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Synthesis and Design of Tetrapyrrole Molecular Receptors for Alkali Metal Cations

Yu. B. Ivanova, O. V. Toldina, V. B. Sheinin, and N. Zh. Mamardashvili

Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045, Russia
e-mail:ngm@isc-ras.ru

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Abstract—*meso*-Phenylporphyrins containing at the benzene ring a conformationally labile polyether fragment with a terminal pyridine ring were synthesized, and their spectral and physicochemical properties were studied. The relations found between the spectral parameters of the tetrapyrrole chromophore, on the one hand, and acid–base equilibria and complex formation with alkali metal cations, on the other, showed the possibility for design of porphyrin-based molecular ensembles possessing useful properties.

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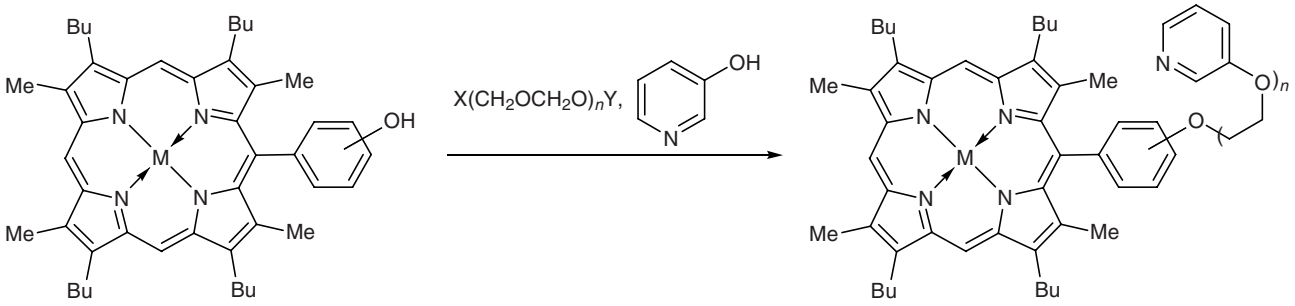
Porphyrins occupy a quite specific place among numerous macroheterocyclic compounds capable of forming self-organized supramolecular ensembles via multisite binding [1–3]. Their unique properties originate from unusual geometric and electronic structure of the tetrapyrrole chromophore which can act as a source of signal reflecting processes occurring in the system under study [4–6]. In the recent years, interest in porphyrin derivatives has increased considerably due to their ability to participate in molecular recognition, i.e., in a selective binding process in which a receptor effectively interacts only with molecules of a definite type through intermolecular forces [7, 8].

In this connection, important results can be obtained by modification of porphyrin macroring with polyether fragments possessing intrinsic complexing ability toward various substrates. Combinations of porphyrin and polyether fragments linked together through covalent bonds could give rise to building blocks for spatially preorganized three-dimensional structures [5, 9].

The present work was aimed at synthesizing supramolecular complexes of *meso*-aryloctaalkylporphyrins and optimizing their parameters. The results of studies on the dependence of spectral parameters of tetrapyrrole chromophore upon acid–base equilibria and complex formation with alkali metal cations indicate that porphyrin derivatives may be used to build up molecular ensembles possessing practically important properties.

By reaction of *meso*-(hydroxyphenyl)porphyrins **I** and **II** with polyethylene glycol bis(4-toluenesulfonates) **III** and **IV**, and 3-hydroxypyridine (**V**) in the presence of cesium carbonate in dimethylformamide–

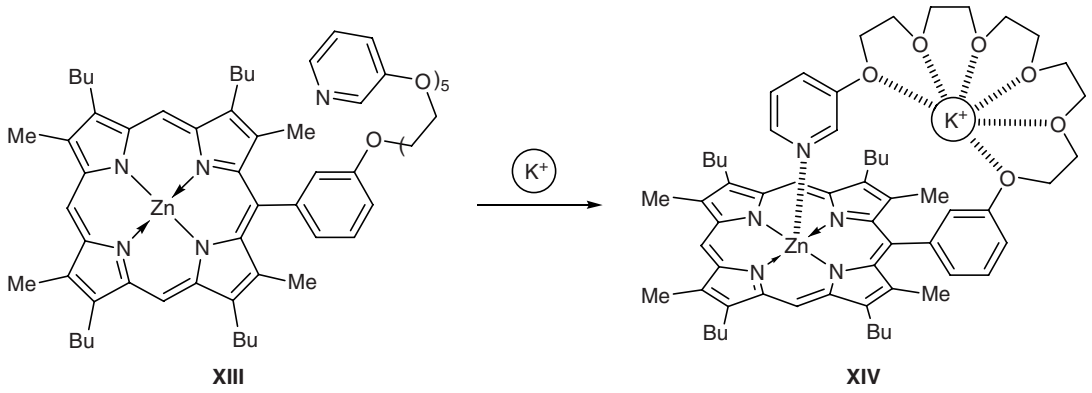
Scheme 1.



