

ACID-BASE EQUILIBRIA OF *MESO*-INDOLO[3,2-*b*]CARBAZOLYL-SUBSTITUTED PORPHYRINS

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The problem of structure and stability of mono- and diprotonated forms of *meso*-aryl-substituted porphyrins attracts considerable interest and has been studied repeatedly (for a contemporary review see Ref. [1]). Two distinct cases were found depending on the rotational degree of freedom for the *meso*-aryl rings.[1,2] In case of 5,10,15,20-tetraphenylporphyrin (H₂TPP), where the phenyl moieties can twist easily, no monoprotonated species have been observed, due to the highly distorted *saddle*-type like geometry of the porphyrin macrocycle adopted already upon attachment of the single proton.[1,2] Simultaneous tilt of the pyrroles and twist of the phenyls allows the macrocycle to adopt the most energy-favourable *saddle*-type conformation. Thus, the geometry of the monoprotonated form of H₂TPP would resemble that of the diprotonated one, but with some asymmetry. In such a geometry, the lone electron pair of the nitrogen atom of the proton-free pyrrolyne ring is exposed to solvent, thus extremely facilitating the accessibility for the second proton and probably lowering the Coulomb repulsion forces. The relationship $pK_a^4 \approx pK_a^3$ holds and the formation of diprotonated species takes place in one step with almost simultaneous binding of two protons.

Formation of a highly distorted macrocycle geometry in case of 5,10,15,20-tetramesitylporphyrin (H₂TMesP) is hindered by the bulky methyl groups in the *ortho*-positions of the mesityl substituents, which prevent the aryl twist. The energetics of the saddling, which mainly consists of pyrrole ring tilting, was found to be practically insensitive to the presence of aryl substituents, provided their planes are orthogonal to the macrocycle plane.[3] Thus, the twisting-tilting synergism, which accounts for the large conformational flexibility of H₂TPP,[3] does not work in the case of H₂TMesP. Therefore, the conformational changes in the monoprotonated form of H₂TMesP, triggered by the attachment of the first proton, can not propagate

over the whole porphyrin macrocycle and are not transmitted to the pyrrolyne ring to be protonated with the second proton. In such a geometry, the relationship $pK_a^4 < pK_a^3$ holds and the second proton attaches much slower, thus allowing to stabilize the monoprotonated species in the appropriate pH range.

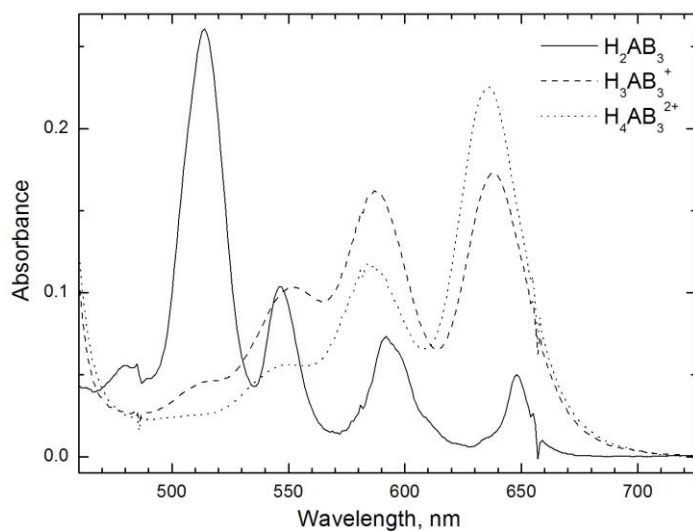


Figure 1. Ground state absorption spectra of free-base H_2AB_3 and its mono- and diprotonated forms in tetrahydrofuran at 293 K.

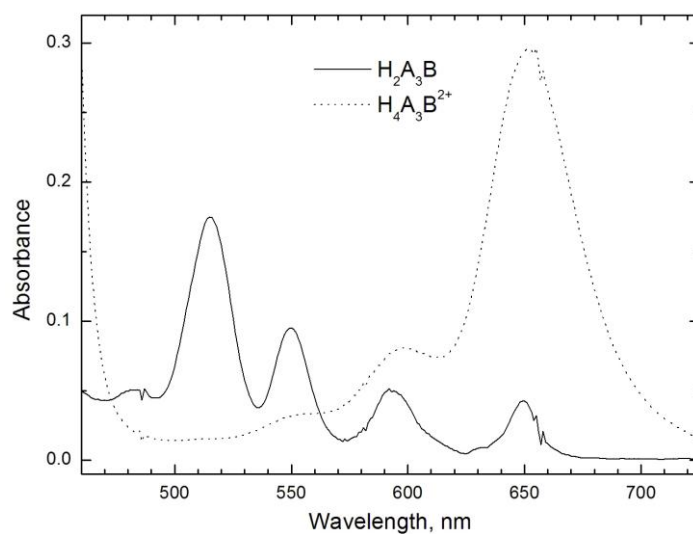


Figure 2. Ground state absorption spectra of free-base H_2A_3B and its mono- and diprotonated forms in tetrahydrofuran at 293 K.

Wide usage of the *meso*-aryl linkages in the design of dendrimers with porphyrin cores and supramolecular assemblies consisting of tetrapyrrolic subunits brings additional importance to the knowledge on the acid-base equilibria in *meso*-aryl-porphyrins. The acid-base equilibria in these supramolecular systems may depend strongly on the type of aryl spacer used. It is the testifying of this hypothesis that our work is aimed at. We have studied the acid-base equilibria for two asymmetrically *meso*-aryl-substituted porphyrins which can be considered as precursors for the design of dendrimers

having the tetrapyrrolic macrocycles as a core with indolo[3,2-*b*]carbazole (ICZ) dendrons *meso*-linked with aryl spacers: free-base 5-ICZ-10,15,20-trimesitylporphyrin (H_2AB_3) and free-base 5,10,15-tri-ICZ-20-mesitylporphyrin (H_2A_3B).

The results of the spectrophotometric titration demonstrate that the two studied porphyrins differ strongly in their acid-base properties (Figure 1,2). Both mono- and diprotonated forms have been observed for the H_2AB_3 porphyrin, but only the diprotonated form has been obtained in the case of the H_2A_3B porphyrin. The H_2AB_3 porphyrin is very close to H_2TMesP in its substitution pattern. It is likely that the three mesityl groups are able to prevent distortions of the whole macrocycle upon binding of the first proton, and as a result the two protonation steps are well separated ($pK_a^4 < pK_a^3$). On the contrary, the molecular flexibility of the H_2A_3B porphyrin approaches that of H_2TPP and the three phenyls can twist easily, giving rise to propagation of the *saddle*-type distortion over the macrocycle at the first protonation step. As a result, the monoprotinated form attaches immediately the second proton. The fluorescence features were found to be also different for these two porphyrins. The free-base forms of the H_2AB_3 and H_2A_3B porphyrins have a strong fluorescence with quantum yields Φ_{fl} being 0,095 and 0,092, respectively. However, in contrast with the Φ_{fl} increase up to 0,183 and 0,244 found for the mono- and diprotonated forms of H_2TMesP , the fluorescence of the protonated H_2AB_3 species is fully quenched. A weak emission with $\Phi_{fl} = 0,0031$ has been detected for the diprotonated H_2A_3B species. Thus, stabilization of the monoprotinated form in supramolecular systems can be predicted on the basis of the twist freedom of the *meso*-aryl spacers. The fluorescence properties of the protonated forms depend on the substitution pattern in a more complicated manner, which will be subject of a following study.

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References

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