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Bisporphyrin–Calix[4]arene Heterotopic Receptors of Multifunctional Substrates

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Abstract—In order to create heterotopic receptors of polyfunctional substrates we have synthesized the bisporphyrin–calix[4]arene crown ethers [6] with the amino and hydroxy groups in tetrapyrrole fragments and polyethyleneoxide complexing cavity in the calix[4]arene fragment of the macrocycle. Their spectral properties and complexing ability toward the alkali metal cations, organic diamines, and dicarboxylic acid esters were investigated.

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The chemistry of macrocyclic functional devices is extremely interesting area of coordination and organic chemistry rapidly developing in the last decade. Its subject of study comprises the compounds combining different classes of organic substances: calix[*n*]arenes, calix[4]pyrroles, crown[*n*] ethers, cyclodextrins, porphyrins, and other macrocycles. Calix[4]areneporphyrins [1–3] and calix[4]pyrroleporphyrins [4, 5] are the examples of compounds formed by covalent fusing of different macrocycles, which retain all individual properties and acquire qualitatively new properties compared with the original fragments.

Calix[4]areneporphyrins have a number of advantages. Firstly, they often possess unique properties as molecular receptors. Secondly, the processes of binding neutral and/or charged particles by different fragments of calix[4]areneporphyrins are interrelated that allows using one process (e.g., complexation of the macrocycle of the calix[4]arene fragment with an alkali metal cation) as a means to control another process (complexation of the macrocycle of the porphyrin fragments with neutral molecules).

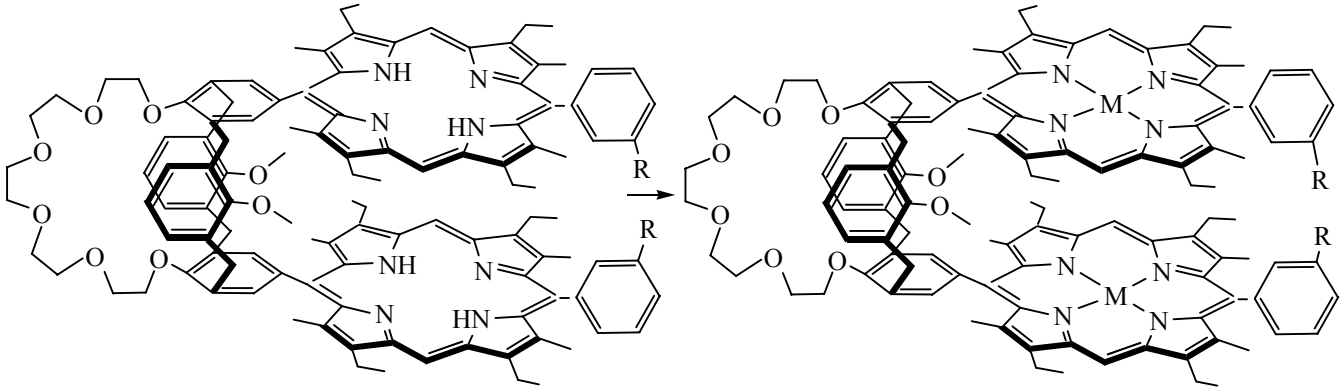
This paper describes the creation of heterotopic receptors on the basis of bisporphyrin–calixarene–crown–ethers containing amino and hydroxy groups in the tetrapyrrole fragments and a polyethylenoxide complexing cavity in the calixarene fragment of the macroheterocycle. It is known that crown ethers and calixarene crown ethers possess receptor properties with respect to metal cations [6–8]. On the other hand, porphyrinate macrocycles possess the ability to axial coordination by the central metal cation of small organic molecules containing electron-releasing atoms or functional groups in their structure [9–11]. If the tetrapyrrole macrocycle has besides the other reaction sites at the periphery of the molecule (amino, hydroxy, carboxy, sulfo, etc.), then such porphyrinate molecules acquire selective complexing ability with respect to the polyfunctional substrates. Covalently combining in one molecule a crown-calixarene fragment and two appropriately functionalized porphyrinate macrocycles allows the creation of sterically preorganized heterotopic receptors possessing polyfunctional complexing power toward both charged particles and neutral molecules of various nature.

In connection with our interests in the field of coordination chemistry of macroheterocyclic compounds, in this work new bisporphyrin–calix[4]arene–crown[6] ethers were synthesized with the amino and hydroxy groups in tetrapyrrole fragments and polyethylenoxide complexing cavity in the calix[4]arene fragment of the macrocycle. We investigated their spectral properties and complexing ability towards alkali metal cations, aromatic diamines, and dicarboxylic acids esters.

