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FREE BASE AND PROTONATED FORM FLUORESCENCE OF THE MIXED 5,10,15,20-ARYLPORPHYRINS

Fluorescence spectra for a series of mixed phenyl-mesityl 5,10,15,20-tetraarylporphyrins – with Mes_4, Mes_3Ph, Mes_2Ph_2-*trans*, Mes_2Ph_2-*cis*, $MesPh_3$ and Ph_4 type architecture (Mes – mesityl, Ph – phenyl) – in their free base, mono- and diprotonated form are reported. Substitution of a single *meso*-phenyl group with a sterically more demanding mesityl group is found to be sufficient to provide stabilization of the monoprotonated porphyrin species. A decrease in the number of mesityl substituents in the macrocycle leads to a decrease in the fluorescence quantum yield for protonated forms. The progressive replacement of ortho,ortho'-substituted mesityl groups with unhindered phenyls results in the additive pattern of spectral changes for the free base porphyrins, whereas for both protonated species a specific jump at the *trans* to *cis* transition is observed, along with a gradual additive pattern before and afterwards. This feature is interpreted as a signature of the transition between the hindered-like and unhindered-like conformations of the tetrapyrrolic macrocycles in the protonated forms. These two molecular conformations provide a different interaction of the two one-electron (a_{1u},e_g) and (a_{2u},e_g) configurations, which leads to changes of their contributions into electronic transitions.

Key words: porphyrins, free bases, protonated forms, molecular conformation, fluorescence.

Introduction. Changes in the spectral, photophysical and physico-chemical properties of 5,10,15,20-arylporphyrins observed during the replacement or modification of aryl moieties, are interpreted as the additive relative to the number of substituted or modified aryl groups [1]. It should be noted that this finding relates to both the free base porphyrins and their metal complexes, for which the steric hindrance caused by *ortho*-substituted *meso*-aryl groups is minimal. It is known that the formation of the protonated forms of tetrapyrrolic molecules is associated with a significant distortion of the macrocycle planarity and the formation of nonplanar saddle type conformers. Saddle distortion overcomes the steric repulsion of protons in the macrocycle core with the most energetically favorable conformation being achieved with a coplanar arrangement of the macrocycle and aryl group planes. To compensate the steric repulsion of internal protons in the diprotonated form (DP) macrocycle core, the tilting angle of the pyrrole rings φ (saddling angle) should be about 10–15°. The pyrrole rings tilting and the aryl groups rotation synergism during the formation of the DP forms of *meso*-tetraaryl-substituted porphyrins leads to the formation of conformers with the saddling angle φ varying from about 20° in 5,10,15,20-tetramesitylporphyrin (Mes_4) up to 28–33° in 5,10,15,20-tetraphenylporphyrin (Ph_4) [2]. Angle change between the median macrocycle plane and aryl substituents (dihedral angle θ) modulates the electronic interaction between their π-electron systems. In case of mesityl substituents due to the steric hindrance of two *ortho*-CH_3 groups, the dihedral angle values is practically 90°, while those of the phenyl substituents are about 60–70° because there is no steric hindrance for the phenyl group rotation [2].

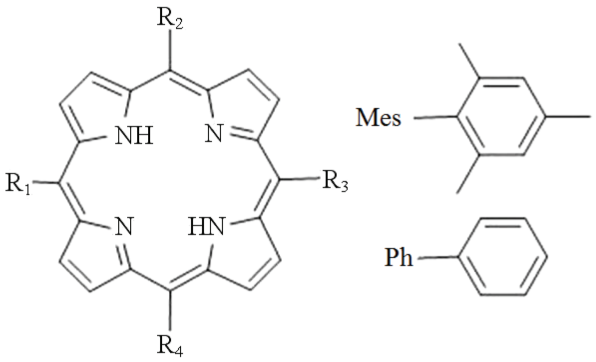

Fig. 1. Molecular structure of the studied compounds: Mes_4 – $R_{1,2,3,4}$ = Mes; Mes_3Ph – $R_{1,2,3}$ = Mes, R_4= Ph; Mes_2Ph_2-*trans* – $R_{1,3}$ =Mes, $R_{2,4}$ = Ph; Mes_2Ph_2-*cis* – $R_{1,4}$ = Ph, $R_{2,3}$ = Mes; $MesPh_3$ – $R_{1,2,3}$ = Ph, R_4 = Mes; Ph_4 – $R_{1,2,3,4}$ = Ph

