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Synthesis, Spectral, and Coordination Properties of Halogen-Substituted Tetraarylporphyrins

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Abstract—2,3,7,8,12,13,17,18-Ocatbromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin have been synthesized. The obtained compounds have been identified by electronic absorption and ^{1}H NMR spectroscopy as well as mass spectrometry. The complex-forming properties of the synthesized porphyrins in the zinc acetate (II)–acetonitrile system at 278–298 K have been studied. Kinetic parameters of the formation of the corresponding zinc complexes in acetonitrile have been determined.

Keywords: 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin, 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin, halogen-substituted tetraarylporphyrins, Co(II) complexes, Zn(II) complexes

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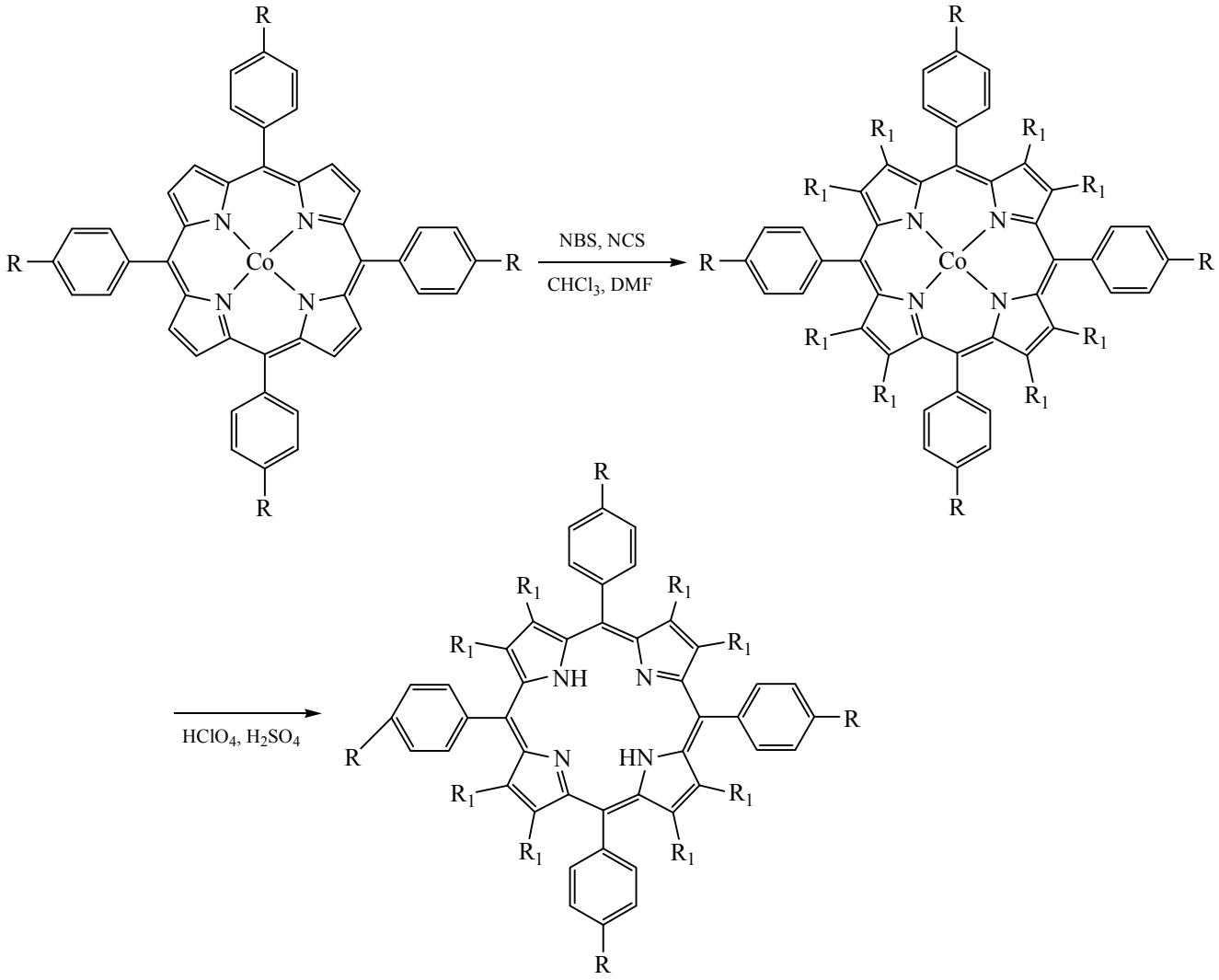
Porphyrins play significant role in natural biochemical and biophysical processes [1–6]. The use of porphyrins in specific practical applications demands certain molecular structure modification aiming to selectively tune the property required for the application. Synthetic porphyrins containing chlorine and bromine atoms in the β-positions are of particular interest, since the induced geometry distortion of the macrocycle allows otherwise impossible chemical modifications. Porphyrins exhibit biological and catalytical functions being a part on metallic complexes [7]. Porphyrin complexes with transition metals are of great interest. In particular, cobalt porphyrinates are efficient catalysts of SO_2 and different hydrocarbons oxidation [8]. The ability of polyhalogenated metalloporphyrins to exhibit catalytic activity in oxygenation reactions is of great interest [9, 10]. In view of the above, this study aimed at the synthesis of porphyrins with halogen substituents in the pyrrole and phenol cycles and investigation of the influence of chlorine and bromine atoms in tetraphenylporphyrin on the complex-forming properties of molecules.