The bisporphyrin–calix[4]arene–crown[6] ethers with nitro (**I**) and methoxy (**II**) groups in the tetrapyrrole fragments were synthesized by a mixed-

aldehyde condensation of 5,5'-unsubstituted dipyrrolylmethane, diformylcalixarene, and an appropriate aromatic aldehyde [12–14]. By reduction of nitro groups in the bis[(3-nitrophenyl)porphyrin]calix[4]arene-crown[6] (**I**) we prepared bis[(3-aminophenyl)porphyrin]calix[4]arene-crown[6] (**III**). By hydrolysis of bis[(3-methoxyphenyl)porphyrin]-calix[4]arene-crown[6] (**II**) was prepared bis[(3-hydroxyphenyl)porphyrin]-calix[4]arene-crown[6] (**IV**) (scheme). By boiling **III** and **IV** with zinc acetate in dimethylformamide the corresponding Zn(II) porphyrinates Zn (**V–VI**) were synthesized.

Compounds **III–VI** are stable: in solid form they are not oxidized under the action of atmospheric oxygen. Electron absorption spectra (EAS) of compounds **III–VI** are characterized by a significant broadening of the Soret band and a reduced coefficients of molar extinction compared to monomeric analogs, 5,15-diphenyl-2,7,12,17-tetramethyl-3,8,13,18-tetraethylporphyrin (**VII**) and its zinc complex (**VIII**) [14]. The shortwave shift (~6 nm) of the Soret band in the EAS of bisporphyrin-calix[4]arene-crowns[6] **III–VI** as compared with **VII** and **VIII** also supports the cyclophane structure, where a significant interaction of π-electronic systems of the tetrapyrrole chromophores in the dimers is observed. ^{1}H NMR spectra of **III–VI** contain the signals of the protons of calixarene, crown ether, and porphyrin fragments. The presence of a clear singlet of protons of methylene groups (at δ ~3.88 ppm) according to published data [3] indicates that the calix[4]arene fragment in **III–VI** is in 1,3-*alternate* conformation. It should also be noted that the signals of all porphyrin fragments in **III–VI** are shifted upfield compared with the corresponding signals in the spectra of **VII** and **VIII** that, according to published data and to the results of our own studies [10–11], confirms the cyclophane structure of compounds **III–VI**.



I–II **III–VI**

R = NO_2 (**I**), OCH_3 (**II**), NH_2 (**III, V**), OH (**IV, VI**); M = 2H (**III, IV**), Zn (**V–VI**).

A characteristic feature of the dimeric porphyrins is the presence of internal complexing cavity, where the bidentate ligands can penetrate and form stable complexes with two points of binding via donor–acceptor bonds. The possibility of varying the size of the cavity due to the length and nature of the bridges binding porphyrin fragments, makes it possible to prepare selective receptors for a particular type of substrates. In [1, 2] and in a series of our works [3, 12, 14, 17] was shown that bisporphyrin-calix[4]arenes can, depending on the structural features of calix[4]arene platform, form stable complexes through two intracavity binding sites with di- and triethylenediamines.

The study of the complexation of amino- (**V**) and hydroxy-substituted (**VI**) bisporphyrinate-calix[4]arene-crowns[6] (**L**^{1}) by spectrophotometric titration and ^{1}H NMR spectroscopy revealed that it proceeds with the formation of stable complexes **IX** with two intracavity donor–acceptor bond. At the formation of the complex **IX** with the ligand taken in a wide concentration range, the spectral curves in the course of complexation have one family of isobestic points (Fig. 1). They are characterized by relatively small shifts of absorption bands because the red shift (axial coordination of the ligand) is compensated partially by a corresponding blue shift and by a slight broadening of the Soret band (the exciton interaction in the porphyrin fragments).

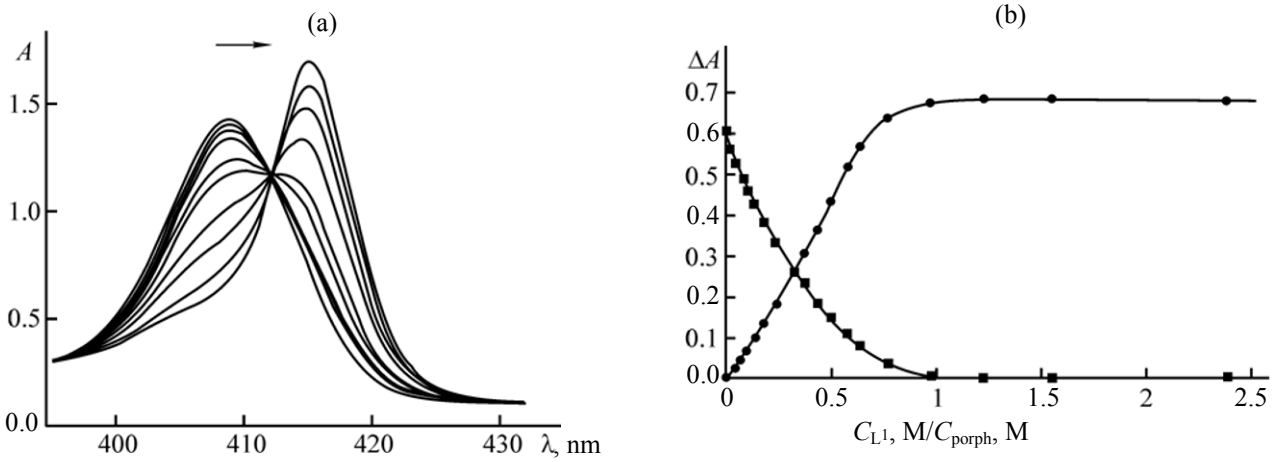
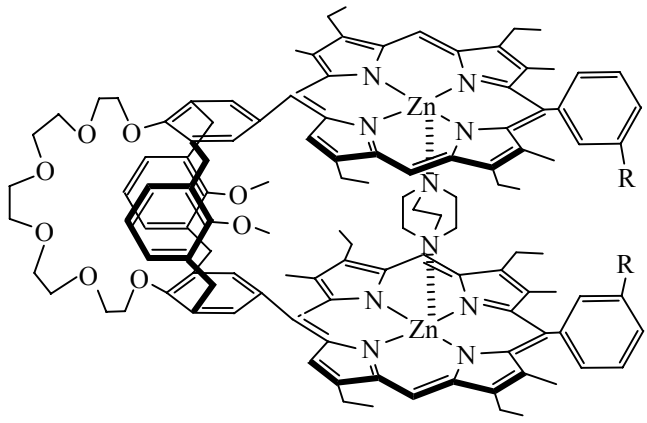


