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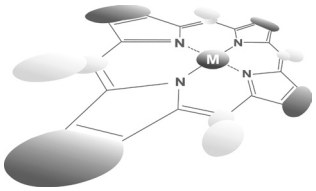

Regioselective bromination of palladium tetraphenyltetrabenzoporphyrin to benzo-rings. Synthesis of mono- and octabromotetrabenzoporphyrins and their properties‡

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ABSTRACT: Bromination of palladium *meso*-tetraphenyl tetrabenzoporphyrin (Pd Ph_4TBP, **1**) by Me_4NBr_3 or Me_4NBr/Br_2 was shown to proceed regioselectively to the benzo-rings annelated to main porphyrin macrocycle. Conditions for preferential mono- and octa-bromination have been established. The respective mono- and octa-bromide (Pd $Ph_4TBP(Br)$, **2** and Pd $Ph_4TBP(Br)_8$, **3**) have been isolated and characterized by UV-vis, NMR and LDI-TOF spectroscopy. Changes of electrochemical properties of tetrabenzoporphyrins induced by Br atoms were found to follow the same trends as the changes in analogous non-extended porphyrins. Room temperature phosphorescence is not substantially influenced by the substitution.

KEYWORDS: palladium *meso*-tetraphenyltetrabenzoporphyrin, benzo-rings bromination, palladium *meso*-tetraphenyltetrabenzoporphyrin monobromide, palladium *meso*-tetraphenyltetrabenzoporphyrin octabromide, phosphorescence, redox properties.

INTRODUCTION

Tetrabenzoporphyrins (TBPs) are an important class of tetrapyrroles with π-extended aromatic system. They possess unique photophysical properties which make them attractive for such applications as organic light-emitting diodes [1], photomedicine [2–4], biomedical sensing systems [5–10], and components of field transistors [11, 12]. In spite of the recent growth of interest in tetrabenzoporphyrins their chemistry is only starting to be developed. The least explored are modifications of pre-formed TBPs by different substitution reactions. Existing examples include electrophilic sulfonation [3], nitration [13] and nucleophilic substitution reaction [14, 15]. Recently developed general methods of synthesis of π-extended porphyrins, with low-temperature condensation being the key step ([16] and references cited therein; [17–19]), make it possible to construct TBPs with a variety of substituents in *meso*-aryl rings. However selection of substituents in benzo-rings is limited. Substituents introduced so far include alkyls: alkoxy, phenyl, and alkoxycarbonyl [20, 21].

In this paper we explore bromination of Pd tetraphenyltetrabenzoporphyrin (Pd Ph_4TBP), the Pd complex of the simplest representative of *meso*-tetraarylated TBPs. Ph_4TBP can also be obtained, although in low yields, by a simple one-step high-temperature condensation reaction ([22, 23] and references cited therein) as opposed to more versatile but multi-step reaction schemes. Bromination of the pre-formed Ph_4TBP could provide a entry point to a variety of functionalized TBP derivatives by way of various Pd-catalyzed reactions [24].

Bromination has been widely used for modification of regular non-extended porphyrins [25, 26]. Brominated porphyrins are valuable as building blocks for

◊SPP full member in good standing

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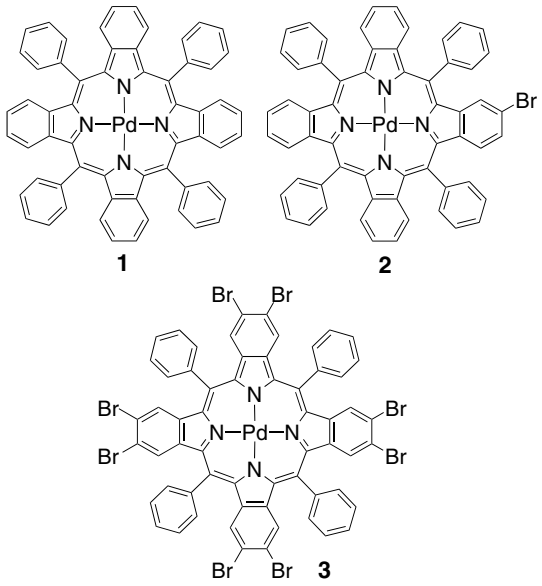


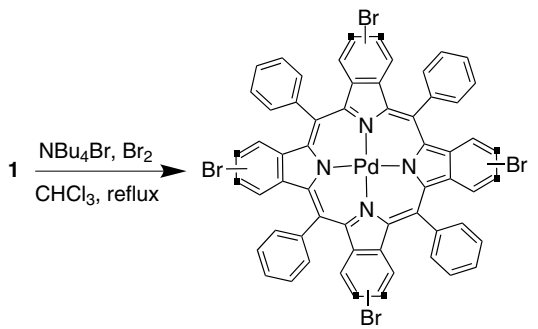
Chart 1.

complex macromolecular systems containing porphyrin rings (for a few recent examples, see [27–32]). To our knowledge, no direct attempts to carry out bromination of TBPs have been disclosed. Herein, we report bromination of Pd Ph_4TBP (**1**) and properties of the *mono*- and *octa*-bromo derivatives Pd $Ph_4TBP(Br)$ (**2**) and Pd $Ph_4TBP(Br)_8$ (**3**).

