

## Evaluating the dependence of electronic properties of dyes with environment using a PCM-based model for lipid monolayer

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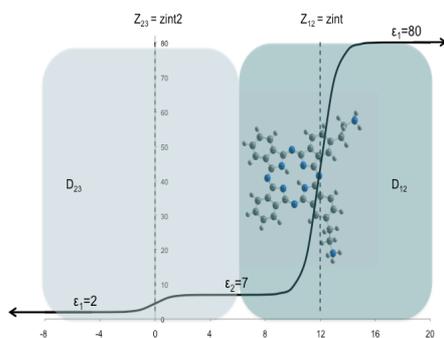
### INTRODUCTION

The interfacial region, as in a membrane, is a peculiar environment where many events occur, such as the absorption of ions and molecules by the cell, fundamental to the maintenance of the organism. In the case of photodynamic therapy (PDT), to understand how this environment affects the electronic absorption and emission of energy by macrocycles, as phthalocyanines (Ph) and porphyrins (Pc), is fundamental to increase the efficiency of the therapy itself.

Usually, the interaction of molecules with membranes is studied by Molecular Dynamics, but this method is computationally demanding and cannot provide electronic properties. As an alternative, this work used the Integral Equation Formalism Polarizable Continuum Model (IEFPCM) [1] to describe a lipid monolayer environment [2].

### METHODS

The lipid monolayer environment was included in TD-DFT/OLYP/6-31g(d) calculations by using a PCM description based on a position dependent dielectric permittivity function (Fig. 1). Free Ph, Pc and Ch (chlorine) and different substituted or complexed Ph and Pc were studied.



**Figure 1.** Position dependent dielectric permittivity used to represent a lipid monolayer. D's are the parameters that give the width of the first and second interfacial zones

### RESULTS AND DISCUSSION

In a previous work [4], the absorption spectrum for the free Ph obtained with PCM-lipid layer was compared to QM/MMPol and experimental data. Both theoretical approaches showed satisfactory results.

So, we have extended the methodology to substituted and complexed macrocycles and the shift induced by the dielectric difference along the z axis of the simulated lipid monolayer was analyzed. For the free Ph and substituted with 1 or 2 amines in cis position, the Q<sub>x</sub> band shift were about 3 nm and for Q<sub>y</sub> band, 6 nm. For the trans substitution, the Q<sub>x</sub> band shift was 25 nm and for Q<sub>y</sub> band, 10 nm; and for the substitution with 3 amines, both bands shift about 10 nm. Free Pc and Ch (chlorine) had 6 nm of shift on Q<sub>x</sub> and 5 nm on Q<sub>y</sub> band. Pc complexed with Al<sup>+3</sup> and Si<sup>+4</sup> with methyl as axial ligand, was shifted by 5 nm, while for the Zn-Pc insignificant effect was observed. The band for Si-Pc with chloride as axial ligand shifted 10 nm and with phenyl, 74 nm.

### CONCLUSIONS

The method here investigated was able to provide the shift in the absorption spectra of Pc, Ph and Ch in a dielectric gradient reproducing a lipid monolayer. In general the shift along the lipid monolayer z axis is not so significant and may not interfere in the PDT efficiency of the studied dyes, except for the Pc complexed with Si<sup>+4</sup> with phenyl as axial ligand.

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