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Self-Organization of Zinc(II) and Tin(IV) Porphyrinates into Supramolecular Trimers

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Abstract—New hybrid porphyrinic oligomers have been obtained via simultaneous coordination of OH group of zinc(II) hydroxyporphyrinate to the central cation of tin(IV) aminoporphyrinate and coordination of NH_2 group of tin(IV) aminoporphyrinate to the central cation of zinc(II) hydroxyporphyrinate; the formed oligomers have been characterized by a complex of physicochemical methods.

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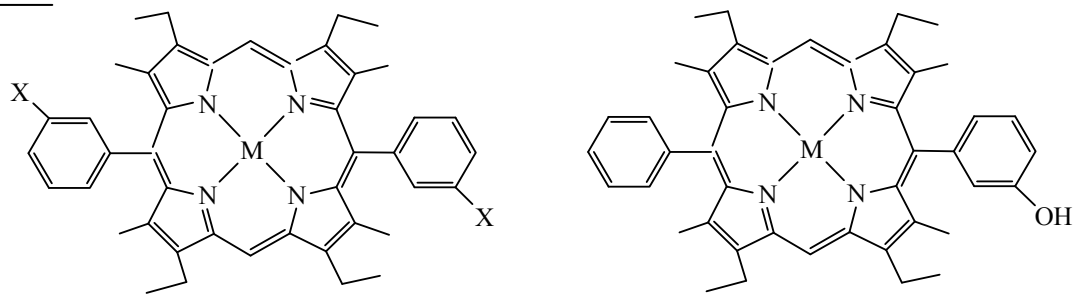
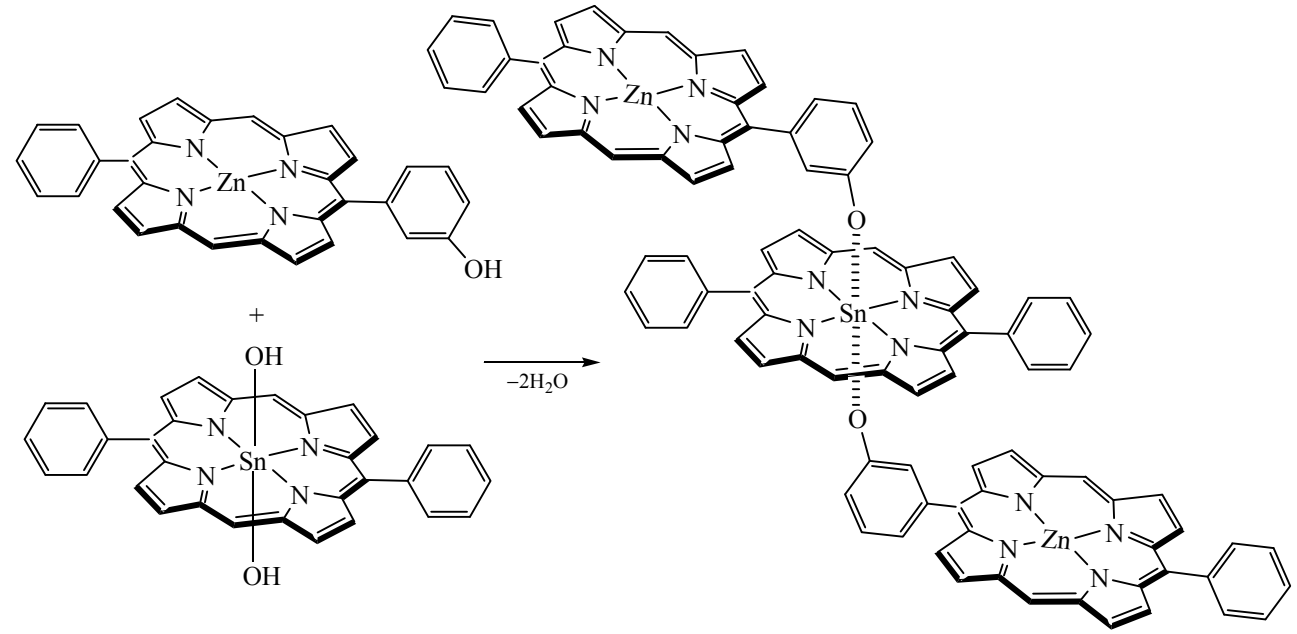
The ability of tin(IV) porphyrinates to coordinate two phenol molecules simultaneously makes it possible to use them as a scaffold of hybrid porphyrin oligomers and dendrimers. Despite numerous descriptions of the supramolecular porphyrinic ensembles available in the literature [1–6], the construction of polyfunctional tetrapyrrole supramolecular dendrimers with useful utilitarian complex formation and photochemical properties has still remained a topical task. The most attractive approach to the construction of photoactive porphyrinic ensembles is probably a method based on the ability of coordination-unsaturated metal porphyrinates to axially coordinate additional electron-donor molecules or molecule fragments [7–11]. This work was aimed at the construction of the porphyrinic trimers via coordination of the OH group of zinc(II) porphyrinate to the central cation of tin(IV) aminoporphyrinate and simultaneous coordination of the NH_2 group of tin(IV) aminoporphyrinate to the central cation of zinc(II) hydroxyporphyrinate.



