

Synthesis and Investigation of Basicity of Diporphyrin with Polyethylenoxide Spacer

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Reaction of 5-(3'-oxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-diamylporphyrin with polyethylene glycol bis(*p*-toluenesulfonates) in the presence of cesium carbonate in boiling mixture of acetonitrile and DMFA leads to diporphyrin-*O,O'*-bis[3-(2,3,7,8,12,18-hexamethyl-13,17-diamylporphyrin-5-yl)phenyl]-pentaethylene glycol (**I**). The porphyrin-precursor was synthesized by condensation of 3,3'-diamyl-4,4'-dimethyldipyrrolylmethane-2,2' with 2-formyl-3,4-dimethylpyrrole in the presence of hydrobromic acid in butanol, and following cyclization (without isolation) of intermediate biladiene-*a,c* dihydrobromide with 3-hydroxybezaldehyde. Values of $\lg K_{b1}$ (13.30 ± 0.01) and $\lg K_{b2}$ (9.70 ± 0.03) for protonation equilibriums of **I** were measured spectropotentiometrically in acetonitrile at 298 K. It was found that two interconnected porphyrin fragments are protonated independently.

Keywords: Podands, bisporphyrins, polyethylenoxide spacer, synthesis, basicity.

Шейнин Владимир Борисович, родился в 1956 г. Выпускник кафедры Технологии органических красителей и промежуточных продуктов Ивановского химико-технологического института (1978). В 1978 – 1981 гг. обучался в очной аспирантуре ИХТИ под руководством Б. Д. Березина и В. Г. Андрианова и в 1981 г. защитил кандидатскую диссертацию на тему: "Исследование кислотно-основной ионизации некоторых природных и синтетических порфиринов". С 1982 занимается исследованиями в области координационной химии ионных форм порфиринов в Институте химии растворов РАН. Ведущий научный сотрудник лаборатории Координационной химии растворов ароматических макроциклических соединений.



Dr. Sheinin Vladimir Borisovich was born in 1956. In 1978 he graduated from Ivanovo Institute of Chemical Technology (Technology of organic dyes and by-products). In 1978 - 1981 he was a post-graduate student in the Department of Organic Chemistry under supervision of Prof. B. D. Berezin and Dr. V. G. Andrianov and in 1981 he received the degree "Candidate of Chemical Sciences" (PhD) for his dissertation "Study of acid-base ionization of some natural and synthetic porphyrins". Since 1982 he held research positions at the Institute of Solution Chemistry RAS. Currently he is leading researcher in the Laboratory of coordination chemistry of solution of aromatic macrocyclic compounds and studies the coordination chemistry of the ionic forms of porphyrins.

Семейкин Александр Станиславович, родился в 1956 г. Окончил Ивановский химико-технологический институт (ИХТИ) в 1978 г. и с 1979 г. начал работать в качестве научного сотрудника на кафедре органической химии ИХТИ. Под руководством Б. Д. Березина в 1983 г. защитил кандидатскую диссертацию на тему "Синтез и исследование функциональных производных тетрафенилпорфина", а в 1995 г. докторскую диссертацию "Синтез и физико-химические свойства синтетических порфиринов в неводных средах". В настоящее время возглавляет лабораторию органического синтеза при кафедре органической химии в должности главного научного сотрудника. Профессор кафедры органической химии (с 2004 г.), Лауреат премии правительства РФ (2003 г.)

