Metalloporphyrins with All the Pyrrole Nitrogens Replaced with Phosphorus Atoms, $MP(P)_4$

(M = Sc, Ti, Fe, Ni, Cu, Zn)

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Abstract

We performed first systematic DFT study of the structures and electronic features (frontier orbitals energies, HOMO/LUMO and optical gaps, IPs and EAs) of the MP(P)_4 compounds, with increasing number of d-electrons: $3d^1 4s^2$ (Sc) $\rightarrow 3d^2 4s^2$ (Ti) $\rightarrow 3d^6 4s^2$ (Fe) $\rightarrow 3d^8 4s^2$ (Ni) $\rightarrow 3d^{10} 4s^1$ (Cu) $\rightarrow 3d^{10} 4s^2$ (Zn). We performed systematic comparison with the tetrapyrrole MP counterparts. Complete substitution of the pyrrole nitrogens by P-atoms does not change the calculated ground spin state of the compound. All the MP(P)_4 species adopt a bowl-like shape, compared to generally planar or slightly distorted shapes of their MP counterparts. Significant positive charge accumulates on P-atoms in MP(P)_4 . Positive charges on the metals in MP(P)_4 are noticeably lower than in the MP counterparts. The calculated MP(P)_4 HOMO/LUMO gaps and optical gaps are noticeably smaller than the corresponding gaps in their MP counterparts, which is explained by stabilization of the MP(P)_4 LUMOs.

Keywords P_4 -substituted transition-metal-porphyrins; density functional theory; strong bowl-like deformations; electronic properties

1. Introduction

Metalloporphyrins and their derivatives have been of great interest because of their roles as enzyme cofactors [1-5] and due to their numerous technological applications [6-17]. The size, shape, electronic properties, and binding ability of porphyrins can be broadly tuned by replacing pyrrole nitrogen(s) with other elements, for example, C, Si, or chalcogens [18-24]. This type of the porphyrin core modification is a highly promising approach for tuning the optical, electrochemical, and coordinating properties as well as reactivity of porphyrins. However, until recent time the effects of one or two pyrrole nitrogen replacement in porphyrins with the heavier congener, phosphorus, were investigated for just a few porphyrins and their derivatives [25-34]. In 2003, Delaere and Nguyen [25] reported the density functional theory (DFT) study of the structural and optical properties of the P-containing porphyrins with one or two pyrrole nitrogens replaced by P-atoms. Substitution of a NH- by a PH-unit showed no distortions of the carbon skeleton which remains essentially planar, whereas replacement of a N- by a P-atom was found to weakly distort the P-containing five-membered ring from the porphyrin mean plane. A nearly equal red shift of both Q- and B-bands was predicted upon substituting NH- by PH-units, whereas the red shift of Q-bands was calculated to be much larger than the red shift of B-bands upon substitution of an N-atom by a P-atom.

Moreover, Matano, Nakabuchi, Imahori and co-workers reported various phosphaporphyrins and their derivatives with only one pyrrole nitrogen replaced by a P-atom [26-35]. In their 2010 review [26], they summarized their previous studies on the synthesis, structures, and aromaticity of phosphole-containing porphyrins and their metal complexes. One of the compounds studied, the 18π -electron porphyrin containing trigonal pyramidal P-center was found to possess a slightly distorted 18π -electron plane. On the contrary, the 22π -electron porphyrin containing tetrahedral P-center was shown to have a highly ruffled structure. The Rh(III) and Pd(II) derivatives of these compounds were also shown to possess significant structural distortions. The metal complexes of these P-substituted porphyrins exhibited only a weak antiaromaticity in terms of the magnetic criterion. In the UV-vis absorption spectra of the P-

substituted porphyrins the characteristic porphyrin transitions, B and Q bands, were clearly observed, with significant red shifts. The 18π -electron Rh-complex also showed characteristic Soret and Q bands, whereas the 20π -electron Pd-complex displayed broad and blue-shifted Soret-like bands and no detectable Q bands. It was stated that the observed structures, reactivities, and coordinating properties of the studied P-porphyrins were undoubtedly produced by the P-atom at the core. Earlier, in the 2009 review [27] Matano and Imahori described the effects of varying the combination of core heteroatoms (P, N, S, and O) on the coordination properties of the hybrid macrocycles. The results were summarized to show that (i) the P,S,N₂-calixpyrroles behave as monophosphine ligands, (ii) the P,X,N₂-calixphyrins behave as neutral, monoanionic, or dianionic tetradentate ligands, and (iii) the P,S,N₂-porphyrins behave as a redox-active π -ligand for Ni, Pd, and Pt. The incorporation of the phosphole subunit into the macrocyclic framework was proved to provide unprecedented coordinating properties for the porphyrin family. In another study [29], P,N₃-porphyrin and P,S,N₂-porphyrin were investigated both experimentally and computationally. The results obtained suggested that the 18π aromaticity inherent in regular N₄-porphyrins was maintained in these phosphaporphyrins. X-ray crystallography revealed a slightly distorted 18π aromatic ring for the P,N₃-porphyrin. DFT calculations on model compounds showed that the P,X,N₂-porphyrins (where X = N, S) possessed considerably small HOMO-LUMO gaps as compared with N₄- and S,N₃-porphyrins, which was reflected in the red-shifted absorptions, low oxidation potentials, and high reduction potentials.

Also, the structures and coordination chemistry of phosphole-containing calixphyrins (P,N₂,X-hybrid calixphyrins) and the catalytic activities of their Pd and Rh complexes were studied both experimentally and computationally [33]. The Pd and Rh complexes were shown to catalyze the Heck reaction and hydrosilylations. It is also worthwhile to mention the 2009 theoretical investigation (using the DFT approach) of electronic structure and reactivity for oxidative addition for the Pd complex of P,S-containing hybrid calixphyrin. The differences in the reactivity among the Pd-containing complexes of P,S-containing hybrid calixphyrin, hybrid porphyrin, and conventional porphyrin were interpreted in terms

of the π^* orbital energies and the flexibility of the ligand frameworks.

Phosphole, C_5H_5P , possesses the following features [36-38]: (i) a trigonal pyramidal geometry of the P-center due to insufficient n- π orbital interaction (and thus much lower aromaticity than pyrrole); (ii) a lower LUMO energy compared to the pyrrole LUMO due to the effective $\sigma^*(P-R)-\pi^*(1,3\text{-diene})$ interaction; (iii) rigid, electron rich, and polarizable P-bridged 1,3-diene unit. These features originate from the intrinsic nature of the P 3s and 3p orbitals. Phospholes behave both as potential building blocks for the π -conjugated materials and as ordinary phosphine ligands [39-40]. The P-atom incorporation in the porphyrin core is a very promising strategy for tuning the properties and reactivity of porphyrin species.

