

Dimeric and Trimeric Supramolecular Systems Formed by Donor–Acceptor Interactions of Zn^{II}, Mn^{III}, and Sn^{IV} Porphyrin Complexes

E. M. Kuvshinova*, O. V. Gornukhina, A. S. Semeikin, and O. A. Golubchikov

Ivanovo State University of Chemistry and Technology, Sheremetevskii pr. 7, Ivanovo, 153000 Russia

*e-mail: kuvshinovae@isuct.ru

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Abstract—The paper presents the methods of synthesis of dimeric and trimeric compounds formed by donor–acceptor interactions of Zn^{II}, Mn^{III}, and Sn^{IV} porphyrin complexes. The structure of the porphyrin ensembles was determined by ¹H NMR spectroscopy. The extra coordination properties of the synthesized dimeric and trimeric supramolecular systems in relation to nitrogen-containing compounds were studied and the stability constants of the resulting porphyrin extra complexes were determined.

Keywords: porphyrins, metal porphyrins, supramolecular systems, donor–acceptor interactions

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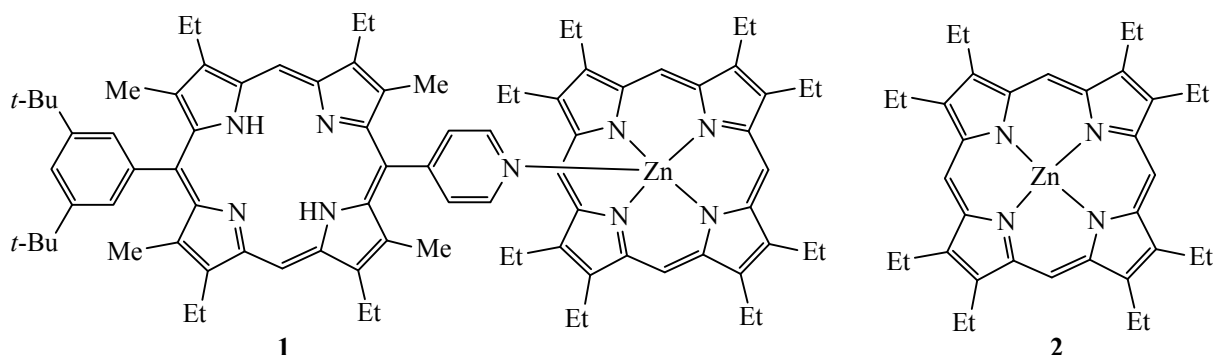
Synthesis and study of dimeric, trimeric, and oligomeric derivatives of macroheterocyclic compounds have attached are receiving much attention all over the world. The results of numerous experimental works in this field have been summarized in a number of monographs [1–4]. Supramolecular porphyrin systems are not only of theoretical interest: they are also considered as a basis for the design of new materials with practically useful properties, for example, light sensors, catalysts, materials with nonlinear optical properties, etc. [5–8]. Quite a promising platform for the design of tetrapyrrole supramolecular systems is provided by coordinately unsaturated metal porphyrins which can react with a great variety of macrohetero-

cyclic compounds containing peripheral electron-donor functional groups. Of key importance for the formation of stable axial complexes of metal porphyrins are the charge of the metal and the nature of the extra ligand [9].

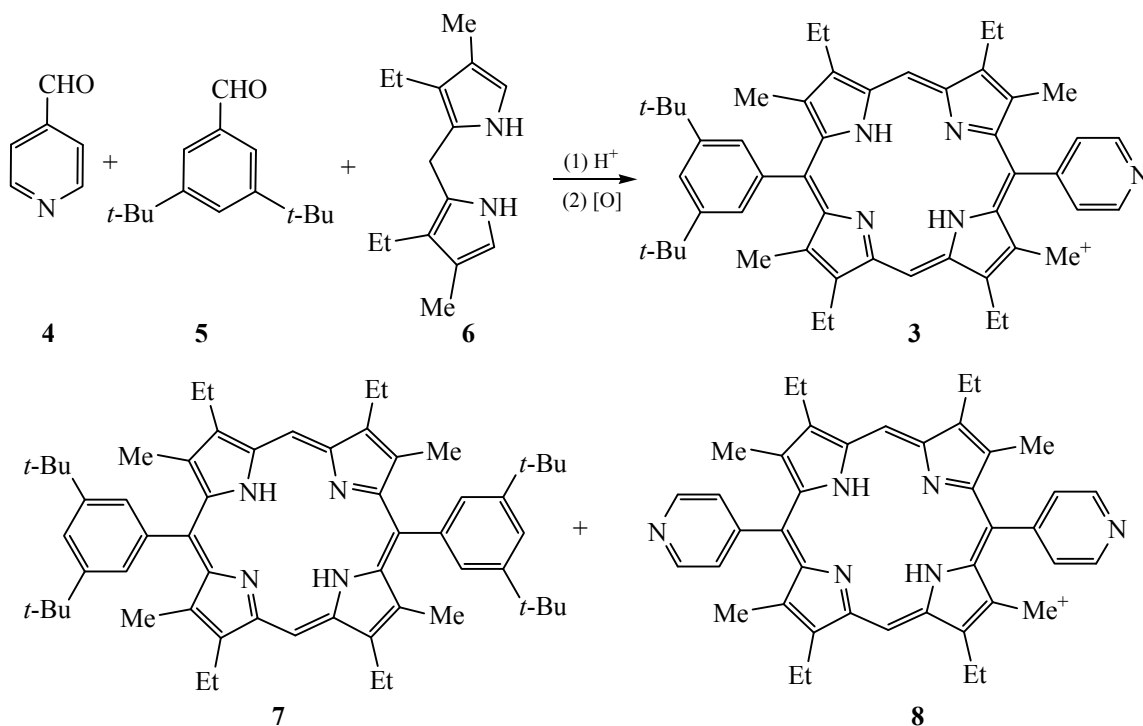
In the present paper we describe the synthesis and properties of dimeric and trimeric compounds formed by donor–acceptor interactions of Zn^{II}, Mn^{III}, and Sn^{IV} porphyrin complex.

