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Acid–Base Properties of Polyhalogenated Tetraphenylporphyrins

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Abstract—[2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) and [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) were synthesized by halogenation of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) with *N*-bromosuccinimide and *N*-chlorosuccinimide, respectively, in a mixture of chloroform with methanol. Treatment of the halogenated zinc porphyrins with trifluoroacetic acid in chloroform gave the corresponding free ligands. The isolated compounds were identified by electronic absorption, ^{1}H NMR, and mass spectra. The acid–base properties of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin, and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin were studied in acetonitrile at 298 K. Their acidity and basicity constants and concentration ranges of their ionized forms were determined.

Keywords: halogen-substituted tetraphenylporphyrins, bromination and chlorination, spectral and acid–base properties

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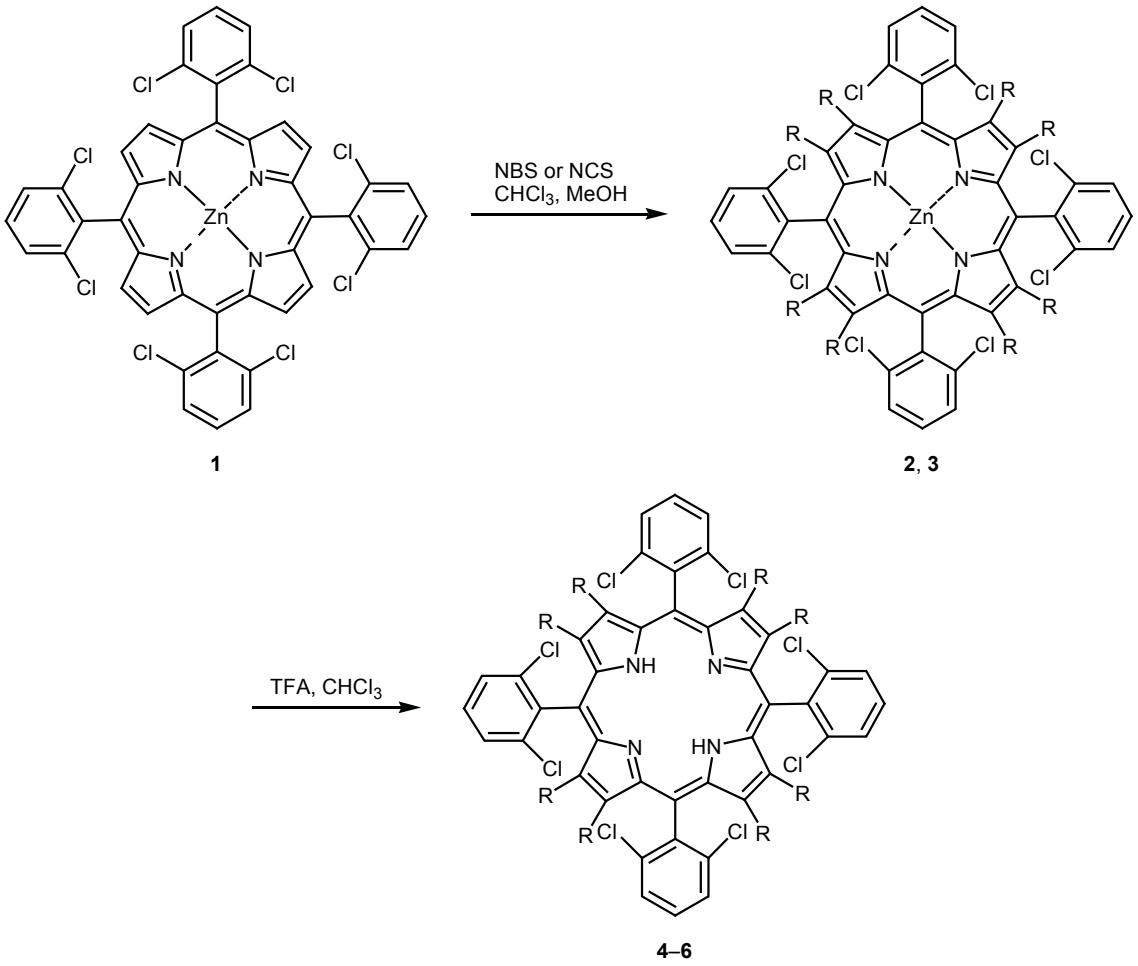
Porphyrins and their metal complexes proved to be efficient semiconductors, components of solar cells, photodynamic therapy agents, and sensors for various substrates [1]. Introduction of electron-withdrawing substituents into porphyrin molecules gives rise to materials with enhanced *n*-conductivity [2]. Halogen-substituted porphyrins are of particular interest among compounds containing electron-withdrawing substituents in the macrocycle. They can be used in the manufacture of new materials with nonlinear optical and catalytic properties [3].

