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Cationic Tetrapyrrole Receptors for Selective Binding Hydroxide Ions

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Abstract—The receptor properties of complexes of 5,10,15,20-tetraphenyl-21,22,23-trimethylporphyrin and 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin toward hydroxide ion were explored by the method of spectrophotometric titration in methanol with iodine and triflate respectively. We found that in the studied complexes the hydroxide ion is replaced by the respective counterion that leads to a strong response in the visible region of absorption spectrum. The formation constants and the concentration ranges of existence of the complexes were determined.

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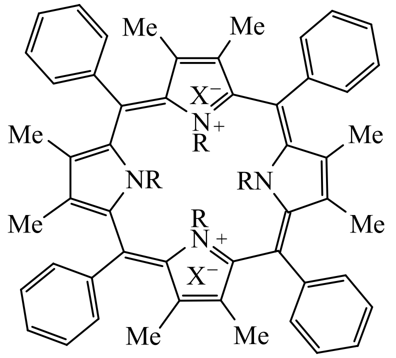
According to the publications [1–9], porphyrins are widely used as receptors for anions at the creation of optical sensors. The coordination processes involving tetrapyrrole chromophore are accompanied by the easily registered changes in the analytical system, which provides good conditions for the detection of anions in solution. The promising agents are both molecular and protonated forms of porphyrins [1,2,5]. Thus, by UV and ^{1}H NMR spectroscopic titration has been revealed selective binding of anions Cl^-, NO_3^-, $H_2PO_4^-$ by the molecular forms of (α,α,α,α)-5,10,15,20-tetrakis[*o*-(*p*-R-phenylureleno)phenylporphyrins [R = H, Cl, Br] with the formation of stable 1:1 complexes [2]. In [3] bisporphyrincalix[4]arene has been used as a receptor binding various anions. Protonated forms of porphyrins themselves [4,5] have also been used as high-performance receptors of halide ions forming stable 1:1 and 1:2 complexes, and has been observed a change in fluorescence of the diprotonated porphyrin molecules in a solution containing halide ions due to quenching along the mechanisms of internal and external heavy atom. Based on these data was proposed a method of fluorescent detection of halide ions (even at the concentration 0.00015 M) [10].

A significant drawback of the protonated forms of porphyrins as receptors is a prerequisite for obtaining mono- and dicationic forms of porphyrins from their molecular form, which is quite difficult, because requires additional highly accurate experiment to determine and stabilize the concentration intervals of cationic forms of the tetrapyrrole macrocycles.

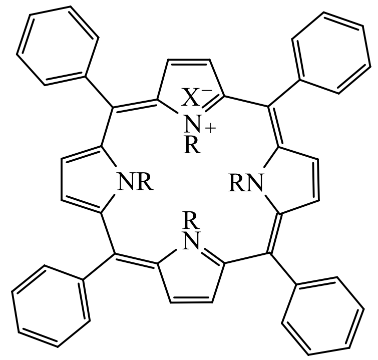
To facilitate solving this task we have carried out the work on the creation of porphyrins in which the tetrapyrrole macrocycle is in a stable dicationic form initially. In particular, in [11], we have synthesized 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate (**I**) and studied its complex-forming properties with respect to the halide ions. It has been shown that the tetrapyrrole dication stabilized by two triflate anions is a high-performance molecular receptor for selective binding fluoride ions in solutions in the concentration range from 0 to 6.22×10^{-5} M.

Continuing studies of receptor properties of the porphyrins cationic forms, we synthesized the 5,10,15,20-tetraphenyl-21,22,23-trimethylporphyrin iodide (**II**) in which the tetrapyrrole macrocycle is in the form of the stable cation with iodide counterion. We investigated the complexing properties of the monocation **II** and dication **I** toward hydroxide ion by the method of spectrophotometric titration in the system of methanol–tetramethylammonium hydroxide.

