ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 5, pp. 1029–1034. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © Yu.B. Ivanova, A.S. Semeikin, N.Zh. Mamardashvili, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 5, pp. 857–862.

Effect of the Macrocycle Chemical Modification on the Tetraphenylporphin Basic Properties

Yu. B. Ivanova[a], A. S. Semeikin[b], and N. Zh. Mamardashvili[a]

[a] *Institute of the Chemistry of Solutions, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: ybi@isc-ras.ru

[b] *Ivanovo State Chemical Technological University, Ivanovo, Russia*

Received November 24, 2008

Abstract—Basic properties of tetraphenylporphin and its derivatives with electron-donor and electron-acceptor substituents in the position 4 of *meso*-aryl fragments are studied by the method of spectrophotometric titration. The process of protonation of endocyclic nitrogen atoms of the macrocycle tetrapyrrole fragment in the ethanol–sulfuric acid system was found to proceed in two steps. Respective ionization constants and concentration ranges of existence of mono- and dicationic forms of the studied tetraarylporphyrins are determined.

DOI: 10.1134/S1070363209050284

The design of tetrapyrrole receptors for their correspondence to certain substrates with the purpose of creation of nano-size molecular sensors for detection of anions in solutions is an actual problem in the chemistry and the material science [1, 2]. The capability of tetrapyrrole macrocycles to selective binding of anions is based on the ability of proton-donor NH groups of pyrrole ring to selective coordination of substrate via the formation of hydrogen bonds [3–11].

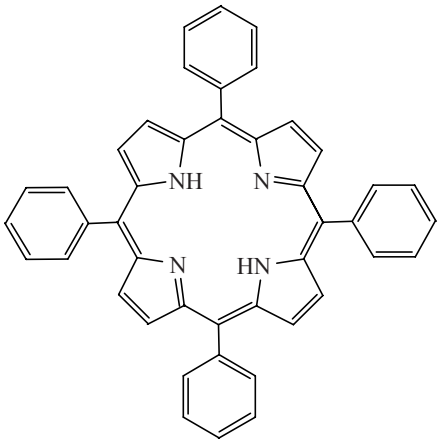
For nonaromatic *meso*-octamethyl-calix-[4]-pyrrole containing in the macrocycle four carbon *meso* atoms in the state of sp^3 hybridization their capability of selective binding anions F^-, Cl^-, Br^-, $H_2PO_4^-$, and HSO_4^- to form 1:1 complexes was detected by the method of spectrophotometric titration [12]. The calixpyrrole selectivity toward the studied anions is as follows: 1.0 (F^-), 0.68 (Cl^-), 0.57 ($H_2PO_4^-$), 0.33 (Br^-) and 0.05 (HSO_4^-).

Porphyrins are undoubtfully interesting compounds for creation of optical molecular sensors for anions. The coordination processes with tetrapyrrole chromophores are commonly accompanied by easily registered changes in the properties of the analyzed system [2]. This provides good conditions for detection of anions in solutions. Therewith, molecular forms of porphyrins [13] and their protonated forms are both promising [1].

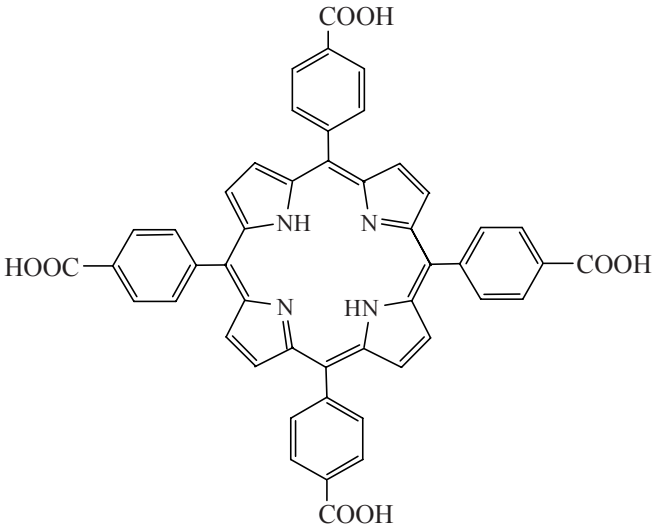
Earlier for the molecular forms of (α,α,α,α)-5,10,15,20-tetra-[*ortho*-(*para*-R-phenylureleno)phenyl]-porphyrins [R = H, Cl, F] by the method of UV-Vis spectroscopy and ^1H NMR titration was shown a selectivity in binding anions Cl^-, NO_3^-, and $H_2PO_4^-$ [13]. The porphyrin was found to bind most effectively the chloride anion: the process proceeds in one step with formation of complexes with stable 1:1 stoichiometry.

