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Photophysics of an octasubstituted zinc(II) phthalocyanine incorporated into solid polymeric magnetic and non-magnetic PLGA–PVA nanoparticles

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ABSTRACT

2,3,9,10,16,17,23,24-octakis[(*N,N*-dimethylaminoethylsulfanyl)]phthalocyaninatozinc (II) (**S1**) was used as a lipophilic photosensitizer to be encapsulated into biodegradable poly(D,L lactide-co-glycolide)-polyvinyl alcohol nanoparticles. The synthesis, size, and spectroscopic, photophysical, and magnetic properties of nanoparticles, were analyzed. A greater number of sonication cycles afforded smaller nanoparticles. The stabilization by means of polyvinyl alcohol of all the nanoparticles synthesized provided a negative charge to the systems in a wide pH range. The thermograms obtained by differential scanning calorimetry showed that the nanoparticles were stabilized by polyvinyl alcohol. The incorporation of magnetite nanoparticles was verified by FT-IR, magnetization measurements by means of hysteresis curves and potential Z. **S1** retained its efficiency in generating singlet oxygen. The incorporation of magnetite into the nanoparticles showed an increase in singlet oxygen quantum yields due to the heavy atom effect.

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1. Introduction

Carriers are frequently used to deliver drugs through the body to protect them from degradation and excretion, to prevent adverse side effects of toxic drugs, or to accomplish targeted drug delivery. Different materials such as liposomes, micelles, gels, mesoporous silica nanoparticles, gold nanoparticles, and semiconductor quantum dots have been postulated as photosensitizer carriers [1–7].

Nanocarriers are used to improve the solubility, bioavailability and controlled release of drugs. However, there are some problems related to toxicity that require special attention [8]. Nanomaterials have special surface, size (0.1–100 nm), and macroscopic quantum tunneling effects. These properties allow nanoparticles to be used in fields such as medicine, electricity, optics, magnetism and catalysis [2,7,9–12].

Nanoparticles of biodegradable polymers can be used as injectable carriers for drug targeting [13]. Among them poly (D,L lactide-co-glycolide) (PLGA) nanoparticles have been used as drug carrier systems for many pharmaceutical drugs and photosensitizers [14,15]. However, the uptake of PLGA nanoparticles by the reticuloendothelial system after intravascular administration presents a major problem to procure an effective targeting to specific sites in the body. The strategy most commonly used to design long-circulating nanoparticles consists in coating them with hydrophilic or hydrophobic copolymers such as Polyethylene glycol (PEG) or polyvinyl alcohol (PVA) [16].

Magnetic nanomaterials are of particular interest and have been used in biological medicine, and also as drug carriers for biological molecular probes [17]. Superparamagnetic iron oxide nanoparticles covered with biocompatible polymers can yield powerful targeted delivery vehicles. These nanoparticles provide a stronger and more rapid magnetic response than bulk magnets when a magnetic field is applied. These nanoparticles can be routed to the target cell by applying a magnetic field [18,19].

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On the basis of these results, further studies have been initiated to investigate the synthesis of magnetic nanoparticles encapsulated into biodegradable PLGA–PVA. In the present study, 2,3,9,10,16,17,23,24-octakis[(*N,N*-dimethylaminoethylsulfanyl)]-phthalocyaninatozinc(II) (S1) [20] was used as a lipophilic photosensitizer to be encapsulated into the nanoparticles. The spectroscopic, photophysical, photochemical, and magnetic properties, as well as the nanoparticle size, were analyzed.

2. Materials and methods

2.1. Materials

Poly(D,L lactide-co-glycolide) 50:50 (PLGA), polyvinyl alcohol (PVA, average Mw 9000–10,000 Da, 80% hydrolyzed), *N,N*-diethyl-4-nitrosoaniline 97%, imidazole $\geq 99\%$, tetrahydrofuran (THF) was of analytical grade, and methylene chloride (distilled) were purchased from Sigma-Aldrich. Methylene Blue (MB) was purchased from Fluka. Monodisperse magnetic nanocrystals stabilized with polyethyleneimine (PEI) was a gift from Centro Atómico Balseiro, Argentina [21]. 2,3,9,10,16,17,23,24-octakis[(*N,N*-dimethylaminoethylsulfanyl)]phthalocyaninatozinc(II) (S1) was synthesized as described elsewhere [22] (Fig. 1)

2.2. Instrumentation

Electronic absorption spectra were determined with a Shimadzu UV-3101 PC spectrophotometer and fluorescence spectra were monitored with a QuantaMaster Model QM-1 PTI spectrofluorometer. pH was measured with a Thermo pH meter Altronix TPX-1. Transmission electron microscopy (TEM) images were obtained by means of an EM 301 Phillips operating at 65 kV. Vortex-mixing was performed by means of a VEP Scientific ZX Classic. The sonicator used was MSE Soniprep 150. Z potential measurements were determined with a Zeta-Potential Analyzer (Brookhaven Instrument Corp.). Magnetic studies were carried out in a commercial superconducting quantum interferometer device (SQUID) magnetometer up to 10 kOe. Infrared spectra were recorded with a Perkin Elmer Spectrum One FT-IR spectrometer. Differential scanning calorimetry and thermal stability of the

samples were performed with an SDT 2960 system (TA Instruments).