Fig. 1. (a) Spectral changes in the region of the Soret band at the titration of **VI** with diamine in toluene in the concentration range of $\mathbf{L^1}$ from 0 to 6.6×10^{-6} M at 25°C ($C_{porph} = 5.6\times10^{-6}$ M); (b) the titration curves at increasing and decreasing wavelengths.

The upfield shift of the signals of CH_2CH_2 protons of the ligand ($\Delta\delta = -3.72$ ppm), their equivalence (they appear as a singlet) and intensity ratio of the signals of protons of the ligand and the porphyrin fragment in ^{1}H NMR spectra of the complex also indicate the formation of intracavity complexes **IX**.

Stability constants of the intracavity complexes **V**–$\mathbf{L^1}$ and **VI**–$\mathbf{L^1}$ in toluene calculated by the formula (1) from the data of spectrophotometric titration of porphyrin dimers with diamine $\mathbf{L^1}$ are 6.3×10^6 l mol^{-1} and 5.5×10^6 l mol^{-1}, respectively.

The study of complexation of **VI** with 1,4-phenylenediamine ($\mathbf{L^2}$) in toluene showed that in the concentration range (C_{ligand} from 0 to 8×10^{-4} M) also a



IX

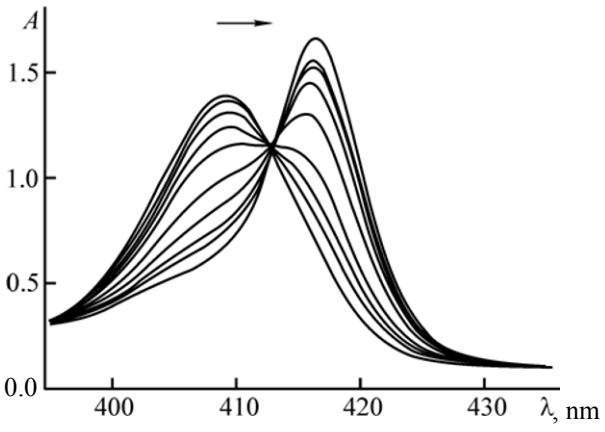
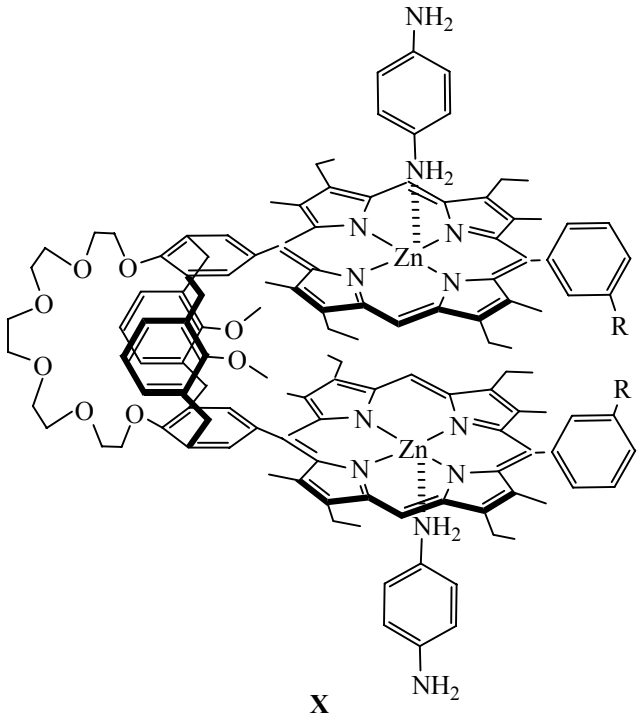


Fig. 2. Spectral changes in the region of the Soret band at the titration of **VI** with diamine in toluene in the concentration range of $\mathbf{L^2}$ from 0 to 5.4×10^{-4} M at 25°C ($C_{VI} = 5.6\times10^{-6}$ M).