So far no computational studies of a free porphyrin or its metal complexes with *all pyrrole nitrogens* replaced with phosphorus (P_4 -porphyrins, or $P(P)_4$) have been reported, except our previous report on $NiP(P)_4$ [41]. We can therefore formulate the following questions to answer:

- (i) What structures will $P(P)_4$ compound and its metal complexes adopt?
- (ii) How will be charges distributed in the metal- $P(P)_4$ compounds compared to tetrapyrrole species?
- (iii) How will the complete replacement of pyrrole nitrogens affect the ground spin state?
- (iv) How different will be the $MP(P)_4$ electronic properties compared to their MP counterparts?

Thus, inspired by the previous studies and by interesting opportunities which $MP(P)_4$ species could provide, we report the structural and electronic properties of the $MP(P)_4$ species containing several transition metals (TM), Sc, Ti, Fe, Ni, Cu, and Zn, and make systematic comparisons with their tetrapyrrole counterparts, metalloporphyrins MP.

The paper is organized as follows: in the next section, we describe the computational approaches used; then we address ground states and the low-lying structures calculated for the $MP(P)_4$ compounds; next, we address the structural features of the $MP(P)_4$ compounds studied; then, we consider their electronic properties; finally, we summarize the research findings and discuss further research perspectives.

2. Computational details

The studies described here were performed with the Gaussian09 package [42]. Geometries of all the MP(P)_4 species were optimized within the C_2 symmetry constraints (the C_2 symmetry was applied because it is the common P_4 -substituted porphyrins symmetry pattern), and the resulting structures were assessed using vibrational frequency analysis to probe whether or not the MP(P)_4 structures represent true minimum-energy geometries. If imaginary frequencies were found, further optimizations along those normal coordinates (without symmetry constraints) were performed. For all the species under investigation, we performed thorough global minimum searches and studied different spin states possible (see supporting information, Table S1). All the calculations were done using the split-valence 6-31G* basis set [43-47] and the hybrid B3LYP functional [48]. This approach was earlier proved to give geometries in good agreement with experiments (see, e.g., Ref. 49), and was also shown to produce the ordering of spin states of metalloporphyrin complexes reasonably well [50]. The approach is subsequently referred to as B3LYP/6-31G*. The same computational approach was applied to the tetrapyrrole MP species (see supporting information, Table S4); the same methodology with respect to the global minimum searches as described above was used, the only difference being starting geometry optimizations within the D_{4h} symmetry constraints.

We studied the MP(P)_4 species both in the gas phase and with implicit solvent effects from water, acetonitrile, and benzene taken into account. With implicit solvent effects the geometries for all of the MP(P)_4 species were calculated at the B3LYP/6-31G* level of theory using the self-consistent reaction field IEF-PCM method [51] (the UFF default model used in the Gaussian09 package, with the electrostatic scaling factor α [52] set to 1.0), with water, toluene, and acetonitrile as solvents (dielectric constants $\epsilon = 78.3553$, 2.2706, and 35.688, respectively). Below we discuss both the gas-phase results without the zero-point correction ZPE (ΔE_0) and with ZPE (ΔE) and results obtained with implicit solvent. The energy differences (in kcal/mol) obtained with the zero-point corrections are given in parentheses.

In order to further demonstrate the reliability of the B3LYP/6-31G* approach in calculating different spin states of the MP(P)_4 compounds, we performed global minimum search calculations on MP(P)_4 using two GGA functionals, PBE [53] and PW91 [53]. All of these calculations were performed in the gas phase, using the 6-31G* basis sets. Results of these calculations are presented in Table S6 in the supporting information.

We also performed time-dependent DFT calculations of the optical gap values for the MP(P)_4 and MP species studied using the TDB3LYP approach [54-58]. All these calculations were done with the gas-phase B3LYP/6-31G* optimized geometries, using the 6-31G* basis set, and number of the states (poles) calculated was chosen to be 30, applying the keywords ‘(nstates=30)’, as implemented in the Gaussian09 package. The vertical ionization potential (IP) and electron affinity (EA), IP_v/EA_v , values were obtained in single-point calculations from the energies of systems with N and $N\pm 1$ electrons calculated with the geometries of the N-electron systems. The adiabatic IPs and EAs ($\text{IP}_{\text{ad}}/\text{EA}_{\text{ad}}$) were obtained from the energies of the systems with N and $N\pm 1$ electrons, calculated using optimized geometries of the $N\pm 1$ electron species. For the charge analysis, we used the Natural Bond Orbital (NBO) analysis scheme implemented in the Gaussian09 software with the keyword ‘pop=NBO’ [59-65]. In order to estimate the contributions of specific atoms to the HOMO and LUMO of the MP(P)_4 and MP compounds, we performed calculations of total densities of states (DOS) and fragment densities of states (projected densities of states, PDOS), using the keywords ‘Fragment’ and ‘Population=orbitals’ as implemented in the Gaussian09 package. For the fragment densities of states calculations, the MP(P)_4 and MP species were ‘split’ into the fragments corresponding to M, P/N, and (C+H) remainder of the ligands. Molecular structures were visualized using Molden 5.0 [66] visualization software.

3. Results and discussion

3.1. $MP(P)_4$ structures and energetics and comparison with the MP compounds.

3.1.1. Ground states and low-lying states and isomers.

Table 1

Ground state (symmetry, spin) and energy gap between the ground state and the next spin state for the neutral $M^{II}P(P)_4$, $M = Sc, Ti, Fe, Ni, Cu, Zn$, and cationic $M^{III/IV}P(P)_4$ species, $M = Sc^{III}, Ti^{IV}, Fe^{III}$ (gas-phase calculated, B3LYP/6-31G* level of theory).

Ground state (symmetry, spin)/					
Energy gap between the ground state and the next spin state, ΔE_0 (ΔE)					
Sc	Ti	Fe	Ni	Cu	Zn
$M^{II}P(P)_4$					
$C_2, ^2B/$	$C_2, ^3B/$	$C_2, ^3B/$	$C_2, ^1A/$	$C_2, ^2A/$	$C_2, ^1A/$
22.1 (21.5)	8.2 (8.5)	16.6 (15.2)	24.7 (18.1)	32.7 (30.7)	17.6 (16.9)
$M^{III/IV}P(P)_4$					
$C_1, ^1A/$	$C_1, ^3A/$	$C_2, ^4A/$			
20.8 (18.8)	4.3 (3.3)	12.0 (12.4)			

Table 2

Ground state (symmetry, spin) and energy gap between the ground state and the next spin state for the neutral $M^{II}P$, $M = Sc, Ti, Fe, Ni, Cu, Zn$, and cationic $M^{III/IV}P$ species, $M = Sc^{III}, Ti^{IV}, Fe^{III}$ (gas-phase calculated, B3LYP/6-31G* level of theory).

