Is there difference in the DMA and the tryptophan photooxidation sensitized by free and encapsulated phthalocyanine derivatives?

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Abstract

It was evaluated the dimethylanthracene and the tryptophan photooxidation sensitized by free and encapsulated phthalocyanines that suffer different photobleaching.

Introduction

Studies have shown that how much more the photosensitizer is photobleached, the greater is the intensity of photobiological damage[1]. Phthalocyanines have tendency to suffer photobleaching[2]. The free Ga(III)-phthalocyanine (GaPc) and In(III)-tetrakis(benzyloxy)phenoxy-phthalocyanine (InTBPPc) suffer different photobleaching due to its photophysical properties. InTBPPc was photobleached faster than the GaPc was in organic solvent, and InTBPPc was also the only photosensitizer photobleached in the phosphate-buffered solution (PBS). However, neither of the encapsulated compounds in PEGlated polylactide-co-glycolide (PLGA-PEG) nanoparticles were photobleached. But how these free and encapsulated compounds act as photosensitizers in different solvents? To answer this question, we investigated the photooxidation of dimethylanthracene (DMA) and tryptophan (Tryp), in organic and aqueous medium, respectively, sensitized by free and encapsulated GaPc and InTBPPc, as well as, the participation of the singlet oxygen in the process.

Results and Discussion

Solutions of free GaPc or free InTBPPc (8 μmol/L) in organic solvent (methylpyrrolidone for the GaPc and dimethylformamide for InTBPPc) containing DMA (19 μmol/L), or in PBS (pH 7.4) containing Tween® 20 (0.24 mmol/L) with 3% of organic solvent and Tryp (19 μmol/L), were irradiated using a laser diode 665 nm with a light dose of 0.025-10 J/cm^2 and a power of 104 mW. The same experiment was performed for the encapsulated compounds in PBS solution but without organic solvent. The fluorescence intensity of DMA (λ_{ex} = 380 nm and λ_{em} = 390-600 nm) and of Tryp (λ_{ex} = 263 nm and λ_{em} = 390-600 nm) was monitored before and after irradiation, in the presence or absence of azide. Free InTBPPc was 2.0 times more efficient to photooxidate the DMA than it was the free GaPc since the rate constant (k) was (1.97 ± 0.05)x10^{-1} s^{-1} and (0.99 ± 0.02)x10^{-1} s^{-1}, respectively (Figure 1). The k value decreased 5.3 and 9.3 times in the presence of azide for GaPc and InTBPPc, corroborating the participation of the singlet oxygen in the photooxidation process. Similar efficiency was observed in the Tryp photooxidation, since the k value was 2.1 times greater when Tryp was photooxidated by free InTBPPc ((1.5 ± 0.3)x10^{-9} s^{-1}) than it was by free GaPc ((0.7 ± 0.1)x10^{-9} s^{-1}). Although the singlet oxygen quantum yield of GaPc (Φ_Δ = 0.41) is 2.3 times smaller than for InTBPPc (Φ_Δ = 0.94), the encapsulated GaPc was 3.3 times more efficiency to photooxidate Tryp than the encapsulated InTBPPc since the k value was (1.9 ± 0.1)x10^{-4} s^{-1} and (0.56 ± 0.03)x10^{-4} s^{-1}, respectively. This result might related to the small loading percentage of InTBPPc into the nanoparticle. The involvement of singlet oxygen was corroborated for all photooxidation in the PBS solution, but the k value with azide was decreased much less than it was in organic solvent.

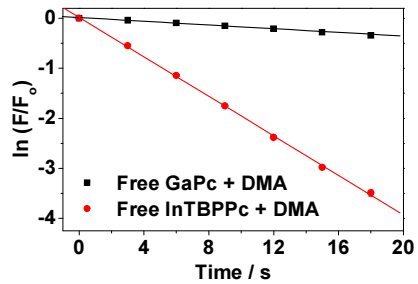

Figure 1. DMA photooxidation in the presence of free GaPc and free InTBPPc

Conclusion

The free InTBPPc was more efficient to photooxidate the DMA and the Tryp in organic and in PBS solution, although the free InTBPPc be more easily photodegraded than the free GaPc. However, the GaPc was the most effective when encapsulated into the PEGlated-PLGA nanoparticles.

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