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Synthesis and Spectral and Coordination Properties of Perhalogenated Tetraphenylporphyrins

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Abstract—The reaction of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) with *N*-halosuccinimides in chloroform–methanol, chloroform–butan-1-ol, or DMF gave [2,3,7,8,12,13,17,18- octachloro(bromo)-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) which were treated with trifluoroacetic acid to obtain the corresponding free porphyrin ligands. The synthesized compounds and their dianions were studied by electronic absorption and ^{1}H NMR spectroscopy and mass spectrometry. The kinetic parameters of the complexation of these ligands with zinc in the systems acetonitrile–$Zn(OAc)_2$ and acetonitrile–$Zn(OAc)_2$–1,8-diazabicyclo[5.4.0]-undec-7-ene in the temperature range 298–318 K were determined.

Keywords: halogen-substituted tetraphenylporphyrins, zinc complexes, bromination, chlorination, spectral and coordination properties

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Porphyrins and their metal complexes have found application as components of solar cells, semiconductors, sensor systems, and photosensitizers for photodynamic therapy [1]. Metal porphyrins containing nitro groups and bromine atoms on the macroheterocycle have been found to be efficient in the treatment of malignant tumors [2]. Halogen-substituted porphyrins are also used in the manufacture of new materials with catalytic and nonlinear optical properties [3].

It is known that bromination of [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (**1**) with *N*-bromosuccinimide (NBS) in boiling methanol gives [2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (**2**) in yield 45% [4]. The reactin of **1** with *N*-chlorosuccinimide (NCS) in boiling methanol afforded [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]-zinc(II) (**3**). We previously synthesized unsymmetrical β-octabromo nitrophenylporphyrins [5] and isomeric tetrachlorooctabromo- and tetrabromoctachloro-tetraphenylporphyrins [6] and studied their acid–base properties.

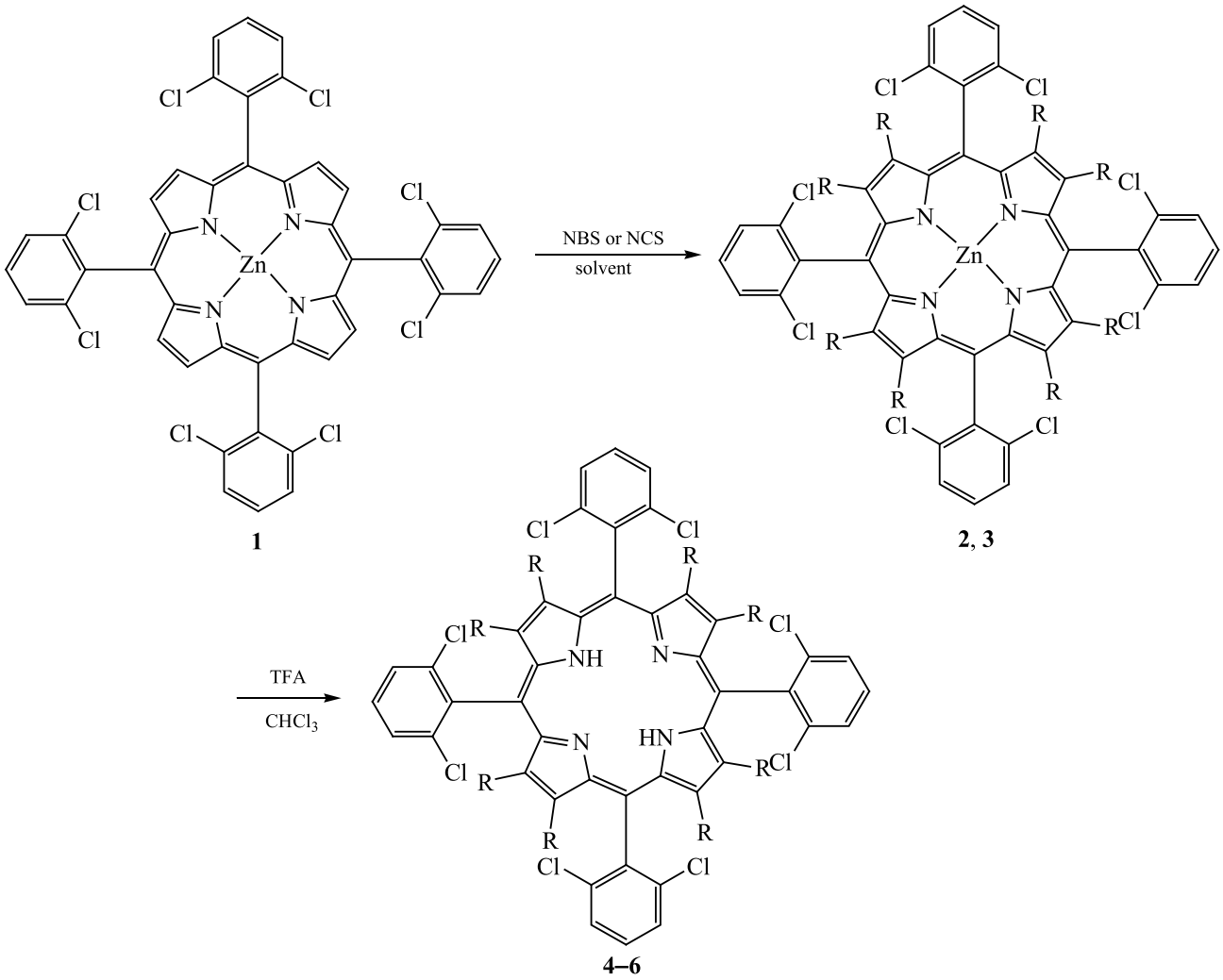
In this work, dichlorophenyl derivative **1** was brominated with NBS in DMF and chloroform–methanol and chlorinated with NCS in chloroform–methanol and chloroform–butan-1-ol. Treatment of the resulting halogenated zinc porphyrins with trifluoroacetic acid afforded 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**4**) and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)-porphyrin (**5**) (Scheme 1).

