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p*H*-Dependent Receptor Based on Dithiaporphyrins for Selective Binding of Perchlorate Ions

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The work presents the synthesis procedure and results of the study of the interconnection between the geometric structure of dithia-substituted analogues of tetraphenylporphyrins and their acid-base and spectral properties. Double-protonated forms of bromine-substituted dithiaporphyrins were found to be able to coordinate perchlorate ions in a neutral solvent, which can be of use in designing a receptor platform of liquid-phase sensor materials.

Keywords: Heterosubstituted porphyrins, base properties, receptor properties, perchlorate ion.

p*H*-Зависимый рецептор на основе дитиапорфиринов для селективного связывания перхлорат-ионов

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В работе представлены методика синтеза и результаты исследования взаимосвязи между геометрической структурой дитиазамещенных аналогов тетрафенилпорфирина и их кислотно-основными и спектральными свойствами. Было обнаружено, что двухпротонированные формы бромзамещенных дитиапорфиринов способны координировать перхлорат-ионы в нейтральном растворителе, что может быть использовано при разработке рецепторной платформы для жидкофазных сенсорных материалов.

Ключевые слова: Гетерозамещенные порфирины, основные свойства, рецепторные свойства, перхлорат-ион.

Introduction

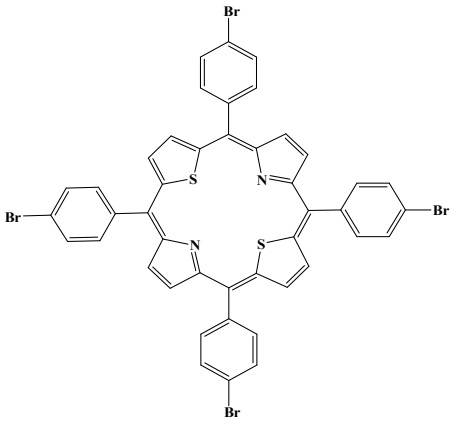
The last few decades have shown a significant increase in the amount of research into the development and investigation of new sensor materials, as well as methods aimed at improving their analytical characteristics. One of the main parameters taken into account when designing effective chemical sensors is the method of analytical signal transduction. At the same time, recording and transmitting optical signals have a number of advantages.

The underlying principle of optical chemical sensors is absorption or reflection of the light reaching them (radiation) and of the resulting luminescence. These phenomena, in turn, are caused by the interaction between the analyte and the receptor platform of the sensor.[1] Of special interest in terms of searching for active components (a receptor platform) for optical sensors are porphyrins and their analogues due to the great variety of properties they possess and potential of their variation within a wide range of values through changes in the molecular structure.[1-12] The

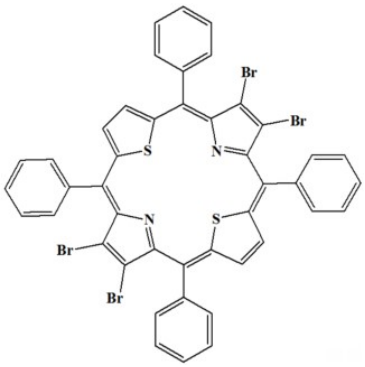
porphyrin macrocycle can be modified in two main ways. The first one is the substitution of hydrogen atoms in the β-positions of pyrrole rings, in the methine bridges, and in the intracyclic nitrogen atoms of the macrocycle. The diversity of organic and inorganic groups that can be used as substituents makes it possible to obtain a large number of porphyrins proper.[13,14] The second way of modification is changing the macrocycle itself through hydrogenation, widening of the conjugation system by adding carbo- or heterocycles, and replacing one or two nitrogen atoms of the reaction center with other donor atoms: O, C, S, Se, and Te. The results of such intracyclic modification are porphyrinoids or heterosubstituted porphyrins, which have significantly different properties from those of classical porphyrins but retain the aromatic character of the molecule as a whole.[15]

Solutions of porphyrins and their structural analogues in organic solvents can change their optoelectronic properties when interacting both with organic and inorganic bases and acids within a wide p*H* range: the intracyclic cavity of the macrocycle can form a charge transforming the molecule into a molecular fragment with high chemical affinity to the cations or anions in the solution. Formation of molecular complexes and associates with porphyrins and their analogues is accompanied by easily identifiable responses, namely shifts and/or changes in the intensity of the bands in electronic absorption spectra, changes in the color of the solutions and other phenomena, with their magnitude and intensity depending on the nature of the ligands participating in the interaction, as well as the acid-base properties of the medium. This fact makes it possible to use changes in the optical properties of porphyrins to make receptors for ions of different nature. It means that it is possible to make receptors for ions of different nature by changing the optical properties of porphyrins. However, these factors require a more detailed study of the acid-base and complexing properties of the molecules of porphyrins and their analogues.

