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2(3), 9(10), 16(17), 23(24)-tetrakis[(3-mercapto)propoxy] phthalocyaninate zinc (II)/gold nanoparticle conjugates: Synthesis and photophysical properties

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In loving memory of Prof. Dr. Josefina Awruch.

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ABSTRACT

Novel stable zinc (II) thiol-phthalocyaninate gold nanoparticle nanoconjugates (PcS-AuNP) with a reproducible and homogeneous distribution size of 16 ± 4 nm were efficiently prepared by means of a ligand exchange reaction. The nanoconjugates were characterized by TEM, DLS, FT-IR and UV–vis. PcS-AuNP were a stable system at least for two months in darkness. Singlet molecular oxygen generation was observed when gold plasmon and phthalocyanine were independently excited at 510 nm and 610 nm, respectively. The PcS-AuNP system obtained is a photosensitive material in a wide range of the UV–vis spectrum (300–400 nm, 500–530 nm and 610–799 nm).

1. Introduction

The design of new multi-functional drug carriers has attracted great interest due to their diverse applications in medicinal chemistry. Gold nanoparticles (AuNP) have shown a great potential in the biomedical field [1–7]. Drug carriers based on gold nanostructures may preferentially and efficiently accumulate in tumor cells, through an enhanced permeation and retention (EPR) effect. The synthesis of AuNP in sizes of 1–150 nm usually requires the reduction of a gold salt with sodium borohydride or sodium citrate and a stabilizing agent [1,8,9]. A wide variety of stabilizing agents such as donor ligands, polymers and surfactants have been successfully employed for the synthetic route of AuNP [10]. Among them, thiols are excellent stabilizers, as they cap AuNP by means of a strong Au-S bonding [11–13].

The combination of a photosensitizer and metal nanoparticle is a powerful method to design photoactive agents with applications in imaging, sensing and in preclinical as well as clinical anti-cancer studies of photodynamic therapy. Many photoactive molecules have been reported to bind and modify the physicochemical properties of the AuNP [11,14]. Metallophthalocyanine complexes exhibit excellent spectroscopic and photochemical properties, such as an intense absorption peak at a longer wavelength in the red light region, where tissue penetration is enhanced; a high efficiency in the generation of reactive oxygen species upon illumination, an increased chemical stability and fluorescence [15–18]. Our group have investigated the synthesis and photodynamic properties of 2(3), 9(10), 16(17), 23(24)-tetrakis[(3-mercapto)propoxy] phthalocyaninate zinc(II) (HSPc) [19]. The UV–vis absorption spectra of phthalocyanine showed a Q band at 686 nm. Moreover, phthalocyanine was an excellent generator of singlet oxygen with a high value of quantum yield production of 0.61, along with a fluorescence quantum yield production of 0.34, these being the basic conditions for biological testing.

The application of conjugates of substituted phthalocyanines with SH terminal groups as well as disulfide moieties and AuNP has previously been reported as efficient singlet oxygen generators for drug delivery [11–13,20,21]. Such great interest in the development of a conjugated AuNP system has prompted us to investigate the synthesis and phototophysical properties of 2(3), 9(10), 16(17), 23(24)-tetrakis [(3-mercapto)propoxy]phthalocyaninatozinc(II)-AuNP (PcS-AuNP) in order to obtained a new non-toxicity nanoparticle system capable of generate singlet molecular oxygen for PDT purposes and also act as a biomarker for the detection of cancer cells.

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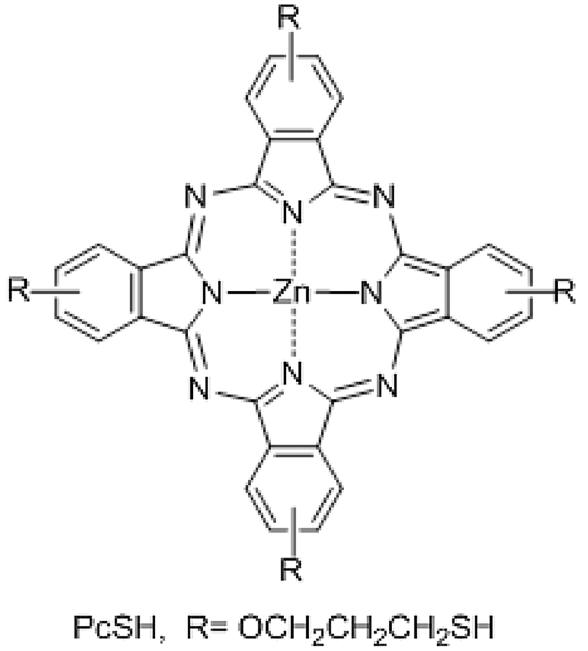

Scheme 1. Chemical structure of zinc(II) thiol-phthalocyanine.

2. Materials and methods

2.1. General

HSPc (Scheme1) were synthetized and characterized in our laboratory as described previously [19]. Sodium citrate, tannic acid, tetrachloroauric acid, *N,N*-dimethylacetamide (DMAc), chloroform ($CHCl_3$), methylene chloride, 1,3-Diphenylisobenzofuran (DPBF) and tetrahydrofuran (THF) were available commercially and were used without further purification. Milli-Q water was used for the preparation of gold nanoparticles.