Initial zinc complex **1** was prepared by the complexation of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**6**) with zinc(II) acetate, as well as by 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 shown that the synthesis of complex **1** via transmetalation [8] using zinc(II) chloride instead of zinc(II) acetate takes an order of magnitude shorter time than that in the direct complexation method.

The mass spectrum of **1** showed the molecular ion peak at *m*/*z* 952.9 (calculated for $C_{44}H_{20}Cl_8N_4Zn$: 953.7). In the ^{1}H NMR spectrum of **1**, protons in the pyrrole rings resonated as a singlet at δ 8.75 ppm, and signals of protons of the benzene rings were observed at δ 7.80 (d, *m*-H) and 7.70 ppm (t, *p*-H).

By heating complex **1** and 20 equiv of NBS in chloroform–methanol (1 : 1) under reflux for 30 min we obtained octabromo derivative **2** (Scheme 1). The electronic absorption spectrum of a sample of the reaction

Scheme 1.



R = Br (**2**, **4**), Cl (**3**, **5**), H (**6**).

mixture dissolved in chloroform showed bands with their maxima at λ 470, 606, and 658 nm. The spectral pattern did not change when the reaction time was prolonged to 50 min. The yield of **2** isolated by column chromatography (basic alumina) was 73%.

The reaction of **1** with excess NBS in DMF at room temperature for 30 h also gave compound **2** with ~80% yield (Scheme 1). After completion of the reaction, the electronic absorption spectrum of a sample of the reaction mixture in DMF showed bands at λ_{max} 474, 612, and 663 nm. The ^{1}H NMR spectrum displayed a multiplet at δ 7.71–7.62 ppm for aromatic protons. The mass spectrum of **2** contained the molecular ion peak at *m*/*z* 1584.7 (calculated for $C_{44}H_{12}Br_8Cl_8N_4Zn$: 1584.9).

Complex **1** reacted with 20 equiv of NCS in chloroform–methanol under reflux for 5 h to produce [2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (**3**) (Scheme 1). The reaction time was almost twice as short as that reported in [4]. When chloroform–butan-1-ol was used as solvent, the reaction was complete in 1 h. Absorption maxima at λ 451, 584, and 635 nm were observed in the electronic spectrum of a sample of the reaction mixture. The ^{1}H NMR spectrum of zinc porphyrin **3** showed an aromatic multiplet at δ 7.73–7.65 ppm. The mass spectrum of **3** contained the molecular ion peak at *m*/*z* 1231.04 (calculated for $C_{44}H_{12}Cl_{16}N_4Zn$: 1229.3). Characteristics of the electronic absorption spectra of halogenated zinc porphyrin complexes **1**–**3** and cadmium porphyrin **7** are given in Table 1.