This work presents the synthesis procedure and results of the study of the interconnection between the geometric structure of dithia-substituted analogues of tetraphenylporphyrins with the acid-base and spectral properties. Double-protonated forms of bromine-substituted dithiaporphyrins (**I** and **II**) were found to be able to coordinate perchlorate ions in a neutral solvent, which can be of use in designing a receptor platform of liquid-phase sensor materials.



5,10,15,20-tetrakis[4'-bromophenyl]-21,23-dithiaporphyrin,
(p-Br)$_4$ PS$_2$ (I)



2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin,
(β-Br)$_4$ PS$_2$ (II)

Experimental

Chemicals and Instruments

The solvents used in this work (perchloric acid and acetonitrile) were purified by standard techniques.[16] The acid-base properties of the porphyrins were studied by spectrophotometric titration. The experimental techniques and methods of experimental data processing are presented in the work[17] in detail. The error in the measurement of the respective constants is ± 3–5%. The electronic absorption spectra (EAS) of the porphyrins were obtained on Shimadzu UV-1800 and Hitachi U-2000 spectrophotometers.

Synthesis

5,10,15,20-Tetrakis[4'-bromophenyl]-21,23-dithiaporphyrin We placed 5 g (11 mmol) of 2,5-bis-(4'-bromophenyl hydroxymethyl)thiophene, 150 mL of *para*-xylene, and 0.75 mL (11 mmol) of pyrrole into a 250 mL three-necked round-bottomed flask equipped with a Dean-Stark trap, a reflux condenser, and an air feed pipe. Then we heated the mixture to the para-xylene boiling point and added 1 mL of trifluoroacetic acid (TFA) from the dropping funnel to 50 mL of *para*-xylene, simultaneously passing air through the mixture. We boiled the mixture for 1 h and distilled *p*-xylene off with water vapour. Then we filtered the precipitate, washed it with water and dried it at room temperature until its weight became constant. The raw product was dissolved in dichloromethane and chromatographed on silica gel with simultaneous dichloromethane elution. We collected the second brownish-orange dithiaporphyrin layer, evaporated the eluate, precipitated the product with methanol, filtered and dried it at room temperature until its weight became constant. Yield: 0.63 g (12%). For further purification, the product was chromatographed on silica gel again. ^{1}H NMR ($CDCl_3$) δ ppm: 9.65s (4H, β-H); 8.59s (4H, β-H); 8.20d (8H 2.6-H-Ph); 7.81d (8H 3.5-H-Ph) (CDCl3). MALDI-TOF MS *m/z* calculated: $C_{44}H_{24}Br_4N_2S_2$: 964.42; found: 963.81 $[M]^+$.

7,8,17,18-Tetrabromo-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin. We placed 120 mg (0.185 mmol) of 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin into a single-necked round-bottomed flask, poured 30 mL of chloroform into it and then added 494 mg (2.78 mmol) of N-bromosuccinimide (NBS) in small portions, stirring the mixture continuously. After that, we refluxed the reaction mixture for 24 h, cooled it down to room temperature and added 2 mL of triethylamine, removed the solvent by vacuum distillation and added an excess of methanol to the residue to achieve product deposition. The residue was filtered off, washed with small amounts of dichloromethane and methanol. Yield: 150 mg (84%). ^{1}H NMR ($CDCl_3$) δ ppm: 7.80 (m, 12H, phenyl), 8.06 (m, 8H, phenyl), 9.39 (s, 4H, β-thiophene). MALDI-TOF MS *m/z* calculated: $C_{44}H_{24}Br_4N_2S_2$: 964.42; found: 964.22 [M]+.

