



Aggregation behavior in unsymmetrically substituted metal-free phthalocyanines



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ABSTRACT

Phthalocyanines (Pcs) generally have a strong tendency for stacking in solution to form dimer and high order oligomers owing to the π - π , metal–ligand coordination, hydrogen bonding and donor–acceptor interactions between planar rings. Large substituents in peripheral positions, solvents and their amount and the central metal affect the aggregation to a remarkable extent. In Pcs, aggregation results in lowering the solubility, bringing purification and characterization problems and decreasing the photosensitizing efficiency. The aim of this study is to determine the predominant reasons inhibiting the aggregation in an unsymmetrically substituted metal-free Pc which contains three naphthoxy units and one carboxy-1,2-dioxyphenyl in THF. Dispersion-corrected density functional theory interaction energy calculations performed at B97-D/TZVP level revealed that aggregation in these complexes are prevented due to the strong solvent–phthalocyanine interactions rather than the existence of large substituents.

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1. Introduction

Phthalocyanine (Pc) derivatives and their analogues are well-known macrocyclic compounds that have very stable physical and chemical properties. In recent years, they have become a subject of increasing research interest due to their possible usage in many fields such as industrial dyes, liquid crystals, optoelectronic devices, gas sensors, catalytic materials, non-linear optics, Langmuir–Blodgett films and nanotechnology [1–8]. One of the most influential application area is the Photodynamic Therapy (PDT) which is a medical treatment that utilizes a photosensitizing molecule [9]. Pcs are effective photosensitizers (PSs) in PDT because of their intense absorption in red region of the visible light.

PDT is an alternative cancer treatment modality that uses the photochemical interaction of three components: light at a specific wavelength (visible or near infrared); drug, called a PS or photosensitizing agent and molecular oxygen at ambient levels. The PS usually binds to unhealthy cells non-specifically and then it is activated by the light that emanates from a laser or other light sources. The excited PS molecule reacts with an oxygen molecule and singlet oxygen is produced. Since the singlet oxygen is a strong oxidant, which is cytotoxic in action, it causes death to the tumor cells [10,11].

PSs can be separated into three generations. The first one absorbs the light at a relatively low wavelength ($\lambda_{\max} \sim 630$ nm) where the light penetration depth in tissue is shallow. The second one absorbs the light at longer wavelengths ($\lambda_{\max} \sim 700$ nm). The last one involves a combination of a second generation PS and a small biomolecule (nucleoside, lipid, peptide, etc.) to improve the selectivity. Due to its peculiar features, the third generation is the most promising novel PS generation. In the last few years, diverse research groups have synthesized a variety of new Pc derivatives belonging to the third generation [12–14].

When choosing a novel PS, its aggregation and photochemical and photophysical properties must be carefully considered. Aggregation is usually a problem for photosensitizing applications of Pc and Pc-like compounds. Pcs form aggregates (dimer and high order oligomers) both in solution and in solid state due to π - π stacking, hydrogen bonding, ligand–metal coordination and donor–acceptor interactions [15,16]. The formation of aggregates decreases solubility and causes problems during purification and characterization. Besides, aggregates reduce the singlet oxygen quantum yield and shorten the triplet-state lifetime [17]. That is, aggregation seriously compromises the effectiveness of PDT. The best approach to suppress the formation of aggregation is the introduction of either long alkyl chains or large substituents to the periphery of the macrocycle. Solvent types and their concentration and the central metal species have also a great influence on the aggregation behavior of the dye [18].

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Theoretical studies on Pcs and their analogues have become widespread in recent years since they supply a quantitative and fundamental strategy helping to elucidate the experimental findings. The electronic structure and optical properties of unsubstituted and substituted Pcs containing different central metal atoms (Zn, Mg, Ni, etc.) have been studied by several research groups [19–23]. In addition to these works including only Pc monomers, it is also possible to see a few studies focusing on the metallated Pc dimers. For example, Ueno et al. [24] investigated the dimer and trimer structures of unsubstituted ZnPc employing

ab initio and DFT methods and they found that stacking in ZnPc is a favorable process. Marom et al. [25] calculated the binding energy curves, geometry, and electronic structure of NiPc and MgPc dimers and they showed the importance of dispersion interactions in Pc dimers. Geometry optimization and time dependent density functional theory (TD-DFT) calculations were carried out by Mack et al. [26] for unsubstituted and substituted naphthalene-ring-bridged coplanar dimers and their parent Pc monomer complexes using the B3LYP functional. In a very recent study [27], aggregation properties of zinc phthalocyanines substituted