Ground state (symmetry, spin)/					
Energy gap with the next lower-lying spin state, ΔE_0 (ΔE)					
Sc	Ti	Fe	Ni	Cu	Zn
$M^{II}P$					
$C_2, ^2B/$	$D_{2h}, ^3B_{2g}/$	$D_{4h}, ^3B_{1g}/$	$D_{2d}, ^1A_1/$	$D_{4h}, ^2B_{1g}/$	$D_{4h}, ^1A_{1g}/$

9					
35.6 (33.1)	2.8 (2.4)	8.1 (6.8)	8.0 (7.0)	42.7 (39.2)	42.1 (38.4)
$M^{III/IV}P$					
$C_1, ^1A/$	$C_1, ^3A/$	$D_{4h}, ^4B_{3g}/$			
37.5 (35.2)	3.2 (4.1)	13.5 (12.1)			

After the initial study of the $Ni^{II}P(P)_4$ compound [41], we decided to extend our computational research further to cover the tetraphosphorus-substituted porphyrins of the following transition elements: Sc, Ti, Fe, Zn, and Cu. We have performed studies of both the neutrals, $Sc^{II}P(P)_4$, $Ti^{II}P(P)_4$, $Fe^{II}P(P)_4$, $Cu^{II}P(P)_4$, $Zn^{II}P(P)_4$, and cations, $Sc^{III}P(P)_4^{1+}$, $Ti^{IV}P(P)_4^{2+}$, and $Fe^{III}P(P)_4^{1+}$. As can be seen, in the neutral compounds, $Sc^{II}P(P)_4$ and $Ti^{II}P(P)_4$, both transition metals exist in non-characteristic oxidation state +2, but these species were studied for the uniformity sake. As mentioned earlier, we included the $Ni^{II}P(P)_4$ compound for the completeness of the study. Thus, we have systematically investigated TM- P_4 -porphyrins, or P_4 -substituted TM-porphyrins, with the increasing number of d-electrons following the sequence of electronic configurations: $3d^14s^2$ (Sc) $\rightarrow$ $3d^24s^2$ (Ti) $\rightarrow$ $3d^64s^2$ (Fe) $\rightarrow$ $3d^84s^2$ (Ni) $\rightarrow$ $3d^{10}4s^1$ (Cu) $\rightarrow$ $3d^{10}4s^2$ (Zn). The $MP(P)_4$ B3LYP/6-31G* gas-phase calculated ground states (symmetry and spin states along with the energy differences between the ground state and the next lower-lying spin state, both without and with ZPE correction, kcal/mol) are provided in Table 1, and the Table 2 contains similar data for the MP species. For the complete spin states data, see supporting information, Tables S1, S2, and S4.

Let us first address the calculated energetics of the $MP(P)_4$ species. For neutral $Sc^{II}P(P)_4$, the doublet C_1 structure was found to be the global minimum, which was calculated to be essentially degenerated with the C_2 structure in the 2B spin state (see Table S1 in supporting information). The quadruplet spin states for the $Sc^{II}P(P)_4$ compound were calculated to be 22.1 (21.5) kcal/mol higher in energy (see Tables 1 and S1). For the neutral $Ti^{II}P(P)_4$ compound, we calculated the global minimum to be the C_2 structure in 3B spin state, with the essentially degenerated triplet C_1 structure (the energy differences between these two

structures is 0.03 (0.03) kcal/mol, see Table S1 in supporting information). The singlets in C_2 and C_1 symmetry are more than 8 kcal/mol higher, and the quintet spin is around 21 kcal/mol higher in energy (Table S1). For the neutral $Fe^{II}P(P)_4$ species the triplet state was calculated to be the lowest-lying one, with the C_2 and C_1 structures being energy-degenerate (Table S1). Both quintets and singlets were computed to be noticeably higher in energy (see Table S1). As for $Ni^{II}P(P)_4$, the singlet structures were calculated to be significantly lower in energy than triplets (by 24.7 (18.1) kcal/mol, Table 1) and quintets. For $Cu^{II}P(P)_4$, the C_2 doublet structure was calculated to be the lowest-lying in energy, with the C_1 doublet species being merely 0.04 (0.04) kcal/mol higher in energy (Table S1). The quadruplets were calculated to be more than 30 kcal/mol higher (Table 1). Finally, for the $Zn^{II}P(P)_4$ species the singlet structure in C_2 symmetry was computed to be the global-minimum structure, being about 17 kcal/mol lower in energy than the triplet structure (see Table S1).

For the cationic $MP(P)_4$ species, $M = Sc^{III}$, Ti^{IV} , and Fe^{III} , the structures were calculated to be energetically aligned as follows. (i) For $M = Sc^{III}$, the singlet C_1 structure was computed to be the global minimum, with the C_2 singlet located at 1.1 (0.9) kcal/mol higher (Table 1). The C_2 singlet was computed to possess one imaginary frequency, and optimization along this imaginary frequency brought to the C_1 global minimum structure. The triplet and quintet structures were computed to be significantly higher, by 20.8 (18.8) and 55.1 (81.4) kcal/mol, respectively (see Table S2). (ii) For $M = Ti^{IV}$, the triplet C_1 structure was calculated to be the global minimum, with the C_1 singlet being 4.3 (3.3) and the C_2 quintet structure being 28.0 (56.3) kcal/mol higher (see Table S2). (iii) And for $M = Fe^{III}$, the quadruplet structures were calculated to be the lowest-lying species, with the C_1 species being merely 0.1 (0.0) kcal/mol lower in energy. The doublets and sextets were calculated to be noticeably higher in energy, by about 12 and more than 30 kcal/mol, respectively (see Table S2).

Comparison between the $MP(P)_4$ and MP species with the same metal M (Tables 1 and 2) shows that the complete substitution of the pyrrole nitrogens by phosphorus atoms does not change the calculated

ground spin state of the compound and also generally does not change the ordering of spin states (compare Tables S1, S2 and S4 in supporting information). This situation is retained for both neutral and cationic species. However, the complete substitution of the pyrrole nitrogens by phosphorus atoms can affect the energy gaps between the ground state and the next lower-lying spin state, with the effect being less pronounced for the cationic species (Tables 1 and 2).

3.1.1.1. Effects of other density functionals and solvents on the ground spin states and energetics.

Table 3

Ground state (symmetry, spin) and energy gap between the ground state and the next spin state for the neutral $M^{II}P(P)_4$, $M = Sc, Ti, Fe, Ni, Cu, Zn$, and cationic $M^{III/IV}P(P)_4$ species, $M = Sc^{III}, Ti^{IV}, Fe^{III}$ (gas-phase, [B3LYP/6-31G*]/[PW91/6-31G*]/[PBE/6-31G*] levels of theory).