Dimeric porphyrin **1** was synthesized by the coordination of zinc 2,3,7,8,12,13,17,18-octaethylporphyrin complex **2** to 15-(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-(pyridin-4-yl)porphyrin (**3**) (Schemes 1, 2).

Scheme 1.



Scheme 2.



The key starting material porphyrin **3** was synthesized by the mixed-aldehyde condensation of pyridine-4-carbaldehyde (**4**) and 3,5-di-*tert*-butylbenzaldehyde (**5**) with 2,2'-methylenebis(3-ethyl-4-methyl-1*H*-pyrrole) (**6**).

Along with porphyrin **3**, the condensation reaction gave as by-products symmetrical 5,15-bis(3,5-di-*tert*-

butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**7**) and 3,7,13,17-tetramethyl-2,8,12,18-tetraethyl-5,15-di(pyridin-4-yl)porphyrin (**8**).

The resulting mixture of porphyrins was separated by column chromatography.

The starting 2,2'-methylenebis(3-ethyl-4-methyl-1*H*-pyrrole) (**6**) was synthesized from 2,2'-methylene bis[3-ethyl-5-(ethoxycarbonyl)-4-methyl-1*H*-pyrrole] by its combined hydrolysis and decarboxylation in ethylene glycol. The resulting compound **6** was used without further purification.

Systematic research into the extra coordination of metal porphyrins to nitrogen-containing molecules showed that zinc porphyrins form fairly stable penta-coordinated complexes with pyridine, piperidine, and other nitrogenous bases. The complex formation was accompanied by large red shifts of bands in the electronic absorption (EA) spectra (Fig. 1).

The stability constants (K_s) of planar Zn porphyrin extra complexes vary in the range $(4-6) \times 10^3$ L/mol depending on the electronic effects of the substituents [2, 9-11]. This allowed spectral detection of molecular complex **1** formed by the donor-acceptor interaction of zinc complex **2** with porphyrin **3**. The bands of the complex appeared in the EA spectrum after con-

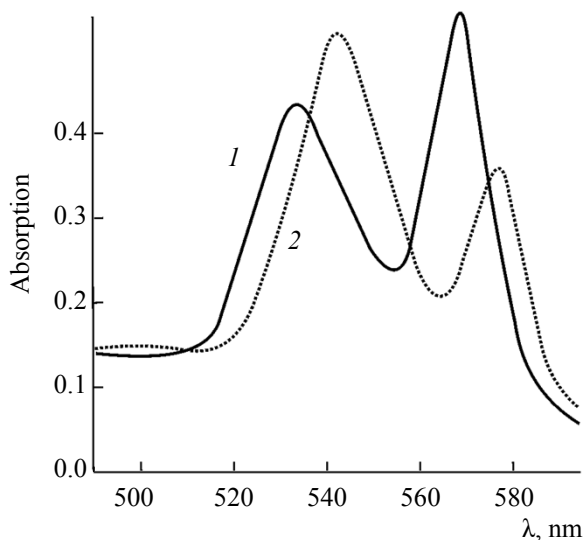


Fig. 1. EA spectra of zinc octaethylporphyrin in (1) benzene and (2) benzene containing 0.2 M pyridine.

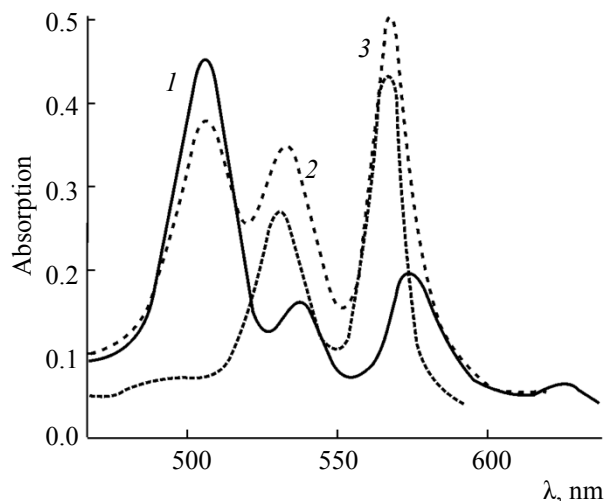


Fig. 2. EA spectra in benzene: (1) 15-(3,5-di-*tert*-butyl-phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-(pyridin-4-yl)porphyrin; (2) zinc octaethylporphyrin; and (3) coordination dimer **1**.