To study the possibility to apply the protonated porphyrins as receptors of the halide anions (Hal^-),we have carried out in [14] a direct titration of mono- (H_3P^+) and diprotonated (H_4P^{2+}) forms of 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin with halide salts solutions and found that in solutions are formed stable complexes $H_4P^+ \cdot Hal^-$ and $H_4P^{2+} \cdot 2Hal^-$, and we have measured their stability constants at 298 K. More recently we have studied [1] the effect of complex formation with iodide anions on the H_4P^{2+} fluorescence properties. On the basis of analysis of dependence of the fluorescence intensity and duration versus the iodide ion concentration in solution we proposed to use H_4P^{2+} as a fluorescent molecular receptor for the halide ions.

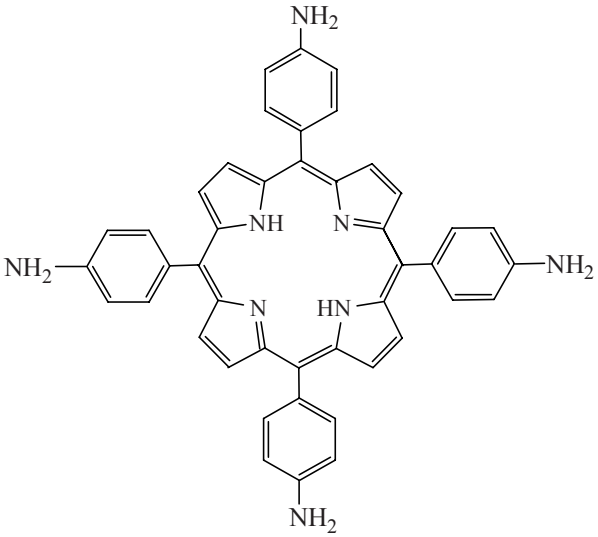
Analysis of publications and results of our own investigations show that the key problem defining the receptor properties of the tetrapyrrole macrocycles



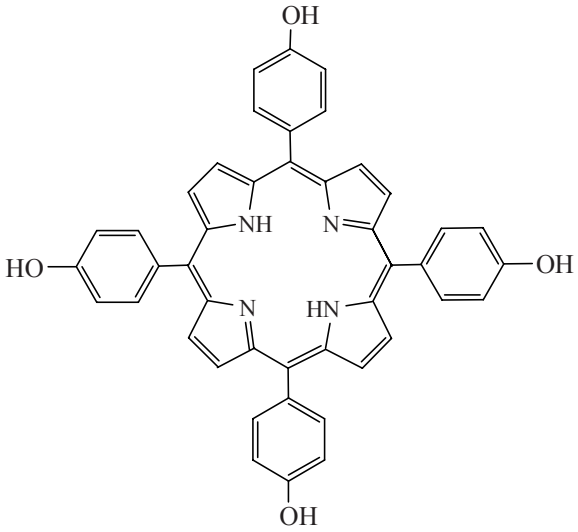
Tetraphenylporphin TPhP (**I**)



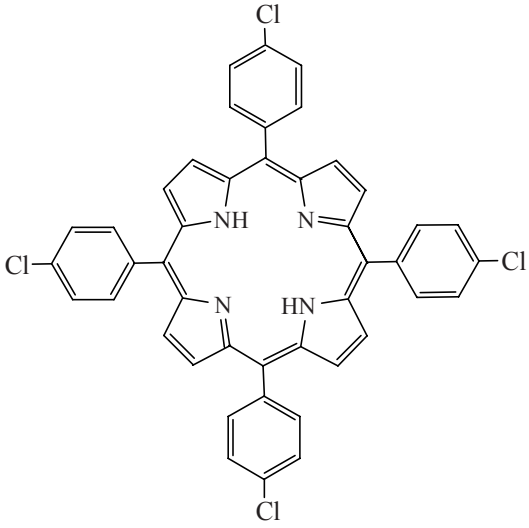
5,10,15,20 tetra-(4-carboxyphenyl)porphin COOH–TPhP (**II**)