Ground state (symmetry, spin)/					
Energy gap between the ground state and the next spin state, ΔE_0 (ΔE)					
Sc	Ti	Fe	Ni	Cu	Zn
$M^{II}P(P)_4$					
$C_2, {}^2B/$	$C_2, {}^3B/$	$C_2, {}^3B/$	$C_2, {}^1A/$	$C_2, {}^2A/$	$C_2, {}^1A/$
22.1 (21.5)//	8.2 (8.5)//	16.6 (15.2)//	24.7 (18.1)//	32.7 (30.7)//	17.6 (16.9)//
18.4 (17.8)//	5.6 (5.4)//	16.7 (16.9)//	23.9 (22.7)//	33.3 (30.4)//	14.0 (13.4)//
18.4 (18.0)	5.4 (5.3)	16.6 (16.0)	25.2 (24.7)	33.2 (30.4)	14.0 (13.5)
$M^{III/IV}P(P)_4$					
$C_1, {}^1A/$	$C_1, {}^3A/$	$C_2, {}^4A/$	-	-	-
20.8 (18.8)//	4.3 (3.3)//	12.0 (12.4)//			
15.1 (14.5)//	3.1 (2.6)//	5.3 (5.1)//			
15.1 (14.5)	3.3 (2.7)	5.6 (5.5)			

The usage of other density functionals, exemplified here by the two GGA functionals, for the global minimum search, does not influence the ground spin state of both neutral and cationic $MP(P)_4$ compounds.

In addition, utilizing other DFT functionals does not affect significantly the energy gaps between the ground state and the next low-lying spin state, as can be seen from Table 3. It is worthwhile to notice that the PW91 and PBE functionals do not affect the energy gaps in systematic way, but generally have slightly more pronounced effects on the energy gaps between the ground state and the next low-lying spin state for $\text{Sc}^{\text{III}}\text{P}(\text{P})_4$ and $\text{Fe}^{\text{III}}\text{P}(\text{P})_4$ species.

We performed geometry optimizations with the implicit solvents for the $\text{MP}(\text{P})_4$ ground states and for the low-lying states within 10 kcal/mol from the ground states, except the $\text{NiP}(\text{P})_4$ case where we optimized both the singlet ground state and the high-lying triplet state with the implicit solvent effects included (see Tables S1 and S2 in supporting information). The effects of the implicit solvents can be summarized as follows. (i) All the three solvents used do not change noticeably the relative energies of $\text{MP}(\text{P})_4$ spin states or isomers (when the structures with the same spin state but with the C_2 and C_1 symmetries are considered, as in the cases of $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$, $\text{Ti}^{\text{II}}\text{P}(\text{P})_4$, $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$, $\text{Cu}^{\text{II}}\text{P}(\text{P})_4$, $\text{Sc}^{\text{III}}\text{P}(\text{P})_4$, and $\text{Fe}^{\text{III}}\text{P}(\text{P})_4$, see Tables S1 and S2). (ii) Using the implicit solvents can result in the structures with small imaginary frequencies, for example, the (C_2 , ^2B) $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ structures optimized with the implicit effects from water and acetonitrile (see Table S1). (iii) Generally, using C_6H_6 as an implicit solvent results in structures without imaginary frequencies and can even invert the isomers ordering, as in the case of $\text{Sc}^{\text{III}}\text{P}(\text{P})_4$. In this case, the optimizations performed within C_2 symmetry constraint both in the gas phase and with implicit H_2O and CH_3CN gave the structures possessing small imaginary frequencies but the optimization with the implicit effects from benzene resulted in the structure somewhat lower than the C_1 isomer (although the total effect regarding the energy difference between the isomers is still very small, less than 1 kcal/mol, see Table S2). Thus, it is safe to consider the gas-phase calculated neutral and cationic species in the following discussion.

3.1.2. Structural features of the $MP(P)_4$ compounds.

Figure 1. Calculated gas-phase structures (B3LYP/6-31G* level of theory) of the neutral $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ (C_1 , ^2A) (a), $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ (C_1 , ^3A) (b), $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$ (C_2 , ^1A) (c), and $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$ (C_2 , ^1A) (d) compounds, along with the labeling scheme (shown at the $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ structure) used throughout the manuscript (for the labeling scheme see also Figure S1).

Table 4

Gas-phase calculated (B3LYP/6-31G* level of theory) principal structural parameters

of the neutral $M^{II}P(P)_4$, $M = Sc, Ti, Fe, Ni, Cu, Zn$, and cationic $M^{III/IV}P(P)_4$ species, $M = Sc^{III}, Ti^{IV}, Fe^{III}$.

[illegible]

	14								
Fe ^{II} P(P) ₄	2.15,	1.78,	1.43,	1.37,	1.40,	141.79	93.01,	166.03,	9.74
(C ₂ , ³ B)	2.20	1.79	1.45	1.39	1.42		93.34	169.73	
Ni ^{II} P(P) ₄	2.12	1.78	1.44	1.38	1.41	146.47	92.94	174.13	4.15
(C ₂ , ¹ A)									
Cu ^{II} P(P) ₄	2.24	1.79	1.44	1.38	1.41	144.94	91.55	178.18	-1.29
(C ₂ , ² A)									
Zn ^{II} P(P) ₄	2.37	1.79	1.45	1.37	1.41	144.55	91.39	173.83	-4.36
(C ₂ , ¹ A)									
M ^{III/IV} P(P) ₄									
Sc ^{III} P(P) ₄	2.43,	1.77,	1.44,	1.38	1.40,	119.26	92.32,	105.18,	47.69
(C ₁ , ¹ A)	2.55,	1.79	1.45		1.41		95.00	136.25	
	2.56								
Ti ^{IV} P(P) ₄	2.35,	1.79	1.43	1.39	1.40,	122.03,	93.12,	124.53,	36.72
(C ₁ , ³ A)	2.36				1.41	122.04	93.34	126.02	
Fe ^{III} P(P) ₄	2.19	1.79	1.43	1.39	1.41	139.50,	92.80,	165.20,	10.38
(C ₂ , ⁴ A)						139.51	92.81	165.24	

Table 5

Gas-phase calculated (B3LYP/6-31G* level of theory) principal structural parameters

of the neutral M^{II}P, M = Sc, Ti, Fe, Ni, Cu, Zn, and cationic M^{III/IV}P species, M = Sc^{III}, Ti^{IV}, Fe^{III}.

Species	Bond length, Å, and angles, deg.								
	M-N	N-C _α	C _α -C _β	C _β -C _β	C _α -C _m	C _m -M-C _m '	C _α -N-C _α	N-M-N	N ₅ -N ₄ -N ₃ -M
Sc ^{II} P	2.10,	1.39	1.42,	1.36,	1.39,	167.69	107.49,	162.29,	10.309
(C ₂ , ² B)	2.11		1.45	1.39	1.42		107.53	165.27	
Sc ^{III} P	2.11	1.39	1.44	1.37	1.40	161.21	106.74	153.85,	18.18
(C ₂ , ¹ A)								153.86	
Ti ^{II} P	2.05,	1.38,	1.43,	1.36,	1.39,	180.0	106.98,	180.0	0.0
(D _{2h} , ³ B _{2g})	2.07	1.39	1.45	1.38	1.41		107.26		

Ti ^{IV} P (C ₁ , ³ A)	2.05	1.37, 1.40	1.43, 1.44	1.37	1.38, 1.42	179.92, 179.94	106.19	179.91	0.07
Fe ^{II} P (D _{4h} , ³ B _{1g})	1.99	1.38	1.44	1.36	1.38, 1.39	180.0	104.75, 105.14	180.0	0.0
Fe ^{III} P (D _{2h} , ⁴ B _{3g}) ^a	1.97	1.39	1.43	1.36	1.38	180.0	104.39	180.0	0.0
Ni ^{II} P (D _{2d} , ¹ A ₁)	1.94	1.38	1.44	1.36	1.38	167.50	104.53	180.0	0.0
Cu ^{II} P (D _{4h} , ² B _{1g})	2.01	1.38	1.44	1.36	1.39	180.0	105.61	180.0	0.0
Zn ^{II} P (D _{4h} , ¹ A _{1g})	2.04	1.37	1.45	1.36	1.40	180.0	106.57	180.0	0.0

^aEssentially, D_{4h} structure.