2.2. Synthesis of gold nanoparticles (CAT-AuNP)

Gold nanoparticles were synthesized according to literature [22]. Briefly, a solution of water (20 mL) containing 4 mL of 1% sodium citrate and 0.05 mL of 1% tannic acid was heated to 60 °C and added under stirring to a solution of 0.25 mM tetrachloroauric acid (1 mL) in water Milli-Q (80 mL) kept at 60 °C. As soon as a ruby-red color solution was obtained, the reaction mixture was maintained at 60 °C under stirring for 10 more minutes. The resultant suspension contained AuNps in the synthesis medium at pH = 5. A solution of sodium citrate (1 mM) and tannic acid (3 μM), with pH = 5, which was analogous to the medium in which the gold nanoparticles were dispersed, was used as control solution. A citrated capped gold nanoparticle (CA-AuNP) was also prepared according to Brust's methods [23].

2.3. Preparation of PcS-AuNP

The PcS-AuNP nanoparticles were prepared by ligand exchange reactions from citrate-tannic acid-capped gold nanoparticles. A solution of 2(3), 9(10), 16(17), 23(24)-tetrakis [(3-mercapto)propoxy]phthalocyaninato zinc(II) (HSPc) [19] in *N,N*-dimethylacetamide (DMAc) (5.8×10^{-4} M, 3 mL) was slowly added by means of a syringe to an aqueous solution of AuNP. The mixture was stirred and heated at reflux for 18 h to promote the coordination of thiol groups onto the nanoparticle surface. The color changed from ruby-red to violet. The nanoparticles became insoluble in water but soluble in the DMAc, indicating that ligand exchange has been achieved. After removing the solvent under reduced pressure, the strong violet residue was dried under vacuum at 60 °C for 3 days. After washing the residue with water, methanol, and methylene chloride, tetrahydrofuran (THF) was added to obtain a pure PcS-AuNP solution.

2.4. Nanoparticle characterization

2.4.1. Transmission electron microscopy (TEM)

Transmission electron microscopy images were obtained by means of a JEON 1210, 120 kV, equipped with an analyzer EDS LINK QX 2000, 200 keV, 5 nm resolution. In order to perform the TEM observations, the concentrated suspensions were diluted in place onto a grid covered with Fomvar film and the excess was drawn off with nitrogen flux. Samples were subsequently stained with uranyl acetate solution for 30 s. The droplet diameter was estimated using a calibrated scale.

2.4.2. Dynamic light scattering

The average hydrodynamic diameter (Dh) and the size distribution of gold nanoparticles were measured by dynamic light scattering (DLS). DLS measurements were performed using a DLS 90 Plus/BI-MAS (Brookhaven Instrument Co, EE.UU.), equipped with a laser He-155 Ne laser operating at 632.8 nm and a Zeta-Potential Analyzer (Brookhaven Instrument Corp, EE.UU). DLS spectra were measured at room temperature in milli-Q water. Experiments were carried out without photosensitizer to prevent fluorescence interference in the DLS signals.

2.4.3. Gold nanoparticle stability

The stability of CAT-AuNP was studied at 25 °C for 2 months. Aliquots of colloid sample were reserved in sealed containers at 25 °C in darkness. All storage mixtures were characterized by UV–vis spectroscopy. The UV–vis spectra of samples were recorded during the incubation time at different intervals and the maximum wavelengths (max) obtained were reported.

2.4.4. Infrared spectra were recorded with a Perkin Elmer Spectrum One FT-IR spectrometer

2.4.4.1. UV–vis and fluorescence measurements. Electronic absorption spectra were determined with a Shimadzu UV-3101 PC spectrophotometer using a 10 x 10 mm quartz cuvette. All the experiments were performed at room temperature. Electron energy spectra were collected with a 150 mm hemispherical analyzer placed at 90° from the light beam in the horizontal plane; all the spectra were recorded with the sample oriented such that the surface normally made an angle of 45° with both the photon beam and the emission direction.

Fluorescence spectra were monitored with a QuantaMaster Model QM-1 PTI spectrofluorometer. The emission spectra of PcS-AuNP were collected at an excitation wavelength of 470 nm, 522 nm and 610 nm and recorded up to 800 nm. Fluorescence quantum yields (Φ_F) were determined by comparison with 2,3,9,10,16,17,23,24-octakis[(*N,N*-dimethylaminoethylsulfanyl)]phthalocyaninate zinc (II) ($\Phi_F = 0.26$ in THF) [24] as a reference at $\lambda_{exc} = 610$ nm. Calculations were performed by Eq. (1).

$$\Phi_F^S = \Phi_F^R \frac{I^S\,(1-10^{-A^R})}{I^R\,(1-10^{-A^S})}\left(\frac{n^S}{n^R}\right)^2 \tag{1}$$

where *R* and *S* superscripts refer to the reference and the sample respectively; *I* is the integrated area under the emission spectrum; *A* is the absorbance of solutions at the excitation wavelength and $(n^S/n^R)^2$ stands for the refractive index correction.

2.4.4.2. Singlet oxygen quantum yield. Standard chemical monitor bleaching rates were used to calculate the singlet oxygen quantum yield (Φ_Δ). [25] For Φ_Δ studies, diphenylisobenzofuran (DPBF) was used as a singlet oxygen chemical quencher. To avoid chain reactions induced by DPBF in the presence of singlet oxygen, the absorbance of DPBF was under 1.9 using a 10 x 10 mm quartz cuvette. DPBF decay at

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