New crown-substituted aluminum(III) porphyrinate as an advanced fluorescent sensor to potassium cations in aqueous media*

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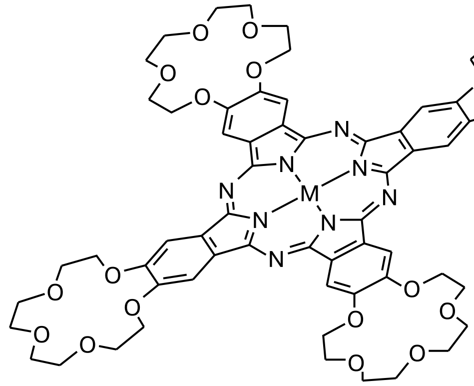
Aluminum(III) and magnesium(II) porphyrinates were synthesized starting from free base *meso*-tetra(benzo-15-crown-5)porphine (H_2TCP), $AlCl_3$, and $Et_2O \cdot MgBr_2$. The structures of the compounds obtained were determined by NMR spectroscopy, electronic absorption spectroscopy (EAS), and MALDI TOF mass spectrometry. A comparative analysis of the fluorescence properties of MgTCP, Al(OH)TCP, and H_2TCP and of stabilities of the metal porphyrinates in an aqueous solution in a wide pH range was carried out. The receptor properties of aluminum(III) porphyrinate to potassium cations in an aqueous solution were examined by the changes in the EAS and fluorescence spectra.

Key words: luminescent sensors to metal cations, crown ethers, porphyrins, transition metal porphyrinates, magnesium porphyrinates, aluminum porphyrinates, luminescence, fluorescence, quenching of fluorescence.

Non-destructive methods for quantitative determination of the concentration of metal cations (K^+, Ca^{2+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Fe^{2+}) in living tissues are being actively developed in the recent years, since their concentration determines normal functioning of human nervous cells, affects the strength of synaptic bonds between neutrons in biological neuron networks, and is related to the development of epilepsy, Alzheimer´s disease, and other diseases of the human nervous system.[1—5] Considerable interest in this area is given to organic fluorescent sensors capable of selective binding of a certain metal cation and changing thus the characteristics of fluorescence, which makes it possible to determine the concentration of metal cations in the living tissue without destructing it.[5—7] Ion-selective electrodes, for example, based on valinomycin[8] and crown ethers[9,10] have previously been used for the determination of potassium ions in solution; however, the valinomycin-based ion-selective electrodes are expensive and unstable, and the most part of crown ethers are not sufficiently well soluble in water and cannot be used for the production of highly efficient ion-selective electrodes obeying the modern requirements. The methods for spectrophotometric determination of potassium cations in solutions were developed on the basis of using crown-substituted metal phthalocyaninates as receptors.[11]


M = Zn^{2+}, Co^{2+}, Cu^{2+}, Al^{3+}

In these molecules, the crown-ether fragments provided binding of potassium cations with a receptor molecule and the phthalocyanine fragment served as a chromophore, which changed the optical properties when potassium cations are bound by a complicated receptor molecule.[11] Difficulties of the use of crown-substituted phthalocyanines as receptors to potassium cations were associated with the fact that transition metal phthalocyaninates (Cu^{2+}, Co^{2+}, Zn^{2+}) were not dissolved in water and water-soluble crown-substituted aluminum(III) phthalocyaninate with intense fluorescence properties lost these properties in an aqueous solution due to self-association processes, which are well known for phthalocyanines.[11] There were attempts to synthesize receptors based on crown-substituted porphyrins, which, as known, can form very stable associates with potassium cation, for instance, *meso*-tetra(benzo-15-crown-5)porphine and the corresponding transition metal

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porphyrinates.[11] For tetra(benzo-15-crown-5)-substituted vanadyl porphyrinate, the equilibrium constant of the formation of supramolecular dimers in a chloroform—methanol solution attains the value of ~$10^{27.6}$ L^5 mol^{-5} (see Refs 12 and 13) (Scheme 1).