Now let us consider the structural features of the neutral and cationic MP(P)₄ compounds studied in more detail (see Table 4 and Figure 1). As can be seen, all the neutral and cationic MP(P)₄ species reported possess one general prominent structural feature: strong deformation of the whole MP(P)₄ unit which adopts a pronounced bowl-like shape, compared to generally planar or slightly distorted from planar shapes of the tetrapyrrole counterparts (compare Table 5, the values of the C_m-M-C_m' and X-P-X angles, and of the X₅-X₄-X₃-M (X = N or P) dihedral angles). This observation is in line with the results reported previously for mono-P-substituted phosphaporphyrins and their derivatives [25-35] where deviations from planarity were found as well. As the measure of this structural deformation, we use the M-P and P-C_α bond distances, the C_α-P-C_α and P-M-P angles, and the P₅-P₄-P₃-M dihedral angle (see Figure 1 and Figure S1 in supporting information for labeling). As was found earlier, in Ni^{II}P(P)₄ the Ni-P and P-C_α bond distances are longer than the Ni-N and N-C_α bond distances in the original Ni^{II}P by *ca.* 0.175 and 0.396 Å in the gas phase, respectively [41]. Interestingly, in all the neutral and cationic MP(P)₄ species studied here, the P-C_α bond distances are essentially the same, ranging from 1.77 to 1.80 Å (see Table 4).

This is also true for all other bond distances listed in Table 4. The only bond distance which changes significantly when going from Sc to Zn is the M-P bond distance: it acquires the largest values for the $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ compound, 2.53 Å, then decreases constantly to $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$ (2.12 Å), and next increases again to $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$ (2.37 Å). For more accurate characterization of the bowl-like $\text{MP}(\text{P})_4$ shape one should use the values of the P-M-P angles and the $\text{P}_5\text{-P}_4\text{-P}_3\text{-M}$ dihedral angles (see Table 4 and Figure 1). The latter characterize the shape of the ‘bowl bottom’. The ‘bowl bottom’ can either have a metal center protruding outwards, as in the case of Sc, Ti, Fe, and Ni, with the positive $\text{P}_5\text{-P}_4\text{-P}_3\text{-M}$ values decreasing from Sc (46.42°) to Ni (4.15°), or have a metal center protruding inwards the ‘bowl’, as in the case of Cu (-1.29°) and Zn (-4.36°). Interestingly, the cationic species have the structures very similar to their neutral counterparts (Table 4): thus, the differences of the $\text{P}_5\text{-P}_4\text{-P}_3\text{-M}$ dihedral angle values between the cationic $\text{MP}(\text{P})_4$ and its neutral counterpart are equal to 1.27° ($\text{Sc}^{\text{III}}\text{P}(\text{P})_4$), 3.75° ($\text{Ti}^{\text{IV}}\text{P}(\text{P})_4$), and 0.64° ($\text{Fe}^{\text{III}}\text{P}(\text{P})_4$). The general structural feature of the $\text{MP}(\text{P})_4$ species investigated can be explained by the smaller hybridization (larger *s*-character) of the P-atom valence orbitals and by the pyramidalization of the P-atom bonds. The changes in the M-P bond distances and in the $\text{P}_5\text{-P}_4\text{-P}_3\text{-M}$ dihedral angles are generally in line with changes of electronegativities of the transition metals under consideration (Sc: 1.36; Ti: 1.54; Fe: 1.83; Ni: 1.91; Cu: 1.90; Zn: 1.65) [67] and thus their polarization abilities, but not with their cationic radii, Å, 0.75 (Sc^{3+}), 0.61 (Ti^{4+}), 0.55 (Fe^{3+}), 0.69 (Ni^{2+}), 0.73 (Cu^{2+}), and 0.74 (Zn^{2+}) [67]. As mentioned above, the tetrapyrrole counterparts of the $\text{MP}(\text{P})_4$ species are essentially flat or not significantly distorted from planarity (see Table 5). We found that the $\text{Sc}^{\text{II}}\text{P}$ and $\text{Sc}^{\text{III}}\text{P}$ tetrapyrrole species possess slightly pronounced bowl-like shape, but this distortion is noticeably smaller than that of the neutral and cationic $\text{Sc}^{\text{II/III}}\text{P}(\text{P})_4$ species (compare Tables 4 and 5). The structural differences between the MP and $\text{MP}(\text{P})_4$ compounds can be summarized as follows. (i) The M-P bond distances are longer than the M-N bond distances by ca. 0.16 ($\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ vs. $\text{Fe}^{\text{II}}\text{P}$) - 0.45 ($\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ vs. $\text{Sc}^{\text{II}}\text{P}$ and $\text{Sc}^{\text{III}}\text{P}(\text{P})_4$ vs. $\text{Sc}^{\text{III}}\text{P}$) Å. (ii) The P-C_α bond distances are generally longer than the N-C_α bond distances by ca. 0.4 Å. (iii) The $\text{C}_\alpha\text{-P-C}_\alpha$ bond angles are generally

smaller than the C_α -N- C_α bond angles by ca. 10-15°. (iv) In the MP compounds the C_m -M- C_m' angles differ from 180° only in $Sc^{II}P$ and $Sc^{III}P$ and very insignificantly in $Ti^{II}P$ (see Table 5), whereas in *all* the $MP(P)_4$ counterparts these angles differ from 180° very strongly, by ca. 35 – 60° (see Table 4). (v) In the MP compounds the N-M-N angles differ from 180° only in $Sc^{II}P$ and $Sc^{III}P$ and very insignificantly in $Ti^{II}P$ (see Table 5), but in *all* the $MP(P)_4$ counterparts the P-M-P angles differ from 180°, the differences ranging from ca. 2° ($Cu^{II}P(P)_4$) up to ca. 75° ($Sc^{III}P(P)_4$), see Table 4. (vi) Finally, the P_5 - P_4 - P_3 -M dihedral angles vary broadly, from 47.69° ($Sc^{III}P(P)_4$) to -4.36° ($Cu^{II}P(P)_4$), whereas the N_5 - N_4 - N_3 -M dihedral angles are different from 0° only for $Sc^{II}P$, $Sc^{III}P$, and $Ti^{II}P$ (compare Tables 4 and 5). (vii) The C-C bond distances are generally not influenced by the N-replacement with P-atoms.