We studied the bromination reaction of Co(II) 5,10,15,20-tetra-(4-chlorophenyl)porphyrinate **1** with *N*-bromosuccinimide (NBS) in a chloroform–DMF mixture and chlorination of Co(II) 5,10,15,20-tetra-(4-bromophenyl)porphyrinate **2** with excess of *N*-chlorosuccinimide (NCS) in a chloroform–DMF mixture, as well as the coordination properties of the halogenated porphyrins with zinc(II) acetate in acetonitrile at 278–298 K (Scheme 1).

Bromination of Co(II)-porphyrin **1** with NBS (molar ratio 1 : 25) in a chloroform–DMF (4 : 1) mixture at room temperature during 6 h led to the formation of a mixture of Co(II) and Co(III) porphyrins complexes. The signals with λ_{max} = 634, 584, and 455 nm corresponding to Co(II) and Co(III) porphyrinates were present in the electronic absorption spectrum of the product. The signals of the starting complex with λ_{max} = 529 and 410 nm are absent. ^{1}H NMR spectrum (in $CDCl_3$) of the cobalt-porphyrins isolated from reaction mixture showed the signals of *ortho*- and *meta*-protons at 8.90–7.80 ppm ($3d^6$

Scheme 1.



R^1 = Cl, R^2 = Br (**3**, **5**); R^1 = Br, R^2 = Cl (**4**, **6**).

configuration) and the signals at 15.10–10.08 ppm ($3d^7$ configuration). Purification of the obtained substance by chromatography on alumina gave Co(II) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrinate **3**. The electronic absorption spectrum of the obtained substance in chloroform contained the bands with λ_{max} = 564 and 449 nm. ^{1}H NMR spectrum of Co(II) porphyrinate **3** in $CDCl_3$ contained the signals of *ortho*- and *meta*-protons at 15.10 and 10.08 ppm. The spectra of paramagnetic Co(II) octaethylporphyrinates have been discussed in detail elsewhere [11].

Chlorination of bromine-substituted cobalt-porphyrin **2** with 130-fold excess of *N*-chlorosuccinimide in the boiling chloroform-DMF mixture during 10 min also led to the formation of a mixture of Co(II) and Co(III) β-octachloro-substituted porphyrins. Purification of the mixture by chromatography on alumina gave Co(II) 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromphenyl)porphyrinate **4**, and only the latest fractions contained the mixture of cobalt-porphyrins. The electronic absorption spectrum of compound **4** in chloroform contained the bands with λ_{max} = 554 and 438 nm (for the latest fraction: λ_{max} = 624, 558, and 445 nm). ^{1}H NMR spectrum of compound **4** in $CDCl_3$ showed broadened signals of *ortho*- and *meta*-protons at 14.30 and 10.14 ppm.