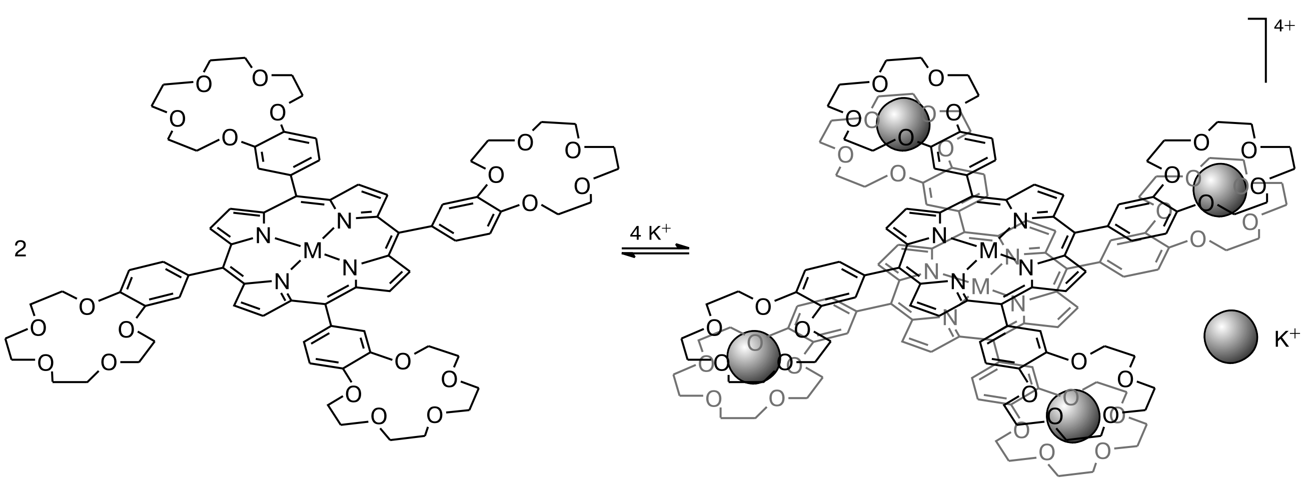
meso-Tetra(benzo-15-crown-5)porphine (H_2TCP) and the corresponding transition metal porphyrinates, as well as crown-substituted phthalocyanines, are poorly soluble in polar organic media and insoluble in water.[12,13] Therefore, association processes of these compounds with potassium cations were studied in a chloroform—methanol mixture to provide the solubility of both potassium salt and a receptor compound. Although many metal porphyrinates based on H_2TCP are known presently, the luminescence properties were studied only for free base *meso*-tetra(benzo-15-crown-5)porphine, the corresponding zinc(II) and ytterbium(III) porphyrinates, and associates of these compounds with potassium cations.[13—15] Interestingly, the method of quenching of fluorescence turned out to be considerably more sensitive for analysis of potassium cations than EAS.[13] However, transition metal porphyrinates have weaker fluorescence properties, as known, than free bases of porphyrins or they have no fluorescence properties at all.[16—18] Therefore, transition metal crown-substituted porphyrinates can hardly be considered as promising fluorescent sensors to potassium cations. At the same time, it is known that porphyrinates of light metals of the nontransition series (magnesium, aluminum), on the contrary, have a higher fluorescence intensity compared to free bases of porphyrins.[19,20]

In this work, we synthesized aluminum(III) and magnesium(II) *meso*-tetra(benzo-15-crown-5)porphyrinates and compared their fluorescence properties with those of porphyrin H_2TCP, studied the stability of the aluminum(III) and magnesium(II) porphyrinates in aqueous solutions in a wide pH range, and examined the receptor properties of tetracrown-substituted aluminum(III) porphyrinate to potassium cations in an aqueous solution by EAS and fluorescence spectroscopy.