The effects of the implicit solvents on the $MP(P)_4$ species geometries were found to be insignificant and are not discussed in details here.

3.2. Electronic properties of the $MP(P)_4$ species.

Table 6

Gas-phase calculated NBO charges for the neutral $MP(P)_4$ species,

M = Sc, Ti, Fe, Ni, Cu, Zn, at the B3LYP/6-31G* level of theory.

Species	NBO charges, e					
	M	P	C_α	C_β	C_m	H
$Sc^{II}P(P)_4$	0.79	0.42,	-0.35,	-0.23	-0.18	0.24
(C_1 , 2A)		0.50	-0.39			
$Ti^{II}P(P)_4$	0.36	0.54	-0.37	-0.22	-0.16	0.23
(C_2 , 3B)						
$Fe^{II}P(P)_4$	0.20	0.55,	-0.37,	-0.22	-0.17	0.24
(C_1 , 3A)		0.62	-0.38			
$Ni^{II}P(P)_4$	-0.19	0.68	-0.38	-0.22	-0.17	0.24

(C ₂ , ¹ A)						
Cu ^{II} P(P) ₄	0.24	0.54	-0.37	-0.22	-0.17	0.24
(C ₁ , ² A)						
Zn ^{II} P(P) ₄	0.61	0.45	-0.35	-0.22	-0.17	0.24
(C ₂ , ¹ A)						

Table 7

Gas-phase calculated NBO charges for the neutral MP species,

M = Sc, Ti, Fe, Ni, Cu, Zn, at the B3LYP/6-31G* level of theory.

Species	NBO charges, e					
	M	N	C _α	C _β	C _m	H
Sc ^{II} P	1.81	-0.71,	0.15,	-0.24	-0.26	0.24
(C ₂ , ² B)		-0.73	0.16			
Ti ^{II} P	1.48	-0.68	0.16	-0.25	-0.25	0.24
(D _{2h} , ³ B _{2g})						
Fe ^{II} P	1.18	-0.60,	0.16	-0.24	-0.23	0.24
(D _{4h} , ³ B _{1g})		-0.62				
Ni ^{II} P	0.93	-0.56	0.16	-0.24	-0.23	0.24
(D _{2d} , ¹ A ₁)						
Cu ^{II} P	1.11	-0.61	0.16	-0.24	-0.23	0.24
(D _{4h} , ² B _{1g})						
Zn ^{II} P	1.28	-0.65	0.17	-0.25	-0.23	0.24
(D _{4h} , ¹ A _{1g})						

Table 6 summarizes the gas-phase calculated NBO charges for the neutral MP(P)₄ species. We used the NBO scheme because previously [68] we found this approach being more robust for the charge distribution analysis. The NBO charges on the central metal were calculated to have the highest positive

value, +0.79e, in the $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ species, then drop through $\text{Ti}^{\text{II}}\text{P}(\text{P})_4$ and $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ to the noticeable negative value, -0.19e, in $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$, and then again increase to significant positive value in $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$, +0.61e (Table 6). This is again generally in line with changes of electronegativities from Sc to Zn, 1.36 (Sc), 1.54 (Ti), 1.83 (Fe), 1.91 (Ni), 1.90 (Cu), and 1.65 (Zn) [67], and thus the TM polarization ability. The unusually small ionic radius of Ni^{2+} (0.69 Å) [67] leads to its unusually high polarization ability and thus very significant charge transfer from the phosphorus centers to Ni^{2+} . The significant positive charge, from +0.42e up to +0.68e, was calculated to accumulate on the P-atoms (see Table 6). The positive charge buildup on the P-atoms, opposite to the negative charge on nitrogens in the MP tetrapyrrole counterparts of the $\text{MP}(\text{P})_4$ species (compare Tables 6 and 7), can result in different reactivity patterns of the $\text{MP}(\text{P})_4$ compounds and their potential novel applications, for example, in catalysis. It is also worthwhile to notice the significant negative charges accumulated on the C_α -atoms in the $\text{MP}(\text{P})_4$ species compared to the positive charge in the MP species (see Tables 6 and 7), which is clearly explained by the lower P electronegativity (2.19) compared to C (2.55), whereas N electronegativity, 3.04, is significantly higher [67]. Also, positive charges on the metals in the $\text{MP}(\text{P})_4$ species are generally noticeably lower than charges on the metals in the MP counterparts, which is again explained by the nitrogen and phosphorus electronegativity differences.

Analysis of the computed $\text{MP}(\text{P})_4$ HOMO/LUMO and optical gaps and comparison with the calculated data for the MP species (see Table 8 and Tables S1 and S4 in supporting information) shows the following trends. (i) The TDB3LYP calculated (optical) gaps have the ‘W’-like profile: they drop quite sharply from the both ends of the transition metals range studied and then rise noticeably again with the highest value, 3.04 eV, for the singlet $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$ species. (ii) Similar pattern is observed for the HOMO/LUMO gaps, with the largest gap value for the triplet $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ compound. (iii) Generally, both the calculated HOMO/LUMO gaps and optical (TDB3LYP) gaps for the $\text{MP}(\text{P})_4$ species are noticeably smaller than the HOMO/LUMO gaps and optical gaps for their MP counterparts (see Table 8).

Table 8

Gas-phase calculated HOMO/LUMO gaps (eV) and optical gaps (eV) for the neutral MP(P)_4 and MP species, $\text{M} = \text{Sc, Ti, Fe, Ni, Cu, Zn}$, at the B3LYP/6-31G* level of theory.

$\Delta(\text{HOMO/LUMO})^a // \text{Optical gap}^b$					
Sc	Ti	Fe	Ni	Cu	Zn
$\text{M}^{\text{II}}\text{P(P)}_4$					
α : 1.45	α : 1.35	α : 2.59	2.57//	α : 1.38	1.97//
β : 1.97//	β : 1.95//	β : 1.74//	3.04	β : 2.67//	2.91
2.48	2.34	2.59		2.77	
$\text{M}^{\text{II}}\text{P}$					
α : 1.30	α : 1.32	α : 3.12	3.13//	α : 3.08	3.07//
β : 2.66//	β : 2.74//	β : 2.37//	3.52	β : 3.11//	3.55
2.85	3.08	3.45		3.52	

^aGaps, eV, given as HOMO-LUMO energy differences.

^bValues calculated using the TDB3LYP approach.

The drastic changes of the HOMO/LUMO gaps for the MP(P)_4 species (see Table 8) can be explained by the following factors. (i) *Slight* stabilization of the HOMO and *much stronger* stabilization of the LUMO, leading to the significant closure of the gap, as occurs for example in the case of $\text{Ni}^{\text{II}}\text{P(P)}_4$. (ii) *Slight* stabilization of the LUMO but *much stronger* stabilization of the HOMO, which results in the opening of the gap, as occurs for example in the case of the α -HOMO/LUMO of $\text{Sc}^{\text{II}}\text{P(P)}_4$ and α -HOMO/LUMO of $\text{Ti}^{\text{II}}\text{P(P)}_4$. (iii) *Slight destabilization* of the HOMO and significant *stabilization* of the LUMO, which causes the noticeable closure of the gap, as occurs for example in the case of the β -HOMO/LUMO of $\text{Sc}^{\text{II}}\text{P(P)}_4$ (see Tables S1 and S4 in supporting information).

