



Synthesis of new water soluble phthalocyanines and investigation of their photochemical, photophysical and biological properties

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ARTICLE INFO

Article history:

Received 26 August 2011

Received in revised form 1 February 2012

Accepted 11 March 2012

Available online 17 March 2012

Keywords:

Water soluble

Phthalocyanines

Fluorescence

Singlet oxygen

Photodynamic therapy

ABSTRACT

With the quaternized derivatives (**4a** and **5a**), the synthesis of new Zn(II) and Co(II) phthalocyanines (**4** and **5**) substituted with 2-(azepan-1-yl)ethoxy moieties are reported. Photochemical and photophysical properties of quaternized Zn(II) and Co(II) phthalocyanines (**4a** and **5a**) are investigated in both dimethyl sulfoxide (DMSO) and water, while non ionic derivatives in DMSO only. General trends are described for fluorescence quantum yields, fluorescence lifetimes, singlet oxygen quantum yields and photodegradation quantum yields. In this work, the effect of substituents and the nature of the metal atoms on the photochemical and photophysical parameters of new phthalocyanines are discussed. The quaternized compounds exhibit excellent solubility in water, making them potential photosensitizers for use in photodynamic therapy (PDT) of cancer. This study also showed that the water-soluble quaternized Zn(II) phthalocyanines strongly bind to blood plasma proteins such as bovine serum albumin (BSA).

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1. Introduction

Phthalocyanines (Pcs) are widely used in the design of new materials such as stable dyes, catalysts, building blocks for nanostructures, active components of optical sensors, semiconductor and electrochromic devices, memory systems, liquid crystal color displays, photoelectric transformers of solar energy, etc. [1–5]. Metallophthalocyanines (MPcs) attract more attention due to additive magnetic or biological properties of metals which they are incorporated.

Recently, pcs have also been widely used as photosensitizers in photodynamic therapy (PDT). PDT is a binary treatment that involves the activation of a tumor-localized photosensitizer with red light. The excited photosensitizer in triplet state reacts with molecular oxygen and forms singlet oxygen that destroys malignant tissues [6,7]. For PDT applications, it is important that MPcs exhibit high absorption coefficients ($\epsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) in visible region and a long triplet lifetime to produce singlet oxygen [8–13].

In order to overcome the insolubility of unsubstituted phthalocyanine parent molecule, peripheral groups have been extensively used to enhance solubility. In this sense, long alkyl, alkyloxy, alkyl-sulfanyl or bulky apolar groups lead to soluble products in common organic solvents while anionic or cationic substituents (e.g. sulfo groups, carboxy groups, ammonium groups) result with products soluble in aqueous media [14,15].

During the last decade, our group has been heavily engaged with the synthesis of phthalocyanines and porphyrazines with substituents such as quaternized amino groups, and multicyclic aromatic rings [16–19]. Water soluble phthalocyanines have appeared as attractive photosensitizers for photodynamic therapy [20–22]. One limitation of these photosensitizers is their high tendency to form aggregated species in aqueous solution. An efficient strategy for number of practical uses might be to add some groups to inhibit aggregation. In this paper we report the synthesis and investigation of photochemical and photophysical properties of some phthalocyanines and their quaternized derivatives bearing four 2-(azepan-1-yl)ethoxy groups which enable the molecules to dissolve in number of organic solvents as well as water.

In this work, the synthesis, characterization and spectroscopic behaviour as well as photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yields) properties of new tetrakis-[2-(azepan-1-yl)ethoxy] substituted non-ionic (**4** and **5**) and quaternized ionic (**4a** and **5a**) Zn(II) and Co(II) phthalocyanine complexes (Fig. 1) are presented. The aim of our ongoing research is to synthesize water-soluble phthalocyanines to be used as potential PDT agents.

2. Experimental

2.1. Materials

All reagents and solvents were of reagent grade quality and were obtained from commercial suppliers. 2-(Azepan-1-yl)ethanol

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