centrated (1×10^{-5} – 2.5×10^{-5} M) solutions of **2** and **3** had been mixed in a 1 : 2 ratio and the mixture allowed to stand under argon. Analytical TLC of the mixture gave three bands, two of which were assigned to zinc complex **2** and ligand **3**. The second, medium band was isolated and characterized spectrally (Fig. 2).

Table 1 lists the characteristics of the EA spectrum and R_f values.

Excess nitrogen-containing reagents, for example, pyridine, destroyed the molecular ensemble. The EA spectrum in this case looked like the superposition of the spectra of **2** and **3** (as pyridinate). The thin-layer chromatogram no longer contained the second band.

The stability constant of the coordination dimer was estimated using the current concentrations of the reagents in the course of spectral changes:

$$K_{st} = 9 \times 10^6 \text{ L/mol.}$$

It should be noted that the stability complex of the dimeric complex is 3–4 orders of magnitude higher compared to those of usual zinc porphyrin extra complexes.

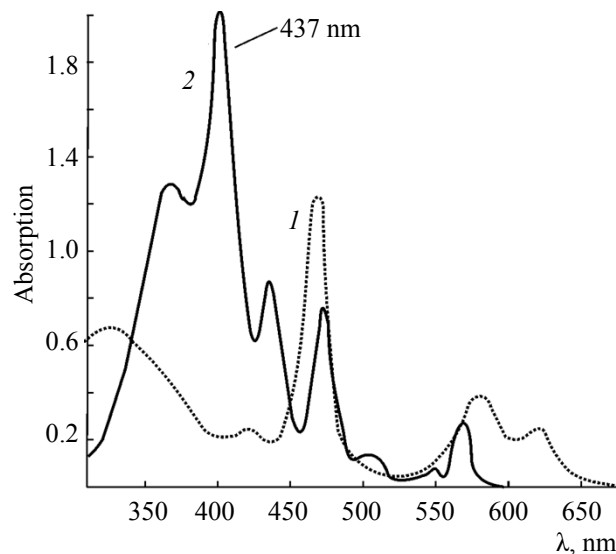


Fig. 3. EA spectra of (1) porphyrin **9** and (2) mixture of porphyrins **9** and **10** in chloroform

The EA spectra of manganese porphyrin complexes having the central atom in different oxidation states strongly differ from each other, which is used for identification purposes [12]. The manganese cation is most frequently present in the stable oxidation state +3. Mn^{III} porphyrins have a characteristic so-called hyper-type EA spectrum with a strong $\pi \rightarrow d$ charge-transfer band in the shortwave region and a great number of well-resolved bands in the near-IR region. An example of a typical EA spectrum is provided by the spectrum of ClMn 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin (**9**) (Fig. 3, curve 1). Mixing solutions of **9** and 2,8,12,18-tetrabutyl-15-(4-hydroxyphenyl)-3,7,13,17-tetramethyl-5-phenylporphyrin (**10**) (Scheme 3) (solvent chloroform, solution concentrations $\sim 10^{-4}$ M) in a 1 : 1 ratio leads to appearance of a new EA band near 437 nm (Fig. 3, curve 2).

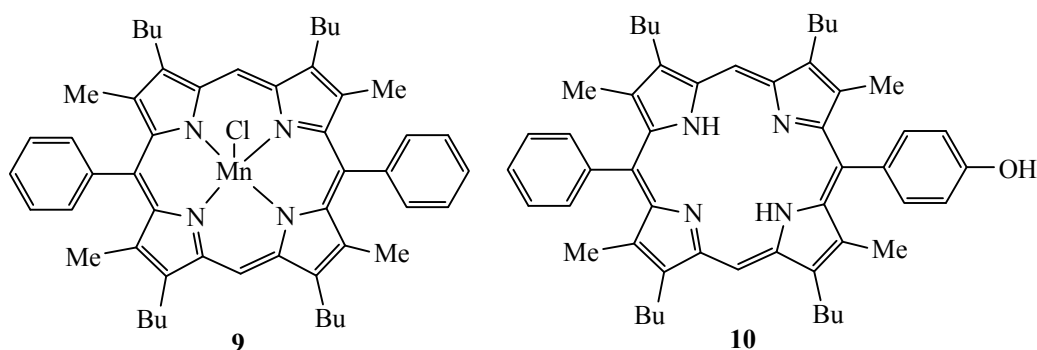
As pyridine is added, the band at 437 nm attenuates until it disappears completely, and the EA spectrum takes the form of a superposition of the spectra of the reagents. This fact suggests that the two porphyrin

Table 1. EA spectra of porphyrins **1**–**3** in benzene at 298 K

| Porphyrin | λ , nm (log ϵ) | | | | | R_f^a |
|-----------|----------------------------------|-----------|-----------|-----------|-----------|---------|
| | | | | | | |
| 1 | | 575 | 539 | 506 | 412 | 0.46 |
| 2 | 625(3.61) | 573(3.79) | 540(3.96) | 507(4.36) | 407(5.39) | 0.21 |
| 3 | – | 568(4.12) | 530(3.93) | – | 403(5.19) | 0.85 |

^a Developer benzene–chloroform (1 : 1) + 2% EtOH.

