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# Design of Novel Classes of Building Blocks for Nanotechnology: Core-Modified Metalloporphyrins and Their Derivatives

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<http://dx.doi.org/10.5772/67728>

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## Abstract

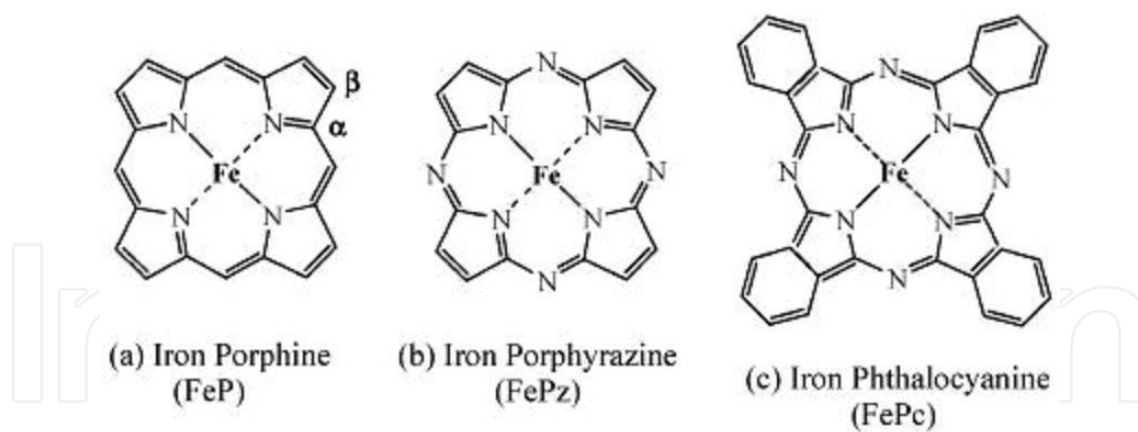
Metalloporphyrins and related macrocycles have been of great interest due to their role in biology and their numerous technological applications. Engineering of the porphyrins by replacing pyrrole nitrogens with other elements is a highly promising approach for tuning properties of porphyrins. To date, numerous efforts have been made to the modification of the porphyrin core with main-group elements, such as chalcogens (O, S, Se) and phosphorus. Thus, the modification of the porphyrin core by incorporation of heteroatoms instead of nitrogens is a very promising strategy for obtaining novel compounds with unusual optical, electrochemical and coordinating properties as well as reactivity. These novel compounds can be used as building blocks in various nanotechnological applications. Within the framework of this research, the following questions can be formulated: (i) what structures will core-modified porphyrins adopt? (ii) How will electronic properties of core-modified porphyrins differ from those of common tetrapyrroles? (iii) Will the core-modified porphyrins be able to form stacks and other arrays like regular porphyrins? (iv) Can core-modified porphyrins form complexes with fullerenes? (v) Can core-modified porphyrins activate small molecules, e.g. O<sub>2</sub> or N<sub>2</sub>? (vi) Will the core-modified porphyrins be able to form complexes with nanoparticles?

**Keywords:** metalloporphyrins, core modification, chalcogens, phosphorus, structural changes

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## 1. Introduction

Various (metallo)tetrapyrrole compounds, for example, porphyrins (P), porphyrazines (Pz) and phthalocyanines (Pc) (**Figure 1**), are representatives of the huge class of  $\pi$ -conjugated



**Figure 1.** Molecular structures of some tetrapyrrole macrocycles. Reprinted (adapted) with permission from Liao et al. [20]. Copyright 2005 American Chemical Society.

(aromatic) organic heterocycles [1–5]. They can be found as cofactors in numerous enzymes: as hemes in various cytochromes, catalases, peroxidases, etc.; as chlorophyll and pheophytin in photosynthetic proteins and as corrin and corphin in other proteins [1–3, 5]. The metalloporphyrins have numerous biological functions such as: (i)  $O_2$  transport and storage, (ii) oxidative metabolism, (iii) gas sensing, (iv) antibactericides/microbicides, (v) collection and transport of light energy, (vi) conversion of solar energy to chemical energy, (vii) electron transfer and (viii) NO scavenging and a significant number of other functions [1–3, 5–10]. Numerous technological applications of porphyrins include: catalysis [1, 2, 4, 11, 12], molecular photonic devices [4, 13, 14], medicine [1, 2, 4, 15], artificial photosynthesis [16, 17], sensitizers for dye-sensitized solar cells [18] and sensor devices [19].

The size, shape, electronic properties and binding ability of porphyrins can be broadly tuned by replacing one or more pyrrole nitrogens with other elements [21–24]. This type of the porphyrin core modification is a highly promising approach for tuning the various properties of porphyrin species. It brings to life the following questions:

(i) What structures will core-modified porphyrins adopt? (ii) How will atomic charges and other electronic properties (frontier orbital energies, HOMO/LUMO and optical gaps, ionization potentials, electron affinities, etc.) in core-modified porphyrins differ from regular tetrapyrroles? How can we tune these properties? (iii) What novel properties will core-modified porphyrins possess?