The computed ionization potential values vary within the ca. 1.40 eV range for all the MP(P)_4

Figure 2. Calculated vertical and adiabatic IP values for the MP(P)₄ and MP species.

Figure 3. Calculated vertical and adiabatic EA values for the MP(P)₄ and MP species.

species studied, and the computed electron affinity values lie within even narrower range of ca. 0.55 eV (see Figures 2 and 3 and Table S3 in supporting information). The triplet $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ species shows both the highest $\text{IP}_v/\text{IP}_{\text{ad}}$ and $\text{EA}_v/\text{EA}_{\text{ad}}$ values which is in line with its highest HOMO/LUMO gap values. The singlet $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$ has the $\text{IP}_v/\text{IP}_{\text{ad}}$ values very close to those of $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ but possesses much lower $\text{EA}_v/\text{EA}_{\text{ad}}$ values. The calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values increase steadily from $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ through $\text{Ti}^{\text{II}}\text{P}(\text{P})_4$ to $\text{Fe}^{\text{II}}\text{P}(\text{P})_4$ then drop sharply through $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$ to $\text{Cu}^{\text{II}}\text{P}(\text{P})_4$ and increase again drastically for $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$ (Figure 2). Interestingly, for $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ and $\text{Ti}^{\text{II}}\text{P}(\text{P})_4$ the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values are higher than the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values for $\text{Sc}^{\text{II}}\text{P}$ and $\text{Ti}^{\text{II}}\text{P}$ but starting from $\text{Fe}^{\text{II}}\text{P}$ the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values are constantly higher for the MP species than for their $\text{MP}(\text{P})_4$ counterparts.

The calculated $\text{EA}_v/\text{EA}_{\text{ad}}$ values for the $\text{MP}(\text{P})_4$ species are noticeably higher than the same values for their MP counterparts (see Figure 3 and Tables S3 and S5 in supporting information), which can be explained by significant stabilization of the LUMOs of the $\text{MP}(\text{P})_4$ compounds compared to their MP counterparts (see Tables S1 and S4 in supporting information). Generally, the $\text{EA}_v/\text{EA}_{\text{ad}}$ values for the $\text{MP}(\text{P})_4$ species and for the MP species follow similar patterns: they increase from Sc to Fe (from Sc to Ti for the MP compounds) then drop quite noticeably from Fe to Ni (from Ti to Ni for MP) and next rise again from Ni to Zn (Figure 3).

The effects of the implicit solvents used in the calculations on the HOMO/LUMO gaps are not systematic and versatile: (i) for some $\text{MP}(\text{P})_4$ species, for example, $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$, all the three implicit solvent just slightly *stabilize* both the HOMO and LUMO resulting in actually unchanged or just slightly changed HOMO/LUMO gap; (ii) in other cases, for example, $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$, all the three implicit solvent just slightly *destabilize* both the HOMO and LUMO again resulting in actually unchanged or just slightly changed HOMO/LUMO gap; (iii) and all the three implicit solvent can also noticeably *stabilize* both the HOMO and LUMO but the net effect is again almost unchanged or just slightly changed HOMO/LUMO gap, as in the case of $\text{Cu}^{\text{II}}\text{P}(\text{P})_4$ (see Table S1 in supporting information). The net effect of the two GGA

functionals used, PW91 and PBE, can be summarized as significant destabilization of HOMOs and stabilization of LUMOs resulting in the very noticeable underestimation of the HOMO/LUMO gaps (see Table S6 in supporting information). It is generally well established that electronic structure calculations using the GGA or LDA functionals tend to severely underestimate HOMO/LUMO energy gaps (see, for example, Ref. 68).

Finally, we estimated the contributions of specific atoms (M, P/N, C+H) to the HOMO and LUMO of the MP(P)_4 and MP compounds. We performed calculations of projected densities of states (PDOS), and contributions of the specific atoms in % to the HOMO and LUMO of the MP(P)_4 and MP species are shown in Table 9.

Table 9

Contributions of the specific atoms in % to the HOMO and LUMO of the neutral MP(P)_4 and MP species, M = Sc, Ti, Fe, Ni, Cu, Zn, at the B3LYP/6-31G* level of theory.

Contributions of the specific atoms in % ^a						
M//P(N)//C+H						
Orbital	Sc	Ti	Fe	Ni	Cu	Zn
$\text{M}^{\text{II}}\text{P(P)}_4$						
HOMO	α : 14//0//78	α : 26//0//72	α : 14//33//52	21//31//48	α : 14//36//50	0//48//47
	β : 0//53//42	β : 0//51//45	β : 32//0//58		β : 0//0//98	
LUMO	α : 12//15//73	α : 25//0//69	α : 0//36//70	0//23//72	α : 0//20//78	0//16//82
	β : 12//0//79	β : 11//0//80	β : 16//0//78		β : 0//17//81	
$\text{M}^{\text{III/IV}}\text{P(P)}_4$						
HOMO	0//53//43	α : 0//50//47	α : 0//47//47	-	-	-
		β : 0//0//98	β : 0//36//57			
LUMO	16//0//78	α : 21//0//74	α : 0//22//76	-	-	-
		β : 0//48//49	β : 30//0//67			
$\text{M}^{\text{II}}\text{P}$						
HOMO	α : 13//0//81	α : 36//0//62	α : 0//0//100	0//0//100	α : 0//0//100	0//0//100

	β : 0//21//76	β : 0//23//76	β : 74//0//24		β : 0//0//100	
LUMO	α : 11//0//83	α : 17//0//78	α : 0//12//85	0//12//86	α : 0//12//88	0//12//88
	β : 11//0//82	β : 10//0//83	β : 0//0//83		β : 0//12//87	
$M^{III/IV}P$						
HOMO	0//0//100	α : 0//0//97	α : 0//0//100	-	-	-
		β : 0//0//95	β : 0//0//100			
LUMO	15//0//79	α : 34//0//64	α : 54//35//10	-	-	-
		β : 0//14//85	β : 105//0//0			

^aDifferences of the sums of atomic contributions from 100% are explained by small errors in calculations due to the program code.

