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Light-driven antimicrobial therapy of palladium porphyrins and their chitosan immobilization derivatives and their photophysical-chemical properties

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ABSTRACT

The emergence of antimicrobial resistance has made the development of photodynamic therapy (PDT) related applications essential, since microorganisms can not form resistance to this method. Porphyrins are well-known photosensitizers for PDT related applications. Thus, the present study outlines the synthesis, characterization and evaluation of the utility of palladium porphyrins and their chitosan inclusion complexes as photosensitizer dye in photodynamic antimicrobial therapy (PACT). Before *in vitro* cell studies, the photophysical-chemical studies of all obtained structures were performed in solution. It was observed that the immobilization of the porphyrins into the chitosan influenced the photophysical-chemical and PACT activity properties. The determined fluorescence quantum yield was very low, in the range of 0.007–0.028 for all samples indicating the efficient triplet state population to cause high singlet oxygen quantum yield (Φ_Δ). The measured Φ_Δ values were in the range of 0.51–0.61 for the porphyrins and 0.53–0.66 for porphyrin chitosan immobilization complexes. Our results demonstrate that the PACT activity of cationic porphyrin (**P3**) and its chitosan immobilization form (**P3-Ct**) were more efficient in decreasing the number of viable cells up to 100% *in vitro*.

1. Introduction

The porphyrins are an important class of macrocyclic bioorganic molecules that occur naturally in biological living organisms. Haemoglobin contains iron porphyrins responsible for oxygen transportation in red blood cells and oxygen storage in living tissue, and magnesium-chlorin (reduced porphyrin) found in chlorophyll are the most important examples [1]. The porphyrins are of particular interest in many applications, such as molecular sensors, light-harvesting, energy and electron transfer, boron neutron capture therapy, nonlinear optics and catalysis, mainly due to their outstanding physical, chemical and spectroscopic properties [2–7].

Porphyrins are suitable molecular dyes for photodynamic therapy (PDT) applications, a therapeutic method for many diseases, including cancer [8]. PDT requires the administration of a photosensitizer (PS) drug in conjunction with the light of appropriate wavelength to form a cytotoxic effect [9]. Upon photoexcitation, the PS is excited to its lowest energy singlet excited state (^{1}PS*). If the PS can undergo non-radiative intersystem crossing (ISC), the converted PS is converted to the triplet excited state (^{3}PS*). Subsequent energy transfer to molecular dioxygen, produces highly cytotoxic species, such as singlet oxygen, causing photoinduced damage to the tumor cells or bacteria [10]. This method has been used to kill cancer cells or microbial infections.

Infectious diseases are still one of the biggest health problems worldwide. The situation has been exacerbated due to the emergence of antibiotic resistance. For this reason, new treatment methods have gained importance in the fight against antimicrobial resistance [11]. Photodynamic antimicrobial therapy (PACT) applying the mechanism described above has been considered as a promising strategy for treating pathogen-associated infections [12]. The PACT method provides significant advantages over traditional antibiotic treatments against a wide range of bacteria for antibiotic-sensitive and antimicrobial resistance since bacteria cannot readily develop resistance to singlet oxygen [13].

Porphyrins are widely used for PACT since they fit the properties required to form an ideal photosensitizer, such as significant absorption in the visible region, high molar absorptivity, and relatively high triplet state quantum and singlet oxygen yields [13]. Among the PS dyes that have been studied, positively charged macrocycles have been found to

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