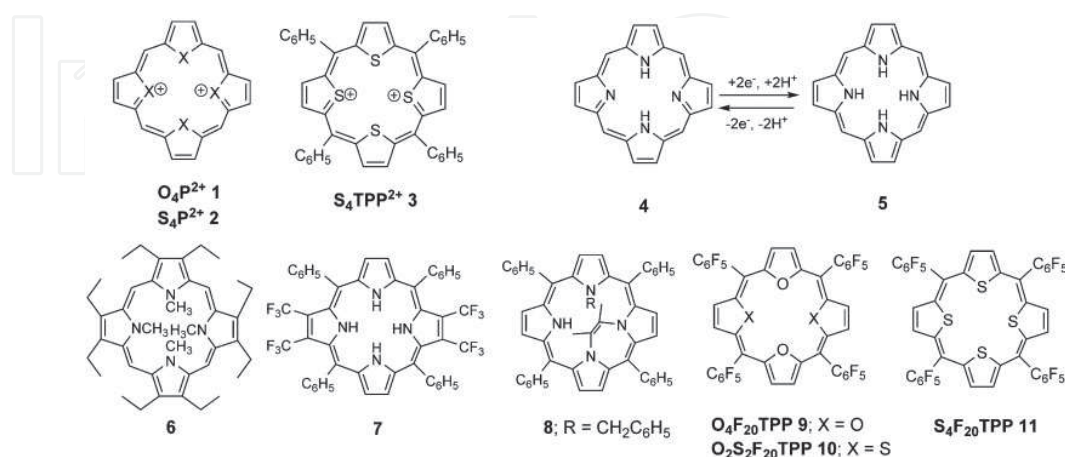
In recent years, there has been increasing interest in porphyrin core modification with the chalcogens (O, S, Se), which resulted in numerous experimental and computational works in this extremely promising area. Core modification of tetrapyrroles by P has been of long-lasting interest as well. Of course, it would not be possible to cover all the studies on core modification of porphyrins in this review. Thus, this chapter will cover the most significant and interesting works devoted to the core modification of porphyrins and derivatives with the principal focus on *completely core-modified* compounds. The important works on *partially core-modified* compounds will be considered as well.

## 2. Core modification with different main-group elements

### 2.1. Core modification with chalcogens

The first porphyrins *fully modified* by the chalcogens, the tetraoxaporphyrin dication **1** [26, 27] and tetrathiaporphyrin dication **2** [27], were reported by Vogel et al. in 1988 and 1989, respectively (**Figure 2**). The X-ray structure and  $^1\text{H}$  NMR and electronic absorption spectroscopy data for the compounds **1** and **2** were consistent with 18  $\pi$ -electron aromatic cycles [26]. However,  $\text{S}_4\text{P}^{2+}$  was found to exhibit low solubility and was shown to be unstable in common organic solvents. To resolve these issues, the octaethyltetrathiaporphyrin dication ( $\text{S}_4\text{OEP}^{2+}$ ) was subsequently prepared [28], but its spectroscopic studies and use in practical applications was found to be problematic. The UV/Vis spectrum of the perchlorate salt of **1** was found to have a sharp, high-intensity B (Soret) band and a series of Q bands in 96%  $\text{H}_2\text{SO}_4$ , whereas the UV/Vis spectrum of the perchlorate salt of the compound **2** showed strongly broadened and red-shifted bands. This difference was ascribed to the planarity of the compound **1** and distorted structure of **2** [27].

Also, research interest was focused on the core modification of the 20  $\pi$ -electron  $N,N'$ -dihydroporphyrins (isophlorins). The possible formation of an isophlorin was first noted during the total synthesis of chlorophyll by Woodward [29] who proposed the 18  $\pi$  porphyrin **4** – 20  $\pi$  isophlorin **5** redox system (**Figure 2**). The first synthesis of the isophlorin, 21,22,23,24-tetramethyloctaethylisophlorin **6** (**Figure 2**), was realized in 1991 [30]. Isophlorin **6** was found to have saddle shape with the *syn,anti,syn,anti*-conformation of the N-attached methyl groups in the solid state. Its UV/vis spectrum was shown to have a band at 356 nm with a shoulder at 516 nm. **Six** was reported to be readily oxidized into the dication and was found to be moderately stable upon exposure to air. Several relatively stable isophlorins were obtained by employing strong electron-withdrawing substituents. Thus, in 2007 Chen et al. reported the synthesis of  $\beta$ -tetrakis(trifluoromethyl)-meso-tetraphenyl-isophlorin **7** [31]. Isophlorins **6** and



**Figure 2.** Dications of tetraoxaporphyrin (**1**) and tetrathiaporphyrins (**2**, **3**), porphyrin (18 $\pi$ )–isophlorin (20 $\pi$ ) redox system (**4**, **5**) and isophlorine derivatives (**6**–**11**). Used with permission from Mishra et al. [25]. Copyright 2016 Wiley.

7 were *nonaromatic*. *Antiaromatic* almost planar isophlorin derivative 21,22-bridged-23-alkylporphyrin 8 was reported by Setsune et al. in 1999 [32]. In 2008, Anand and Reddy reported fully core-modified tetraoxa- and dithiadioxaisophlorines 9 and 10 [33], with planar structures and *antiaromatic* properties [33].

In 2012, Kon-no et al. reported the synthesis, structures, optical properties, and electronic structures of the *fully core-modified*  $18\pi$ -electron 5,10,15,20-tetraphenyl-21,22,23,24-tetrathiaporphyrin dication,  $S_4TPP^{2+}$  (6) and the  $20\pi$ -electron 5,10,15,20-tetrakis-(penta-fluorophenyl)-21,22,23,24-tetrathiaisophlorin,  $S_4F_{20}$ -TPP (7) [34]. The tetraaryl tetrathiaisophlorin was supposed to be *non-planar* owing to the larger size of the S-atom [34]. The X-ray analysis of the  $[S_4TPP^{2+}][B(C_6F_5)_4]_2$  and compound 7 showed the following: (i) The thiophene moieties located on the  $y$ -axis of  $[S_4TPP^{2+}][B(C_6F_5)_4]_2$  were tilted above and below the plane formed by the four *meso*-carbons so that the four S-atoms could be accommodated inside the central cavity, and the two thiophene rings on the  $x$ -axis were located within the  $x/y$  plane. Thus,  $S_4TPP^{2+}$  had a wave conformation. The structure of  $S_4TPP^{2+}$  inside  $[S_4TPP^{2+}][B(C_6F_5)_4]_2$  was considered as being very similar to that of the tetrathiaporphyrin dication  $S_4P^{2+}$  (2) [27]. (ii) In the structure of 7, two thiophene rings were shown to be tilted out of the plane of the four *meso*-carbons along one axis in a disordered manner with an occupancy factor of 0.50 above and below the plane, whilst the other two thiophene rings were found to be almost coplanar with the rest of the  $\pi$ -system (saddle conformation). The bond-alternation pattern for  $S_4F_{20}$  TPP was found to be consistent with that normally anticipated for an isophlorin. (iii) The B3LYP/6-31G(d) optimized geometries of  $S_4TPP^{2+}$  and  $S_4F_{20}$  TPP were shown to be very similar to their X-ray structures.

