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Tetrapyrrole Cation Receptor for Selective Binding Fluoride Ion

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Abstract—The 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate was synthesized and its complexing properties toward fluoride ion were investigated by spectrophotometric titration in the acetonitrile–tetrabutylammonium fluoride system. We found that at the complexation the two triflate counterions are replaced by the fluoride ions. The stability constants of the complexes and the concentration ranges of their existence were determined.

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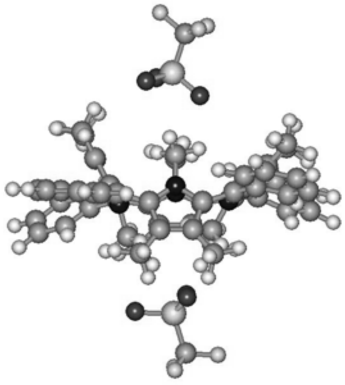
Detection of chemical compounds in various media using tetrapyrrole macrocyclic compounds and their cationic forms as the sensors gives rise to application the porphyrins protonated forms as the receptors for anions [1–7]. Previously [3] we showed the effective quenching of fluorescence by the protonated porphyrin molecules in a solution containing halide ions, along the mechanisms of internal and external heavy atom. Based on the analysis of dependence of the fluorescence intensity and lifetime on the concentration of iodide ions in the solution the protonated forms of porphyrins were proposed for the use as a fluorescent molecular receptor of halide ions [8]. For the obtaining protonated forms of porphyrins required a careful analysis of the conditions of their existence: the determination of pH values, the choice of solvent with a specific donor property and dielectric permeability, and selecting appropriate protonating reagent taking into account the influence of its counterion on the macrocycle cationic form.

In this study we synthesized 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate (**I**) which contains the tetrapyrrole chromophore as a dication (denoted as H_4P^{2+}), with the triflate anions (T = $CF_3SO_2^-$) as the stabilizing counterions.

The complexing properties of compound **I** toward fluoride ion were studied by the method of spectrophotometric titration [2] in the system of acetonitrile–tetrabutylammonium fluoride [Eq. (1)].



I, $H_4P^{2+}T_2$

$$H_4P^{2+}T_2–(C_4H_9)_4NF–CH_3CN. \quad (1)$$

The results of the interaction of **I** with fluoride ions (system 1) are seen from the EAS (electron absorption spectroscopy) data and the titration curve of the process. Upon increase in the concentration of fluoride ion [F^-], in the absorption spectra of the reaction system occurs a sequential formation of two families of spectral curves, each curve corresponds to a certain point in the titration curve. In the tetrabutylammonium fluoride concentration range from 0 to 2.65×10^{-5} M in

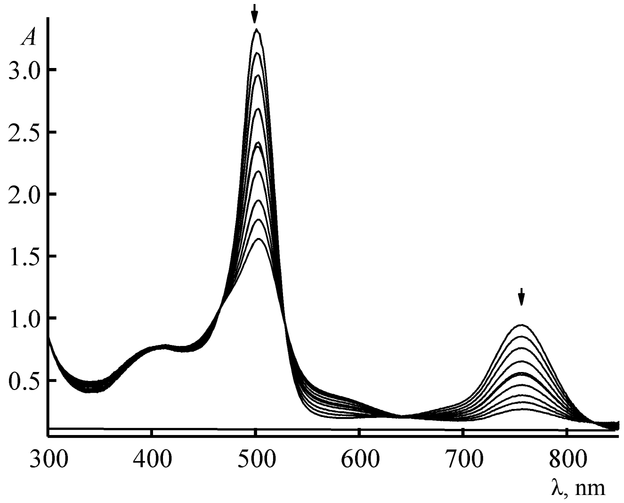


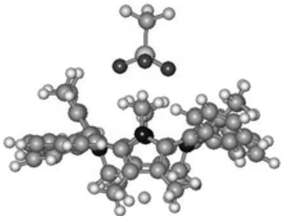
Fig. 1. Electron absorption spectra of the system $H_4P^{2+}T_2$–$(C_4H_9)_4NF$–CH_3CN $\{c_{\mathrm{Porphyrin}} = 1.5\times10^{-5}$, $c[(C_4H_9)_4NF] = 0$–2.65×10^{-5} M$\}$.

the EAS appears the first family of spectral curves with its own set of isobestic points (Fig. 1).