As shown in [4], the bromination of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (**1**) with *N*-bromosuccinimide (NBS) in a boiling methanol suspension gave 45% of [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (**2**). Likewise, heating of **1** with *N*-chlorosuccinimide (NCS) in methanol for 11 h gave [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrinato]zinc(II) (**3**). The synthesis and acid–base properties of β-octabromo-substituted unsymmetrical nitrophenylporphyrins [5] and isomeric tetrachlorooctabromo- and tetrabromo-octachlorotetraphenylporphyrins [6] were reported previously.

With the goal of studying spectral and acid–base properties of polyhalogenated tetraphenylporphyrins, in this work we performed bromination and chlorination of zinc porphyrin **1** with NBS and NCS in a mixture of chloroform with methanol. The free ligands, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**4**) and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin (**5**), were synthesized by treatment of the corresponding zinc porphyrins with trifluoroacetic acid (Scheme 1). Initial complex **1** was prepared by two methods: (1) complexation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**6**) with zinc(II) acetate and (2) metal exchange of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]cadmium(II) (**7**) with zinc(II) chloride in boiling DMF [7]. It was found that the synthesis of **1** by the transmetalation method [8] takes much less time (by an order of magnitude) than the complexation method.

The mass spectrum of **1** (see Supplementary Materials) contained the molecular ion peak at *m*/*z* 952.9

Scheme 1.



1 **2**, **3** **4–6**

4, R = Br; **5**, R = Cl; **6**, R = H.

(calculated for $C_{44}H_{20}Cl_8N_4Zn$: 953.7). The ^1H NMR spectrum of **1** in $CDCl_3$ showed a singlet at δ 8.75 ppm from the pyrrole ring protons, a doublet at δ 7.80 ppm from protons in the *meta* positions of the phenyl rings, and a triplet at δ 7.70 ppm from protons in the *para* position (Fig. 1a).

By heating complex **1** with 20 equiv of in a boiling chloroform–methanol mixture (1:1) for 50 min we obtained β-octabromo-substituted zinc porphyrin **2**. The yield of **2** isolated by chromatography on basic alumina was 70%. In the ^1H NMR spectrum of **2** in $CDCl_3$ we observed a multiplet in the region δ 7.71–7.62 ppm from *meta*- and *para*-protons in the phenyl rings (Fig. 1b). The mass spectrum of **2** (see Supplementary Materials) showed the molecular ion peak at *m*/*z* 1584.7 (calculated for $C_{44}H_{12}Br_8Cl_8N_4Zn$: 1584.9).

The reaction of **1** with *N*-chlorosuccinimide at a molar ratio of 1:20 under similar conditions (reaction time 5 h) afforded [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]-zinc(II) (**3**). The reaction time was approximately two times shorter than that given in [4]. The ^1H NMR spectrum of **3** in $CDCl_3$ showed a multiplet at δ 7.73–7.65 ppm due to protons in the 2,6-dichlorophenyl rings, and its mass spectrum (see Supplementary Materials) contained the molecular ion peak at *m*/*z* 1231.04 (calculated for $C_{44}H_{12}Cl_{16}N_4Zn$: 1229.3).