Table 1. Electronic absorption spectra of halogen-substituted tetraphenylporpyrin complexes **1**–**3** and **7**

Compound	Solvent	λ, nm (log ε)	
		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].

Treatment of a solution of **2** in chloroform with trifluoroacetic acid (TFA) for 30 min led to the formation of doubly protonated metal-free octabromoporphyrin (H_4OBP^{2+}) (Scheme 1). Its electronic absorption spectrum in chloroform showed bands at λ_{max} 494, 636, and 696 nm. The free 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 the doubly protonated form with a solution of $NaHCO_3$. The electronic absorption spectrum of **4** in chloroform displayed bands with their maxima at λ 463, 559, and 644 nm. In the ^1H NMR spectrum of **4**, aromatic protons resonated at δ 7.71–7.67 ppm, and the NH protons resonated at δ –1.26 ppm. The mass spectrum of **4** showed the molecular ion peak at *m*/*z* 1523.7 (calculated for $C_{44}H_{14}Br_8Cl_8N_4$: 1521.6).

Likewise, treatment of zinc complex **3** with trifluoroacetic acid afforded 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (**5**) (Scheme 1) which showed the molecular ion at *m*/*z* 1168.3 in the mass spectrum (calculated for $C_{44}H_{14}Cl_{16}N_4$: 1165.9).

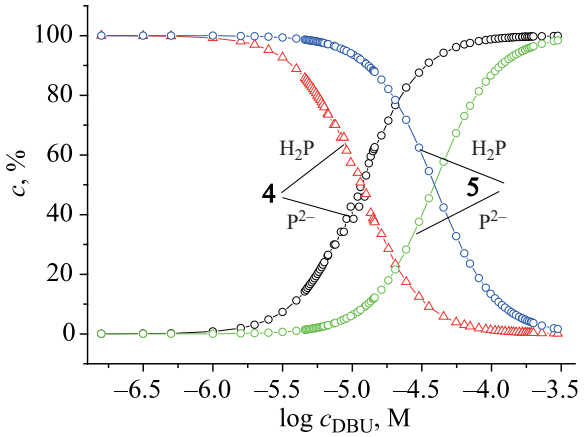


Fig. 1. Concentrations of the neutral (H_2P) and doubly deprotonated forms (P^{2-}) of porphyrins **4** and **5** in the system MeCN–DBU versus logarithm of the DBU concentration.

The spectral and complexing properties of porphyrins **4** and **5** in comparison to tetrakis(2,6-dichlorophenyl)-porphyrin (**6**) were studied by spectrophotometric titration [9, 10] in the systems acetonitrile–$Zn(OAc)_2$ and acetonitrile–$Zn(OAc)_2$–1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the temperature range 298–318 K.

The nature and position of substituents on the macrocycle largely affect acid–base properties of porphyrins. Comparison of the deprotonation constants of porphyrins **4** and **5** [equilibria (1) and (2)] in the system acetonitrile–DBU showed that the overall acidity of chlorinated porphyrin **5** is higher by an order of magnitude than the acidity of bromine-containing analog **4**; furthermore, the deprotonation steps are visually distinguishable [11]. Compound **6** did not undergo deprotonation in the same system. However, all porphyrins **4**–**6** were protonated in acetonitrile–$HClO_4$, and their basicity decreased in the series **6** > **4** > **5** [11].

$$H_2P \underset{}{\overset{k_{a1}}{\rightleftharpoons}} HP^- + H^+, \quad (1)$$

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

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

The complexation of porphyrins **4** and **5** in the systems MeCN–$Zn(OAc)_2$ and MeCN–$Zn(OAc)_2$–DBU follows Eqs. (3) and (4) [9]:

$$H_2P + [Zn(OAc)_2(Solv)_{n-2}] \rightarrow ZnP + 2HOAc - (n-2)Solv, \quad (3)$$

$$P^{2-} + [Zn(OAc)_2(Solv)_{n-2}] \rightarrow ZnP + 2OAc^- - (n-2)Solv. \quad (4)$$

where H_2P and P^{2-} are, respectively, neutral and double deprotonated forms of porphyrins **4** and **5**; ^-OAc is anionic ligand (acetate ion); Solv is a solvent molecule; and *n* is the metal coordination number. With account taken of deprotonation equilibria (1) and (2), the acid dissociation constants of compounds **4** and **5** in the

