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A Molecular Receptor Based on the 2,3,7,8,12,13,17,18-Octaethyl-21,23-dimethylporphyrin for Detection of Fluoride Ions: Synthesis, Spectral and Complexation Properties

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Abstract—2,3,7,8,12,13,17,18-Octaethyl-21-methylporphyrin and 2,3,7,8,12,13,17,18-octaethyl-22,23-dimethylporphyrin monotriflate based on the former were synthesized. Basic and complexing properties of these compounds were studied by the method of spectrophotometric titration in acetonitrile–perchloric acid and acetonitrile–tetrabutylammonium fluoride systems at 298 K. It was established that in the system of acetonitrile–perchloric acid the cationic forms of 2,3,7,8,12,13,17,18-octaethyl-21-methylporphyrin do not form complexes with fluoride ions, whereas 2,3,7, 8,12,13,17,18-octaethyl-22,23-dimethylporphyrin monotriflate forms complexes of 1:1 composition with the fluoride ions. The protonation constant of 2,3,7,8,12,13,17,18-octaethyl-21-methylporphyrin and the stability constant of the complex of 2,3,7,8,12,13,17,18-octaethyl-22,23-dimethylporphyrin with fluoride ions in acetonitrile at the standard temperature were determined.

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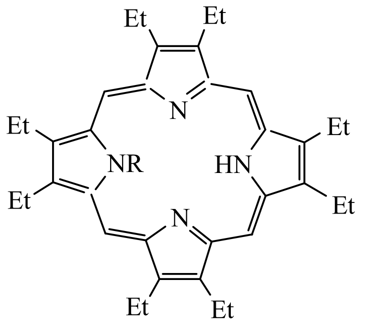
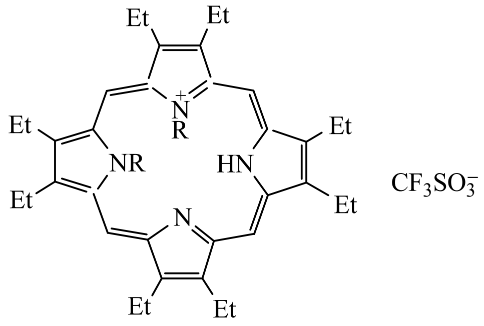
Tetrapyrrole macrocycles are known as amphoteric compounds: the presence of NH groups imparts them an opportunity to show weak acidic properties, while tertiary nitrogen atoms provide the basic properties. The loss of protons leads to restructuring and shortening of the conjugation chain while apparent aromaticity of the system is retained. Adding protons to the tertiary nitrogen atoms does not affect the planar structure of the molecule. Cationic and anionic forms of tetrapyrrole macrocycles have the same isoelectronic conjugation chains and similar electronic spectra, differing only by a shift of the absorption bands. Protonated forms of porphyrins are known as excellent chromophores possessing conformationally flexible complexing cavity that can selectively bind anions of different nature [1–8]. This property of the protonated forms is reflected in the change of optical signals of the electronic spectrum. Dicationic forms of tetrapyrrole macrocycles are capable of forming associates of 1:1 and 1:2 composition with the molecules and anions. Thus, the dication forms of mezoporphyrin **IX** in acetonitrile form associates of 1:1 and 1:2 composition with water molecules [9] and halide ions (iodide, bromide, and chloride) [1]. Pronounced electron-acceptor properties of chemoreceptors are largery determined by the medium acidity function and the structure of the molecule. The simplicity and accessibility of spectral analysis techniques to determine anions in solutions using protonated forms of porphyrins makes these studies interesting and relevant.

In this study, we synthesized 2,3,7,8,12,13,17,18-octaethyl-21-methylporphyrin (**I**) and converted it into 2,3,7,8,12,13,17,18-octaethyl-22,23-dimethylporphyrin monotriflate (**II**) where the porphyrin is in the protonated form stabilized by the triflate ion.

Basic properties of **I** were studied by the method of spectrophotometric titration [5] in an acetonitrile–perchloric acid system. Increasing concentration of acid in the system of acetonitrile–perchloric acid leads to two sets of spectral curves in the electron absorption spectra (Fig. 1, the EAS parameters are listed in the table), to each set corresponds its own set of isosbestic points.



