psi \) values.

**NiTPPF20(py).** Of the two six-coordinate complexes, only NiTPPF20(py) has been structurally characterized by X-ray analysis. The experimental data show that in the complex the coordination sphere of the nickel is pseudo-octahedral (square bipyramidal) and the porphyrin macrocycle is perfectly planar. The pyridines are coplanar, are perpendicular to the porphyrin plane, and are rotated by ~25° with respect to the Np—Ni—Np axis. The meso aryl groups are tilted only slightly toward the porphyrin plane (\( \theta = 70.4° \)), not enough, however, to guarantee \( \pi \) conjugation with the macrocycle. The elongation of the Ni—Np bond
predicted from theory for the five-coordinate complexes stays nearly the same upon addition of the second pyridine ligand, in line with the strongly Ni–Nπ σ antibonding α-spin 3d⊥pπ* orbital being occupied in both the five- and six-coordinate complexes (vide infra). Optimization of NiTPPF20(py)2 under a C3-symmetry constraint in its triplet (S = 1) ground state yielded the structure of D2h symmetry shown in Figure 3, regardless of the level of theory. As can be inferred from the structural data reported in Figure 3 and Table S3, there is a satisfactory agreement between theory and experiment, especially at the BP86/TZP level of theory. The only significant discrepancy with the experiment concerns the rotation of the pyridine ligands with respect to the Np−Ni–Np axis, which is predicted to be 45° instead of the experimentally observed ~25°. This discrepancy is most likely related to packing effects.

For NiTPP(py)2, the calculations predict the S4-symmetry structure of Figure 3 with the pyridine planes orthogonal to each other and going through the meso carbons. The porphyrin macrocycle shows an appreciable degree of ruffling and a much less pronounced degree of saddling, as indicated by the ω and ψ values reported in Figure 3 and Table S3. The saddling of the macrocycle, although quite modest, is sufficient to allow the meso phenyl groups to rotate toward the pyrrole plane by ~30°, with θ ranging from 62.5 to 71.5°, depending on the level of theory. Bond lengths and bond angles do not differ significantly from those computed for the fluorinated complex.

Energetics of the Coordination Processes. Formation of the complexes of NiTPP with pyridine was initially investigated by Cole et al., in benzene and chloroform, through spectrophotometric titrations. In both solvents, these authors were only able to detect formation of the five-coordinate complex NiTPP(py), for which K1 and the related thermodynamic parameters ΔH1, ΔS1, and ΔG1 were determined. More accurate experiments by Herges and co-workers have recently ruled out the formation of NiTPP(py) in noncoordinating solvents and even in pyridine, where the six-coordinate species was detected instead. Using variable-temperature (VT) 1H NMR experiments in pyridine, these authors obtained a quite reliable estimate of the association constant of two pyridines to NiTPP (eq 3) and related thermodynamic parameters.

For the pyridine complexes of NiTPPF20, they have been both detected in toluene solution and thermodynamically characterized by Herges and co-workers through VT 1H NMR titrations. We have computed, at different levels of theory, the energies and enthalpies associated with the formation of NiTPPF20(py) in noncoordinating solvents and even in pyridine, where the six-coordinate species was detected instead. Using variable-temperature (VT) 1H NMR experiments in pyridine, these authors obtained a quite reliable estimate of the association constant of two pyridines to NiTPPF20 (eq 3) and related thermodynamic parameters.

If we consider first the formation of the five-coordinate complexes (Table 1), the ΔH1 values computed at the BP86 level are positive in the gas phase and in toluene, especially in the case of NiTPP. In contrast, the ΔH1 values computed at the B3LYP level are invariably negative, much less for NiTPP(py) than for NiTPPF20(py); however, this is in line with the uncertainty of the experimental data concerning the formation of the former. Remarkably, the ΔH1 values predicted for NiTPPF20(py) in toluene are in nice agreement with the experimental data obtained by Herges and co-workers in the same solvent.

The BP86 inadequacy to correctly describe the energetics of the formation of the five-coordinate complexes can be related to the fact that this process involves a singlet to triplet spin state change and this functional underestimate the exchange contribution to the energy of the five-coordinate complexes in their ground triplet state. This contribution is evaluated more correctly at the B3LYP level, due to the inclusion of the
Hartree–Fock (HF) exchange contribution. This interpretation of the different performance of the hybrid and GGA functionals seems to be supported by the fact that for the formation of the six-coordinate complexes from the five-coordinate parents, a process that does not involve a spin state change, the enthalpy and energy values (ΔH and ΔE) predicted by BP86 and B3LYP functionals (see Table 2) do not diverge. In agreement with the experiment, both functionals predict the formation of the six-coordinate complex in toluene for NiTPP but not for NiTPF. For the latter (slightly) negative ΔH values are computed only in the gas phase. When the gas-phase and toluene ΔH values are compared, it is apparent that the inclusion of solvent effects disfavors formation of the six-coordinate complexes.

Considering now the formation of the six-coordinate complexes by the reaction of NiTPP and NiTPPF with two pyridines (eq 3), we note that the ΔH values in Table 3 are, just as the ΔH values, markedly different for the two functionals, with the BP86 enthalpies being almost invariably positive, in disagreement with the experiment. This is not surprising, since this process also involves a singlet to triplet spin state change. In agreement with the experiment, the B3LYP calculations predict the formation of NiTPPF in toluene, although the ΔH values are underestimated. The ΔH value in the gas phase is, instead, much closer to the experimental data by Herges and co-workers.