RESULTS AND DISCUSSION

Synthesis

In our preliminary studies we found that bromination of **1** using classic S_E systems (Br_2-$AlBr_3$, Br_2-$FeBr_3$ (*in situ*)) resulted in unresolvable mixtures of bromides, presumably *benzo*- and aryl-substituted derivatives [33]. Milder agents, such as Br_2-NMe_4Br, permitted bromination exclusively into the *benzo*-rings, with the formation of mixtures of *tetra*- to *hepta*-substituted bromides (Scheme 1). Attempts to apply these conditions to other metalated Ph_4TBPs lead to demetalation of the macrocycle, such as in the case of $ZnPh_4TBP$, or to complete absence of the reaction, *e.g.* in the case of $CuPh_4TBP$.



Scheme 1. Bromination of **1** by NMe_4Br-Br_2 yielding mixture of bromides $Ph_4TBP(Br)_n$, n = 4–7. Sites of substitution are marked with dots

Further studies [34] have shown that two consequent bromination reactions performed on the same sample of **1** made it possible to obtain octabromide **3** in 88% yield, although the product was contaminated by heptabromide and traces of hexabromide.

Pd $Ph_4TBP(Br)_8$. In this study we extended the search for the optimal conditions for the formation of pure octabromide **3**. NMe_4Br was used in excess to make saturated solution at the solvent reflux temperature, whereas Br_2 amount varied. Pure NMe_4Br_3 was also tested as brominating agent. Besides $CHCl_3$ used earlier, lower-boiling CH_2Cl_2 was employed as a solvent, as well as higher-boiling $CHBr_3$. Reaction time was chosen so that neither starting compound nor Pd $Ph_4TBP(Br_n)$ (n = 1–4) were seen on TLC. These spots are distinguishable from the mixture Pd $Ph_4TBP(Br_n)$ (n = 5–8), which appeared as one spot.

Identification of reaction products was performed by Laser Desorption Ionization Time-of-Flight (LDI-TOF) mass spectroscopy. No matrix was added, as LDI-TOF can be successfully used for porphyrin analysis [35]. Moreover, porphyrins can serve as matrices themselves, as shown in the analysis of B_{12}-related compounds [36].

Variation of the number of Br_2 equivalents was found to strongly influence the outcome of the reaction (Table 1, entries 1–2, 4–5). The concentration of Pd Ph_4TBP also had a considerable effect (Table 1, entries 4–5, 9–10). On the other hand, carrying the reaction in inert atmosphere (argon or nitrogen), as opposed to air, did not have noticable effect (entries 3–4, 7–8). These results show good reproducibility of product distribution that allows one to consider this method as a possible route to the whole spectrum of brominated derivatives of **1**, provided adequate methods of separation of individual derivatives can be established.

Bromination at higher concentrations of both **1** and bromine lead to formation of Pd $Ph_4TBP(Br)_7(Cl)$ (Fig. 1). Similar results were obtained in the case of non-extended porphyrins [37]. However, the increase in reaction temperature by way of refluxing in $CHBr_3$ leads to appearance of nona-brominated product Pd $Ph_4TBP(Br)_9$, by analogy with $CHCl_3$ brominations at high substrate concentrations (Table 1, entries 5, 6, 11). LDI-TOF spectra additionally illustrate the reliability of determining the number of bromine and chlorine atoms in Pd-containing porphyrins. For example, isotope multiplet corresponding to $PdBr_9$ was reproducibly different from that to $PdClBr_8$ (note intensity difference between 1625 and 1626 peaks (inset b) and respective peaks in (inset a) in Fig. 1). Relative intensities of isotope peaks in the experiment coincide with calculated ones.

Reaction at lower temperature in refluxing CH_2Cl_2 yielded almost unchanged starting compounds.

Thus, considering all data, the following conclusions can be made. Despite very close properties of polybrominated Pd Ph_4TBP containing 6- to 9-bromine atoms

Table 1. Bromination products distribution as the result of reaction conditions variations[a]

Entry	Agent	Eq.[b]	C (**1**)	t, h	n[c]	%[d]	Reference
1	Br_2/Me_4NBr	9	1.5×10^{-2}	2	4	**63**	[34]
					5	34	
					6	3	
2	Br_2/Me_4NBr	15	1.5×10^{-2}	2	0	2	[34]
					5	2	
					6	24	
					7	**55**	
					8	17	
3	Br_2/Me_4NBr	160	1.5×10^{-2}	15	6	5	this study
					7	16	
					8	**74**	
4[e]	Br_2/Me_4NBr	160	1.5×10^{-2}	15	6	5	this study
					7	17	
					8	**66**	
5	Br_2/Me_4NBr	400	5×10^{-2}	4	8	97	this study
					9	3	
6	Br_2/Me_4NBr	400	5×10^{-2}	4	7	16	this study
					8	**78**	
					9	6	
7	Me_4NBr_3	16	8.4×10^{-3}	8	2	1.7	this study
					3	5.5	
					4	20	
				5	**44**		
					6	22	
					7	3	
8[e]	Br_2/Me_4NBr	16	8.4×10^{-4}	8	2	1.9	this study
					3	4.2	
					4	31	
					5	**44**	
					6	15	
					7	0.9	
9[f]	Br_2/Me_4NBr	11	8.4×10^{-4}	8	5	3.9	this study
				6	8		
					7	22	
					8	**57**	
10[f]	Br_2/Me_4NBr	15	1.5×10^{-2}	6	6	1	[34]
					7	11	
					8	**88**	
11[f]	Br_2/Me_4NBr	100	1.7×10^{-5}	12	7	23	this study
					8	**59**	
				9	6		
12[f]	Br_2/Me_4NBr	160	5×10^{-1}	15	8	**93**	this study
13[f]	Br_2/Me_4NBr	200	1.4×10^{-3}	1	6	10	this study
					7	19	
					8	**71**	