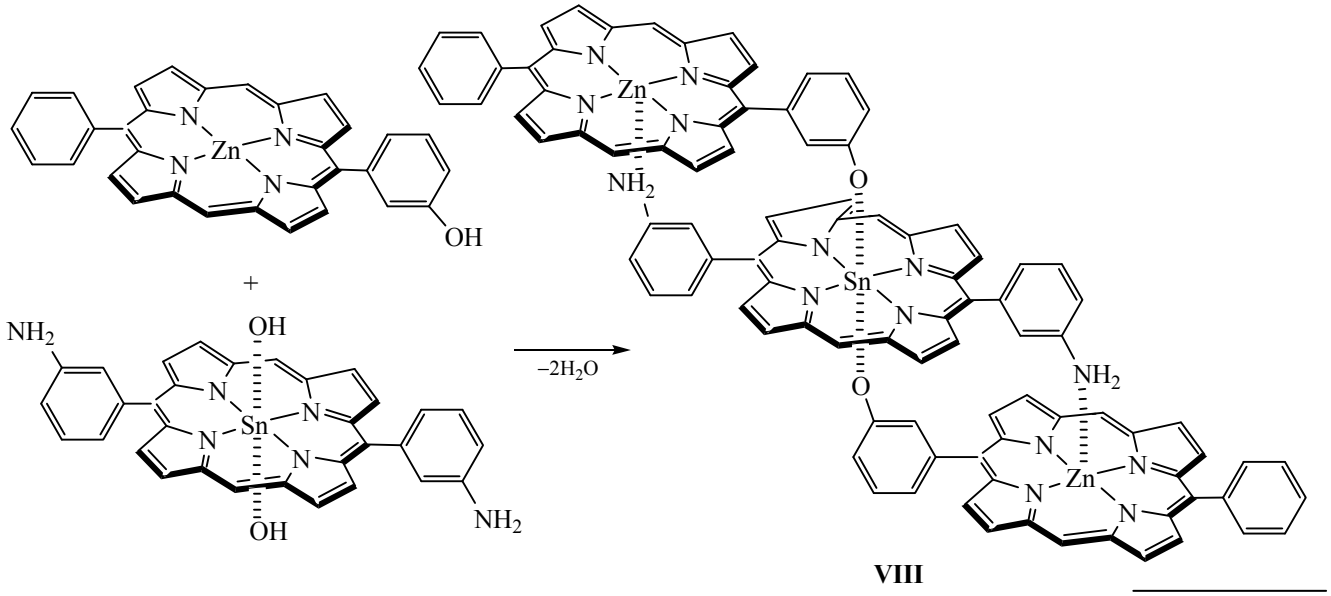
M = H_2 (**I, II, V**), $Sn(OH)_2$ (**III, IV**), Zn (**VI**); X = H (**I, III**), NH_2 (**II, IV**).