The results of time-dependent DFT and ZINDO/s calculations were compared to the observed magnetic circular dichroism (MCD) spectra and the electronic absorption spectra to study the effects of core modification on the electronic structures of  $S_4TPP^{2+}$  and  $S_4F_{20}$  TPP. For  $[S_4TPP^{2+}][ClO_4]_2$ , the MCD spectrum showed correspondence with the weaker bands at 948 and 733 nm in the near-IR region of the electronic absorption spectrum and a more intense band in the visible region at 491 nm. These bands were assigned as  $Q_{00}$ ,  $Q_{01}$  and  $B_{00}$  bands, respectively. In contrast to 21- and 21,23-core-modified porphyrinoids [35], a marked red-shift of the Q bands into the near-IR region was observed owing to a narrowing of the HOMO–LUMO gap. *Full core modification was shown to result in a marked destabilization of the HOMO*. The ring current calculations were carried out for model compounds  $S_4P^{2+}$  in  $C_s$  and  $D_{4h}$  symmetries and  $S_4P$  in  $C_{2v}$  symmetry. The optimized  $S_4P^{2+}$   $C_s$  structure was comparable to the B3LYP-optimized structure of  $S_4TPP^{2+}$  and the X-ray structure for  $[S_4TPP^{2+}][B(C_6F_5)_4]_2$ . The calculations for the  $S_4P^{2+}$   $C_s$  and  $S_4P^{2+}$   $D_{4h}$  model structures predicted the *aromatic* character of  $S_4P^{2+}$ . The current density map of the  $S_4P$  in  $C_{2v}$  symmetry showed *nonaromatic* character of the  $S_4P$  and, therefore,  $S_4F_{20}$  TPP,  $\pi$ -system. In general, current density map calculations for the model structures predicted the core modification and non-planarity of the macrocycles to modify patterns of the ring currents significantly. Nuclear independent chemical shift (NICS) values obtained for the structure of  $S_4TPP^{2+}$  (6) were consistent with a *diamagnetic* ring current and an *aromatic*  $\pi$ -system. The NICS values computed for the compound 7 were essentially nonaromatic. The greater stability of tetraaryl tetrathiaporphyrins, as stated by



the authors, makes these species potentially suitable for use as organic devices in practical applications.

Also in 2012, Rurack and coworkers reported the synthesis of novel *partially core-modified* and fused-ring-expanded tetraphenyldiphenanthroporphyrins [36], denoted as  $N_2O_2$ ,  $N_2S_2$ ,  $N_2Se_2$  and  $N_2Te_2$ . In these compounds, chalcogens replaced the pyrrole NH-groups along the *y*-axis. Peripheral-fused phenanthrene rings were substituted onto the pyrroles on the *x*-axis. Trends in the optical properties and electronic structures were explored and the suitability of these compounds for near IR region dye applications was studied. The terminology  $N_2Y_2$  ( $Y = O, S, Se, Te$ ) used in this publication referred to the four core atoms on the inner perimeter of the porphyrin  $\pi$ -system that can coordinate a central metal atom (**Figure 4**). Other notations used in the paper were as follows:  $P$  = porphyrin;  $TPP$  = 5,10,15,20-tetraphenylporphyrin;  $P_1$ ,  $P_1-Bz_y$ , and  $P_3$ ,  $P_3-Bz_y$  = core-modified diphenanthro- and diacenanthroporphyrins, respectively, with fused bicyclo[2.2.2]octadiene (BCOD) and benzene rings along the *y*-axis;  $TPTPhenPn$  = *meso*-tetraphenyltetraphenanthroporphyrin;  $TPhenP$  = tetraphenanthroporphyrin;  $2Phen_xN_4$  = non-core-modified tetraphenyldiphenanthroporphyrin. The partially chalcogen core-modified macrocycles have a potential to stabilize metals in unusual oxidation states. Thus, 5,10,15,20-tetraphenyl-21-oxaporphyrin was shown to stabilize Ni(I) [37], which was not possible for  $TPP$ , due to the presence of an  $N_3O$ , rather than an  $N_4$ , core. The effects of the heteroatoms on the electronic structures and optical properties of the porphyrinoids were examined using TD-DFT calculations and MCD and fluorescence measurements. MCD measurements were carried out on a series of compounds with *n*-hexadecyloxy groups attached at the *para*-positions of the phenyl substituents ( $N_2Y_2OC_{16}H_{33}$ ): these groups enhanced the solubility of the compounds in optically transparent solvents. To examine the extent to which the aryl substituents could be used to fine-tune the optical properties of core-modified porphyrins, electron-donating OMe- and  $N(CH_3)_2$ -groups (giving compounds denoted as  $N_2Se_2-OMe$  and  $N_2Se_2-NMe_2$ ) and electron-withdrawing F-atoms (giving compounds denoted as  $N_2O_2-F$  and  $N_2S_2-F$ ) were employed.