Treatment of a solution of complex **3** in a mixture of perchloric and sulfuric acids (4 : 3) during 2 h afforded the double-protonated form (H_4OBP^{2+}) of the

free base. The bands with maximums at 746, 499, and 434 nm were observed in the electronic absorption spectrum of H_4OBP^{2+} in chloroform. After removal of the inorganic acids and the treatment of a solution of the protonated form H_4OBP^{2+} with a solution of ammonia, 2,3,7,8,12,13,17,18-octabomo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin **5** was obtained. ^{1}H NMR spectrum of the brominated porphyrin **5** in $CDCl_3$ showed the signals of *ortho*- and *meta*-protons at 8.14 and 7.78 ppm.

Treatment of complex **4** with a mixture of perchloric and sulfuric acids (4 : 3) during 5 h did not lead to, complete demetalation of the cobalt porphyrinate. Repeated treatment the obtained solution of free base and cobalt complex in chloroform with the same acids mixture during 3 h gave the double-protonated form (H_4OCP^{2+}) of the chlorinated porphyrin. The electronic absorption spectrum of H_4OCP^{2+} in chloroform contained the bands with maximums at 734, 489, and 422 nm. After removal of the acids and the treatment of the protonated form H_4OCP^{2+} with ammonia solution, 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin **6** was obtained. ^{1}H NMR spectrum of the chlorinated porphyrin **6** in $CDCl_3$ showed the signals of *ortho*- and *meta*-protons at 8.04 and 7.92 ppm.

Parameters of electronic absorption spectra of Co(II) tetraphenylporphyrinates are given in Table 1. Halogenation of the β-positions of cobalt-porphyrins led to bathochromic shift of the absorption bands in comparison with unsubstituted complexes **1** and **2**. The signals corresponding to molecular ions of compounds **1-6** were observed in the mass spectra of halogen-substituted Co(II)-porphyrins and their free bases.

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin could be protonated and deprotonated at the trans-annular nitrogen atoms in the presence of acids and bases dissolved in acetonitrile [12]. The acid-base properties of porphyrins **5** and **6** have been earlier studied [12] in the acetonitrile–$HClO_4$ and acetonitrile–1,8-diasobicyclo[5.4.0]-undec-7-ene systems by means of spectrophotometric titration [13] at 298 K. Results of this study (in particular, analysis of the values of porphyrins protonation and deprotonation constants) showed that the introduction of bromine atom at the β-positions of tetraphenylporphyrin led to the change in π-electron density in the macrocycle so that the basic properties were weakened and, correspondingly, the acidic properties were enhanced in comparison with the unsubstituted tetraphenylporphyrin. The compounds acidity was strengthened in the H_2Br_8TPP < $H_2Br_8T(4\text{-}ClPh)P$ < $H_2Cl_8T(4\text{-}BrPh)P$ series (Table 2).

Table 1. Electronic absorption spectra data for Co(II) tetraphenylporphyrinates **1**–**4**

Complex	Solvent	λ, nm, (log ε)	
		band I	Soret band
1	$CHCl_3$	529 (4.23)	410 (5.32)
2	$CHCl_3$	528 (4.50)	411 (5.57)
3	$CHCl_3$	564 (4.17)	449 (5.04)
	DMF	567 (4.29)	457 (5.12)
4	$CHCl_3$	554 (4.16)	438 (5.01)
	DMF	557 (4.31)	446 (5.07)

The porphyrins possessing pronounced acidic properties in acetonitrile are capable of coordination of zinc cation via two mechanisms [molecular (1) and ionic (2)], depending on the molecular state in the solution [16, 17].

$$H_2P + [Zn(OAc)_2(Solv)_{n-2}] \rightarrow ZnP + 2HOAc + (n-2)Solv, \quad (1)$$

$$[DBU\cdot 2H]^{2+}P^{2-} + [Zn(OAc)_2(Solv)_{n-2}] \rightarrow ZnP + 2HOAc + (n-2)Solv + DBU, \quad (2)$$

where (H_2P) porphyrin, (OAc) acido ligand (salt anion), (Solv) solvent molecule, (*n*) coordination number of the metal cation.

The complex formation reaction of porphyrins **5** and **6** conducted at low temperatures occurred exclusively via the mechanism (1). In the presence of the organic base, the zinc complexes were formed instantly via the mechanism (2), which complicated the determination of reaction kinetic parameters.