The ΔH and ΔE values reported in Table 3 suggest that the formation of NiTPPF in toluene is unlikely. This fits with the formation of NiTPPF, having been detected only in pyridine, most likely thanks to a large excess of the ligand.

**Electronic Structure of NiTPP and NiTPPF** Effects of the Peripheral Fluorine Atoms. The highest occupied and lowest unoccupied one-electron levels of NiTPP and NiTPPF are shown in Figure 4, where the relevant molecular orbitals are also displayed.

Among the one-electron levels in the figure one may recognize the Gouterman orbitals of the porphyrin system, the occupied “a_2u” and “a_1u” and the unoccupied “e_u”, and additionally the metal 3d orbitals. In the virtual spectrum there is the 3d<x,y,z> orbital that is pushed up by antibonding with the N<sub>p</sub> lone pairs.

The highest occupied 3d levels are the nearly degenerate 3d<sub>x</sub> and 3d<sub>y</sub>. The latter is an almost pure metal orbital, largely 3d<sub>x</sub>, with some 4s character. The former are heavily mixed with the N<sub>p</sub>-based π orbitals of the porphyrin ring, their bonding counterpart being in both complexes ~1.5 eV lower in energy. The energy ordering and composition of the frontier orbitals are nearly identical in the two complexes, the outstanding difference being the generalized downshift of the MOs (~0.9 eV) and the “a_1u” inversion in NiTPPF.

Inspection of the Hirshfeld and NBO atomic charges (Table S4) reveals that the electronic density distributions are nearly the same in the two complexes, suggesting that the downshift of the NiTPPF<sub>20</sub> levels cannot be ascribed to the electronic density redistribution perfluorophenyl groups. On the other hand, the molecular

---

**Table 1. Calculated ΔH (ΔE) Values (kJ/mol) for the Formation of the NiTPP(py) and NiTPPF<sub>20</sub>(py) Complexes in Comparison to the Experimental Data**

<table>
<thead>
<tr>
<th></th>
<th>NiTPP</th>
<th></th>
<th>NiTPPF&lt;sub&gt;20&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas phase</td>
<td>toluene</td>
<td>gas phase</td>
<td>toluene</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>−19.1 (−10.6)</td>
<td>−14.1 (−5.6)</td>
<td>−32.7 (−33.2)</td>
<td>−23.7 (−23.2)</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;b&lt;/sup&gt;</td>
<td>−18.5 (−10.0)</td>
<td>−13.5 (−5.0)</td>
<td>−30.2 (−29.7)</td>
<td>−23.1 (−22.6)</td>
</tr>
<tr>
<td>BP86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+34.3 (+37.7)</td>
<td>+33.9 (+41.8)</td>
<td>+15.9 (+13.8)</td>
<td>+24.7 (+22.6)</td>
</tr>
<tr>
<td>expt</td>
<td>−17.6 ± 2.9&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−26.4 ± 1.3</td>
<td>−10.9 ± 4.2</td>
<td>−25.0 ± 2.0&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>ADF (ZORA/TZP). <sup>b</sup>Turbomole (def2-TZVP). <sup>c</sup>ΔH value determined in chloroform. <sup>d</sup>ΔH value determined in benzene. 

---

**Table 2. Calculated ΔH (ΔE) Values (kJ/mol) for the Formation of the NiTPP(py) and NiTPPF<sub>20</sub>(py) Complexes in Comparison to the Experimental Data**

<table>
<thead>
<tr>
<th></th>
<th>NiTPP</th>
<th></th>
<th>NiTPPF&lt;sub&gt;20&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas phase</td>
<td>toluene</td>
<td>gas phase</td>
<td>toluene</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>−1.3 (−12.2)</td>
<td>+12.3 (+1.4)</td>
<td>−15.3 (−20.3)</td>
<td>−1.7 (−6.7)</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;b&lt;/sup&gt;</td>
<td>−0.5 (−10.9)</td>
<td>+9.1 (−1.3)</td>
<td>−13.0 (−18.0)</td>
<td>−5.5 (−10.5)</td>
</tr>
<tr>
<td>BP86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>−6.7 (−17.6)</td>
<td>+11.7 (−6.3)</td>
<td>−23.4 (−21.8)</td>
<td>−7.9 (−10.9)</td>
</tr>
<tr>
<td>expt</td>
<td>−21.8 ± 0.8&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−25.0 ± 2.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−25.0 ± 2.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−46.9 ± 2.1&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>ADF (ZORA/TZP). <sup>b</sup>Turbomole (def2-TZVP). <sup>c</sup>ΔH value determined in toluene.

---

**Table 3. Calculated ΔH<sub>f</sub> (ΔE<sub>f</sub>) Values (kJ/mol) for the Formation of the NiTPP(py) and NiTPPF<sub>20</sub>(py) Complexes in Comparison to the Experimental Data**

<table>
<thead>
<tr>
<th></th>
<th>NiTPP</th>
<th></th>
<th>NiTPPF&lt;sub&gt;20&lt;/sub&gt;</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gas phase</td>
<td>toluene</td>
<td>gas phase</td>
<td>toluene</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;a&lt;/sup&gt;</td>
<td>−20.4 (−22.8)</td>
<td>−1.8 (−4.2)</td>
<td>−49.0 (−53.5)</td>
<td>−25.6 (−30.1)</td>
</tr>
<tr>
<td>B3LYP&lt;sup&gt;b&lt;/sup&gt;</td>
<td>−18.4 (−20.9)</td>
<td>−3.4 (−5.9)</td>
<td>−43.5 (−48.1)</td>
<td>−28.5 (−33.1)</td>
</tr>
<tr>
<td>BP86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>+27.6 (+20.1)</td>
<td>+45.6 (+35.6)</td>
<td>−7.5 (−7.9)</td>
<td>+16.7 (+11.7)</td>
</tr>
<tr>
<td>expt</td>
<td>−19.2 ± 0.8&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−46.9 ± 2.1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−46.9 ± 2.1&lt;sup&gt;e&lt;/sup&gt;</td>
<td>−46.9 ± 2.1&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup>ADF (ZORA/TZP). <sup>b</sup>Turbomole (def2-TZVP). <sup>c</sup>ΔH<sub>f</sub> value determined in pyridine. 