This process corresponds to the first stage section of the titration curve (Fig. 2), which probably corresponds to the substitution of one triflate ion by fluorine ion. The interaction can be described by Eq. (2).

$$H_4P^{2+}T_2 + F^- \overset{k_{b1}}{\rightleftarrows} H_4P^{2+}TF + T^-. \tag{2}$$

In favor of the replacing triflate ion by fluoride ion indicates the character of spectral changes in going from H_4P^{2+} T_2, H_4P^{2+} TF (Fig. 1). When the concentration of fluoride reaches 2.65×10^{-5} M, the two-band absorption spectrum of $H_4P^{2+}T_2$ is transformed into a single-band spectrum. The band intensity at 501 nm decreases, it is broadened and shifted bathochromically. Such spectral changes are explained by a change in the π-conjugation in the tetrapyrrole chromophore under the influence of halide ion [9]. Thus, the complex formed in the first stage can be represented as **Ia**.



Ia, $H_4P^{2+}TF$

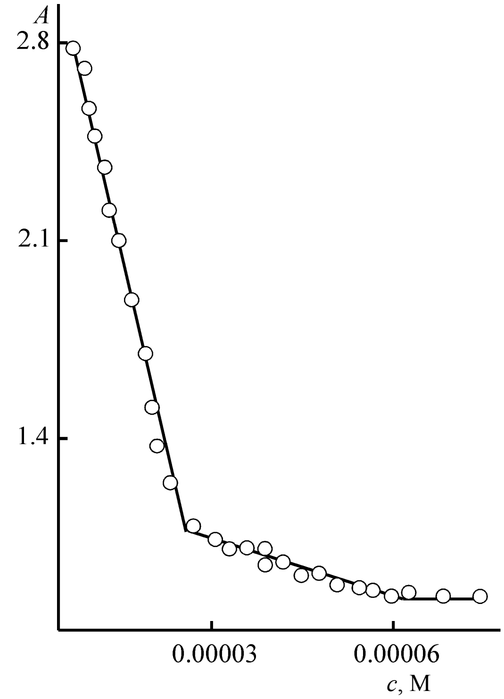


Fig. 2. The curve of spectrophotometric titration of $H_4P^{2+}T_2$ ($c_{\mathrm{Porphyrin}} = 1.5\times10^{-5}$ M) with a solution of $(C_4H_9)_4NF$ in acetonitrile $\{c[(C_4H_9)_4NF] = 0$–6.22×10^{-5} M$\}$ at λ = 500 nm, 298 K.

Upon further increase in the fluoride concentration to 6.22×10^{-5} M in the spectrum of the system (1) is formed a new family of spectral curves with its own set of isobestic points (Fig. 3). This process corresponds to the second section of the titration curve (Fig. 2). In the EAS of the reaction system occurs formation of new absorption band at 467 nm (see Fig. 3 and the table).

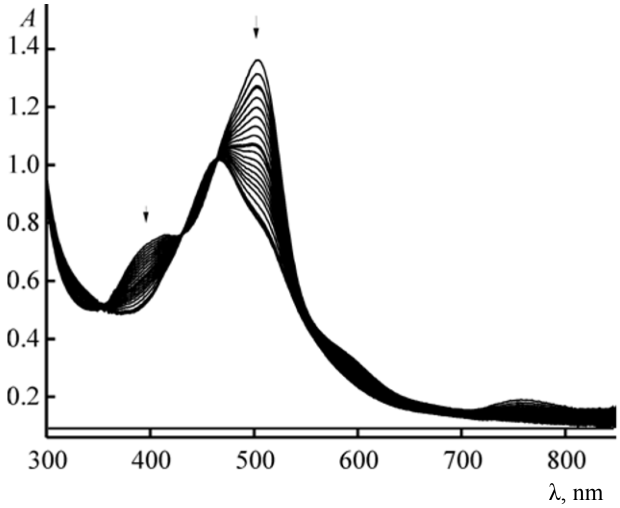
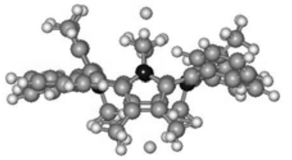


