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Spectral Signature of the Equilibrium Distribution of the Free Base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin Atropisomers in Solution

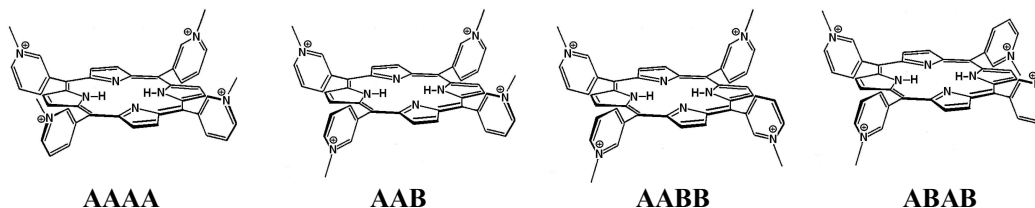
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It is known that the molecules of the *ortho*-, *meta*- and *para*-methyl substituted derivatives of the 5,10,15,20-tetrakis-pyridyl-porphyrin have pronounced photocytotoxic effect and are considered as promising candidates for inactivation of bacteria and viruses. The absorption and luminescence spectra of the *meta*-methyl substituted free base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin was found to reveal large flexibility, in contrast to those reported for *ortho* and *para*-methyl substituted derivatives. We suggest that the most probable reason of such a behavior is the heterogeneity of the solutions appearing due to the formation of labile atropisomers, differing in the position of the substituted methyl group in the pyridine ring relative to the macrocycle mean plane (**A** – above, **B** – below, see scheme) due to weakly restricted rotation of substituents around the C_m-C₁ bond.



The detailed study of the spectral properties of the free base 5,10,15,20-tetrakis-(3-*N*-methylpyridyl)-porphyrin has been carried out with elaboration of the absorption and luminescence spectroscopies [1]. The spectral changes was found to reflect the redistribution of the atropisomers concentrations upon establishing of the equilibrium distribution which ends approximately within 300 hours after the preparation of solution at the temperature 290±2 K. The atropoisomerization is suggested to be inherent property of all the 5,10,15,20-tetraarylporphyrins with asymmetric substitution of aryl groups with respect to the axis passing through the C_m-C₁ bond, which does not relate with the sterical hindrances between the *ortho*-substituents in the aryl ring with tetrapyrrolic macrocycle. The prospects for the practical applications of revealed phenomenon are discussed.

REFERENCES

1. Liulkovich L.S., Pukhovskaya S.G., Ivanova Yu.B., Semeikin A.S. and Kruk M.M., *Doklady of the National Academy of Science of Belarus*. 2017; **61**: 56-65.