I, **II** **VI–XIII**

I, **II**, **VI**–**IX**, M = H_2; **X**–**XIII**, M = Zn; **VI**, **VII**, **X**, **XI**, n = 4; **VIII**, **IX**, **XII**, **XIII**, n = 5; X = p-$MeC_6H_4SO_3$, Y = p-$MeC_6H_4SO_2$.

Scheme 2.



acetonitrile we synthesized porphyrins **VI–IX** having a conformationally labile polyether fragment with a terminal pyridine group in the *meso* position of the macroring (Scheme 1). The reaction of **VI–IX** with zinc(II) acetate in boiling dimethylformamide gave porphyrin metal complexes **X–XIII**. The assumed structure of tetrapyrrole compounds **VI–XIII** was consistent with the data of elemental analysis and electronic absorption, ^{1}H NMR, and mass spectra.

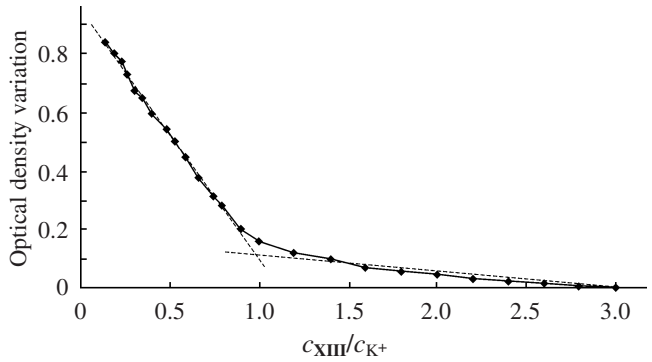


Fig. 1. Spectrophotometric titration curve of compound **XIII** with potassium cation in toluene–MeOH (2:1) at the ascending wavelength (λ = 415 nm, 298 K, $c_{XIII} = 5.32\times10^{-6}$ M).

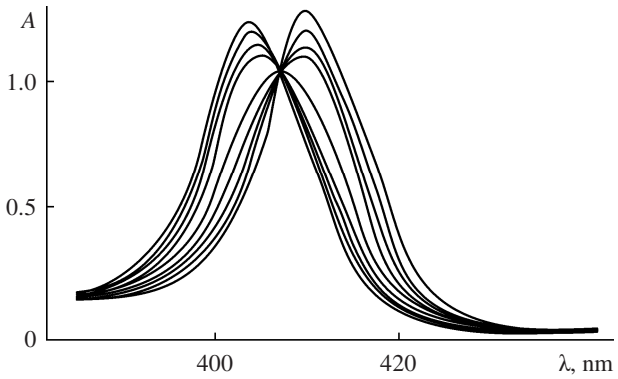


Fig. 2. Variations of the electronic absorption spectra of compound **XIII** (Soret band region) upon addition of K^+ ions from 0 to 10^{-3} M.

The complexing ability of porphyrins **VIII–XIII** toward alkali metal cations (Li^+, Na^+, and K^+) was studied in a 2:1 toluene–methanol mixture. Among the examined compounds, only 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5-{3-[14-(pyridin-3-yloxy)-3,6,9,12-tetraoxatetradecyloxy]phenyl}porphyrinatozinc(II) (**XIII**) turned out to be capable of binding potassium cations with formation of complex **XIV** due to appropriate geometric parameters of the polyether cavity (Scheme 2). Conformational flexibility of the polyether bridge enables the terminal pyridine ring to approach the tetrapyrrole macroring, which is readily detected by the electronic absorption and ^{1}H NMR spectra. Donor–acceptor interaction between the pyridine nitrogen atom and zinc cation in the system porphyrin complex **XIII**–potassium tetrafluoroborate leads to a red shift of the absorption band (up to 10 nm), and shielding of the pyridine fragment by the porphyrin ring current induces upfield shift of signals from protons in the pyridine ring, which reside in the vicinity of the macroring.