---

With the formation of NiTPPF, having been detected only in pyridine, most likely thanks to a large excess of the ligand.
To verify this, we performed single-point calculations on (i) the NiP_{NiTPP} and NiP_{NiTPPF20} fragments, that is the “NiP” fragments derived from NiTPP and NiTPPF20 by removing the aryl groups and saturating the meso carbons by hydrogen atoms (these fragments differ slightly in geometry) and (ii) the same “NiP” fragments in the presence of the electrostatic field generated by replacing the carbon and hydrogen/flourine atoms of the aryl groups with the corresponding Hirshfeld charges obtained from single-point calculations on NiTPP and NiTPPF20 (Table S4).

The energies of the frontier orbitals of the species defined in (i) and (ii) are compared in Table 4 with those of the corresponding MOs of NiTPP and NiTPPF20. Relatively small changes can be observed on passing from NiTPP to NiP_{NiTPP} apart from the “a1u”/“a2u” inversion in the latter. Application of the electrostatic potential generated by point charges corresponding to the Hirshfeld charges of the aryl C and H atoms leaves substantially unaltered the energy of the NiP_{NiTPP} MOs. This is in agreement with the fact that the point charges are not very pronounced (Table S4) and the electrostatic field is weak in this case.

The situation of the fluorinated compound is different. The NiP_{NiTPPF20} frontier MOs, which are very close to those of the NiP_{NiTPP} fragment and thus are ca. 0.8 eV higher in energy than those of NiTPPF20 to begin with, shift down by 0.5 eV upon application of the stronger electrostatic field of the Hirshfeld charges of the C and F atoms. This supports our hypothesis on the origin of the downshift of the NiTPPF20 levels, although the downshift of the NiP_{NiTPPF20} levels under the effect of the electrostatic field is less pronounced than in the full NiTPPF20, most likely due to the approximation inherent to the calculated Hirshfeld charges.

Additional support to our hypothesis comes from the calculation of the electron densities and electrostatic (Coulomb) potential based on the SCF electron density of NiTPP, NiTPPF20, and the species defined in (i) and (ii).

Figure 5a shows the plots of the electron density and electrostatic (Coulomb) potential of NiTPP, NiTPPF20, and the species defined in (i) and (ii). It is evident that the total electrostatic potential generated by the presence of the phenyl groups. Similarly, we find that the total electrostatic potential generated by the electron density and the nuclear charges does not change in a significant way on passing from NiTPP to NiP_{NiTPP} and NiP_{NiTPPF20+EField(TP)}. Substantially the same results are obtained in (i) and (ii). We hypothesize that the total electrostatic potential is due to the presence of the phenyl groups.

Table 4. B3LYP/TZP Energies (eV) of the Frontier MOs of the NiP_{NiTPP} and NiP_{NiTPPF20} Fragments before and after Application of the Electrostatic Field Generated by Replacing the Atoms of the Phenyl Groups, EField(TP), and the Perfluorophenyl Groups, EField(TPF20), with the Corresponding Hirshfeld Charges in Comparison to Those of the NiTPP and NiTPPF20 Complexes, Respectively

<table>
<thead>
<tr>
<th>MO</th>
<th>NiP_{NiTPP}</th>
<th>NiP_{NiTPPF20+EField(TP)}</th>
<th>NiTPPF20</th>
<th>NiP_{NiTPPF20}</th>
<th>NiP_{NiTPPF20+EField(TPF20)}</th>
<th>NiTPPF20</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d_{x,y}^z</td>
<td>−1.54</td>
<td>−1.60</td>
<td>−1.45</td>
<td>−1.63</td>
<td>−2.13</td>
<td>−2.37</td>
</tr>
<tr>
<td>“e”</td>
<td>−2.40</td>
<td>−2.46</td>
<td>−2.34</td>
<td>−2.38</td>
<td>−2.91</td>
<td>−3.25</td>
</tr>
<tr>
<td>“a1u”</td>
<td>−5.56</td>
<td>−5.61</td>
<td>−5.32</td>
<td>−5.56</td>
<td>−6.11</td>
<td>−6.39</td>
</tr>
<tr>
<td>“a2u”</td>
<td>−5.46</td>
<td>−5.52</td>
<td>−5.39</td>
<td>−5.46</td>
<td>−5.97</td>
<td>−6.23</td>
</tr>
<tr>
<td>3d_{x}</td>
<td>−6.24</td>
<td>−6.30</td>
<td>−6.13</td>
<td>−6.28</td>
<td>−6.78</td>
<td>−7.00</td>
</tr>
<tr>
<td>3d_{y}</td>
<td>−6.38</td>
<td>−6.44</td>
<td>−6.30</td>
<td>−6.41</td>
<td>−6.90</td>
<td>−7.14</td>
</tr>
</tbody>
</table>
In both complexes an evident flatness on the whole porphyrin core, including the area around the central metal; they only diverge in the outer regions corresponding to the aryl groups.