Thus, Mes_4 and Ph_4 represent two extreme cases of sterically hindered and sterically unhindered *meso*-aryl-substituted porphyrins. Being almost indistinguishable as the free base forms, these compounds lose their similarity upon protonation. For Mes_4 porphyrin there is a sequential formation of both mono- (MP) and diprotonated forms, while the formation of DP form takes place only for the Ph_4 porphyrin in one step with simultaneous attachment of two protons. Peripheral substitution architecture is essential for the macrocycle basicity and photophysical properties of protonated forms. In the present study, we have investigated the role of the rotational degree of freedom of aryl substituents in the formation of the spectral-luminescent characteristics of *meso*-aryl-substituted porphyrins. As an object of study a series of mixed phenyl-mesityl 5,10,15,20-tetraarylporphyrins with Mes_4, Mes_3Ph, Mes_2Ph_2-*trans*, Mes_2Ph_2-*cis*, $MesPh_3$ and Ph_4 substitution architecture (see Fig. 1) have been chosen.

Main part. Analysis of the fluorescence spectra of all studied meso-tetraarylporphyrins during acid-base titration in dichloromethane solution at room temperature shows that the fluorescence spectra position and form, as well as the magnitude of fluorescence quantum yield Ph_{fl} undergo the significant changes as compared to the values measured by us for the free base compounds (Fig. 2).

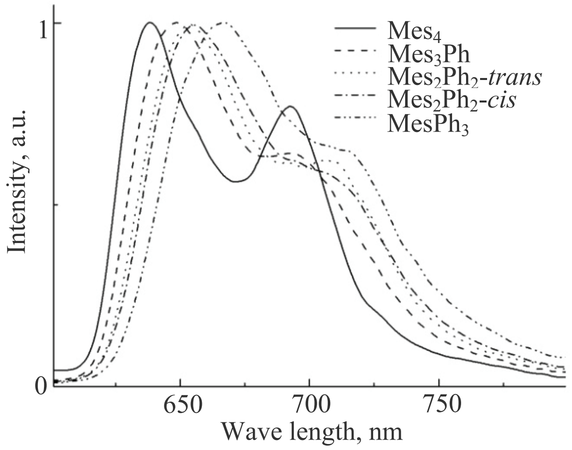

Fig. 2. Peak intensity normalized fluorescence spectra of the MP forms of studied compounds

The spectral shape of the fluorescence spectra of the free bases and DP was determined immediately at the beginning and at the end of the titration process. For MP forms the fluorescence spectra were calculated using the methodology developed earlier by us (Fig. 2). It has been found that the position of the band maxima $Q_x(0,0)$ in the fluorescence spectra are virtually unchanged for all the studied mesityl-containing derivatives (within ± 0.5 nm), but for the Ph_4 porphyrin the $Q_x(0,0)$ band maximum has 2 nm bathochromic shift (Table).

The Stokes shift value ($\Delta\lambda_{Stokes} = \lambda_{abs} - \lambda_{fl}$) for free bases is weakly dependent on the substitution of mesityl for phenyl (Fig. 3). The DP forms fluorescence spectra undergo increasing bathochromic shift and show a decrease in the relative intensity of the vibronic band $Q_x(0,1)$ in comparison with the electronic band $Q_x(0,0)$. The Stokes shift value $\Delta\lambda_{Stokes}$ can be considered as an estimate for the conformational mobility (degree of freedom) of the tetrapyrrolic macrocycle. Thus, the Stokes shift value $\Delta\lambda_{Stokes}$ for the DP forms in going from the Mes_4 porphyrin to the Ph_4 porphyrin gradually increases with the number of sterically unhindered substituents amounting of about 270 cm^{-1}. Substantially larger magnitude of $\Delta\lambda_{Stokes}$ value for the DP forms compared with the free bases indicates a significant amount of structural rearrangements in the excited state S_1 of the DP form. The dependence of the $\Delta\lambda_{Stokes}$ value on the number of the phenyl substituents is not of simple additive nature.

