



Fluorescence behavior and singlet oxygen generating abilities of aluminum phthalocyanine in the presence of anisotropic gold nanoparticles



Thandekile Mthethwa, Tebello Nyokong*

Department of Chemistry Rhodes University, Grahamstown 6140, South Africa

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ABSTRACT

Gold nanoparticles (spheres, rods and bipyramids) were synthesized. The nanocrystals were characterized by UV–visible spectrometry, transmission electron microscopy (TEM) and X-ray diffractometry (XRD). The as prepared gold nanoparticles were then conjugated to a quaternized 2,(3)-tetra [2-(dimethylamino) ethanethio] substituted Al(OH) phthalocyanine (complex **1**). The conjugation of phthalocyanines with gold nanoparticles resulted in a decrease in the fluorescence quantum yields and lifetimes. Conversely, an increase in the singlet oxygen quantum yields was observed for the conjugated complex **1** in the presence of AuNPs.

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1. Introduction

Metal nanoparticles have attracted a great deal of attention due to their unique optical properties. The synthesis of anisotropic gold nanoparticles has opened up many opportunities in a wide variety of applications such as in electronics [1], biomedicine [2] and imaging [3]. The optical properties of gold nanoparticles depend on their size and morphology, for example their surface plasmon absorption can be tuned to longer wavelengths in the UV–vis spectrum. There are a number of methods that have been developed for the synthesis of anisotropic gold nanoparticles such as an electrochemical synthesis [4] and a seed-mediated method [5,6]. The seed-mediated method involves the synthesis of small spherical particles in the first step, followed by shape directed growth by the addition of excess gold ions and a shape directing surfactant. In this work the seed-mediated method was used to synthesize differently shaped gold nanoparticles.

Photothermal therapy (PTT) is a method of treating cancer that employs light absorbing materials that can generate heat and cause the thermal ablation of tumor cells. Gold nanoparticles have the ability to absorb light and rapidly convert it to heat through non-radiative processes. For this reason, gold nanoparticles have potential as photothermal agents in PTT [7–9].

On the other hand, phthalocyanine (Pc) molecules are diverse and robust materials that are useful for a variety of applications ranging from medicine (e.g. as photosensitizers in photodynamic therapy, PDT) to molecular electronics [10–13]. The PDT modality combines the selectivity of fiber optic directed light with the cell destruction properties of singlet oxygen (or radicals). It is believed that during photosensitization in PDT, the photosensitizer (PS) molecule is first excited to the triplet state, and then transfers the energy to ground state oxygen to generate singlet oxygen, the chief cytotoxic species, which is responsible for oxidizing the substrate. The current manuscript reports on the conjugation of gold nanoparticles to phthalocyanine photosensitizers for possible combined PTT or PDT. Conjugates of phthalocyanines with spherical gold nanoparticles (AuNPs) have been reported [14–17], but there have been no reports on the conjugation of phthalocyanines with non-spherical AuNPs. Spherical AuNPs have a surface plasmon resonance (SPR) absorption band from 400 to 600 nm whereas anisotropy in AuNPs extends this absorption to the near infrared (NIR) region where there is greater light penetration of tissue. The Pc complex (**1**, Fig. 1) is linked to different shapes of AuNPs (rods, stars and bipyramids) and the fluorescence behavior and singlet oxygen generating ability is compared to the previously reported conjugate of complex **1** with spherical AuNPs [18]. Complex **1** is water soluble and contains Al as the central metal. Aluminum phthalocyanines are well known photosensitizers for PDT [10]. Tetrasulfonated AlPc (negatively charged) has been linked to gold nanorods (AuNRs) resulting in a two-fold enhancement ascribed to the surface plasmon coupling

* Corresponding author. Tel.: +27 46 6038260; fax: +27 46 6225109.

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

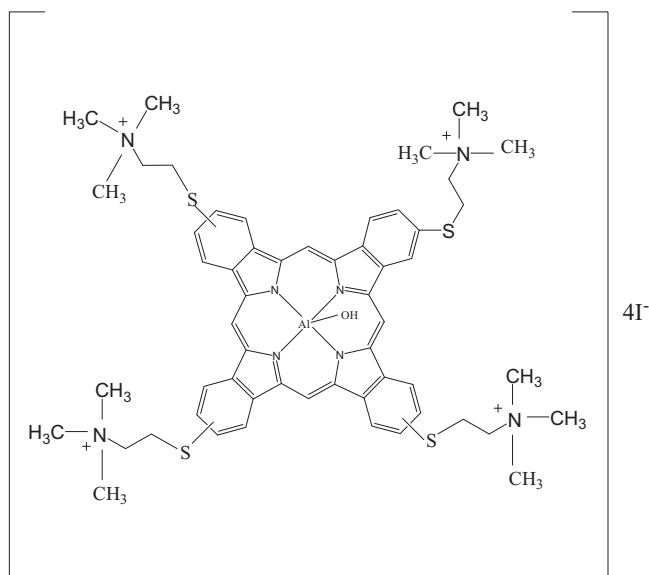


Fig. 1. Molecular structure of AlPc derivative (complex 1).

[19]. However, in this work we chose to use positively charged complex **1**, because quaternized MPC complexes are known to be more selectively accumulated in the mitochondria and improve cellular uptake [20,21], compared to anionic MPC complexes.