The results of the interaction of compounds **I** and **II** with tetramethylammonium hydroxide in the systems (1)

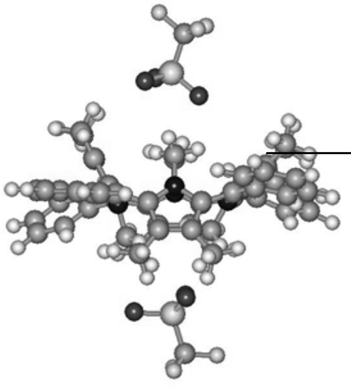


I

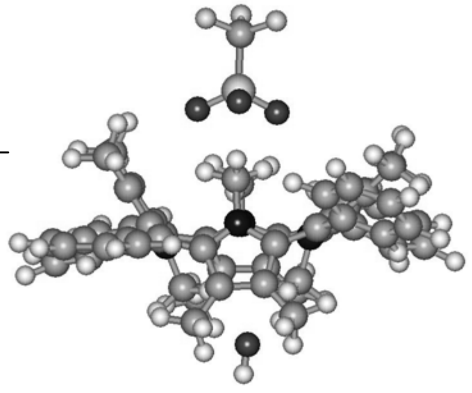


II

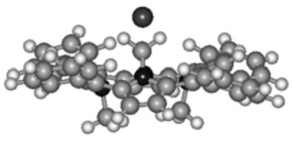
$R = CH_3$, $X = F_3CSO_2^-$ (**I**); $R = CH_3$, $X = I^-$ (**II**).



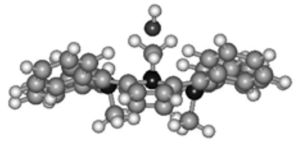
I, H_4P^{2+} $(F_3CSO_2^-)_2$



Ia, H_4P^{2+} $(F_3CSO_2^-)OH^-$



II, $H_3P^+I^-$



IIa, $H_3P^+OH^-$

and (2) are presented by the data of electron absorption spectra (EAS, Figs. 1 and 3) and the titration curves (Figs. 2 and 4).

$$H_3P^+I–(CH_3)_4NOH–CH_3OH, \quad (1)$$

$$H_4P^{2+}(F_3CSO^-)_2–(CH_3)_4NOH–CH_3OH. \quad (2)$$

Upon increase in the hydroxide ion $[OH^-]$ concentration from 0 to 0.0613 M, the absorption spectra of the reaction system (1) gave a family of spectral curves (Fig. 1), which corresponds to one section on the corresponding titration curve (Fig. 2). From the results of changes in the EAS of the reaction system and the titration curve we assume that in complex **II** the counterion stabilizing the molecule (iodide ion) is probably replaced by hydroxide ion. This interaction can be represented by the Eq. (3).

$$H_3P^+I^- + OH^- \overset{k}{\rightleftarrows} H_3P^+OH^- + I^-. \quad (3)$$

In favor of the iodide ion substitution by the hydroxide also indicates the nature of spectral changes in going from $H_3P^+I^-$ to $H_3P^+OH^-$ (Fig. 1). When the hydroxide ion concentration reaches 0.0613 M the four-band absorption spectrum of $H_3P^+I^-$ is transformed into a two-band (see the table). The intensity of the band at 459 nm decreases, the band broadens and exerts hypsochromic shift. As known, the iodide ion with its large ionic radius and low ionic potential forms weak associates with the porphyrin cationic forms [4]. The shift to shorter wavelengths characteristic of the dissociation of the complexes of porphyrins dicationic forms with iodide ions [Eq. (4)] [4, 5] also indicates the substitution of the iodine ion by hydroxide ion.

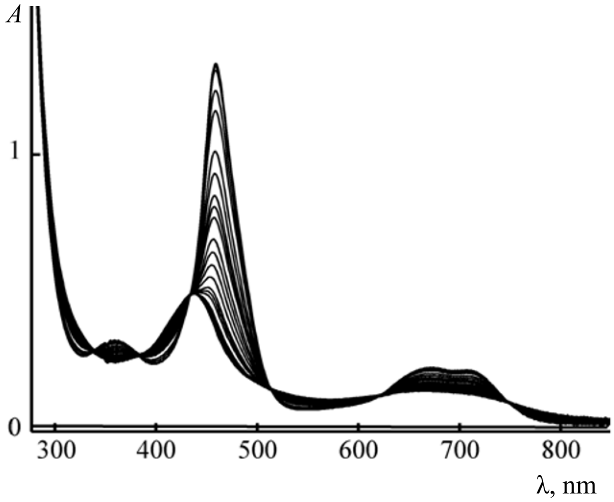


Fig. 1. Changes in EAS of the system $H_4P^{2+}I_2$–$(CH_3)_4NOH$–CH_3OH ($c_{porph.}$ = 1.3×10^{-5}, c_{TMA} = 0–0.0613 M).

