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### ACID-BASE AND PHOTOPHYSICAL PROPERTIES OF ASYMMETRIC DENDRIMERS WITH PORPHYRIN CORE

The spectral and photophysical properties of mixed 5,10,15,20-arylporphyrins with  $A_2B_2$ -*cis* and  $A_2B_2$ -*trans* peripheral substitution and the porphyrin core dendrimers with the same spacer architecture between tetrapyrrolic macrocycle and indolocarbazole dendrons as well as those of their mono- and doubly protonated forms have been studied. Sequential formation of both mono- and doubly protonated forms of all the studied compounds was found during the acid-base titration. However, the concentration of monoprotinated form is small compared to those of the free base and doubly protonated one due to close values of protonation constants  $pK_{a1}$  ( $H_2P \leftrightarrow H_3P^+$ ) and  $pK_{a2}$  ( $H_3P^+ \leftrightarrow H_4P^{2+}$ ) in both ground singlet  $S_0$  state and first excited singlet  $S_1$  state. Different position of peripheral substituents/spacers of A (phenyls) and B (mesityls) type, which is known to have different sterical hindrances with tetrapyrrolic macrocycle, does not result in any noticeable differences in the acid-base properties. The free bases of all the compounds have similar photophysical properties. Doubly protonated forms of dendrimers and parent porphyrins were found to have different probabilities of lowest singlet  $S_1$  state deactivation. Compared to the free base molecules the fluorescence quantum yield value for dendrimers reduces for 50–1,000 times, whereas the parent porphyrins demonstrate about three fold increase.

**Key words:** porphyrin, dendrimer, acid-base equilibria, fluorescence.

**Introduction.** Physico-chemical and optical properties of tetrapyrrolic compounds and supramolecular systems depend strongly on the degree of freedom of the aromatic aryl substituents. These compounds and systems include tetrapyrrolic chromophores in which tetrapyrrolic macrocycles are linked to adjacent molecular fragments via aryl spacers [1–3]. Obviously, by varying the substituents (spacers) and/or the place of their joining to the tetrapyrrolic macrocycle, it is possible to achieve a graduate change of photophysical and fluorescent characteristics of molecules in a desired direction. This is especially important in the case of forming the protonated forms of tetrapyrrolic molecules, because their formation is associated with a significant distortion of the macrocycle planarity and the formation of nonplanar saddle type conformers [4]. For aryl substituents, characterized by a high degree of steric interactions with macrocycle due to the presence of bulky groups at one or both *para*-positions of aryl fragments, the degree of the macrocycle saddle distortion is significantly lower [5]. Thus it becomes possible to stabilize the monoprotinated porphyrin form, as opposed to 5,10,15,20-tetraphenylporphyrin molecule for which the formation of the monoprotinated form is not observed. Obviously, in the case of substitutions providing mixed sterically hindered and sterically free rotation of the aryl substituents, a more complex spectral pattern should be expected. However, the sequential change in the steric interaction magnitude in such systems can provide the conditions for a smooth change in the acid-base, photophysical and spectral-luminescence characteristics. Introduction of the sterically hindered aryl substituents will influence the mutual synergism of the pyrrole rings

tilt and aryl rings rotation on the magnitude and type of the tetrapyrrolic macrocycle saddle distortions [5]. At the same time, the geometrical parameters and the weight (size, method of branching, generation number for the dendritic shell, and nature of terminal groups of supramolecular systems) of molecular fragments, attached via aryl spacers may also influence the acid-base equilibrium in the core of the tetrapyrrolic macrocycle.

To determine the influence pattern of a dendritic shell on optical and acid-base properties of dendrimers with a porphyrin core, a number of compounds has been selected, which included: mixed 5,10,15,20-arylporphyrins with  $A_2B_2$ -*cis*,  $A_2B_2$ -*trans* structure, where A is phenyl, B is mesityl (2,4,6-methyl-phenyl) (Fig. 1, *a, b*); porphyrin-indolocarbazole dendrimers with substitution architecture  $A_2B_2$ -*cis*,  $A_2B_2$ -*trans* (Fig. 1, *c, d*).

The aim of this work is to establish the role of indolocarbazole dendrons in the formation of acid-base, photophysical and luminescent properties of the studied systems.