Results and Discussion

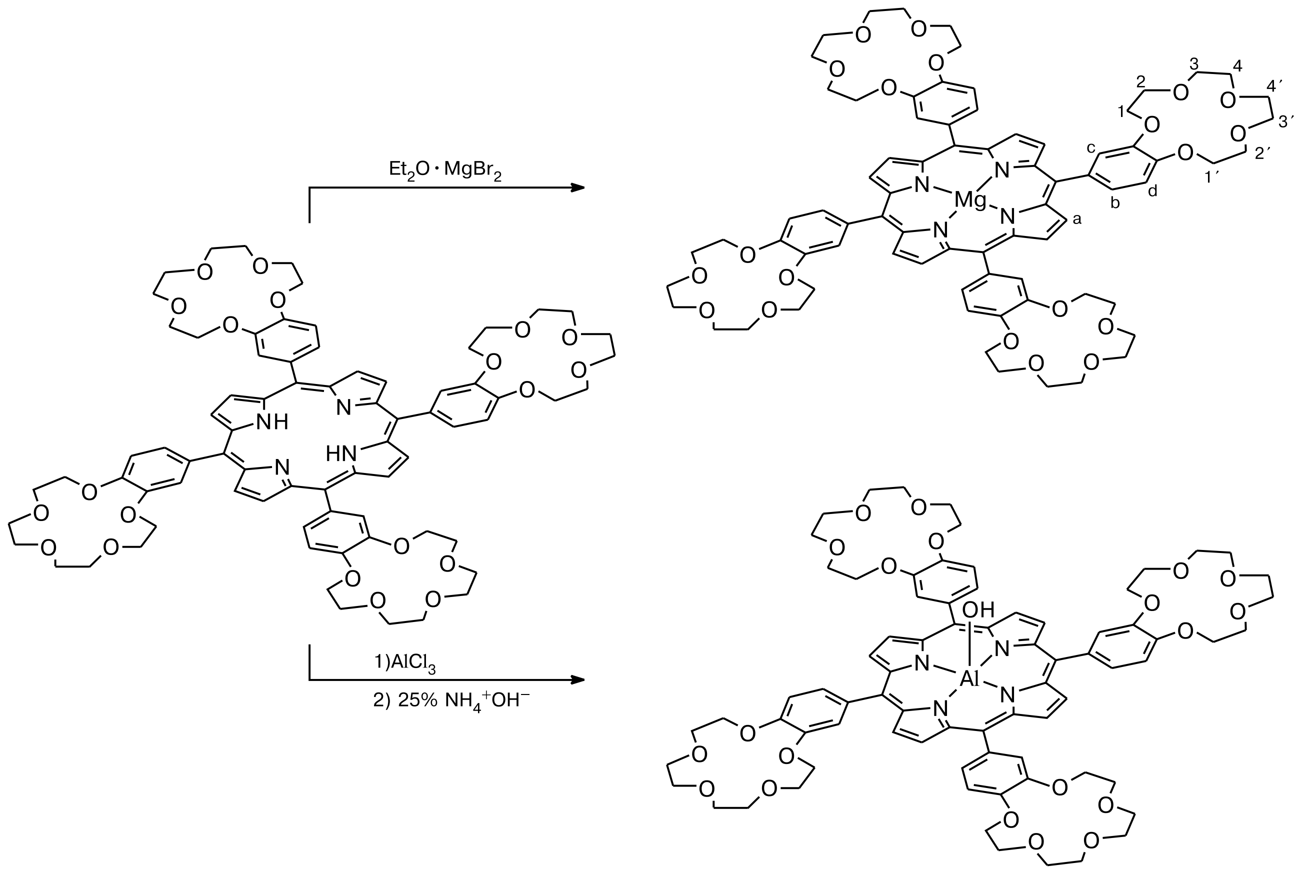
Tetracrown-substituted aluminum(III) porphyrinate was synthesized from $AlCl_3$ and H_2TCP in boiling pyridine followed by the hydrolysis of the obtained product in a 25% solution of ammonia (Scheme 2). The structure of aluminum(III) porphyrinate was determined by the data of ^{1}H NMR spectroscopy, MALDI TOF mass spectrometry, and EAS. The NMR spectrum of Al(OH)1TCP exhibits the downfield shift of the signals from the C—H protons of the tetrapyrrole cycle compared to the starting porphyrin due to the effect of the metal cation on the electron density distribution in the porphyrin cycle. The signal at −2.7 ppm corresponding to the signal of the N—H protons of the porphyrin cycle is absent from the ^{1}H NMR spectrum of Al(OH)TCP, indicating the formation of the aluminum(III) complex with tetracrown-substituted porphyrin. The MALDI TOF mass spectrum of Al(OH)TCP contain the signal of the fragmentation ion $[AlTCP]^+$ (m/z = 1400, I_{rel} = 100%), the signal from the $[(AlTCP)_2OH]^+$ dimer (m/z = 2817, I_{rel} = 37%) formed, most likely, during the mass spectrometric experiment,[21] and the signal of the molecular ion $[Al(OH)TCP]^+$ (m/z = 1417, I_{rel} = 18%). The EAS of aluminum(III) porphyrinate contains the bathochromic shift of the Soret band and a decrease in the number of Q bands compared to the spectrum of H_2TCP, which agrees well with the increase in the symmetry of the complex molecule to C_{4v} for Al(OH)1TCP compared to D_{2h} for the initial tetracrown-substituted porphyrin. Crown-substituted magne-

Scheme 1



M = Zn^{2+}, Cu^{2+}, VO^{2+}

Scheme 2



sium(II) porphyrinate was synthesized using the method proposed by Lindsey and Woordford[22] from the $MgBr_2 \cdot Et_2O$ complex and H_2TCP in 1,2-dichloroethane. The structure of magnesium(II) porphyrinate was also reliably determined by the data of NMR spectroscopy, MALDI TOF mass spectrometry, and EAS (see Experimental).

The fluorescence spectra of magnesium(II) and aluminum(III) porphyrinates measured in a dimethylformamide solution are shifted to the blue region compared to the spectrum of the free porphyrin base, most likely, due to the effect of the complexing metal on the electronic structure of the porphyrin cycle and an increase in the symmetry group of the metal porphyrinate molecules compared to the starting H_2TCP (Fig. 1). The increase in the intensity of the observed fluorescence spectra of MgTCP and Al(OH)TCP over to that of the spectrum of the free porphyrin base is most likely due to, on the one hand, an increase in the quantum yield of fluorescence of metal porphyrinates compared to H_2TCP, because the channel of nonradiative degradation of the excited state involving the N—H vibrations of the porphyrin ring is close in metal porphyrinates, unlike the free porphyrin base,[19] and the heavy atom effect cannot substantially contribute to the