Parameters of the electronic absorption spectra of halogen-substituted zinc and cadmium porphyrins are given in Table 1.

Treatment of a solution of **2** in chloroform with trifluoroacetic acid for 30 min gave doubly protonated form (H_4P^{2+}) of the free porphyrin ligand, which displayed absorption bands with their maxima at λ 696, 636, and 494 nm in the electronic spectrum ($CHCl_3$). The neutral ligand, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**4**) was obtained by treatment of H_4P^{2+} with aqueous

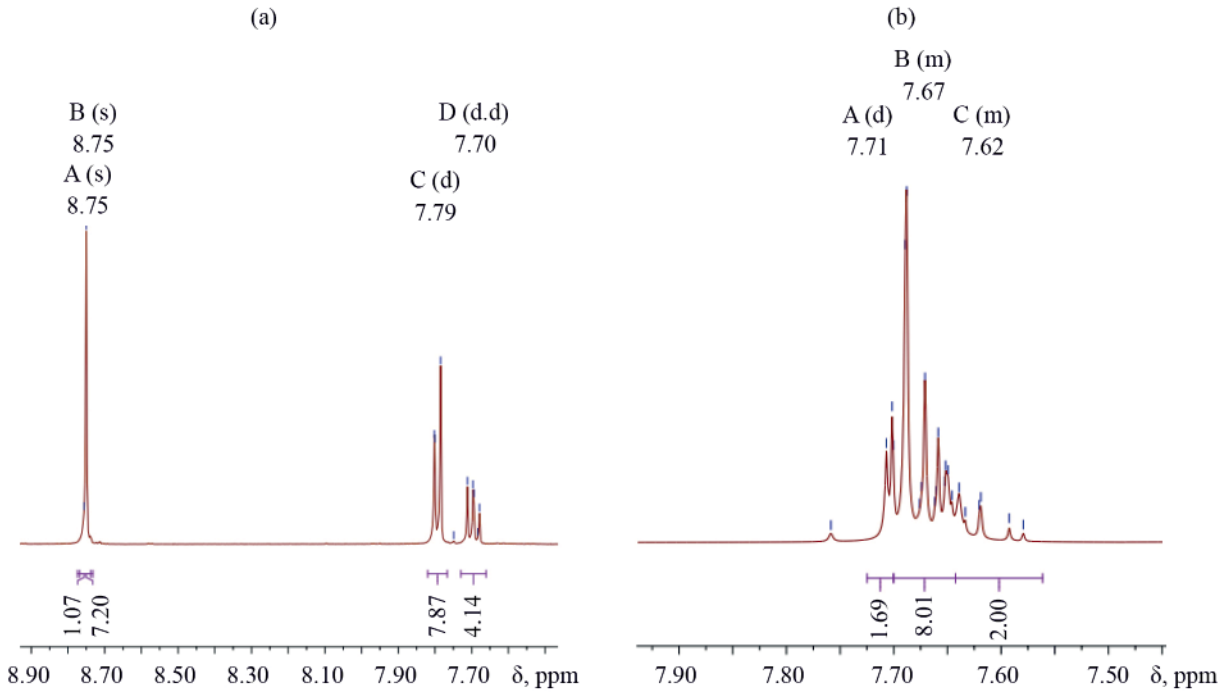


Fig. 1. ^{1}H NMR spectra of compounds (a) **1** and (b) **2** in $CDCl_3$.

sodium hydrogen carbonate. The electronic absorption spectrum of **4** in chloroform showed bands at λ_{max} 644, 559, and 463 nm. Its ^{1}H NMR spectrum ($CDCl_3$) contained signals of the *meta*- and *para*-protons in the region δ 7.71–7.67 ppm, and the NH protons resonated at δ –1.26 ppm The molecular ion of **4** was observed in the mass spectrum (Fig. 2) at *m*/*z* 1523.7 (calculated for $C_{44}H_{14}Br_8Cl_8N_4$: 1521.6). Likewise, treatment of complex **3** with trifluoroacetic acid in chloroform afforded 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**5**). Its mass spectrum is shown in Fig. 3.

