

Synthesis, spectroscopy and photochemistry of octasubstituted thiol-derivatized phthalocyaninatozinc(II) complexes

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Abstract

Synthesis, spectroscopic and photochemical characterization of phenylthiol-derivatized zinc phthalocyanine complex: 2,3,9,10,16,17,23,24-octa(4-methylphenylthio-)phthalocyaninatozinc(II) [$\text{ZnPc}(\text{SC}_6\text{H}_4\text{CH}_3)_8$] (**3a**) and its alkanethiol derivative, 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatozinc(II) [$\text{ZnPc}(\text{SC}_4\text{H}_9)_8$] (**3b**) are described. Spectroscopic analyses show that **3a** has a higher aggregation tendency than **3b** in organic solvents. Photochemical studies indicate that **3b** is more photostable and more efficient at singlet oxygen generation than **3a**.

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1. Introduction

Zinc (II) phthalocyanine (ZnPc) complexes have been found very attractive as sensitizers for photodegradation of pollutants [1–4] and photodynamic therapy (PDT) [5,6]. Thiol-derivatized metallophthalocyanine (MPc) complexes show rich spectroscopic and photochemical properties. For example, they are known to absorb at longer wavelengths (>700 nm) [7–10] than other MPc complexes – a very useful feature for application in PDT, optoelectronics and near-IR devices. Also, there has been a growing interest in thiol-derivatized phthalocyanines for the fabrication of thin films such as the self-assembled monolayers (SAMs) [11–13]. Preparation of thiol-derivatized metallophthalocyanine complexes is relatively more difficult than other MPc derivatives, which explains why MPcs containing sulphur donors rank among the least reported MPc complexes in literature. Hence, simpler strategies for their preparation, as shown in this work, are important.

During PDT action and photosensitized degradation of pollutants using MPc sensitizer, the photosensitizer is excited to its triplet state, and then transfers the energy to the ground state triplet oxygen, O_2 ($^3\Sigma_g$) generating the excited state singlet oxygen, $^1\text{O}_2$ ($^1\Delta_g$) which is the chief cytotoxic or oxidative species, through the so-called Type II mechanism. Hence, studies of the photooxidative stability of these MPcs during photosensitized reactions as well as their ability to generate the singlet oxygen cannot be over-emphasized. Thus, in this work we also report photochemical properties of 2,3,9,10,16,17,23,24-octa(4-methylphenylthio-)phthalocyaninatozinc(II) [$\text{ZnPc}(\text{SC}_6\text{H}_4\text{CH}_3)_8$] (**3a**) and 2,3,9,10,16,17,23,24-octabutylthiophthalocyaninatozinc(II) [$\text{ZnPc}(\text{SC}_4\text{H}_9)_8$] (**3b**) (Scheme 1).

2. Experimental

2.1. Materials and measurements

Dimethylformamide (DMF), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), 1,3-diphenylisobenzofuran (DPBF), diazabicyclooctane (DABCO), butanethiol, 4-methyl-

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