To compare the relative effects of the heavy atoms and core modification on the emission properties of the core-modified porphyrins, Cl, Br and I were used to generate the compounds denoted as  $N_2O_2-Cl$ ,  $N_2O_2-Br$  and  $N_2O_2-I$ . The effects of steric crowding and peripheral-fused-ring expansion were explored by synthesizing core-modified diphenanthro- ( $P_1$  and  $P_1-Bz_y$ ) and diacenanthroporphyrins ( $P_3$  and  $P_3-Bz_y$ ), with fused BCOD and benzene rings along the *y*-axis. The results of the research might be summarized as follows. (i) Steric hindrance between the *meso*-phenyl substituents and the peripheral-fused-ring moieties resulted in a significant saddling distortion of the  $\pi$ -systems. According to the results of computational studies, when the porphyrin cores were modified by introducing furan, thiophene, selenophene, or tellurophene moieties along the *y*-axis of the porphyrin core, the obtained core-modified porphyrin structures remained highly non-planar but the saddling distortion of the  $\pi$ -system steadily diminished as the heteroatoms became progressively larger on going from O to Te to form  $N_2O_2$ ,  $N_2S_2$ ,  $N_2Se_2$  and  $N_2Te_2$ . One of the selenophene or tellurophene moieties was found to tilt out of the saddled structure that was formed by the rest of the  $\pi$ -system, due to a marked increase in the

length of the C-Se and C-Te bonds. However, the twofold axis of symmetry was retained in the X-ray structure of  $N_2Se_2$  and also when the structure was optimized with the 3-21G\*\* rather than the 6-31G(d) basis sets. (ii) Upon core modification with chalcogens, a slight increase of the average HOMO–LUMO gap was predicted from O to S, with slight decrease from S to Se to Te, primarily based on a slight relative destabilization of the so-called *s* MOs (the MOs with nodal planes along the *y*-axis of the compound were referred to as ‘*a*’ and ‘-*a*’ MOs, whereas MOs with large coefficients were referred to as ‘*s*’ and ‘-*s*’ MOs [36]). The TD-DFT predicted average HOMO–LUMO gaps for the  $N_2Y_2$  compounds were found to vary from ca. 2.15 to ca. 2.4 eV [36]. Core modification was found to result in a red shift of the lowest-energy Q and B bands on moving from  $N_2O_2OC_{16}H_{33}$  to  $N_2Se_2OC_{16}H_{33}$  and then to  $N_2Te_2$ , as well as from  $N_2S_2OC_{16}H_{33}$  to  $N_2O_2OC_{16}H_{33}$ .  $N_2Te_2$  was found to be unstable to oxidation due to the destabilization of the HOMO and thus considered as not useful for optoelectronic or photodynamic applications. The absorption spectra of  $N_2O_2$  and  $N_2Te_2$  were shown to be markedly different from those of  $N_2S_2$  and  $N_2Se_2$  and the bands in the UV region were found to increase in intensity relative to the Q and B bands. This increase was explained by the effect of changes in the degree of saddling of the phenanthrene moieties and, where  $N_2Te_2$  is concerned, by the effect on the vibrational bands of tilting one of the tellurophene moieties out of the saddled  $C_{2v}$  symmetry structure. The  $Q_{00}$  bands of  $N_2O_2$ ,  $N_2S_2$ ,  $N_2Se_2$  and  $N_2Te_2$  were found to be relatively weak. (iii) Incorporation of electron donating  $-NMe_2$  groups at the *para*-positions of *meso*-attached benzene rings was shown to introduce a strong mesomeric interaction with the main porphyrin macrocycle which resulted in a significant intensification and red-shift of the Q bands. (iv) The diphenanthro- and diacenaphtho-fused  $N_2S_2$  compounds containing two benzo-fused thiophene moieties were shown to exhibit a narrowing of the HOMO–LUMO gap relative to TPP due to primarily a stabilization of the LUMO rather than a destabilization of the HOMO and enhanced absorption intensity in the NIR region. (v) The differing effects of incorporating benzene, phenanthrene and acenaphthalene fused ring moieties along the *x* and *y* axes were shown to substantially modify the relative energies of the four frontier  $\pi$ -MOs of the compounds studied. Some of the core-modified compounds studied were shown to be promising candidates for use in photodynamic therapy.

In 2016, Goto, Shinmyozu and coworkers reported the synthesis, optical and redox properties, and electronic structure of the completely core-modified tetrakis(pentafluorophenyl)tetrathiaisophlorin dioxide (**12**) [25]. After the synthesis of the fully core-modified 5,10,15,20-tetrakis(pentafluorophenyl)-21,22,23,24-tetrathiaisophlorin (**11**) (**Figure 2**) [25], the authors aimed to oxidize the S-atoms of the thiophene moieties of **11** to reveal its reactivity toward oxidation, compared to that of simple thiophene derivatives and to elucidate the structure and electronic properties of the oxidized products. Earlier, Bongini et al. reported that oxidation of thiophene to the corresponding 1-oxide led to only a minor change in the ionization potential, but to a dramatic change in electron affinity [38]. The product of oxidation of the compound **11** was found to be the 20  $\pi$ -electron tetrathiaisophlorin dioxide **12**, stable at room temperature. The thiophene moieties and S-atoms of the thiophene 1-oxide moieties of **12** were found to be tilted above and below the plane formed by the four *meso*-carbons. Cyclic voltammetry measurements indicated for **12** a significant stabilization of the HOMO, but the LUMO energy remained essentially unaltered. This corresponded to the significant blue shift of the  $\lambda_{\max}$  of the absorption band (348 nm), compared with that of the parent compound **11**. This result was also supported by MCD spectra and molecular orbital calculations (B3LYP/6-31G\* level).

The MCD spectrum of **12** was interpreted as that of a  $4n$   $\pi$ -antiaromatic system. Based on the computed NICS values and  $^1\text{H}$  NMR spectroscopy data, compound **12** was assigned more antiaromatic character than **11** (which was aromatic). This study demonstrated, for the first time, the following: (i) a tetrathiaporphyrin can be oxidized to the dioxide stable at room temperature; (ii) an attachment of O-atoms to the S-atoms of a tetrathiaporphyrin could modify its redox potentials and optical and electronic properties, along with its aromaticity properties.

Within this chapter, it is also of interest to mention the work of Sukumaran, Detty, and coworkers who in 2002 reported their studies of Te-containing 21- and 21,23-core-modified porphyrins [39]. Ono and coworkers who also studied the partial core modification of tetrabenzoporphyrins and tetraphenyltetrabenzoporphyrins with O and S observed only minor changes in the optical spectra of 21- and 21,23-core-modified tetrabenzoporphyrins [35].