The acid–base properties of porphyrins **4** and **5**, as well as of tetrakis(2,6-dichlorophenyl)porphyrin (**6**) and previously reported halogenated tetraphenylporphyrins [6], were studied by spectrophotometric titration [9] in the systems acetonitrile–perchloric acid and acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 298 K.

Porphyrins (H_2P) in organic solvents behave as amphoteric compounds capable of undergoing protonation in the presence of acids and deprotonation in the presence of bases at the inner nitrogen atoms (Scheme 2).

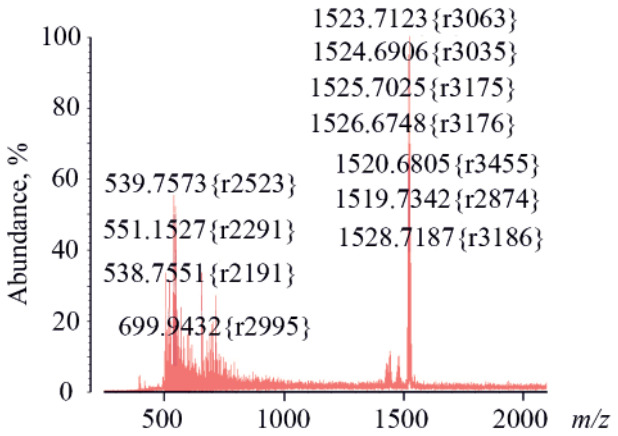


Fig. 2. Mass spectrum of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**4**).

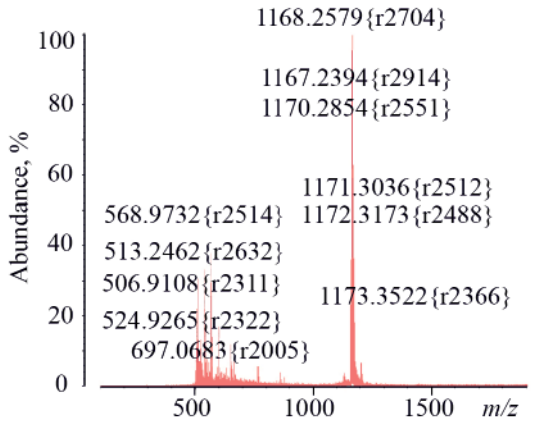


Fig. 3. Mass spectrum of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**5**).

Table 1. Electronic absorption spectra of zinc porphyrins **1**–**3** and cadmium porphyrin 7, λ, nm (log ε)

Compound no.	Solvent	Soret band	*Q* band
1	DMF	405 (4.66), 426 (5.50)	559 (4.35), 594 sh
1	$CHCl_3$	405 (4.64), 425 (5.53)	557 (4.32), 592 sh
2	DMF	368 (4.52), 474 (5.31)	612 (4.16), 660 (4.06)
2	$CHCl_3$	368 (4.64), 469 (5.45)	604 (4.35), 656 (4.16)
3	DMF	364 (4.66), 455 (5.40)	592 (4.34), 643 sh
3	$CHCl_3$	362 (4.63), 451 (5.45)	584 (4.38), 635 sh
7[a]	DMF	418 (4.77), 438 (5.53)	578 (4.34), 620 (3.98)

[a] Data of [7].

Scheme 2.

$$H_4P^{2+} \overset{K_{b1}}{\rightleftharpoons} H_3P^{+} + H^{+} \quad (1)$$

$$H_3P^{+} \overset{K_{b2}}{\rightleftharpoons} H_2P + H^{+} \quad (2)$$

$$H_2P \overset{K_{a1}}{\rightleftharpoons} HP^{-} + H^{+} \quad (3)$$

$$HP^{-} \overset{K_{a2}}{\rightleftharpoons} P^{2-} + H^{+} \quad (4)$$

Here, H_2P, HP^-, P^{2-}, H_3P^+, and H_4P^{2+} are, respectively, neutral, singly and doubly deprotonated, and singly and doubly protonated forms.