Spectral-luminescent characteristics of the free bases, MP and DP forms of mixed phenyl-mesityl 5,10,15,20-tetraarylporphyrins

Porphyrin	Form	λ_{fl}^{max}, nm		$Ph_{fl} \times 10^2$
		$Q_x(0.0)$	$Q_x(1.0)$	
Mes_4	H_2P	649.0	717.0	8.3
	H_3P^+	638.0	693.0	20.8
	H_4P^{2+}	649.0	705.0	30.0
Mes_3Ph	H_2P	649.0	717.0	7.1
	H_3P^+	647.0	694.0	13.0
	H_4P^{2+}	657.0	715.0	21.5
Mes_2Ph_2-*trans*	H_2P	649.0	717.0	6.6
	H_3P^+	653.0	~710.0	13.5
	H_4P^{2+}	667.0	~720.0	21.0
Mes_2Ph_2-*cis*	H_2P	649.0	717.0	6.6
	H_3P^+	656.0	~710.0	10.0
	H_4P^{2+}	667.0	~725.0	17.6
$MesPh_3$	H_2P	649.0	717.0	7.0
	H_3P^+	666.0	~715.0	6.0
	H_4P^{2+}	676.0	~740.0	10.2
Ph_4	H_2P	651.0	717.0	9.0
	H_3P^+	–	–	–
	H_4P^{2+}	687.0	~750.0	10.5

The data presented in Fig. 3 show an abrupt change of the $\Delta\lambda_{Stokes}$ value in going from *trans*- to *cis*-form in disubstituted compounds.

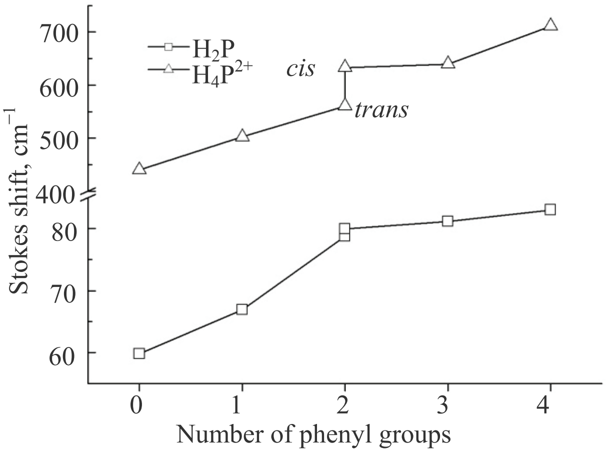

Fig. 3. Stokes shift dependence on the phenyl groups number for the free bases (H_2P) and DP forms (H_4P^{2+}) of the studied compounds

Therefore, one can conclude that in goiing from the Mes$_4$ to the Ph$_4$, the molecular conformation of the DP macrocycle changes in the following manner: a) attachment of the first unhindered phenyl group and the second one for the *trans*-conformer increases the macrocycle mobility which contributes to a certain increase in the saddling angle φ of the adjacent pyrrole and has an additive character; b) attachment of two phenyl groups in neighboring *meso*-positions (*cis*-conformer) allows pyrrole ring, located between them, take a maximum saddling angle φ thus increasing the size of the distorted region of the macrocycle, i.e. has a sharp jumping character.

For the free bases and the DP forms, the fluorescence quantum yield was measured directly by the method with the standard sample, while the indirect method, previously described by us in [3], was used to obtain the Ph$_{fl}$ value of MP forms. For all the compounds an increase of the Ph$_{fl}$ value was observed in going from the free bases to the protonated forms, however, it turned out to be different for all tested derivatives (Fig. 4). In the case of the Ph$_4$ porphyrin whose the peripheral substitution favors the stabilization of significantly distorted conformer macrocycle, increase of the Ph$_{fl}$ value for the DP form compared to the free base, is barely exceeding the measurement accuracy range (0.105 vs. 0.09, Table). The Ph$_{fl}$ value for the Mes$_4$ porphyrin increases for more than 3 times and amounts to 0.30 for the DP form. The differences in Ph$_{fl}$ values for the MP and DP forms of the studied compounds are associated with changes in the macrocycle molecular flexibility and the stabilization of conformers with different degrees of nonplanar distortions.

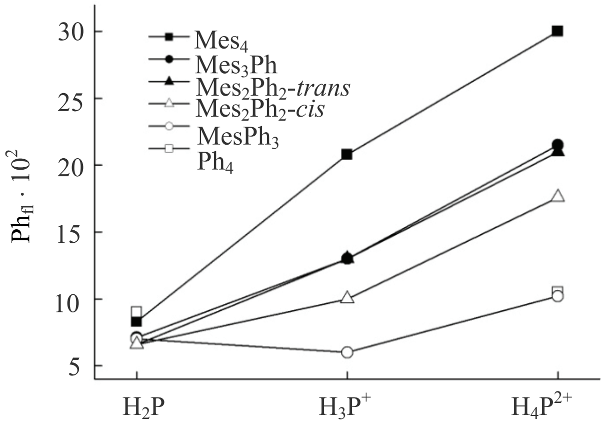

Fig. 4. Changes in the fluorescence quantum yield in going from the free bases (H_2P) to the MP (H_3P^+) and the DP (H_4P^{2+}) forms

In the framework of the Gouterman four orbital model, the weights of two one electron (a_{2u},e_g) and (a_{1u},e_g) configurations were determined as described previously in [4]. The squared weight A^2 of the one electron (a_{2u},e_g) configuration for the Mes$_4$ and Ph$_4$ porphyrin free bases was found to be 0.57, and for all asymmetric derivatives about 0.55.