**Main part.** The electronic absorption spectra of the free bases of 5,10,15,20-tetraarylporphyrins and porphyrin-indolocarbazole dendrimers with spacer architecture  $A_2B_2$ -*cis* and  $A_2B_2$ -*trans* do not differ from each other. Variation of the architecture of the  $A_2B_2$ -*cis*/ $A_2B_2$ -*trans* spacer location for each pair of compounds does not result in spectral changes. At the same time, during the transition from the parent porphyrin to dendrimers small shifts of the absorption bands are observed (less than 2 nm), which are caused by the electron density redistribution between the macrocycle and peripheral substituents due to the weak increase in electron-donating ability of the latter.

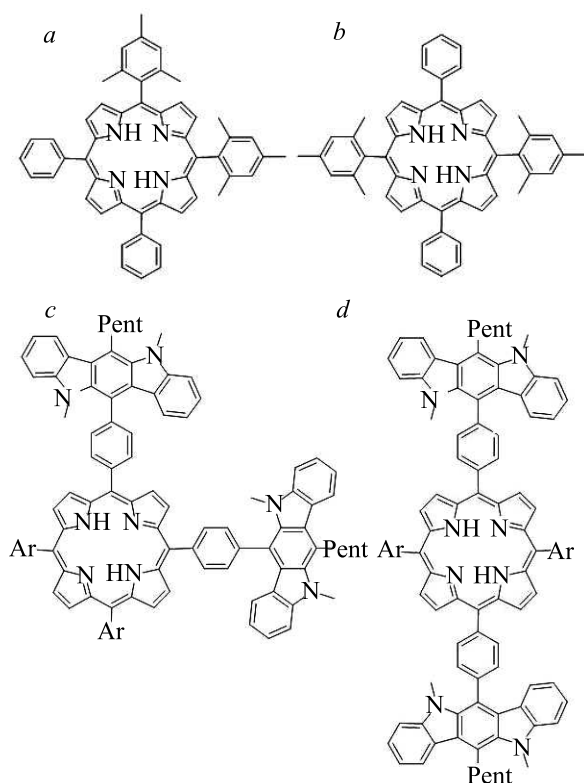


Fig. 1. The molecular structure of mixed 5,10,15,20-arylporphyrins (top) and porphyrin-indolocarbazole dendrimers (bottom) with  $A_2B_2$ -*cis* (a, b) and  $A_2B_2$ -*trans* (c, d) architecture

Protonation of the tetrapyrrolic macrocycle core in both the parent porphyrin and the dendrimers leads to the sequential formation of mono- and doubly protonated forms. It is reflected by absence of isobestic points in absorption spectra in the course of acid-base titration. At the same time due to the proximity of protonation constants  $pK_{a1}$  ( $H_2P \leftrightarrow H_3P^+$ ) and  $pK_{a2}$  ( $H_3P^+ \leftrightarrow H_4P^{2+}$ ) the mono-protonated form concentration appears to be small compared with the concentrations of the free base and doubly protonated form. Hence spectral changes observed in the acid-base titration of all the compounds studied in the ground singlet  $S_0$  state, reflect primarily the equilibrium between free base and doubly protonated porphyrin form (Fig. 2).

The overall picture of the spectral changes proved to be the same for all of the compounds studied. However, there are slight differences in the absorption spectra of doubly protonated forms of the compounds with different peripheral substitution architecture. Thus, the Cope band absorption maximum of the free bases of the  $A_2B_2$ -*cis* and  $A_2B_2$ -*trans* compounds is at 417 nm and detects a bathochromic shift of 20–21 nm in the formation of a doubly protonated form. At the same time, the maximum wavelength of the long wavelength absorption band undergoes a hypsochromic shift

from 646 to 641 nm in the  $A_2B_2$ -*cis* porphyrin and to 643 nm in  $A_2B_2$ -*trans* porphyrin. This can be explained by differences in the nonplanar distortion degree of doubly protonated *cis*- and *trans*-conformers, which as it has previously been shown [5] can be related uniquely to the energy of long wavelength electronic transition.