Analysis of the electronic absorption spectra showed that increase of the concentration of $HClO_4$ or 1,8-diazabicyclo[5.4.0]undec-7-ene gave rise to two families of spectral curves with their own sets of isosbestic points. Figures 4 and 5 (see also Supplementary Materials) show variations of the electronic absorption spectra of porphyrins **4**–**6** in acetonitrile upon titration with 0.01 M $HClO_4$ and of **4** and **5** upon titration with 0.01 M DBU.

The presence of two families of isosbestic points in the electronic absorption spectra is typical of stepwise protonation processes. However, the spectrophotometric titration curves plotted on the basis of the experimental data displayed no clearly defined steps, except for the titration curves obtained for compound **6**. This does not rule out stepwise process but implies close protonation constants in each step [10]. The observed variations of the electronic absorption spectra suggest that the ratio of the ionized forms in equilibria (1)–(4) does not change as the concentrations of two absorbing centers of the porphyrin molecule change.

The molar absorption factors of all porphyrin species involved in equilibria (1)–(4) were determined from the electronic spectra parameters and overall

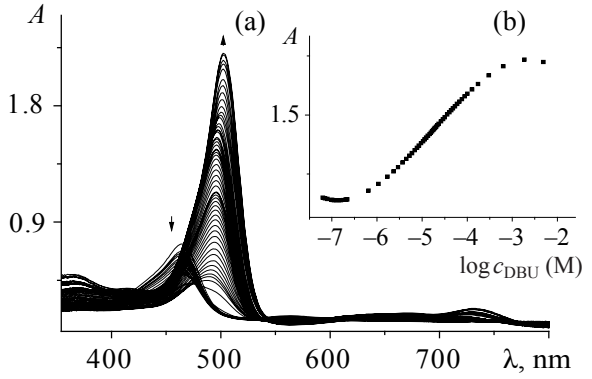


Fig. 4. (a) Variation of the electronic absorption spectrum and (b) spectrophotometric titration curve (λ 502 nm) of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**4**) in the system MeCN–DBU; c_4 = 5.41×10^{-6} M; c_{DBU} = 0–3.31×10^{-2} M; temperature 298 K.

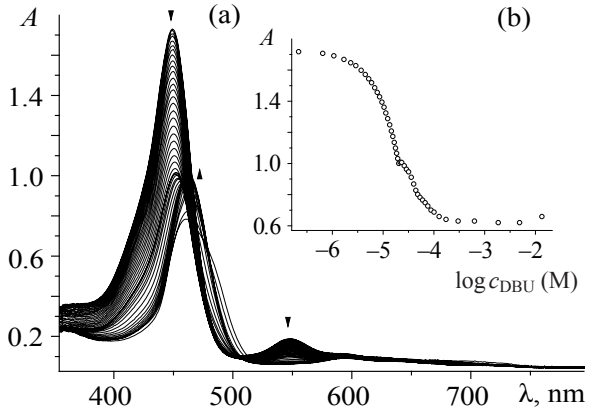


Fig. 5. (a) Variation of the electronic absorption spectrum and (b) spectrophotometric titration curve (λ 449 nm) of 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**5**) in the system MeCN–DBU; c_5 = 1.34×10^{-5} M; c_{DBU} = 0–3.31×10^{-2} M; temperature 298 K.

concentration of each porphyrin (Table 2). The overall protonation constant [equilibria (1) and (2)] was calculated by Eq. (5):

$$pK_{b1,2} = -\log K = \log I + pH, \quad (5)$$

where K is the overall protonation constant for the first and second steps, and I is the indicator ratio $[H_2P]/[H_4P^{2+}]$. Using the previous data of potentiometric study of the pH function of a glass electrode (ESL 43-07) in acetonitrile and temperature calibration of the electrode system ESL 43-07–silver chloride electrode [EVL 1 M3, filled with a solution of Et_4NCl and saturated at 293 K with respect to *m*-nitroaniline (pK_a 7.6)] [11–14], we obtained the dependence pH—$\log c_{HClO_4}$ [15] which was used to calculate protonation constants.