Very recently, Anand and coworkers reported extremely interesting synthesis and characterization of the meso-meso linked antiaromatic tetraoxaisophlorin dimer [40]. It should be noted that antiaromatic units are seldom used as components of functional  $\pi$ -materials [41], although they can be employed in organic electronics due to their noticeable paramagnetic properties [42]. The chemistry of antiaromatic systems is severely hindered by the very small number of stable antiaromatic compounds. The  $4n\pi$  isophlorins offer a rare opportunity to explore novel antiaromatic organic materials for potential applications in optoelectronics. The 20  $\pi$ -electrons isophlorin derivatives of thiophene and furan represent the simplest of the stable and planar antiaromatic compounds. Isophlorin can non-covalently bind to  $\text{C}_{60}$  through conventional  $\pi$ - $\pi$  interactions, as was shown by the same research group in 2015, thus highlighting the utility of isophlorin as a synthon for supramolecular chemistry [43]. It was found that the compound **3** formed the co-crystallized product  $\mathbf{3}\cdot\text{C}_{60}$  along with the unexpected *meso-meso* linked dimer, **4**, bound non-covalently to  $\text{C}_{60}$ . The formation of the dimer was confirmed by MALDI TOF-TOF mass spectrometry and by  $^1\text{H}$  NMR spectroscopy. The compound **3** was found to exhibit a flat geometry (as observed for other tetraoxaisophlorins) with very close contacts (2.58 and 2.61 Å) between its  $\pi$ -surface and the surface of  $\text{C}_{60}$ . The macrocycles in the compound **4** were found to make an angle of  $35.57^\circ$ , which supported the single bond nature of the meso-meso link between these two macrocycles. The macrocycles in the compound **4** were found to bind the fullerene through uncommon short  $\pi$ - $\pi$  interactions (2.70, 2.78 and 2.93 Å) between their surface and the surface of the  $\text{C}_{60}$ . The antiaromatic character of **4** was further supported by NICS calculations. The estimated NICS values in the centre of the macrocycle, NICS(0), of +30.38 and +12.90 for **3** and **4**, respectively, showed *antiaromaticity* of these compounds. The reduced antiaromaticity of **4** was attributed to the loss of planar structure upon binding the fullerene  $\text{C}_{60}$  at the centre of the macrocycle. The electronic absorption spectrum of the dimer **4** in dichloromethane displayed a red shift with respect to the monomer **3**. An intense absorption similar to the Soret-like band at 372 nm, and Q-like bands at 436, 466 and 503 nm were considered as suggesting electronic coupling between the macrocyclic units in spite of the non-coplanar orientation of the both the macrocycles. The compound **4** was found to exhibit a strong resistivity towards oxidation as was observed for tetraoxaisophlorins by Reddy and Anand before [65]. Moreover, **4** was also found to resist the formation of  $\beta$ - $\beta$  links upon action of strong oxidants to yield the completely fused macrocyclic dimer.



Also, it is worthwhile to mention the following several works on *partially core-modified* porphyrins. The 2009 micro-review on aza-deficient porphyrins considered briefly, among other compounds, 21-heteroporphyrins containing O, S, Se, Te or P, and 21,23-ditellura-porphyrin, which possessed significant distortion due to the size of Te-atom [44]. The 2015 report by Maeda et al., considered the synthesis and photophysical properties of cyano and ethynyl-substituted carbazole-based chalcogen-porphyrins containing either two S- or the Se-atoms [45]. One year earlier, Maeda et al. reported the synthesis of carbazole-based hetero-core-modified (by S and Se) porphyrins [46]. In 2015, Zhang and coworkers reported the DFT study of the magnetically induced current strengths as well as NICS of aromatic heteroporphyrins and antiaromatic 22,24-dideazaheteroporphyrins [47]. Heteroporphyrins were shown to sustain a diatropic induced current while 22,24-dideazaheteroporphyrins revealed paratropic ring current. The substitution of pyrrole NH groups by O and S atoms was shown to not change the total induced current strengths and total NICS(0)<sub>πzz</sub> values.

## 2.2. Core modification with phosphorus

In this section, we will first address the studies on *partially core-modified* porphyrins and their derivatives reported by Matano et al. [53–62] for the series of *mono-phosphorus*-substituted porphyrins, calixphyrins and calixphospholes [48] and then will proceed to the *fully core-modified* porphyrins recently studied by Kuznetsov.

*Partial* core modification of tetrapyrroles by P has been of long-lasting interest [48]. The *mono-P-modified* Matano/Imahori structures showed interesting redox chemistry both in their coordination compounds with Pd, Pt, Rh, Zn, Au and Ni and as free ligands, along with the catalytic activity (see the discussion below). Therefore, more heavily P-modified metalloporphyrins should possess intriguing structural, electronic and optical properties. Stepwise syntheses of tri- and tetraphosphaporphyrinogens with numerous groups attached to the porphyrin core were reported by Carmichael et al. [48].

Now a few words should be said about the phosphole, C<sub>5</sub>H<sub>5</sub>P, as the phosphorus isologue of pyrrole, C<sub>5</sub>H<sub>5</sub>N. C<sub>5</sub>H<sub>5</sub>P has much lower aromaticity than pyrrole due to insufficient π-conjugation between the cis-dienic π-system and the lone electron pair of the P-atom [49, 50]. The phosphole species possesses the following prominent features affecting its structure, electronic properties and reactivities [50]: (1) the P-centre adopts a trigonal pyramidal geometry due to insufficient n-π orbital interaction; (2) the LUMO is located at a lower energy compared to the pyrrole LUMO due to the effective σ\*(P–R) – π\*(1,3-diene) hyperconjugation; (3) orbital energies of the C<sub>5</sub>H<sub>5</sub>P π-system are easily tunable by chemical modification at the P-centre and (4) the P-bridged 1,3-diene unit is rigid, electron rich and polarizable. These features of phospholes originate from the intrinsic nature of the P 3s and 3p orbitals. Consequently, phospholes behave both as potential building blocks for the π-conjugated materials and as ordinary phosphine ligands [51].