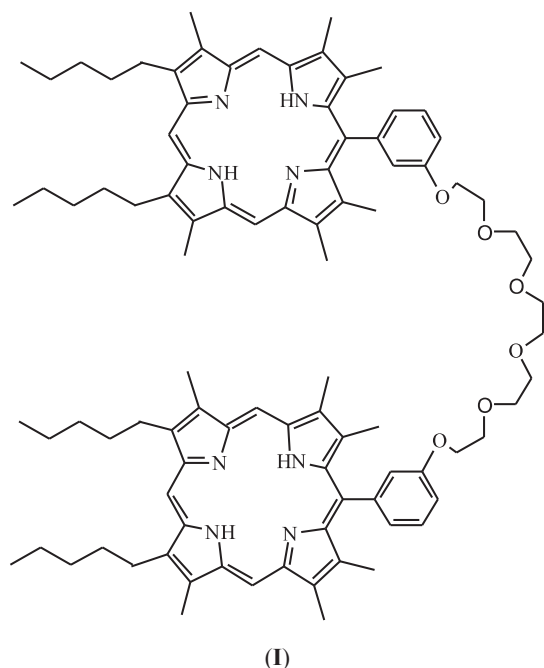


Prof. Semeikin Aleksandr Stanislavovich was born in 1956. In 1978 he graduated from Ivanovo Institute of Chemical Technology and since 1979 held research positions in the Department of Organic Chemistry at Ivanovo State University of Chemical Technology. Under supervision of Prof. B. D. Berezin he received in 1983 the degree "Candidate of Chemical Sciences" (PhD) for his dissertation "Synthesis and study of the functional derivatives of tetraphenylporphin" and in 1995 the degree "Doctor of Chemical Sciences" for the dissertation "Synthesis and physical chemical properties of synthetic porphyrins in non-aqueous media". Currently he has positions of the chief researcher and professor at the Department of Organic Chemistry and is head of the laboratory of organic synthesis. In 2003 he became laureate of the Russian Federation Government Award.

Introduction

Porphyrins are considered as perspective molecular blocks for design of supramolecular systems, which are intensively investigated as biomimetic models and molecular devices for different applications.^[1]

The present work describes synthesis of diporphyrin **I** with flexible polyethylenoxide spacer and investigation of basicity of linked porphyrin fragments, which is closely connected with coordination properties of porphyrins,^[2] metalloporphyrins^[3] and diprotonated porphyrins.^[4-6]



The diporphyrin **I** is considered as an element with porphyrinic “fastener”, because of intra- and intermolecular binding of two porphyrins of metalloporphyrinic fragments it can be used for construction of linear and cyclic supramolecular systems (Figure 1). Coordination chemistry of this unique molecule gives the impressive perspectives for design of different types of “fasteners” (Figure 2).

The important feature of diporphyrin **I** and compounds on its basis is a possibility of stereochemical control of their properties due to complexation with polyethylenoxide chain, which should be accompanied by optical response of porphyrin chromophore.

Experimental

¹H NMR spectra were recorded on Bruker Avance-III spectrometer at 500 MHz. Chemical shifts are given in ppm

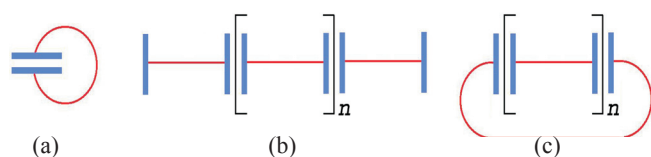


Figure 1. I-type diporphyrins as elements with porphyrin “fastener” (blue – porphyrinic fragment, red – polyethylenoxide spacer); (a) – cyclic intramolecular complex, (b) – linear intermolecular complex; (c) – cyclic intermolecular complex.

relatively tetramethylsilane (TMS), solvent deuteriochloroform. Electronic absorption spectra were obtained in acetonitrile using Agilent 8453 ChemStation for UV-visible spectroscopy.