Scheme 3.



macrocycles react by way of extra coordination to form supramolecular structure **11** via manganese–oxygen bonding.

Thin-layer chromatography of the mixture of **9** and **10** on Alufol plates (eluent 1 : 1 chloroform–benzene + 0.5% ethanol) gave two bands. The spectrum of the first band corresponded to porphyrin **10**, and the spectrum of the second band, to molecular complex **11**.

The addition of a solution of phenol in chloroform ($c = 1.35 \times 10^{-2}$ M) to a solution of **11** leads to minor changes in the EA spectrum (bathochromic shifts of the charge-transfer and *I* bands: 475 → 478 and 555 → 566, respectively); no new bands appear. However, the addition of sodium phenolate in alkaline medium results in disappearance of the band at 477 nm and appearance of new bands at 426 and 437 nm, which suggests redox processes. Similar spectra with a maximum at 437 nm are characteristic of Mn(II) porphyrin complexes [12–14]. We can suggest that the molecular dimer formation in the present case involves the change of the oxidation state of manganese from Mn^{III} in **11** to Mn^{II} and stabilization of the latter state by the porphyrin macrocycle with a peripheral phenoxy group.

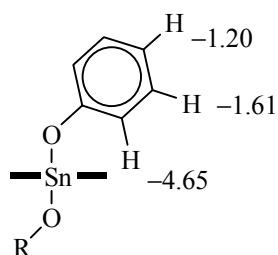


Fig. 4. Relative chemical shifts ($\Delta\delta$) of the proton signals of the phenoxy group in the complex $[\text{SnTTP}(\text{OC}_6\text{H}_5)_2]$ (300 MHz).

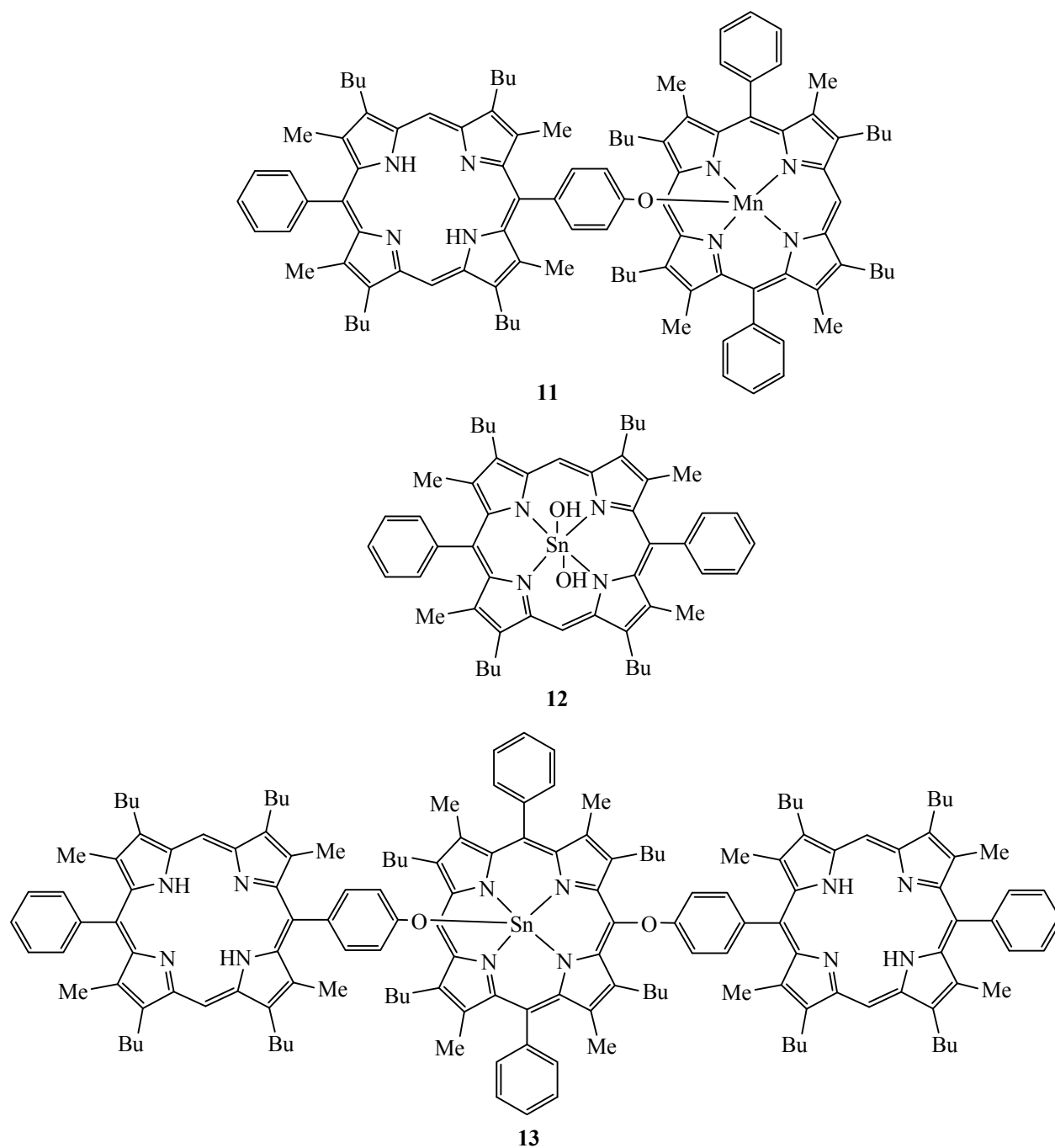
As known, Sn^{IV} in its coordination compounds with porphyrins shows a high affinity to oxygen-containing extra ligands [15] (Scheme 4).