The isosbestic points were clearly observed in the electronic absorption spectra of the reacting systems, and reaction (1) followed the first reaction rate order with respect to porphyrin, which was confirmed by the linearity of the log $[c^0(H_2P)/c(H_2P)]$ vs $\tau(c)$ dependence. The reaction order with respect to the salt was estimated from the slope of the log K_{eff} dependence on log $c[Zn(OAc)_2]$.

Electronic absorption spectra parameters for porphyrins, their double-deprotonated forms, and the

Table 2. Parameters of electronic absorption spectra of molecular and ionic forms of porphyrins and theirs zinc complexes in acetonitrile and the corresponding basicity and acidity constants

Form, compound	λ, nm (log ε)		p$K_{b1,2}$	p$K_{a1,2}$
	Soret band	Q-band		
H_2TPP	413 (5.02)	512 (3.56), 546 (3.12), 589 (2.92), 646 (2.96)	19.8 [14]	
H_3TPP^+	413 (5.01)	512 (3.69), 547 (3.42), 660 (3.47)	18.61 [15]	
H_4TPP^{2+}	441 (5.04)	661 (4.17)		
H_2Br_8TPP	471 (5.14)	646 (4.16), 765 (3.92)	16.60	10.77 [15]
$H_4Br_8TPP^{2+}$	490 (5.19)	741 (4.52)		
Br_8TPP^{2-}[29]	497 (5.30)	734 (4.80)		
H_2Br_8T(4-ClPh)P (**5**)	475 (5.09)	646 (4.17), 763 (3.94)	16.06	10.15 [12]
H_4Br_8T(4-ClPh)P^{2+}	495 (5.21)	743 (4.54)		
Br_8T(4-ClPh)P^{2-}	500 (4.96)	733 (4,18)		
$ZnBr_8T$(4-ClPh)P	472 (5.20)	611 (4.04), 675 (4.10)		
H_2Cl_8T(4-BrPh)P (**6**)	458 (5.04)	554 (4.07), 623 (4.16), 732 (3.99)	14.76	9.66 [12]
H_4Cl_8T(4-BrPh)P^{2+}	486 (5.23)	736 (4,56)		
Cl_8T(4-BrPh)P^{2-}	491 (5.03)	755 (4.32)		
$ZnCl_8T$(4-BrPh)P	455 (5.18)	593 (4.18), 647 (4.18)		

corresponding metal complexes are given in Table 2, and the kinetic parameters of the zinc complexes formation in the acetonitrile–$HClO_4$ system are given in Table 3.

Introduction of electronegative substituents at the β-positions of the porphyrin molecule promotes the distortion of the macrocyclic plane, and the degree of the macrocycle distortion increases along with the increase in electronegativity of the introduced atom [15]. Deformation of the porphyrin structure leads to the partial isolation of the π-electron systems of pyrrole fragments and the increase in electron density on tertiary nitrogen atoms [18, 19]. In turn, electron-accepting atoms such as bromine or chlorine draw off the electron density from transannular nitrogen atoms, creating an excessive positive charge on transannular nitrogen atoms of the reactive site. The listed factors affect the zinc complexes formation rate: the deceleration of the complex formation was observed along with the change in the electronegativity and the number of the introduced substituents. The reaction rate constant for compound **6** was lower than that for compound **5**, and the increase in enthalpy of the reaction process was observed. The comparative analysis of the rate constants for compounds **5** and **6**, unsubstituted tetraphenylporphyrin (H_2TPP) [14], and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (H_2Br_8TPP) [15] (Table 3) showed that the introduction of bromine and chlorine atoms at the β-positions of the macrocycle and the *para*-positions of the phenyl rings reduced the reaction complex forma-

Table 3. Kinetic parameters of the formation of zinc–porphyrins complexes in the zinc(II) acetate–acetonitrile system