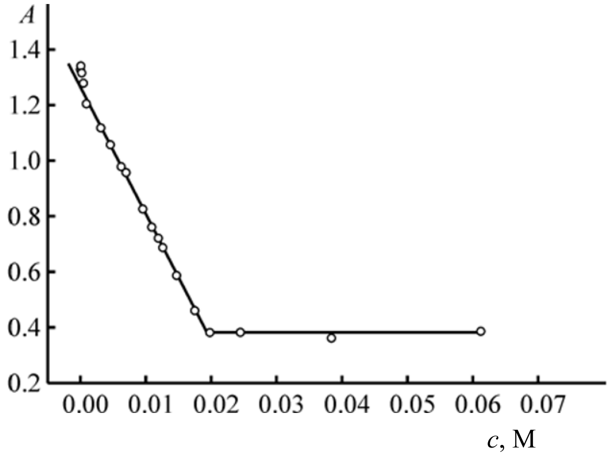


Fig. 2. The spectrophotometric titration curve of $H_4P^{2+}I_2$ (c_{porph} = 1.3×10^{-5} M) with the solution of $(CH_3)_4NOH$ (c_{TMA} = 0–0.0613 M) in methanol, λ = 460 nm, 298 K.

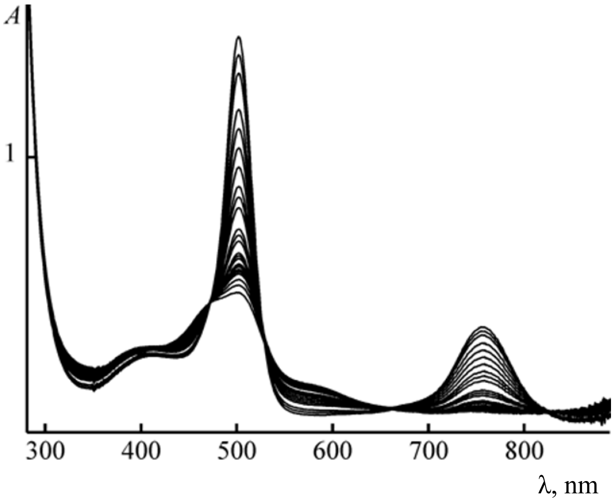


Fig. 3. Changes in the EAS of the system $H_4P^{2+}(F_3CSO^-)_2$–$(CH_3)_4NOH$–CH_3OH (c_{porph} = 1.1×10^{-5}, c_{TMA} = 0–0.00067 M).

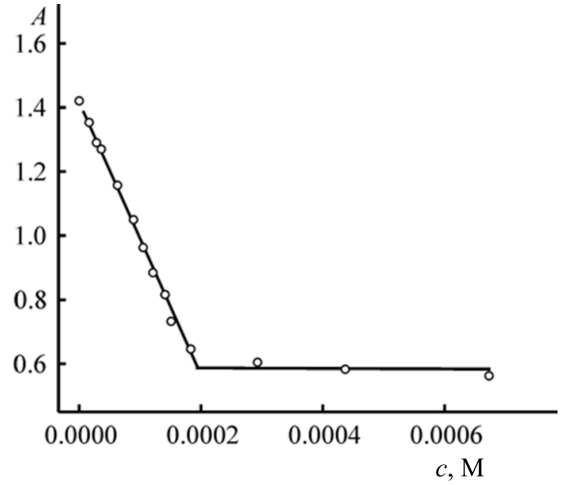


Fig. 4. The spectrophotometric titration curve of $H_4P^{2+}\cdot(F_3CSO^-)_2$ (c_{porph} = 1.1×10^{-5} M) with the solution of $(CH_3)_4NOH$ (c_{TMA}= 0– 0.00067 M) in methanol, λ = 500 nm, 298 K.