The acidity constants [equilibria (3) and (4)] were calculated by Eq. (6):

$$\log K_{a1,2} = \log I + n \log c_{an}, \quad (6)$$

where K_a is the overall acidity constant, c_{an} is the analytical concentration of DBU in solution, I is the indicator ratio P^{2-}/H_2P, and n is the number of released protons (n = 2); $pK_{a1,2} = -\log K_{a1,2}$. The error in the determination of the acidity and basicity constants did not exceed 3–5% (Table 2).

Analysis of the data presented in Table 2, in particular protonation and deprotonation constants of the porphyrins under study and published data [6, 15–18] on halogen-substituted tetraphenylporphyrins, showed that the presence of electron-withdrawing chlorine atoms both in the β-positions and in the *meso*-phenyl

Table 2. Electronic absorption spectra of halogenated porphyrins and their ionized forms and their acidity and basicity constants in acetonitrile; temperature 298 K

Porphyrin	Soret band, λ, nm, (log ε)	*Q* Band, λ, nm, (log ε)	$pK_{b1,2}$	$pK_{a1,2}$
H_2TPP	413 (5.02)	512 (3.56), 546 (3.12), 589 (2.92), 646 (2.96)	19.8 [15, 16]	–
H_3TPP^+	413 (5.01)	512 (3.69), 547 (3.42), 660 (3.47)		
H_4TPP^{2+}	441 (5.04)	661 (4.17)		
H_2Br_8TPP	471 (5.14)	646 (4.16), 765 (3.92)	16.60 [6, 17]	10.77 [6, 17]
$H_4Br_8TPP^{2+}$	490 (5.19)	741 (4.52)		
Br_8TPP^{2-}	497 (5.30)	734 (4.80)		
H_2(3,5-BrPh)P	417 (5.01)	513 (3.91), 546 (3.67), 588 (3.66), 649 (4.59)	17.50 [18]	
(3,5-BrPh)P^{2+}	442 (4,95)	492 sh (3.76), 596 sh (3.72), 650 (4.06)		
H_2(4-MeO-3- BrPh)P	418 (5.03)	515 (3.84), 552 (3.70), 593 (3.62), 651 (3.75)	18.09 [18]	
H_4(4-MeO-3-BrPh)P^{2+}	452 (4.90)	685 (4.21)		
H_2Br_8(2,6-ClPh)P (**4**)	463 (5.13)	560 (4.21), 646 (3.92), 603 sh, 713 (3.73)	15.63	9.9
Br_8(2,6-ClPh)P^{2+}	495 (5.08)	639 (4.02), 698 (4.06)		
Br_8(2,6-ClPh)P^{2-}	502 (4.97)	674 (3.90),729 (3.99)		
H_2Cl_8(2,6-ClPh)P (**5**)	449 (5.11)	548 (4.13), 590 sh, 636 (3.67), 706 (3.42)	13.25 (pK_{b1} 9.63, pK_{b2} 3.62)	8.82 (pK_{b1} 4.72, pK_{b2} 4.1)
HCl_8(2,6-ClPh)P^+	465 (4.89)	643 (4.01), 710 (3.85)		
Cl_8(2,6-ClPh)P^{2+}	483 (4.92)	629 (3.91), 688 (3.97)		
HCl_8(2,6-ClPh)P^-	454 (4.86)	548 (3.87), 591 (3.11)		
Cl_8(2,6-ClPh)P^{2-}	461 (4.77)	599 (3.84), 643 (3.82)		
H_2T(2,6-ClPh)P (**6**)	409 (5.42)	510 (4.20), 543 sh, 586 (3.78)	17.04	–
T(2,6-ClPh)P^{2+}	425 (5.41)	574 (4.29), 620 (4.09)		

rings is the main factor affecting the acid-base properties of porphyrins.