[a] Earlier results are included for clarity. [b] Number of equivalents of brominating agent (Br_2 or Me_4Br_3) relative to Pd Ph_4TBP. [c] *n*-bromosubstituted component and [d] its percentage in the resulting mixture (minor unidentified Pd-containing peaks were not taken into account). [e] Reactions were carried out in argon. [f] Reactions were carried out with mixtures of Pd $Ph_4TBP(Br)_{4-7}$ as starting material.

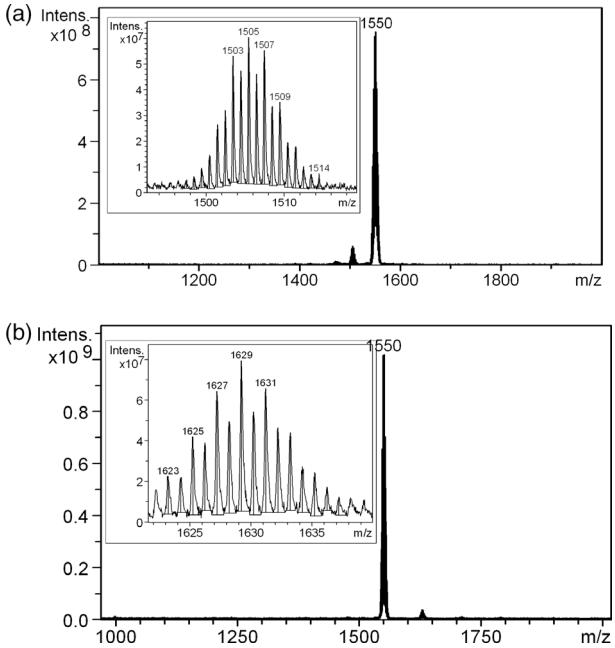


Fig. 1. LDI-TOF spectra of (a) **3** contaminated with Pd $Ph_4TBP(Br)_7(Cl)$, (b) **3** contaminated with Pd $Ph_4TBP(Br)_9$

that preclude their chromatographic isolation, conditions can be established leading to the octabromide product of 97% purity. Best results are obtained for 50 mg load **1**. Repetitive bromination improves the octabromide purity (entries 10–13). Highest purity of the octabromide **3** can be achieved by high porphyrin and bromine concentrations, and **3** can be isolated in 46% yield.

Pd $Ph_4TBP(Br)$. During the course of the above studies we have determined that mono-, di-and tri-bromo derivatives of **1** can be distinguished by TLC on silica gel from each other and from derivatives containing a higher number of bromine atoms. This prompted us to develop a method of synthesis of mono-bromo derivative **2**.

Initially the reaction conditions were optimized to maximize the amount of monobromide in the reaction mixture (Table 2). It was found that pure NMe_4Br_3 leads to the mixture of mono- and di-bromides (Table 1, entries 7–8). Thus, we varied Pd Ph_4TBP concentration, reagent-substrate mole ratio, and reaction time. An additional parameter to change was mode of the reagent addition, *i.e.* simultaneous or in small portions during the reaction, as organic tribromide salts at elevated temperatures are

Table 2. Optimization of bromination conditions for maximum contents of **2** in the mixture

Entry	Solvent	Eq.[a]	C (**1**), M	Addition mode	t, h	n[b]	%[c]
1	$CHCl_3$	0.7	4.5×10^{-4}	simultaneous	15	**0**	**57**
						1	39
						2	2.5
2	$CHCl_3$	1.2	4.5×10^{-4}	-"-	6	0	44
						1	**48**
						2	8
3	$CHCl_3$	2	1.65×10^{-3}	in portion	11	0	4
						1	**62**
						2	30
4	$CHCl_3$	2.5	1.65×10^{-3}	-"-	8	0	18
						1	**67**
						2	15
5	$CHCl_3$	4	3.3×10^{-4}	-"-	9	0	19
						1	**67**
						2	14
6[d]	$CHCl_3$	6.6	1.5×10^{-2}	dropwise (Br_2)	3	1	14
						2	**34**
						3	25
7	CH_2Cl_2	2	1.65×10^{-3}	dropwise (Me_4NBr_3)	5.5	**0**	**52**
						1	21
						2	5
8	CH_2Cl_2	16	1.08×10^{-2}	-"-	15	0	**TLC main spot**
						1	TLC traces

[a] Number of equivalents of brominating agent (Br_2 or Me_4Br_3) relative to Pd Ph_4TBP. [b] *n*-bromosubstituted component and [c] its percentage in the resulting mixture. [d] Br_2 in the presence of Me_4NBr was used as brominating agent.

known to be unstable [38]. It was assumed that portion-wise mode of addition would diminish the fraction of the decomposed reagent.