Having demonstrated the electrostatic origin of the downshift of the NiTPPF$_{20}$ levels, we now address the question of whether and to what extent the electrostatic field generated by the external perfluorophenyl groups affects the energy of the frontier orbitals of the incoming pyridine axial ligand(s). To this end we have computed the energy of the frontier orbitals of the pyridine fragment derived from NiTPPF$_{20}$(py) before and after application of the electrostatic field generated by replacing the atoms of the aryl groups with the corresponding Hirshfeld charges. According to the energy values gathered in Table S, the downshift of the pyridine levels upon application of the electrostatic field amounts to no more than $-0.10$ eV. In particular, the 11a$_1$-HOMO, the nitrogen lone pair $\sigma$-donor orbital, is downshifted by $-0.10$ eV. Such a downshift is clearly much smaller than that experienced by the nickel porphyrin MOs (Table 4). As expected, almost no energy change is observed in the pyridine frontier MOs when the same analysis is performed on the pyridine fragment derived from NiTPP-(py) with the EField(TP) (Table S).

The important conclusion is that the energy gap between the frontier orbitals of the incoming pyridine ligand(s) and those of the nickel(II) porphyrins is reduced on going from NiTPP and those of the perfluorophenyl groups in NiTPPF$_{20}$.
The aforementioned small energy changes observed for the pyridine frontier MOs upon application of the electrostatic field generated by the aryl groups in NiP_{NiTPPF20}+EField(TPF20), on moving away from the porphyrin mean plane (Figure 7a). In contrast, in NiP_{NiTPPF20}+EField(TP), the potential is almost independent of distance from the porphyrin mean plane and is smaller than in NiP_{NiTPPF20}+EField(TPF20) (Figure 7b).

One may wonder whether the solvent (toluene) would screen to a significant extent the electrostatic field generated by the perfluorophenyl groups of NiTPPF20 (a) and of the phenyl groups of NiTP (b) computed at different distances from the porphyrin mean plane, along the N_p−Ni−N_p axis.

NiP_{NiTPPF20}+EField(TP) the potential is almost independent of the distance from the porphyrin mean plane and is smaller than in NiP_{NiTPPF20}+EField(TPF20) (Figure 7b).

The formation energy $\Delta E_1$ is made up of two major components, the preparation energy, $\Delta E_{\text{prep}}$, and the interaction energy, $\Delta E_{\text{int}}$. $\Delta E_{\text{prep}}$ comprises the energy needed to deform the interacting fragments from their equilibrium geometry to the one they attain in the final complexes, $\Delta E_{\text{geo}}$, and the energy required to excite the deformed nickel(II) porphyrins from their ground-state electronic structure to the excited triplet state where the 3d\text{z}\text{z} and 3d_x^2−3d_y^2 orbitals are singly occupied, $\Delta E_{\text{excit}}$. According to the data in Table 6, the $\Delta E_{\text{geo}}$ term, which is almost entirely attributable to the energy required for the geometrical deformation of the metalloporphyrins (the energy required for the pyridine deformation is negligible), does not differ significantly in the two complexes and largely accounts for the preparation energy, especially in the case of the fluorinated complex. However, the difference in $\Delta E_{\text{prep}}$ between NiTPPP20(py) and NiTPPF20(py) has significant (counteracting) contributions from both $\Delta E_{\text{geo}}$ and $\Delta E_{\text{excit}}$, the smaller $\Delta E_{\text{excit}}$ term dropping more than half on going from NiTPPP20(py) to NiTPPF20(py).

**Table 6.** B3LYP/TZP Energy Decomposition Analysis of the Formation Energy, $\Delta E_1$ (kJ/mol), of NiTPPP20(py) and NiTPPF20(py) from the Nickel(II) Porphyrin and Pyridine Fragments

<table>
<thead>
<tr>
<th></th>
<th>NiTPPP20(py)</th>
<th>NiTPPF20(py)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{geo}}$</td>
<td>49.3</td>
<td>52.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{excit}}$</td>
<td>12.6</td>
<td>5.8</td>
</tr>
<tr>
<td>$\Delta E_{\text{prep}}$ ($\Delta E_{\text{geo}} + \Delta E_{\text{excit}}$)</td>
<td>61.9</td>
<td>58.0</td>
</tr>
<tr>
<td>$\Delta E_{\text{excit}}$</td>
<td>267.9</td>
<td>270.4</td>
</tr>
<tr>
<td>$\Delta V_{\text{elstat}}$</td>
<td>-243.3</td>
<td>-255.4</td>
</tr>
<tr>
<td>$\Delta E^\text{elstat}$ ($\Delta E_{\text{elstat}} + \Delta V_{\text{elstat}}$)</td>
<td>24.6</td>
<td>15.0</td>
</tr>
<tr>
<td>$\Delta E_{\text{exc}}$</td>
<td>-76.7</td>
<td>-83.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$</td>
<td>-3.0</td>
<td>-3.4</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$</td>
<td>-7.4</td>
<td>-8.4</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$ ($\sum \Delta E_i$)</td>
<td>-10.0</td>
<td>-11.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$ ($\Delta E^\text{elstat} + \Delta E_{\text{Ei}}$)</td>
<td>-97.1</td>
<td>-106.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$ ($\Delta E_{\text{prep}} + \Delta E_{\text{Ei}}$)</td>
<td>-72.5</td>
<td>-91.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{Ei}}$ ($\Delta E_{\text{excit}}$)</td>
<td>-10.6</td>
<td>-33.2</td>
</tr>
</tbody>
</table>
Due to a 7 kJ/mol less demanding excitation energy, the \( \Delta E_{\text{prep}} \) term is in NiTPPF\(_{20}\)(py) some 4 kJ/mol smaller than in NiTPP(py).