In 2003, Delaere and Nguyen [52] reported the DFT study of the structural and optical properties of the core-modified porphyrins with one or two pyrrole nitrogens replaced by P-atoms. The geometries of the ground states were optimized using the B3LYP/6-31G\* approach and energies of the lower-lying excited singlet states of P-modified porphyrins were computed using

the TD-B3LYP/SV(P) method and compared with those of N-porphyrins. The substitution of a NH- by a PH-unit did not distort the carbon skeleton which remains essentially planar, whereas replacement of a N- by a P-atom was found to weakly distort (by 15.3°) the P-containing 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.

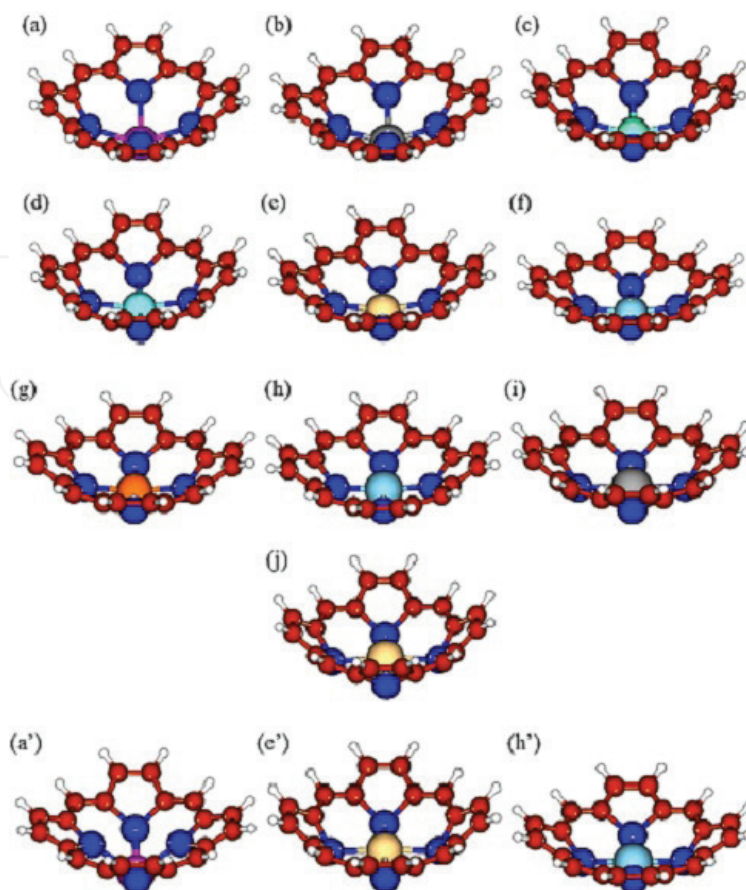
Later, Matano et al. [53–62] reported syntheses and characterization of various phosphaporphyrins and their derivatives with only one pyrrole nitrogen replaced by a P-atom. Thus, in their 2010 review [53], the researchers summarized their previous studies on the phosphole-containing porphyrins and their metal complexes. One of the compounds studied, the porphyrin containing trigonal pyramidal P-centre was found to possess a slightly distorted 18 $\pi$ -electron plane, wherein the phosphole and three pyrrole rings were found to be somewhat tilted from the 24-atom mean plane. It was suggested that the porphyrin 18 $\pi$ -electron circuit does not involve the lone electron pair of the trigonal pyramidal P-atom. On the contrary, the 22 $\pi$ -electron porphyrin containing tetrahedral P-centre was shown to have a highly-ruffled structure, with the P-atom deviated significantly from the porphyrin  $\pi$ -plane (1.20 Å) to avoid the steric congestion at the core. The Rh(III) and Pd(II) derivatives of these compounds were also shown to possess significant structural distortions. The metal complexes of these P-modified porphyrins exhibited only a weak antiaromaticity in terms of the magnetic criterion. In the UV/vis absorption spectra of the P-modified porphyrins, the characteristic two transitions of the porphyrin core, B and Q bands, were clearly observed, with significant red shifts. These results showed that the incorporation of a P-atom in the porphyrin core considerably reduced both the  $S_0$ – $S_2$  and  $S_0$ – $S_1$  excitation energies. The 18 $\pi$ -electron Rh-complex also showed characteristic Soret and Q bands, whereas the 20 $\pi$ -electron Pd-complex displayed broad and blue-shifted Soret-like bands and no detectable Q bands, which is typical of highly ruffled, nonaromatic 4n $\pi$  porphyrinoids. It was stated that the observed structures, reactivities, and coordinating properties of the studied P-core-modified porphyrins were undoubtedly produced by the P-atom at the core. In this context, the phosphole-containing porphyrins were regarded as metal-affinitive macrocyclic  $\pi$ -systems and could be developed as new classes of metal sensors, sensitizers and catalysts.

Earlier, in the 2009 review [54], Matano and Imahori described the exploration of the utility of phosphole-containing porphyrins and porphyrinogens as macrocyclic, mixed-donor ligands. The convenient methods for the synthesis of calixpyrroles, calixphyrins and porphyrins with P and either O or S substitutions (P,X,N<sub>2</sub>-hybrids) were described. Also, the effects of varying the combination of core heteroatoms (P, N, S and O) on the coordination properties of the hybrid macrocycles were investigated. The results were summarized to show that: (i) the P,S,N<sub>2</sub>-calixpyrroles behave as monophosphine ligands, (ii) the P,X,N<sub>2</sub>-calixphyrins behave as neutral, monoanionic or dianionic tetradentate ligands and (iii) the P,S,N<sub>2</sub>-porphyrins behave as a redox-active  $\pi$ -ligand for group 10 metals (Ni, Pd, Pt), affording a novel class of core-modified isophlorin complexes. The incorporation of the phosphole subunit into the macrocyclic framework was proved to provide unprecedented coordinating properties for the porphyrin family.