5,10,15,20 tetra(4-aminophenyl)porphin NH_2–TPhP (**III**)



5,10,15,20 tetra-(4-hydroxyphenyl)porphin OH–TPhP (**IV**)



5,10,15,20 tetra(4-chlorophenyl)porphin Cl-TPhP (**V**)

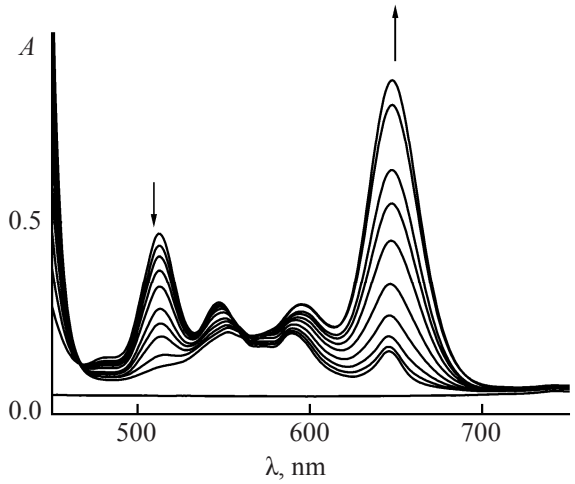


Fig. 1. Variations in electron absprption spectra of TPhP in the system of $C_2H_5OH–H_2SO_4$ at 298 K, $C(H_2SO_4)$ = 0–0.007 mol l^{-1}.

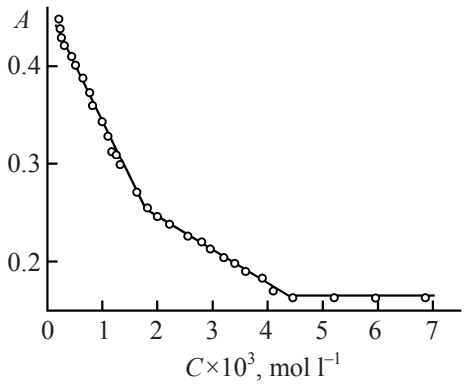


Fig. 2. Titration curve of TPh**P** on the analytical wavelength 512 nm in the system of $C_2H_5OH–H_2SO_4$, $C(H_2SO_4)$ = 0–0.007 mol l^{-1}.

toward the anions of different nature is the basicity of the nitrogen atoms in the porphyrin molecule coordination center. In connection with our interest in designing tetrapyrrole receptors for anions, in the present work we studied the effect of donor and acceptor substituents on the acid-base properties of tetraphenylporphin. We found that the process of protonation of nitrogen atoms of the studied tetrapyrrole macrocycles in the system of ethanol – sulfuric acid proceeded in two steps. We measured the corresponding ionization constants and concentration ranges of the existence of mono- and dianionic forms of the studied compounds.

In acid medium, porphyrins (H_2P) are protonated at the tertiary nitrogen atoms to form mono- (H_3P^+) and dications (H_4P^{2+}) [Eqs. (1) and (2)].

$$H_2P + H^+ \overset{k_{b1}}{\rightleftharpoons} H_3P^+, \quad (1)$$

$$H_3P^+ + H^+ \overset{k_{b2}}{\rightleftharpoons} H_4P^{2+}, \quad (2)$$

$$H_2P–C_2H_5OH–H_2SO_4. \quad (3)$$

Therewith, the four-band spectrum of initial porphyrin is transformed into the two-band one. In some cases, the acidification of solution leads to the appearance of electronic spectra as two alternating sets of curves (each has its own isobestic point) that indicates the protonation sequence in the first and the second step. In other cases, the increase in the acid concentration in the porphyrin solution leads to a smooth change of spectral image from the neutral form to the dication with one isobestic point up to the completion of the titration.

In the absence of specific interaction of the porphyrin protonated forms with the solvent and the solution components, the main ionization proceeds commonly in two separate steps, and the second proton is expectably added more difficultly than the first one. Each form occupies its own area depending on the concentration of initial reagents.