Computer simulation methods

The geometric structure of the obtained 5,10,15,20-tetrakis[4'-bromophenyl]-21,23-dithiaporphyrin (I) and 2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (II) was optimized by computer simulation methods using the Becke functional with Perdew gradient corrections - BP86.[20,21] Application of this functional ensures the highest accuracy of the geometric parameters for tetrapyrrole macrocycles and their derivatives.[22,23] Besides, an additional polarization function - Def2-SVPP - was used to increase the accuracy of the results.[24] The effect of the solvent (acetonitrile in this case) was taken into account by applying the RSM models of dissolution described in literature.[25] The calculations were made in the Gaussian V16 program.

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2},$$

$$\eta = \frac{(E_{LUMO} - E_{HOMO})}{2} = \frac{\Delta E}{2}$$

$$\omega - \frac{\mu^2}{2\eta}$$

Here, μ is the electronic chemical potential, η is the absolute hardness, ω is the electrophilicity dipole moment (D).[26]

Spectrophotometric titration

The acid-base properties of dithia-substituted porphyrins were studied by the method of spectrophotometric titration in the $HClO_4$ - CH_3CN system at 298 K by a technique similar to the one used in [17,25]. During the titration procedure, the UV-vis spectra of compounds **I** and **II** showed four families of spectral curves, each with its own set of isobestic points (Figures S1, S2 of the *Supplementary Materials*) indicating four successive processes (1-4).

$$HPS_2^+ \xrightleftharpoons{K_{b1}} PS_2 + H^+ \quad (1)$$

$$H_2PS_2^{2+} \overset{k_{b2}}{\rightleftarrows} HPS_2^+ + H^+ \quad (2)$$

$$H_2PS_2(ClO_4)^+ \overset{k_1}{\rightleftarrows} H_2PS_2^{2+} + ClO_4^- \quad (3)$$

$$H_2PS_2(ClO_4)_2 \overset{k_2}{\rightleftarrows} H_2PS_2(ClO_4)^+ + ClO_4^- \quad (4)$$

$$Co = PS_2 + HPS_2^+ + H_2PS_2^{2+} + H_2PS_2(ClO_4)^+ + H_2PS_2(ClO_4) \quad (5)$$

Here, PS_2, HPS_2^+, $H_2PS_2^{2+}$, $H_2PS_2(ClO_4)^+$, and $H_2PS_2(ClO_4)_2$ are the molecular, mono- and double-protonated (doubly protonated) forms and associates of double-protonated (doubly protonated) forms of porphyrin ligands (**I**) and (**II**).

The intracyclic NH-groups are capable of coordinating solvent molecules and anions to form individual and/or mixed complexes. That is why a double-protonated (doubly protonated) porphyrin macrocycle can act as an anion-molecular receptor in some cases.[27,28] Acetonitrile is a weakly solvating solvent both for cation and anion particles.[29] Probably, as it was shown in work [17], in case of compounds **I** and **II**, the titration process in the $HClO_4$ - CH_3CN system consists in sequential addition of two protons (titration stages 1 and 2, processes 1 and 2) and then, possibly, of one (stage 3) and the other ClO_4^- anions (stage 4, processes 3 and 4) (Figures S1, S2). The material balance of the system, according to the composition of particles, can be represented by equation (5).

The calculation of the double-protonated (doubly protonated) form concentration region by equation (5) was carried out in a similar way. The reaction mixture at pH ~ 5 (Figure S3) (99.99 % dicationic species) was titrated by an acetonitrile solution $(C_2H_5)_4ClO_4$ (0.01 mol/L). As a result, the UV-vis spectra showed a transition from the double-protonated (doubly protonated) forms to the one reproducing the parameters of the $H_2PS_2(ClO_4)_2$ associate (Figure S4), which also indicates the possibility of association between the dication and perchlorate ions.

The effective extinction coefficients for all the studied porphyrin forms participating in equilibria (3,4) of system (1) were determined using the absorption data (UV-vis spectra) and the total concentration of particles of each of the porphyrins. The quantitative values of the stepwise and total base ionization constants for the studied compounds at 298 K were calculated by equation (6). The respective values and UV-vis parameters of the molecular and ionized species in the $HClO_4$–CH_3CN system are given in Table 2.

$$pK = -\lg K = pH + \lg Ind \quad (6)$$

Here K is the basicity constant for steps 1-4 (Kb_1, Kb_2, K_1, and K_2); *Ind* is the indicator ratio for steps 1-4, respectively: $[PS_2]/[HPS_2^+]$, $[HPS_2^+]/[H_2PS_2^{2+}]$, $[H_2PS_2^{2+}]/[H_2PS_2(ClO_4)^+]$, and $[H_2PS_2(ClO_4)^+]/[H_2PS_2(ClO_4)_2]$.

