Dyes and Pigments 82 (2009) 244-250

Contents lists available at ScienceDirect

Dyes and Pigments



The synthesis and photophysicochemical behaviour of novel water-soluble cationic indium(III) phthalocyanine

Mahmut Durmuş^a, Ali Erdoğmuş^{b,c}, Abimbola Ogunsipe^{b,d}, Tebello Nyokong^{b,*}

^a Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Turkey

^b Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

^cYıldız Technical University, Faculty of Arts and Science, Department of Chemistry, 34210 Esenler, Istanbul, Turkey

^d Department of Chemistry, University of Lagos, Lagos, Nigeria

ARTICLE INFO

Article history: Received 9 November 2008 Received in revised form 12 January 2009 Accepted 16 January 2009 Available online 27 January 2009

Keywords: Indium(III) phthalocyanine Synthesis Photophysics Photochemistry Photodynamic therapy Singlet oxygen

ABSTRACT

The syntheses and characterization of 2,3-octakis (2) pyridyloxyphthalocyaninato) indium(III) and quaternized 2,3-octakis-(3-pyridyloxyphthalocyaninato) indium(III) are described. The ground state electronic absorption spectra, photophysics and photochemistry of both dyes in DMSO as well as that of the quaternized compound in aqueous solution are also presented. A comparison of the photophysical and photochemical parameters of the two dyes revealed that quaternized 2,3-octakis-(3-pyridyloxyphthalocyaninato) indium(III) was a potter photosensitizer than its unquaternized counterpart. The quantum yield values of fluorescence ($\Phi_{\rm F}$), triplet state formation ($\Phi_{\rm T}$) and singlet oxygen formation (Φ_{Δ}) for the cationic dye were found to be 0.03, 0.68 and 0.66 respectively in DMSO; these values were higher than those for 2,3-octakis-(3-pyridyloxyphthalocyaninato) indium(III), which exhibited values of 0.02, 0.66 and 0.63, respectively in DMSO. The values for the cationic dye in aq. solution were 0.02, 0.59 and 0.56 respectively, suggesting that the water-soluble quaternized 2,3-octakis-(3-pyridyloxyphthalocyaninato) indium(III) offers potential as a photosensitizer in photodynamic therapy treatment.

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PIĞMĔNTS

1. Introduction

Phthalocyanines (Pcs) are an interesting class of compounds which exhibit both chemical and physical stabilities [1–3]. The Pc macrocycle can engage most metal ions in its cavity; hence scores of different metallophthalocyanines (MPcs) have been synthesized. The nature of the metal ion encapsulated within the Pc cavity plays a vital role in the properties, reactions and of course, applications of the resulting MPc. MPcs exhibit a wide range of applications ranging from industrial [4,5], technological [6–8] to medical [9,10]. MPc derivatives in which the central metal is diamagnetic and nontransitional are photoactive, and are often employed in photosensitization and energy conversion [11-13]. Worth emphasizing is the Pcs' application as photosensitizers (PSs) in the photodynamic therapy (PDT) of tumours. The photophysics and photochemistry of InPc derivatives are well documented [14–17]. Such studies reveal that these complexes show great promise for photocatalytic and photosensitizing applications [18,19]. However, studies on watersoluble indium phthalocyanine (InPc) derivatives are scarce in the

literature [20]. In PDT administration, the drug is injected into the patient's blood stream, and since the blood itself is a hydrophilic system, water solubility becomes crucial for a potential PS in PDT.

The advantages of MPcs bearing cationic substituents over those with neutral and anionic substituents are numerous [21], and include the following: (i) they are able to improve water solubility and prevent aggregation [22,23]; aggregation seriously compromises the PDT value of the PS, (ii) they are more efficient as PDT agents [24–26] and also improve cell uptake [27], (iii) they are selectively localized in the cell mitochondria, which when impaired induces apoptosis [28,29]. The advantages that go with cation-substituted MPcs are too striking to overlook, hence our interest in these complexes. In this work, the synthesis, photophysical and photochemical studies on new water-soluble cationic octasubstituted indium phthalocyanine derivative (Scheme 1) are presented.

During PDT, singlet oxygen is the predominant cytotoxic agent produced. Singlet oxygen is produced when the PS undergoes electronic excitation from a ground singlet (S_0) state to an excited singlet (S_1) state; the S_1 state is highly unstable, and rapidly undergoes intersystem crossing to a longer-lived excited triplet (T_1) state. One of the few chemical species present in tissue is triplet state oxygen. When the PS and an oxygen molecule are in



^{*} Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109. *E-mail address*: t.nyokong@ru.ac.za (T. Nyokong).

^{0143-7208/\$ –} see front matter \odot 2009 Elsevier Ltd. All rights reserved. doi:10.1016/j.dyepig.2009.01.008