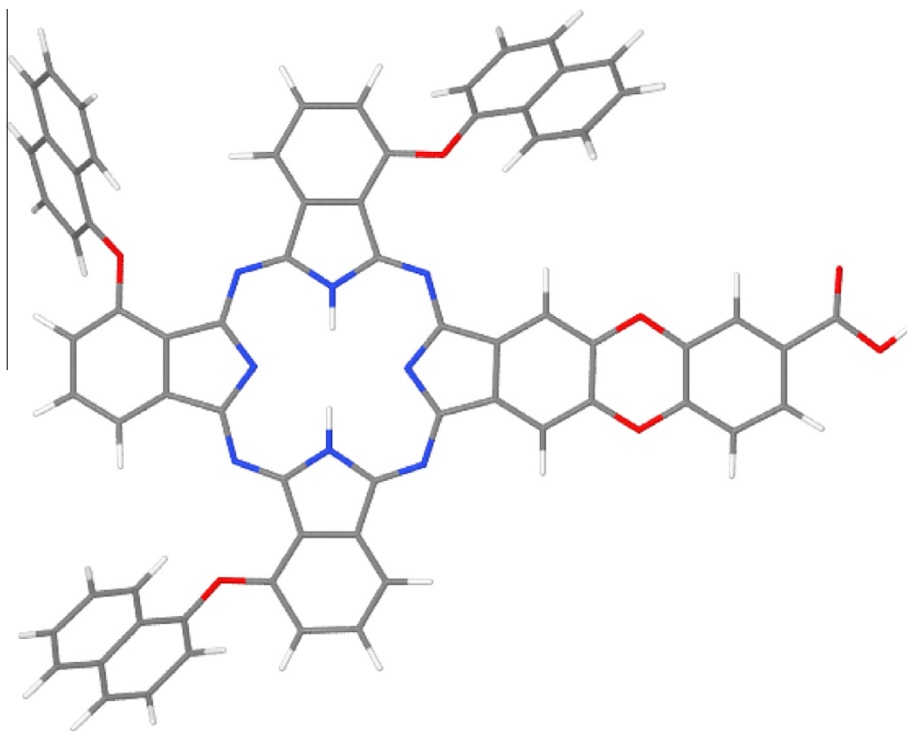


Fig. 1. H₂Pc monomer.

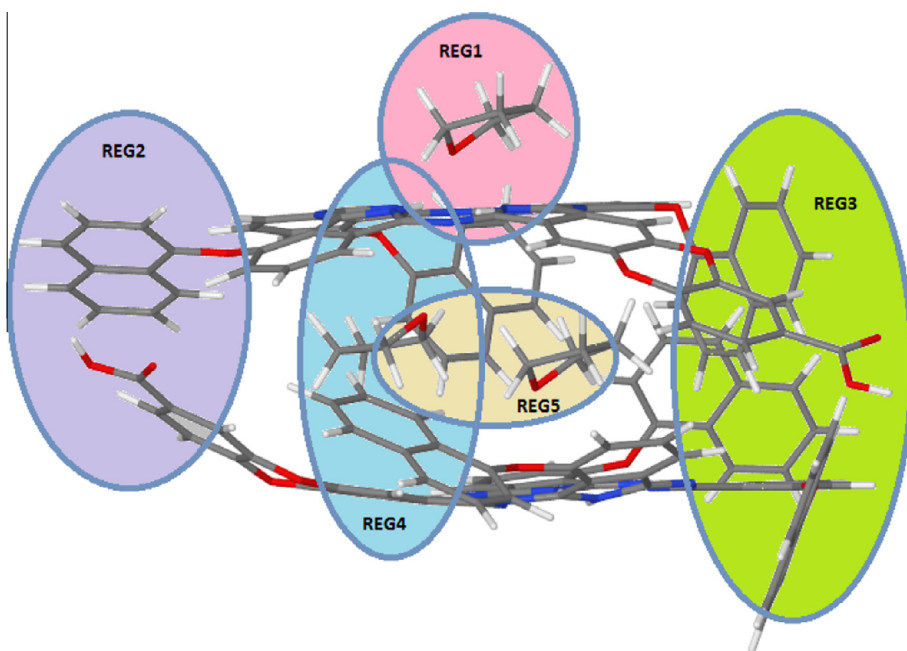


Fig. 2. Interaction regions in H₂Pc dimer including THF.

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