In 2008, the syntheses, structures and coordination chemistry of phosphole-containing hybrid calixphyrins ( $P,N_2,X$ -hybrid calixphyrins) and the catalytic activities of their transition metal complexes were reported [60]. The 5,10-porphodimethene type  $14\pi-P,(NH)_2,X$ - and  $16\pi-P,N_2,X$ -hybrid calixphyrins (where  $X = O, S, NH$ ) were prepared. The  $\sigma^3-P,(NH)_2,S$ - and  $\sigma^3-P,N_2,S$ -compounds were shown to produce the same  $Pd(II)-P,N_2,S$ -hybrid complex. In this complex, the calixphyrin ligand was regarded as a dianion. In the complexation with  $[RhCl(CO)_2]_2$  in  $CH_2Cl_2$ , the  $\sigma^3-P,N_2,S$ -compound was shown to behave as a neutral ligand producing an ionic  $Rh(I)-P,N_2,S$ -hybrid complex. The  $\sigma^3-P,N_2,NH$ -compound was found to behave as an anionic ligand to produce  $Rh(III)-P,N_3$ -hybrid complexes. The complexation of  $AuCl(SMe_2)$  with the  $\sigma^3-P,N_2,X$ -compounds ( $X = S, NH$ ) was shown to lead to the formation of the corresponding  $Au(I)$ -monophosphine complexes. The calixphyrin- $Pd$  and - $Rh$  complexes were shown to catalyse the Heck reaction and hydrosilylation reaction, respectively, implying that the metal centre in the core was capable of activating the substrates under appropriate reaction conditions. The study results demonstrated the potential utility of the phosphole-containing hybrid calixphyrins as a new class of macrocyclic  $P,N_2,X$ -mixed donor ligands for designing highly reactive transition metal complexes.

It is also worthwhile to mention the 2009 theoretical investigation of electronic structure and reactivity for oxidative addition for the  $Pd$ -complex of  $P,S$ -containing hybrid calixphyrin [62]. Two kinds of valence tautomers were shown for the  $Pd$ -complex **1**: (i) with the calixphyrin moiety having -2 charges and the  $Pd$ -centre with +2 oxidation state, (ii) with the calixphyrin neutral and the  $Pd$ -centre with 0 oxidation state. Complex **1** was shown to take the first form in the ground state. DFT computations clearly showed that the oxidative addition of phenyl bromide ( $PhBr$ ) to **1** occurred with moderate activation enthalpy, as experimentally proposed. On the other hand, the oxidative additions of  $PhBr$  to  $Pd$ -complexes of  $P,S$ -containing hybrid porphyrin **2** and of conventional porphyrin **3** needed much larger activation enthalpies. The differences in the reactivity among the complexes **1**, **2**, and **3** were theoretically investigated. In **1**, the valence tautomerization was shown to occur with moderate activation enthalpy to afford the form with  $Pd(0)$  which was reactive for the oxidative addition. In **2**, the tautomerization from the  $Pd(+2)$  form to the  $Pd(0)$  form needed very large activation enthalpy. In **3**, such valence tautomerization did not occur at all, indicating that the  $Pd(+2)$  must change to the  $Pd(+4)$  in the oxidative addition of  $PhBr$  to **3**, which is a very difficult process. These differences were interpreted in terms of the  $\pi^*$ -orbital energies of the compounds and the flexibility of their frameworks.

So far, as can be seen, no computational studies (metallo)porphyrins completely core-modified with  $P$ -atoms ( $P(P)_4$ ) have been reported, except the 2012 report by Barbee and Kuznetsov on the  $NiP(P)_4$  compound [63]. Motivated by the above-listed works on mono- $P$ -core-modified porphyrins and derivatives, Kuznetsov reported the computational studies of the structures and electronic properties of the fully  $P$ -core-modified metallocporphyrins,  $MP(P)_4$ ,  $M = Sc-Zn$  [64, 65], along with the computational design of the stacks formed by the  $ZnP(P)_4$  species [66]. The prominent structural feature of all the  $MP(P)_4$  compounds studied was found to be their significant distortion from planarity (**Figure 3**) [63–66].



**Figure 3.** Structures of the  $MP(P)_4$  species calculated at the B3LYP/6-31G\* level: neutrals:  $Sc^{II}P(P)_4$  (a),  $Ti^{II}P(P)_4$  (b),  $V^{II}P(P)_4$  (c),  $Cr^{II}P(P)_4$  (d),  $Mn^{II}P(P)_4$  (e),  $Fe^{II}P(P)_4$  (f),  $Co^{II}P(P)_4$  (g),  $Ni^{II}P(P)_4$  (h),  $Cu^{II}P(P)_4$  (i) and  $Zn^{II}P(P)_4$  (j), and cations:  $Sc^{III}P(P)_4$  (a'),  $Mn^{IV}P(P)_4$  (e'), and  $Ni^{III}P(P)_4$  (h'). Reprinted from Kuznetsov [65]. Copyright (2016), with permission from Elsevier.

In the 2015 work, the first *systematic* DFT study of the  $MP(P)_4$  compounds was performed [64]. The  $MP(P)_4$  species with increasing number of d-electrons were studied:  $3d^14s^2$  (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). Systematic comparison with the tetrapyrrole MP counterparts was made. As mentioned above, all the  $MP(P)_4$  species were calculated to adopt a bowl-like shape, compared to generally planar shapes of their MP counterparts. Significant positive charges were computed to be accumulated on P-atoms in  $MP(P)_4$ . Positive charges on the metals in  $MP(P)_4$  were found to be noticeably lower than in the MP counterparts. The calculated  $MP(P)_4$  HOMO-LUMO gaps and optical gaps were noticeably smaller than the corresponding gaps in their MP counterparts, which was explained by stabilization of the  $MP(P)_4$  LUMOs.