Fig. 3. Electron absorption spectra of the system $H_4P^{2+}T_2$–$(C_4H_9)_4NF$–CH_3CN $\{c_{\mathrm{Porphyrin}} = 1.5\times10^{-5}$, $c[(C_4H_9)_4NF] = 2.65\times10^{-5}$–$6.22\times10^{-5}$ M$\}$.

The chemical interaction in this range of concentrations of the reagents can be described by Eq. (3), and the structure of the complexes is shown by **Ib**, $H_4P^{2+}F_2$.

$$H_4P^{2+}TF + F^- \overset{k_{b1}}{\rightleftarrows} H_4P^{2+}F_2 + T^-. \tag{3}$$



Ib, $H_4P^{2+}F_2$

The stability constants of the respective complexes in the system (1) are calculated by Eq. (4):

$$\log k_b = \log(\mathrm{Ind}) - n\log c_{\mathrm{tetrabutylammonium\ fluoride}}, \tag{4}$$

where k_b is the constant of association of the tetrapyrrole chromophore with fluoride ion in the first and second stages, respectively; Ind is indicator ratio $H_4P^{2+}TF/H_4P^{2+}T_2$ for the first stage and $H_4P^{2+}F_2/H_4P^{2+}TF$ for the second stage of the processes (2) and (3), respectively; $c[(C_4N_9)_4NF]$ is analytical concentration of tetrabutylammonium fluoride in solution (M); $n = 1$ (the number of connected fluoride ionss formed at the dissociation of tetrabutylammonium fluoride). The log k_b values for the first and second stages of complex formation are 4.75 and 4.68 respectively.

The spectrophotometric studies showed that under the comparable conditions adding of either Cl^-, or Br^-, or I^- ions to a solution of **I** does not results in significant spectral changes (Fig. 4), that is, the processes similar to the interaction of **I** with the fluoride ion do not occur in the case of other halide ions. The ability of compound **I** selectively bind fluoride ions was also confirmed by additional research consisted in the spectrophotometric titration of compound **I** by the fluoride ion on the background of 100-fold excess of Cl^-, or Br^-, or I^- ion. The experimental data show that the presence of another halide ion as a background does not affect significantly the complexation of **I** with the fluoride ion. The values of log $k_{b1,2}$ for processes (2) and (3) in the presence of Cl^-, or Br^-, or I^- ion are close (they differ within experimental error only) to the corresponding values for the interaction of **I** with the fluoride ion in the solvent not containing a halide.

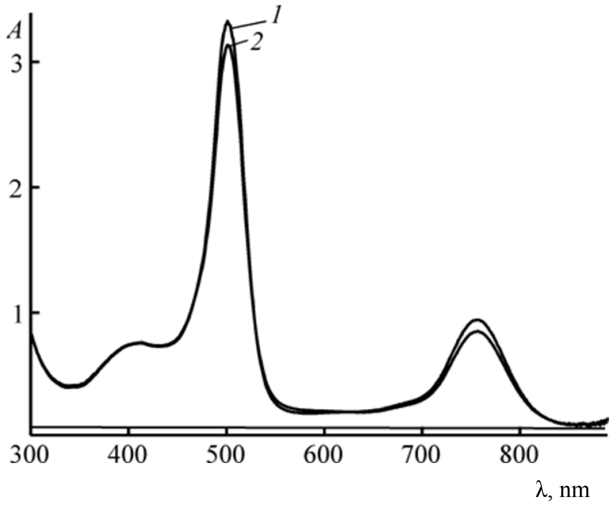


Fig. 4. Electron absorption spectra of the system (*1*) $H_4P^{2+}T_2$–$(C_4H_9)_4NF$–CH_3CN in the absence and (*2*) the presence of 100-fold excess of $(C_4H_9)_4NCl$, $c_{\mathrm{Porphyrin}} = 1.5\times10^{-5}$ M.

