Dyes and Pigments 91 (2011) 153–163

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Water-soluble quaternized mercaptopyridine-substituted zinc-phthalocyanines: Synthesis, photophysical, photochemical and bovine serum albumin binding properties

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ARTICLE INFO

Article history:
Received 3 January 2011
Received in revised form
4 February 2011
Accepted 7 February 2011
Available online 8 March 2011

Keywords:
Phthalocyanine
Quaternization
Water soluble
Photosensitizer
Bovine serum albumin
Photodynamic therapy

ABSTRACT

The synthesis and characterization of the new zinc phthalocyanine derivatives, tetra- (non-peripheral, **5**) and octa-(peripheral, **6**) substituted with 2-mercaptopyridine and their respective quaternized derivatives (**8** and **9**) are reported. Photochemical and photophysical properties of the new complexes are compared with those of the previously reported peripherally tetra-substituted complexes **7** and **10**. The quaternized compounds exhibit excellent solubility in water, making them potential photosensitizers for use in photodynamic therapy (PDT) of cancer. Spectroscopic, aggregation, photophysical and photochemical properties of these complexes are also investigated and compared. Photophysical (fluorescence quantum yields and lifetimes) and photochemical (singlet oxygen and photodegradation quantum yield) properties of these phthalocyanine photosensitizers are very important for the assessment of these complexes as PDT agents. In this study, the effects of the position of the substituents and quaternization of the substituents on the photophysical and photochemical parameters of the zinc phthalocyanines are also reported. This study also showed that the water-soluble quaternized zinc phthalocyanines strongly bind to blood plasma proteins such as bovine serum albumin (BSA).

1. Introduction

Phthalocyanines (Pcs) are remarkable macrocyclic compounds having magnificent physical and chemical properties [1]. Metallophthalocyanines (MPc) have been investigated in detail for many years due to their wide applications in many fields, mostly in terms of their uses as blue-green dyes and catalysts [2,3]. They have also found different applications in many fields ranging from industrial [4], technological [5,6] to medical [7,8]. Most metal ions can be engaged in the Pc macrocyle's cavity; therefore, a large number of different MPc complexes have been synthesized. When the central metal is diamagnetic and non-transitional, MPc derivatives are photoactive and may be employed in photosensitization [9,10]. In this regard, it is worth emphasizing the Pcs' application as photosensitizers in the photodynamic therapy (PDT) of tumours. High triplet state quantum yields and long triplet lifetimes are required for efficient sensitization by MPc complexes. The photophysical properties of the Pc dyes are strongly influenced by the presence and nature of the central metal ion. MPcs containing transition metals give short triplet lifetimes. Closed shell and diamagnetic ions, for example Zn^{2+}, Ga^{3+} and Si^{4+}, give Pc complexes excellent properties such as high triplet yields and long lifetimes [11–13]. ZnPcs in particular have been extensively studied because of d^{10} configuration of the central Zn^{2+} ion results in optical spectra that are not complicated by additional bands, as in transition-metal Pc complexes. ZnPcs have intensive red-visible region absorption and high singlet and triplet yields, making them valuable photosensitizers for PDT applications.

In PDT applications, the drug is injected into the patient's blood stream, and since the blood itself is a hydrophilic system, water solubility plays a very important role for a potential photosensitizer in PDT [14–17]. The advantages of MPcs bearing cationic substituents over those with neutral and anionic substituents are numerous [18], for examples: (i) they are able to improve water solubility and prevent aggregation [19]; aggregation seriously compromises the PDT value of the photosensitizer, (ii) they are more efficient as PDT agents [20] and also improve cell uptake [21], (iii) they are selectively localized in the cell mitochondria and cause apoptosis [22].

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doi:10.1016/j.dyepig.2011.02.007