As seen in Table 2, addition of reagent in small portions together with long reaction time gives the best results. Pd $Ph_4TBP(Br)$ **2** is isolated from this mixture in 63% yield.

NMR spectra

^1H NMR spectra of **1**, **2** and **3**, together with that of the bromides Pd $Ph_4TBP(Br)_{5\text{-}7}$ mixture (Chart 3), exhibit the following features, which are reproduced for molecules with different numbers of substituents.

Analyzing the ^1H NMR spectrum in the region corresponding to the protons of benzo rings, one can conclude that the presence of the following structural fragments accounts for the shape and multiplicity of ^1H signals, *i.e.* non-substituted benzo-rings (Type A), mono-substituted benzo-rings (Type B) and di-substituted benzo-rings (Type C). Structures of **1**, **2**, **3** and that of hexabromide [39] with marked protons for spectral assignments are shown in Chart 2.

In mono-substituted bromide **2** (Chart 3b), one can see AA'BB' multiplets with changed BB' part for Type A benzo-ring having approximately the same chemical shifts as protons of Type A benzo-ring in **1**. Signals of AMX spin system can be assigned due to their multiplicity, whereas H^4 proton is hidden within H^O protons of Type A ring (Type B benzo ring).

Spectrum of mixture of Pd $Ph_4TBP(Br)_{5\text{-}7}$ (Chart 3c) exhibits two sets of AMX multiplets (corresponding to Type B benzo-rings), referred to as minor and major according to their integral intensities. Also, there are two sets of singlets corresponding to Type C benzo-rings. Integral intensities of these peaks correspond to actual numbers of the unsubstituted protons, making Type B to Type C benzo-rings ratio approximately 1:1 in this mixture.

Finally, only signal of Type C benzo-ring (that of H^C) is present in the spectrum of **3**. Thus, ^1H NMR spectra of **1**, **2** and **3**, together with that of the bromides mixture are consistent with each other. Substitution pattern of a benzo-ring does not influence the chemical shifts of other benzo rings present in the molecule.

Signals corresponding to the phenyl rings show some complicated shape when the number of susbtitutents increases, but, in the case of symmetrical octabromide **3**, they are simplified again, the spectra resembling unsubstituted Pd Ph_4TBP.

UV-vis spectra

The number of bromine substituents (Table 3) has little effect on UV-vis bands maxima positions, slightly changing B- to Q-intensity ratio. In comparison, β-pyrrole substitution for bromine in non-extended porphyrins leads to significant red shift in their absorption spectra. For both unsubstituted and *meso*-tetraphenyl-substituted porphyrins "each bromine substitution contributes a shift of 6 nm" [40, 41]. An overall band shift in Pd Ph_4TBP system in octabromide is 6–8 nm to the red region.

A possible explanation of such difference in the behaviour is that introduction of beta-pyrrolic bromines into Pd TPP drastically changes its conformation, bringing flat Pd TPP **4** to saddle-shaped octabromide **5** [42–44] due to the steric overlap of the bromine atoms with *meso*-aryl substituents. Such overlap is absent or negligibly small in the case of **3**. Optimized geometries (see Supplementary material) of **1** and **3** show approximately the same distortion, *i.e.* N(1)-N(2)-N(3)-N(4) dihedral angles are 8.6 and 8.3 degrees, respectively, which is close to the distortion observed in **5** [44].