I



II

After determination of the inflection point in the titration curve (Fig. 2) we separated two electron absorption spectra in correspondence with the sequential biprotonation (Scheme 1) and calculated the corresponding protonation constants, log k_{b1} = 6.1 and log k_{b2} = 5.2 (the standard technique is described in detail in [1, 5]).

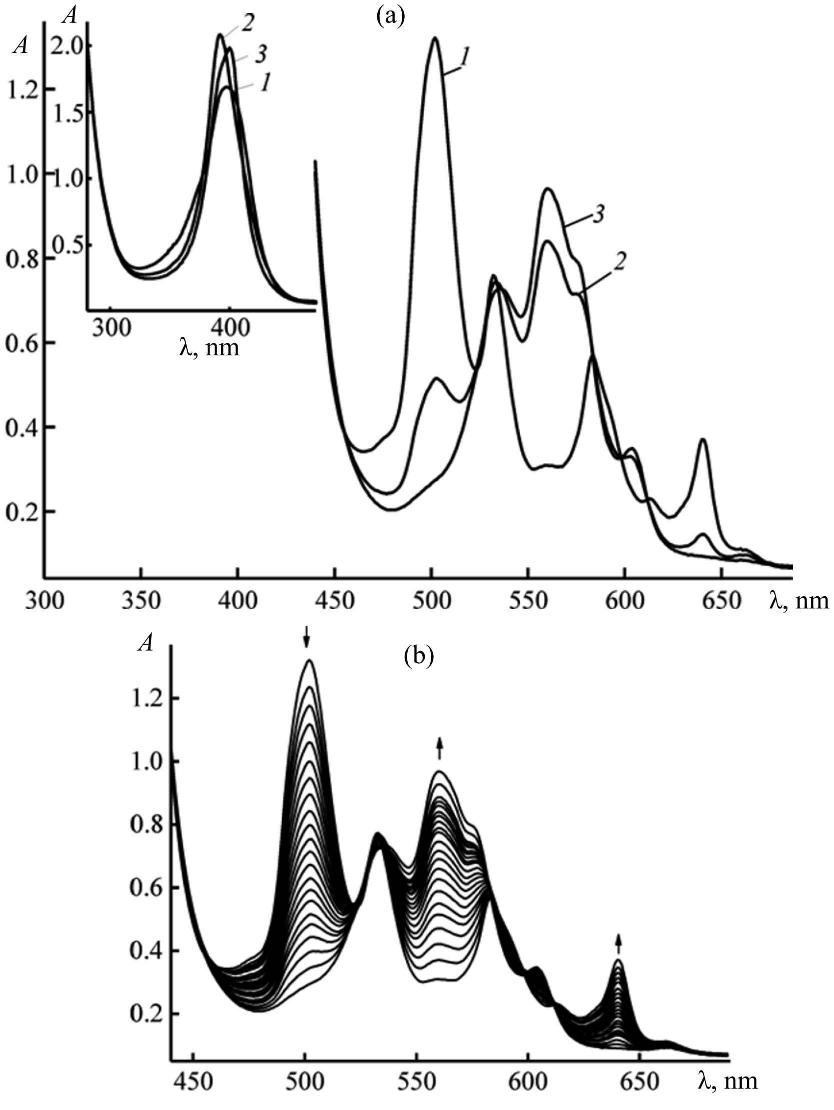
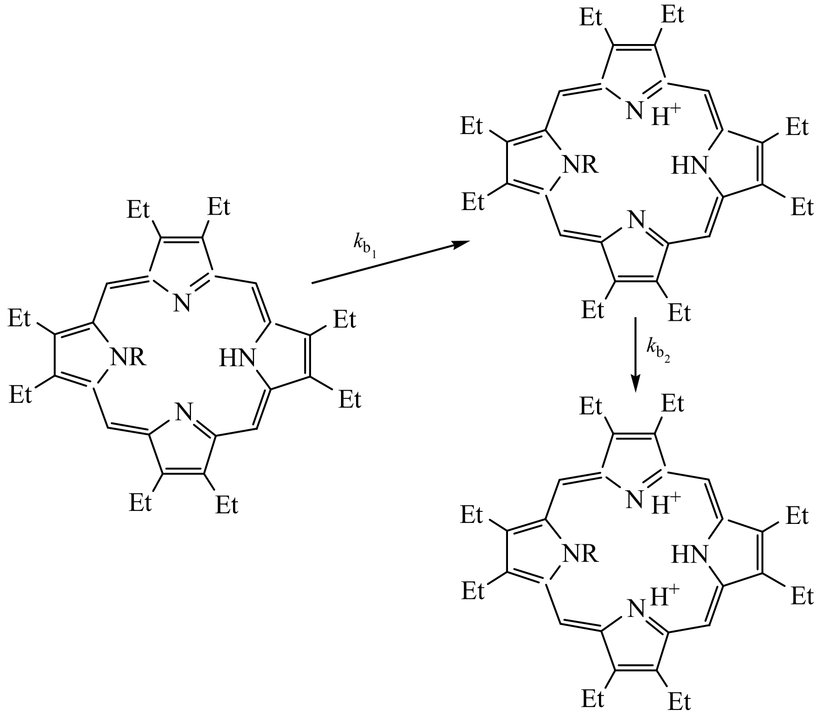


