### Polyhedron 60 (2013) 59-67

Contents lists available at SciVerse ScienceDirect

# Polyhedron

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

# Physicochemical properties of zinc monoamino phthalocyanine conjugated to folic acid and single walled carbon nanotubes



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

#### ARTICLE INFO

Article history: Received 11 April 2013 Accepted 13 May 2013 Available online 23 May 2013

Keywords: Single walled carbon nanotubes Folic acid Monoamino phthalocyanine Triplet quantum yields Fluorescence and singlet oxygen quantum yields

## ABSTRACT

FUL

This study reports on the photophysical and photochemical behavior of the conjugates formed by covalent and non-covalent bonding between zinc monomino phthalocyanine (ZnMAPc) and either single walled carbon nanotubes (SWCNTs) or folic acid (FA). The conjugates were characterized using FTIR, Xray powder diffractometry, thermogravimetric gnalyses, transmission electron microscopy and Raman spectroscopy. <sup>1</sup>H NMR and mass spectroscopies were only employed for ZnMAPc–FA conjugate. There was a slight increase in the triplet and single oxygen quantum yields on conjugating ZnMAPc to SWCNTs (or FA), while a decrease in the photophysical and photochemical parameters were observed upon adsorption of the ZnMAPc–FA conjugate to SWCNTs.

© 2013 Elsevier Ltd. All rights reserved.

# 1. Introduction

Metallophthalocyanines (MPcs) are a family of promising photosensitizers with a wide variety of applications including as photosensitizers in photodynamic therapy (PDF) due to their distinctive properties such as an intense absorption in the red region of the visible spectrum, effective singlet, oxygen generation, coupled together with their low-toxicity (a the absence of light) [1]. The main limitation with the use of phthalocyanines (Pcs) as photosensitizers for PDT is their lack of selectivity towards cancerous cells. There is therefore a need to develop tumor specific therapeutics, which could be done by the attachment of cancer specific molecules (such as folic acid) onto the Pc. Cancer cells that are most difficult to treat with classical methods can be easily targeted with folic acid (FA) linked therapeutics [2,3]. Folate receptors are over expressed in a number of carcinomas, including malignancies of the ovary, brain, kidney, breast, colon and lung [4-6]. In this study, an MPc molecule is linked to FA which will provide the advantage of selectivity as well as biocompatibility to the Pc. We recently reported on a conjugate between folic acid and zinc tetraamino phthalocyanine (ZnTAPc) [7]. However, since the complex contained four amino groups, the number of folic acid moieties attached to the MPc was difficult to determine. We herein report on the linking of FA to a monoamino substituted Pc which provides the advantage of a single folic acid substituent linked to the MPc.

The problem of the transportation of drugs across cellular barriers is a major setback in the development of anti-cancer therapeutics. Several delivery systems including quantum dots, silica nanoparticles, dendrimers, micelles, molecular conjugates and liposomes have been reported [8,9]. Single walled carbon nanotubes (SWCNTs) belong to the family of nano materials, which have emerged as potential delivery systems for therapeutic molecules due to their remarkable properties which include their high aspect ratio, hollow and cage like interior [10], and high surface area [11]. Functionalized SWCNTs have the advantage of moving across cellular membranes with less cytotoxicity when compared to the unfunctionalized SWCNTs [12]. SWCNTs absorb light in the nearinfrared region and they may induce cell death by a localized photothermal (PT) effect [13]. In this work SWCNTs are linked to a phthalocyanine photosensitizer. We have reported on the chemical conjugation of SWCNTs to symmetrical or asymmetrical phthalocyanines containing electroactive central metals for electrocatalytic applications [14-17]. The central metals employed were not appropriate for MPcs aimed for use as photosensitisers. Conjugation of SWCNTs to asymmetric ZnPc derivatives containing a single NH group has been reported [18], but the resulting conjugate showed no triplet decay or singlet depletion curves. This work reports for the first time on the conjugation of a SWCNT to a ZnPc derivative monosubstituted with an amino group. The resulting conjugate shows triplet decay curves. The adsorption of Pc-FA onto SWCNT is also reported for the first time.

In this study, the photophysical and photochemical behaviour of zinc monoamino phthalocyanine (ZnMAPc) is investigated upon conjugation to SWCNTs (or FA). The resulting conjugates are







<sup>\*</sup> Corresponding author. Tel.: +27 46 603 8260; fax: +27 46 622 5109. *E-mail address:* t.nyokong@ru.ac.za (T. Nyokong).

<sup>0277-5387/\$ -</sup> see front matter @ 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2013.05.025