In this case, the stepwise character of protonation and deprotonation becomes more distinct, and separate steps corresponding to processes (1)–(4) can be observed for the "most acidic" porphyrin **5**, which is typical of a distorted porphyrin macrocycle. It is known that distortion of the porphyrin macrocycle is commonly achieved via introduction of substituents into the neighboring *meso* and β-positions and that the degree of distortion increases in parallel with the number and size of these substituents [15].

It should be noted that halogen-substituted porphyrins containing substituents only in phenyl rings showed no acidic properties due to weak effect of chlorine and bromine atoms on the electron density transfer from the functional substituent to the reaction center of porphyrin through the inductive mechanism. Peripheral halogenation in combination with β-halogenation of porphyrins endowed them with acidic properties. As noted above, introduction of chlorine atoms exerted the strongest effect on the acid–base properties of porphyrins.

The maximum effect was observed for β-octachloro derivative **5**, and the difference in the basicity constants of **5** and unsubstituted tetraphenylporphyrin (H_2TPP) was more than 6.5 orders of magnitude; analogous difference between **5** and 2,3,7,8,12,13,17,18-octabromotetraphenylporphyrin (H_2Br_8TPP) was more than 3 orders of magnitude. The corresponding differences for octabromoporphyrin **4** were more than four orders and one order of magnitude, respectively. Compound **6** showed a lower acidity due to specific features of the system acetonitrile–DBU (larger titrant molecule), and only compounds **4** and **5** displayed acidic properties. However, stepwise deprotonation was observed in the titration of **5** with DBU, so that we were able to calculate acidity constants for each deprotonation step. Leveling of the deprotonation processes in the case of H_2Br_8TPP and compound **4** is likely to be related to weaker effect of bromine atoms than chlorines. It is interesting that introduction of bromine atoms into the 3,5-positions of *meso*-phenyl rings changes the basicity by 0.5 order of magnitude relative to double *ortho*-chlorine substitution in **6**. Analogous pattern was observed for 3-bromo-4-methoxy derivative. The basicity of the latter is higher by 0.5 order of magnitude than that of H_2(3,5-BrPh)P and by an order of magnitude than that of **6**. These findings do not contradict classical views on substituent effects, but make it possible to vary acid–base properties of porphyrin molecules.

Thus, the results of our study have shown that chemical modification of a porphyrin macrocycle is an important tool for controlling their spectral and acid–base properties, which makes it possible to create systems with required physicochemical properties for definite purposes.

EXPERIMENTAL

Commercial 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (Porphychem), *N*-bromosuccinimide, *N*-chlorosuccinimide, trifluoroacetic acid (Acros), aluminum oxide, solvents, cadmium acetate, zinc acetate, and zinc chloride (Merck) were used without further purification. The electronic absorption spectra were recorded on a Varian Cary-100 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AV III-500 spectrometer at 500 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal standard. The mass spectra were obtained with a Shimadzu Biotech Axima Confidence MALDI TOF spectrometer using 2,5-dihydroxybenzoic acid as matrix. The acid–base properties were studied according to the procedure described in [9, 10]. Solutions of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) and perchloric acid with a concentration of 0.01 M were prepared from dry acetonitrile (Aldrich, water content 0.03%), DBU (Aldrich, purity 98%), and perchloric acid (analytical grade, 66.76% aqueous solution).

[5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato]cadmium(II) was synthesized according to the procedure described in [7].