Porphyrin	$[Zn(OAc)_2]\times10^3$, mol/L	$k_v^{298}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
H_2TPP[14]	1.84	302±1	70±2	–28± 2
H_2Br_8TPP [15]	4.50	69±1	56±1	–88±2
H_2Br_8T(4-ClPh)P	4.50	60±1	65±1	–58±3
H_2Cl_8T(4-BrPh)P	4.50	48±1	75±2	–26±2

tion rate constant k_v in ~4–6 times. For β-substituted porphyrins, the rate constant was increased in the following series: H_2Br_8TPP > $H_2Br_8T(4\text{-ClPh})P$ > $H_2Cl_8T(4\text{-BrPh})P$. It is known that the reactivity of porphyrins as ligands in the complex formation reactions depends on the interaction of macrocyclic tertiary nitrogen atoms in the transition state with the metal cations entering the coordination site of porphyrine, and the activation energy of reaction (1) increases along with the strength of this interaction [1]. In our case, the increase in the activation energy of the complex formation reaction (Table 3) was probably related to the weakening of that interaction due to the appearance of excessive positive charge on macrocyclic transannular nitrogen atoms caused by the influence of the introduced halogen atoms.

In summary, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin were synthesized and identified by electronic absorption and ^{1}H NMR spectroscopy as well as mass spectrometry. Spectrophotometric determination of the complex-forming properties of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin and 2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin in the zinc(II) acetate–acetonitrile system at 278–298 K and the determination of kinetic parameters of the formation of the zinc complexes in acetonitrile pointed out that it was possible to tune the properties of the porphyrin molecule as a whole so that they matched a specific application by changing the substituent type in β- and *para*-positions of the phenyl ring of tetraphenylporphyrin.

EXPERIMENTAL

Tetra-(4-chlorophenyl)-porphyrin and tetra-(4-bromophenyl)porphyrin (Porphychem) were used. Coordination properties of the halogenated porphyrins were studied in solutions in acetonitrile purchases from Lab-Scan. The measurements were performed at 278–298 K in a closed cell (at least three measurements at each temperature; temperature was maintained constant within ±0.1 K) using a Cary-100 spectrophotometer (Varian). The details of the preparative chemistry and experimental data processing are given elsewhere [13, 16]. The solvents (dimethylformamide, chloroform, and dichloromethane of "chemical pure" grade), *N*-bromosuccinimide and *N*-chlorosuccinimide (Acros), and alumina (Merck) were used as received. Mass spectra were registered with the use of a MALDI TOF Shimadzu Biotech Axima Confidence mass spectrometer (matrix: dihydroxybenzoic acid). ^{1}H NMR spectra (in $CDCl_3$) were registered with the use of a Bruker AV III-500 (internal reference: TMS). Electronic absorption spectra were registered at room temperatureusing a Cary-100 spectrophotometer.

Co(II) 5,10,15,20-tetra-(4-chlorophenyl)porphyrinate (1). A mixture of 0.04 g (0.065 mmol) tetra-(4-chlorophenyl)porphyrin and 0.096 g (0.65 mmol) of $Co(OAc)_2$ in 30 mL of DMF was boiled for 30 s and then cooled to ambient. The mixture was poured into water, and NaCl was added. The precipitate was filtered off, washed with water, dried, and purified by chromatography on alumina eluting with dichloromethane. Yield 0.033 g (0.0407 mmol, 77%). ^{1}H NMR spectrum, δ, ppm: 15.82 br. s (8H, pyrrole),13.00 br. s (8H, H^o), 8.15 d (8H, H^m, J = 7.6 Hz). Mass spectrum, *m/z* (I_r, %): 809.02 (97) $[M]^+$ (calculated for $C_{44}H_{24}N_4Cl_4Co$: 810).

Co(II) 5,10,15,20-tetra-(4-bromophenyl)porphyrinate (2) was obtained similarly from 0.04 g (0.043 mmol) of tetra-(4-bromophenyl)porphyrin, 0.075 g (0.43 mmol) of $Co(OAc)_2$ and 40 mL of DMF. Yield 0.034 g (0.0344 mmol, 80%). ^{1}H NMR spectrum, δ, ppm: 15.88 br. s (8H, pyrrole), 12.94 br. s (8H, H^o), 10.10 br. s (8H, H^m). Mass spectrum, *m/z* (I_r, %): 986.63 (98) $[M]^+$ (calculated for $C_{44}H_{24}N_4Br_4Co$: 987.3).