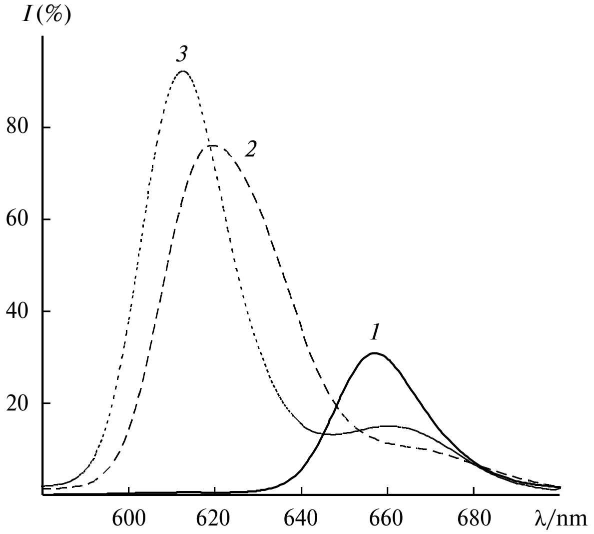


Fig. 1. Comparison of the intensity of the fluorescence spectra of solutions of free *meso*-tetra(benzo-15-crown-5)porphine (H_2TCP, *1*) and the corresponding magnesium(II) porphyrinate (MgTCP, *2*) and aluminum(III) porphyrinate (Al(OH)TCP, *3*) in DMF upon excitation with the light at the wavelength 430 nm.

processes of distribution of the excited state energy between the singlet and triplet level of the porphyrin luminophore for such light elements as magnesium and aluminum.[16,18] On the other hand, the intensity of the fluorescence spectra detected with an instrument depends on the wavelength of the fluorescence transition, and upon the shift of the spectra to the blue region their intensity increases due to an increase in the sensitivity of a photomultiplier tube of the instrument.[23] In addition to an increase in the intensity of the observed fluorescence spectra compared to free porphyrin, magnesium(II) and aluminum(III) porphyrinates have another advantages over H_2TCP from the viewpoint of using these compounds as receptors to potassium cations in a solution. Magnesium(II) and aluminum(III) porphyrinates are well soluble in alcohols and other polar organic solvents (DMSO, DMF), especially Al(OH)TCP. Even for a high dilution with water of these solutions, magnesium(II) and aluminum(III) porphyrinates are not transformed into associates due to π—π-stacking, as it occurs in phthalocyanines,[11] but exist in an aqueous solution as monomers according to the EAS and fluorescence spectral data. As already mentioned, a chloroform—methanol mixture was used in the earlier studies of the receptor properties of crown-substituted metal porphyrinates to potassium cations in order to provide the solubility of both the potassium salt and crown-substituted porphyrin. An analysis of the stability of magnesium(II) and aluminum(III) porphyrinates in aqueous solutions showed that MgTCP is prone to fast hydrolysis at the metal—tetrapyrrole ligand bonds to form free porphyrin in the neutral and protonated forms of the free porphyrin base H_4TCP^{2+} in an acidic medium, which is a substantial drawback from the point of view of using this compound as a receptor to potassium cations. On the contrary, aluminum(III) porphyrinate is highly stable in an aqueous solution in a wide pH range. No hydrolysis of this compound at the metal—tetrapyrrole ligand bonds occurs even in 3 *M* hydrochloric acid and in a 25% aqueous solution of ammonia according to the data of EAS and MALDI TOF mass spectrometry (no signal of free porphyrin or its protonated form was detected even in such aggressive media).

The receptor properties of aluminum(III) porphyrinate to potassium cations were studied by EAS and fluorescence spectroscopy in a DMF—water (1 : 100, vol/vol) solution in a neutral medium. Upon the addition of potassium cations, the EAS of a solution of Al(OH)TCP ($C = 1.4 \cdot 10^{-6}$ mol L^{-1}) exhibited a decrease in intensity of the Soret band with a maximum at 432 nm and the appearance of a new absorption band with a maximum at 417 nm (Fig. 2), which indicates the formation of cofacial dimers (Scheme 2). Similar effects were observed for the formation of cofacial dimers of other crown-substituted porphyrins in a chloroform—methanol solution.[12,13] The changes in the spectra were also detected in the region of the Soret bands (see Fig. 2). The value of the equilibrium constant for dimer formation was $\sim 6 \cdot 10^{22}$ L^5 mol^{-5} (20 °C) according to the data of the calculation by the method used earlier.[20] The decrease in the equilibrium constant of the formation of dimers based on Al(OH)TCP in an aqueous solution compared to the values of *K* for analogous processes of the formation of cofacial dimers in a chloroform—methanol solution for VOTCP ($K \approx 10^{27.6}$ L^5 mol^{-5} at 28 °C)[12], $Ni^{II}TCP$ ($K \approx 10^{27.31}$ L^5 mol^{-5}), $Pd^{II}TCP$ ($K \approx 10^{27.16}$ L^5 mol^{-5}), and $Pt^{II}TCP$ ($K \approx 10^{26.15}$ L^5 mol^{-5}) at 20 °C (see Ref. 24) is probably caused by the fact that the energy necessary for the destruction of the hydrate shell of potassium cations in an aqueous solutions is higher than the energy of destruction of the solvate shell of potassium cations in the previous experiments for VOTCP, $Ni^{II}TCP$, $Pd^{II}TCP$, and $Pt^{II}TCP$. In addition, in an aqueous solution of Al(OH)TCP water molecules are coor-