Synthesis

O,O'-Bis[3-(2,3,7,8,12,18-hexamethyl-13,17-di-*n*-amylporphyrin-5-yl)phenyl]-pentaethylene glycol (**I**) was prepared according to the modified procedure.^[7] Pentaethylene glycol bis(*p*-toluenesulfonates) (78.5 mg, 0.144 mmol), 5-(3'-oxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-di-*n*-amylporphyrin (100 mg, 0.160 mmol), and cesium carbonate (50 mg, 0.153 mmol), were mixed with acetonitrile (3 ml) and dry DMFA (6 ml), and the mixture was heated with stirring for 24 h. After that it was poured into water (100 ml), the precipitate was filtered off, rinsed with water, and dried at 70°C. The product was dissolved in chloroform, separated by column chromatography on silica gel (eluent mixture of chloroform–methanol 50:1). The second porphyrin zone was evaporated to minimal volume, the product was precipitated with methanol, the residue was filtered off, rinsed with methanol and dried at 70°C. Yield: 73 mg (35%). *R_f* (silufol): 0.27 (benzene–methanol, 10:1). UV-vis (CHCl₃) λ_{max} nm (lg ε): 503 (4.29), 536 (3.40), 572 (3.35), 622 (3.23). ¹H NMR δ ppm: 10.18s (4H, 10,20-H); 9.99s (2H, 15-H); 7.89s (2H, Ph_{2-H}); 7.67m (4H, Ph_{4,5-H}); 7.41m (2H, Ph_{6-H}); 4.31t (4H, OCH₂); 4.01t (8H, AmCH₂); 3.92t (4H, OCH₂); 3.74-3.49m (24H, 12,18-CH₃+OCH₂CH₂O); 3.45s (12H, 2,8-CH₃); 2.45s (12H, 3,7-CH₃); 2.30m (4H, Am_{CH₂}); 1.76qv (8H, Am_{CH₂}); 1.59sc (4H, Am_{CH₂}); 1.01t (6H, Am_{CH₃}).

5-(3'-Oxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-diamylporphyrin (**II**) was obtained by condensation of 3,3'-di-*n*-amyl-4,4'-dimethyldipyrrolylmethane-2,2'^[8-10] with 2-formyl-3,4-dimethylpyrrole^[8-11] in the presence of hydrobromic acid in butanol, and following cyclization (without precipitation) of intermediate biladiene-*a,c* dydibromide with 3-hydroxybenzaldehyde, according to the procedure described earlier.^[12] The concentrated hydrobromic acid (1.0 ml, 8.3 mmol) was added with stirring to the mixture of 3,3'-di-*n*-amyl-4,4'-dimethyldipyrrolylmethane-2,2' (0.7 g, 2.23 mmol) and 2-formyl-3,4-dimethylpyrrole (0.55 g, 4.46 mmol) in butanol (50 ml) at r.t. After 1 hour the precipitate of biladiene-*a,c* dydibromide was mixed with 3-hydroxybenzaldehyde (2.0 g, 16.4 mmol, 8-fold excess). The mixture was heated, and boiled during 4 hours. After that it was cooled and mixed gradually with concentrated ammonia solution (2 ml). The precipitate was filtered off, rinsed with methanol, and dried at 70°C. The product was purified by column chromatography on silica gel (the eluent mixture of chloroform–methanol (100:1)). The porphyrin eluate was evaporated to minimal volume, the product was precipitated with methanol, the residue was filtered off, rinsed with methanol, and dried at 70°C. Yield: 0.67 g (48%). *R_f* (silufol): 0.68 (benzol – methanol, 10:1). UV-vis (CHCl₃) λ_{max} nm (lg ε): 623 (3.56); 570 (3.91); 537 (3.94); 503 (4.23); 404 (5.32). ¹H NMR δ ppm: 10.15s (2H, 10,20-H); 9.92s (1H, 15-H); 7.49m (2H, Ph_{4,5-H}); 7.10d (1H, Ph_{6-H}); 6.98s (1H, Ph_{2-H}); 4.01t (4H, Am_{CH₂}); 3.62s (6H, 12,18-CH₃); 3.52s (6H, 2,8-CH₃); 2.39s (6H, 3,7-CH₃); 2.30qv (4H, Am_{CH₂}); 1.74qv (4H, Am_{CH₂}); 1.56sc (4H, Am_{CH₂}); 0.99t (6H, Am_{CH₃}); -3.14bs (2H, NH).

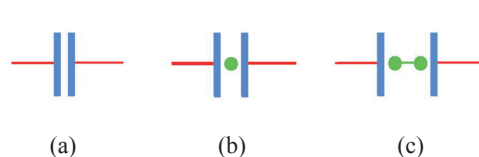
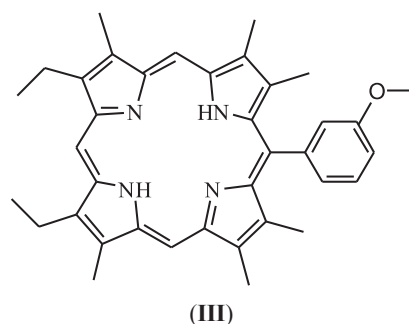


Figure 2. “Fasteners” (a) – bis-porphyrinate complexes, (b) – bis-nuclear complexes of metalloporphyrins or porphyrin dications with monoatomic anion, (c) – bis-nuclear complexes of metalloporphyrins or porphyrin dications with polyatomic anion.