Study of the complex formation between compound **XIII** and K^+ ion by spectrophotometric titration showed that complex **XIV** has a composition of 1:1. The titration curve is characterized by one step (Fig. 1) which corresponds to an isosbestic point in the electronic absorption spectra (Fig. 2). An upfield shift of signals from protons in the pyridine fragment (as compared to pyridine) was observed in the ^{1}H NMR spectrum of the complex ($\Delta\delta$ = 4.5 and 1.1 ppm for α-H and β-H, respectively) in the reactant concentration range corresponding to the inflection on the spectrophotometric titration curve. The stability constant of complex **XIV** ($K_s = 0.361\times10^6$ l/mol) was calculated according to standard procedure [9] on the basis of spectrophotometric data obtained at two wavelengths (descending and ascending) using formula (1):

$$K_s = \frac{[ZnP \cdot K^+]}{[ZnP][K^+]} = \frac{1}{[K^+]}\left(\frac{\Delta A_{i,\lambda_1}}{\Delta A_{0,\lambda_1}}\frac{\Delta A_{0,\lambda_2}}{\Delta A_{i,\lambda_2}}\right). \quad (1)$$

Here λ_1 is the descending wavelength, λ_2 is the ascending wavelength, $[K^+]$ is the concentration of K^+ ions, [ZnP] is the concentration of the porphyrin zinc complex, ΔA_0 is the maximal variation of the optical density at a given wavelength, and ΔA_i is the optical density variation at given wavelength and concentration [9]. The error in the determination of K_s was 7–10%. No binding with Li^+ or Na^+ ions was observed.

With a view to design sterically preorganized complexing cavities for selective binding of alkali metal cations we also examined the effect of acid–base equilibria on the spectral parameters of the tetrapyrrole chromophore. Spectrophotometric–potentiometric titration of porphyrin **VIII** in the system $HClO_4$–H_2O–MeCN showed that the process can be represented by equilibria (2) and (3).

$$H_2P + H^+ \underset{}{\overset{K_{b1}}{\rightleftharpoons}} H_3P^+ \quad (2)$$

$$H_3P + H^+ \underset{}{\overset{K_{b2}}{\rightleftharpoons}} H_4P^{2+} \quad (3)$$

The titration curve is characterized by two steps (Fig. 3), each corresponding to a family of isosbestic points (Fig. 4). At the limiting values of the examined acidity range we observed absorption spectra of individual neutral porphyrin **VIII** [H_2P, λ_{max}, nm ($\log\varepsilon$): 496 (4.17), 528 (4.01), 565 (3.87), 618 (3.74)] and its dication [H_4P^{2+}, λ_{max}, nm ($\log\varepsilon$): = 543 (4.45), 585 (3.94)]. The equilibrium constants calculated according to standard procedure [10] were $\log K_{b1} = 11.58 \pm 0.01$ (2) and $\log K_{b2} = 8.77 \pm 0.01$.

In all cases, the constants K_{b1} and K_{b2} were calculated, and their accuracy was estimated, from two parallel measurements using SigmaPlot program by fitting parameters in Eq. (4) which relates optical density to pH of solutions of dibasic acids [11]:

$$A_c = \frac{A_{H_2P} + 10^{pH}K_{b1}A_{H_3P^+} + 10^{2pH}K_{b1}K_{b2}A_{H_4P^{2+}}}{1 + 10^{pH}K_{b1} + 10^{2pH}K_{b1}K_{b2}}. \quad (4)$$

Here, A_c is the current optical density of H_2P solution at an analytical wavelength, and A_{H_2P}, $A_{H_4P^{2+}}$, and $A_{H_3P^+}$ are the optical densities of solutions of individual H_2P, H_4P^{2+}, and H_3P^+ species with an analytical concentration (c_0). The titration curve shown in Fig. 3 has a stepwise shape since the difference between the first and second protonation constants is about three orders of magnitude [11].