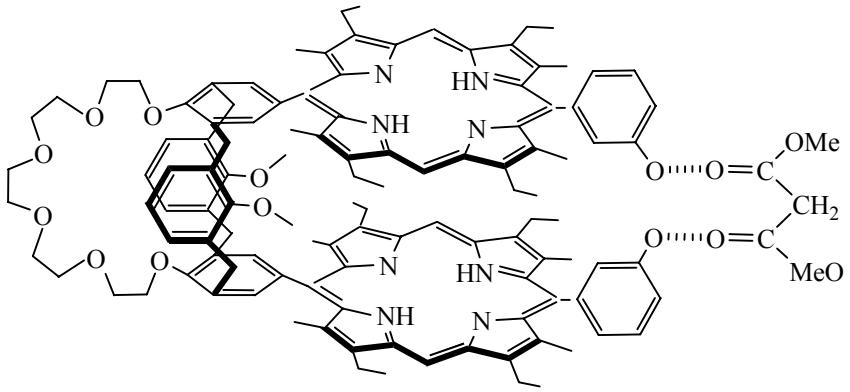
complex of one type is produced (Fig. 2). The splitting of proton signals of $\mathbf{L^2}$ and the ratio of the intensities of the signals of porphyrinate protons and the protons of the ligand in the ^{1}H NMR spectrum of the **VI**–$\mathbf{L^2}$ complex support the formation of "external" complex **X** of 1:2 composition when the ligand molecules cannot penetrate the interporphyrin complexing cavity and are located outside the tetrapyrrole macrocycles. Protons of the aryl moiety $\mathbf{L^2}$ are no longer equivalent, and some of them are located close to the tetrapyrrole macrocycle, experiencing the ring current shielding effect of π-electrons of the porphyrin fragment to a greater extent shifting upfield their signals (4H, at 2.69 ppm). Another part of the protons being more distant from the macrocycle give rise to the signals in a weak field (4H, at 5.71 ppm). Similarly the proton signals of the amino groups of the substrate are split in



X

the ^{1}H NMR spectrum of complex **VI**–**L**^{2} (singlets at 0.29 (4H) and 3.96 (4H) ppm, respectively). Stability constant (K_{st}) characterizing the process of binding one ligand **L**^{2} with one porphyrin fragment of **VI**, calculated by Eq. (1) from the data of spectrophotometric titration (1480 l mol^{-1}) corresponds to the stability constants of the monomeric zinc porphyrinate complex **VIII**–**L**^{2}, K_{st} = 1320 l mol^{-1}) [8]. The stability constants of **VI**–2**L**^{2} complex of 1:2 composition calculated by Eq. (2) is 1.96×10^6 l^2 mol^{-2}.

Compounds **III**–**VI** can form complexes with the esters of dicarboxylic acids through the hydrogen bonding. The complexation is accompanied by a change in the distance between the porphyn fragments of the macrocycle which is reflected in the electron absorption spectrum of the reaction system bisporphyrin–carboxylic acid ester as a blue or red shift and broadening or narrowing of the absorption bands, which allows to examine the process by spectrophotometric titration.



XI

The study of the complexation of **III** and **IV** with methyl esters of several dicarboxylic acids [malonic (**L**^{3}), maleic (**L**^{4}), fumaric (**L**^{5}), succinic (**L**^{6}), and isophthalic (**L**^{7})] showed that the spectral changes typical of the formation of 1:1 complex **XI** with a family of isobestic points occur in the case of malonic ester. Figure 3 shows the changes in EAS of **III** at adding methyl malonate (**L**^{3}). Probably, the formation