Co(II) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrinate (3). 0.11 g (0.618 mmol) of NBS was added to a solution of 0.02 g (0.0247 mmol) of complex **1** in 12 mL of chloroform and 3 mL of DMF. The mixture was kept at room temperature during 6 h and evaporated to minimal volume; 4 mL of DMF, water, and NaCl were then added. The precipitate was filtered off, washed with water, dried, and purified by column chromatography on alumina (eluent: dichloromethane, chloroform). Yield 0.027 g (0.0187 mmol, 77%). ^{1}H NMR spectrum, δ, ppm: 15.10 br. s (8H, H^o), 10.07 br. s (8H, H^m). Mass spectrum, *m/z* (I_r, %): 1440.9 (48) $[M]^+$ (calculated for $C_{44}H_{16}N_4Cl_4Br_8Co$: 1440.5).

Co(II) 2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrinate (4). 0.165 g (1.015 mmol) of NCS was added to a solution of 0.02 g (0.0203 mmol) of complex **2** in a mixture of 10 mL of chloroform and 2.5 mL of DMF. The mixture was boiled for 4 min, and then 1.5 mL of DMF and 0.165 g of NCS were added to the mixture which was boiled

for 2 min more. After cooling, the mixture was evaporated to minimal volume, and 3 mL of DMF, water, and NaCl were added. The precipitate was filtered off, washed with water, dried, and purified by column chromatography on alumina (eluent: hexane, dichloromethane, chloroform). Yield 0.015 g (0.0119 mmol, 60%). ^{1}H NMR spectrum, δ, ppm: 14.30 br. s (8H, H^o), 10.14 br. s (8H, H^m). Mass spectrum, *m/z* (I_r, %): 1263.05 (42) $[M]^+$ (calculated for $C_{44}H_{16}N_4Cl_8Br_4Co$: 1262.7).

2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetra-(4-chlorophenyl)porphyrin (5). 3 mL of 58% perchloric acid and 2.5 mL of 96% sulfuric acid were added to a solution of 0.02 g (0.0139 mmol) of compound **3** in 10 mL of chloroform. The mixture was stirred for 2 h at room temperature. After the reaction was complete, the organic fraction was separated, washed with water, ammonia solution, then again with water, and dried over Na_2SO_4; after that, the residue was evaporated. The residue was purified by column chromatography on alumina eluting with dichloromethane, and then reprecipitated from hexane. Yield: 0.014 g (0.0101 mmol, 72%). EAS (MeCN), λ_{max}, nm (log ε): 763 (3.94), 646 (4.17), 474 (5.09), 372 (4.44). ^{1}H NMR spectrum, δ, ppm: 8.14 d (8H, H^o, J = 7.7 Hz), 7.78 d (8H, H^m, J = 7.6 Hz). Mass spectrum, *m/z* (I_r, %): 1385 (39) $[M]^+$ (calculated for $C_{44}H_{18}N_4Cl_4Br_8$: 1383.7).

2,3,7,8,12,13,17,18-Octachloro-5,10,15,20-tetra-(4-bromophenyl)porphyrin (6). 3 mL of 58% perchloric acid and 2.5 mL of 96% sulfuric acid were added to a solution of 0.02 g (0.0158 mmol) of compound **4** in 10 mL of chloroform. The mixture was stirred for 5 h at room temperature. 3 mL of prchloric acid and 2.5 mL of sulfuric acid were added to the separated organic fraction. The obtained mixture was stirred for 3 h and then treated as described above. The product were isolated via chromatography on alumina, eluent: dichloromethane–hexane (1 : 1). Yield 0.01 g (0.0083 mmol, 54%). EAS (MeCN), λ_{max}, nm (log ε): 732 (3.99), 623 (4.16), 554 (4.07), 458 (5.04). ^{1}H NMR spectrum, δ, ppm: 8.04 d (8H, H^o, J = 7.7 Hz), 7.92 d (8H, H^m, J = 7.6 Hz). Mass spectrum, *m/z* (I_r, %): 1207.3 (53) $[M]^+$ (calculated for $C_{44}H_{18}N_4Cl_8Br_4$: 1205.9).

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CONFLICT OF INTEREST

No conflict of interest was declared by authors.

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