The photobleaching of cationic porphyrins - 5,10,15,20-tetrakis (1-methyl-X-pyridyl)porphyrin ($H_2TMXPyP^{4+}$), with X = 2, 3, and 4

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Abstract

The 5,10,15,20-tetrakis(1-methyl-X-pyridyl)porphyrin, with X = 2, 3, and 4, manifested an insignificant degree of photobleaching.

Introduction

Photodynamic Therapy (PDT) is an alternative treatment for different types of diseases. It is based on the accumulation of a photosensitizer compound (PS) in diseased tissue, followed by its excitation by light at the appropriate wavelength. The PS in the excited state reacts with molecular oxygen of tissues generating reactive oxygen species (ROS).[1] These species can act in a way that causes the death of diseased cells. However, ROS can also act on the PS destroying it. This phenomenon is known as photobleaching.[2] The analysis of this process is important in evaluating the photostability of photosensitizers and it can assist in determining the PS dosage required for use in PDT.[2]

In this paper, the photobleaching (PB) process of the series of cationic porphyrins - the 5,10,15,20-tetrakis(1-methyl-X-pyridyl)porphyrin ($H_2TMXPyP^{4+}$), with X = 2, 3, and 4 (Figure 1), was studied.

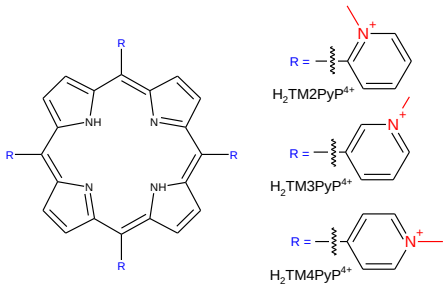

Figure 1. Studied porphyrins.

Results and Discussion

Solutions with porphyrin (5.0×10^{-5} M) in a potassium phosphate buffer and sodium hydroxide (pH = 7.6) were subjected to continuous illumination with a red LED system (625-740 nm) at room temperature. The process was monitored every 10 minutes, over a period of 120 minutes, using absorption spectra in the UV-visible region.

All the porphyrins have a very small degree of photobleaching, according to the literature data (Table 1).[2-4]

Table 1. The degree of photobleaching of some compounds.

Compound	Degree of photobleaching (%)
$H_2TM2PyP^{4+}$	**4.25**
$H_2TNBByP$[a]	5.20
$H_2TM3PyP^{4+}$	**9.20**
$H_2TM4PyP^{4+}$	**12.60**
ChlorophyllA[b]	70.00

[a] 5,10,15,20–tetrakis(N-4-nitrobenzil-4-piridil)porphyrin ($H_2TNBByP$) under 60 minutes of irradiation with red LED.[3]

[b] Chlorophyll A was subjected to 50 minutes of irradiation with red LED.[4]

The degradation of porphyrins by ROS is modified by changing the pyridyl methyl substituent position with respect to the porphyrin macrocycle. The degree of PB follows an ascending order with the change in group substituent position: ortho<meta<para.

The intensity of the PB is related to the value of the photodynamic activity (PA) of Fischer's Method.[5] In a study in development, we determined that PA($H_2TM3PyP^{4+}$) = 166 and PA($H_2TM4PyP^{4+}$) = 51. Although the $H_2TM3PyP^{4+}$ generated more singlet oxygen than $H_2TM4PyP^{4+}$, the first was less sensitive to PB. This is a fundamental characteristic of the photosensitizer to photodynamic therapy.

The $H_2TM2PyP^{4+}$ had the lower PB characteristics which could increase the probability of a reaction between formed ROS and diseased cells. Quantitative studies, measuring the ability to generate singlet oxygen (PA), are already in development with the $H_2TM2PyP^{4+}$ utilizing Fischer's Method.[5]

Conclusions

All three cationic porphyrins examined were relatively photostable under the studied conditions. Therefore, the series of porphyrins 5,10,15,20-tetrakis(1-methyl-X-pyridyl)porphyrin ($H_2TMXPyP^{4+}$), with X = 2, 3, and 4, demonstrated potential as photosensitizers in photodynamic therapy.

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