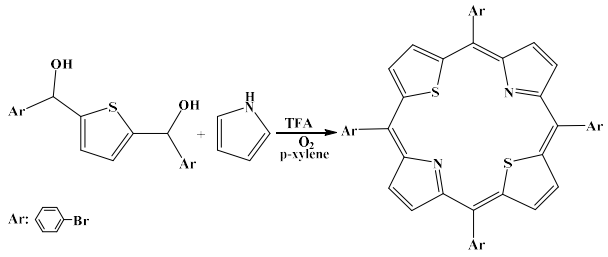
The pH-function of the glass electrode was calculated in accordance with [17]. The error in the constants measurement did not exceed 3-5%.

Results and Discussion

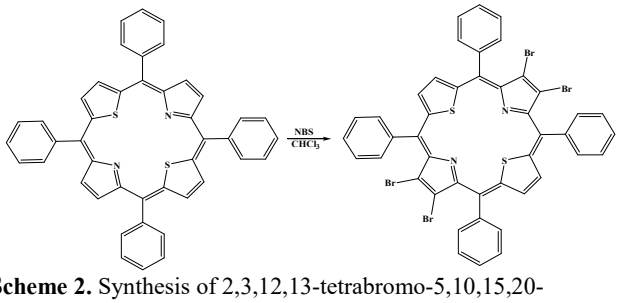
Synthesis

5,10,15,20-Tetrakis(4'-bromophenyl)-21,23-dithiaporphyrin was synthesized (Scheme 1) at the boiling temperature of *p*-xylene in the presence of trifluoroacetic acid (yield 12%) by the technique described in the literature.[18]

The bromination of 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin obtained by a technique similar to the one applied in [19] was carried out in chloroform and consisted in adding N-bromosuccinimide in small portions (Scheme 2).



Scheme 1. Synthesis of 5,10,15,20-tetrakis[4'-bromophenyl]-21,23-dithiaporphyrin.



Scheme 2. Synthesis of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin.

Computer simulation methods

The optimized geometry of the porphyrins is shown in Figure 1. All the quantum-chemical data are presented for the lowest-energy conformer of each of the compounds.

The reactivity of a compound is known to depend on the electron density distribution in the molecule. The analysis of the energy distribution of molecular orbitals in the region of the highest occupied molecular orbitals (HOMO and $HOMO^{-1}$) and the lowest unoccupied molecular orbitals (LUMO and $LUMO^{+1}$), as well as the LUMO-HOMO energy gap value (ΔE) are presented in Table 1.

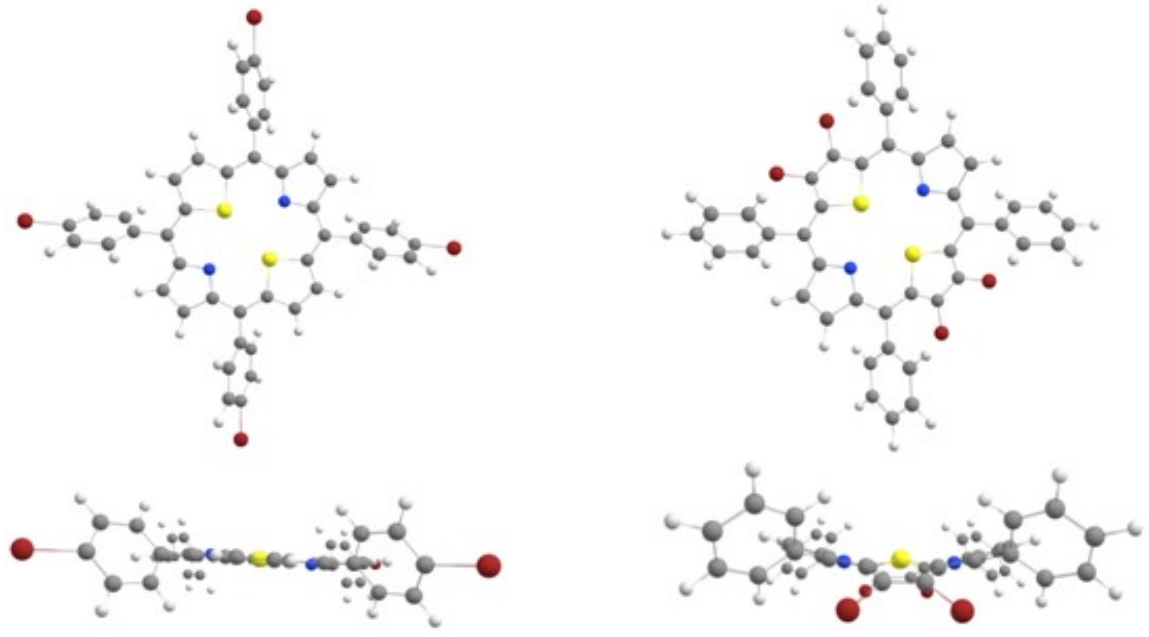
Table 1 shows that porphyrin **I** and porphyrin **II** have similar donor-acceptor properties, according to the μ values. However, porphyrin **II** is more stable (η 2 > η 1).

