Resonance Raman spectra of diacids of octaalkylporphyrins

Alexander Starukhin\(^1\), Michał Kijak\(^2\), Aleksander Górski\(^2\), S. Gawinkowski\(^2\), and Solomon Stavrov\(^3\)

\(^1\) B.I. Stepanov Institute of Physics, National Academy of Sciences of Belarus, Independence Av. 68, 220072, Minsk, Belarus, e-mail: a_starushin@ifanbel.bas-net.by
\(^2\) Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland
\(^3\) Sackler Institute of Molecular Medicine, Department of Human Molecular Genetics and Biochemistry, Sackler School of Medicine, Tel Aviv University, Tel Aviv 69978, Israel

It is well known that metal-incorporation reactions (i.e. syntheses of metalloporphyrins) require acidic conditions and that the porphyrin diacids may play an important role in the chemical synthesis of such metallocomplexes. In acidic conditions the free-base porphyrins are transformed to N-protonated diacids and their photophysical parameters drastically change in comparison to their neutral forms. The protonation leads to the formation of nonplanar macrocycles, as results of the steric hindrance and electrostatic repulsion of the central hydrogen atoms.

In this report we present results of the study of acidic forms of 2,3,7,8,12,13,17,18-octamethylporphyrin (H\(_4\)OMP\(^{2+}\)), as well as H\(_4\)OMP\(^{2+}\) with hydrogen atoms in meso-position exchanged by atoms of deuterium (H\(_4\)OMP\(^{2+}\)-d\(_4\)) and 2,3,7,8,12,13,17,18-octaethylporphyrin (H\(_4\)OEP\(^{2+}\)), by method of Raman microscopy in a crystal powder. The methodology of sample preparation and the experimental setup have been described in details previously \([1]\). The frequencies of normal modes and their Raman activities were simulated by means of DFT methods and compared with the experimental results. All spectra recorded for diacids were compared with Raman data of their parent neutral forms.

The formation of diacid species, with four hydrogen atoms in the centre of the porphyrin macrocycle, leads to significant changes in the Raman spectrum of H\(_2\)OMP (see Fig. 1). The set of new intense lines with frequencies of 248, 283, 333, 662, 680, 697, 753, 860 and 879 cm\(^{-1}\) manifests itself in the spectral range below 900 cm\(^{-1}\). It is explained by the saddle type distortion of the macrocycle upon protonation, induced by the crowding effect provided by two additional inner protons, as well as by the electrostatic repulsion between them. The interaction with the two counterions placed on the opposite sides of the molecule cannot be also neglected and its influence on the Raman spectrum will be analyzed by quantum-chemical modeling.

**Keywords:** diacids of octaalkylporphyrins; Raman microscopy; out-of-plane modes

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**References**