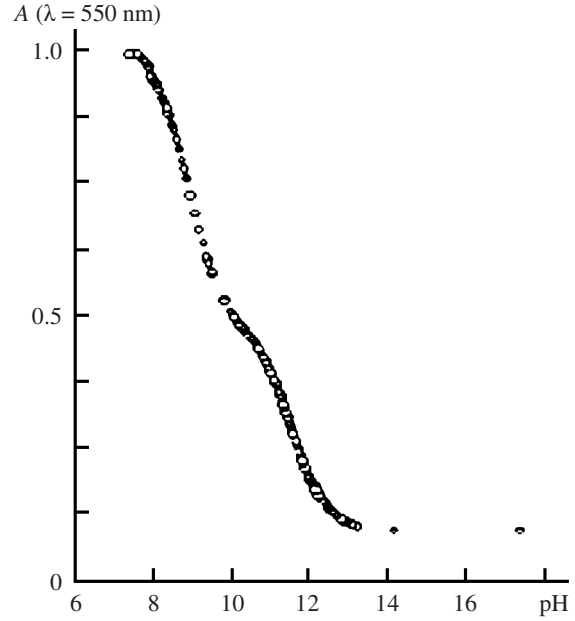


Fig. 3. Plot of the optical density of a solution of porphyrin **VIII** versus pH in the system $HClO_4$–H_2O–MeCN at 298 K.

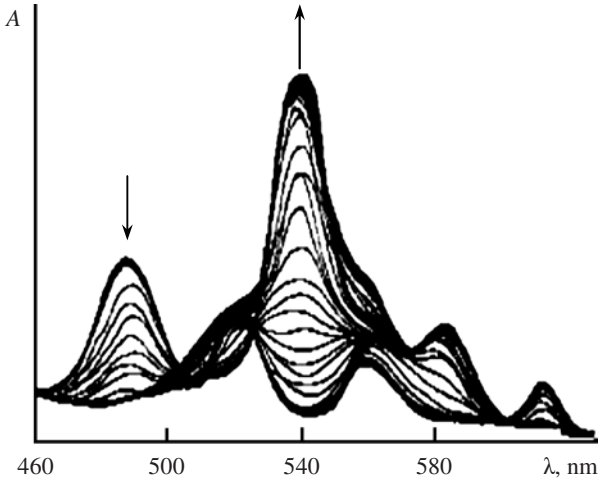
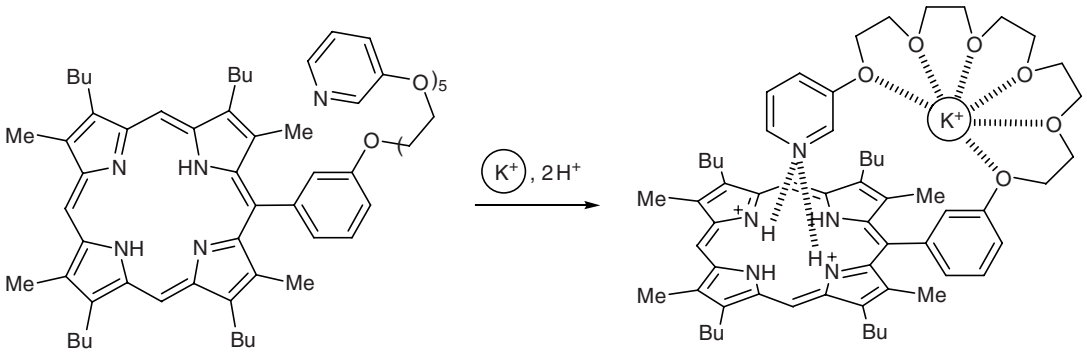


Fig. 4. Variations in the visible region of the electronic absorption spectrum of porphyrin **VIII** with decrease in pH (from 18 to 6) in the system $HClO_4$–H_2O–MeCN at 298 K ($c_{VIII} = 1.51 \times 10^{-5}$ M).

Taking into account that in the presence of potassium cation the conformation of the polyether chain changes in such a way that the pyridine and tetrapyrrole fragments of molecule **VIII** become spatially close (Scheme 2), the pyridine nitrogen atom is likely to be capable of interacting with hydrogen atoms in the coordination entity of the protonated tetrapyrrole macroring (Scheme 3). Such self-organization seems to be fairly promising from the viewpoint of design of supramolecular receptors for alkali metal cations. It

Scheme 3.



VIII **XV**

provides means for optimization of geometric parameters of a receptor cavity so that to match substrate parameters.