$$(H_4P)^{2+}(I^-)_2 \rightleftarrows (H_4P)^{2+}(I^-) + I^-. \qquad (4)$$

Stability constant of complex **IIa** in the system (1) calculated with Eq. (5) equals 2.09.

$$\log k = \log\,(\mathrm{Ind}) - n\log c_{TMA}, \qquad (5)$$

where k is association constant of tetrapyrrole chromophore with hydroxide ion; Ind is the indicator ratio H_3P^+OH/H_3P^+I (for the proces 3) and H_4P^{2+} TOH^-/$H_4P^{2+}T_2$ (for the process 6), c_{TMA} is analytical concentration of tetramethylammonium hydroxide in solution (M); n = 1 (the number of the hydroxide ions produced at the dissociation of tetramethylammonium hydroxide and entering to the complex).

Study of complexation of **I** with tetramethylammonium hydroxide in the range of the hydroxide ion concentration 0 to 0.00067 M showed that the spectrum of the reaction system (2) as well as in the case of (1) gives a family of spectral curves, to which corresponds one section of the corresponding titration curve (Figs. 3, 4).The EAS of compound **I** in the process of titration of hydroxide ions is transformed from a two-band to a single band pattern (see the table). As far as the spectrum of the product of

Parameters of the electron absorption spectra of the complexes **I, Ia, II** and **IIb** in the systems (1) and (2): λ_{max}, nm (log ε, l mol^{-1} cm^{-1})

Ion	λ_1 (log ε)	λ_2 (log ε)	λ_3 (log ε)	λ_4 (log ε)
H_3P^+I	359 (4.39)	459 (4.99)	674 (4.24)	709 (sh) (4.47)
H_3P^+OH	–	439 (4.57)	666 (4.05)	–
$H_4P^{2+}T_2$	–	502 (5.16)	755 (4.59)	–
$H_4P^{2+}TOH$	–	498 (4.70)	–	–

complexation in the system (2) is identical to the spectrum of the complex H_4P^{2+} TF^- (Fig. 5) formed at the complexation of $H_4P^{2+}T_2$ with fluoride ion [11], the interaction of **I** with tetramethylammonium hydroxide can be represented by the Eq. (6).

$$H_4P^{2+}(F_3CSO^-)_2 + OH^- \xrightleftharpoons{k} H_4P^{2+}(F_3CSO^-)(OH^-) + F_3CSO^-. \tag{6}$$

That is, in contrast to the interaction of **I** with the fluoride ion proceeding in accordance with [11] in two stages with successive replacement of two triflate ions by the fluoride ions with the formation finally of 5,10,15,20-tetraphenyl-2,3,7,8,12,13,17,18,21,22,23,24-dodecamethylporphyrin difluoride [$H_4P^{2+}(F^-)_2$], the interaction in the system (2) ends with the replacement of one triflate ion by the hydroxide ion [Eq. (6)]. Stability constant of the corresponding complex **Ia** in the system (2) calculated with Eq. (5) is 3.93.

Thus, in this work we studied by spectrophotometric titration in methanol the receptor properties of 5,10,15,20-tetraphenyl-21,22,23-trimethylporphyrin iodide and 5,10,15,20-tetraphenyl-2, 3,7,8,12,-13,17,18,21,22,23,24-dodecamethylporphyrin ditriflate with respect to the hydroxide ion. We established that in the studied complexes occurs substitution of the counterion by the hydroxide ion accompanied by a strong response in the visible absorption spectrum of the system. The formation constants of the complexes and the concentration ranges of their existence are determined. The sensitivity of the proposed porphyrin cationic forms covers a wide range of the substrate concentrations, which allows us to consider these tetrapyrrole chromophores as highly selective molecular sensors for registration hydroxide ions in solution. Formation of analytical signal by the sensor is due to chemical interaction of the macrocyclic receptor molecules with the substrate molecules.