The electrophilicity values for both porphyrins allows them to be classified as highly electrophilic compounds.[2] The dipole moment values indicate that porphyrin **II** is more polar than porphyrin **I**.

A comparison of the calculation data for compounds **I** and **II** showed that the bond lengths in the porphyrin core change by ~1-2 Å when going from compound **I** to compound **II**, which is accompanied by a significant distortion of the macrocycle plane, which takes a saddle shape. The other geometric parameters, such as the bond angles of the pyrrole ring, increase when bromine atoms are introduced into the *β*-positions of the pyrrole rings at the C_2, C_3, C_{12}, and C_{13} atoms. The tilt angle of the phenyl ring to the macrocycle plane becomes slightly bigger – by 2-3 degrees.

Evidently, the nonplanarity of the porphyrin core of compound **II** caused by steric repulsion of the large peripheral substituents lowers the strain by changing the bond lengths and angles. The deviation of the N_{22}-S_{21}-N_{24} and N_{22}-S_{23}-N_{24} angles from 180 degrees indicates the S atom position out of the macrocycle plane. The pyrrole rings shift symmetrically upwards and downwards from the central plane of the macrocycle in the opposite directions. The phenyl rings tilt towards the macrocycle plane to reduce the repulsive interaction between the substituents. The data obtained show that the substitution in the C_2, C_3, C_{12}, and C_{13} positions makes the macrocycle core lengthen towards the bromine atoms as a result of the macrocycle distortion caused by the steric effect.

The states of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are extremely important quantum-chemical parameters that may affect electric and optical properties. In a redox reaction, the oxidizer has a low LUMO value and the reducing agent has a high HOMO value. The nature of substituents and their position in the macrocycle have a great effect on the acid properties of tetrapyrrole macrocycles. The obtained HOMO and LUMO values show that compound II has the lowest LUMO (-3.833 eV) (Table 1) and is probably a good oxidizing agent.



I **II**

Figure 1. Optimized structures: 5,10,15,20-tetrakis[4'-bromophenyl]-21,23-dithiaporphyrin (**I**) and 2,3,12,13-tetrabromo-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (**II**).

Table 1. Quantum-chemical parameters of compounds **I** and **II**.

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (eV)	η (eV)	ω (eV)	D (Debye)
$(p\text{-}Br)_4$ PS2 (**I**)	-5.2954	-3.6812	-1.6142	-4.4883	0.8071	12.4798	0.002
$(\beta\text{-}Br)_4$ PS2 (**II**)	-5.2472	-3.833	-1.4142	-4.5401	0.7071	14.5754	0.179

Table 2. Indicators of base ionization constants and spectral characteristics of molecular and protonated forms of the porphyrins in the AN–$HClO_4$ system, 298 K.