Fig. 1. Variation of EAS (280–700 nm) of **I** in the system of $CH_3CN–HClO_4$. (a) $c(HClO_4)$ = (0–2.42)×10^{-5} M, c_{porph}=. 6.39×10^{-6} M, λ = 280–700 nm; (b) $c(HClO_4)$ (0–2.42)×10^{-5} M, c_{porph}= 4.91×10^{-5} M, λ = 400–700 nm; $N(CH_3)Et_8$, (*1*) $H(CH_3)Et_8P$, (*2*) $H_2(CH_3)Et_8P^+$, and (*3*) $H_3(CH_3)Et_8P^{2+}$.

Scheme 1.

$$H(CH_3)Et_8P + H^+ \overset{k_{b_1}}{\rightleftarrows} H_2(CH_3)Et_8P$$

$$H_2(CH_3)Et_8P^+ + H^+ \overset{k_{b_2}}{\rightleftarrows} H_3(CH_3)Et_8P^{++}$$



We revealed the region of concentrations of perchloric acid where the concentration of the dications of **I** in the system of acetonitrile–perchloric acid is maximal, and carried out a direct titration of the dication forms of porphyrin **I** with a solution of the fluoride salt in the system of acetonitrile–tetrabutylammonium fluoride.The formation of stable complexes H_4P^{2+} Hal^- and $H_4P^{2+}\cdot 2Hal^-$ was not observed, which is probably due to the screening effect of the methyl group at the intracyclic nitrogen atom on the coordination cavity of the porphyrin. Previously obtained data on similar systems have shown that there is a dependence of receptor properties of tetrapyrrole macrocycles with quartenated methyl groups on the number and nature of the substituents and counterions [8, 10, 11].

Taking into account the basic properties of 2,3,7,8,12,13,17,18-octaethyl-21-methylporphyrin **I** we synthesized 2,3,7,8,12,13,17,18-octaethyl-22,23-dimethylporphyn monotriflate **II.** Compound **II** has

Parameters of electron absorption spectra of porphyrin **I** and its mono- and diprotonated forms in the system of $HClO_4$–CH_3CN, and porphyrin **II** and its fluoride complex **IIa** in the system of $(C_4H_9)_4NF$–CH_3CN[a]

Porphyrin	λ_1 (log ε)	λ_2 (log ε)	λ_3 (log ε)	λ_4 (log ε)	λ_5 (log ε)
$H(CH_3)Et_8P$	397 (5.42)	502 (4.43)	532 (4.21)	583 (4.09)	640 (3.92)
$H_2(CH_3)Et_8P^+$	392 (5.51)	503 (4.41)	534 (4.54)	560 (4.58)	640 (3.86)
$H_3(CH_3)Et_8P^{++}$	400 (5.49)	–	535 (4.52)	560 (4.61)	604 (4.19)
$(CH_3)_2Et_8P^+T^-$	400 (5.08)	–	541 (4.19)	572 (4.25)	619 (3.72)
$(CH_3)_2Et_8P^+F^-$	426 (4.76)	–	539 (4.03)	597 (3.97)	–

