chemistry proceedings

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Theoretical rationalization of chirality sensors on the basis of mono- and bis-porphyrins

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Abstract: In the present work, two mono-porphyrin and three bis-porphyrin zinc complexes were modelled using DFT and TD-DFT approaches in order to understand a role of various controlling factors being able to influence on circular dichroism (CD) spectra. The decisive value of the position of secondary chromophores in mono-porphyrins and the relative position of porphyrin subunits in bis-porphyrin complexes for induced circular dichroism is shown. The weak deformation of porphyrin plane, observed in this work, had only minor influence on CD spectra.

Keywords: TD-DFT; circular dichroism; porphyrin; supramolecular chemistry; host–guest binding

1. Introduction

Circular dichroism (CD) is an absorption spectroscopy method based on the differential absorption of left and right circularly polarized light [1,2]. However, for non silent CD spectra, investigated molecules should be chiral and have both electric and magnetic transition moments, since CD intensity (rotatory strength) is a scalar product of electric and magnetic transition moments (equation 1), in contrast to UV-Vis intensity (oscillator strength), where only electric transition moments are taken into account (equation 2) [3].

$$R = Im(\mu \cdot m) \tag{1}$$

$$f = \propto |\mu|^2 \tag{2}$$

where f is oscillator strength, R is rotary strength, μ – electric and m – magnetic transition moments, and Im refers to the imaginary part.

Porphyrins are a class of macrocyclic aromatic compounds consisting of four modified pyrrole subunits interconnected at α carbon atoms via methine bridges. Porphyrins have a specific electronic structure that results in unique optical properties and strong absorption around 400 nm (B band). In addition, in free-base porphyrins two protons could be substituted by one metal ion (such as Zn, Fe, Mn, etc.) forming four-coordinate metal complexes that are able to bind one or two axial ligands, depending on a metal ion. The combination of the above mentioned properties has led to the broad application of porphyrins in supramolecular chemistry and in the field of optical- and chemo-sensors [4,5].

In this work, B-bands of CD spectra will be rationalized using mono- and bis-porphyrin zinc complexes and TD-DFT approach. The influence of guest conformation and position of second chromophore on CD profile of mono- and bis-porphyrins will be shown. The synergies between axial ligation and peripheral replacement will be discussed. The reflection of porphyrin plane distortion in CD spectra will be considered. Finally, the critical importance of relative position of porphyrin subunits in

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Chem. Proc.* **2021**, 3, x. https://doi.org/10.3390/xxxxx

Published: date

bis-porphyrins will be shown.

2. Materials and Methods

In all of the molecules, except fully optimized, a part of molecule was fixed in a certain position and corresponding calculations were carried out in order to understand how the particular factor affects the CD spectrum. Dynamic factors were not considered.

The geometry optimization was performed using RI-BP86-D3/def2-SV(P) implemented in Turbomole 7.0 [6]. The CD spectra were simulated using Gaussian16 [7] software, TD-DFT method and ωB97X-D/cc-pVTZ level of theory. All CD spectra simulations were performed using the SMD continuum solvent model as it gives a better agreement with the experiment [8,9] and dichloromethane was chosen as one of the most popular solvents for CD spectroscopy of porphyrins. To ensure the B-band region of absorption spectrum is covered the first six excited states were calculated for mono-porphyrins and first ten – for bis-porphyrins. The rotatory strengths were calculated on the basis of the dipole velocity formalism. The CD spectra were visualized using GaussView 6.1 [10] and a bandwidth of 0.1 eV.

The geometries of the complexes, transition energies and rotatory strengths are provided in the Supplementary Materials.

3. Results and discussions

3.1. Mono-porphyrins

Porphyrins are chromophores that in addition to electric transition moments also have strong magnetic transition moments. In contrast, organic molecules are often chiral, but do not have magnetic transition moments. For this reason as sensors are usually used achiral metalloporphyrins with a silent CD spectrum. By axial coordination of a chiral guest with a porphyrin, a supramolecule is formed, where the chirality is determined by the chirality of the guest. In addition, this supramolecule also have a strong magnetic moment because of a porphyrin part.