It should also be noted that in different solvents the protonation of the same porphyrin can proceed differently. According to [20], the first and the second steps of tetraphenylporphin protonation with perchloric acid in acetonitrile are not resolved. However, our study of ionization of tetraphenylporphin in the system ethanol–sulfuric acid [Eq. (3)] showed that protonation of tetrapyrrole macrocycle results (as far as the acid concentration grows) in stepwise appearance of two sets of spectral curves in the electron spectrum of the system (Fig. 1), each set has its own isobestic points and its own inflection point on the titration curve (Fig. 2). The increase in sulfuric acid concentration results in a red shift of the five-band spectrum of the tetraphenylporphin molecular form with stepwise transformation initially into six-band spectrum (monocation) and then into four-band one (dication) (Table 1). After detecting inflection points on the titration curves using procedure described in [19] we

Table 1. Electron absorption spectra of porphyrins **I–V** and respective mono- and dicationic forms in the system of C_2H_5OH – H_2SO_4: λ_{max}, nm ($\varepsilon\times10^{-3}$, l mol^{-1} cm^{-1})

Compound	I	II	III	IV	V	$C(H_2SO_4)$, mol l^{-1}
TPhP						
H_2P	409 (3.51)	512 (2.65)	547 (2.43)	589 (2.29)	646 (2.18)	0
H_3P^+	411, 433 (3.52, 3.44)	513 (2.50)	550 (2.39)	592 (2.36)	647 (2.50)	0.0016
H_4P^{2+}	428 (3.5)	–	553 (2.30)	595 (2.42)	648 (2.91)	0.0070
COOH–TPhP						
H_2P	401 (4.72)	512 (4.27)	546 (4.02)	588 (3.88)	645 (3.74)	0
H_3P^+	412 (4.73)	512 (4.06)	547 (3.90)	591 (3.90)	648 (4.08)	0.0038
H_4P^{2+}	430 (4.70)	–	–	597 (3.86)	649 (4.34)	0.0157
NH_2–TPhP						
H_2P	419 (4.41)	522 (3.96)	563 (4.01)	653 (3.85)	–	0
H_3P^+	426 (4.42)	460 (4.32)	561 (3.97)	–	720 (4.19)	$1.18\cdot10^{-9}$
H_4P^{2+}	385 (3.97)	461 (4.34)	–	–	781 (4.32)	$3.44\cdot10^{-9}$
HO–TPhP						
H_2P	410 (4.73)	516 (4.18)	554 (4.10)	592 (3.68)	650 (3.91)	0
H_3P^+	422 (4.76)	444 (4.70)	516 (3.60)	554 (3.97)	652 (4.16)	$2.03\cdot10^{-9}$
H_4P^{2+}	–	445 (4.74)	–	–	694 (4.52)	$1.20\cdot10^{-8}$
Cl–TPhP						
H_2P	412 (4.34)	512 (3.60)	545 (3.43)	587 (3.36)	645 (3.26)	0
H_3P^+	415 (4.33)	439 (4.19)	511 (3.48)	590 (3.38)	655 (3.55)	0.002
H_4P^{2+}	–	438 (4.34)	–	599 (3.41)	653 (3.79)	0.006

separated the protonation processes in the system (3) into steps (Figs. 3 and 4) and calculated respective constants for the Eqs. (1) and (2). The ionization processes of COOH-tetraphenylporphin (Fig. 5), Cl-tetraphenylporphin (Fig. 6), NH_2-tetra-phenylporphin (Fig. 7) and HO-tetraphenylporphin (Fig. 8) proceed similarly. The equilibrium constants of the processes described by Eqs. (1) and (2) for the porphyrins **I–V** are listed in Table 2.

The porphyrins **II–V** differ from **I** by inclusion of substituents in positions 4 of benzene fragments of the

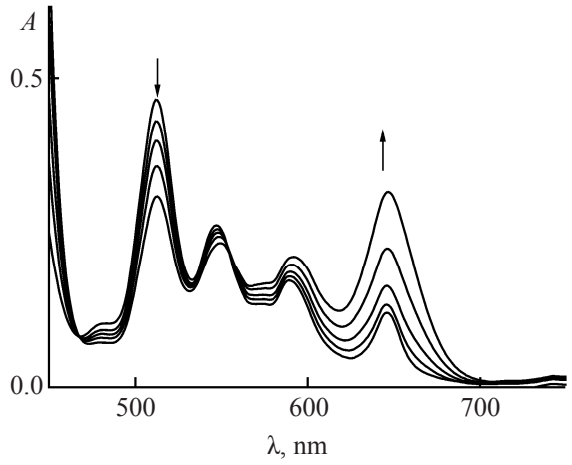


Fig. 3. Variations in electron absprption spectra of TPhP in the system of C_2H_5OH–H_2SO_4, at 298K, $C(H_2SO_4)$ = 0–0.0016 mol l^{-1}.

