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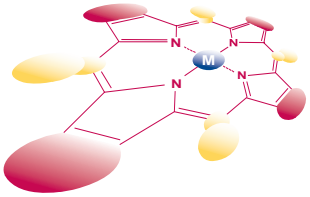

Influence of cyclodextrins on the fluorescence, photostability and singlet oxygen quantum yields of zinc phthalocyanine and naphthalocyanine complexes

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ABSTRACT: The effects of formation of cyclodextrin inclusion complexes on the photochemical and photophysical properties of zinc phthalocyanine (ZnPc) and various peripherally substituted zinc phthalocyanines as well as zinc naphthalocyanine (ZnNPc) are investigated. The cyclodextrins employed were the hydroxypropyl-γ-cyclodextrin and unsubstituted β-cyclodextrin. Job's plots were employed to confirm the stoichiometry of the inclusion complexes and showed 2:1 and 4:1 (cyclodextrin:phthalocyanine) inclusion behavior. The phthalocyanine inclusion complexes showed larger singlet oxygen quantum yield (ϕ_Δ) values when compared to the free phthalocyanines before inclusion, for complexes **1** (zinc naphthalocyanine), **2** (zinc tetranitrophthalocyanine) and **4** (zinc tetra-*tert*-butylphenoxyphthalocyanine). The fluorescence quantum yields generally remained unchanged following inclusion.

KEYWORDS: zinc phthalocyanine, cyclodextrin, singlet oxygen, photobleaching, fluorescence.

INTRODUCTION

Cyclodextrins (CDs) are naturally occurring cyclic oligosaccharides composed of six, seven and eight D-glucopyranose residues, called α-CD, β-CD and γ-CD. CDs are soluble to a varying extent in water and have a relatively hydrophobic cavity in the centre. Many different types of organic compounds can be incorporated into the cavities to form inclusion complexes. Inclusion complexes between porphyrin derivatives and CDs have been reported [1-8]. Due to the large nature of the porphyrin molecule, it has been observed that only parts of the molecule are included within the CD cavity. The formation of inclusion complexes of CDs with porphyrins changes the photochemical and photophysical properties of the latter. 1:1 and 2:1 CD:porphyrin inclusion complexes are known [1, 5, 8] in aqueous and non-aqueous solvents (such as dimethylsufoxide, DMSO).

Porphyrins and the structurally related phthalocyanines have been used successfully as photosensitizers for photodynamic therapy (PDT). Inclusion of these complexes into CDs is useful for PDT, since CDs may solubilize the otherwise insoluble photosensitizers. Phthalocyanines are generally less soluble than porphyrins. Much less attention has been given to the inclusion of phthalocyanines into CD compared to porphyrins. This work reports on the effects of cyclodextrins on some photophysical and photochemical properties of different peripherally substituted zinc phthalocyanine complexes. ZnPc complexes that are peripherally substituted with hydrophobic substituents were previously found to bind to CD, forming water soluble complexes [9]. ZnPc complexes have good photosensitizing properties for photodynamic therapy [10-12]. Many ZnPc complexes form aggregates in solution. Zinc tetracarboxyphthalocyanine complexes, in

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