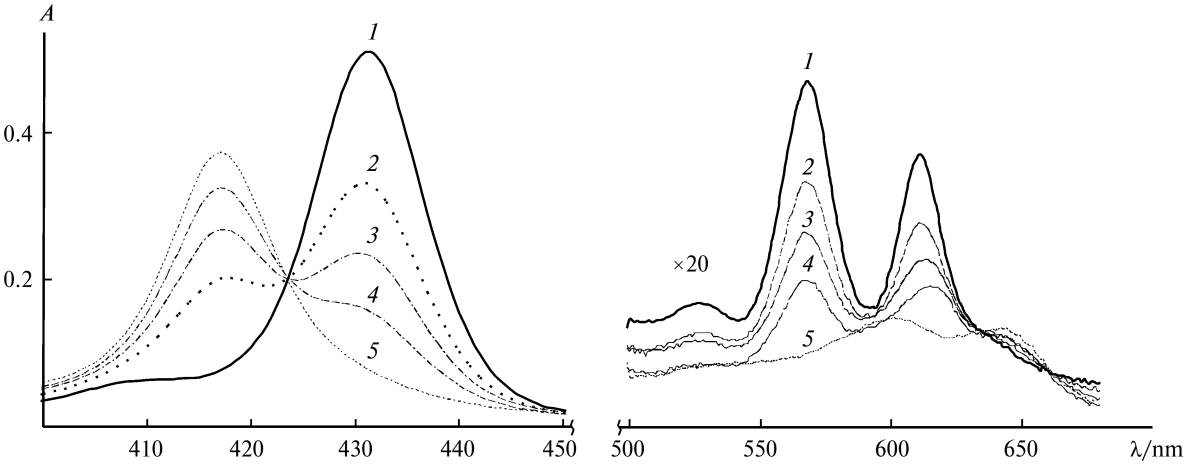


Fig. 2. Changes in the EAS upon the interaction of Al(OH)TCP ($C = 1.4 \cdot 10^{-6}$ mol L^{-1}) with $KClO_4$ in the H_2O—DMF system (100 : 1, vol/vol). The number of mole equivalents of K^+ to Al(OH)TCP was 0 (*1*), 37.5 (*2*), 50 (*3*), 75 (*4*), and 375 (*5*).

dinated, most likely, by the aluminum atoms of the Al(OH)TCP molecules, which should result in a decrease in the value of the equilibrium constant of this reaction. The octahedral structure of the coordination node of Al(OH)TCP in an aqueous solution is indicated by the ratio of the Q band intensities in the EAS of the solution of crown-substituted aluminum(III) porphyrinate.[25] For aluminum(III) porphyrinates with the octahedral structure of the coordination node, the Q bands have approximately equal intensities, whereas they considerably (more than tenfold) differ in intensity for aluminum(III) porphyrinates with the square pyramidal structure.[25]

The addition of potassium cations to an aqueous solution of Al(OH)TCP ($C = 0.7 \cdot 10^{-7}$ mol L^{-1}) results in a decrease in the intensity of the fluorescence transition with the emission maximum at 612 nm (Fig. 3) and the appearance of a new fluorescence transition of the associate of aluminum(III) porphyrinate with potassium cations at 653 nm. Similar changes were observed for the interaction of ZnTCP with potassium cations in a chloroform—methanol solution.[13] An analysis of the dependence of the fluorescence intensity of Al(OH)TCP (excitation at 430 nm, the studied fluorescence transition with $\lambda_{max} = 612$ nm) upon the addition of $KClO_4$ in the Stern—Volmer coordinates (Fig. 4) showed that both the effect of static quenching of fluorescence related to the formation of dimers with potassium cations and the effect of dynamic quenching of fluorescence caused by collisions of the metal cations and molecules of crown-substituted aluminum(III) porphyrinate in the electron-excited state in a solution contribute to the quenching processes, which is indicated by a significant deviation of the dependence from linearity (the plot has the convex shape characteristic of the mixed type of quenching).[26] The appearance of fluorescence of the supramolecular dimer with the emission maximum at 653 nm was more pronounced upon the irradiation of the solution with the light with a wavelength of 415 nm, since the absorption band maximum of the associate of Al(OH)TCP with potassium cations $[(Al(OH)TCP)_2(K^+)_4]$ lies in this region (Fig. 5).