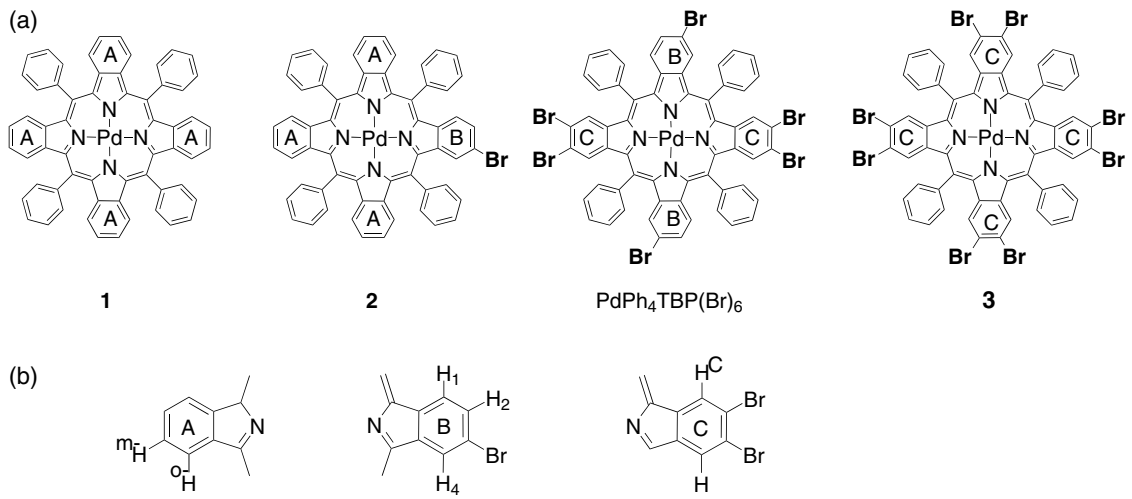


Chart 2. (a) Designation of distinct structural fragments of **1** and brominated porphyrins **2** and **3** as marked in Chart 3. Hexabromide was shown for Pd $Ph_4TBP(Br)_{5\text{-}7}$ mixture. (b) designation of the protons types of different benzo rings

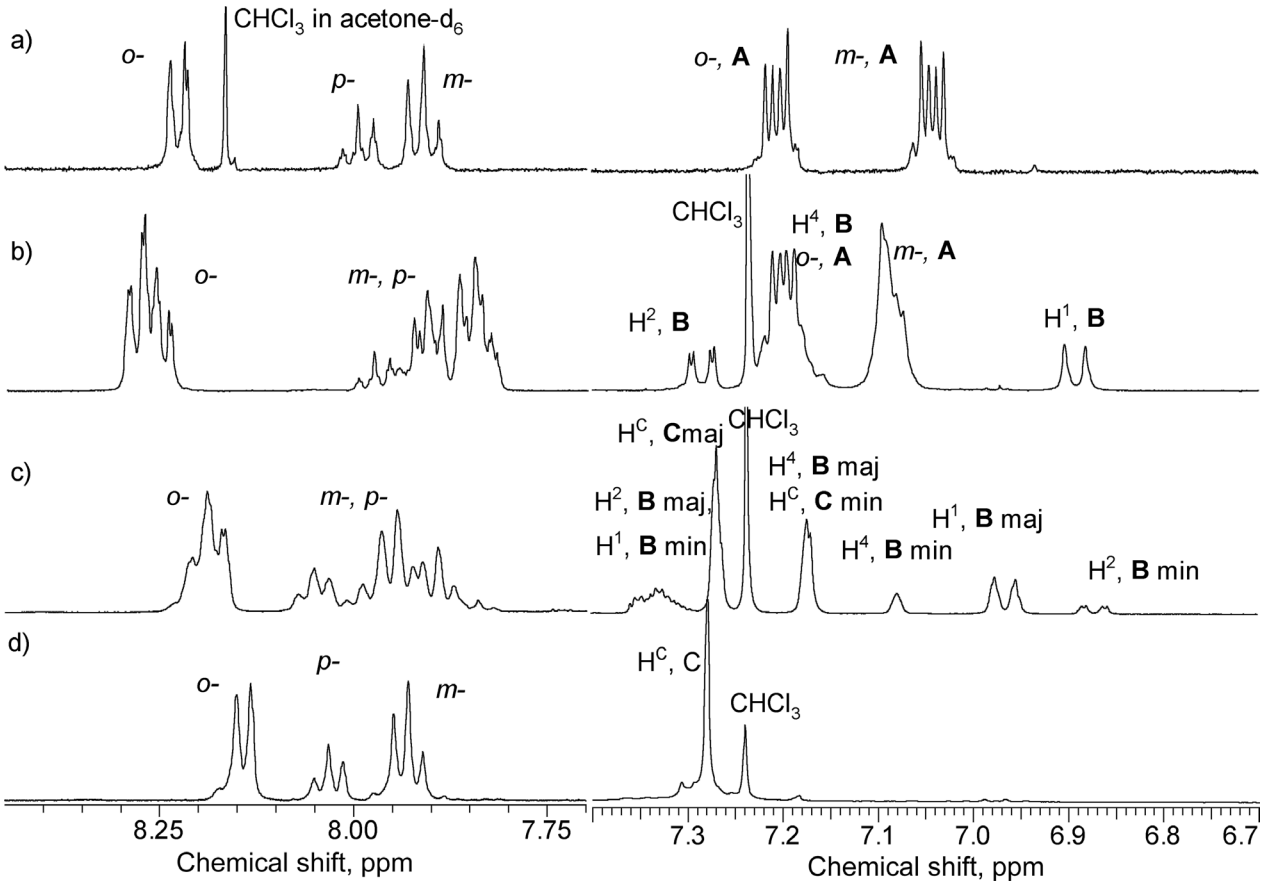
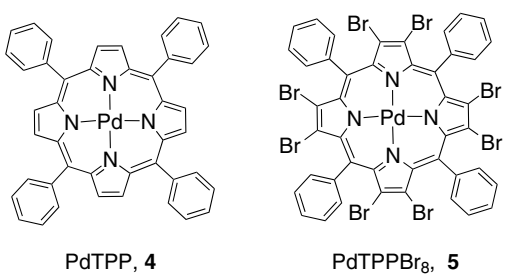