The experimental study by Mizutani *et al.* showed that similar chiral guests bound by the same achiral porphyrin (host) give very similar absorption energies and differ by intensities of CD signal (**Figure 1, Table S1**) [11]. The authors concluded that the rotational strength correlates with a bonding free energy, and that conformational change effects the CD spectra. This agrees with conclusion by Osadchuk [9,12] that the same supramolecule discerned only by the conformation of a guest, give spectra of opposite signs and different shape.

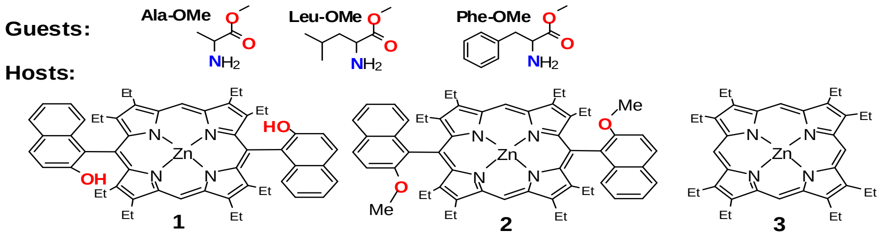
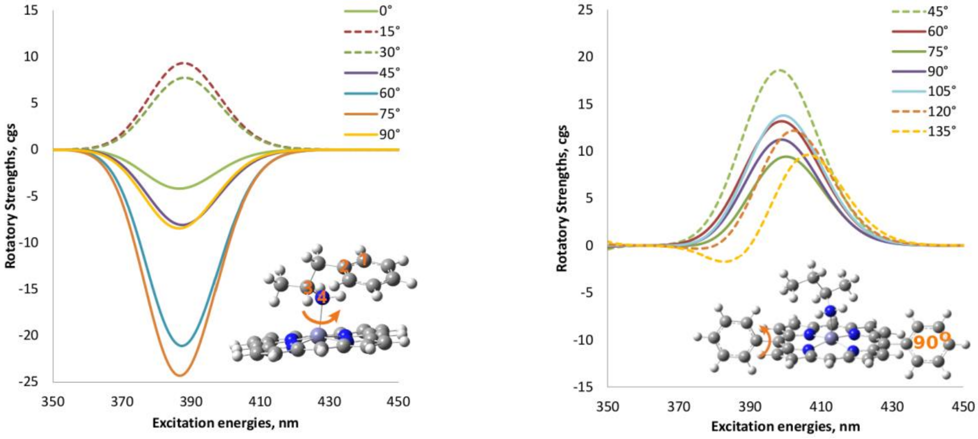


Figure 1. Host-guest systems studied by Mizutani *et al.* [11]

To prove that a change in the position of the second chromophore can determine the CD spectrum, calculations were performed, in which the position of the second chromophore was changed by varying the C_{host}-Zn-N_{guest}-C_{guest} dihedral angle form 0° to 90°. In order to ensure the same position of the second chromophore (phenyl) relative to the porphyrin plane, geometry optimization was done with the frozen C_1-C_2-C_3-N_4 dihedral angle. The results are shown in **Figure 2a.** Depending on the position of the guest's chromophore relative to the porphyrin plane, sign of a band can be positive or negative.

Thus, CD spectra are highly sensitive to conformers' geometry and population of a chiral guest.

Contrary, when the same organic molecule bound by varying hosts, the CD spectra differ significantly. This was shown in experimental work by Mizutani *et al.* [11] (**Table S1**) and theoretical work by Osadchuk *et at.* [9]. One of the reasons is different main conformations of a chiral guest, and as a result varying positions of guest's chromophore (**Figure 3**). However, two of three studied porphyrins have chromophoric peripheral substituents which can also influence CD septum. Mizutani *et al*. concluded that split of CD is caused by the hydrogen bonding interaction between host 1 and guests [11].



(**a**) (**b**)

Figure 2. Dependence of CD spectra on a position of (**a**) guest's chromophore; (**b**) porphyrin's chromophoric peripheral substituent.