Our results indicate that tetrapyrrole macroheterocycles modified by polyether moieties can be used as base structures in the design of new molecular receptors for alkali metal cations. Such receptors are more advantageous than traditionally used crown ethers due to the presence of a tetrapyrrole chromophore which makes it possible to apply spectrophotometric and potentiometric methods intrinsic to the chemistry of porphyrins while studying complex formation processes. As a result, the potential and prospects in the application of tetrapyrrole compounds as selective receptors for extraction and membrane transfer processes and supersensitive switchers for data storage could be considerably extended. The selectivity and high sensitivity of porphyrins to low-energy effects provide the possibility for controlling chemical processes involving these compounds.

EXPERIMENTAL

2,8,12,18-Tetrabutyl-5-(2-hydroxyphenyl)-3,7,13,17-tetramethylporphyrin (**I**) and 2,8,12,18-tetrabutyl-5-(3-hydroxyphenyl)-3,7,13,17-tetramethylporphyrin (**II**) were synthesized according to the procedure described in [12]. Tetraethylene glycol bis(4-toluenesulfonate) (**III**), pentaethylene glycol bis(4-toluenesulfonate) (**IV**), and 3-hydroxypyridine (**V**) were commercial products (Acros). Individual compounds were isolated by column chromatography on neutral aluminum oxide using methylene chloride–hexane (1:1) as eluent. Organic solvents were purified by standard procedures [13]. The progress of reactions was monitored by TLC on Silufol UV-254 plates. The ^{1}H NMR spectra were recorded on a Bruker VC-200 spectrometer at 200 MHz using benzene-d_6 as solvent and tetramethylsilane as internal reference. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1310 instrument (ion source temperature 150–200°C). The electronic absorption spectra were measured from solutions in toluene and acetonitrile on a Carry-100 spectrophotometer.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{2-[11-(pyridin-3-yloxy)-3,6,9-trioxaundecyloxy]phenyl}porphyrin (VI). Porphyrin **I**, 100 mg (0.12 mmol), and 3-hydroxypyridine (**V**), 12.84 mg (0.12 mmol), were dissolved in 9 ml of a 1:2 dimethylformamide–acetonitrile mixture, 32.51 mg (0.10 mmol) of cesium carbonate and 42.96 mg (0.12 mmol) of tetraethylene glycol bis(4-toluenesulfonate) were added to the solution under argon, and the mixture was stirred for 24 h on heating. The solvent was distilled off under reduced pressure, the residue was treated with a mixture of 30 ml of methylene chloride and 5 ml of 10% hydrochloric acid, and the organic phase was separated, washed with two portions of water, dried over sodium sulfate, and evaporated to a volume of 20 ml. The residue was subjected to chromatography on aluminum oxide using methylene chloride–hexane (1:1) as eluent. The product was recrystallized from CH_2Cl_2–MeOH (1:1). Yield 30.51 mg (27%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (logε): 406.7 (4.92), 507.1 (4.01), 542.5 (3.51), 574.1 (3.77), 628.1 (3.19). ^{1}H NMR spectrum, δ, ppm: 10.02 s (2H, *meso*-H), 9.91 s (1H, *meso*-H), 7.92 d (1H, 2′-H), 7.75 d (1H, 4″-H), 7.69 t (1H, 5″-H), 7.61 t (1H, 3′-H or 5′-H), 7.53 m (2H, 2″-H, 6″-H), 7.42 d (1H, 5′-H or 3′-H), 7.28 t (1H, 4′-H), 3.80 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.26 m (16H, OCH$_2$CH$_2$O), 2.40 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.49 m (8H, C**H**$_2$CH$_3$), 1.24 s (6H, CH$_3$), 1.18 s (6H, CH$_3$), 1.01 t (12H, CH$_2$C**H**$_3$), –2.67 s (2H, NH). Mass spectrum: *m/z* 934.02 $[M]^+$ (I_{rel} 54%).

Found, %: C 75.68; H 8.20; N 7.44. $C_{59}H_{77}N_5O_5$. Calculated, %: C 75.72; H 8.23; N 7.48.