Porphyrin	λ(lgε)					pKb_1, pK_1	pKb_2, pK_1	$\sum pKb_{1,2}$, $\sum pK_{1,2}$
H_2TPP	413(5.02)	512(3.56)	546(3.12)	589(2.92)	646(2.96)	-	-	18.67[29]
H_4TPP^{2+}	441(5.04)	-	-	-	661(4.17)			19.8[28]
	369sh(4.45)	471(5.14)	646(4.16)	765 (3.92)				
$H_4Br_8TPP^{2+}$	490(5.19)	-	-	741(4.52)				16.60[30]
H_2Br_4TPP	431(4.20)	537(3.25)	693(3.15)					
$H_4Br_4TPP^{2+}$	465(4.36)			699(3.63)				17.96[30]
PS_2	412sh(5.12)	429(5.30)	509(4.36)	541(3.80)	700(3.66)	12.25	8.95	21.20[17]
HPS_2^+	413sh(4.97)	444(5.24)	546(4.19)	594(3.70)	693(3.66)			
$H_2PS_2^{2+}$	345(5.01)	445 (5.37)	548(3.77)	594(3.83)	694(3.82)			
$H_2PS_2^{2+}ClO^{4-}$	381sh(5.10)	412 (4.77)	451(5.39)	689(4.17)	738(4.12)	5.93	4.29	10.22[17]
$H_2PS_2^{2+}(ClO_4)_2^{2-}$	385sh(5.27)	411(5.30)	454(5.82)	686(5.33)	735(5.32)			
(p-Br)$_4$ PS_2	430(5.03)	511(4.38)	544(4.21)	692(4.01)	728(3.92)	12.19	7.10	19.29
(p-Br)$_4$ HPS_2^+	434(4.89)	509(4.20)	543sh(4.01)	698(3.86)	730(3.82)			
(p-Br)$_4$ $H_2PS_2^{2+}$	448(4.93)	598(3.92)		696(3.95)	724(sh)(3.88)			
(p-Br)$_4$ $H_2PS_2^{2+}ClO^{4-}$	462(4.91)				709(4.13)	6.80	3.00	9.8
(p-Br)$_4$$H_2PS_2^{2+}(ClO_4)_2^{2-}$	465(5.02)			694(4.24)	734(4.91)			
(β-Br)$_4$$PS_2$	438(4.96)	521(4.24)	636(3.65)	698(3.96)		10.88	7.45	18.33
(β-Br)$_4$$HPS_2^+$	441(4.79)	466sh(4.67)	519(4.17)		751(4.04)			
(β-Br)$_4$$H_2PS_2^{2+}$	470(4.89)	572(4.06)	633(4.06)		745(4.15)			
(β-Br)$_4$$H_2PS_2^{2+}ClO^{4-}$	475(4.86)		704(4.17)		783(4.19)	5.78	3.64	9.42
(β-Br)$_4$$H_2PS_2^{2+}(ClO_4)_2^{2-}$	477(4.85)		690(4.27)		789(4.29)			
	490(4.85)							

Spectrophotometric titration

The presence of several families of isosbestic points in the UV-vis spectra is characteristic of step-wise protonation processes (Figures S1, S2). The spectrophotometric titration curves plotted based on the experimental data had pronounced steps. The presence of isosbestic points and the character of changes in the absorption spectra indicate that, as the concentrations of the two centers of the porphyrin molecule absorption changed, the ratio between the ionized forms during the porphyrin deprotonation remained the same.[30]

An analysis of the data in Table 2 showed that the introduction of bromine atoms into the macrocycle weakens the base properties of the compound both in case of tetraphenylporphyrin derivatives and in case of dithia-substituted analogues of tetraphenylporphyrins – in the ascending order of the basicity constants the compounds can be arranged as follows: H_2TPP > H_2 (β-Br)$_4$TPP > H_2 (β-Br$_8$)TPP and PS_2 > (*p*-Br)$_4$$PS_2$ > PS_2(β-Br)$_4$. By comparing the formation constants of the perchlorate associates of compounds **I** and **II**, it can be concluded that compound **I** can more easily associate with perchlorate ions.

The electron-acceptor capacity of the porphyrins increases as follows: **II** > **I**, indicating weaker base properties of compound **II**, which agrees well with the spectrophotometric titration results.

Conclusion

Analyzing the data obtained, it can be concluded that the nature of the substituent and its position in the macrocycle have a great effect on the base and spectral properties of dithia-substituted analogues of tetraphenylporphyrins. The study conducted showed that chemical modification of the properties of dithia-substituted analogues of tetraphenylporphyrins changed the ligand molecule geometry, which was reflected in changes in the base and receptor properties of the molecule.

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