We made use of this property to prepare trimeric molecular ensemble **13** by reacting Sn(II) 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin **12** and 2,8,12,18-tetrabutyl-15-(4-hydroxyphenyl)-3,7,13,17-tetramethyl-5-phenylporphyrin (**10**). The synthesis was performed by mixing benzene solutions of porphyrin **10** ($c = 6.6 \times 10^{-5}$ M) and complex **12** ($c = 6.2 \times 10^{-5}$ M) in a 2 : 1 ratio. The mixture was stirred for 8 h under argon. Thin-layer chromatography of the resulting mixture gave three bands which were isolated and characterized by spectral methods (see Experimental).

The structure of molecular ensemble **13** was determined using the ¹H NMR spectra and published chemical shifts the *ortho*- and *meta*-protons of the phenoxy group coordinated to metal porphyrins: $\Delta\delta = \delta(\text{complex}) - \delta(\text{phenol})$ (Fig. 4). The chemical shifts of the proton signals of coordination trimer **13**, porphyrin **9**, and complex **12** are compared in Table 2. The presence of the electron-donor OH group in one of the phenyl groups in porphyrin **10** increases the electron density, thereby enhancing proton shielding. The proton signals of the substituted ring are shifted upfield compared to those of an unsubstituted phenyl ring and appear at 6.67–6.71 ppm (*o*-H with respect to oxygen) and 7.34 ppm (*m*-H with respect to oxygen).

In molecular ensemble **13**, the porphyrin phenoxy group protons are shielded by the metal porphyrin macrocyclic current. The signals of these protons are strongly shifted upfield with respect to those in uncoordinated porphyrin **10** and appear at 2.64 ppm (2H, *ortho* with respect to oxygen) and 7.07 ppm (2H; *meta* with respect to oxygen). These findings provide

Scheme 4.



evidence for the interaction of the oxygen atom with the coordination center of the Sn complex and, consequently, formation of a trimeric structure.

EXPERIMENTAL

The electronic absorption spectra were measured on Hitachi U-2000 and Shimadzu UV-1800 scanning spectrophotometer in the range 300–900 nm at 298 K,

using quartz ground glass stoppered cells. The wavelength settings were accurate to within ± 0.1 nm and reproducible to within ± 0.002 nm (by wavelength); the photometric accuracy was ± 0.002 nm.

The ^1H NMR spectra were recorded on a Bruker-200 spectrometer at 200 MHz in CDCl_3 (internal standard TMS).

Table 2. ^1H NMR data for porphyrins **10**, **12**, and **13** in CDCl_3

| Porphyrin | NH | $\beta\text{-CH}_3$ | <i>ms</i> -H | β -Alk | Phenyl H |
|-----------|--------------|--|-----------------------------|--|--|
| 10 | -2.40 s (2H) | 2.53 s (6H) 2.45 s (6H) | 10.21 s (2H) | 3.97 t (8H) 2.14 quintet (8H) 1.73 sextet (8H) 1.10 t (12H) | 8.06 m (2H, <i>o</i> -H) 7.93 m (3H, <i>m</i> , <i>p</i> -H) 6.71–6.67 d (2H, <i>o</i> -H to OH) 7.34 d (2H, <i>m</i> -OH) |
| 12 | – | 2.46 s (6H) 2.53 s (6H) 2.55 s (12H) | 10.22 s (2H) 10.6 s (2H) | 3.93–4.02 m (16H) 2.23 m (16H) 1.78 sextet (16H) 1.11 m (24H) | 2.64 s (2H, <i>o</i> -H to OH) 7.07 m (2H, <i>m</i> -H to OH) 7.82 m (3H, <i>m</i> , <i>p</i> -H) 8.07 m (2H, <i>o</i> -H) |
| 13 | -2.40 s (2H) | 2.52 s (12H) | 10.55 s (2H) | 4.02 t (8H) 2.25 quintet (8H) 1.80 sextet (8H) 1.15 t (12H) | -4.95 d (4H, <i>o</i> -H) -1.61 t (4H, <i>m</i> -H) -1.20 t (4H, <i>p</i> -H) |

Solvents (benzene, chloroform, pyridine, DMF) were purified by published procedures [15, 16].

