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The effects of silica based nanoparticles on the photophysical properties, *in vitro* dark viability and photodynamic therapy study of zinc monocarboxyphenoxy phthalocyanine

David O. Oluwole^a, Imran Uddin^a, Earl Prinsloo^b, Tebello Nyokong^{a,*}^a Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa^b Biotechnology Innovation Centre, Rhodes University, Grahamstown 6140, South Africa

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ABSTRACT

Aminopropyl triethoxysilane functionalized core SiO₂ and core/shell ZnO/SiO₂ nanoparticles (NP) were covalently linked to zinc monocarboxyphenoxy phthalocyanine (ZnMCPPc, complex **1**) *via* amide bond formation. The photophysical behavior, *in vitro* dark viability and photodynamic therapy (PDT) activity against human breast adenocarcinoma cell line (MCF-7 cells) of the conjugates were studied. The nanoconjugates showed enhanced photophysical behavior as compared to complex **1** alone. Complex **1** showed higher dark toxicity against MCF-7 cells when compared to the conjugates. In the dark, complex **1** accounted for less than 50% viable cells at 28.6 μg/mL and 57.1 μg/mL compared to the conjugates which accounted for more than 50% cell viability at these concentrations. The *in vitro* dark viability and PDT activity of complex **1** was reduced in the presence of these nanoparticles.

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1. Introduction

Photodynamic therapy (PDT) involves the combination of a photosensitizing drug, oxygen and light to cause selective damage to the target tissue. The overall effectiveness of PDT requires careful planning of both drug and light dosimetry [1]. Metallophthalocyanines (MPcs) have been found to be suitable PDT photosensitizers for the treatment of cancerous cells due to their unique photophysical properties which include intense and tunable light absorption in the near-infrared region as well as their ability to efficiently generate singlet oxygen, which is the chief cytotoxic species for PDT [2,3].

On the other hand nanoparticles effectively improve the photophysical and PDT activities of photosensitizers [4,5]. The ease of functionalization of nanoparticles (NPs) such as silica (SiO₂ NPs) and zinc oxide (ZnO NPs) with different materials such as fluorophores, drugs, bio-molecules, dendrimers and polymers, has led to the development of improved and multifunctional materials that have found applications in areas such as drug delivery, sensing, diagnosis, imaging and theranostics [6–12].

In this study, aminopropyl triethoxysilane (APTES) functionalized silica nanoparticles (SiO₂ NPs) and ZnO nanoparticle core with SiO₂ nanoparticle shell (ZnO/SiO₂ NPs) were covalently linked to zinc monocarboxyphenoxy phthalocyanines (ZnMCPPc, complex **1**, Scheme 1) *via* the carboxyl functional moiety of the latter and the amine functional moiety of the former. The photophysical properties, the *in vitro* dark cytotoxic and PDT activity (against MCF-7 cells) of complex **1** and its conjugates with NPs are investigated in this work. Silica nanoparticles have been linked to phthalocyanines with improved photophysical behavior [13,14]. But there have been no studies on their activity on cancer cells, until this report. Also, this is the first time core shell ZnO/SiO₂ NPs are linked to phthalocyanines. The presence of Zn in the ZnO/SiO₂ NPs is expected to result in even more improved triplet state population of complex **1** due to the heavy atom effect of Zn in the NPs, which encourages intersystem crossing to the triplet state. A ZnPc derivative was chosen due to the heavy atom effect of Zn and a mono carboxy substituent allows for a single coordination for the NPs.

