Journal of Photochemistry & Photobiology, A: Chemistry 402 (2020) 112813

Contents lists available at ScienceDirect

Journal of Photochemistry & Photobiology, A: Chemistry

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

The photodynamic antimicrobial chemotherapy of *Stapphylococcus aureus* using an asymmetrical zinc phthalocyanine conjugated to silver and iron oxide based nanoparticles

Sivuyisiwe Mapukata, Nnamdi Nwahara, Tebello Nyokong *

Institute for Nanotechnology Innovation, Department of Chemistry, Rhodes University, Makhanda, 6140, South Africa

ARTICLE INFO

Keywords:
Photodynamic antimicrobial chemotherapy
Singlet oxygen quantum yield
Phthalocyanine
Magnetic nanoparticles

ABSTRACT

The synthesis and characterisation of asymmetrical zinc(II) 2(3)-mono-isophthalic acid-9(10),16(17),23 (24)-tri (*tert*-butylphenoxy) phthalocyanine (complex **4**) are reported. The phthalocyanine is conjugated to cysteamine capped silver nanoparticles (Cys-Ag NPs), amine functionalised iron oxide magnetic nanoparticles (NH_2-Fe_3O_4 NPs) and a core-shell composite of the two (Cys-Fe_3O_4@Ag) via amide bonds. The photo-physico-chemical properties of complex **4** and its respective nanoconjugates (**4**-Ag, **4**-Fe_3O_4 NPs and **4**-Fe_3O_4@Ag NPs) are also reported. The nanoconjugates showed improved triplet and singlet oxygen quantum yields compared to complex **4**. The antibacterial activity of complex **4** and its nanoconjugates were also evaluated on *S. aureus* wherein their activity was found to be mainly visible light driven with the best catalyst being **4**-Fe_3O_4@Ag. The work therefore demonstrates the feasibility of phthalocyanine-nanoparticle based compounds as potential agents in real life antibacterial treatment.

1. Introduction

Photodynamic antimicrobial chemotherapy (PACT) is the method of photoinactivation of bacteria in the presence of a photosensitizer. In PACT a photosensitizer is activated by light of appropriate wavelength, and upon interaction with oxygen, the photosensitizer generates various reactive oxygen species (ROS) (including singlet oxygen) which are lethal and damage bacteria [1–3]. Phthalocyanines (Pcs) are amongst the photosensitisers that have been effectively applied in antimicrobial studies [4,5]. Pcs are synthetic tetrapyrrolic macrocycles containing four iminoisoindoline rings with a conjugated 18 π electron system [6]. They possess attractive properties such as excellent visible/near infrared absorption [7] and the ability to generate singlet oxygen; which is the active species in bacterial inactivation. Pcs are also used for other applications such as in nonlinear optics, dye-sensitized solar cells (DSSC) and as gas sensors amongst others [8–10].

A zinc Pc (complex **4**) is synthesised in this work because diamagnetic metals such as zinc and indium have been reported to exhibit high triplet and singlet oxygen quantum yields, attributes which are attractive for photosensitised catalytic applications [11,12]. In addition, asymmetry in porphyrin type compounds has been reported to improve singlet oxygen generation [13]. The existence of different functional groups in low symmetry Pcs allows for the coexistence of several features in a molecule, and therefore an improvement in the Pc's properties. Zinc(II) 2(3)-mono-isophthalic acid-9(10),16(17),23 (24)-tri (*tert*-butylphenoxy) phthalocyanine (complex **4**) has *tert*-butylphenoxy substituents which were chosen for their bulkiness which will prevent aggregation, as well as carboxylic acid groups which aid in amide bond formation between the Pcs and nanoparticles (NPs). Various NPs including silica, gadolinium oxide and gold NPs have been conjugated to Pcs before [14–16]. In this work, complex **4** is conjugated to cysteamine capped silver NPs (Cys-Ag NPs), amine functionalised iron oxide magnetic NPs (NH_2-Fe_3O_4 NPs) as well as a composite of the two NPs; Cys-Fe_3O_4@Ag with the aim of creating and comparing a variety of antimicrobial agents.

Fe_3O_4 NPs and Ag NPs have been found to increase the singlet oxygen quantum yield of Pcs [17,18]. In addition, they have both been successfully applied for antimicrobial studies [19,20]. The composite NPs (Cys-Fe_3O_4@Ag NPs) was prepared because it has been reported that combining magnetic nanoparticles (MNPs) with Ag NPs results in enhanced magneto-optic response relative to MNPs alone [21]. Another attractive attribute about these bimetallic NPs is that improved triplet and singlet oxygen quantum yields have been reported when similar NPs were conjugated to Pcs [22,23] as well as improved PACT against *E. coli*

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

https://doi.org/10.1016/j.jphotochem.2020.112813
Received 12 November 2019; Received in revised form 6 July 2020; Accepted 28 July 2020
Available online 1 August 2020