Comparing the changes in the optical absorption and fluorescence spectra in the reaction of Al(OH)TCP with

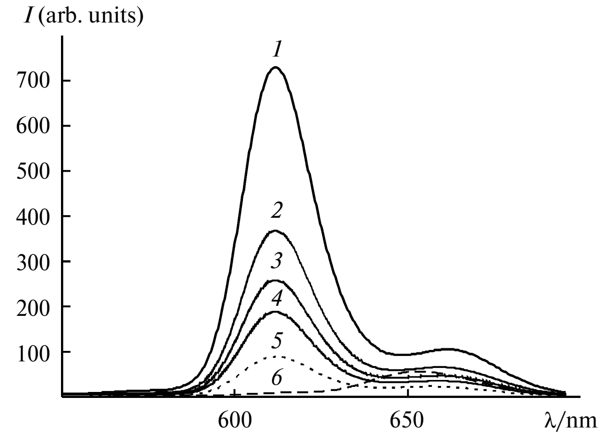


Fig. 3. Changes in the fluorescence spectra after the addition of $KClO_4$ to a solution of Al(OH)TCP ($C = 0.7 \cdot 10^{-7}$ mol L^{-1}) in the water—DMF (100 : 1, vol/vol) system upon the excitation with the light at the wavelength 430 nm. The number of mole equivalents of K^+ to Al(OH)TCP was 0 (*1*), 25 (*2*), 37.5 (*3*), 50 (*4*), 75 (*5*), and 375 (*6*).

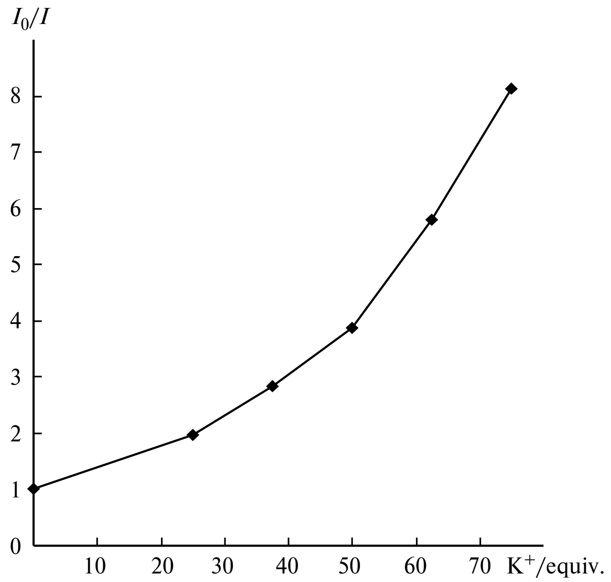


Fig. 4. Quenching of the fluorescence (emission transition with a maximum at 612 nm) of Al(OH)TCP ($C = 0.7 \cdot 10^{-7}$ mol L^{-1}) in the water—DMF (100 : 1, vol/vol) system *vs* concentration of potassium cations in the Stern—Volmer coordinates at a wavelength of the exciting light of 430 nm.

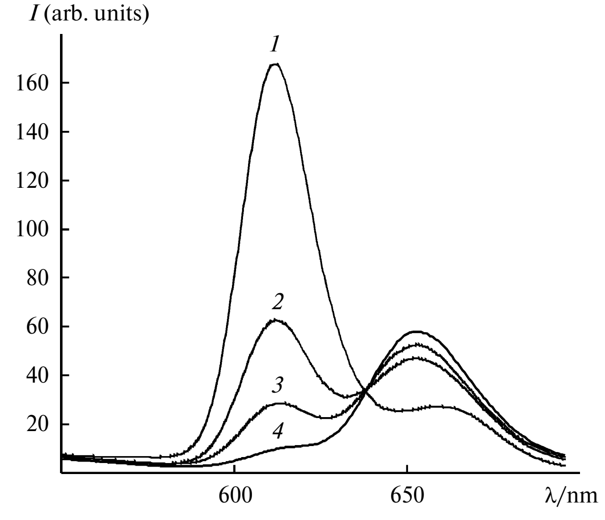


Fig. 5. Changes in the fluorescence spectra in the Al(OH)TCP—$KClO_4$ system upon the excitation with the light at the wavelength 415 nm ($C_{Al(OH)TCP} = 0.7 \cdot 10^{-7}$ mol L^{-1}). The number of mole equivalents of K^+ to Al(OH)TCP was 0 (*1*), 25 (*2*), 75 (*3*), and 375 (*4*).

potassium cations (Fig. 6), one can mention that the addition of 25 equivalents of $KClO_4$ to a $1.4 \cdot 10^{-6}$ mol L^{-1} solution of Al(OH)TCP resuts in the 27% decrease of the Soret band intensity in the EAS of the solution, whereas the addition of 25 equivalents of $KClO_4$ to a more dilute ($0.7 \cdot 10^{-7}$ mol L^{-1}) solution of Al(OH)TCP leads to the 50% decrease of the intensity of the fluorescence transition with a maximum at 612 nm, *i.e.*, the method of quenching of fluorescence is considerably more sensitive for the determination of potassium cations in a solution compared to electronic absorption spectroscopy.