Porphyrins **VII–IX** were synthesized in a similar way.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{3-[11-(pyridin-3-yloxy)-3,6,9-trioxaundecyloxy]phenyl}porphyrin (VII). Yield 26.09 mg (21%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 406.1 (4.89), 507.4 (4.07), 542.9 (3.56), 574.6 (3.81), 629.1 (3.21). ^{1}H NMR spectrum, δ, ppm: 10.05 s (2H, *meso*-H), 9.97 s (1H, *meso*-H), 7.93 d (1H, 6′-H), 7.85 s (1H, 2′-H), 7.77 d (1H, 4″-H), 7.67 t (1H, 5″-H), 7.59 t (1H, 5′-H), 7.51 m (2H, 2″-H, 6″-H), 7.31 t (1H, 4′-H), 3.81 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.28 m (16H, OCH$_2$-CH$_2$O), 2.42 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.51 m (8H, C**H**$_2$CH$_3$), 1.22 s (6H, CH$_3$), 1.16 s (6H, CH$_3$), 1.02 t (12H, CH$_2$C**H**$_3$), –2.65 s (2H, NH). Mass spectrum: *m*/*z* 933.96 $[M]^+$ (I_{rel} 57%). Found, %: C 75.66; H 8.21; N 7.42. $C_{59}H_{77}N_5O_5$. Calculated, %: C 75.72; H 8.23; N 7.48.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{2-[14-(pyridin-3-yloxy)-3,6,9,12-tetraoxatetradecyloxy]phenyl}porphyrin (VIII). Yield 23.19 mg (20%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 406.9 (4.83), 508.1 (4.11), 543.6 (3.52), 575.1 (3.86), 630.1 (3.19). ^{1}H NMR spectrum, δ, ppm: 10.07 s (2H, *meso*-H), 9.96 s (1H, *meso*-H), 7.90 d (1H, 6′-H), 7.71 d (1H, 4″-H), 7.65 t (1H, 5″-H), 7.59 t (1H, 3′-H or 5′-H), 7.51 m (2H, 2″-H, 6″-H), 7.39 d (1H, 5′-H or 3′-H), 7.24 t (1H, 4′-H), 3.79 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.21 m (20H, OCH$_2$CH$_2$O), 2.36 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.45 m (8H, C**H**$_2$CH$_3$), 1.22 s (6H, CH$_3$), 1.15 s (6H, CH$_3$), 1.04 t (12H, CH$_2$C**H**$_3$), –2.61 s (2H, NH). Mass spectrum: *m*/*z* 978.01 $[M]^+$ (I_{rel} 49%). Found, %: C 74.73; H 8.23; N 7.11. $C_{61}H_{81}N_5O_6$. Calculated, %: C 74.77; H 8.27; N 7.15.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{3-[14-(pyridin-3-yloxy)-3,6,9,12-tetraoxatetradecyloxy]phenyl}porphyrin (IX). Yield 20.69 mg (18%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 407.2 (4.87), 508.9 (4.14), 544.2 (3.55), 576.0 (3.87), 630.8 (3.21). ^{1}H NMR spectrum, δ, ppm: 10.01 s (2H, *meso*-H), 9.93 s (1H, *meso*-H), 7.91 d (1H, 6′-H), 7.81 s (1H, 2′-H), 7.74 d (1H, 4″-H), 7.62 t (1H, 5″-H), 7.58 t (1H, 5′-H), 7.52 m (2H, 2″-H, 6″-H), 7.33 t (1H, 4′-H), 3.78 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.22 m (20H, OCH$_2$-CH$_2$O), 2.41 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.55 m (8H, C**H**$_2$CH$_3$), 1.21 s (6H, CH$_3$), 1.12 s (6H, CH$_3$), 0.98 t (12H, CH$_2$C**H**$_3$), –2.61 s (2H, NH). Mass spectrum: *m*/*z* 977.86 $[M]^+$ (I_{rel} 46%). Found, %: C 74.71; H 8.24; N 7.09. $C_{61}H_{81}N_5O_6$. Calculated, %: C 74.77; H 8.27; N 7.15.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{2-[11-(pyridin-3-yloxy)-3,6,9-trioxaundecyloxy]phenyl}porphyrinatozinc(II) (X). Porphyrin **VI**, 30 mg, was dissolved in 70 ml of dimethylformamide, excess zinc(II) acetate (molar ratio 1:10) was added, the mixture was heated for 30 min at the boiling point, cooled, and diluted with an equal volume of water, and the precipitate was filtered off, dried, and subjected to chromatography on aluminum oxide using methylene chloride–hexane (1:1) as eluent. The subsequent recrystallization from methylene chloride–methanol (1:1) gave 30.10 mg (86%) of zinc complex **X**, R_f 0.72 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 409.5 (5.06), 539.7 (4.20), 574.2 (3.89). ^{1}H NMR spectrum, δ, ppm: 10.00 s (2H, *meso*-H), 9.89 s (1H, *meso*-H), 7.90 d (1H, 6′-H), 7.71 d (1H, 4″-H), 7.67 t (1H, 5″-H), 7.58 t (1H, 3′-H or 5′-H), 7.51 m (2H, 2″-H, 6″-H), 7.40 d (1H, 5′-H or 3′-H), 7.26 t (1H, 4′-H), 3.77 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.21 m (16H, OCH$_2$CH$_2$O), 2.36 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.46 m (8H, C**H**$_2$CH$_3$), 1.20 s (6H, CH$_3$), 1.16 s (6H, CH$_3$), 0.96 t (12H, CH$_2$C**H**$_3$). Mass spectrum: *m*/*z* 996.92 $[M]^+$ (I_{rel} 61%). Found, %: C 70.91; H 7.46; N 6.95. $C_{59}H_{75}N_5O_5Zn$. Calculated, %: C 70.94; H 7.51; N 7.01.

