

# NH-TAUTOMERISM, ELECTRONIC STRUCTURE AND FORMATION OF EXCITED STATES IN TETRAPYRROLES WITH NON-SYMMETRICAL SUBSTITUTION: EXPERIMENT AND THEORETICAL CALCULATIONS

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Characteristic peculiarity of tetrapyrrole free bases is NH-tautomerism, caused by pair displacement of labile protons from one pair of nitrogens to the other one in the center of macrocycle. Typically, for symmetrical porphyrins proton migration at ambient temperature is manifested by NMR methods, while at low T it may be detected by FLN optical methods as far as spectral difference between these two NH-tautomers does not exceed  $\sim 100\text{ cm}^{-1}$ . In contrast, we have shown for the first time that in tetrapyrroles with non-symmetrical substitution [including porphyrins, chlorins and recently phthalocyanines) pair displacement of two protons leads to drastic changes of absorption spectra (spectral difference for tautomers amounts  $380\text{-}800\text{ cm}^{-1}$ ).

With these results in mind, we have carried out the systematic analysis of our absorption, polarized fluorescence, magnetic circular dichroism data as well as literature data on confocal microscopy for individual NH-tautomers being obtained for various tetrapyrroles with non-symmetrical substitution in order to evaluate energetic parameters, thermodynamics and stability of these structurally different forms of tetrapyrrolic macrocycle. In addition, optimized geometries for non-symmetrical tetrapyrroles (in the form of x- and y-tautomers) as well as their electronic structure were calculated using the Gaussian 09 [the B3LYP/6-31G(d) and CAM-B3LYP/ 6-31G(d) levels of theory for the geometry optimizations and TD-DFT calculations, respectively].

Recently, compounds of this type have been attracting considerable attention as novel functional materials; moreover, control over NH-tautomerism in tetrapyrroles is expected to give rise to novel switchable molecular devices and multi-valued logic elements.

Financial support by the grant from Council under the President of the Russian Federation for State Support of Young Scientists and Leading Scientific Schools (MK-3230.2015.3) and Belarussian SPSR “Convergence 2020 - 3.03” is gratefully acknowledged.