Table 2. Electronic absorption spectra of halogen-substituted porphyrins, their dianions, and zinc complexes in the systems MeCN–$Zn(OAc)_2$ and MeCN–$Zn(OAc)_2$–DBU

Porphyrin species	λ, nm (log ε)		$pK_{b1,2}$	$pK_{a1,2}$
	Soret band	*Q* band		
H_2Br_8TPP [12]	471 (5.14)	646 (4.16), 765 (3.92)	16.60	10.77
Br_8TPP^{2-}	497 (5.30)	734 (4.80)		
H_2Br_8(2,6-ClPh)P (**4**) [11]	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-}	502 (4.97)	674 (3.90), 729 (3.99)		
$ZnBr_8$(2,6-ClPh)P	367 (4.46), 467 (5.17)	603 (4.13), 667 (3.79)		
$Zn^{2+}Br_8$(2,6-ClPh)P^{2-}	421 sh (4.49), 480 (5.08)	620 (4.07), 674 (3.93)		
H_2Cl_8(2,6-ClPh)P (**5**) [11]	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
Cl_8(2,6-ClPh)P^{2-}	461 (4.77)	599 (3.84), 643 (3.82)		
$ZnCl_8$(2,6-ClPh)P	362 sh (4.52), 452 (5.25)	428 sh (5.09), 547 (4.22), 592 (4.13)		
$Zn^{2+}Cl_8$(2,6-ClPh)P	361 (4.21), 457 (4.88)	593 (3.83), 648 (3.51)		
H_2T(2,6-ClPh)P (**6**)	409 (5.42)	510 (4.20), 543 sh, 586 (3.78)	17.04	–

Table 3. Kinetic parameters for the complexation of halogen-substituted porphyrins with zinc in the systems MeCN–$Zn(OAc)_2$ and MeCN–$Zn(OAc)_2$–DBU

Porphyrin	$[Zn(OAc)_2]\times10^3$, M	$k_v^{298}\times10^3$,[a] L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
H_2Br_8TPP [15]	4.50	69±1	56±1	–88±2
H_2Br_8(2,6-ClPh)P (**4**)	1.84	50±1	68±1	–48±2
Br_8(2,6-ClPh)P^{2-}	1.84	98±1	38±1	–141±2
H_2Cl_8(2,6-ClPh)P (**5**)	1.84	40±1	80±2	–11±2
Cl_8(2,6-ClPh)P^{2-}	1.84	83±1	45±1	–122±2

[a] Determined with an accuracy of 3–5%.

system acetonitrile–DBU determined previously [11], and material balance equation (5) (proportionality of the optical density of a solute and its concentration according to the Beer–Lambert–Bouguer law), we determined the concentrations of the neutral and doubly deprotonated forms of porphyrins **4** and **5**, depending on the DBU concentration (Fig. 1).

$$c = c_{H_2P} + c_{P_2}. \quad (5)$$

We thus were able to determine the DBU concentration corresponding to complete deprotonation of ligands **4** and **5**. Zinc complexes of porphyrins **4** and **5** were synthesized in the system MeCN–$Zn(OAc)_2$–DBU where the ligands were present as dianions.

Analysis of the electronic absorption spectra and rates of formation of complexes from the neutral porphyrins **4** and **5** and their dianions [reactions (3) and (4)] revealed distinct isosbestic points (Fig. 2) and first reaction order in the ligand. This followed from the linear dependences of $\ln(c^0_{H_2P}/c_{H_2P})$ versus time in the temperature range 298–318 K. Tables 2 and 3 contains the electronic absorption spectra parameters of porphyrins **4** and **5** and their zinc complexes and kinetic parameters of reactions (3) and (4) in the systems MeCN–$Zn(OAc)_2$ and MeCN–$Zn(OAc)_2$–DBU. The rate constants k_v^{298} and activation parameters E_a and $\Delta S^{\neq}$ for reactions (3) and (4) were calculated according to the known procedure [9]. Our attempts to obtain zinc complex directly from