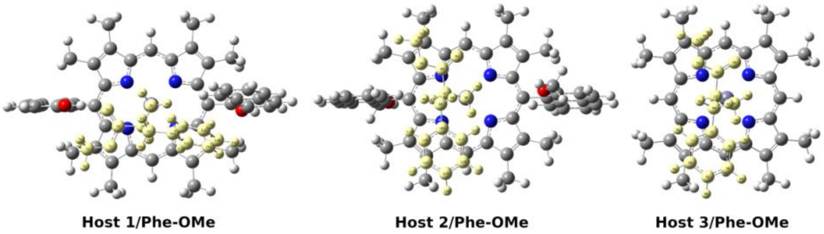
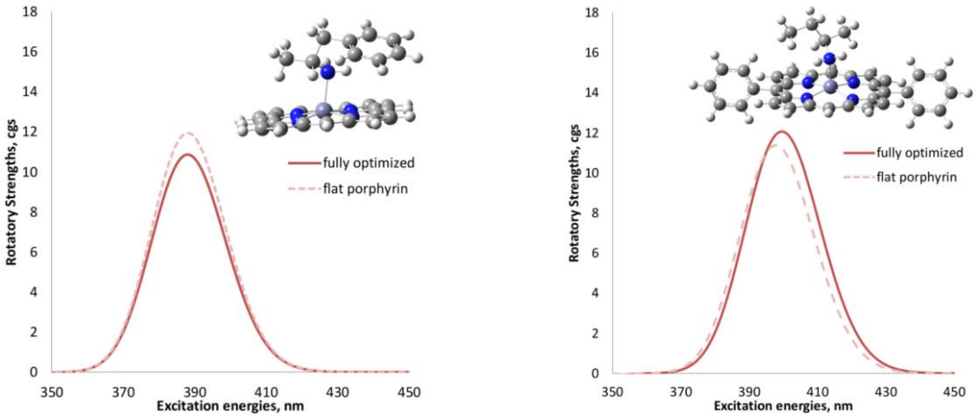


Figure 3. The main conformation of a supramolecules where guests are marked in yellow. (Geometries are taken from ref. 9).

To understand how significant a role of chromophoric peripheral substituents is, was modeled a supramolecule with two phenyl substituents in *meso*-position on porphyrin, and a chiral axial ligand was chosen so that it does not contain any chromophoric groups. In the studied supramolecule, one phenyl was fixed in perpendicular position respective to the porphyrin plane and position of other was altering in range from 45° to 135° (**Figure 2b**). The usual position of peripheral substituents is characterized by angle in the range of 60° - 120° [13,14], but in the present study the area was expanded to test extreme cases. The deviation of porphyrin's chromophoric peripheral substituent by 120° - 135° results in bisigned bands. This agrees with conclusion by Mizutani *et al*. [11] and previous theoretical studies of free-base porphyrins and non-ligated metalloporphyrins [15–17]. The deviation of porphyrin's chromophoric peripheral substituent from perpendicular position also causes a change in the energy and intensity of the bands.

It is well known that axial ligation, bulky peripheral substituents, non-covalent interactions can distort a porphyrin plane. Numerous works associate the distortion of porphyrin plane with the shift of transitions to the lower energy [18,19]. In ZnP/R-2-phenylisopropylamine, axial ligation caused only minor changes in the geometry of the porphyrin. Thus, C_{β}–C_{β}–$C_{\beta opp}$–$C_{\beta opp}$ dihedral angles were -0.5° and 0.5° and N–