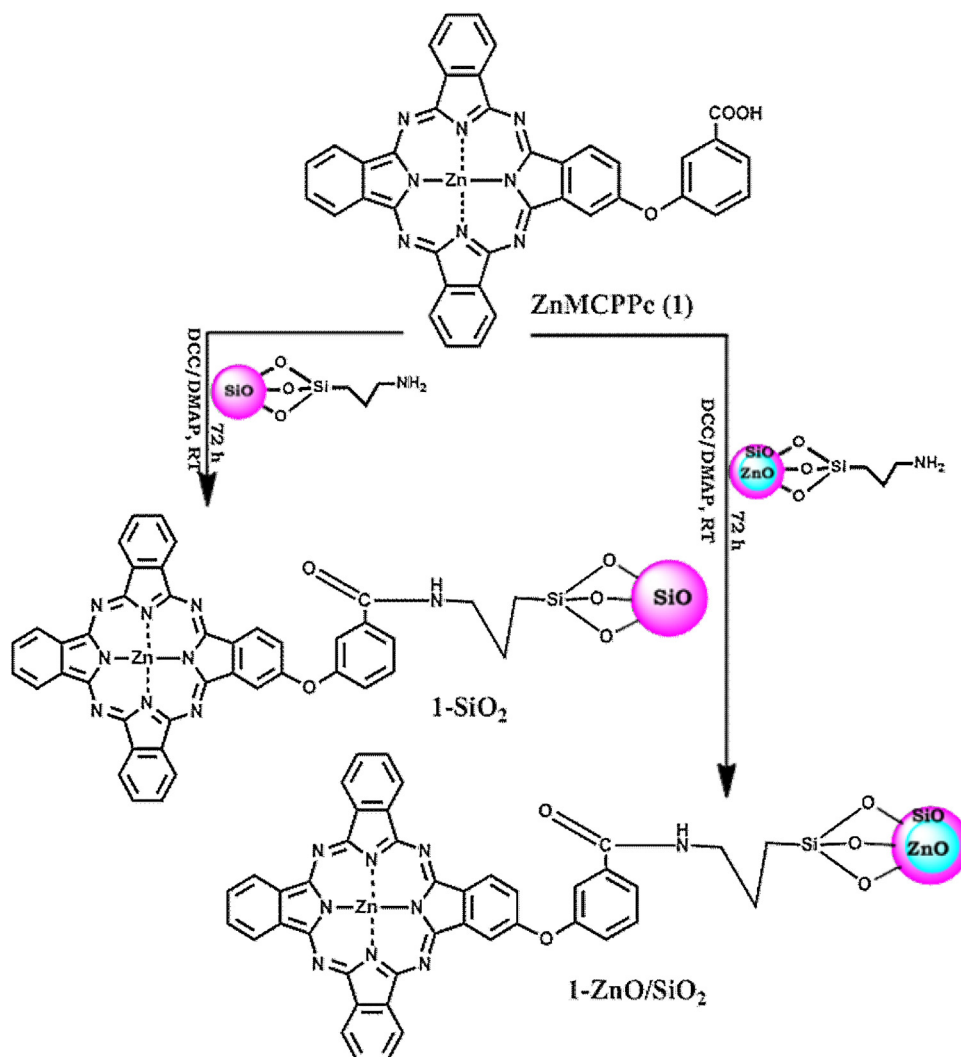
2. Experimental

2.1. Materials

Ultra-pure water was obtained from a Milli-Q Water System, dimethylsulfoxide (DMSO), *N,N'*-dicyclohexylcarbodiimide (DCC),

* Corresponding author.

E-mail address: t.nyokong@ru.ac.za (T. Nyokong).



Scheme 1. Covalent linkage of ZnMCPc to SiO₂ NPs or ZnO/SiO₂ NPs.

4-(dimethylamino)pyridine (DMAP), zinc phthalocyanine (ZnPc) and trypan blue were obtained from Sigma Aldrich[®]. Methanol (MeOH), dimethylformamide (DMF), and absolute ethanol (EtOH) were obtained from SAARCHEM[®]. Cultures of MCF-7 breast cancer cell lines were obtained from Cellonex[®]. Dulbecco's phosphate-buffered saline (DPBS), trypsin ethylenediaminetetra acetic acid (EDTA) and Dulbecco's modified Eagle's medium (DMEM) were obtained from Sigma Aldrich[®], 10% (v/v) heat-inactivated fetal calf serum (FCS), neutral red cell proliferation reagent (WST) and 100 unit/mL penicillin-100 μg/mL streptomycin-amphotericin B were obtained from Lonza[®]. SiO₂ NPs and ZnO/SiO₂ NPs coated with aminopropyl triethoxysilane (APTES) were synthesized according to literature [15–17]. ZnMCPc was also synthesized as reported before [18].

2.2. Equipment

The ground state electronic absorption spectra were recorded on Shimadzu[®] UV-2550 spectrometer. FT-IR spectra were measured on Bruker[®] ALPHA FT-IR spectrometer with universal attenuated total reflectance (ATR) sampling accessory. Fluorescence emission and excitation spectra were acquired on Varian Eclipse[®] spectrofluorometer using a 360–1100 nm filter. Fluorescence lifetimes were measured using a time correlated

single photon counting setup (TCSPC) (FluoTime 300, Picoquant[®] GmbH) with LDH-P-670, Picoquant[®] GmbH, 20 MHz repetition rate, 44 ps pulse width. Details have been provided before [19].

X-ray powder diffraction patterns were recorded using a Cu K radiation (1.5405 Å, nickel filter), on a Bruker[®] D8 Discover equipped with a proportional counter and the X-ray diffraction data were processed using the Eva[®] (evaluation curve fitting) software. The morphologies of the nanoparticles and nanoconjugates were assessed using transmission electron microscope (TEM) ZEISS LIBRA[®] model 120 operated at 90 kV and micrograph were processed with iTEM[®] software. Energy dispersive X-ray spectrometer (INCA PENTA FET coupled with VAGA TESCAM[®] operated at 20 kV) was used to qualitatively determine the elemental compositions of the NPs and the nanoconjugates. Micrometrics ASAP[®] 2020 Surface Area and Porosity Analyzer was used to acquire the nitrogen adsorption/desorption isotherms of the NPs operated at 77 K.

X-ray photoelectron spectroscopy (XPS) data were collected using a Kratos Axis Ultra DLD with an Al (monochromatic) anode, equipped with charge neutralizer. The operational protocol has been reported before [20].

Triplet quantum yields were determined using laser flash photolysis system. The excitation pulses were produced using a tunable laser system consisting of a Nd:YAG laser (355 nm, 135 mJ/

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