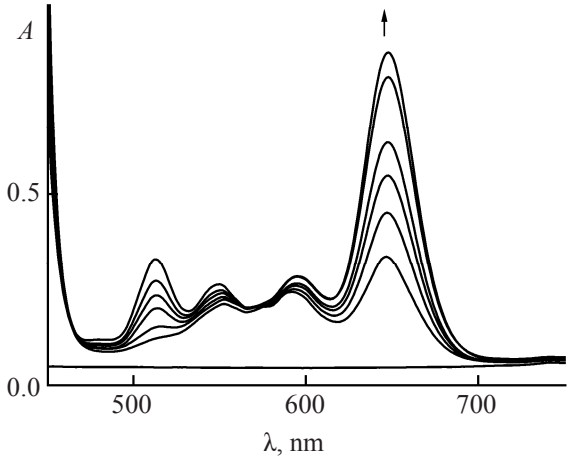


Fig. 4. Variations in electron absprption spectra of TPhP in the system of C_2H_5OH–H_2SO_4, at 298K, $C(H_2SO_4)$ = 0.0016–0.007 mol l^{-1}.

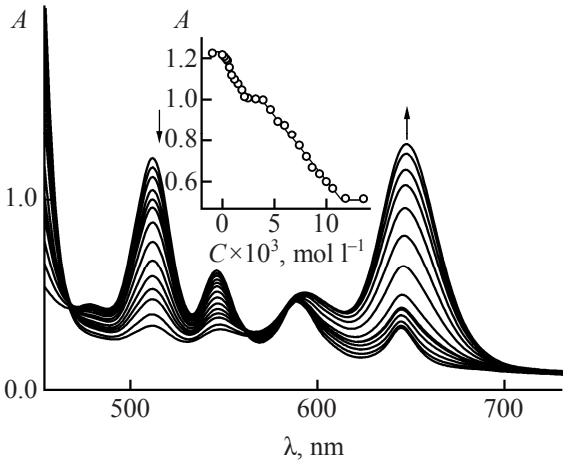


Fig. 5. Variations in electron absprption spectra and titration curve on the analytical wavelength 512 nm of COOH–TPhP in the system of C_2H_5OH–H_2SO_4, at 298K, $C(H_2SO_4)$ = 0–0.0157 mol l^{-1}.

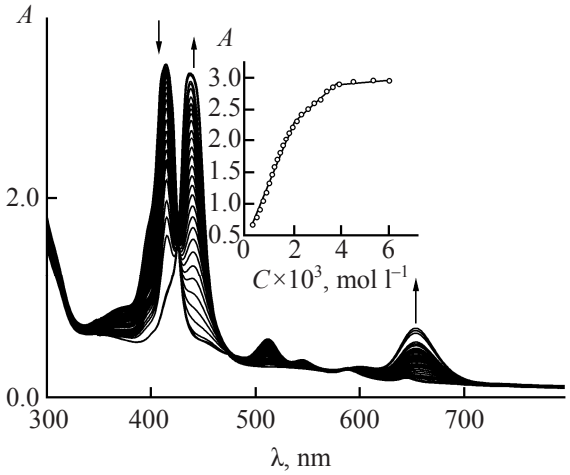


Fig. 6. Variations in electron absprption spectra and titration curve on the analytical wavelength 450 nm of Cl–TPhP in the system of C_2H_5OH–H_2SO_4, at 298K, $C(H_2SO_4)$ = 0–0.006 mol l^{-1}.

