

Photochemistry, photophysics and nonlinear optical parameters of phenoxy and *tert*-butylphenoxy substituted indium(III) phthalocyanines

Vongani Chauke^a, Mahmut Durmuş^{a,b}, Tebello Nyokong^{a,*}

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

^b Department of Chemistry, Gebze Institute of Technology, PO Box 141, Gebze 41400, Turkey

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Abstract

This work hereby presents the syntheses, photochemistry and photophysics of octaphenoxy ((Cl)InOPPC) and octakis(4-*tert*-butylphenoxy)chloroindium ((Cl)InOTBPPC) phthalocyanines. Calculated nonlinear parameters of these complexes are compared with those of the corresponding GaPc derivatives and tetrasubstituted GaPc and InPc complexes. Fluorescence quantum yields do not vary much between (Cl)InOPPC and (Cl)InOTBPPC complexes in different solvents. High quantum yields of triplet state (Φ_T ranging from 0.70 to 0.91 in dimethylsulphoxide, DMSO) and singlet oxygen generation (Φ_{Δ} , ranging from 0.61 to 0.79 in DMSO) were obtained. Short triplet lifetimes 50–60 μ s were obtained in DMSO. The optical limiting threshold intensity (I_{lim}) for the InPc derivatives were calculated and compared with those of corresponding tetrasubstituted InPc and GaPc complexes. The latter were found to be better optical limiters.

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1. Introduction

Metallophthalocyanines (MPcs), a family of aromatic macrocycles based on an extensive delocalized π - π electron system, are known not only as classical dyes in practical use but also as modern functional materials in scientific research. There has been growing interest in the use of phthalocyanines in a variety of new technology fields including nonlinear optics [1] semiconductor devices [2], Langmuir–Blodgett films [3], electrochromic display devices [4], liquid crystals [5], and as photosensitizers in photodynamic therapy (PDT) [6]. For nonlinear optical applications MPcs have advantages over inorganic compounds currently in use due to their small dielectric constants [7], fast response times, ease of processibility into optical components and their economic feasibility [1,7]. The MPcs can be modulated in a plethora of ways by changing the peripheral and non-peripheral substituents on the ring in addition to changing the central metal and the axial ligands.

Heavy metals, especially diamagnetic metals, play a major role in photosensitising and optical limiting mechanisms because they enhance intersystem crossing through spin orbit coupling. This is desirable because it improves the chances of getting a large population in the triplet state. Axial ligands in MPcs are useful in preventing or minimizing intermolecular interactions which result in aggregation in solution. Aggregation can result in the fast decay of the excited states. Indium is a useful central metal in MPc complexes since it is diamagnetic and able to host axial ligands. Indium phthalocyanines have been reported to have good photosensitising and optical limiting properties [1,7–11]. Mainly tetrasubstituted InPc derivatives have been reported in the literature, since they have much higher solubility due to lower degree of order which facilitates salvation, compared to octasubstituted derivatives. Octasubstituted MPcs on the other hand have isomeric purity. In this work we study the photochemical (singlet oxygen and photodegradation quantum yields) properties and photophysical (triplet state lifetimes and quantum yields, and fluorescence quantum yields and lifetimes) behaviour of octasubstituted indium phthalocyanines in different solvents. These are substituted on the peripheral position with large ligands (phenoxy, (Cl)InOPPC, and *tert*-butyl phenoxy,

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