For the interaction energy, the contribution of the steric interaction term, \( \Delta E_\text{fi} \), is moderately repulsive in both five-coordinate complexes because the repulsive \( \Delta E_{\text{Pauli}} \) term slightly overcomes the attractive \( \Delta V_{\text{elstat}} \) term, less however in NiTPPF\(_{20}\)(py), where the electrostatic contribution is more stabilizing than in NiTPP(py) by 12.1 kJ/mol. This can be attributed to the more stabilizing electrostatic field due to the perfluorophenyl substituents.

With regard to the orbital interaction term \( \Delta E_{\text{eo}} \), we first note that it gives the important stabilizing contribution (around \(-100 \) kJ/mol) to \( \Delta E_1 \) (more stabilizing in NiTPPF\(_{20}\)(py) by \(-9.1 \) kJ/mol). Due to the repulsive \( \Delta E_\sigma \) and \( \Delta E_{\text{prep}} \) terms, the net bond between the nickel(II) porphyrins and the axial pyridine ligand is, in agreement with the experiment, still rather weak.

The analysis of the contributions to \( \Delta E_{\text{eo}} \) shows that each irreducible representation of the \( C_2 \) symmetry group of the complexes allows assessment of the nature and strength of the bonding interactions. From the data in Table 6 it is apparent that the major contribution (78% in both cases) to \( \Delta E_{\text{eo}} \) comes from the \( \Delta E_{\text{A}_1} \) term. This term, which is more stabilizing by 6.5 kJ/mol in NiTPPF\(_{20}\)(py) than in NiTPP(py), accounts for the \( \sigma \) interaction between the singly occupied \( \mathrm{Ni} \) 3d\(_z^2\) orbital of the nickel(II) porphyrins and the lone pair of the pyridine ligand, the 11a\(_1\)-HOMO. According to the schematic level diagrams of the key MOs of NiTPP(py) and NiTPPF\(_{20}\)(py) displayed in Figure 8, the interaction between the 3d\(_z^2\) orbital and the pyridine nitrogen lone pair allows the doubly occupied Ni–N\(_\text{py} \) bonding \( \sigma \) and the singly occupied Ni–N\(_\text{py} \) antibonding \( \sigma^* \) spin orbitals and, hence, is configured as a three-electron–two-orbital interaction.

Due to the surplus of \( \alpha \) electrons, the \( \alpha \)-spin orbitals are stabilized relative to the \( \beta \)-spin orbitals. The \( \alpha \)-spin components of \( \sigma \) and \( \sigma^* \) show significant mixing of the pyridine lone pair and the nickel orbitals, mainly 3d\(_z^2\) with a minor 4p\(_z\)/4s contribution. Since both these \( \alpha \)-spin \( \sigma \) and \( \sigma^* \) orbitals are occupied, the 3d\(_z^2\)–N\(_\text{py} \) mixing in the \( \alpha \)-spin manifold represents mostly Pauli repulsion, although, due to the admixture of the \( \alpha \)-3d\(_z^2\) with the \( \alpha \)-spin 4p\(_z\) and 4s some charge transfer occurs from the \( \alpha \)-N\(_\text{py} \) into these orbitals (0.06e in NiTPP(py) and 0.07e in NiTPPF\(_{20}\)(py)).

There is much less mixing in the \( \beta \)-spin \( \sigma \) and \( \sigma^* \) orbitals, these orbitals remaining mainly localized on the N\(_\text{py} \) lone pair (\( \beta \)-\( \sigma \)) and the 3d\(_z^2\) metal orbital (\( \beta \)-\( \sigma^* \)). As the \( \beta \)-3d\(_z^2\) metal orbital is unoccupied to begin with, it can interact favorably with the occupied \( \beta \)-N\(_\text{py} \). Mulliken population analysis reveals that, in both complexes, there is a modest, but larger than that in the \( \alpha \)-spin manifold, \( \sigma \) donation from the pyridine lone pair to the \( \beta \)-spin 3d\(_z^2\), 4p\(_z\), and 4s metal orbitals (0.13e in NiTPP(py) and 0.14e in NiTPPF\(_{20}\)(py)).

Thus, it can be concluded that the \( \Delta E_{\text{A}_1} \) term mostly describes the formation of a two-orbital–three-electron (2o-3e) bond, which is typically rather weak. The somewhat more negative value of the \( \Delta E_{\text{A}_1} \) term for NiTPPF\(_{20}\)(py) amounts to a stronger 2o-3e bond. This is plausible, as the Ni–3d\(_z^2\) and the lone pair of the incoming pyridine (the MOs involved in the bond formation) are in NiTPPF\(_{20}\) closer in energy than in NiTPP, due to the energy lowering by \(-0.84 \) eV of the 3d\(_z^2\) orbital of the former induced by the electrostatic field associated with the perfluorophenyl groups (cf. Table 4). Other effects accounting for small negative contributions of other irreps in Table 6, such as \( \pi \) back-donation from the nickel 3d\(_{xz}\) and 3d\(_{yz}\) orbitals to the lowest unoccupied pyridine MOs of pertinent symmetry (\( \Delta E_{\text{B}_1} \) and \( \Delta E_{\text{B}_2} \) terms in Table 6).
and polarization ($\Delta E_{\text{pol}}$) are closely similar in NiTPP(py) and NiTPPF$_{20}$(py).