[5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (1). *a*. A mixture of 0.04 g (0.0225 mmol) of porphyrin **6** and 0.082 g (0.450 mmol) of zinc(II) acetate in 30 mL of DMF was refluxed for 30 min. The mixture was cooled and poured into water, and the precipitate was filtered off, washed with water, dried, and purified by alumina chromatography using chloroform as eluent. Yield 0.035 g (0.0367 mmol, 82%).

b. A mixture of 0.04 g (0.040 mmol) of complex **7**, 0.054 g (0.40 mmol) of zinc(II) chloride, and 25 mL of DMF was refluxed for 2 min, and the product was isolated as described above in *a*. Yield 0.034 g (0.0357 mmol, 89%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.70 t (4H, *p*-H, J = 7.65 Hz), 7.79 d (8H, *m*-H, J = 7.6 Hz), 8.75 s (8H, β-H). Mass spectrum: m/z 952.9 (I_{rel} 98%) $[M]^+$. Calculated for $C_{44}H_{20}Cl_8N_4Zn$: 953.7.

[2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (2). Complex **1**, 0.02 g (0.021 mmol), was dissolved in a mixture of 5 mL of chloroform and 5 mL of methanol, 0.075 g (0.420 mmol, 20 equiv) of NBS was added, and the mixture was refluxed for 50 min. The mixture was cooled and evaporated, the residue was dissolved in methylene chloride, and the product was isolated by alumina chromatography using first CH_2Cl_2 and then $CHCl_3$ as eluent. Yield 0.023 g (0.0145 mmol, 70%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.71–7.62 m (H_{arom}). Mass spectrum: m/z 1584.7 (I_{rel} 98%) $[M - H]^+$. Calculated for $C_{44}H_{12}Br_8Cl_8N_4Zn$: 1584.9.

[2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (3). Complex **1**, 0.02 g (0.021 mmol), was dissolved in a mixture of 5 mL of chloroform and 5 mL of methanol, 0.028 g (0.21 mmol) of NCS was added, and the mixture was refluxed for 2 h. An additional portion of NCS, 0.028 g (0.210 mmol), was added, and the mixture was refluxed for 3 h more, cooled, and evaporated. The residue was treated as described above in the synthesis of **2**. Yield 0.017 g (0.0138 mmol, 66%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.73–7.65 m (H_{arom}). Mass spectrum: m/z 1231.04 (I_{rel} 97%) $[M + 2H]^+$. Calculated for $C_{44}H_{12}Cl_{16}N_4Zn$: 1229.3.

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (4). Trifluoroacetic acid, 1.5 mL, was added to a solution of 0.02 g (0.0126 mmol) of complex **2** in 7 mL of chloroform. The mixture was stirred at room temperature for 1 h and treated with water, the organic layer was separated, washed with water, a solution of sodium hydrogen carbonate, and water again, and dried over Na_2SO_4, and the product was isolated by alumina chromatography using chloroform as eluent. Yield 0.014 g (0.0092 mmol, 75%). Electronic absorption spectrum (CH_2Cl_2), λ, nm (logε): 713 (3.73), 645 (3.92), 604 sh, 558 (4.21), 462 (5.13), 369 (4.43). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: –1.26 s (NH), 7.71–7.67 m (12H, H_{arom}). Mass spectrum: m/z 1523.7 (I_{rel} 96%) $[M + 2H]^+$. Calculated for $C_{44}H_{14}Br_8Cl_8N_4$: 1521.6.

2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (5) was synthesized in a similar way from 0.02 g (0.0163 mmol) of complex **3** using 7 mL of chloroform and 2 mL of trifluoroacetic acid; reaction time 3 h. Yield 0.013 g (0.0112 mmol, 70%). Electronic absorption spectrum (CH_2Cl_2), λ, nm (logε): 700 (3.42), 631 (3.67), 585 sh, 543 (4.13), 446 (5.11). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH), δ, ppm: –1.03 s (4H, NH), 7.85–7.79 m (12H, H_{arom}). Mass spectrum: m/z 1168.3 (I_{rel} 96%) $[M + 2H]^+$. Calculated for $C_{44}H_{14}Cl_{16}N_4$: 1165.9.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIALS

Supplementary materials are available for this article at https://doi.org/10.1134/S1070428020060147 and are accessible for authorized users.

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