Crown-substituted aluminum(III) porphyrinate Al(OH)TCP can evidently be considered as an advanced fluorescent sensor to potassium cations in an aqueous medium due to its intense fluorescence properties, solubility in water at a low content of an additional solvent (dimethylformamide, dimethyl sulfoxide, or ethanol), and high stability of this compound in an aqueous solution in a wide pH range. An analogous approach, namely, the synthesis of aluminum(III) porphyrinates from free porphyrins, can be used for the improvement of the properties of other fluorescent sensors, whose molecular structures include the porphyrin luminophore, for example, the receptor to zinc cations known in "metalloneurochemistry" $(DPA\text{-}C_2)_2\text{-}TPPS_3$ (see Ref. 5).

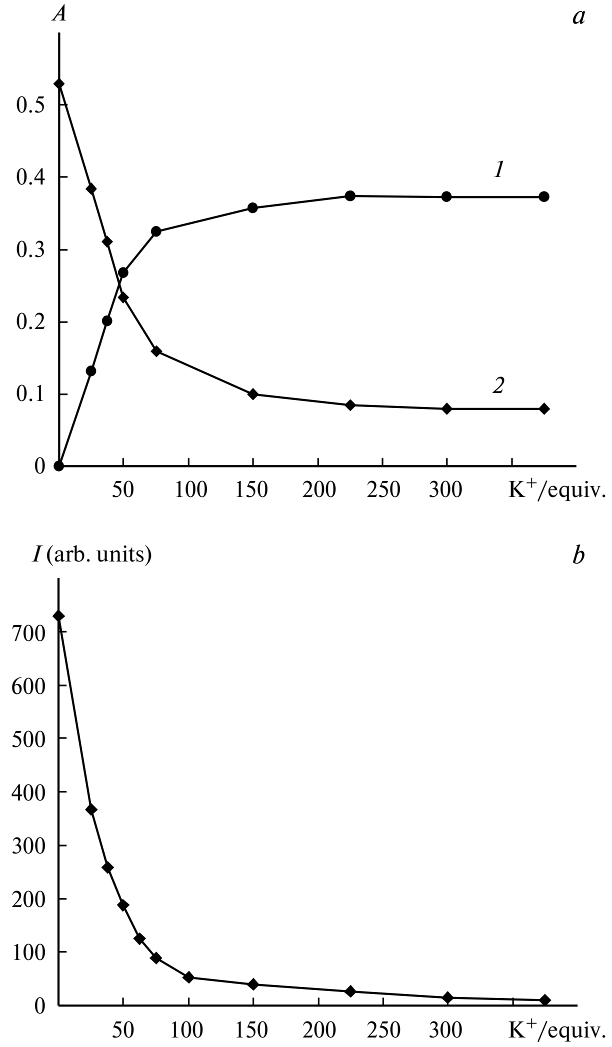


Fig. 6. Changes in the intensities of the Soret band of Al(OH)TCP (*1*) and the Soret band of $[(Al(OH)TCP)_2(K^+)_4]$ (*2*) after the addition of $KClO_4$ to a $1.4 \cdot 10^{-6}$ *M* solution of Al(OH)TCP in the H_2O—DMF (100 : 1, vol/vol) system (*a*) and the changes in the Intensity of the fluorescence transition of Al(OH)TCP with the emission maximum at 612 nm upon the addition of $KClO_4$ to a $0.7 \cdot 10^{-7}$ *M* solution of Al(OH)TCP in the H_2O—DMF (100 : 1, vol/vol) system (*b*).

Experimental

Toluene, dimethylformamide (ACRUS) and potassium perchlorate (analytical purity grade) were used. Chloroform, 1,2-dichloroethane, triethylamine, toluene, and dimethylformamide were purified and dried prior to use.[27] Free *meso*-tetra(benzo-15-crown)porphine (H_2TCP) was synthesized according to a known procedure.[28] ^1H NMR spectra were recorded on a Bruker 600 instrument (A. N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences) with a working frequency of 600 MHz. Mass spectra were measured on a Bruker Daltonics Ultraflex MALDI TOF instrument without using a matrix. Electronic absorption spectra were recorded on a Perkin Elmer Lambda 35 instrument at 20 °C. Fluorescence spectra were detected on a Perkin Elmer LS-55 instrument at 20 °C. To compare the fluorescence intensities of H_2TCP and the corresponding metal porphyrinates, solutions of these compounds in dimethylformamide were used with the concentration selected in such a way that the absorbance at the wavelength 430 nm would be 0.04 for all compared solutions. The exciting radiation intensity was constant in all measurements.