Supramolecular complexes **VII** and **VIII** were obtained by boiling tin porphyrinates **III** and **IV** with excess of zinc porphyrinate **VI** in benzene. Complexes **VII** and **VIII** were purified by column chromatography and recrystallization from mixture of dichloromethane–methanol 9:1. Tin porphyrinates **III** and **IV** acted as the tetrapyrrole scaffolds of the complexes **VII** and **VIII**, zinc hydroxyporphyrinate **VI** was axially coordinated to that scaffolds. In the case of complex **VII** the self-assembly was achieved due to Sn–O bonds, whereas in the case of complex **VIII** the assembly occurred due to simultaneous formation of the bonds Sn–O and Zn–N.

Significant differences of the electron absorption spectra of the complexes **VII** and **VIII** (see table and Fig. 1) indicated the different spatial organization of the porphyrinic fragments in those compounds. The



VII



VIII

relatively large blue shift and a noticeable broadening of the Soret band in the case of complex **VIII** as compared with the initial monomeric porphyrins showed that in **VIII** all three porphyrin fragments occurred in the cyclophane orientation which allowed exciton interaction between the π-electronic systems of the macrocycles. The *edge-over-edge* orientation [12] in this oligomer, apart from the hydroxy groups of zinc porphyrinates coordination to tin porphyrinates, was assured by additional donor-acceptor bonding between tin porphyrinate amino groups and the coordination-unsaturated zinc atom of the zinc porphyrinate. The blue shift, resulting in this case from the cyclophane orientation, prevailed over the red shift due to amino groups coordination to zinc.

The electron absorption spectrum of **VII** was a sum of two porphyrinic monomers spectra, which according to the literature data indicated weak mutual influence of the porphyrinic fragments in the complex. The single-centered binding of the porphyrinic fragments did not provided likely their fixation in the parallel planes, and the π-electronic systems conjugation in the complex **VII** did not occur due to mobile conformation.

Electron absorption spectra of porphyrinates (**III**, **IV**, **VI**–**VIII**) in toluene ($c_{porph} \sim 10^{-5}$ M)

Comp. no.	λ_{max}, nm (log ε)		
	Soret band	*Q*-bands	
III	408.5 (5.28)	541.4 (3.99)	574.0 (4.43)
IV	410.4 (5.27)	544.2(4.08)	576.4 (4.25)
VI	409.2 (5.32)	542.7 (4,16)	574.9 (4.52)
VII	408.3 (5.24)	542.2 (4.02)	574.5 (4.21)
VIII	401.0 (5.01)	537.2 (3.91)	568.7 (4.10)

In the ^{1}H NMR spectra of the complexes **VII**, **VIII** the strongest shifts were observed for the protons of hydroxyphenyl and aminophenyl groups in porphyrin fragments, just in those aryl fragments that directly participated in the formation of donor-acceptor bonds between porphyrin macrocycles, and thus were the most subjected to the screening effect of the adjacent macrocycle.