C_α–C_α–N dihedral angles varied in the range of -2.4° – +1.5° (**Table S2**). In ZnDPP/R-2-aminobutane, the changes were larger and less symmetric. Thus, C_β–C_β–$C_{\beta opp}$–$C_{\beta opp}$ dihedral angles were -1.0° and 2.3° and N–C_α–C_α–N dihedral angles varied in the range of -2.5° – +3.1°. Corresponding spectra of fully optimized complexes as well as supramolecules where porphyrin plane was kept planar are given in **Figure 4**. In ZnP/R-2-phenylisopropylamine (**Figure 4a**), a change in the geometry of the porphyrin does not cause a shift in the absorption energy. The only difference between the spectra of the optimized structure and the supramolecule with planar porphyrin is the decrease in intensity. On the contrary, distortion of the porphyrin plane in ZnDPP/R-2-aminobutane (**Figure 4b**) shifts the CD band to the low energy region and slightly increases intensity of the band. This agrees with the conclusion by Graves *et al*. about a nonlinear dependence of the B-band shift on distortion of a porphyrin plane [20].



(**a**) (**b**)

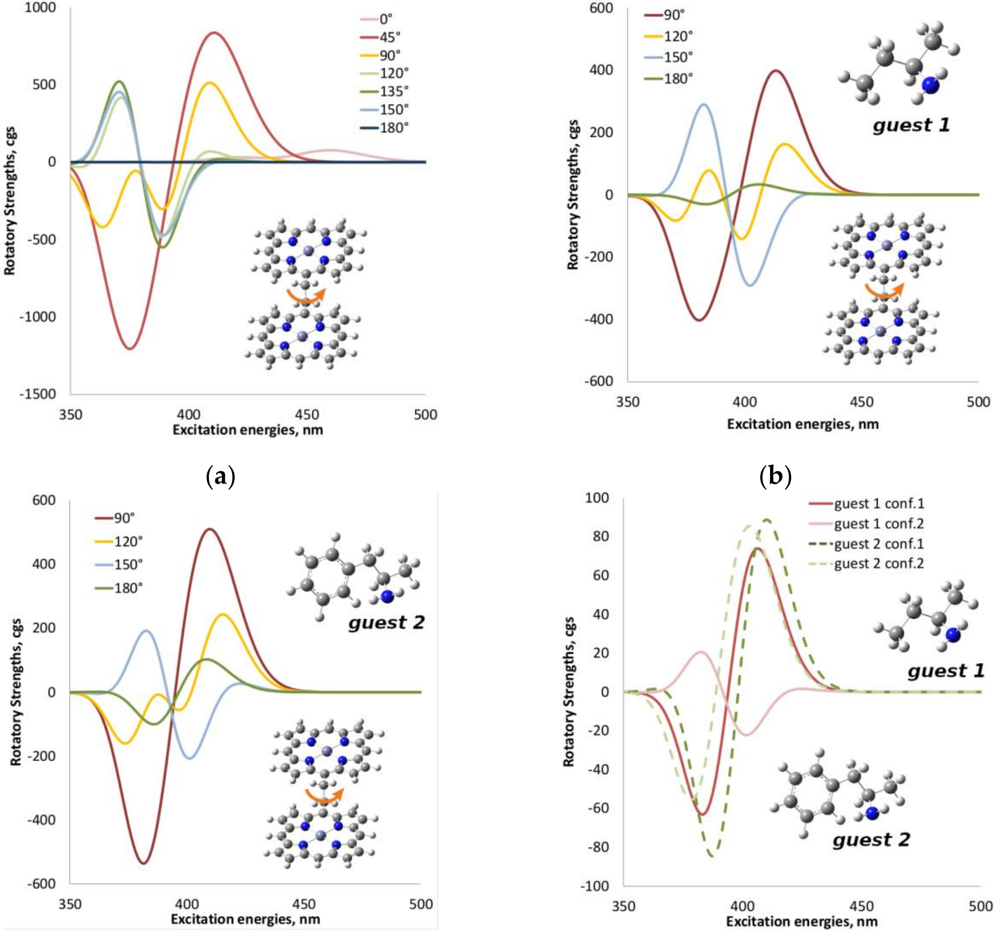
Figure 4. Dependence of CD spectra on a distortion of a porphyrin plane in (**a**) ZnP/R-2-phenylisopropylamine; (**b**) ZnDPP/R-2-aminobutane.

