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Enhanced triplet state yields in aqueous media of asymmetric zinc phthalocyanines when conjugated to silver nanoflowers

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ABSTRACT

Novel low symmetry water-soluble zinc phthalocyanines (ZnPcs, complexes **1** and **2**) were synthesized and then mixed with silver nanoflowers. Photophysical and photochemical studies were performed in order to determine the efficiency of complexes **1** and **2** as photosensitizers when alone and when combined with the silver nanoflowers. The Pcs show low fluorescence quantum yields and excellent triplet quantum yields of 0.78 (for **1**) and 0.66 (for **2**) in aqueous media. The triplet quantum yield values increased to 0.80 and 0.89, respectively, in the presence of silver nanoflowers. Long triplet lifetimes ranging from 180 to 200 μs in DMSO were obtained for complexes **1**, **2** and their conjugates with silver nanoflowers.

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1. Introduction

Phthalocyanines are versatile aromatic macrocycles with high absorption in the region of maximum light penetration in tissue [1–3]. As such, there has been great interest in researching these macromolecules for use as second generation photosensitizers in photodynamic therapy of cancer [4–6].

In order to enhance the properties of phthalocyanines (Pcs), functional groups can be added to either the peripheral (β) or non-peripheral (α) positions of the Pc ring. Hydrophobic and hydrophilic substituents can be incorporated in order to introduce solubility and to allow uptake into the cancerous cells [7]. In this work, photophysical and photochemical behavior of low symmetry zinc phthalocyanines containing three 2-[2-(2-ethoxyethoxy) ethoxy]-1-[2-((2-ethoxyethoxy)-ethoxy) methyl] ethoxy and one aminoethoxy or 2-(2-(2-ethoxyamino)-2-oxoethoxy) acetic acid groups at non-peripheral positions (complexes **1** or **2**, respectively, Scheme 1) are studied in the absence and presence of silver nanoparticles with flower like shape (designated as silver nanoflowers, AgNFs). The peripherally substituted derivative of **1** has been reported before [8]. The ring substituents in this work were chosen in order to enhance solubility and the bulky polyoxythylene groups are to reduce aggregation. Substitution at non-peripheral positions results in a red shift of the Q band when compared to the peripherally substituted derivatives [8] and this shift is more towards the therapeutic window, hence making Pcs studied in this work more ideal as photosensitizers.

Silver has a high affinity for N atoms. The possible interaction between the MPcs and silver nanoparticles may be via the NH_2 for **1** and NH for **2**, which may be achieved by ligand exchange where some of the *p*-phenylenediamine (PPD) or polyvinyl pyrrolidone (PVP) capping is replaced by the Pc. Silver nanoparticles are known to exhibit antimicrobial properties [9–12]. In addition, AgNPs are expected to increase the triplet quantum yields and subsequently the singlet oxygen production of the studied Pcs since AgNPs nanoparticles contain heavy atoms which enhance intersystem crossing. Research into shaped nanoparticles has recently drawn interest [13,14], since anisotropic nanoparticles [15] have been reported to have superior long blood circulation time. Thus, when Pcs are coordinated to anisotropic silver nanoparticles, their effectiveness as photosensitizers in photodynamic therapy or photodynamic antimicrobial chemotherapy (PACT) is expected to improve. Hence, we use nanoflowers in this work. The photophysical behavior of phthalocyanines have been studied in the presence of spherical silver nanoparticles [10]. This work reports for the first time on the photophysical and photochemical behavior of asymmetric phthalocyanines in the presence of silver nanoparticles in aqueous media. There have been studies of photophysical behavior of Pcs in the presence of AgNPs but in organic media [10–12]. This