In conclusion, the energy decomposition analysis indicates that both five-coordinate complexes can be formed because the stabilizing orbital interaction term overcomes the destabilizing preparation energy and steric interaction terms. The formation of NiTPPF$_{20}$(py) is, however, by far more favorable energetically, due to the more stabilizing $\Delta E_{\text{st}}$ term (essentially the $\Delta E_{\text{orb}}$ term) and less destabilizing $\Delta E_{\text{prep}}$ and $\Delta E^0$ terms.

To evaluate the solvent (toluene) effects on the energy terms and the additional terms related to the solvation/desolvation of the interacting fragments and the final complexes, the energy decomposition analysis was also performed in toluene, with the COSMO model. The results are gathered in Table S7, where the gas-phase results are also shown for comparison purposes. As inferred from the data in the table, inclusion of solvation effects only slightly modifies the terms contributing to $\Delta E_{\text{tot}}$, which is less than that in the gas phase by only 3.4 and 5.0 kJ/mol in NiTPP(py) and NiTPPF$_{20}$(py), respectively, leaving almost unaltered the $\Delta E_{\text{det}}$ gap computed for the two species in the gas phase. These results confirm that the electrostatic field generated by the dipole moments of the C–F bonds is only slightly screened by the solvent and, more generally, the solvent perturbation does not modify the gas-phase scenario.

As is apparent from Table S7, the $\Delta E_{\text{solv}}$ term, which accounts for the differential solvation of the isolated fragments and the final complex, is appreciably destabilizing (positive) only in the case of the fluorinated complex. This term favors the isolated fragments with respect to the five-coordinated complexes, especially in the case of NiTPPF$_{20}$(py), due to a larger solvation energy of NiTPPF$_{20}$ relative to that of NiTPP.

NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ from NiTPP(py) and NiTPPF$_{20}$(py). The six-coordinate complexes are formed by addition of a second pyridine ligand to the five-coordinate complexes and/or by simultaneous addition of two pyridine ligands to the nickel(II) porphyrins (see the next section). Both of these processes have been considered in performing the energy decomposition analysis. The calculated energy terms are reported in Tables 7 and 8.

The formation of NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ from the parent five-coordinate complexes does not involve any spin state change; thus, the preparation energy term in Table 7 only accounts for the geometrical deformation of the five-coordinate nickel(II) porphyrins (the energy required for the pyridine deformation is again negligible).

When the six-coordinate complexes are formed, the porphyrin macrocycle of NiTPP(py) and NiTPPF$_{20}$(py) flattens and expands (compare the geometrical parameters in Figures 2 and 3). The expansion energy cost is partially covered by the flattening energy gain. The result is that the $\Delta E_{\text{geo}}$ term is much less destabilizing than for the formation of the five-coordinate complexes. The opposite happens with the $\Delta E^0$ term, especially in the case of the fluorinated species. When the $\Delta E_{\text{tot}}$ terms in Tables 6 and 7 are compared, it is apparent that the orbital interaction energy for the addition of the second pyridine is less stabilizing than for the addition of the first pyridine. According to the decomposition of the $\Delta E_{\text{tot}}$ into the contributions from the A and B irreducible representations of the $C_2v$ symmetry group of the complexes, the major contribution to the orbital interaction energy comes from the $\Delta E_{\text{orb}}$ term. This term is ca. 30% less stabilizing than in the case of the addition of the first pyridine, although now it also comprises the polarization effects that in the $C_2v$ symmetry of the five-coordinate complexes are included in the $\Delta E_{\text{A}}$ term.

In addition to polarization effects, the $\Delta E_{\text{A}}$ term accounts for the $\sigma$ interaction between the singly occupied Ni–N$_{\text{py}}$ antibonding $\sigma^*$ spin orbital of the five-coordinate complexes and the nitrogen lone pair of the second pyridine ligand. The salient electronic structure effects of this interaction are visible in the schematic level diagrams of Figure 9.

Among the levels in Figure 9, one may recognize the doubly occupied $\sigma$ and the singly occupied $\sigma^*$ orbitals reported in the level diagrams of the five-coordinate complexes (Figure 8). These MOs are now an admixture of nickel orbitals, mainly 3d$_{x^2}$ with some 4p$_{yz}$/4s contribution, and the plus combination of the nitrogen lone pair of the two pyridine ligands, N$_{\text{py}}$(py)$_2$. In addition to the $\sigma$- and $\sigma^*$-spin orbitals there is a doubly occupied MO ($\sigma$-100a and $\beta$-99a) localized on the minus combination of the N$_{\text{py}}$(py)$_2$ lone pairs, which does not play a part in the bonding. Just as seen in the five-coordinate complexes, the $\alpha$-spin components of the $\sigma$ and $\sigma^*$ show a significant mixing between the orbitals of the interacting fragments (note the stabilization of the $\alpha$-$\sigma$ with respect to $\alpha$-100a, viz. $\alpha$-141a). The $\alpha$-$\sigma$/$\alpha$-$\sigma^*$ bonding/antibonding pair represents Pauli repulsion in the $\alpha$-spin manifold. A bonding contribution can come from occupied/unoccupied interaction ($\beta$-N$_{\text{py}}$/3d$_{x^2}$, $\beta$-4s, $\beta$-4p$_{yz}$). The mixing of these $\beta$-spin orbitals is not large; the