From the data presented in Table 9 we can see both similarities and drastic differences between $MP(P)_4$ and their MP counterparts. They can be summarized as follows. (i) The LUMOs of the $M^{II}P(P)_4$ compounds in general have compositions qualitatively similar to the LUMOs of the $M^{II}P$ counterparts, except the cases of $Sc^{II}P$ and $Fe^{II}P$. (ii) The HOMOs of $Sc^{II}P(P)_4$ and $Ti^{II}P(P)_4$ have compositions similar to the HOMOs of their $M^{II}P$ counterparts. (iii) The HOMOs of $Fe^{II}P(P)_4$ (α -HOMO), $Ni^{II}P(P)_4$, $Cu^{II}P(P)_4$ (α -HOMO), and $Zn^{II}P(P)_4$ have significant contributions from the metal and phosphorus atoms compared to zero contributions of the metal and nitrogen atoms in the HOMOs of their $M^{II}P$ counterparts. (iv) There are noticeable composition differences for the HOMOs of the cationic $MP(P)_4$ species compared to their MP counterparts: significant contributions of the phosphorus atoms compared with zero contributions of the nitrogen atoms in the MP species. The LUMOs of $Sc^{III}P(P)_4$ and $Ti^{IV}P(P)_4$ have compositions qualitatively similar to the LUMOs of their $M^{II}P$ counterparts, and the $Fe^{III}P(P)_4$ LUMOs are very different in composition compared to the $Fe^{III}P$ species.

4. Conclusions and perspectives

We performed first systematic DFT (B3LYP/6-31G*) study of the structures and electronic features (frontier orbitals energies, HOMO/LUMO and optical gaps, IPs and EAs) of the TM- P_4 -porphyrins, or P_4 -

substituted TM-porphyrins, with increasing number of d-electrons following the sequence of electronic configurations $3d^1 4s^2$ (Sc) $\rightarrow 3d^2 4s^2$ (Ti) $\rightarrow 3d^6 4s^2$ (Fe) $\rightarrow 3d^8 4s^2$ (Ni) $\rightarrow 3d^{10} 4s^1$ (Cu) $\rightarrow 3d^{10} 4s^2$ (Zn). For Sc, Ti, and Fe, we studied both the neutral $MP(P)_4$ species with M in non-characteristic oxidation state +II and the cationic $MP(P)_4^{n+}$ species, where $n = 1$ for Sc^{III} , 2 for Ti^{IV} , and 1 for Fe^{III} . We also performed systematic comparison of the results obtained with the tetrapyrrole MP counterparts of the compounds studied. The principal findings of our research are summarized below as follows:

(i) Complete substitution of the pyrrole nitrogens by phosphorus atoms does not change the calculated ground spin state of the compound and does not change the ordering of spin states. This situation is retained for both neutral and cationic species. However, the complete substitution of the pyrrole nitrogens by phosphorus atoms can affect the energy gaps between the ground state and the next lower-lying spin state.

(ii) All the neutral and cationic $MP(P)_4$ species reported possess prominent deformation of the whole $MP(P)_4$ unit which adopts a pronounced bowl-like shape, compared to generally planar or slightly distorted from planar shapes of their tetrapyrrole counterparts. The only bond distance which changes significantly from Sc to Zn in the $MP(P)_4$ species is the M-P bond distance. The cationic species have the structures very similar to their neutral counterparts. The general structural features of the $MP(P)_4$ species can be explained by the smaller hybridization of the P-atom valence orbitals and by the pyramidalization of the P-atom bonds. The changes in the M-P bond distances and in the $P_5-P_4-P_3-M$ dihedral angles are in line with M electronegativity changes. The M-P bond distances are longer than the M-N bond distances by ca. 0.16 - 0.45 Å. The $P_5-P_4-P_3-M$ dihedral angles in the $MP(P)_4$ species vary broadly, from 47.69° to -4.36° , whereas the $N_5-N_4-N_3-M$ dihedral angles in the MP species differ from 0° only for $Sc^{II}P$, $Sc^{III}P$, and $Ti^{II}P$. The C-C bond distances are generally not influenced by the N-replacement with P-atoms. The effects of the implicit solvents on the $MP(P)_4$ species geometries were found to be insignificant.

(iii) The NBO charges on the central metal of $MP(P)_4$ were calculated to have the positive value,

+0.79e, in $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$, then drop to the noticeable negative value, -0.19e, in $\text{Ni}^{\text{II}}\text{P}(\text{P})_4$, and then again increase to the positive value in $\text{Zn}^{\text{II}}\text{P}(\text{P})_4$, +0.61e. This observation is generally in line with changes of electronegativities from Sc to Zn. The unusually small ionic radius of Ni^{2+} leads to its unusually high polarization ability. The significant positive charge, from +0.42e up to +0.68e, calculated to accumulate on the P-atoms, is opposite to the negative charge on nitrogens in the tetrapyrrole counterparts of the $\text{MP}(\text{P})_4$. Also, positive charges on the metals in the $\text{MP}(\text{P})_4$ species are generally noticeably lower than charges on the metals in the MP counterparts, which is explained by the nitrogen and phosphorus electronegativity differences.

(iv) Both the calculated HOMO/LUMO gaps and optical gaps for the $\text{MP}(\text{P})_4$ species are noticeably smaller than the HOMO/LUMO gaps and optical gaps for their MP counterparts. For $\text{Sc}^{\text{II}}\text{P}(\text{P})_4$ and $\text{Ti}^{\text{II}}\text{P}(\text{P})_4$ the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values are higher than the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values for $\text{Sc}^{\text{II}}\text{P}$ and $\text{Ti}^{\text{II}}\text{P}$ but starting from $\text{Fe}^{\text{II}}\text{P}$ the calculated $\text{IP}_v/\text{IP}_{\text{ad}}$ values are constantly higher for the MP species than for their $\text{MP}(\text{P})_4$ counterparts. The calculated $\text{EA}_v/\text{EA}_{\text{ad}}$ values for the $\text{MP}(\text{P})_4$ species are noticeably higher than the same values for their MP counterparts, which can be explained by significant stabilization of the LUMOs of the $\text{MP}(\text{P})_4$ compounds compared to their MP counterparts.

Based on these findings, we can raise the following questions, which are of high interest for the follow-up research:

- (i) How will different counterions affect structures and properties of cationic $\text{MP}(\text{P})_4$ species?
- (ii) How will annulation with different rings affect structures and electronic properties of $\text{MP}(\text{P})_4$ species?
- (iii) How strongly can $\text{MP}(\text{P})_4$ species interact with each other or with other molecules?

Some of these problems are currently under investigation and will be the subject of the follow-up reports. Also, the preliminary investigations showed that the $\text{MP}(\text{P})_4$ species are able to form stacks with the binding energies of several kcal/mol [69]. Other problems are planned to be investigated and the questions raised will be answered later.

Acknowledgments

The author first expresses his gratitude to the computational resources of Duke University and specifically of the research group of Professor David N. Beratan at Duke University. This work was partially supported by DOE grant ER 46430 and partially supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) grant “Estudo Teórico Computacional de Sistemas Nanoestruturados com Potencial Aplicação Tecnológica”, number 402313/2013-5, approved in the call N° 70/2013 Bolsa de Atração de Jovens Talentos - BJT - MEC/MCTI/CAPES/CNPq/FAPs / Linha 2 - Bolsa de Atração de Jovens Talentos – BJT. The computational resources of the centers Centro Nacional de Processamento de Alto Desempenho em São Paulo and Núcleo de Tecnologia da Informação are highly appreciated as well.

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