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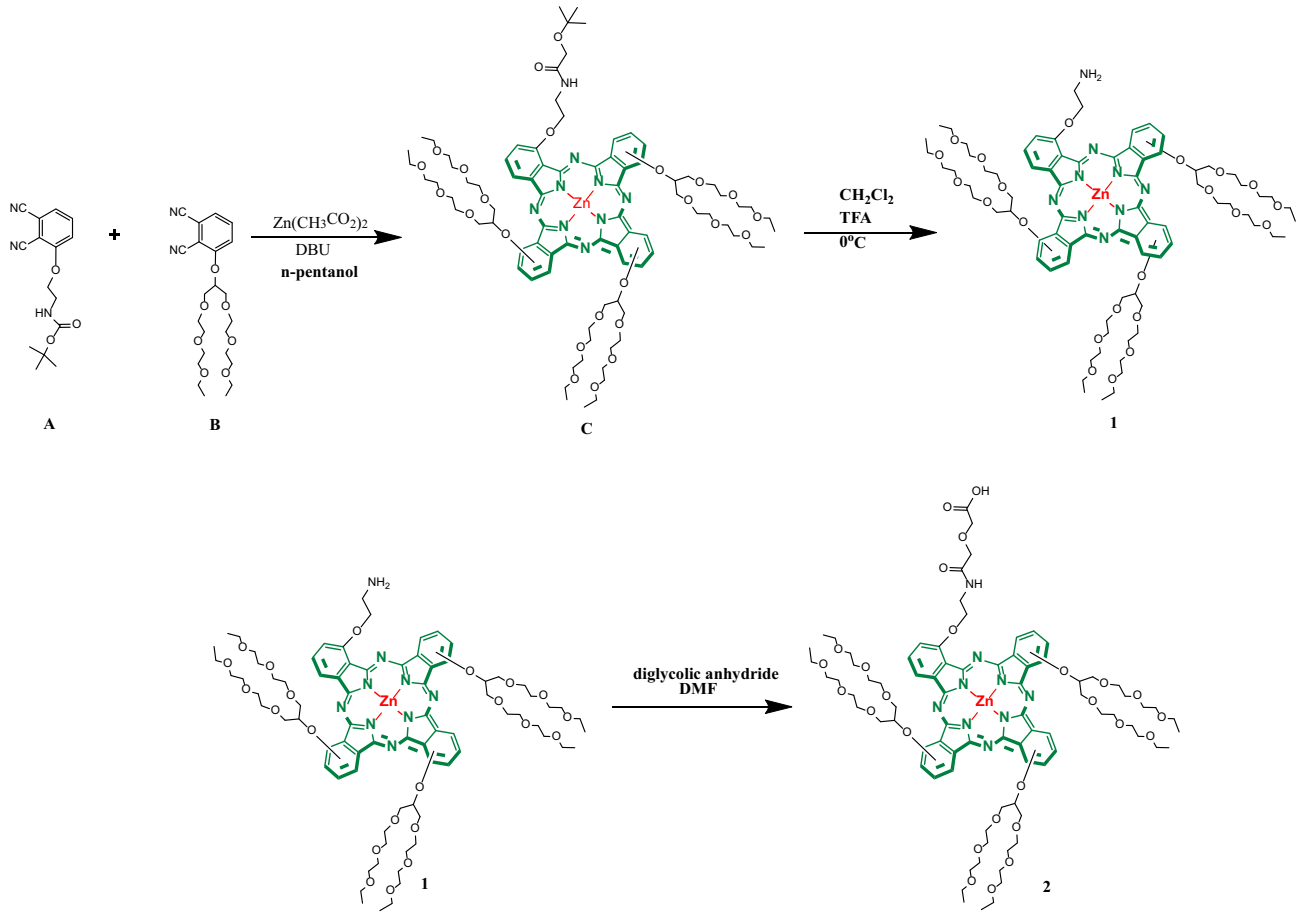

Scheme 1. Synthesis route of asymmetrically substituted zinc(II) phthalocyanine complexes **1** and **2**.

work reports for the first time on the photophysical behavior Pc-AgNPs conjugate in aqueous media. Large triplet state quantum yields are reported in this work in aqueous media even though water is known to quench the triplet state of phthalocyanines [16]. Studies in water are essential for practical applications.

2. Experimental

2.1. Materials

All solvents were reagent-grade quality and obtained from commercial suppliers. Column chromatography was performed on silica gel 60 (0.04–0.063 mm) and thin layer chromatography (TLC) was performed on silica gel 60 P F_{254}. All reactions were monitored by TLC using 0.25 mm silica gel plates with UV indicator ($60F_{254}$). Triton-X 100, ethyl glycol, diglycolic anhydride, 1,3-diphenylisobenzofuran (DPBF), *p*-phenylenediamine (PPD), polyvinyl pyrrolidone (PVP), $AgNO_3$, and trifluoroacetic acid (TFA) were purchased from Sigma–Aldrich. AlPcSmix (containing a mixture of sulfonated derivatives and used as a standard) was synthesized according to literature methods [17]. The rest of the reagents were obtained from commercial supplies and used as received.

3-{2-[2-(2-Ethoxyethoxy)ethoxy]-1-[2-((2-ethoxyethoxy)-ethoxy) methyl] ethyloxy} phthalonitrile (A) [18], 3-{2′-[(*tert*-butoxycarbonyl) amino]ethoxy}phthalonitrile (B) [19], and 1-{[(2-*tert*-butoxycarbonyl) amino]ethoxy}–8(11),15(18),22(25)-tris-{2-[2-(2-ethoxyethoxy) ethoxy]-1-[2-((2-ethoxyethoxy ethoxymethyl]ethyloxy} phthalocyninato Zn(II) (C) [19] were synthesized and purified according to literature procedures.

2.2. Equipment

Elemental analyses were obtained from Thermo Finnigan Flash 1112 Instrument. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 spectrophotometer. ^1H and ^{13}C NMR spectra with TMS as the internal standard were recorded on a Varian 500 MHz spectrometer. The mass spectra were recorded on a MALDI (Matrix Assisted Laser Desorption Ionization) BRUKER Microflex LT using 2,5-dihydroxybenzoic acid (DHB) as matrix.

Fluorescence emission and excitation spectra were recorded on a Varian Eclipse spectrofluorimeter. Ground-state electronic absorption spectra were recorded on a Shimadzu, UV–Vis 2550 UV–Vis spectrometer.

Fluorescence lifetimes were measured using a time correlated single photon counting setup (TCSPC) (FluoTime 200, Picoquant GmbH) with a diode laser (LDH-P-670 with PDL 800-B, Picoquant GmbH, 670 nm, 20 MHz repetition rate, 44 ps pulse width). Details of the equipment have been described before [20].

A laser flash photolysis system was used for the determination of triplet absorption and decay kinetics. The excitation pulses were produced by a Quanta-Ray Nd:YAG laser (1.5 J/90 ns), pumping a Lambda Physic FL 3002 dye laser (Pyridin 1 in methanol). Details of the equipment have been described before [20].

Photo-irradiations for singlet oxygen determinations were done using a General Electric Quartz line lamp (300 W). A 600 nm glass cut off filter (Schott) and a water filter were used to filter off ultraviolet and infrared radiations, respectively. An additional interference filter (Intor, 700 nm with a band width of 40 nm) was placed in the light path before the sample for singlet oxygen determination studies. Light intensities were measured with a POWER MAX

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