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Photophysical and photochemical studies of long chain-substituted zinc phthalocyanines

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Abstract

Photochemical and photophysical measurements were conducted on peripheral and non-peripheral tetra(13,17-dioxanonacosane-15-hydroxy)substituted zinc phthalocyanines (1, 2). General trends are described for quantum yields of photodegradation, fluorescence yields, triplet lifetimes and triplet quantum yields as well as singlet quantum yields of these compounds in dimethylformamide (DMF) and toluene. The effects of the solvents on the photophysical and photochemical parameters of the zinc(II) phthalocyanines (1, 2) are reported. © 2006 Elsevier B.V. All rights reserved.

Keywords: Phthalocyanine; Quantum yields; Singlet oxygen; Triplet; Photodegradation

1. Introduction

Phthalocyanines and metallophthalocyanines have been investigated in detail for many years because of their wide applications in many fields, including use in chemical sensors, liquid crystals, Langmuir-Blodgett films, non linear optics, optical data storage and as carrier generation materials in near-IR devices. Substituted derivatives carealso be used for photodynamic cancer therapy and other processes driven by visible light [1,2]. A decisive disadvantage of phthalocyanine and metal phthalocyanines is their low solubility in organic solvents or water. The solubility can be increased, however, by introducing alkyl or alkoxy groups into the peripheral and non-peripheral positions of the phthalocyanine framework [3]. Because of their lower degree of order in solid state, tetra-substituted phthalocyanines are more soluble than the corresponding octa-substituted ones. In contrast to octa-substituted systems tetra-substituted phthalocyanines are obtained as a mixture of constitutional isomers by statistical synthesis starting from mono-substituted phthalonitriles or corresponding diiminoisoindolines. Depending on their substituent positions two types (non-peripherally

1010-6030/\$ - see front matter © 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jphotochem.2006.08.025 and peripherally substituted) of tetra-substituted macrocycles, which show significant differences in their chemical and physical behaviour, can be distinguished.

For photodynamic therapy (PDT), a combination of a photosensitizing drug and light in the presence of molecular oxygen is used to obtain a therapeutic effect, and has been proposed as an alternative treatment to complement conventional protocols in the management of malignant tumors and many other nononcologic diseases [4]. The use of photosensitizing agents for inactivation of several cancer cells has been widely studied [5].

Many groups of compounds have been shown to possess photosensitizing tendencies. Metallophthalocyanines (MPcs), in particular, have proved to be highly promising in this respect, due to their intense absorption in the red region of visible light. High triplet state quantum yields and long lifetimes are required for efficient sensitization and these criteria may be fulfilled by the incorporation of a diamagnetic metal such as zinc, aluminum or silicon into the phthalocyanine macrocycle.

Zinc phthalocyanine complexes have attracted much interest because of their appreciably long triplet lifetimes [6–8]. Such long lifetimes constitute a great advantage since the number of diffusional encounters between the triplet excited state and ground state molecular oxygen increases with the lifetime of the excited state. The introduction of peripheral and nonperipheral substituents onto the MPc ring is expected to affect

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