Wavelength dependence of the efficiency of singlet oxygen generation upon photoexcitation of photosensitizers

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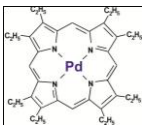
Abstract. The dependence of the efficiency of singlet oxygen ($^1\Delta_g$) generation upon excitation of photosensitizer at different wavelength was observed for several derivatives of palladium porphyrin in carbon tetrachloride. The efficiency of singlet oxygen generation upon excitation in a blue region of the spectrum (Soret band) exceeds by several times the efficiency at excitation in the red spectral region (Q band). The effect of enhancement of singlet oxygen generation upon CW photoexcitation to Soret band of photosensitizer may be explained by influence of high laying triplet states of a donor molecule on the triplet-triplet energy transfer.

Metallocomplexes of porphyrins have been widely used as photosensitizers for the singlet oxygen generation during more than 40 years [see 1.2 and references therein]. The singlet oxygen generation in this case occurs by means of triplet-triplet energy transfer between primarily populated triplet state of photosensitizer and the ground state of molecular oxygen (triplet state - $^3\Sigma^-_g$). The singlet oxygen luminescence has been often used for determination of efficiency of singlet oxygen generation. In many cases, a monochromatic laser light at the visible spectral range has been used as a source of population of the triplet state of photosensitizer. It seems quite interesting to study how the efficiency of singlet oxygen generation depend on wavelength of photoexcitation. The detection of excitation spectra of singlet oxygen luminescence at a whole spectral range of absorption of photosensitizer looks as an appropriate tool for this goal. The method allows to determine the spectral ranges in the absorption spectrum of the sensitizer with the most efficient singlet oxygen generation.

Two peripherally substituted derivatives of porphyrin: Pd-2,3,7,8,12,13,17,18-octaethylporphyrin and Pd-5,10,15,20-tetraphenylporphyrin were investigated (Fig. 1).



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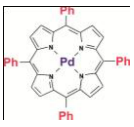

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Fig. 1. Structure of Pd-OEP(**1**) and Pd-TPP(**2**)

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Fluorescence, phosphorescence and fluorescence excitation spectra as well as excitation spectra of Pd-TPP measured at wavelength of singlet oxygen luminescence ($\lambda_{rec.}$=1274 nm) have been recorded at ambient temperature and normal pressure in carbon tetrachloride solution (Fig. 2).

As is evident from Fig. 2, the excitation spectrum of singlet oxygen luminescence for Pd-TPP photosensitizer (1) has significantly higher intensity in the region of the Soret band in comparison to the Pd-TPP fluorescence excitation spectrum (2) which, at the same time, is well correlated with

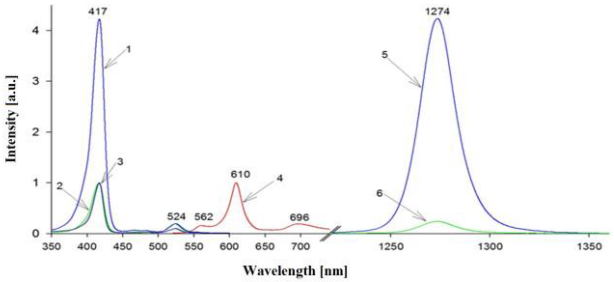

Fig. 2. Excitation spectrum of Pd-TPP at $\lambda_{rec.}$=1274 nm (1), fluorescence excitation spectra at λrec.=610 nm (2), absorption spectrum (3), fluorescence spectrum at $\lambda_{exc.}$=417 nm (4), luminescence spectra of singlet oxygen excited at 417 nm (5) and 524 nm (6)

Pd-TPP absorption spectrum (3). The experimental data allows to conclude that the efficiency of singlet oxygen generation in the case of Pd-TPP photosensitizer is significantly higher for excitation in the Soret band ($\lambda_{exc.}$= 417 nm) than for excitation in the visible region of the spectrum - Q band ($\lambda_{exc.}$=562 nm). Previously, the similar behavior of excitation spectra of singlet oxygen luminescence measured in spectral range of absorption of photosensitizer were reported in [3,4] for other porphyrin derivatives, but the origin of this effect was not well explained.

Photochemical generation of singlet oxygen occurs in result of a triplet-triplet energy transfer between the excited lowest triplet state of photosensitizer and the ground (triplet) state of molecular oxygen. The Pd-TPP exhibits a very strong and wide triplet-triplet absorption band centered at 462 nm (Fig. 3). Taking into account a continuous wave excitation used during the above-mentioned experiment, as well as, an overlap of that strong triplet-triplet absorption band with the ground state absorption in the region of Soret band, an influence of higher triplet states of Pd-TPP on singlet oxygen generation can be postulated. To answer what is the exact origin of the dependency of singlet oxygen generation on wavelength of excitation of photosensitizer an additional experiments needed.

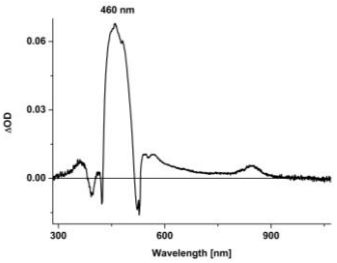

Fig. 3. Triplet-triplet absorption spectrum of Pd-TPP.

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