2.3. Preparation of nanoparticles

Nanoparticles were prepared by an oil/water emulsion-solvent evaporation method [23]. PLGA was dissolved in methylene chloride at a final concentration in the range of 2×10^{-5} M– 7×10^{-6} M. For blank nanoparticles (NPs), 10 mL of polymer solution was mixed with 20 mL of PVA 3% water solution and emulsified by one or more cycles for 10 min each in a 450 W ultrasonicator. The solution was then concentrated under reduced pressure with constant stirring, removing the organic solvent. Finally, the NPs obtained as a suspension were lyophilized and stored at 4 °C until further use.

Dye and magnetite were incorporated in the organic phase. The final concentration of the dye was 0.5 μ M and 53 μ M, whereas the magnetite concentration was 30 mg/mL solution.

2.4. Differential scanning calorimetry (DSC)

The composition of NPs was characterized by the analysis of the DSC curves. The curves were obtained in a DSC cell (Shimadzu DSC 60) using aluminium crucibles with about 3 mg of samples, under dynamic air atmosphere (100 mL/min) and heating rate of 30 °C/min at a temperature range from 20 to 500 °C. The DSC cell was calibrated with indium (m.p. 156.6 °C; $\Delta H_{\text{fus}} = 28.54$ J/g) and zinc (m.p. 419.6 °C).

2.5. Z potential of blank nanoparticles (NPs) and nanoparticles with magnetite (NPs-Fe₃O₄)

The electrophoretic mobility of the particles was recorded from a total of 10 cycles of 50 seconds each according to Smoluchowsky's model with a residual error < 0.035 [24].

Measurements were performed at a concentration of 10^{-5} M for all nanoparticles. For all experiments, the ionic strength was kept constant by incorporating 0.15 M KNO₃ and adjusting the pH from 1.9 to 10.2.

2.6. Magnetic measurements

Magnetic measurements were performed at room temperature ($T = 300$ K) and $T = 4$ K for magnetite and at $T = 5$ K for NPs-Fe₃O₄ in the range of $H = \pm 10$ kOe. The magnetization was normalized to the saturation value of the particles (about 40 emu/g in the systems studied).

2.7. Determination of S1 incorporation into NPs and NPs-Fe₃O₄

The incorporation efficiency was determined using UV–vis spectroscopy. The maximum absorbance intensity of S1 at 680 nm of the supernatant and washings after the incorporation of S1 into the NPs and NPs-Fe₃O₄ was subtracted from the starting concentration. The percentage of incorporation of S1 in all the nanoparticles was 33%.

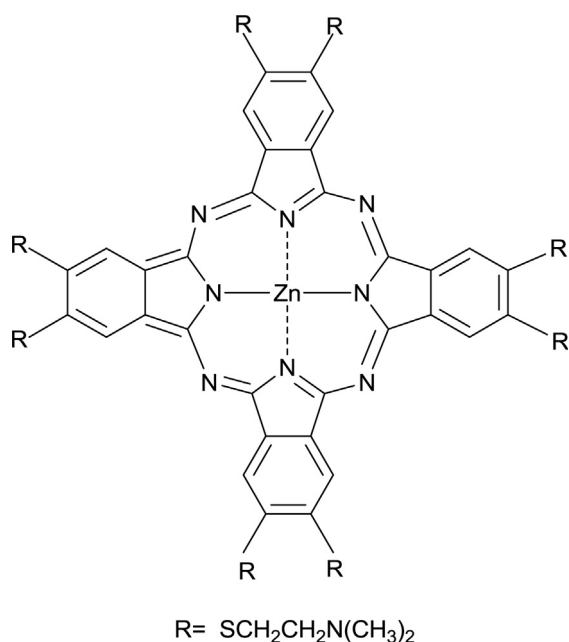


Fig. 1. Chemical structure of phthalocyanine S1.

Table 1

Monomer–dimer ratio and photophysical parameters of S1 in THF, S1–NPs and S1–NPs–Fe₃O₄.

| | S1-THF ^a | S1-NPs | S1-NPs-Fe ₃ O ₄ |
|---------------|---------------------|---|---|
| [S1]/M | 1×10^{-7} | 3.2×10^{-7} ; 4.8×10^{-5} | 3.2×10^{-7} ; 4.8×10^{-5} |
| Monomer/Dimer | 7.0 | 0.58; 0.46 | 0.60; 0.44 |
| Φ_F | 0.26 | 0.25; 0.11 | 0.03; 0.04 |
| Φ_Δ | 0.69 | 0.22; 0.11 | 0.23; 0.22 |

^a Ref. [35].

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