3.1. Bis-porphyrins

Bis-porphyrins are also capable to form supramolecular assemblies with different chiral guest molecules, and provide strong CD signal. This enables their broad application as sensors for the determination of absolute configuration of various chiral organic compounds [4,5]. However, the mechanism of formation of CD signals in bis- and mono-porphyrins is different due to the presence of the second porphyrin subunit. In bis-porphyrins, CD bands appear due to exciton coupling [21,22], when the molecule adopts a screw conformation either a clockwise or anticlockwise. Herein, the shape of the CD spectra changes depending on the position of the porphyrin subunits relative to each other. The **Figure 5a** shows that a change in the orientation of the of the porphyrin subunits already leads to the appearance of CD spectra even in the absence of a chiral ligand, since the molecule adopt directional helicity. The number of peaks and their sign vary with a change in the Zn-C-C-Zn dihedral angle, and spectra of conformations oriented clockwise and anticlockwise are mirror images of each other (**Figures S5a** and **S1**).

Coordination of a chiral guest forces bis-porphyrins to adopt a screw conformation, as consequence, a supramolecule gain a directional helicity and a non silent CD spectrum. Moreover, by binding of a chiral guest the bis-porphyrin becomes chiral that results in significantly change in the shape of the CD spectra (**Figures 5b, 5c, S1**). For example, bisign signal appears for anti-conformation (Zn-C-C-Zn dihedral angle is 180°), previously silent. The relative position of porphyrin subunits still plays an important role determining the shape of the spectra. This is in agreement with previous researches [21,23,24]. Herein, CD spectra with varying guests are similar by shapes and differ by intensities (**Figures 5a** and **5c**), that also agrees previous researches [25].

Figure 5d shows CD spectra of two fully optimized conformers of bis-ZnP with two guests (R-2-aminobutane and R-2-phenylisopropylamine). Depending on the conformation that the supramolecule adopts, the spectra can differ significantly. That can be explained by different position of porphyrin subunits determined by steric hindrance. Herein, the phenyl of the guest and its position seems to play a minor role.



(**a**) (**b**)

(**c**) (**d**)

Figure 5. Dependence of CD spectra on a position of porphyrin subunits in (**a**) bis-ZnP without axial ligands; (**b**) bis-ZnP/R-2-aminobutane; (**c**) bis-ZnP/R-2-phenylisopropylamine; (**d**) two fully optimized conformers of bis-ZnP/R-2-aminobutane and bis-ZnP/R-2-phenylisopropylamine.

5. Conclusions

In the present work, two mono-porphyrin and three bis-porhyrin zinc complexes were modeled and their CD spectra were simulated using TD-DFT approach in order to understand a role of various controlling factors being able to influence on circular dichroism (CD) spectra. Based on the performed calculations, it is concluded that in mono-porphyrins the position of secondary chromophores has the decisive value, since it determinates the sign of a band and is responsible for its splitting. In bis-porphyrins the relative position of porphyrin subunits determines the shape of the CD spectra; herein CD spectra of bis-porhyrin zinc complexes with varying guests are similar and differ only by intensities. In all studied cases axial ligation caused only minor deformation of a porphyrin plane, and its influence on CD spectra was insignificant.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Table S1: Excitation energies and rotatory strength of supramolecules, Table S2: Changes in the geometry of the porphyrin caused by axial ligation, Figure S1: Dependence of CD spectra on a position of porphyrin subunits in bis-ZnP, bis-ZnP/R-2-phenylisopropylamine and bis-ZnP/R-2-aminobutane, Table S3: Transition energies, oscillator strengths and rotational strengths, Cartesian coordinates.

Funding: This work was supported by the Estonian Research Council grant PUTJD749.

Data Availability Statement: Data presented in this study are available in the article and Supplementary Material.

Acknowledgments: Computations were performed on the HPC cluster at Tallinn University of Technology, which is part of the ETAIS project and partly on at Computational Chemistry laboratory at Tallinn University of Technology, Estonia. The author acknowledges prof. T. Tamm for his help.

Conflicts of Interest: The authors declare no conflict of interest.

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