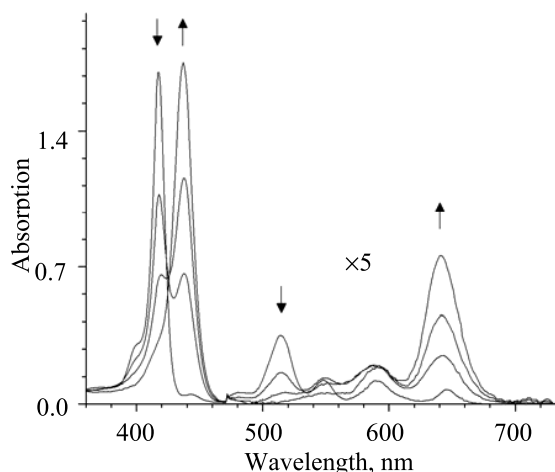


Fig. 2. Absorption spectra changes of 5,10,15,20-arylporphyrins of the  $A_2B_2$ -*trans* type during titration in the  $H_2SO_4 - CH_2Cl_2$  system.

Arrows here and at Fig. 3 show the direction of spectral changes when passing from the free base to the doubly protonated form

The shapes of the fluorescence spectra are almost identical for the free bases of all the compounds studied, but the values of fluorescence quantum yield  $\Phi_f$  in case of dendrimers increases by 40% (Fig. 3, Table). For the protonated products the significant differences of spectral-luminescent properties are detected between the parent porphyrins on the one hand and in the porphyrin-indolocarbazole dendrimers on the other.

Thus, the formation of the protonated forms of 5,10,15,20-arylporphyrins is accompanied by a significant increase in the fluorescence quantum yield. In  $A_2B_2$ -*trans* porphyrin the magnitude of the fluorescence quantum yield  $\Phi_f$  is increased more than 3-fold and equals 0.21, while for  $A_2B_2$ -*cis* porphyrin the  $\Phi_f$  is 0.176.

This increase has been previously noticed by us for the symmetrically substituted 5,10,15,20-tetramesitylporphyrin [5], in which all the substituents are sterically strained: due to the presence of methyl groups in the *ortho*-positions of the benzene ring a sterically hindered conformer is formed in which the mesityl groups are arranged almost orthogonally to the mean plane of the macrocycle. Consequently, the growth of the fluorescence quantum yield can be attributed to the restriction of conformational mobility of the molecule. Thus it is possible to assume that the conformational flexibility and therefore the

degree of nonplanar distortion of the  $A_2B_2$ -*cis* porphyrin molecule is slightly higher.

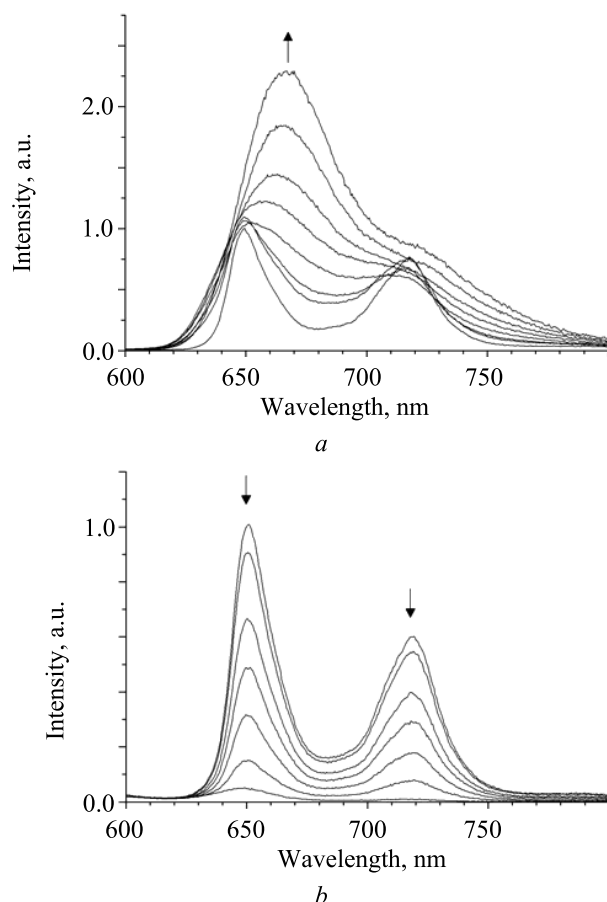


Fig. 3. Fluorescence spectra changes of 5,10,15,20-arylporphyrins of the  $A_2B_2$ -*trans* type (a) and porphyrin-indolocarbazole dendrimer with  $A_2B_2$ -*trans* architecture (b) during titration