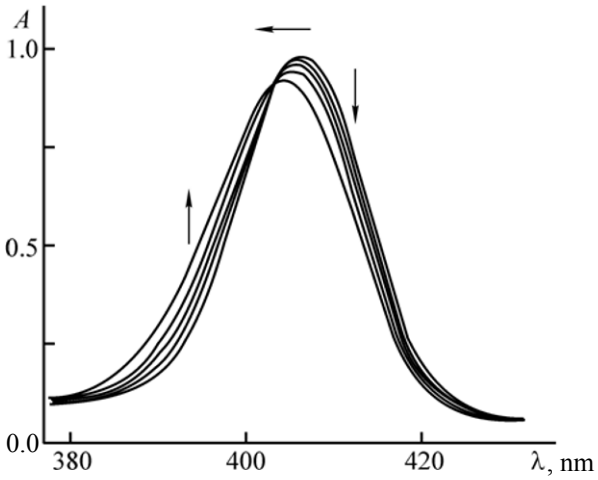
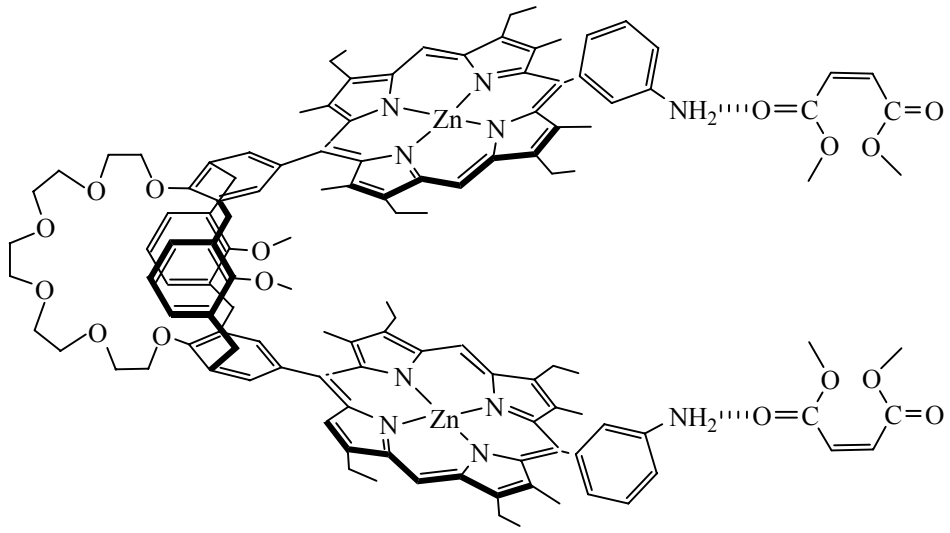


Fig. 3. Spectral changes in the region of the Soret band at the titration of **III** with dimethyl dicarboxylate in toluene in the concentration range of $\mathbf{L}^3$ from 0 to 5.2×10^{-3} M at 25°C ($C_{porph} = 6.6\times10^{-6}$ M).

of complex **XI** in the case of methyl malonate is accompanied by a approachment of the porphyrin fragments, which is characterized by the corresponding blue shift of the bands in the EAS. Spectral changes in the **IV**–$\mathbf{L}^3$ system are similar. The stability constants of the complexes **III**–$\mathbf{L}^3$ and **IV**–$\mathbf{L}^3$ calculated by Eq. (1) from the data of spectrofotometric titration are respectively 680 and 1320 l mol^{-1}.

The analysis of experimental data allows us a conclusio that the size of intramolecular binding cavities in compounds **III** and **IV** are best consistent with the size of malonic acid among all the investigated dicarboxylic acids, and these bisporphyrinates form intracavity complexes through two hydrogen bonds only with the malonate ester.

The study of the complexation process of porphyrinate **V** with dimethyl maleate ($\mathbf{L}^4$) showed that in a wide concentration range of ligand (C_{ligand} from 0 to 5.3×10^{-5} M) the spectral changes during the reactions occur with the preservation of the family of isobestic points (Fig. 4). The titration curve has one jump indicating the formation of the bisporphyrinate–ligand complex of one type, and the slope of the plot log $[(A_0 - A_{eq})/(A_{eq} - A_c)]$ vs. log C of the ligand equals two, indicating that the formed complex has a composition of 1:2. The process of complexation of **V** with $\mathbf{L}^4$ is accompanied, in contrast to the complexes **III**–$\mathbf{L}^3$ and **IV**–$\mathbf{L}^3$, by a red shift of the bands in the EAS, which probably indicates that the distance between the porphyrin fragments increases upon the formation of **V**–$\mathbf{2L}^4$ (**XII**). The stability constant of the complex calculated by Eq. (3) is $K_{st} = 2.45\times10^5$ l^2 mol^{-2}. The complexation of **V** with dimethyl fumarate ($\mathbf{L}^5$) proceeds similarly. The stability constants of the complex **V**–$\mathbf{2L}^5$ is 1.81×10^5 l^2 mol^{-2}.



XII

Conformational changes of bisporphyrin-calix[4]-arene-crown[6] molecules caused by the binding of alkali metal cation by the polyether complexing cavity of the supramolecule calix[4]arene fragment due to the approachment or, conversely, removal of the porphyrin fragments from each other, are also reflected in the electron absorption spectra. The change in the position and intensity of the absorption bands in the EAS

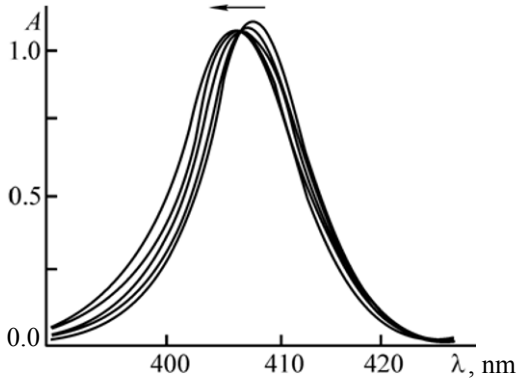


Fig. 4. Spectral changes in the region of the Soret band at the titration of **V** with dimethyl dicarboxylate in toluene in the concentration range of $\mathbf{L}^4$ from 0 to 5.3×10^{-5} M at 25°C ($C_{porph} = 6.6\times10^{-6}$ M).

