

# Synthesis, photophysical and photochemical properties of tetra- and octa-substituted gallium and indium phthalocyanines

Mahmut Durmuş<sup>a,b</sup>, Tebello Nyokong<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

<sup>b</sup> Gebze Institute of Technology, Department of Chemistry, P.O. Box 141, Gebze 41400, Turkey

Received 13 February 2007; accepted 6 March 2007

Available online 12 March 2007

## Abstract

The synthesis, photophysical and photochemical properties of the tetra- and octa-[4-(benzyloxyphenoxy)] substituted gallium(III) and indium(III) phthalocyanines are reported for the first time. The new compounds have been characterized by elemental analysis, IR, <sup>1</sup>H NMR spectroscopy and electronic spectroscopy. General trends are described for quantum yields of photodegradation, fluorescence quantum yields and lifetimes, triplet lifetimes and triplet quantum yields as well as singlet oxygen quantum yields of these compounds in dimethylsulfoxide (DMSO). Substituted indium phthalocyanine complexes (**7b–9b**) showed much higher quantum yields of triplet state and shorter triplet lifetimes, compared to the substituted GaPc derivatives due to enhanced intersystem crossing (ISC) in the former. The gallium and indium phthalocyanine complexes showed phototransformation during laser irradiation due to ring reduction. The singlet oxygen quantum yields ( $\Phi_{\Delta}$ ), which give an indication of the potential of the complexes as photosensitizers in applications where singlet oxygen is required (Type II mechanism) ranged from 0.51 to 0.94. Thus, these complexes show potential as photodynamic therapy of cancer.

© 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Phthalocyanine; Photosensitizer; Gallium; Indium; Quantum yields; Singlet oxygen; Photodegradation

## 1. Introduction

Phthalocyanines, a family of aromatic macrocycles based on an extensive delocalized 18- $\pi$  electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research [1]. There has been growing interest in the use of phthalocyanines in a variety of new high technology fields including semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], gas sensors [5], liquid crystals [6], non-linear optics [7] and various catalytic processes [8]. The attractive characteristics of phthalocyanines in these applications arise from their great diversity, thermal and chemical stability, redox versatility and intense colour.

One of their most important applications is functioning as photosensitizers for photodynamic therapy (PDT) [9–12]. Due to the intense absorption in the visible region, high efficiency to generate reactive oxygen species (such as singlet oxygen), and low dark toxicity, phthalocyanines have been used in this avenue for the treatment of various cancers and photoinactivation of viruses [13–15]. However, their insolubility in common organic solvents causes difficulties for many applications, rendering the syntheses of soluble derivatives an important task. Phthalocyanine derivatives of increased solubility have been obtained using substituents such as alkyl, alkoxy, alkylthio chains and bulky groups. Peripheral substitution with bulky groups or long alkyl, alkoxy or alkylthio chains leads to phthalocyanine products which are soluble in apolar solvents. Sulfo or quaternary ammonium groups enhance solubility in aqueous media over a wide pH range of aqueous solutions. The size and the nature of the substituents are not

\* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.  
E-mail address: [t.nyokong@ru.ac.za](mailto:t.nyokong@ru.ac.za) (T. Nyokong).