**Spectral-luminescence characteristics of the free bases, mono- and doubly protonated forms of 5,10,15,20-arylporphyrins and porphyrin-indolocarbazole dendrimers with  $A_2B_2$ -*cis* and  $A_2B_2$ -*trans* architecture**

Architecture	Form	$\lambda_{fl}^{max}, nm$		$\Phi_{fl} \cdot 10^2$
		$Q_x(0.0)$	$Q_x(1.0)$	
5,10,15,20-arylporphyrins				
$A_2B_2$ - <i>cis</i>	$H_2P$	649.0	717.0	6.6
	$H_3P^+$	—	—	—
	$H_4P^{2+}$	667.0	—	17.6
$A_2B_2$ - <i>trans</i>	$H_2P$	649.0	717.0	6.6
	$H_3P^+$	—	—	—
	$H_4P^{2+}$	667.0	—	21.0
Porphyrin-indolocarbazole dendrimers				
$A_2B_2$ - <i>cis</i>	$H_2P$	650.5	718.5	9.3
	$H_3P^+$	—	—	—
	$H_4P^{2+}$	671.0	—	0.17
$A_2B_2$ - <i>trans</i>	$H_2P$	650.5	718.5	9.3
	$H_3P^+$	647.0	—	1.76
	$H_4P^{2+}$	669.0	—	0.009

On the contrary, a strong fluorescence quenching is observed in porphyrin-indolocarbazole dendrimers upon porphyrin core protonation (Table, Fig. 4).

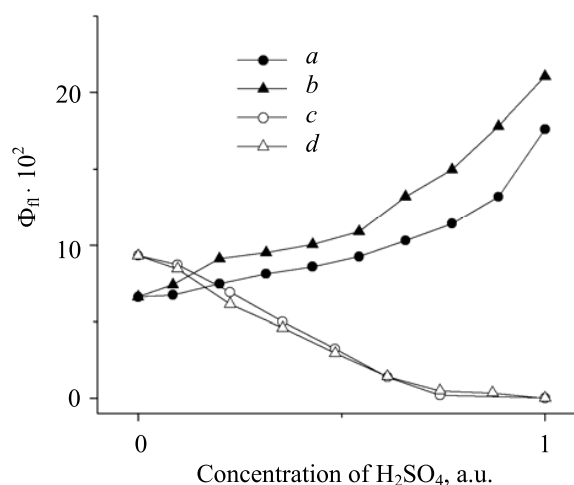


Fig. 4. Fluorescence quantum yield changes of the studied compounds in solutions during titration

It was found that for doubly protonated species the fluorescence quantum yield value  $\Phi_{fl}$  decreases for about 50 times for the  $A_2B_2$ -*cis* dendrimer and almost 1,000 times for the  $A_2B_2$ -*trans* dendrimer. Obviously, this is due to the specific intramolecular interactions in the formation of a dendritic shell. The fluorescence quantum yield value  $\Phi_{fl}$  for the monoprotonated form of the  $A_2B_2$ -*trans* dendrimer has been obtained which was almost 10 times less than the value measured for the corresponding free base. In case of  $A_2B_2$ -*cis* dendrimer no fluorescence from monoprotonated species was found.

Acid concentration in solution is given in relative units. Normalization on the acid concentration required for complete conversion of the free base of  $A_2B_2$ -*cis* porphyrin into doubly protonated form has been performed. Analysis demonstrates that within the measurement error, all the compounds form doubly protonated forms at the acid same concentration, i.e. they have very similar  $pK_{a1}$  values for the  $H_3P^+ \leftrightarrow H_4P^{2+}$  equilibrium. Thus, we can conclude that the formation of the dendrimer has no significant effect on acid-base properties of the porphyrin core. The monotonous character of the dependences shown in Fig. 4, indicates that the magnitude of the fluorescence quantum yield with successive formation of the protonated products in the series  $H_2P \rightarrow H_3P^+ \rightarrow H_4P^{2+}$  changes monotonically: it increases in the parent porphyrins while in the porphyrin-indolocarbazole dendrimers it goes down.

**Conclusion.** Thus, the formation of dendrimers was found does not change acid-base properties of the porphyrin macrocycle, but leads to the substan-

tial changes of its fluorescent properties. The porphyrin dendrimers synthesis can be suggested to diversify the fluorescent response of such

supramolecular systems, and the latter can be used as basic compounds for the development of sensitive molecular sensors for acids and bases.

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