Porphyrins **11** and **12** were synthesized by published procedures [17, 18].

Thin-layer chromatography was performed on alumina (Brockmann activity grade III).

Zinc(II) 2,3,7,8,12,13,17,18-octaethylporphyrin (2). A boiling solution of 2.0 g (3.68 mmol) of 2,3,7,8,12,13,17,18-octaethylporphyrin was poured into a solution of 1.3 g (4.9 mmol) of zinc acetylacetonate in 150 mL of methylene chloride, the mixture was refluxed for 1 h, reduced to 100 mL, cooled down, the complex that precipitated was filtered off, washed with methylene chloride, and dried in air at 70°C. Yield 1.7 g. The filtrate was reduced by half and chromatographed on alumina, eluent methylene chloride. The eluate was evaporated, and the product was precipitated with methanol. Yield 0.3 g. Total yield 2.0 g (90.9 %). R_f (Silufol): 0.85 (1 : 1 benzene–chloroform + 2% ethanol). EA spectrum, λ_{max} , nm (log ϵ): 568 (4.12); 530 (3.93); 403 (5.19) (chloroform). ^1H NMR spectrum, δ , ppm: 10.07 s (4H, *ms*-H); 3.98 q (16H, CH_2CH_3); 1.70 t (24H, CH_2CH_3).

2,2'-Methylenebis(3-ethyl-4-methyl-1H-pyrrole) (6). A mixture of 1 g 2,2'-methylenebis[3-ethyl-5-(ethoxycarbonyl)-4-methyl-1H-pyrrole], 0.1 g of hydrazine sulfate, 1 g of potassium hydroxide, and 30 mL of ethylene glycol was refluxed for 1 h and then poured into 200 mL of water, left to stand at room temperature for 3 h, the precipitate was filtered off, washed with water, and dried at room temperature. Yield 0.56 g (2.43 mmol). The product was further used without purification.

15-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5-(pyridin-4-yl)porphyrin (3). A solution of 0.45 g (4.79 mmol) of chloroacetic acid in 20 mL of methylene chloride was added with stirring under CO_2 at room temperature to a solution of 0.56 g (2.43 mmol) of compound **6**, 0.13 g (1.22 mmol) of pyridine-4-carbaldehyde (**4**), and 0.26 g (1.22 mmol) of 3,5-di-*tert*-butylbenzaldehyde (**5**) in 150 mL of methylene chloride. The mixture was stirred for 4 h under light-proof conditions, after which a solution of 0.9 g (3.66 mmol) of *p*-chloranil in 20 mL of THF was added. The resulting mixture was stirred for 16 h at room temperature, and the solvent was removed completely on a rotary evaporator. The residue was stirred with 5% KOH, the precipitate was filtered off, washed with water, and dried in air at 70°C. The porphyrin mixture was dissolved in chloroform and chromatographed on alumina, eluent chloroform. The first band contained 5,15-bis(3,5-di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (**7**), the second band contained the target compound **3**, and the last eluted was 2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-5,15-di(pyridin-4-yl)porphyrin (**8**). For further purification the eluate of the second band was reduced to a small volume and subjected to repeated chromatography under the same conditions. The eluate was evaporated, the product was precipitated with methanol, filtered off, washed with ethanol, and dried in air at 70°C. Yield 0.20 g (22%). EA spectrum, λ_{max} , nm (log ϵ): 625 (3.68); 573 (4.06); 540 (3.98); 507 (4.36); 408 (5.39) (chloroform). ^1H NMR spectrum, δ , ppm: 10.20 s (2H, *ms*-H); 8.95 d (2H, α -H); 8.06 d (2H, β -H); 7.84 d (2H, *o*-H); 7.74 t (1H, *p*-H); 3.95 q (8H, CH_2CH_3); 2.46 s (6H, 13,17- CH_3); 2.39 s (6H,

3,7-CH₃); 1.71 t (12H, CH₂CH₃); 1.49 s (18H, *t*-Bu); -2.52 s (2H, NH) (CDCl₃).

15-(3,5-Di-*tert*-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (7). *M*_r 855.312. *R*_f (Silufol): 0.80 (benzene–hexane, 1 : 1). EA spectrum, λ_{max}, nm (log ε): 626 (3.26); 574 (3.90); 542 (3.73); 509 (4.27); 410 (5.40) (chloroform). ¹H NMR spectrum (CDCl₃), δ, ppm: 10.21 s (2H, *ms*-H); 7.91 d (4H, *J* = 1.6 Hz, 2,6-H-Ar); 7.86 t (2H, *J* = 1.6 Hz, 4-H-Ar); 4.03 q (8H, ¹*J* = 7.5 Hz, CH₂-Et); 2.45 s (12H, CH₃); 1.76 t (12H, *J* = 7.5 Hz, CH₃-Et); 1.49 s (36H, *t*-Bu); -2.45 br.s (2H, NH).