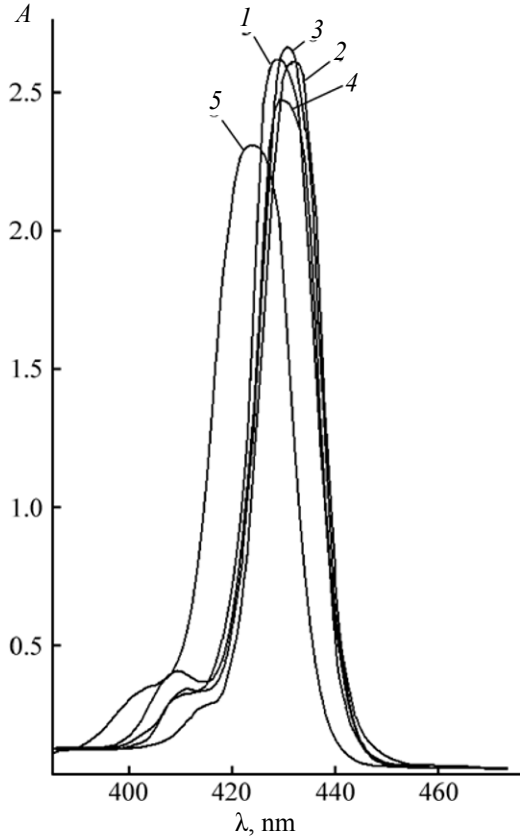


Fig. 1. Electron absorption spectra (Soret band range) ($c_{porph} \sim 10^{-5}$ M, 25°C) in toluene. (*1*) compound **III;** (*2*) compound **IV;** (*3*) compound **VI;** (*4*) compound **VII;** (*5*) compound **VIII**.

With the axial orientation of the hydroxyphenyl-substituted Zn(II) porphyrinate to Sn(IV) porphyrinate in complex **VII**, signals of protons of aryl participating in coordination shifted upfield. The closer were the protons to the adjacent porphyrin macrocycle, the larger was the signal shift. Signals of the *ortho*-, *meta*-, and *para*-protons of the second phenyl fragment of zinc porphyrinate and of two phenyl fragments of tin porphyrinate, as well as signals of protons of β-alkyl substituents in porphyrinate fragments **III**, **VI** in complex **VII** appeared as multiplets in the same spectral ranges as respective monomer macrocycles signals.

In complex **VIII**, upon binding of porphyrin macrocycles via two axial bonds, the signals of protons participating in coordination of hydroxyphenyl and aminophenyl fragments shifted upfield. The protons of β-alkyl substituents of porphyrin fragments in complex **VIII** were no more equivalent because they were screened by the ring currents of the adjacent porphyrin fragments to a different extent. Thus, in the ^{1}H NMR spectrum of complex **VIII** signals were observed of methyl and ethyl groups of two types. The signals of "inner" protons (protons of eight methyl and ethyl groups located between porphyrin fragments) appeared in the strong field, whereas signals of "outer" protons (four methyl and four ethyl groups at the periphery part of the complex) are very similar to the chemical shifts of the respective protons in the initial monomers.

A preliminary study of the photochemical properties revealed fluorescence quenching in the cases of hybrid trimer porphyrinate complexes **VII**, **VIII** as compared with the individual monomeric porphyrin fragments (Fig. 2). In the case of complex **VIII**, with the fixed position of porphyrin macrocycles one above the other, the fluorescence quenching was more pronounced.

Comp. no.	λ_{max} 410 nm (φ, %*Q*)	λ_{max} 450 nm (φ, %*Q*)
VII	0.005 (88)	0.005 (90)
VIII	0.001 (96)	0.001 (98)

The quenching efficiency was calculated as: Q = φ(mon.) − φ(trim.)/φ(mon.), with mon. being a comparison compound (ZnP at 410 nm, $SnP(OH)_2$ at 450 nm) [7]. The error in the φ (quantum yield) estimation did not exceed ±10%.

The analysis of the literature data [9–10] leads to the conclusion that the origin of the fluorescence quenching in the case of the studied complexes could

be either fast intramolecular electron transfer (from the central tin porphyrinate to the side zinc porphyrinate) or photoinduced electron transfer (from the side zinc porphyrinate to the central tin porphyrinate). We are currently in the process of detailed investigation of the photochemical and electrochemical properties of the prepared hybrid porphyrinate complexes **VII** and **VIII** in order to estimate the impact of the intramolecular and photoinduced electron transfer along the Sn–O and Zn–N bonds.

To conclude, the new hybrid porphyrinate oligomers were prepared by single-centered coordination of the OH group of zinc(II) hydroxyporphyrinate to the central cation of tin(IV) porphyrinate, or by simultaneous (two-centered) coordination of the OH group of zinc(II) hydroxyporphyrinate to the central cation of tin(IV) porphyrinate and coordination of the NH_2 group of tin(IV) aminoporphyrinate to the central cation of zinc(II) porphyrinate. The complexes thus obtained are promising for the investigation of the electron transfer processes along the chain of the interacting porphyrin fragments of different nature.