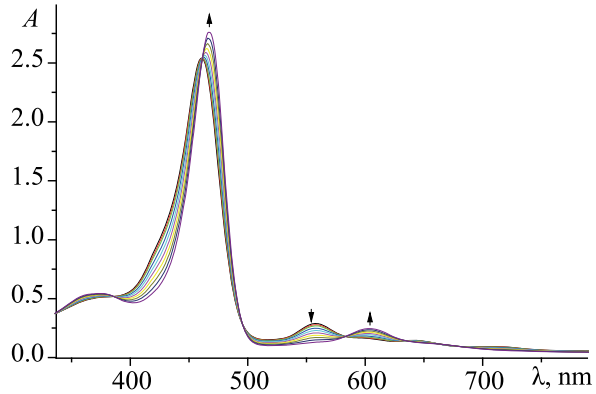


Fig. 2. Electronic absorption spectra of porphyrin **4** in the system $Zn(OAc)_2$–acetonitrile in the temperature range 298–318 K; [**4**] = 1.88×10^{-5} M, $[Zn(OAc)_2] = 1.84\times10^{-3}$ M.

neutral ligand **6** in acetonitrile were unsuccessful even at elevated temperature. As we already noted, porphyrin **6** does not undergo deprotonation in acetonitrile–DBU. Anionic forms of porphyrins are better solvated, which favors stronger polarization of the ligand molecule [9]. As seen from Table 3, the complexation rate constants for porphyrins **4** and **5** in MeCN–$Zn(OAc)_2$–DBU are almost twice as high as those in the system MeCN–$Zn(OAc)_2$.

The rate of formation of zinc complexes with porphyrins **4** and **5** depends on the acidity of the latter. Introduction of halogen atoms into the *meso*-phenyl rings and β-pyrrole positions is likely to increase the NH acidity and favor deprotonation due to stabilization of the resulting anions. Correspondingly, more acidic ligand **5** with a higher deprotonation constant reacts at a lower rate and is characterized by a higher energy of activation (in comparison to **4**; Table 3). The same conclusion followed from analysis of reported data for 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (H_2Br_8TPP) [12] and comparison with those for compounds **4** and **5** in the system MeCN–$Zn(OAc)_2$ (Table 3). Presumably, higher strength of the N→M bond in the transition state for more basic ligand **4** is responsible for the higher rate of its complexation with zinc. Deprotonation of ligands **4** and **5** reduces the difference in the rates of their complexation with zinc, which may be due to higher symmetry of their dianions and lower energy consumption for dissociation of the N–H bond. It should be noted that the electronic absorption spectra of zinc complexes **2** and **3** in Me–$Zn(OAc)_2$ and MeCN–$Zn(OAc)_2$–DBU showed a red shift of the absorption maxima relative to those of free ligands **4** and **5**. In particular, the red shift of the Soret band for porphyrin **4** was 27 nm, and the corresponding shift for ligand **5** was as small as 5 nm in MeCN–$Zn(OAc)_2$–DBU relative to Me–$Zn(OAc)_2$. This may be rationalized by extra coordination of DBU to the zinc complex, as was described in detail in [13–15]. Increase of the complexation rate constant implies reduction of the energy of activation due to higher polarity of the complex than the polarity of the initial ligand. This assumption is also confirmed by the negative value of the entropy of activation.

In summary, we have synthesized and identified [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). Treatment of these complexes with trifluoroacetic acid gave the corresponding free ligands, and spectral properties of the latter and their dianions in acetonitrile have been studied. Kinetic parameters for complexation the ligands with zinc in the systems acetonitrile–$Zn(OAc)_2$ and acetonitrile–$Zn(OAc)_2$–DBU at 298–318 K have been determined. The obtained results may be useful for the design of new materials with enhanced *n*-type conductivity. Chemical modification of porphyrin macrocycle is an important tool for controlling spectral and coordination properties of porphyrins, which provides the possibility of obtaining systems with desired physicochemical characteristics.