Thus, the performed synthesis of 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate and studied its complexing properties toward fluoride ion by spectrophotometric titration in acetonitrile. We found that during the complexation process occurs substitution of the two triflate counterions by the fluoride ions. The complexes stability constants and the concentration ranges of the complexes existence were determined. Sensitivity of the proposed macrocycle covers a wide range of the substrate concentrations, 0 to 6.22×10^{-5} M, which allows us to consider this tetrapyrrole chromophore as a highly selective molecular sensor registering fluoride ions in solutions. Formation by the sensor of analytical signal is provided by the chemical interaction of the macrocyclic receptor with the substrate molecules.

EXPERIMENTAL

Synthesis of 5,10,15,20-tetraphenyl-2,3,7,8,12,-13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate. To a solution of 0.5 g (0.6 mmol) of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenyl-

Electron absorption spectra of porphyrin **I** and its mono- (**Ia**) and difluoride (**IIb**) complexes in the system of $H_4P^{2+}T_2$–$(C_4H_9)_4NF$–CH_3CN: $\lambda_{\max}$, nm [$\varepsilon\times10^{-5}$, l mol^{-1} cm^{-1}]

Ion	λ_1 (log ε)	λ_2 (log ε)	λ_3 (log ε)
$H_4P^{2+}T_2$	413 (sh) (4.77)	501 (5.43)	756 (4.94)
$H_4P^{2+}TF$	413 (sh) (4.75)	504 (5.10)	758 (4.31)
$H_4P^{2+}F_2$	–	467 (4.90)	–

porphyrine in 50 ml of water-free methylene chloride was added successively 1.2 g (9.0 mmol) potassium carbonate, which was dried preliminary at 80ºC, and 4.7 g (28.6 mmol) of methyl trifluorormethylsulfonate. The reaction mixture was refluxed for 8 h, then cooled and filtered. The residue on filer was washed with methylene chloride, the filtrate was evaporated to minimum volume and diluted with petroleum ether (1:1 by volume). Yield 0.6 g (~92%). ^{1}H NMR spectrum, δ, ppm (internal TMS): 8.42 m (8H, *o*-HPh), 7.92 m (12H, *m,p*-HPh), 1.74 s (24H, CH_3), –3.11 s (12H, NH). EAS in dichloromethane: λ_{max}, nm (log ε): 762 (4.64), 505 (5.24), 417 (4.48). Prior to obtain the data of the elemental analysis, the samples were dried in a vacuum pistol at the boiling point of toluene. Found, %: H 5.19, C 64.27, N 5.20, S 5.97. $C_{58}F_6S_2H_{56}O_6N_4$. Calculated, %: H 5.21, C 64.31, N 5.17, S 5.92.

The ball–rod images of the complexes **I**, **Ia**, and **Ib** are drawn using the Hyper Chem Professional 8.07 program. Acetonitrile from ALDRICH was used without an additional purification. The water content was determined by Fisher method, it did not exceed 0.04%. Tetrabutylammonium halide solutions were prepared on the basis of acetonitrile. The salts used were purified by the action of acetonitrile in a Soxhlet apparatus and dried in a vacuum (1.33 Pa) at 393 K to constant weight. Spectrophotometric titration of **I** with a solution of $(C_4H_9)_4NF$ in acetonitrile was carried out using a Varian Cary 100 spectrophotometer. The experimental procedure and data processing are described in [2, 8]. Error in the determination of the constants was ±(3–5)%. The ^{1}H NMR spectra were recorded on a Bruker VC-500 spectrometer from solutions in deuterochloroform, internal reference TMS.

ACKNOWLEDGMENTS

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