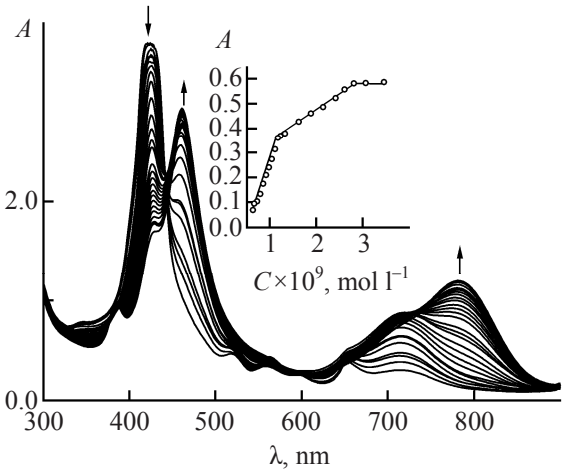


Fig. 7. Variations in electron absprption spectra and titration curve on the analytical wavelength 777 nm of NH_2–TPhP in the system of C_2H_5OH–H_2SO_4, $C(H_2SO_4)$ = 0–3.44×10^{-9} mol l^{-1}.

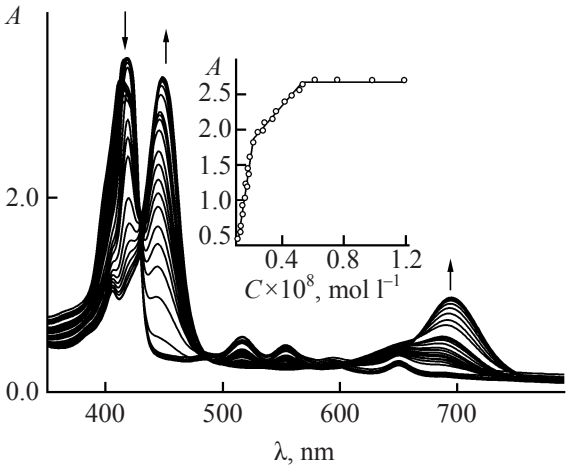


Fig. 8. Variations in electron absprption spectra and titration curve on the analytical wavelength 450 nm of HO–TPhP in the system of C_2H_5OH–H_2SO_4, $C(H_2SO_4)$ = 0–1.20×10^{-8} mol l^{-1}.

macrocycle. Analysis of the values of K_{b1}, K_{b2} listed in Table 2 shows that the observed changes in the porphyrins basicity correspond to the inductive effects of substituents at the chemical modification of porphyrin molecule. The inductive effect (+*I*) of electron-donor substituents (OH, NH_2) obviously leads to an increase in the electron density on the tertiary nitrogen atoms of pyrrole fragments of the tetrapyrrole macrocycle and as a consequence, to an increase in the basicity of porphyrins **IV** and **V** (Table 2). Basicity of amino-substituted porphyrin **IV** grows by a factor 1.3 compared to the tetraphenylporphin **I**.

Table 2. Values of the constants k_{b1} and k_{b2} for the processes (1) and (2) with the porphyrins **I–V**

Compound	k_{b1}	k_{b2}
TPhP	525	58
COOH–TPhP	151	41
NH_2–TPhP	707	64
HO–TPhP	562	56
Cl–TPhP	537	56

The electron-acceptor COOH group affects maximally the macrocycle basicity. The decrease in the electron density on the macrocycle tertiary nitrogen atoms (*–I* effect of substituent) leads to 3.5-fold decrease in the basicity of the carboxy-substituted porphyrin **III** compared to porphyrin **I**. Chlorine substitution leads only to a small change in the macrocycle basicity probably because the conjugation effect (*+C* effect) between the halide lone pairs and π-electron cloud of the macrocycle benzene fragments overrides *–I* effect of this substituent. Eventually, the basicity of porphyrin **III** slightly grows compared to porphyrin **I**. Note that the effect of substituents is more pronounced on the first step of the macrocycle protonation [Eq. (1)]. The process of addition of the second proton is less dependent on the nature of substituent (Table 2).

Thus, the protonation of the reaction centers of *meso*-tetraarylporphyrins **I–V** at the increased concentration of sulfuric acid proceeds in two steps and occurs at intracyclic nitrogen atoms. Each step of protonation leads to strong response in the visible region of the absorption spectrum, therefore a possibility appears to control the physicochemical properties of tetrapyrrole chromophore at varying the medium acidity. The results obtained show that the most basic amino-substituted tetraphenylporphin can be used as a basic compound for creation of pH-switch-selectable molecular device for detection of anions in a solution.

EXPERIMENTAL

Tetraphenylporphin (TPhP, **I**) and tetra(4-chlorophenyl)porphin (Cl–TPhP, **II**) are synthesized along the procedure in [16]. Tetra(4-carboxyphenyl)-porphin (COOH–TPhP, **III**) is synthesized along the procedure in [17]. Tetra(4-aminophenyl)porphin (NH_2–TPhP, **IV**) is synthesized along the procedure in [18]. Tetra(4-hydroxyphenyl)porphin (HO–TPhP, **V**) is synthesized along the procedure in [19].