EXPERIMENTAL

Commercial acetonitrile (water content 0.03%, Aldrich), DBU (Aldrich, 98%), 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (Porphychem), *N*-bromosuccinimide, *N*-chlorosuccinimid, trifluoroacetic acid (Acros), alumina, solvents, cadmium(II) acetate, zinc(II) acetate, and zinc(II) chloride (Merck) were used without further purification. [5,10,15,20-Tetrakis(2,6-dichlorophenyl)porphyrinato]cadmium(II) was synthesized according to the procedure described in [7].

The electronic absorption spectra were measured on a Varian Cary-100 spectrophotometer. The ^{1}H NMR spectra were recorded on a Bruker AV III-500 spectrometer at 500 MHz using tetramethylsilane as internal standard. The mass spectra (MALDI TOF) were run on a Shimadzu Biotech Axima Confidence mass spectrometer using 2,5-dihydroxybenzoic acid as matrix. The complexations reactions were studied according to the reported procedures [9, 10].

[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 $Zn(OAc)_2$ 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%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.75 s (8H, CH=), 7.79 d (8H, *m*-H, J = 7.6 Hz), 7.70 t (4H, *p*-H, J = 7.65 Hz). Mass spectrum: m/z 952.9 (I_{rel} 98%) $[M]^+$. Calculated for $C_{44}H_{20}Cl_8N_4Zn$: 953.7.

b. Complex **1** was synthesized in a similar way from 0.04 g (0.040 mmol) of complex **7** and 0.054 g (0.40 mmol) of $ZnCl_2$ in 25 mL of DMF; reaction time 2 min. Yield 0.034 g (0.0357 mmol, 89%).

[2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II)

(2). *a*. *N*-Bromosuccinimide, 0.038 g (0.210 mmol), was added to a solution of 0.02 g (0.0210 mmol) of complex **1** in a mixture of 5 mL of chloroform and 5 mL of methanol. The mixture was refluxed for 15 min, an additional 0.038 g (0.210 mmol) of NBS was added, and the mixture was refluxed for 15 min more, cooled, and evaporated. The residue was dissolved in methylene chloride, and the product was isolated by alumina chromatography using first methylene chloride and then chloroform as eluent. Yield 0.024 g (0.0151 mmol, 73%). ^{1}H NMR spectrum ($CDCl_3$): δ 7.71–7.62 ppm, 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.

b. *N*-Bromosuccinimide, 0.075 g (0.420 mmol), was added to a solution of 0.02 g (0.0210 mmol) of complex **1** in 5 mL DMF. The mixture was kept at room temperature for 24 h, an additional 0.075 g (0.420 mmol) of NBS was added, and the mixture was kept for 6 h. The mixture was then diluted with water and treated with sodium chloride, and the precipitate was filtered off, washed with water, and dried. Yield 0.026 g (0.0164 mmol, 80%).

[2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato]zinc(II) (3). *a*. *N*-Chlorosuccinimide, 0.028 g (0.21 mmol), was added to a solution of 0.02 g (0.021 mmol) of complex **1** in a mixture of 5 mL of chloroform and 5 mL of methanol. The mixture was refluxed for 2 h, an additional 0.028 g (0.210 mmol) of NCS was added, and the mixture was refluxed for 3 h more, cooled, and evaporated. The residue was dissolved in methylene chloride, and the product was isolated by alumina chromatography using first methylene chloride and then chloroform as eluent. Yield 0.017 g (0.0138 mmol, 66%). ^{1}H NMR spectrum ($CDCl_3$): δ 7.73–7.65 ppm, 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.

b. *N*-Chlorosuccinimide, 0.028 g (0.21 mmol), was added to a solution of 0.02 g (0.021 mmol) of complex **1** in a mixture of 5 mL of chloroform and 5 mL of butan-1-ol. The mixture was refluxed for 30 min, an additional 0.028 g (0.210 mmol) of NCS was added, and the mixture was refluxed for 30 min more, cooled, and evaporated. The residue was dissolved in methylene chloride, and the product was isolated by alumina chromatography using first methylene chloride and then chloroform as eluent. Yield 0.018 g (0.0146 mmol, 70%).

