Absorption Spectral Shift of Tetrasubstituted Phthalocyanine due to Dimerization

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INTRODUCTION

Research in PDT (photodynamic therapy) is very broad covering both theoretical and experimental investigations. Emphasis is placed on physical and chemical study of new lead compounds. Several phthalocyanines are approved for clinical such as the drug Photosens® employed for the treatment of skin and endobronchial lesions[1,2]. In this work we studied a tetrasubstituted phthalocyanine complexed with Zn^{+2} using DFT to investigate the changes in its spectra due to aggregation. We analyze the dimerization energy with respect to dimer sliding, stacking, and inter-rotation.

METHODS

The ZnPcOH (Fig. 1) geometry was obtained in the gas-phase by using the BLYP functional and def2SVP basis set along Grimme's D3 dispersion correction.

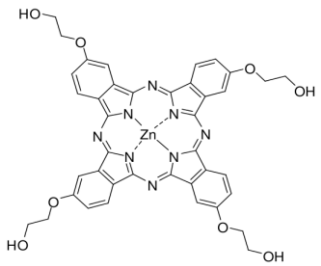


Figure 1. Phytalocyanine structure of ZnPcOH.

The potencial-energy scans (PES) for the rigid scans were produced by sliding, rotatating, and stacking the monomers in gas-phase. The aggregation energy ΔG_{Agg} was calculated using a thermodynamical given by equation 1 in DMSO using COSMO.

$$\Delta G_{Agg} = 2\Delta H_{gf} + \Delta G_{DMSO}(D) - 2\Delta G_{DMSO}(M) \quad (1)$$

The absorption spectra was obtained by means of TD-DFT at the equilibrium geometries of the dimers.

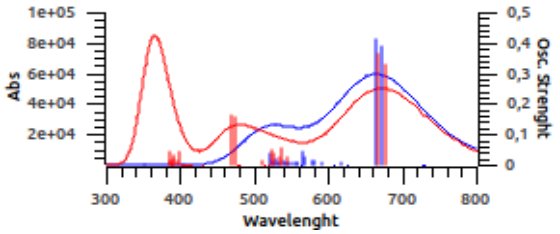
RESULTS AND DISCUSSION

Geometry optimization of monomers lead to planar structures. Table 1 displays the aggregation energy (ΔG_{Agg}) for the first proposed dimer.

$2\Delta H_{gf}$	$\Delta G_{DMSO}(D)$	$2\Delta G_{DMSO}(M)$	ΔG_{Agg}
-0,14766553	-0,05773955	-0,08171583	-0,04197342

Table 1. Aggregation energy for ZnPcOH optimized dimer (Δ in a.u.).

Figure 2. Spectral shift due to dimerization for



ZnPcOH. Red line is monomer absorption and blue is dimer absorption.

CONCLUSIONS

The results confirm the experimental evidence of dimerization due the interaction of the phthalocyanine rings. Solvating by DMSO destabilizes the dimer but not enough to dissociate it. Aggregation has a strong negative effect on the B band, making it non-absorptive, and reduces the Q band absorption. Therefore, dimerization strongly affects the absorption at the spectral region relevant to PDT for ZnPcOH.

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