Chart 3. ^{1}H NMR spectra of (a) **1**($CDCl_3$ + acetone-d_6); (b) **2**; (c) mixture of Pd $Ph_4TBP(Br)_n$ (n = 5–7); (d) **3** (all - $CDCl_3$). Phenyl part is on the left; benzo- part is on the right. Chemical shifts can be seen in Experimental section. See Chart 2 for assignment designations

Table 3. UV-vis (CH_2Cl_2) spectra of the studied compounds and their phosphorescence (DMF) data (cf. Fig. 3)[a]

	$\lambda_{max,\ abs}$ Soret (log ε)	$\lambda_{max,\ abs}$ Q band (log ε)	$\lambda_{max,\ phos}$ nm	ϕ_{phos}
1[b]	441 (5.48)	627 (5.04)	803	0.09 ± 0.01
2	442 (5.31)	628 (4.85)	799	0.09 ± 0.01
3	449 (5.45)	633 (5.07)	791	0.11 ± 0.01

[a] For the sake of clarity of representation data on emission of the studied compounds are also included in this table. Discussion is given below. [b] Although UV-vis spectrum of Pd Ph_4TBP in DMF is reported [5], no such measurements in CH_2Cl_2 have been made.



PdTPP, **4** PdTPPBr$_8$, **5**

Chart 4.

Electrochemical measurements

Electrochemical properties of porphyrins **1**–**3** were studied by the cyclic voltammetry and the rotating disk electrode methods. Combined results of electrochemical studies are presented in Table 1; the cyclic voltammetry curves CV curves for **1** and **2** are shown in Fig. 2.

First reduction and oxidation processes are found to be reversible for all three compounds, whereas second redox processes are quasi-reversible for **1** and **2**.

Electrochemical properties of β-brominated porphyrins were extensively studied previously. Kadish *et al.* [26] performed systematic research on the series of metalated

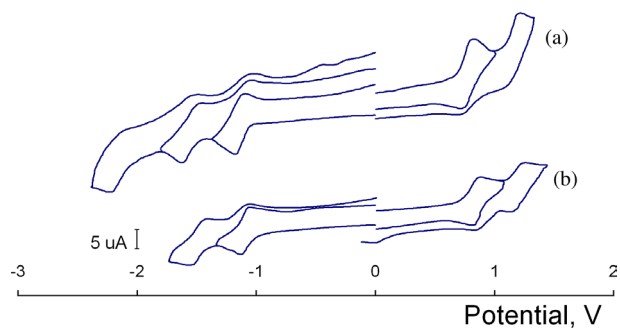


Fig. 2. CVA redox curves for **1** (a) and **2** (b)

Table 4. Redox potentials for Pd Ph_4TBP **1**, Pd $Ph_4TBP(Br)$ **2** and Pd $Ph_4TBP(Br)_8$ **3** in DMF *vs.* Ag/AgCl, 0.1 M of TBAP (number of electrons in the electrode process are given in parentheses)

Compound	$E_{1/2\ II\ red}$	$E_{1/2\ I\ red}$	$E_{1/2\ I\ ox}$	$E_{1/2\ II\ ox}$
1	$-1.60(1)^{qrev}$	$-1.15(1)^{rev}$	$0.80(1)^{rev}$	$1.21(1)^{rev}$
2	$-1.54(1)^{qrev}$	$-1.09(1)^{rev}$	$0.83(1)^{rev}$	$1.22(1)^{qrev}$
3	$-1.27(1)^{qrev}$	$-0.83(1)^{rev}$	0.80^{qev}	1.03^{irr}

(Fe(III), Mn(III), Co, Zn) mono- to octabrominated porphyrins, whereas Bhyrappa *et al.* [41] investigated electrochemistry of β-octabromo-*meso*-tetraphenylporphyrin and some of its metal derivatives, including Pd.

Direct comparison of the results of this and earlier studies of the influence of bromination on potentials is difficult, because the latter were done in other solvent [41, 45–48].

However, the trends found for ring-originated redox potentials can be compared. Our results show similar behavior as those for $MTPPBr_x$ (x = 0 to 8) [26], including anode shift of first two reduction potentials, stability (within experimental error) of first oxidation one and cathode shift of second oxidation one with increase of the number of bromine substituents.

At this stage we are unable to obtain individual Pd $Ph_4TBPBr_{2\text{-}7}$ due to the statistical character of bromine substitution and products separation problem. Hence, more detailed trends of the potential changes, similar to non-extended porphyrin bromides, are to be studied for TBP series.

Phosphorescence studies

Halogenation of porphyrins and chlorins is known to have dramatic effects on their photophysical properties [49]. In Pd tetrabenzoporphyrins intersystem crossing results in rapid depopulation of singlet-excited states, resulting in nearly quantitative formation of emissive triplet states [50]. Introduction of heavy atoms, such as bromine, could further influence the rates of intersystem crossings, leading to both formation and deactivation of the triplet state, as well as the radiative rate of the triplet emission. Since phosphorescence of Pd tetrabenzoporphyrins is important for several applications (*vide supra*), it was interesting to examine triplet emissivity of the brominated derivatives of **1**.