Spectrophotometric investigations of equilibriums (1) and (2) in system (3) of compounds **I–V** was carried out on a Varian Cary 100 instrument. The experimental technique, equipment and procedures of the spectrophotometric titration were described in detail in [20]. The error in the determination of the respective constants is ±(3–5)%.

ACKNOWLEDGMENTS

This work was financially supported by Russian Foundation for Basic Research (grants nos. 08-03-0009-a, 08-03-9000-Bel.)

REFERENCES

1. Kruk, N.N., Starukhin, A.S., Mamardashvili, N.Zh., Sheinin, V.B., and Ivanova, Yu.B., *Zh. Prikl. Spectr*., 2007, vol. 74, no. 6, p. 750.
2. Koifman, O.I., Mamardashvili, N.Zh., and Antipin, I.S., *Sinteticheskie retseptory na osnove porfirinov i ikh kon'yugatov s kaliks4.arenami* (Synthetic Receptors Based on Porphyrins and Their Complexes with Calyx4.arenes), Moscow: Nauka, 2006.
3. Amemiya, S., Buhlmann, P., Umezawa, Y., Jagessar, R., and Burns, D.H., *Anal. Chem*., 1999, vol. 71, p. 1049.
4. Jagessar, R.C., Shang, M., Scheidt, W.R., and Burns, D.H., *J. Am. Chem. Soc*., 1998, vol. 120, p. 11684.
5. Burns, D.H., Caderon-Kawasaki, K., and Kularatne, S., *J. Org. Chem*., 2005, vol. 70, p. 2803.
6. Panda, K.P. and Lee, C.-H., *J. Org. Chem*., 2005, vol. 70, p. 31483.
7. Gale, P.A., Sessler, J.L., Kral, V., and Lynch, V., *J. Am. Chem. Soc*., 1996, vol. 118, p. 5140.
8. Sessler, J.L., Gale, P.A., and Genge, J.W., *Chem. Eur. J*., 1998, vol. 4, p. 1095.
9. Sessler, J.L., Anzenbacher, P., Jr., Miyaji, H., Jursikova, K., Bleasdale, E.R., and Gale, P., *Ind. Eng. Chem. Res*., 2000, vol. 39, p. 3471.
10. Sessler, J.L., Genge, J.W., Gale, P.A., and Kral, V., *ACS Symp., Ser*., 2000, no. 757, p. 238.
11. Gale, P.A., Anzenbacher, P.Jr., and Sessler, J.L., *Coord. Chem. Rev*., 2001, vol. 222, p. 57.
12. Gale, P.A., Twyman, L.J., Handlin, C.I., and Sessler, J.L., *Chem. Commun*., 1999, p. 1851.
13. Jagessar, R.C. and Burns, D.H., *Chem. Commun*., 1997, p. 1685.
14. Ivanova, Yu.B., Sheinin, V.B., and Mamardashvili, N.Zh., *Zh. Obshch. Khim*., 2007, vol. 77, no. 8, p. 1380.
15. Ushakova, L.I., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1988.
16. Lomova, T.N., Klyueva, M.E., Mamardashvili, G.M., and Mamardashvili, N.Zh., Abstarct of Papers, *Int. Conf. Fiziko-khimicheskie osnovy noveishikh tekhnologii XXI veka* (Physicochemical Fundamentals of the Newest Technologies of 21th Century), Moscow, 2005, p. 25.
17. Longo, F.R., Finarelly, M.G., and Kim, J.B., *J. Heterocycl. Chem*., 1969, vol. 6, p. 927.
18. Semeikin, A.S., Koifman, O.I., and Berezin, B.D., *Khim. Geterotsikl. Soed*., 1982, no.10, p. 1354.
19. Semeikin, A.S., Koifman, O.I., Berezin, B.D., and Syrbu S.A., *Khim. Geterotsikl. Soed*., 1983, no. 10, p. 1359.
20. Ivanova, Yu.B., Churakhina, Yu.I., and Mamardashvili, N.Zh., *Zh. Obshch. Khim*., 2008, vol. 78, no. 4, p. 691.