### Table 7. B3LYP/TZP Energy Decomposition Analysis of the Formation Energy, $\Delta E_{\text{f}}$ (kJ/mol), of NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ from NiTPP(py), NiTPPF$_{20}$(py), and Pyridine Fragments

<table>
<thead>
<tr>
<th></th>
<th>NiTPP(py)$_2$</th>
<th>NiTPPF$_{20}$(py)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{geo}}$</td>
<td>18.7</td>
<td>21.1</td>
</tr>
<tr>
<td>$\Delta E_{\text{prep}}$</td>
<td>18.7</td>
<td>21.1</td>
</tr>
<tr>
<td>$\Delta E_{\text{pol}}$</td>
<td>206.1</td>
<td>202.6</td>
</tr>
<tr>
<td>$\Delta V_{\text{solv}}$</td>
<td>$-169.4$</td>
<td>$-171.7$</td>
</tr>
<tr>
<td>$\Delta E_{\text{orb}}$</td>
<td>36.7</td>
<td>30.9</td>
</tr>
<tr>
<td>$\Delta E_{\text{A}}$</td>
<td>$-57.5$</td>
<td>$-60.7$</td>
</tr>
<tr>
<td>$\Delta E_{\text{B}}$</td>
<td>$-10.1$</td>
<td>$-11.6$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-67.6$</td>
<td>$-72.3$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-30.9$</td>
<td>$-41.4$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-12.2$</td>
<td>$-20.3$</td>
</tr>
</tbody>
</table>

### Table 8. B3LYP/TZP Energy Decomposition Analysis of the Formation Energy, $\Delta E_{\text{f}}$ (kJ/mol), of NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ from the Nickel(II) Porphyrin and Two Pyridine Fragments

<table>
<thead>
<tr>
<th></th>
<th>NiTPP(py)$_2$</th>
<th>NiTPPF$_{20}$(py)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_{\text{geo}}$</td>
<td>42.1</td>
<td>41.9</td>
</tr>
<tr>
<td>$\Delta E_{\text{prep}}$</td>
<td>18.0</td>
<td>11.2</td>
</tr>
<tr>
<td>$\Delta E_{\text{pol}}$</td>
<td>60.1</td>
<td>53.1</td>
</tr>
<tr>
<td>$\Delta E_{\text{pol}}$</td>
<td>389.0</td>
<td>383.6</td>
</tr>
<tr>
<td>$\Delta V_{\text{solv}}$</td>
<td>$-332.5$</td>
<td>$-338.6$</td>
</tr>
<tr>
<td>$\Delta E_{\text{orb}}$</td>
<td>65.5</td>
<td>45.0</td>
</tr>
<tr>
<td>$\Delta E_{\text{A}}$</td>
<td>$-114.9$</td>
<td>$-123.1$</td>
</tr>
<tr>
<td>$\Delta E_{\text{B}}$</td>
<td>$-24.5$</td>
<td>$-28.5$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-139.4$</td>
<td>$-151.6$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-82.9$</td>
<td>$-106.6$</td>
</tr>
<tr>
<td>$\Delta E_{\text{f}}$</td>
<td>$-22.8$</td>
<td>$-53.5$</td>
</tr>
</tbody>
</table>
Figure 9. Schematic energy level diagram of the key MOs of NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ in their $S = 1$ triplet ground spin state obtained at the B3LYP/TZP level. The two unpaired electrons are indicated with red arrows.

$\beta$-spin $\sigma$ and $\sigma^*$ are mainly localized on the plus combination of the pyridine lone pairs and on the nickel 3d$_z^2$ orbital, respectively. In summary, we are again faced with a two-orbital-three-electron interaction, where now one orbital is the N$_{py}$ lone pair of the second pyridine and the other orbital is the 3d$_z^2$ destabilized by the interaction with the N$_{py}$ lone pair of the first pyridine. Because of this destabilization, this second 2o-3e bond is considerably weaker than the first bond (compare the $\Delta E_{oi}$ term in Table 7 with the $\Delta E_{fl}$ term in Table 6). Due to the concomitant decrease (less negative) on the stabilizing $\Delta E_{oi}$ term and increase (more positive) of the repulsive $\Delta E_{fl}$ term, the total interaction energy $\Delta E_{int}$ is much less stabilizing (by 40–50 kJ/mol) than for the addition of the first pyridine. This is largely compensated by less preparation energy (ca. 40 kJ/mol) for the addition of the second pyridine (no excitation energy to the triplet required), yielding overall comparable bond strength for bonding of the second pyridine in comparison to the first. Because of a more stabilizing $\Delta E_{int}$ term, the formation energy $\Delta E_2$ of NiTPPF$_{20}$(py)$_2$ is slightly more negative than that of NiTPP(py)$_2$.

NiTPP(py)$_2$ and NiTPPF$_{20}$(py)$_2$ from the Nickel(II) Porphyrins and Two Pyridines. Let us consider now the formation of the six-coordinate complexes by simultaneous addition of two pyridine ligands. The results of the energy decomposition analysis are gathered in Table 8.

When the $\Delta E_{prep}$ terms in Tables 8 and 6 are compared, it is evident that the energy required to prepare the interacting fragments to form the six-coordinate complexes is not significantly different from that required to form the five-coordinate species (in both cases an electronic excitation energy to the triplet is required).