Phosphorescence spectra of **1**, **2** and **3**, studied in DMF solution at room temperature showed the features presented in Fig. 3. Although the sensitivity range of our detector did not cover full emission bands, these measurements can provide initial information about relative emissivity of the Pd porphyrins. Phosphorescence maxima proved to gradually shift to the blue region as the number of substituents increase, whereas maxima increase. On the other hand, phosphorescence quantum yields (Table 3) remain approximately constant. However,

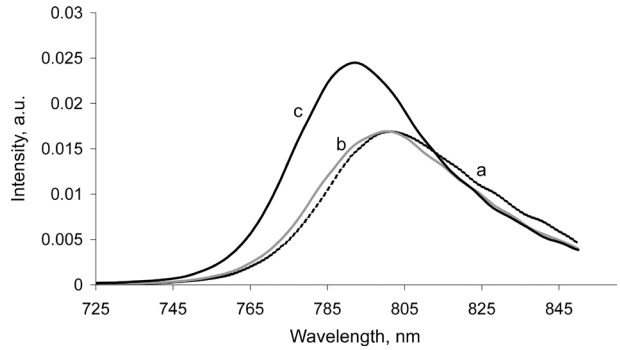


Fig. 3. Room-temperature (25 °C) phosphorescence spectra of DMF solutions of (a) Pd Ph_4TBP; (b) Pd $Ph_4TBP(Br_1)$; (c) Pd $Ph_4TBP(Br_8)$, normalized for the quantum yield of the standard and OD of the studied solution. l_{exc} = 635 nm. Other details of the measurements can be found in the Experimental section

comparative studies of the emissive properties of **3** *vs.* **1** at 77 K reveal much higher emission of the former (see Supplementary material).

According to reference 49, halogen atoms in the porphyrin molecule, appearing in addition to central metal atom, can either enhance or reduce phosphorescence quantum yield due to a number of reasons. The quantum yield, being virtually independent of the number of bromine substituents for the new compounds, is to be the subject of future detailed studies, as well as temperature dependence of these compounds phosphorescence.

EXPERIMENTAL

All solvents and commercial reagents were obtained from Aldrich, Khimmed and Reachim. Deuterated solvents were purchased from "Applied Chemistry" SciTech Plant, St. Petersburg. **1** was synthesized according to the literature procedures [18].

^1H NMR spectra were measured on Bruker Avance 400 spectrometer in $CDCl_3$, unless stated otherwise. LDI-TOF spectra on Bruker Autoflex II mass spectrometer. UV-vis spectra were obtained on Agilent 8453 spectrophotometer. Cyclic voltammetric experiments were carried out using a PI-50-1.1 potentiostat (Gomel, Belarus) equipped with PR-8 programmable module. The system consisted of the three-electrode assembly, glassy carbon (GC) electrode (working electrode, disk d = 2 mm), Ag/AgCl/KCl (aq., satur.) (reference electrode) and platinum electrode (counter electrode, plate s = 0.5 cm^2). Tetrabutylammoniumperclorate (TBP) (Fluka) 0.1 M, was used as received in acetonitrile. The anhydrous solvents had electronic grade purity. Measurements were performed using 1 mM concentration of porphyrins. A 1 mM solution of ferrocene along with 0.1 M TBAP was employed during calibration. The cyclic voltammetric experiments were carried out after deaerating the experimental solutions by purging pure argon gas. All the measurements were carried out at 22 °C. Scan rate: 200 mV/s.

Phosphorescence spectra and quantum yields were measured on Fluorolog-3 instrument equipped with HORIBA Jobin Yvon FL 1073 detector. Right-angle detection was used in all measurements. Assemblies of quartz cuvette with graded quatz-borosilicate seal and a side flask for freeze-pump-thaw degassing were used. DMF solutions of the substances with OD no more than 0.1 at the excitation wavelength were placed in the flask and the assembly attached to a vacuum (10^{-2} Torr) line. After 5 to 7 freeze-pump-thaw cycles the assembly was seal-detached in vacuum, then frozen solution was melted and poured into the cuvette. An identical cuvette was used for the standard – tetraphenylporphyrin, which was measured in benzene solution in ambient atmosphere (quantum yield 0.11 [51]). Solutions were irradiated at 635 nm, range of emission detector was 640–850 nm. Slit widths in both excitation and emission channels were 3 nm. Instrument built-in correction factors are used to obtain true emission spectra. Phosphorescence quantum yields were determined according to [52], correction having been applied to amount of absorbed light and to the difference of refraction indices of the solvents. For details of phosphorescence measurements at 77 K, see Supplementary material.

Geometry optimizations were performed using Gaussian 03 software at B3LYP/LanL2MB level of theory. Optimized geomeries showed no imaginary frequencies in vibrational analyses.

