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Synthesis, photophysicochemical properties and TD-DFT calculations of tetrakis(2-benzoyl-4-chlorophenoxy) phthalocyanines

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ABSTRACT: The synthesis of metal free, magnesium and zinc tetrakis(2-benzoyl-4-chlorophenoxy) phthalocyanine derivatives (**2–4**) is described along with their characterization by elemental analysis, IR, UV-visible absorption, and ^{1}H NMR spectroscopy and mass spectrometry. Trends observed in the fluorescence, triplet state, singlet oxygen and photodegradation quantum yields and the triplet state lifetimes are also analyzed. The compounds exhibit high solubility in a wide range of organic solvents and no evidence of aggregation was observed over a wide concentration range. The Zn(II) complex (**4**) was found to have a very high singlet oxygen quantum yield ($\Phi_\Delta = 0.78$) in dimethylsulfoxide (DMSO) and a reasonably large triplet state quantum yield ($\Phi_T = 0.82$). The photophysical and photochemical properties clearly demonstrate that these compounds could prove useful in singlet oxygen applications such as photodynamic therapy (PDT). DFT and TD-DFT calculations were used to assess the impact of the positional isomerism of the 2-benzoyl-4-chlorophenoxy substituents on the electronic structures and optical spectroscopy.

KEYWORDS: phthalocyanine, singlet oxygen quantum yields, TD-DFT calculations.

INTRODUCTION

Phthalocyanines (Pcs) have long been used as industrial organic pigments and dyestuffs, since their accidental discovery at a Scottish dye factory in the late 1920s [1–3]. In recent years, in addition to these traditional applications, phthalocyanines have been extensively studied for use in a wide range of high technology fields [4]. The focus of this study is the preparation of new phthalocyanines for use as photosensitizers in photodynamic therapy (PDT) for the treatment of cancer. The PDT properties of these compounds are largely shaped by the central metal ion and the peripheral substituents that are introduced on the Pc ligand. Zinc and aluminium phthalocyanines have been the most extensively studied in this regard [5–7]. The metallation of phthalocyanines with transition metals typically leads to the formation of dyes with short triplet state lifetimes [8]. MgPcs have been studied less extensively than ZnPcs, since the smaller size of the Mg(II) ion has been reported to result in higher fluorescence intensities, which minimizes the rate of intersystem crossing to the triplet state [9]. The introduction of biocompatible diamagnetic metals, such as Zn, into the central cavity results in large triplet state quantum yields, leading to the generation of higher concentrations of singlet oxygen and hence improved PDT activity.

The solubility of Pcs is often very important in the context of singlet oxygen applications. Many Pcs are

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◊SPP full member in good standing

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