The stability of magnesium(II) and aluminum(III) porphyrinates in alkaline and acidic media was analyzed as follows. A solution of metal porphyrinate in ethanol ($1 \cdot 10^{-4}$ mol L^{-1}) was diluted with an aqueous solution of HCl or an aqueous solution of ammonia in such a way that the ethanol to an aqueous solution of HCl or NH_3 would be 1 : 100 (vol/vol). The obtained solution was stirred and left to stay for 24 h at 25 °C in a closed flask. Then the solution was stored *in vacuo* for the partial removal of HCl or ammonia. A less aggressive solution obtained was used for analysis by EAS and for the preparation of samples for analysis by MALDI TOF mass spectrometry was used .

Synthesis of aluminum(III) *meso*-tetra(benzo-15-crown-5)porphyrinate. Aluminum chloride (119 mg, 0.8724 mmol) was added to a solution of H_2TCP (20 mg, 0.01454 mmol) in pyridine (2 mL). The solution was heated to boiling allowing the solvent to partially evaporate, and the temperature of the reaction mixture increased to 140 °C. The reaction mixture was stored at this temperature for 30 min and then cooled to 20 °C. Pyridine (3 mL) was added to the reaction mixture, and the solution was transferred onto a chromatographic column packed with alumina. Aluminum porphyrinate was isolated by elution with pyridine. The solvent was removed *in vacuo*. The dry residue was dissolved in a mixture of pyridine (2 mL) and a 25% solution of ammonia (2 mL). The obtained solution was heated to 45 °C and stirred at this temperature for 20 min. The solvents were removed *in vacuo*.

The residue was dissolved in chloroform, and the solution was transferred to a chromatographic column packed with alumina. Aluminum porphyrinate was isolated by elution with chloroform. The solvent was evacuated *in vacuo*, and the product was dried *in vacuo* at 120 °C. The yield of aluminum porphyrinate was 12 mg (60% of the theoretical value).

^{1}H NMR (DMSO-d$_6$), δ: 9.11 (s, 8 H, H$_a$); 7.90—7.75 (m, 4 H, H$_b$); 7.75—7.57 (m, 4 H, H$_c$); 7.46—7.34 (m, 4 H, H$_d$); 4.41—4.34 (m, 8 H, H(1)); 4.30—4.22 (m, 8 H, H(1´)); 4.03—3.96 (m, 8 H, H(2)); 3.92—3.83 (m, 8 H, H(2´)); 3.81—3.69 (m, 32 H, H(3), H(3´), H(4), H(4´)). EAS in an H$_2$O—DMF (100 : 1, vol/vol) solution, λ_{max}/nm (logε): 432 (5.56), 526 (3.90), 568 (4.27), 612 (4.18). MS (MALDI TOF), m/z (I_{rel} (%)): 1400 [AlTCP]$^+$ (100), 1417 [Al(OH)TCP]$^+$ (18), 2817 [(AlTCP)$_2$OH]$^+$ (37).

Synthesis of magnesium(II) *meso*-tetra(benzo-15-crown-5)-porphyrinate. Pre-dried triethylamine (0.075 mL) was added to a solution of MgBr$_2$·Et$_2$O (50 mg, 0.1934 mmol) in 1,2-dichloroethane (10 mL), and then a solution of H$_2$TCP (15 mg, 0.01091 mmol) in 1,2-dichloroethane (10 mL) was added. The obtained mixture was heated to 40 °C and vigorously stirred at this temperature for 10 min. The reaction mixture was cooled down and washed with 3 portions of 30 mL of a 10% aqueous solution of sodium hydrocarbonate. The organic phase was dried above sodium sulfate, and the solution was separated by filtration and concentrated *in vacuo* to 3 mL. The solution was transferred onto a chromatographic column with alumina preliminarily wet with a 0.5% solution of triethylamine in 1,2-dichloroethane. Unreacted porphyrin was isolated by elution with a 0.5% solution of triethylamine in 1,2-dichloroethane. Magnesium porphyrinate was washed from the column with a 1% solution of acetone in 1,2-dichloroethane. The solvents were removed *in vacuo*, and the product was dried *in vacuo*. The yield of magnesium porphyrinate was 14 mg (92% of the theoretical value).

^{1}H NMR (CDCl$_3$), δ: 8.96 (s, 8 H, H$_a$); 7.74—7.57 (m, 8 H, H$_b$, H$_c$); 7.16—7.08 (m, 4 H, H$_d$); 4.47—4.30 (m, 8 H, H(1)); 4.25—4.01 (m, 8 H, H(1´)); 3.95—3.80 (m, 8 H, H(2)); 3.80—3.61 (m, 40 H, H(2´)). EAS in DMF, λ_{max}/nm (logε): 438 (5.57), 528 (3.85), 568 (4.11), 609 (4.06). MS (MALDI TOF), m/z (I_{rel} (%)): 1397 [MgTCP]$^+$ (100).

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