5-(3'-Methoxyphenyl)-2,3,7,8,12,18-hexamethyl-13,17-diethylporphyrin (**III**) was obtained according to the procedure described earlier.^[12]



Spectropotentiometry

The investigation of basicity of **I** and **III** was carried out by the spectropotentiometric method in system (1) at 298 K, as it was described in^[6].



Calculations

Basicity constants K_{b1} , K_{b2} were calculated by the method of fitting parameters using Equation (2).

$$A_T = \frac{C_0 \ell (\varepsilon_{\text{H}_2\text{P}} + \varepsilon_{\text{H}_3\text{P}^+} K_{b1} 10^{-\text{pH}} + \varepsilon_{\text{H}_4\text{P}^{2+}(\text{CH}_3\text{CN})_2} K_{b1} K_{b2} 10^{-2\text{pH}})}{\Sigma_b} \quad (2)$$

$$\Sigma_b = 1 + K_{b1} 10^{\text{pH}} + K_{b1} K_{b2} 10^{2\text{pH}}$$

$$C_0 = [\text{H}_2\text{P}] + [\text{H}_3\text{P}^+] + [\text{H}_4\text{P}^{2+}(\text{CH}_3\text{CN})_2]$$

Results and Discussion

The comparative investigation of **I** and **III** (as precursor) showed that polyethylenoxide spacer has no effect on the protonation. The dependences of UV-vis spectra on pH for **I** and **III** are similar. That is why the experimental results are shown for **I**, as an example.

The presence of two protonation equilibria (3), (4) is proved by experimental data (Figures 3–5).

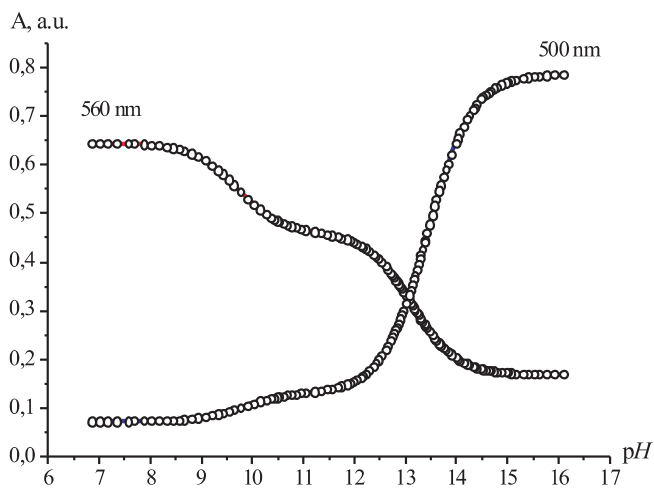


Figure 4. (a) - The titration curves for **I** in system (1); (°°°) experiment, (—) calculations, (b) - correlation dependence A_{500}/A_{560} for **I** in the system (1).

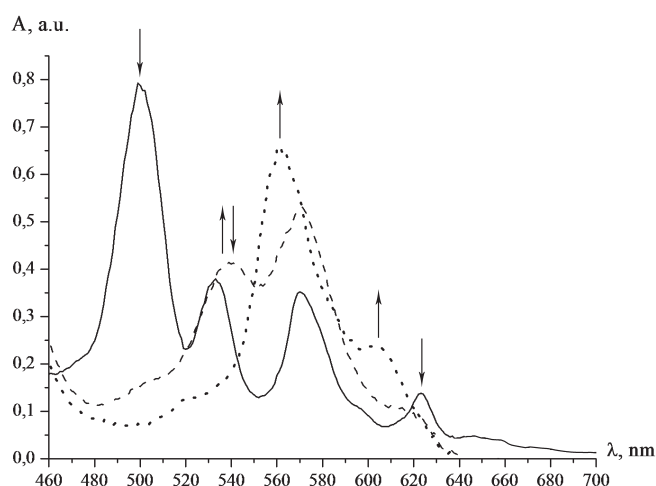
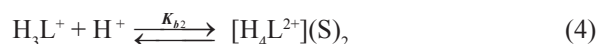