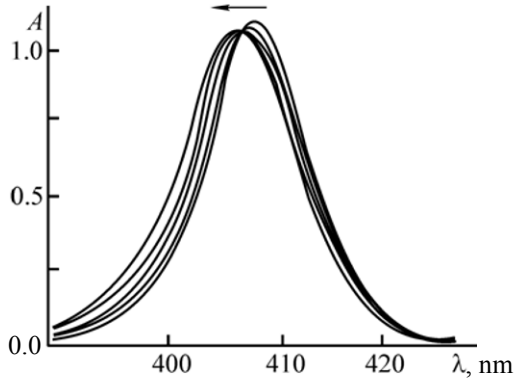
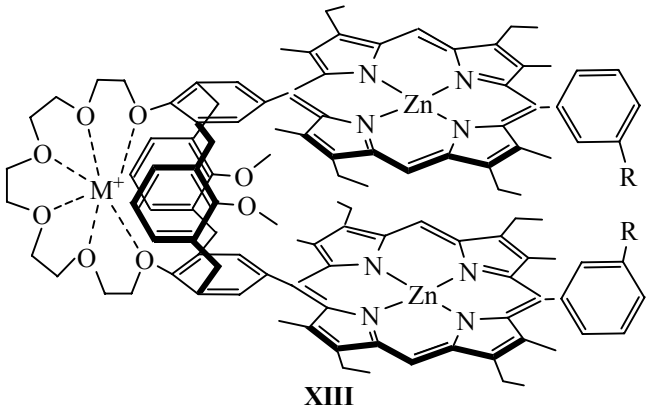


Fig. 5. Spectral changes in the region of the Soret band at the titration of **VI** with K^+ cation in dichloromethane in the concentration range of KBF_4 from 0 to 1.2×10^{-4} M at 25°C ($C_{porph} = 9.4\times10^{-6}$ M).

accompanying the process of complexation allows the application of the method of spectrophotometric analysis to the study of the binding of metal cations by the polyether cavity of the calixarene fragment.

Figure 5 shows the spectral changes in the reaction system at the interaction of **VI** with KBF_4. These changes and spectrophotometric titration curves derived from them indicate that the resulting complex has a stoichiometry of 1:1 (**XIII**). Similar processes take place between **VI** and $NaBF_4$. Stability constants of the complexes calculated by Eq. (1) from the data on spectrophotometric titration of **VI** with tetrafluoroborates (KBF_4 and $NaBF_4$) are 8.2×10^7 and 9.6×10^4 l mol^{-1}, respectively. These data are in good agreement with the published data obtained for calix[4]arene-crown[6] of similar structure but without the porphyrin fragments [18].



XIII

Thus, the results obtained indicate that the synthesized bisporphyrin-calix[4]arene-crown[6] are multifunctional receptors forming stable complexes with potassium and sodium cations, triethylenediamine, and methyl malonate. The most significant conditions for the formation of such complexes is the geometric correspondence by size of the substrate and the intramolecular complexing cavity of the receptor and the presence of several (two or more) complementary binding sites.

EXPERIMENTAL

Bisporphyrin-calix[4]arene-crowns[6] **I** and **II** were synthesized by the methods [12–14]. Individual compounds were isolated by column chromatography on neutral alumina. As an eluent we used methylene chloride–hexane 1:1 mixture. Organic solvents were purified by known methods [19]. The reaction course was monitored by TLC on the Silufol UV-254 plates. ^{1}H NMR spectra of compounds **III–VI** were recorded on a Bruker VC-500 spectrometer at the operating frequency 500.17 MHz in deuterochlroform, internal reference TMS. Electron absorption spectra (EAS) of compounds **III–VI** in toluene were recorded on a Varian Cary 100 spectrophotometer. EAS of **III–VI** and their changes upon adding to the system of the substrates of different nature are depicted in Figs. 1–5.

Stability constants (K_{st}) of the porphyrin complexes with different substrates the for the 1:1 complexes was calculated by the Eq. (1).

$$K_{st} = [A\cdot B]/([A]\cdot[B])$$
$$= (1/[B])[(\Delta A_{i,\lambda1}/\Delta A_{0,\lambda1})\cdot(\Delta A_{0,\lambda2}/\Delta A_{i,\lambda2})]\ \ (\mathrm{M})^{-1}, \quad (1)$$

where λ_1 is the wavelength of decreasing band, λ_2 is wavelength of the increasing band, [A] is the porphyrinate concentration, [B] is the substrate concentration, ΔA_0 is maximum change in optical

density of the solution at a given wavelength, ΔA_i is the change in optical density of the solution at a given wavelength, at a given concentration [20].

