



Spectroscopic and physicochemical behavior of magnesium phthalocyanine derivatives mono-substituted with a carboxylic acid group

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ABSTRACT

This work reports on the synthesis of novel unsymmetrically substituted magnesium phthalocyanine complexes containing one carboxyl group. The physicochemical behavior of these complexes were compared with those of their unmetallated and zinc counterparts. The MgPcs showed interesting absorption spectra with [8,15,22-Tris-(naphtho)-4,5-(3-carboxy-1,2-dioxyphenyl)phthalocyaninato]magnesium (II) showing a large split in the Q band whereas [8,15,22-Tris-(naphtho)-2-(carboxy) phthalocyaninato]magnesium(II) presented only a small splitting. The magnesium phthalocyanine derivatives displayed higher fluorescence quantum yields compared to unmetallated and zinc phthalocyanine counterparts. The latter gave admirable triplet and singlet oxygen quantum yields. These molecules can distinctly be employed in the field of photodynamic therapy in combination with fluorescence imaging.

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1. Introduction

Research associated with phthalocyanines (Pcs) has spanned across various disciplines including sensing [1,2], non-linear optics [3] and photovoltaic energy conversion [4]. Of particular interest in recent times, is their use as photosensitizers in medicine, specifically, the treatment of cancers with light in photodynamic therapy (PDT) [5]. PDT is a cancer treatment that necessitates the activation of a photosensitizer in cancer cells, with the appropriate wavelength of light [6,7]. It is the activation of the photosensitizer by light that elicits the toxic action. The non-invasive nature and lack of severe side effects of PDT renders it an advantage over conventional treatments. The effectiveness of the photosensitizer is highly influenced by its ability to localize within cancer cells together with singlet oxygen generation [8–10]. Phthalocyanines containing zinc as a central metal have been used for PDT due to their ability to produce high singlet oxygen quantum yields [11]. The major disadvantage of using Pcs for PDT is their poor bio-distribution and selectivity to target tissue [12]. To improve the biological effectiveness, Pcs have been recently conjugated to different molecules such as peptides [13]. Such macromolecules enable the Pc to have a longer retention time inevitably leading to higher drug concentration in the targeted tissue. Recently much focus is on asymmetrically substituted phthalocyanines [14–18], due to their selectivity when conjugated to other molecules. Low symmetrically substituted phthalocyanines (e.g., with only one carboxylic acid group) can be selectively coupled to biological compounds (peptides and

proteins) and nanoparticles. Thus, the synthesis of Zn (ZnPc) and Mg (MgPc) phthalocyanines containing one carboxyl group are discussed in this work. MgPc complexes have been less studied compared to their ZnPc counterparts due to the small central atom which encourages fluorescence rather than intersystem crossing to the triplet state [19]. The presence of diamagnetic metals (which are also biocompatible) such as Zn in the Pc core results in large triplet state quantum yields, leading to the generation of higher concentration of singlet oxygen, hence improved PDT activity.

Very high fluorescence quantum yields have been reported for Mg phthalocyanine derivatives symmetrically substituted with naphthol groups [19], hence our interest in this substituent. In addition, the bulky nature of the substituents will prevent aggregation. For ZnPc, the metal is larger than the equilibrium cavity of the ring, nevertheless the Zn ion is still located in plane. However, MgPc has been found not to be planar but forms a pyramidal structure [20,21] in the Pc cavity.

In the solid state, magnesium phthalocyanines exhibit an intense absorption band in the near-IR spectral region due to the non-planar nature that arises from the Mg atom being displaced from the Pc plane. This is caused by the interaction of a Mg ion of one molecule with the N-azamethine atom of a neighboring MgPc molecule [20]. This effect will be observed more for MgPcs than ZnPcs due to differences in planarity as mentioned above. This lack of planarity for MgPc has mainly been reported in the solid state, though the split in the Q-band in solution has also been reported [21]. The spectra and photophysical behavior of MgPc and ZnPc complexes will thus depend on their planarity. Thus, the effects of low symmetry and planarity of the MPc complexes on their photophysical and photochemical behavior will be reported in this work.

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