Zinc complexes **XI–XIII** were synthesized in a similar way.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{3-[11-(pyridin-3-yloxy)-3,6,9-trioxaundecyloxy]phenyl}porphyrinatozinc(II) (XI). Yield 28.59 mg (81%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 409.1 (5.03), 539.1 (4.22), 574.5 (3.82). ^{1}H NMR spectrum, δ, ppm: 10.03 s (2H, *meso*-H), 9.95 s (1H, *meso*-H), 7.91 d (1H, 6′-H), 7.81 s (1H, 2′-H), 7.75 d (1H, 4″-H), 7.65 t (1H, 5″-H), 7.53 t (1H, 5′-H), 7.49 m (2H, 2″-H, 6″-H), 7.29 t (1H, 4′-H), 3.79 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.24 m (16H, OCH$_2$CH$_2$O), 2.39 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.47 m (8H, C**H**$_2$CH$_3$), 1.20 s (6H, CH$_3$), 1.17 s (6H, CH$_3$), 1.05 t (12H, CH$_2$C**H**$_3$). Mass spectrum: *m*/*z* 997.07 $[M]^+$ (I_{rel} 71%). Found, %: C 70.90; H 7.49; N 6.97. $C_{59}H_{75}N_5O_5Zn$. Calculated, %: C 70.94; H 7.51; N 7.01.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{2-[14-(pyridin-3-yloxy)-3,6,9,12-tetraoxatetradecyl-

oxy]phenyl}porphyrinatozinc(II) (XII). Yield 24.96 mg (78%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 409.6 (5.11), 539.6 (4.27), 574.9 (3.87). ^{1}H NMR spectrum, δ, ppm: 10.01 s (2H, *meso*-H), 9.93 s (1H, *meso*-H), 7.89 d (1H, 6′-H), 7.67 d (1H, 4″-H), 7.60 t (1H, 5″-H), 7.57 t (1H, 3′-H or 5′-H), 7.49 m (2H, 2″-H, 6″-H), 7.37 d (1H, 5′-H or 3′-H), 7.21 t (1H, 4′-H), 3.77 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.19 m (20H, OCH$_2$CH$_2$O), 2.33 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.44 m (8H, C**H**$_2$CH$_3$), 1.20 s (6H, CH$_3$), 1.13 s (6H, CH$_3$), 1.03 t (12H, CH$_2$C**H**$_3$). Mass spectrum, *m*/*z* 1041.21 $[M]^+$ (I_{rel} 52%). Found, %: C 70.20; H 7.56; N 6.69. $C_{61}H_{79}N_5O_6Zn$. Calculated, %: C 70.25; H 7.58; N 6.72.