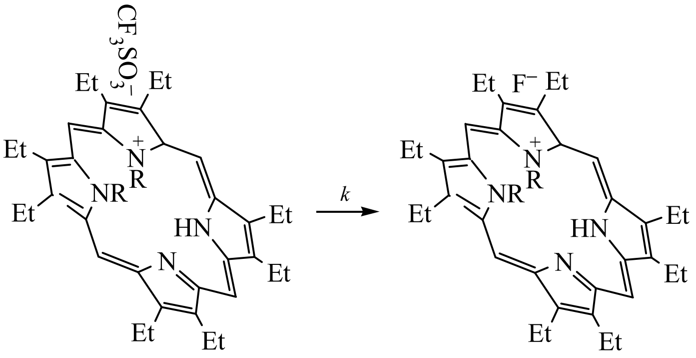
[a] λ_{max}, nm ($\varepsilon\times10^{-3}$, l mol^{-1} cm^{-1}).

several advantages compared with compound **I**: The tetrapyrrole macrocycle is initially in the protonated form, and the obtaining of the porphyrin protonated forms does not require performing additional experiments with a careful selection of the conditions of their existence (the determination of pH, solvent nature, and the protonating agent with accounting for the influence of its counterion on the cationic forms of the macrocycle).

Using the method of spectrophotometric titration [5] in the acetonitrile–tetrabutylammonium fluoride system we investigated the complexing properties of **II** with fluoride ion. Synthetically modified macroheterocycle **II** forms the analtical signal due to chemical interaction of the receptor molecules with the substrate (fluoride) in the region of concentration of the fluoride salts from 0 to 2.27×10^{-5} M. In the EAS of the system of acetonitrile–tetrabutylammonium fluoride a formation of a set of spectral curves with individual isosbestic point was observed (Fig. 3).The titration curve is of a single-stage character (Fig. 4). These experimental data provided a possibility to express the process by Scheme 2.

Scheme 2.

$$H(CH_3)_2Et_8P^+T^- + F^- \overset{k}{\rightleftarrows} H(CH_3)_2Et_8P^+F^- + T^-$$



II **IIa**

Replacement of the triflate ion in H(CH$_3$)$_2$Et$_8$$^+T^-$ by the fluoride ion with the formation of H(CH$_3$)$_2$Et$_8$$^+F^-$ leads to a strong red shift in the EAS, which is typical for such processes [8]. The increase in the fluoride concentration to 2.27×10^{-5} M also leads to a red shift (26 nm), as well as to broadening of the Soret band and a decrease in its intensity. Simultaneously the intensity of the band λ_{572} decreases and a`band at λ_{597} appears (Fig. 3).

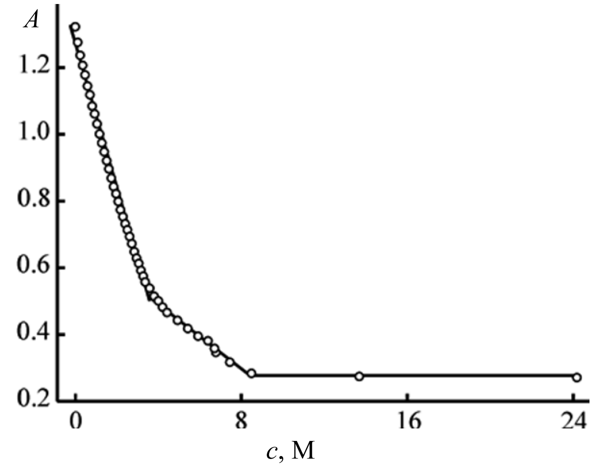


Fig. 2. Spectrophotometric titration curve of the porphyrin (**I**) ($c_{\text{porph.}}$= 4.91×10^{-5} M) in system of CH$_3$CN–HClO$_4$; c(HClO$_4$) = (0–2.42)×10^{-5} M, λ = 502 nm, 298 K.