The value of A^2 ranged from 0.645 to 0.680 for the DP forms of porphyrins. The A^2 value increase upon the formation of the DP form indicates an increase in the energy gap between the highest occupied a_{2u} and a_{1u} orbitals. We have studied the dependence of one electron (a_{2u},e_g) configuration A^2 value on the number of attached phenyl groups. The dependence obtained (Fig. 5) clearly demonstrates that the configuration interaction changes abruptly in going from the Mes$_2$Ph$_2$-*trans* to the Mes$_2$Ph$_2$-*cis* derivative, along with weak additive changes before and after this transition.

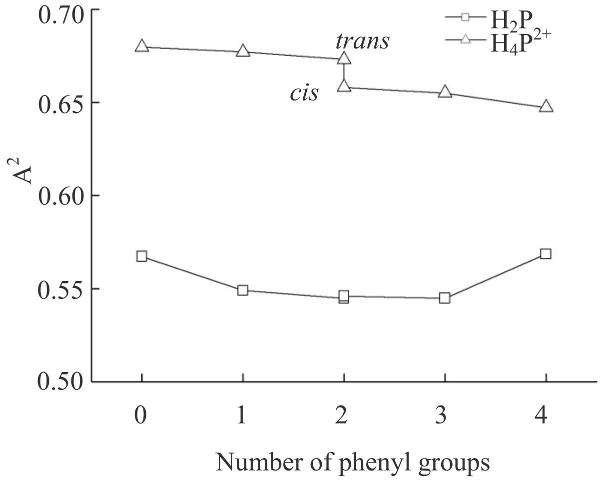

Fig. 5. Dependence of the one electron (a_2u, e_g) squared configuration weight A^2 on the number of the attached phenyl groups for the free bases (H_2P) and the DP forms (H_4P^{2+})

Thus, the position of the molecular orbitals of the tetrapyrrolic macrocycle also reflects a conformational transition, which is observed when changing the architecture of the peripheral substitution from the Mes$_2$Ph$_2$- *trans* to Mes$_2$Ph$_2$-*cis* pattern.

Conclusion. In summary, the analysis of the obtained data for the series of phenyl-mesityl mixed *meso*-tetraarylsubstituted porphyrins shows that the spectral-fluorescent properties essentially depend on the difference in the rotational degree of freedom of *meso*-aryl groups and substitution architecture. In case the free base from the substituents make an additive effect, whereas for the protonated forms there is a sharp change of the molecular conformation in going from the *trans*- to the *cis*-form.

References

1. Maes W., Ngo T. H., Rong G., Starukhin A. S., Kruk M. M., Dehaen W. Meso-indolo[3,2-b]carbazolyl-substituted porphyrinoids: synthesis, characterization and effect of the number of indolocarbazole moieties on the photophysical properties. *Eur. Journal of Organic Chemistry*, 2010, no. 13, pp. 2576–2586.

2. Presselt M., Dehaen W., Maes W., Klamt A., Martinez T. J., Beenken W. J. D., Kruk M. M. Quantum chemical insights into the dependence of porphyrin basicity on the *meso*-aryl substituents: thermodynamics, buckling, reaction sites and molecular flexibility. *Phys. Chem. Chem. Phys.*, 2015, vol. 17, no. 21, pp. 14096–14106.

3. Kruk M. M., Ngo T. H., Verstappen P., Starukhin A. S., Hofkens J., Dehaen W., Maes W. Unraveling the fluorescence features of individual corrole NH tautomers. *Journal of Physical Chemistry*, *A.*, 2012, vol. 116, no. 44, pp. 10695–10703.

4. Liulkovich L. S., Kruk M. M. Configuration interaction upon nonplanar distortion of tetrapyrrolic macrocycle. *Trudy BGTU* [Proceedings of BSTU], 2015, no. 6: Physical-Mathematical Sciences and Informatics, pp. 63–67 (In Russian).

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