For 1: 2 complexes (A-2B) at stepwise (parallel or sequential) complexation was used Eq. (2).

$$K_{st} = K^1_{st} \cdot K^2_{st} \ (M)^{-2}. \quad (2)$$

At simultaneous complexation (third order reaction) was used Eq. (3).

$$K_{st} = [A \cdot 2B]/([A] \cdot [B]^2) = (1/[B]^2)[(\Delta A_{i,\lambda 1}/\Delta A_{0,\lambda 1}) \cdot (\Delta A_{0,\lambda 2}/\Delta A_{i,\lambda 2})]. \ (M)^{-2} \quad (3)$$

The error in determining K_{st} is about 7–10%.

5,17-Bis-[*meso*-(3-aminophenyl)tetramethyltetraethylporphyrin]-25,27-dimethoxy-26,28-crown[6]-calix[4]arene, 1,3-*alternate* (III). A mixture of tin dichloride dihydrate (0.67 g, 3.0 mmol), **I** (0.62 g, 0.3 mmol) and hydrochloric acid (50 ml) was stirred at 90–100°C for 30 min. The mixture was cooled, filtered, and diluted with an equal volume of water. Hydrochloride **IV** precipitate formed was filtered off and washed in succession with dilute (1:2) hydrochloric acid, ammonia and hot water. Compound **IV** was dried, dissolved in benzene and subjected to chromatography on aluminum oxide (II degree of activity by Brockmann). The eluate was evaporated and **IV** was precipitated with hexane. Yield 0.43 g, 71%. R_f 0.67 (Al_2O_3, eluent is a mixture CH_2Cl_2–C_6H_{14}, 1:2). Electron absorption spectrum (toluene), λ_{max}, nm (log ε): 406.0 (5.19), 530 (4.15), 566 (3.98), 602 (4.13), 650 (4.32). ^{1}H NMR spectrum of **III**, δ, ppm: 10.2 br.s (4H, NH_2), 9.79 s. (4H, *ms*-H), 7.64–7.69 m (4H, Ar_o, porphyrin + 4H, Ar, calixarene) 7.51–7.55 pm (2H, Ar_p, porphyrin + 4H, Ar, calixarene), 7.02–7.07 m (4H, Ar_p, porphyrin. Ar_p, calixarene), 4.13 s (6H, OCH_3), 3.82 s (8 H, $ArCH_2Ar$), 3.76 q (8H, CH_2CH_3), 3.70 m (8H, CH_2CH_3), 3.61 s (4H, OCH_2CH_2O), 3.57 m (16H, OCH_2CH_2 O), 2.03 s (12H, CH_3), 2.11 s (12H, CH_3), 1.06 t (12H, CH_2CH_3), 0.85 t (12H, CH_2CH_3), –2.48 br.s. (4H, NH).

5,17-Bis-[*meso*-(3-hydroxyphenyl)tetramethyltetraethylporphyrin]-25,27-dimethoxy-26,28-crown[6]-calix[4]arene, 1,3-*alternate* (IV). To a solution of **II** (0.54 g, 0.3 mmol) in chloroform (10 ml) was added a solution of boron tribromide (0.35 ml, 3.0 mol) in chloroform (8 ml), and the mixture was stirred at room temperature for 1 h. To the reaction mixture was added methanol (5 ml) and the stirring was continued for 30 min. The resulting mixture was neutralized with a solution of ammonia, evaporated to a minimum volume, and subjected to chromatography on aluminum oxide (II degree of activity by Brockmann), eluent chloroform. The eluate was evaporated and porphyrin was precipitated with hexane. Yield 21.2 g, 40%. R_f 0.57 (Al_2O_3, eluent a mixture of CH_2Cl_2–C_6H_{14}, 1:2). Electron absorption spectrum (toluene), λ_{max}, nm (log ε): 407 (5.22), 532 (4.19), 567 (4.02), 603 (4.11), 653.4 (4.37). ^{1}H NMR spectrum of IV, δ, ppm: 9.81 s (4 H, *ms*-H), 8.67 br.s (2H, OH), 7.69–7.76 m (4H, Ar_o, porphyrin + 4H, Ar, calixarene) 7.55–7.59 m (2H, Ar_m, porphyrin + 4H, Ar, calixarene), 7.06–7.09 m (4H, Ar_p, porphyrin, Ar_p, calixarene), 4.11 s (6H, OCH_3), 3.88 s (8H, $ArCH_2Ar$), 3.80 q (8 H, CH_2CH_3), 3.72 m (8H, CH_2CH_3), 3.63 s (4H, OCH_2 CH_2 O), 3.59 m (16 H, OCH_2 CH_2 O), 2.01 s (12H, CH_3), 2.14 s (12H, CH_3), 1.03 t (12H, CH_2CH_3), 0.89 t (12H, CH_2CH_3), –2.23 br.s. (4H, NH).

