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EVIDENCES OF 5,10,15,20-TETRAKIS-(3-*N*-METHYLPYRIDYL)-PORPHYRIN ATROPOISOMERIZATION IN SOLUTION

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The water-soluble 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin has been known of about 40 years [1] and its spectral-luminescent properties have been studied repeatedly. Due to unrestricted rotation of the pyridyl substituents around the C_{meso}-C_1 bond, the quaternized nitrogen atom of *meta*-substituted pyridyl may reside either on the one, or on the another side of the porphyrin macrocycle plane, giving rise to the different structural atropoisomers. However, up until now the possibility of formation of several atropoisomeric conformations have not been considered, most likely, due to the opinion that electronic communication between the aryl substituent in the *meta*-position and the porphyrin macrocycle is too weak to be able to give rise to the noticeable spectral changes. However, the accurate spectral studies in the time scale up to 1600 hours after the sample preparation have revealed the temporal evolution of the ground state absorption spectrum as well as that of the fluorescence spectrum [2]. In this work we present the results of the detailed study of this issue.

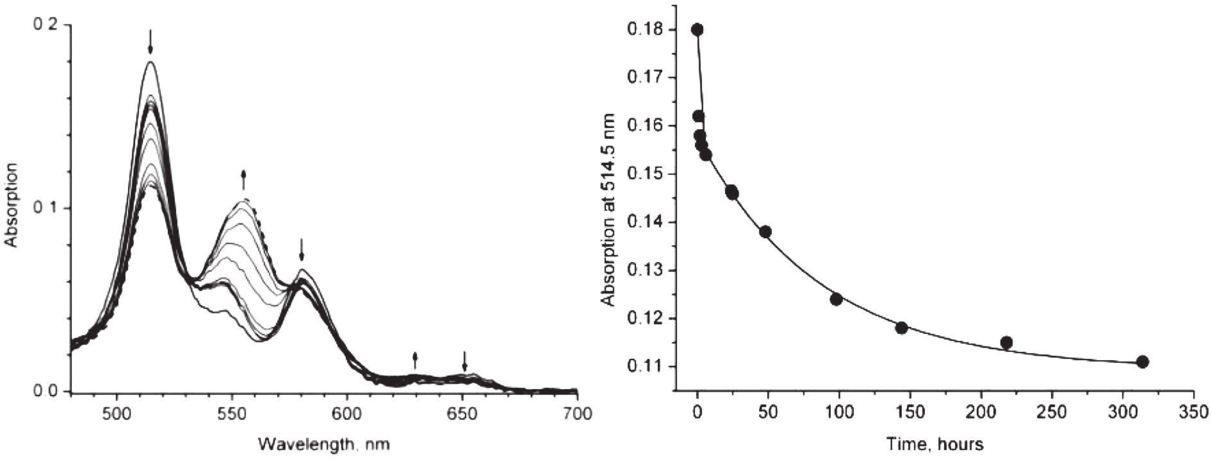

Fig. 1. *Time dependence of the 5,10,15,20-tetrakis-(3-N-methylpyridyl)-porphyrin ground state absorption spectra in the visible range (left) and absorbance at 514.5 nm (right). Equilibrium spectrum (after 1550 hours) is shown with dashed line. Arrows indicate the direction of spectral changes*

According to the statistical analysis, there is a possibility of formation of four doubly degenerated atropoisomers of *meta*-aryl (or *ortho*-aryl) substituted tetraarylporphyrins in solution. The statistical weights of these conformers relate as 1:4:2:1.

Analysis of the ground state absorption spectra in water solutions indicates the pronounced temporal evolution (Fig. 1, left). Thus, the most intense in the visible range band IV with maximum at 514.5 nm loses its intensity, whereas the absorption of the neighboring band III increases. We treat these spectral changes as the evidence of the atropoisomerization. The porphyrin aggregation has been excluded based on the separate check of the concentration dependence of the spectra. Decrease in the optical density at 514.5 nm as a function of the sample keeping time can be treated with two exponential function. The characteristic decay times are 0.63 and 79 hours (Fig. 1, right). The solution reaches the equilibrium after approximately 350 hours and no further spectral changes were found upon the sample handling up to the 1600 hours.

The measurements of the 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin fluorescence excitation spectra with different observation wavelengths reveals also the heterogeneity of solution, due to presence of several emissive conformers. Three atropoisomers have been identified with this procedure. The fluorescence excitation spectrum with observation at 708 nm is identical to the ground state absorption spectrum of isomer dominating immediately after the solution preparation. Another atropoisomer with high relative intensity of the long wavelength transition band has been identified with measurements of the fluorescence excitation spectrum with observation at 670 nm. The third atropoisomer with substantially lower concentration (or with decreased fluorescence quantum yield) has been found upon observation of the fluorescence excitation spectrum at 613 nm.

In summary, as a result of coexistence of several atropoisomers of the 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin in the solution, the ground state absorption spectra reveal the temporal evolution which reflects the trend to reaching the equilibrium between atropoisomers in the solution. The spectral features of three atropoisomers have been identified in the equilibrium solution with the fluorescence excitation spectra technique.

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