2,8,12,18-Tetraethyl-3,7,13,17-tetramethyl-5,15-di(pyridin-4-yl)porphyrin (8). *M*_r 632.856. *R*_f (Silufol): 0.39 (benzene–methanol, 10 : 1). EA spectrum (chloroform), λ_{max}, nm (log ε): 625 (3.48); 574 (3.88); 540 (3.85); 507 (4.23); 408 (5.32). ¹H NMR spectrum (CDCl₃), δ, ppm: 10.28 s (2H, *ms*-H); 9.04 d.d (2H, *J* = 5.8 Hz, ¹*J* = 1.5 Hz, 3',5'-H-Py); 8.11 d.d (2H, *J* = 5.8 Hz, ¹*J* = 1.5 Hz, 2',6'-H-Py); 4.03 q (8H, ²*J* = 7.7 Hz, CH₂-Et); 2.53 s (12H, CH₃); 1.80 t (12H, ²*J* = 7.7 Hz, CH₃-Et); -2.45 br.s (2H, NH).

2,8,12,18-Tetrabutyl-15-(4-hydroxyphenyl)-3,7,13,17-tetramethyl-5-phenylporphyrin (10). A solution of 0.45 g (4.79 mmol) of chloroacetic acid in 20 mL of methylene chloride was added at room temperature under argon to a stirred solution of 0.52 g (1.82 mmol) of compound **6** (prepared from 1.0 g of 2,2'-methylenebis[3-ethyl-5-(ethoxycarbonyl)-4-methyl-1*H*-pyrrole], yield 78,2 %), 0.12 g (0.98 mmol) of 4-hydroxybenzaldehyde, and 0.1 mL (0.99 mmol) of benzaldehyde in 150 mL of methylene chloride. The mixture was stirred for 4 h under light-proof conditions, after which a solution of 0.7 g (2.84 mmol) of *p*-chloranil in 20 mL of THF was added. The resulting mixture was stirred for 16 h at room temperature, and the solvent was removed completely on a rotary evaporator. The porphyrin mixture was dissolved in chloroform and chromatographed on alumina. The first band contained 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin, yield 0.23 g (33.3%), the second band contained the target compound **10**, yield 0.25 g (36.2%), and the last eluted was 2,8,12,18-tetrabutyl-5,15-bis(4-hydroxyphenyl)-3,7,13,17-tetramethylporphyrin, yield 0.08 g (11.3%). For further purification the eluate of the second band was reduced to a small volume and subjected to repeated chromatography under the same conditions. The eluate was evaporated, the product was precipitated with

methanol, filtered off, washed with ethanol, and dried in air at 70°C.

Compound 10. *M*_r 759.095. *R*_f (Silufol): 0.19 (chloroform); 0.20 (0.25) (1 : 1 benzene–chloroform + 2% ethanol). EA spectrum (chloroform), λ_{max}, nm (log ε): 626 (3.36); 575 (3.89); 542 (3.78); 509 (4.24); 411 (5.33). ¹H NMR spectrum (CDCl₃), δ, ppm: 10.21 s (2H, *ms*-H); 8.06 d (2H, *J* = 7.2 Hz, 2,6-H-Ph); 7.93 d (2H, ¹*J* = 8.0 Hz, 2,6-H-Ar); 7.71–7.67 m (3H, 3,4,5-H-Ph) 7.34 d (2H, ¹*J* = 8.0 Hz, 3,5-H-Ar); 2.53 s, 2.45 s (2×6H, CH); 3.97 t (8H, ²*J* = 7.5 Hz, CH₂-Bu); 2.14 q (8H, ²*J* = 7.5 Hz, CH₂-Bu); 1.73 sextet (8H, ²*J* = 7.5 Hz, CH₂-Bu); 1.10 t (12H, ²*J* = 7.5 Hz, CH₃-Bu); -2.40 br.s (2H, NH).

2,8,12,18-Tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin. *M*_r 743.096. *R*_f (Silufol): 0.50 (benzene–heptane, 1 : 1); 0.87 (chloroform). EA spectrum (chloroform), λ_{max}, nm (log ε): 625 (3.42); 574 (3.84); 541 (3.73); 507 (4.20); 409 (5.31). ¹H NMR spectrum (CDCl₃), δ, ppm: 10.27 s (2H, *ms*-H); 8.09 d (4H, *J* = 7.2 Hz, 2,6-H-Ph); 7.80 t (2H, *J* = 7.2 Hz, 4-H-Ph); 7.76 t (4H, *J* = 7.2 Hz, 3,5-H-Ph); 4.01 t (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 2.51 s (12H, CH₃); 2.19 q (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 1.77 sextet (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 1.12 t (12H, ¹*J* = 7.4 Hz, CH₃-Bu); -2.37 br.s (2H, NH).