The total bond energy $\Delta E_1$ must be the sum of $\Delta E_1$ and $\Delta E_2$. This needs not be exactly the case for the individual contributions. We find the orbital interaction energy $\Delta E_{oi}$ to be somewhat more stabilizing than the sum of these terms for the first and second additions of a pyridine moiety. What is more, $\Delta E_{oi}$ is again more stabilizing in the fluorinated complex by virtue of a stronger 2o-3e bonding interaction. Understandably, the preparation energy is close to that for the coordination of the first pyridine, while the repulsive $\Delta E_{fl}$ term is comparable to the sum of the two steps. The net effect is indeed a bond strength that is the sum of those for the first and second addition of a pyridine.

## CONCLUSIONS

It emerges from these studies that the electrostatic potential generated by the dipole moments of the perfluorophenyl C–F bonds makes NiTPPF$_{20}$ have a greater propensity than NiTPP to axially bind the pyridine ligand(s) either in the gas phase or in toluene solution. Contrary to the common view, the perfluorophenyl groups do not alter the electron density distribution of the “NiP” core, which is identical in NiTPPF$_{20}$ and NiTPP. Rather, they induce a downshift of the NiTPPF$_{20}$ levels, which is driven by the electrostatic potential generated by the dipole moments of the C–F bonds. This has been assessed by explicit calculations of the electron densities and electrostatic (Coulomb) potential based on the SCF electron density of NiTPP, NiTPPF$_{20}$, and their “NiP” cores (NiP$_{NiTPP}$ and NiP$_{NiTPPF_{20}}$), in the presence and absence of the electrostatic field generated by replacing the carbon and hydrogen/fluorine atoms of the aryl groups with the corresponding Hirshfeld charges. Interestingly, the electrostatic potential generated by the perfluorophenyl groups barely affects the frontier orbitals, notably the HOMO nitrogen lone pair, of the incoming pyridine ligand(s), in keeping with the drop in the electrostatic potential produced by the Hirshfeld atomic charges on moving away from the porphyrin mean plane. As a result, the energy gap between the frontier orbitals of the incoming pyridine ligand(s) and those of the nickel(II)
porphyrins (notably the higher lying Ni 3d,2) is reduced on going from NiTPP to NiTPPF20, leading in the pyridine complexes of the latter to a stronger two-orbital–three-electron bond between the pyridine nitrogen lone pair(s) and the singly occupied Ni 3d,2 orbital (in the excited triplet state). The enhanced binding capability of NiTPPF20 toward the pyridine ligand(s) has been analyzed by a bond energy decomposition analysis for the formation of the five- and six-coordinate complexes. According to this analysis, pyridine binding to the fluorinated complex is energetically favored mainly because of a more stabilizing orbital interaction energy term, in keeping with our suggested explanation.

**ASSOCIATED CONTENT**

| Supporting Information | The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c01327. |

Salient geometrical features of NiTPP and NiTPPF20 and their five- and six-coordinate pyridine complexes computed at different levels of theory. B3LYP Hirshfeld and NBO charges of selected atoms of NiTPP and NiTPPF20, B3LYP/TZP energies (eV) of the frontier MOs of NiTPP and NiTPPF20, computed in the gas phase and in toluene solution (COSMO), B3LYP/TZP energies (eV) of the frontier MOs of pyridine computed in the gas phase and in toluene solution (COSMO), B3LYP/TZP energy decomposition analysis of the formation energy, $\Delta E_f$ (kJ/mol), of NiTPP(py) and NiTPPF20(py) from the nickel(II) porphyrin and pyridine fragments in the gas phase and in toluene solution (COSMO model), electrostatic potentials (SCF potential, ev) computed at different distances from the macrocycle mean plane, along the $N_p-N_i-N_p$ and $C_{\text{max}}-N_i-C_{\text{max}}$ axes in NiTPP (full SCF computation), NiP NiTPP and NiP NiTPPF+EFIELD(TP) and deviation of the NiP NiTPPF+EFIELD(TP) and NiP NiTPPF potentials from the NiTPPF20 full potential (PDF).

**AUTHOR INFORMATION**

**Corresponding Authors**

Giampaolo Ricciardi — Università della Basilicata, Scuola di Scienze Agrarie, Forestali, Alimentari e Ambientali (SAFE), 85100 Potenza, Italy; orcid.org/0000-0002-6034-8813; Email: giampaolo.ricciardi@unibas.it

Angela Rosa — Università della Basilicata, Dipartimento di Scienze, 85100 Potenza, Italy; orcid.org/0000-0003-4592-244X; Email: angela.rosa@unibas.it

**Authors**

Mario Amati — Università della Basilicata, Dipartimento di Scienze, 85100 Potenza, Italy

Evert Jan Baerends — VU University Amsterdam, Theoretical Chemistry, FEW, 1081 HV Amsterdam, The Netherlands; orcid.org/0000-0002-3045-4906

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.0c01327

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This research work was supported by the Università degli Studi della Basilicata, Potenza, Italy.

**REFERENCES**


(d) Tang, Q.; Carrington, P. E.; Horng, Y.-C.; Ragsdale, S. W.; Hoffman, B. M. Cryoreduction of Methyl-Coenzyme M Reductase: EPR Characterization of Forms, MCRred1, MCRred2, MCRred1, and MCRred2. Inorganic Chemistry pubs.acs.org/IC

1999, 38, 7875−7889.