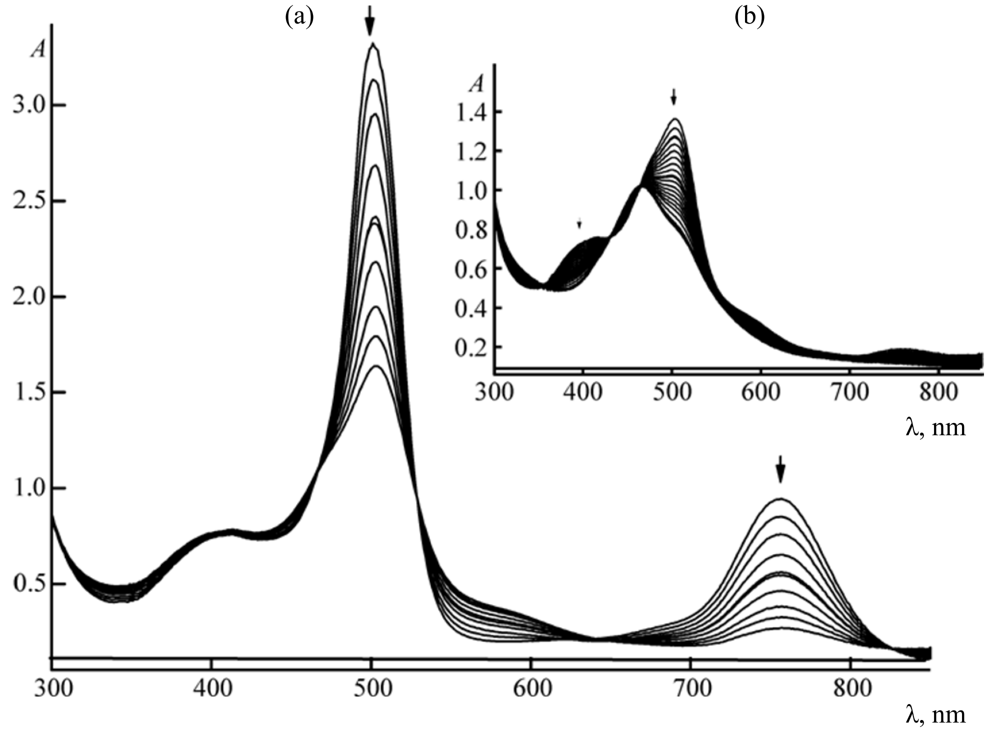


Fig. 5. The changes in the EAS of the system of $H_4P^{2+}(F_3CSO^-)_2$–$(C_4H_9)_4NF$–CH_3CN. (a) $c_{porph} = 1.5\times10^{-5}$, $c_{TMA} = 0$–2.65×10^{-5} M, (b) $c_{porph} = 1.5\times10^{-5}$, $c_{TMA} = 2.65\times10^{-5}$–$7.46\times10^{-5}$ M.

EXPERIMENTAL

The ball-rod models of the complexes **I, Ia, II** and **IIa** were optimized using Hyper Chem Professional 8.07 software.

Methanol from Aldrich was used, water content (0.04%) was monitored by the Fisher's mrthod. Tetramethylammonium hydroxide solution in methanol was prepared based on the industrially available concentrated solution of tetramethylammonium hydroxide in methanol (from Acros). The water content at the end of the titration monitored by Fisher did not exceed 0.044%. The spectrophotometric titration of **I** and **II** with a solution of $(CH_3)_4NOH$ in methanol was carried out using a Varian Cary 100 spectrophotometer. The experimental procedure and data processing are given in [4, 10]. Error in the determination of the constants was ± (3–5)%.

***N',N'',N'''*-Trimethyl-5,10,15,20-teraphenylporphyrin iodide (II).** 0.5 g (0.81 mmol) of 5,10,15,20-tetraphenylporphyrin was refluxed for 8 h with 10 ml (0.16 mol) of methyl iodide and 1 g (7.23 mmol) of potassium bicarbonate in 50 ml of chloroform. The precipitate formed was filtered off, and the solution was chromatographed on alumina of IInd degree of activity by Brockmann, eluting with a chloroform-methanol mixture (100:1), collecting the second (green) zone of the target product. The eluate was evaporated to a minimum volume, and porphyrin was precipitated by adding petroleum ether. The precipitate was filtered off, washed with petroleum ether and dried at 70°C. Yield 0.2g (31.5%). Found, %: H 4.71, C 71.89, N 7.12. $C_{47}H_{38}N_4I$. Calculated, %: H 4.75, C 71.94, N 7.14.

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