EXPERIMENTAL

Dimethylformamide, pyridine, benzene, toluene, $Zn(OAc)_2$, and $SnCl_2{\cdot}2H_2O$ (all Sigma-Aldrich) were used without further purification. Complex formation reaction was followed by means of spectrophotometry (sampling method). The same volumes of the reaction mixture were sampled at regular intervals and diluted with dimethylformamide. The electron absorption spectra were recorded with Cary-100 spectrophotometer at 25°C, fluorescence spectra were recorded with CM 2203 spectrofluorimeter. ^{1}H NMR spectra were recorded with Bruker AV III-500 spectrometer. The elemental analysis was performed with Flash EA 1112. Thin layer chromatography analysis was performed with the Silufol plates.

Tin (IV) 10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrinate (III) [13]. 1.5-fold (molar) excess of $SnCl_2{\cdot}2H_2O$ was added to the solution of **I** [14] (30 mg, 0.05 mmol) in 50 ml of pyridine. The reaction mixture was boiled during 8 h. After cooling the mixture, the solution was filtered, the solvent was evaporated under reduced pressure, and the residue was recrystallized from the dichloromethane–hexane mixture (2:1). Thus obtained tin dichloroporphyrinate (40 mg, 0.045 mmol) and potassium carbonate (0.21 g, 1.50 mmol) were dissolved in 100 ml of tetrahydrofuran and 25 ml of water, the reaction mixture was boiled during 4 h. The solvent was evaporated to the volume of 30 ml on a rotory evaporator and the residue was left in the refrigerator overnight. The precipitated crystals were filtered off, washed with cold water, and dried in a vacuum. Yield 30 mg (85%). R_f 0.47 (Silufol, dichloromethane–hexane, 1:1). ^{1}H NMR spectrum, δ, ppm: 9.91 s (2H, *ms*-H), 7.69 d (4H, *o*-H_{Ar}), 7.27 m (6H, *m*, *n*-H_{Ar}), 6.01 s (2H, OH), 2.90 m (8H, $\underline{CH_2}CH_3$), 3.12 s (12H, CH_3), 0.94 t (12H, $CH_2\underline{CH_3}$). Found, %: C 67.27; H 5.83; N 7.02. Calculated, %: C 67/63; H 5.89; N 7.17.

Tin(IV) 10,20-di(3-aminophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrinate (IV) was obtained similarly from **II** [15]. Yield 79%, R_f 0.36 (Silufol, dichloromethane–hexane, 1:1). ^{1}H NMR spectrum, δ, ppm: 9.93 s (2H, *ms*-H), 7.72 m (4H, *o*-H_{Ar}), 7.31–7.39 m (4H, *m*, *n*-H_{Ar}), 6.05 s (2H, OH), 4.27 s (4H, NH_2), 2.92 m (8H, $\underline{CH_2}CH_3$), 3.15 s (12H, CH_3), 1.03 t (12H, CH_2CH_3). Found, %: C 64.85; H 5.87; N 10.04. Calculated, %: C 65.13; H 5.92; N 10.36.

Zinc 10-(3-hydroxyphenyl)-20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrinate (VI) [16]. Ten-fold (molar) excess of zinc acetate was added to the solution of **V** [17] (30 mg, 0.05 mmol) in 70 ml of dimethylformamide, and the reaction mixture was boiled during 30 min. The mixture was then cooled and diluted with water (1:1). The precipitate formed was filtered off and purified via chromatography on the aluminum oxide column (eluent: CH_2Cl_2–C_6H_{14}, 1:1). The solvents were evaporated under reduced pressure, and the porphyrinate was recrystallized from CH_2Cl_2–CH_3OH,