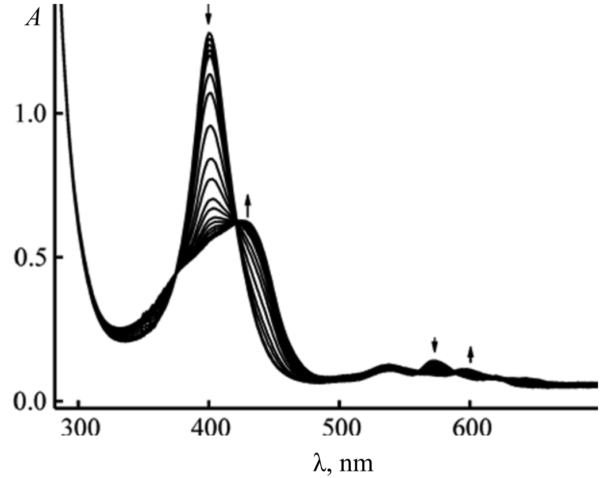


Fig. 3. Variation of EAS of the H(CH$_3$)$_2$Et$_8$P$^+$T$^-$ in the system of CH$_3$CN–(C$_4$H$_9$)$_4$NF, c_{porph} = 1.08×10^{-5} M, c(C$_4$H$_9$) = (0–2.27)×10^{-5} M.

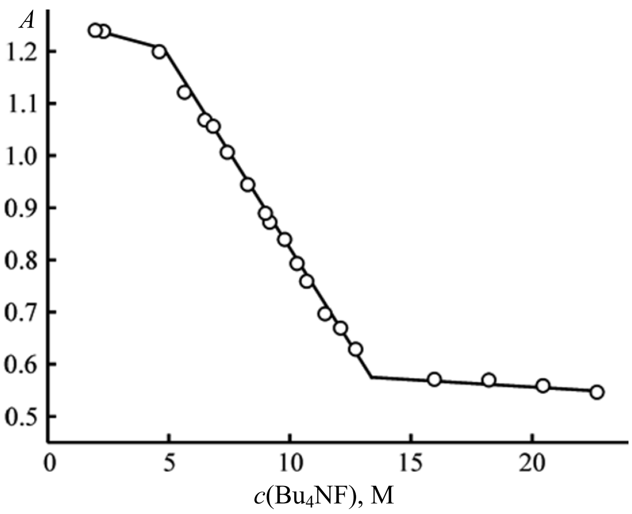


Fig. 4. Spectrophotometric titration curve of $H(CH_3)_2Et_8P^+T^-$, c_{porph} = 1.5×10^{-5} M in the system of CH_3CN–$(C_4H_9)_4NF$, $c[(C_4H_9)_4NF]$ = (0–2.27) $\times10^{-5}$ M, λ = 400 nm, 298 K.

The complexation constant log *k* of the process shown in the Scheme 2 in the system of acetonitrile–tetrabutylammonium fluoride calculated with the equation log *k* = log (Ind) – *n*log *S*$[(C_4N_9)_4NF]$, where *k* is association constant of porphyrin molecules with fluoride ion, Ind is indicator ratio $[H(CH_3)_2\overset{+}{Et_8}F/$ $[H(CH_3)_2\overset{+}{Et_8}T^-]$, *c* is analytical concentration of tetrabutylammonium fluoride in solution in M, *n* = 1 (the number of added fluoride ions formed at the dissociation of tetrabutylammonium fluoride) gives the value log *k* = 5.18.

Comparing the parameters of the EAS for monocationic forms obtained by different methods it is possible to see that the absorption bands in the EAS of monocationic forms of compound **II** suffer a red shift (8 nm of the Soret band, 7, 12, and 21 nm in the long-wavelength region) compared with the monocationic forms of compound **I.** At the replacement of triflate ions by fluoride (formation of compound **IIa**) the red shifts in the EAS significantly increase (up to 26 nm), easily detecting the presence of fluoride in acetonitrile solutions of compound **II.** The sensitivity of the proposed macroheterocycle **II** covers a wide range of the halogen concentration in solution {$c[(C_4H_9)_4NF]$ = (0–2.27×10^{-5} M), λ 400 nm, 298 K}, which shows a possibility to propose the tetrapyrrole chromophore as an effective molecular receptor for the registration of fluoride ions. The studies provide estimates of receptor properties of the protonated forms of tetrapyrrole compounds by different methods, which significantly expands the possibilities of creating new macroheterocyclic compounds for the detection and selective binding anions of different nature.

