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The photobleaching of the free and encapsulated metallic phthalocyanine and its effect on the photooxidation of simple molecules

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ABSTRACT

The photobleaching of an unsubstituted phthalocyanine (gallium(III) phthalocyanine chloride (GaPc)) and a substituted phthalocyanine (1,4-(tetrakis[4-(benzyloxy)phenoxy]phthalocyaninato) indium(III) chloride (InTBPPc)) was monitored for the free photosensitizers and for the phthalocyanines encapsulated into nanoparticles of PEGylated poly(D,L-lactide-*co*-glycolide) (PLGA-PEG). Phosphate-buffered solutions (PBS) and organic solutions of the free GaPc or the free InTBPPc, and suspensions of each encapsulated photosensitizer (2–15 μmol/L) were irradiated using a laser diode of 665 nm with a power of 1–104 mW and a light dose of 7.5 J/cm^2. The relative absorbance (RA) of the free GaPc dissolved in 1-methyl-2-pyrrolidone (MP) decreased 8.4 times when the laser power increased from 1 mW to 104 mW. However, the free or encapsulated GaPc did not suffer the photobleaching in PBS solution. The RA values decreased 2.4 times and 22.2 times for the free InTBPPc dissolved in PBS solution and in dimethylformamide (DMF), respectively, but the encapsulated InTBPPc was only photobleached when the laser power was 104 mW at 8 μmol/L. The increase of the free GaPc concentration favored the photobleaching in MP until 8 μmol/L while the increase from 2 μmol/L to 5 μmol/L reduced the photodegradation in PBS solution. However, the photobleaching of the free InTBPPc in DMF or in PBS solution, and of each encapsulated photosensitizer was not influenced by increasing the concentration. The influence of the photobleaching on the capability of the free and encapsulated GaPc and InTBPPc to photooxidate the simple molecules was investigated monitoring the fluorescence of dimethylanthracene (DMA) and the tryptophan (Trp). Free InTBPPc was 2.0 and 1.8 times faster to photooxidate the DMA and Trp than it was the free GaPc, but the encapsulated GaPc was 3.4 times more efficient to photooxidize the Trp than it was the encapsulated InTBPPc due to the photodegradation suffered by the encapsulated InTBPPc. The participation of the singlet oxygen was confirmed with the sodium azide in the photobleaching of all free and encapsulated photosensitizer, and in the photooxidation of the DMA and Trp. The asymmetry of InTBPPc increased the solubility of the free compound, decreasing the aggregation state of the photosensitizer and favoring the photobleaching process. The encapsulation shows capability in decreasing the photobleaching of both photosensitizers but the confocal micrographs showed that the increase of the solubility favored the InTBPPc photobleaching during the acquisition of optical cross section.

1. Introduction

Phthalocyanines are a class of compounds used as photocatalysts [1], dyes and pigments [2], photosensitizers in the cancer treatment [3], the photoinactivation of bacteria and viruses [4], semiconductor devices [5] and in routine diagnostic procedure [6]. These applications are because of the phthalocyanines excellent electronic, spectroscopic and chemical properties [7].

In particular, there is a great interest in the study of these compounds for use in photodynamic therapy (PDT) due to their intense absorption in the therapeutic window (600–800 nm) and their ability to generate singlet oxygen under light irradiation. PDT is a therapeutic modality that combines a photosensitizer, a source of light and oxygen molecules to generate cytotoxic species (singlet oxygen and/or reactive oxygen species) that cause the death of diseased tissue. Researchers have shown that the presence of heavy-atom in the phthalocyanine structure (such as indium and gallium) favors the generation of singlet

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