Bromination of Pd Ph_4TBP. Synthesis of palladium 2-bromo-6,13,20,27-tetraphenyltetrabenzo[b:g:l:q]-porphyrin (2). Amount of Pd Ph_4TBP relevant to concentration specified in Table 2 was dissolved in the mentioned solvent. Then reflux and stirring was begun, and Me_4NBr_3 added by equal portions in equal time periods (or added dropwise if CH_2Cl_2 used as a the solvent). Reflux and reagent addition was continued until TLC showed mainly the formation of the target porphynate. At the end reaction mixture was washed by 10% aq. Na_2SO_3 and brine. Organic layer was dried over Na_2SO_4. Then the solvent was evaporated and the residue was analysed by LDI-TOF. For preparative purposes (Table 2, entry 4) **1** (50 mg, 54.4 μmol) were dissolved in $CHCl_3$ (3.3 mL) and NMe_4Br_3 (44 mg, 0.14 mmol) were added in portions for specified time. After workup, residue was chromatographed on silica, eluent CCl_4/hexanes. Yield 33 mg, 63%. Molecular ion isotope distribution spectrum is identical with simulated one. UV-vis spectrum see in Table 3. ^{1}H NMR (400 MHz, $CDCl_3$, HMDS, ring designation – bold letter – see in Chart 3): δ_H, ppm 8.25–8.20 (8H, m, *o*-Ph), 7.98–7.81 (12H, *p*-, *m*-Ph), 7.28 (1H, dd, $J_{H^1H^2\text{-}\mathbf{B}}$ = 8.7, $J_{H^2H^4\text{-}\mathbf{B}}$ = 1.7 Hz, H^2-**B**), 7.21–7.19 (7H, m(quasi-AA' part of AA'BB'), *o*-**A**, H^2-**B**)), 7.10 (6H, m, *m*-**A**), 6.89 (1H, d, $J_{H^1H^2\text{-}\mathbf{B}}$ = 8.7, H^1-**B**). LDI-TOF mass spectrum (see Supplementary material) shows isotope distribution identical to the calculated one.

Bromination of Pd Ph_4TBP. Synthesis of palladium 2,3,9,10,16,17,23,24-octabromo-6,13,20,27-tetraphenyltetrabenzo[b:g:l:q]porphyrin (3). To the mixture of NMe_4Br (17 mg, 54 μmol) and Br_2, (3.5 g, 22 mmol, 400 equiv.) dissolved in of $CHCl_3$ (3.6 mg) **1** (50 mL, 54 μmol) was added. Then the reaction mixture was brought to reflux and the reflux continued for 4 h. Reaction mixture was quenched and processed as for the previous compound. 38 mg of **3** (25 μmol, 46%) was obtained. Molecular ion isotope distribution spectrum is identical with simulated one. UV-vis spectrum see in Table 3. ^{1}H NMR (400 MHz, $CDCl_3$, HMDS, ring designation – bold letter – see in Chart 2): δ_H, ppm 8.14 (8H, d, *o*-Ph), 8.03 (4H, t, *p*-Ph), 7.93 (8H, t, *m*-Ph), 7.28 (8H, s, H-**C**). LDI-TOF mass spectrum (see Supplementary material) shows isotope distribution identical to the calculated one.

Mixture of palladium 2,9,16,23,-tetrabromo-6,13,20,27-tetraphenyltetrabenzo[b:g:l:q]porphyrin [53], palladium 2,3,9,16,23,-pentabromo-6,13,20,27-tetraphenyltetrabenzo[b:g:l:q]porphyrin, palladium 2,3,9,10,16,23,-hexabromo-6,13,20,27-tetraphenyl-tetrabenzo[b:g:l:q]porphyrin, palladium 2,3,9,10,16,17,23-heptaromo-6,13,20,27-tetraphenyltetrabenzo[b:g:l:q]porphyrin. This mixture was obtained on according to Table 1, entry 7. Spectrum is shown in Chart 3c. ^{1}H NMR (400 MHz, $CDCl_3$, HMDS, ring designation – bold letter – see in Chart 2): δ_H, ppm 8.20–8.11 (8H, m, *o*-Ph), 8.06–7.80 (12H, *p*-,*m*-Ph), 7.36–7.29 (2H, m, H^2-**B**maj and H^1-**B**min), 7.27 (s, H-**C**maj), 7.17 (*quasi*-d, H-**C**min and H^4-**B**maj), 7.08 (6H(together with 7.27 and 7.17), s H^4-**B**min), 6.97 (d, $J_{H^1H^2\text{-}\mathbf{B}maj}$ = 8.8, H^1-**B**maj), 6.87 (2H(together with 6.97), dd, $J_{H^1H^2\text{-}\mathbf{B}min}$ = 8.9, $J_{H^2H^4\text{-}\mathbf{B}min}$ = 2.0, H^2-**B**min).

SUMMARY AND CONCLUSION

Bromination of Pd Ph_4TBP **1** yields mono- and octabromoderivative **2** and **3**. These derivatives were isolated and characterized. UV-vis, redox and phosphorescence properties have been studied. Bromination was found to exert little influence on UV-vis data. Reduction potentials showed anode shift upon bromination, whereas at first oxidation one remained unchanged; for second oxidation one moved to cathode region. Unlike the results at 77 K, octabromosubstitution did not give rise to increased phophorescence quantum yield at room temperature.

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Supporting information

Figures S1–S5 are given in the supplementary material. This material is available free-of-charge via the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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