EXPERIMENTAL

Acetonitrile from ALDRICH was not subjected to further purification. The water content determined by Fisher did not exceed 0.04%. The solution of $(C_4H_9)_4NF$ was prepared on the basis of acetonitrile. The salt was purified in a Soxhlet apparatus with acetonitrile and dried in a vacuum (1.33 Pa) at 393 K to the constant weight. The spectrophotometric titration of **I** with a solution of $(C_4H_9)_4NF$ in acetonitrile was carried out using a Varian Cary 100 spectrophotometer.

A working solution of perchloric acid was prepared using dried acetonitrile and perchloric acid (8.75 M aqueous solution of chemically pure grade). The experimental procedure and data processing are given in [1, 5]. Error in the determination of the constants was ±(3–5)%. Mass spectra were obtained on electron impact mass spectrometer complex MX-1310 at the of ionizing electrons energy 70 eV and ionization chamber temperature 150–200°C. ^1H NMR spectra were recorded on a Bruker VC-200 spectrometer with the operating frequency 200 MHz from solutions in deuterochloroform, internal reference TMS.

2,3,7,8,12,13,17,18-Octaethyl-21-methylporphyrin. To a solution of 3,7,8,12,13,17,18-octaethylporphyrin (250 mg, 0.47 mmol) in 30 ml of chloroform was added 5 ml (2.2 g, 15.5 mmol) of methyl iodide and excess of freshly dried sodium formate. The mixture was refluxed for 24 h, then cooled to room temperature, filtered from the precipitate, evaporated to minimum volume, and chromatographed on aluminum oxide of III degree of activity by Brockmann, eluting with chloroform–light petroleum ether. Eluate containing 3,7,8,12,13,17,18-octaethyl-21-methylporphyrin was evaporated to the minimum volume, the product was precipitated with methanol, filtered off, washed with methanol, and dried at 70ºC in air. Yield 0.15 g (61%). ^1H NMR spectrum, δ, ppm: 9.95 s, 9.89 s (2×2H, *ms*-H); 4.04 m, 3.97 m, 3.78 m (16H, $C\underline{H}_2CH_3$), 1.93 t, 1.91 t, 1.1 t (24H, $CH_2C\underline{H}_3$), –4,79 s (3H, CH_3) ($CDCl_3$, int. TMS). Found, %: C 80.97, H 8.84, N 10.19. $C_{39}H_{51}F_3N_4O_3S$. Calculated, %: C 80.98, H 8.82, N 10.21.

2,3,7,8,12,13,17,18-Octaethyl-22,23-dimethylporphyrin monotriflate. To a mixture of 250 mg (0.46 mmol) of octaethyl porphin and 1,25 g (4.6 mmol) of potassium carbonate was added to 70 ml of dry chloroform, and then 0.53 ml (4.6 mmol) of methyl trifluoromethanesulfonate in 20 ml of chloroform. The mixture was stirred at room temperature for several hours. The reaction monitoring was carried out by TLC every 2 h. After completion, the reaction mixture was filtered of through a glass frit filter from inorganic precipitate, evaporated to a half of its volume, and chromatographed on aluminum oxide of III degree of activity, eluting with chloroform. Porphyrin eluate was evaporated to minimum volume, precipitated with methanol, the precipitate was filtered off, washed with methanol, and dried at 70ºC in air. Yield 0.32 g (96%). ^{1}H NMR spectrum ($CDCl_3$, int. TMS), δ, ppm: 10.35 s, 10.22 s, 10.19 (2×2H, *ms-H*); 3.86 m, 4.13 m (16H, $C\underline{H}_2CH_3$); 1.99 t, 1.93 t, 1.69 t, 1.50 t (24H, $CH_2C\underline{H}_3$); –5.88 s (6H, 22,23-CH_3). Found, %: C 65.73, H 7.25, N 7.83, S 4.59. $C_{39}H_{51}F_3N_4O_3S$. Calculated, %: C 65.71, H 7.21, F 7.99, N 7.86, O 6.73, S 4.50.

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