2. Experimental

2.1. Materials

Gold(III) chloride trihydrate, diphenylisobenzofuran (DPBF), sodium borohydride, trisodium citrate (99%), cetyltrimethylammonium bromide, (CTAB), silver nitrate and ascorbic acid were purchased from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) was obtained from Fluka. Nitric and hydrochloric acids were purchased from B&M Scientific. Deionized water was used for all solution preparations. The synthesis of AlPc complex **1** has recently been reported [18].

2.2. Instrumentation

Ground state electronic absorption spectra were performed on a Shimadzu UV-2550 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Varian Eclipse spectrofluorimeter. Fluorescence lifetimes were measured using a time correlated single photon counting (TCSPC) setup (FluoTime 200, Picoquant GmbH), as described before [22,23]. The concentration of gold nanoparticles (Au^0) was determined using a ThermoElectron ICAP 6000 inductively coupled plasma (ICP) spectrometer with an optical Emission spectroscopy (OES) detector. Gold nanoparticles were digested by addition of 3 mL of aqua regia for ICP measurements. Standard calibration was achieved at concentrations ranging from 0.5 to 5 ppm. A minimum of three measurements were made for each sample of gold nanoparticles. Gold was analyzed at wavelengths of 208, 242 and 267 nm.

Transmission electron microscope (TEM) images were obtained using a Zeiss Libra TEM 120 model operated at 90 kV accelerating voltage. TEM samples were prepared by placing a drop of the conjugates or nanoparticle solution on the sample grid and allowing it to dry before measurements. X-ray powder diffraction patterns were recorded on a Bruker D8 Discover equipped with a LynxEye detector, using $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$, nickel filter).

Details have been reported before [22]. Photodegradation for singlet oxygen quantum yields was carried out using a Halogen lamp, 600 nm glass (Schott) and water filters, to filter off ultraviolet and far infrared radiation, respectively as described before [24]. An interference filter (Intor, 670 nm with bandwidth of 40 nm) was placed in the light path just before the reaction vessel (which was a glass vial). The intensity of the light reaching the reaction vessel was measured with a power meter (POWER MAX 5100 Molelectron Detector Inc) and found to be 2.4×10^{20} photons $\text{cm}^{-2} \text{ s}^{-1}$.

2.3. Fluorescence and singlet oxygen quantum yields

Fluorescence (Φ_F) and singlet oxygen (Φ_Δ) quantum yields for the Pc and the conjugates were determined using the comparative methods as described before [25–28], using ZnPc as a standard in DMSO. Values of the ZnPc standard in DMSO used were as follows: $\Phi_F = 0.20$ [26] and $\Phi_\Delta = 0.67$ [27].

2.4. Synthesis of spherical gold nanoparticles, represented as AuSph

Spherical gold nanoparticles (represented as **AuSph**) were synthesized according to the method reported previously [29]. Briefly, a solution of $2.5 \times 10^{-4} \text{ M}$ (5 mL) trisodium citrate was added to $2.5 \times 10^{-4} \text{ M}$ (5 mL) HAuCl_4 solution at room temperature under vigorous stirring. A solution of NaBH_4 (0.1 M, 1 mL) was added and the mixture stirred at room temperature for 2 h. Gold nanospheres were purified by centrifuging the gold solutions at 2000 rpm for 20 min. The supernatant was removed and the solid nanoparticles were dispersed in 3 mL of distilled water.

2.5. Synthesis of non-spherical nanoparticles

Non-spherical gold nanoparticles of various shapes were synthesized by seed-mediated method as described by Chen et al. [5]. The syntheses of each cetyltrimethylammonium bromide (CTAB) coated shaped gold nanoparticles are described briefly below and the conditions are summarized in Table 1.

2.5.1. Seed solution

The seed AuNPs solution was prepared following the literature methods [5], using CTAB instead of sodium citrate (used in reference 5) as follows: an aqueous solution of $2.5 \times 10^{-4} \text{ M}$ (5 mL) HAuCl_4 was mixed with 10 mL of a 0.1 M CTAB solution, and the mixture stirred for 2 min. Then, 0.6 mL of an ice cold aqueous solution of 0.01 M NaBH_4 was added, and the mixture shaken for 2 min. The solution was allowed to stand for 30 min, and then used for the subsequent synthesis of shaped AuNPs.

2.5.2. Synthesis of gold nanorods (represented as AuRod) and gold bipyramids (represented as AuBP)

The growth solution was prepared according to the literature [5] by mixing 10 mL of 0.1 M CTAB, 5 mL of $2.5 \times 10^{-4} \text{ M}$ HAuCl_4 and 0.5 mL of 0.004 M AgNO_3 (for Au nanorods). To this solution, 0.4 mL of 0.1 M

Table 1
Reaction conditions for the synthesis of anisotropic gold nanoparticles.

Sample	[CTAB] (M)	[HAuCl_4] (M)	[AgNO_3] (M)	^a [AA] (M)	NaBH_4 (M)
AuSph	0.1	2.5×10^{-4}	–	–	0.01
AuRod	0.1	2.5×10^{-4}	0.004	0.1 M	–
AuBP	0.1	2.5×10^{-4}	0.04	0.1 M	–

^a AA=ascorbic acid.

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