Figure 3. UV-vis spectra of **I** in system (1); (—) H_2L (pH = 16.00), (---) H_3L^+ (pH = 12.00), (····) $[\text{H}_4\text{L}^{2+}](\text{CH}_3\text{CN})_2$ (pH = 7.0).



The titration curves also have two well-defined steps (Figure 4,a) which are accompanied by corresponding transformations of UV-vis spectra (Figure 3). The existence of equilibria only between two light-absorbing centres: $\text{H}_2\text{I} / \text{H}_3\text{I}^+$ (3) and $\text{H}_3\text{I}^+ / \text{H}_4\text{I}^{2+}(\text{CH}_3\text{CN})_2$ (4) was evidenced by the presence of the isosbestic points (Table 1) and two linear areas of the correlation dependence A_{500}/A_{560} (Figure 4,b). The two titration steps are separated by plateau, which points out the stable monocation H_3I^+ formation (as it was shown for β -octaalkylporphyrins).^[6] Reversibility of equilibria (3), (4) was proved by additional titration of final solution of H_3I^+ or $\text{H}_4\text{I}^{2+}(\text{CH}_3\text{CN})_2$ with ammonia solution in acetonitrile. In all cases equilibria became stable after 1 minute, what is needed for pH balancing in the solution volume and achievement of equilibrium electrode potential. The experimental dependence $A_\lambda = f(\text{pH})$ corresponds to the model of two-step protonation (Equation (2)) with correlation coefficient $R=0.9990$.

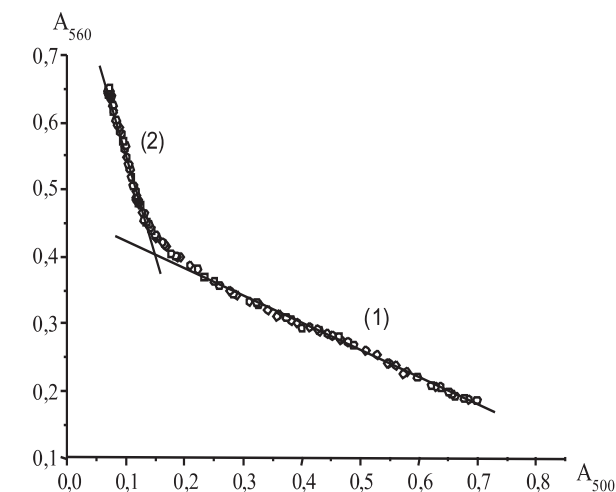


Table 1. The results of spectropotentiometric investigation of reactions (3), (4) in the system (1).

Parameters	I	III	IV ^[5]
$\lg K_{b1}$	13.30 ± 0.01	13.58 ± 0.01	11.93 ± 0.02
$\lg K_{b2}$	9.70 ± 0.03	9.47 ± 0.02	7.91 ± 0.03
maximum absorption (nm)	H ₂ Π	499, 532, 568, 622	497, 531, 568, 621
	H ₃ Π ⁺	540, 571	532, 558, 603
	H ₄ Π ²⁺	560	550, 593
isosbestic points (nm)	Eq. (3)	466, 516, 620, 628	462, 610, 633
	Eq. (4)	549, 586, 621	539, 583, 598
concentration (mol/l)	4.07·10 ⁻⁵	2.45·10 ⁻⁵	

The results of spectropotentiometric investigations are shown in Table 1 together with literature data for dimethylester of mesoporphyrin IX (IV),^[5] as a typical β-octaalkylporphyrin.

Conclusions

Comparative investigation of compounds I and III has shown that the interconnected porphyrin fragments in I are protonated independently. The effect of coupling in the reactions of I protonation is extremely weak, what exhibits as decreasing of ($\lg K_{b1} - \lg K_{b2}$) only in half.

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