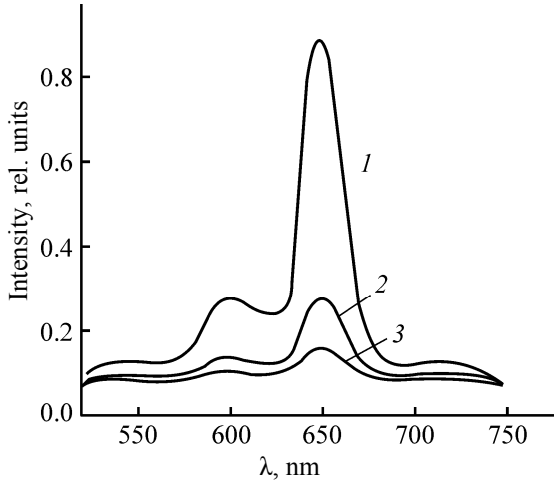


Fig. 2. Fluorescence spectra of compounds (*1*) **VI**, (*2*) **VII**, and (*3*) **VIII** in toluene with λ_{ex} = 410 nm.

1:2. Yield 27 mg (82%), R_f 0.52 (Silufol, dichloromethane–hexane, 1:1). ^{1}H NMR spectrum, δ, ppm: 9.94 s (2H, *ms*-H), 7.75 br. s (1H, OH), 7.59 m (4H, *o*-H_{Ar}), 7.20–7.27 m (5H, *m*-, *n*-H_{Ar}), 2.91 m (8H, $\underline{CH_2}CH_3$), 3.13 s (12H, CH_3), 1.05 t (12H, $CH_2\underline{CH_3}$). Found, %: C 74.07; H 6.28; N 7.51. Calculated, %: C 74.32; H 6.33; N 7.88.

Complex VII. 30 mg (0.04 mmol) of tin porphyrinate **III** was boiled with four-fold excess (molar) of zinc porphyrinate **VI** in 50 ml of benzene during 8 h. The reaction mixture was cooled and applied to the chromatography column filled with aluminum oxide. Dichloromethane–ethanol (9:1) was used as eluent. Eluate was evaporated to the minimal volume, and 2 ml of methanol was added to the dichloromethane solution of the porphyrinate. The precipitate formed was filtered off and dried. Yield 68%, R_f 0.32 (Silufol, dichloromethane–hexane, 1:1). ^{1}H NMR spectrum, δ, ppm: 9.93 s (6H, *ms*-H), 8.79 br.s (2H, OH), 7.68 m (10H, *o*-H_{Ar}), 7.22–7.29 m (12H, *m*-, *n*-H_{Ar}), 3.24 s (2H, *o*-H_{Ar}), 3.28 d (2H, *n*-H_{Ar}), 2.92 m (24H, $\underline{CH_2}CH_3$), 3.09 s (36H, CH_3), 0.92 m (36H, $CH_2\underline{CH_3}$). Found, %: C 72.88; H 6.06; N 7.42. Calculated, %: C 73.14; H 6.10; N 7.76.

Complex VIII was obtained similarly by boiling tin porphyrinate **IV** with zinc porphyrinate **VI** in benzene. Yield 79%, R_f 0.41 (Silufol, dichloromethane–hexane, 1:1). ^{1}H NMR spectrum, δ, ppm: 9.91 s (6H, *ms*-H), 8.82 br. s (2H, OH), 7.70 m (8H, *o*-H_{Ar}), 7.24–7.30 m (8H, *m*-, *n*-H_{Ar}), 3.21 s (4H, *o*-H_{Ar}), 3.26 d (4H, *n*-H_{Ar}), 2.65 m (16H, $\underline{CH_2}CH_3$), 2.66 s (24H, CH_3), 0.69 t (24H, $CH_2\underline{CH_3}$), 2.89 m (8H, $\underline{CH_2}CH_3$), 3.01 s (12H, CH_3), 0.84 t (12H, $CH_2\underline{CH_3}$), –0.25 br.s (4H, NH_2). Found, %: C 71.73; H 6.03; N 8.69. Calculated, %: C 72.15; H 6.10; N 8.92.

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