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5-{3-[14-(pyridin-3-yloxy)-3,6,9,12-tetraoxatetradecyloxy]phenyl}porphyrinatozinc(II) (XIII). Yield 23.19 mg (71%), R_f 0.54 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 409.3 (5.08), 539.1 (4.29), 573.6 (3.90). ^{1}H NMR spectrum, δ, ppm: 10.03 s (2H, *meso*-H), 9.95 s (1H, *meso*-H), 7.94 d (1H, 6′-H), 7.83 s (1H, 2′-H), 7.75 d (1H, 4″-H), 7.61 t (1H, 5″-H), 7.55 t (1H, 5′-H), 7.49 m (2H, 2″-H, 6″-H), 7.31 t (1H, 4′-H), 3.75 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.20 m (20H, OCH$_2$-CH$_2$O), 2.39 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.51 m (8H, C**H**$_2$CH$_3$), 1.19 s (6H, CH$_3$), 1.10 s (6H, CH$_3$), 0.97 t (12H, CH$_2$C**H**$_3$). Mass spectrum: *m*/*z* 1041.01 $[M]^+$ (I_{rel} 69%). Found, %: C 70.21; H 7.55; N 6.68. $C_{61}H_{79}N_5O_6Zn$. Calculated, %: C 70.25; H 7.58; N 6.72.

Complex XIV. Electronic absorption spectrum (toluene), λ_{max}, nm (log ε): 419.1 (5.01), 543.9 (4.21), 576.3 (3.81). ^{1}H NMR spectrum, δ, ppm: 10.01 s (2H, *meso*-H), 9.93 s (1H, *meso*-H), 7.96 d (1H, 6′-H), 7.85 s (1H, 2′-H), 7.71 d (1H, 4″-H), 6.51 t (1H, 5″-H), 6.42 t (1H, 5′-H), 3.25 m (2H, 2″-H, 6″-H), 7.28 t (1H, 4′-H), 3.71 m (8H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.18 m (20H, OCH$_2$CH$_2$O), 2.36 q (8H, C**H**$_2$CH$_2$CH$_3$), 1.50 m (8H, C**H**$_2$CH$_3$), 1.16 s (6H, CH$_3$), 1.08 s (6H, CH$_3$), 0.95 t (12H, CH$_2$C**H**$_3$).

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REFERENCES

1. Koifman, O.I., Mamardashvili, N.Zh., and Antipin, I.S., *Sinteticheskie retseptory na osnove porfirinov i ikh kon"yugatov s kaliks[4]arenami* (Synthetic Receptors Based on Porphyrins and Their Conjugates with Calix[4]arenes), Moscow: Nauka, 2006, p. 246.
2. Mamardashvili, N.Zh. and Koifman, O.I., *Russ. J. Org. Chem*., 2005, vol. 41, p. 787.
3. Mamardashvili, N.Zh. and Golubchikov, O.A., *Usp. Khim*., 2000, vol. 69, p. 337.
4. Wylie, R.S., Levy, E.G., and Sanders, J.K.M., *Chem. Commun*., 1997, p. 1611.
5. Anderson, H.L., Hunter, C.A., Meah, M.N., and Sanders, J.K.M., *J. Am. Chem. Soc*., 1990, vol. 112, p. 5780.
6. Pukhovskaya, S.G., Guseva, L.Zh., Kuvshinova, E.M., Mamardashvili, N.Zh., and Golubchikov, O.A., *Koord. Khim*., 1998, vol. 29, p. 851.
7. Anderson, H.L., Anderson, S., and Sanders, J.K.M., *J. Chem. Soc., Perkin Trans. 1*, 1995, p. 2231.
8. Jokic, D., Asfari, Z., and Weiss, J., *Org. Lett*., 2002, vol. 4, p. 2129.
9. Hunter, C.A., Meah, M.N., and Sanders, J.K.M., *J. Am. Chem. Soc*., 1990, vol. 112, p. 5773.
10. Sheinin, V.B., Ivanova, Yu.B., and Chizhova, N.V., *Zh. Neorg. Khim*., 2004, vol. 49, p. 112.
11. Bernshtein, I.Ya. and Kaminskii, Yu.L., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectrophotometric Analysis in Organic Chemistry), Leningrad: Khimiya, 1986, p. 200.
12. Mamardashvili, N.Zh., Abstracts of Papers, *XXV nauchnaya sessiya Vserossiiskogo seminara po khimii porfirinov i ikh analogov* (XXVth Scientific Session of the All-Russian Seminar on the Chemistry of Porphyrins and Their Analogs), Ivanovo, 2004, p. 13.
13. *Organikum. Organisch-chemisches Grundpraktikum*, Berlin: Wissenschaften, 1976, 15th edn. Translated under the title Organikum, Moscow: Mir, 1979, vol. 2, p. 422.