Zinc 5,17–bis[*meso*-(3-aminophenyl)tetramethyltetraethylporphyrinate]-25,27-dimethoxy-26,28-crown[6]-calix[4]arene, 1,3-*alternate* (V). To a solution of **III** (30 mg) in dimethylformamide (70 ml) was added an excess (1:10 mol) of zinc acetate. The reaction mixture was refluxed for 30 min, cooled, diluted with water (1:1), and the precipitate was filtered off. The precipitate was dried and subjected to chromatography on aluminum oxide, eluent a mixture CH_2Cl_2–C_6H_{14}, 1:1. Solvent was distilled off in a vacuum, the porphyrin was recrystallized from a mixture CH_2Cl_2–CH_3OH, 1:1. Yield 28.4 mg, 89%. R_f 0.69 (Al_2O_3), eluent a mixture CH_2Cl_2–C_6H_{14}, 1:1. EAS (toluene), λ_{max}, nm (log ε): 408 (4.89), 537 (4.19), 570 (3.82). ^{1}H NMR spectrum of **V**, δ, ppm: 9.79 s (4 H, *ms*-H), 8.64 br.s (2H, OH), 7.65–7.71 m (4H, Ar_o, porphyrin + 4H, Ar, calixarene), 7.52–7.56 m (2H, Ar_m, porphyrin + 4H, Ar, calixarene), 7.01–7.05 m (4H, Ar_p, porphyrin, Ar_p, calixarene), 4.07 s (6H, OCH_3), 3.86 s (8H, $ArCH_2Ar$), 3.82 q (8 H, CH_2CH_3), 3.70 m (8H, CH_2CH_3), 3.60 s (4H, OCH_2CH_2O), 3.52 m (16H, OCH_2CH_2O), 2.06 s (12H, CH_3), 2.15 s (12H, CH_3), 1.06 t (12H, CH_2CH_3), 0.93 t (12H, CH_2CH_3).

Similarly was synthesized **zinc 5,17-Bis-[*meso*-(3-hydroxyphenyl)tetramethyltetraethylporphyrinate]-25,27-dimethoxy-26,28-crown[6]-calix[4]arene, 1,3-*alternate* (VI)**. Yield 76%. R_f 0.46 (Al_2O_3), eluent a mixture CH_2Cl_2–C_6H_{14}, 1:1. EAS (toluene), λ_{max}, nm (log ε): 409 (4.67), 535 (4.02), 568 (3.78). ^{1}H NMR spectrum of **VI**, δ, ppm: 9.75 s (4H, *ms*-H), 8.62 br.s (2H, OH), 7.61–7.67 m (4H, Ar_o, porphyrin + 4H, Ar, calixarene) 7.50–7.53 pm (2H, Ar_m, porphyrin + 4H,

Ar, calixarene), 6.98–7.01 m (4H, Ar_p, porphyrin, Ar_p, calixarene), 4.02 s (6H, OCH_3), 3.84 s (8H, $ArCH_2Ar$), 3.76 q (8H, CH_2CH_3), 3.73 m (8H, CH_2CH_3), 3.62 s (4H, OCH_2CH_2O), 3.50 m (16H, OCH_2CH_2O), 2.01 s (12H, CH_3), 2.11 s (12H, CH_3), 1.02 t (12H, CH_2CH_3), 0.87 t (12H, CH_2CH_3). ^{1}H NMR spectrum of complex **VI–L**^{1} 1:1, δ, ppm: 9.72 s (4H, *ms*-H), 8.60 br.s (2H, OH), 7.63–7.70 pm (4H, Ar_o, porphyrin + 4H, Ar, calixarene) 7.52–7.55 m (2H, Ar_m, porphyrin + 4H, Ar, calixarene), 7.01–7.04 m (4H, Ar_p, porphyrin, Ar_p, calixarene), 4.05 s (6H, OCH_3), 3.82 s (8H, $ArCH_2Ar$), 3.77 q (8H, CH_2CH_3), 3.71 m (8H, CH_2CH_3), 3.65 s (4H, OCH_2CH_2O), 3.52 m (16 H, OCH_2CH_2O), 2.03 s (12H, CH_3), 2.15 s (12H, CH_3), 1.07 t (12H, CH_2CH_3), 0.89 t (12H, CH_2CH_3), –3.72 s (12H, $N(CH_2CH_2)_3N$). ^{1}H NMR spectrum of complex **VI–2L**^{2} 1:2, δ, ppm: 9.74 s (4H, *ms*-H), 8.63 br.s (2H, OH), 7.67–7.72 m (4H, Ar_o, porphyrin + 4H, Ar, calixarene) 7.57–7.60 m (2H, Ar_m, porphyrin + 4H, Ar, calixarene), 7.03–7.08 m (4H, Ar_p, porphyrin, Ar_p, calixarene), 4.09 s (6H, OCH_3), 3.96 s (4H, NH_2), 3.83 s (8H, $ArCH_2Ar$), 3.79 q (8 H, CH_2CH_3), 3.73 m (8H, CH_2CH_3), 3.67 s (4H, OCH_2CH_2 O), 3.55 m (16H, OCH_2CH_2O), 5.71 d (4H Ar, ligand), 2.07 s (12H, CH_3), 2.17 s (12H, CH_3), 1.09 t (12H, CH_2CH_3), 0.91 t (12H, CH_2CH_3), 2.69 d (4H, Ar, ligand), 0.29 s (4H, NH_2).

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