The photobleaching of cationic porphyrins - 5,10,15,20-tetrakis (1-methyl-X-pyridyl)porphyrin (H₂TMXPyP⁺⁺), with X = 2, 3, and 4

Camila Soares Monteiro (PG), Sophia Vieira Macedo (IC), Ynara Marina Idemori (PQ), Dayse Carvalho da Silva Martins* (PQ)

Departamento de Química – ICEX – Universidade Federal de Minas Gerais. *daysecsm@yahoo.com.br

Keywords: Photodynamic therapy, Porphyrins, Photobleaching.

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 with light at the appropriate wavelength. The PS in the excited state reacts with molecular oxygen of tissues generating reactive oxygen species (ROS). 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. 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.

In this paper, the photobleaching (PB) process of the series of cationic porphyrins - the 5,10,15,20-tetrakis(1-methyl-X-pyridyl)porphyrin (H₂TMXPyP⁺⁺), with X = 2, 3, and 4 (Figure 1), was studied.

![Figure 1. Studied porphyrins.](image)

Table 1. The degree of photobleaching of some compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Degree of photobleaching (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂TM2PyP⁺⁺</td>
<td>4.25</td>
</tr>
<tr>
<td>H₂TNBBByP⁺⁺</td>
<td>5.20</td>
</tr>
<tr>
<td>H₂TM3PyP⁺⁺</td>
<td>9.20</td>
</tr>
<tr>
<td>H₂TM4PyP⁺⁺</td>
<td>12.60</td>
</tr>
<tr>
<td>ChlorophyllA⁺⁺</td>
<td>70.00</td>
</tr>
</tbody>
</table>

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. In a study in development, we determined that PA(H₂TM3PyP⁺⁺) = 166 and PA(H₂TM4PyP⁺⁺) = 51. Although the H₂TM3PyP⁺⁺ generated more singlet oxygen than H₂TM4PyP⁺⁺, the first was less sensitive to PB. This is a fundamental characteristic of the photosensitizer to photodynamic therapy.

The H₂TM2PyP⁺⁺ 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 H₂TM2PyP⁺⁺ utilizing Fischer’s Method.

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 (H₂TMXPyP⁺⁺), with X = 2, 3, and 4, demonstrated potential as photosensitizers in photodynamic therapy.

Acknowledgements

UFMG, CAPES, CNPq, Fapemig.

---