2,8,12,18-Tetrabutyl-5,15-bis(4-hydroxyphenyl)-3,7,13,17-tetramethylporphyrin. *M*_r 775.094. *R*_f (Silufol): 0.07 (chloroform). EA spectrum (chloroform), λ_{max}, nm (log ε): 626 (3.04); 574 (3.56); 543 (3.46); 509 (3.90); 410 (5.00). ¹H NMR spectrum (CDCl₃-CF₃COOH), δ, ppm: 10.19 s (2H *ms*-H); 8.06 d (4H, *J* = 8.1 Hz, 2,6-H-Ar); 7.47 d (4H, *J* = 8.1 Hz, 3,5-H-Ar); 2.27 s (12H, CH₃); 3.67 t (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 1.71 q (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 1.43 sextet (8H, ¹*J* = 7.4 Hz, CH₂-Bu); 0.91 t (12H, ¹*J* = 7.4 Hz, CH₃-Bu); -2.70 br.s (4H, NH).

Manganese 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin chloride (9) was synthesized by the reaction of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin with a 10-fold excess of manganese chloride in DMF under reflux for 8 h. The reaction mixture was then diluted by half with chloroform, and excess manganese chloride removed by washing with water. The target complex was purified by chromatography on alumina, eluent chloroform. EA spectrum (chloroform), λ_{max}, nm (log ε): 567 (4.00); 477 (4.78); 365 (4.84).

Tin(II) 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin chloride (12) was synthesized by the reaction of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin with a 10-fold excess of tin chloride in DMF under reflux for 10 h. The solvent was removed in a vacuum. The tin complex was extracted from the residue and purified by chromatography on alumina, eluent chloroform. The solution of tin(IV) 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin dichloride in chloroform was successively washed with aqueous ammonia and water. The resulting dihydroxytin(IV) 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-diphenylporphyrin was chromatographed on silica, eluent chloroform R_f (Silufol): 0.15 (1 : 1 benzene–chloroform +2% ethanol). EA spectrum, λ_{\max} , nm (log ϵ): 580 (3.69); 547 (4.36); 507 sh; 420 (5.57).

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REFERENCES

- Sanders, J.K.M., Bampos, N., Clude-Watson, Z., Darling, S.L., Hawley, J.C., Kim, H.-J., Mak, C.C., and Webb, S.J., *The Porphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., Eds., New York: Academic, 2000, vol. 3, p. 1.
- Ageeva, T.A., Koifman, O.I., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Peterb. Gos. Univ., 2004, vol. 4, p. 218.
- Mamardashvili, G.M., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Peterb. Gos. Univ., 2007, vol. 5, p. 168.
- Tsvadze, A.Yu., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Peterb. Gos. Univ., 2007, vol. 5, p. 198.
- Wasielowski, M.R., *Chem. Rev.*, 1992, vol. 92, no. 3, p. 435. doi 10.1021/cr00011a005
- Zen'kevich, E.I., Shul'ga, A.M., Sagun, E.I., von Borczyskowski, C., Rempel, U., and Chernook, A.V., *Uspekhi khimii porfirinov* (Advances in Porphyrin Chemistry), Golubchikov, O.A., Ed., St. Petersburg: Sankt-Peterb. Gos. Univ., 1997, vol. 1, p. 270.
- Sessler, J.L., Wang, B., and Harriman, A., *J. Am. Chem. Soc.*, 1995, vol. 117, p. 704. doi 10.1021/ja00107a014
- Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
- Zielenkiewicz, W., Lebedeva, N.Sh., Kaminski, M., Antina, E.V., and Vyugin, A.I., *J. Thermal Anal. Calorim.*, 1999, vol. 58, p. 741. doi 10.1023/A:1010133318556
- Berezin, B.D. and Koifman, O.I., *Rus. Chem. Rev.*, 1980, vol. 49, no. 12, p. 1188. doi org/10.1070/RC1980v049n12ABEH002537
- Karmanova, T.V., Koifman, O.I., and Berezin, B.D., *Koord. Khim.*, 1983, vol. 9, no. 6, p. 772.
- Klyueva, M.E., *Doctoral (Chem.) Dissertation*, Ivanovo, 2006.
- Gonzalez, B., Kouba, J., Yee, S., Kirner, J.F., Scheidt, W.R., *J. Am. Chem. Soc.*, 1975, vol. 97, no. 11, p. 3247. doi 10.1021/ja00844a070
- Valentine, J.S. and Quinn, A.E., *Inorg. Chem.*, 1976, vol. 15, no. 8, p. 1997. doi 10.1021/ic50162a058
- Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
- Organic Solvents*, Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., Eds., New York: Wiley, 1955.
- Syrbu, S.A., Lyubimova, T.V., and Semeikin, A.S., *Russ. J. Gen. Chem.*, 2001, vol. 71, no. 10, p. 1656.
- Syrbu, S.A. and Semeikin, A.S., *Russ. J. Org. Chem.*, 1999, vol. 35, no. 8, p. 1236.