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin (4). Trifluoroacetic acid, 2 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 20 min and treated with water, and the organic layer was separated, washed with water, a solution of sodium hydrogen carbonate, and water again and dried. The solvent was removed, and the residue was purified by alumina chromatography using chloroform as eluent. Yield 0.014 g (0.0092 mmol, 75%). Electronic absorption spectrum (CH_2Cl_2), λ, nm (logε): 369 (4.43), 462 (5.13), 558 (4.21), 604 sh, 645 (3.92), 713 (3.73). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.71–7.67 m (12H, H_{arom}), –1.26 s (2H, NH). 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 3 mL of trifluoroacetic acid; reaction time 1.5 h. Yield 0.013 g (0.0112 mmol, 70%). Electronic absorption spectrum (CH_2Cl_2), λ, nm (logε): 446 (5.11), 543 (4.13), 585 sh, 631 (3.67), 700 (3.42). ^{1}H NMR spectrum ($CDCl_3$–CF_3COOH), δ, ppm: 7.85–7.79 m (12H, H_{arom}), –1.03 s (4H, NH). 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 the absence of conflict of interest.

REFERENCES

1. Li, L.-L. and Diau, E.W.-G., *Chem. Soc. Rev*., 2013, vol. 42, no. 1, p. 291. https://doi.org/10.1039/C2CS35257E
2. Stuzhin, P.A., Goryachev, M.Yu., Ivanova, S.S., Nazarova, A., Pimkov, I., and Koifman, O.I., *J. Porphyrins Phthalocyanines*, 2013, vol. 17, p. 905. https://doi.org/10.1142/S1088424613500892
3. Chumakov, D.E., Khoroshutin, A.V., Anisimov, A.V., and

Kobrakov, K.I., *Chem. Heterocycl. Compd*., 2009, vol. 45, no. 3, p. 259. https://doi.org/10.1007/s10593-009-0277-8
4. Chorghade, M.S., Dolphin, D., Dupré, D., Hill, D.R., Lee, E.C., and Wijesekera, T.P., *Synthesis*, 1996, vol. 11, p. 1320. https://doi.org/10.1055/s-1996-4401
5. Ivanova, Yu.B., Chizhova, N.V., and Mamardashvili, N.Zh., *Russ. J. Org. Chem*., 2019, vol. 55, no. 10, p. 1554. https://doi.org/10.1134/S1070428019100142
6. Mamardashvili, N.Zh., Ivanova, Yu.B., and Chizhova, N.V., *Makrogeterotsikly*, 2019, vol. 12, no. 1, p. 22. https://doi.org/10.6060/mhc180900m
7. Chizhova, N.V., Mamardashvili, G.M., Dmitrieva, O.G., Mamardashvili, N.Zh., and Koifman, O.I., *Makrogeterotsikly*, 2019, vol. 12, no. 4, p. 364. https://doi.org/10.6060/mhc190556m
8. Hambright, P., *Coord. Chem. Rev*., 1971, vol. 6, nos. 2–3, p. 247. https://doi.org/10.1016/S0010-8545(00)80041-7
9. Berezin, B.D., *Coordination Compounds of Porphyrins and Phthalocyanines*, Chechester: Wiley, 1981.
10. Ivanova, Yu.B., Pukhovskaya, S.G., Semeikin, A.S., and Syrbu, S.A., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 7, p. 1406. https://doi.org/10.1134/S1070363213070177
11. Ivanova, Yu.B., Chizhova, N.V., Shumilova, I.A., Rusanov, A.I., and Mamardashvili, N.Zh., *Russ. J. Org. Chem*., 2020, vol. 56, no. 6, p. 1054. https://doi.org/10.1134/S1070428020060147
12. Pukhovskaya, S.G., Ivanova, Yu.B., Semeikin, A.S., Syrbu, S.A., and Kruk, N.N., *Ross. Khim. Zh*., 2017, vol. 61, no. 1, p. 56.
13. Ivanova, Yu.B., Chizhova, N.V., and Kruk, N.N., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 3, p. 558. https://doi.org/10.1134/S1070363213030250
14. Ivanova, Yu.B., Semeykin, A.S., Pukhovskaya, S.G., and Mamardashvili, N.Zh., *Russ. J. Org. Chem*, 2019, vol. 55, no. 12, p. 1878. https://doi.org/10.1134/S107042801912011X
15. Lebedeva, N.Sh., Pavlycheva, N.A., and V'yugin, A.I., *Russ. J. Org. Chem*., 2004, vol. 40, no. 12, p. 1727. https://doi.org/10.1007/s11178-005-0090-5