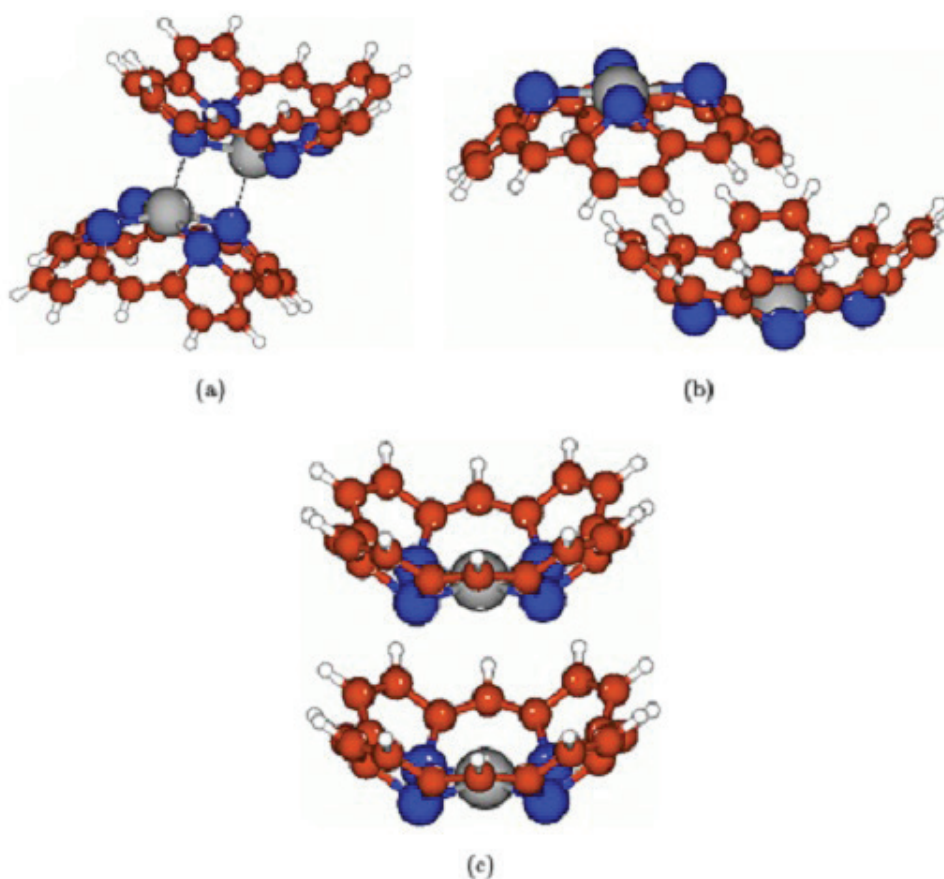
In the follow-up 2016 work [65], the comparative DFT study, including Natural Bond Orbitals analysis, of the binding energies between all the first-row transition metals  $M^{n+}$  ( $M = Sc-Zn$ ) and two ligands of the similar type, porphine,  $P^{2-}$ , and its completely P-modified counterpart,  $P(P)_4^{2-}$ , was reported. The main findings were as follows: (i) generally, for the  $MP(P)_4$  compounds the calculated HOMO-LUMO gaps and optical gaps were shown to be smaller than for their MP counterparts; (ii) the trends in the change of the binding energies between  $M^{n+}$



and  $\text{P(P)}_4^{2-}/\text{P}^{2-}$  were shown to be very similar for both ligands. The full P-modification of the porphyrin core was found to decrease the  $\text{M}^{n+}$ -ligand binding energies; however, the  $\text{MP(P)}_4$  compounds studied were shown to be stable according to the  $E_{\text{bind}}$  values and therefore can be potentially synthesized.

Also in 2016, due to motivation by the phenomenon of formation of stacks by regular metalloporphyrins, the computational check of the stack formation between the  $\text{MP(P)}_4$  species without any linkers or substituents was performed [66]. Three modes of binding or coordination were found to be possible between the monomeric  $\text{ZnP(P)}_4$  units (**Figure 4**).

The ‘convexity-to-convexity’ dimer I was found to be the most stable compound with the highest binding energy. In the dimer I, the strongly convex shape of both monomer units was demonstrated. The Zn–Zn distances in the dimer I, ca. 3.5 Å, were computed to be significantly shorter than in two other dimers. In the dimer I, significant decrease of the charge was found on the Zn-centres.



**Figure 4.** Structures of the  $[\text{ZnP(P)}_4]_2$  stacks, binding modes I (a), II (b), and III (c), calculated at the B3LYP/6-31G\* level of theory. Republished with permission of Journal of Theoretical and Computational Chemistry, Kuznetsov [66]; permission conveyed through Copyright Clearance Center, Inc.

### 3. Conclusions and perspectives

Thus, as can be seen from this micro-review, core modification of the porphyrins and their derivatives with other elements than N is a very promising and productive approach to modify and fine-tune their structures, electronic and coordination properties and reactivities. The research in this area has already been quite productive and brought for our attention numerous compounds with unusual novel structures and properties, which makes these species great candidates for different fields in chemistry and nanotechnology. Without any doubts, studies in this area will be continued and broadened. Based on the considered studies of porphyrin derivatives core-modified by other elements, we can summarize subareas (or research directions), which would be necessary to focus on to employ the core-modified porphyrins for the design of building blocks for nanotechnology:

- i. Ability of core-modified porphyrins to form stacks and other arrays like regular porphyrins. Would be core-modified porphyrins and their derivatives form stacks/arrays without any linkers or substituents?
- ii. Ability of core-modified porphyrins to form complexes with fullerenes, similar to regular porphyrins. How stable will be such complexes and what properties and potential applications they will have?
- iii. Catalytic properties of core-modified porphyrins. Can they activate, in particular, small molecules, like  $H_2$ ,  $O_2$ ,  $N_2$ , hydrocarbons?
- iv. Ability of core-modified porphyrins to form complexes with various nanoparticles, including semiconductor NPs. What properties and potential applications with these complexes have? How can we tune structures and properties of these complexes?
- v. Possibility to develop general synthetic strategies for obtaining the core-modified porphyrins with desired structures and properties. Development of approaches for synthesis of building nanoblocks from these compounds.
- vi. Broad and profound application of computational approaches in this area, both to assist the synthesis of novel core-modified porphyrins and to provide insight in their properties. Also, the computational approaches could be broadly used to assist in obtaining various building nanoblocks from these compounds.

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