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Synthesis and Design of Supramolecular Systems on the Basis of Tetrapyrrole Macrocycles

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Abstract—Three new cyclophane-like calixarene–bis-porphyrins were synthesized, and their spectral properties were studied. Zinc complex of *meso*-(aminophenyl)-substituted calixarene–bis-porphyrin was found to form a stable 1:1 complex with dimethyl maleate in toluene. Its stability constant was determined by spectrophotometric titration.

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Synthesis and design of nanosize (1 to 10^2 nm) molecules capable of selectively binding metal ions and small organic molecules is an important problem in organic chemistry [1, 2]. Its significance is determined by the necessity of determination and separation of various biologically active substrates.

In this connection, convenient model structures are bis-porphyrins where appropriate orientation of the tetrapyrrole macrorings is ensured by both flexible linkers (hydrocarbon or ether) and rigid aromatic bridges (naphthalene, anthracene, or calixarene) [3–7]. The tetrapyrrole chromophore in such polyfunctional molecules is the main structural unit (host fragment) bearing substituents that are capable of interacting in different modes with guest molecules [8, 9]. Available published data demonstrate the significance and wide potential of using tetrapyrrole macrorings in practice; however, no detailed interpretation of the effects of electronic and structural factors on the selectivity of complex formation was given.

By reaction of dipyrrolylmethane **II** with aldehydes **I** and **III** in acetonitrile–methylene chloride (1:1.5) in the presence of trichloroacetic acid and subsequent oxidation of the condensation product with tetrachlorobenzoquinone we obtained *meso*-nitrophenyl-substituted bis-porphyrin zinc complex (**IV**). Reduction of the nitro groups in **IV** gave bis-amine **V** which reacted with zinc(II) acetate to form zinc complex **VI** (Scheme 1).

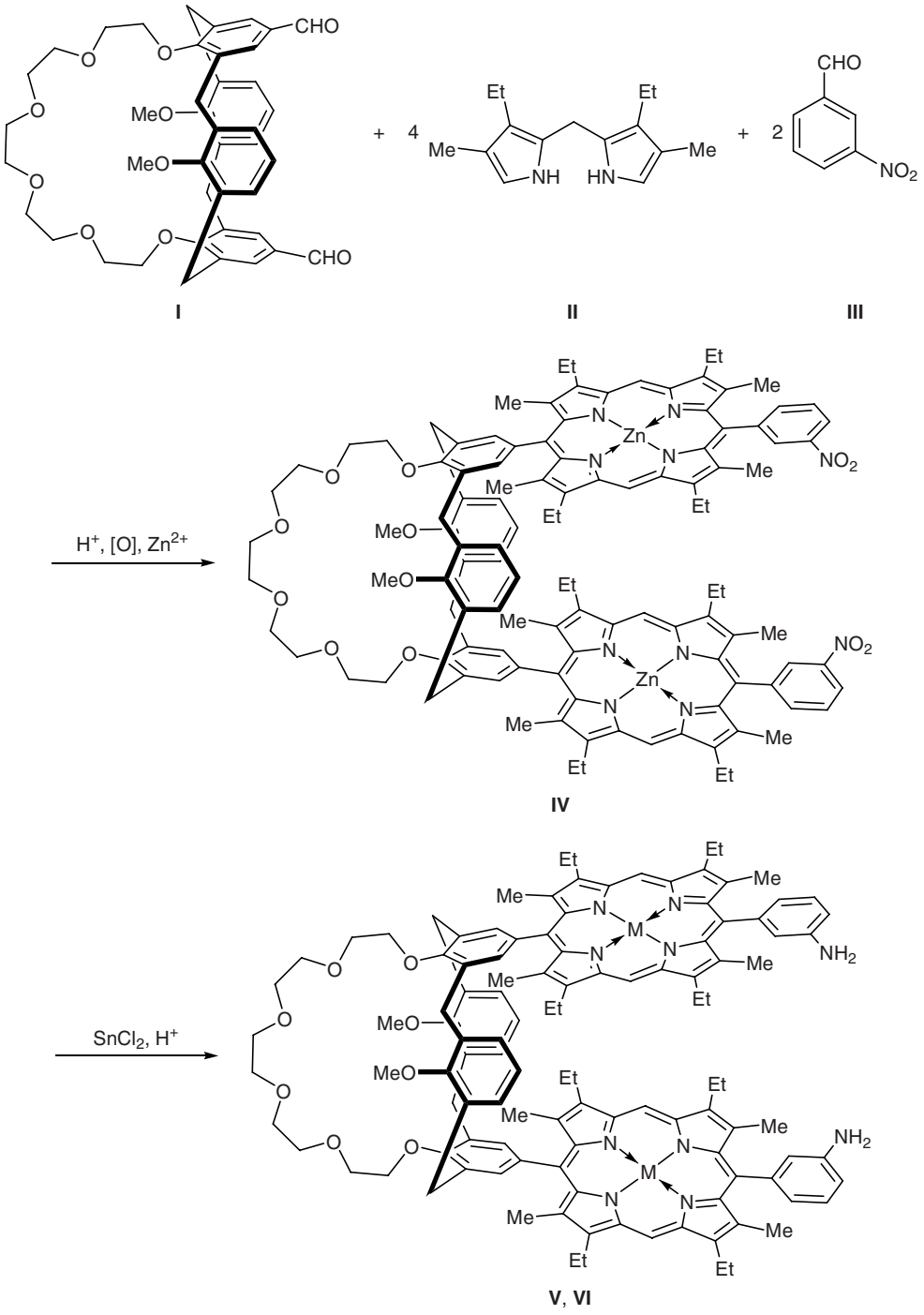
Compounds **IV**–**VI** are stable in the crystalline state and are not oxidized with atmospheric oxygen. Their mass spectra contain strong molecular ion peaks. The electronic absorption spectra of **IV**–**VI** are characterized by considerable broadening of the Soret band and reduced molar absorption coefficients as compared to porphyrin complex **VII**. The short-wave shift (by ~2–4 nm) of the Soret band in the spectra of **IV** and **VI** relative to that of **VII** also suggests their cyclophane-like structure where π-electron systems of the tetrapyrrole chromophores strongly interact with each other.

In the ^{1}H NMR spectra of **IV**–**VI** we observed signals from protons in the calixarene and porphyrin fragments. Protons in the methylene groups of the calixarene moiety resonated as two well resolved symmetric doublets at δ ~3.3 and 4.0 ppm, indicating *cone* conformation of that fragment. Signals from all protons in the porphyrin fragments appear in a stronger field relative to the corresponding signals of **VII**.

We examined complex formation between zinc complex **VI** and dimethyl maleate (L) and toluene. For comparison, complex formation of the same substrate with zinc porphyrin **VII** as model of the tetrapyrrole fragment in **VI** was also studied. Two modes of coordination of dimethyl maleate to bis-porphyrin **VI** are possible. If the distance between the tetrapyrrole macrorings is insufficient to accommodate molecule L, less stable 1:2 complex **VIII** ($Zn_2P \cdot L_2$) could be formed; otherwise, stable 1:1 complex **IX** ($Zn_2P \cdot L$) may be obtained, where the dimethyl maleate molecule is located between the macrorings and is coordinated to each of them.

Spectrophotometric titration showed that the complex formation between **VI** and dimethyl maleate

Scheme 1.

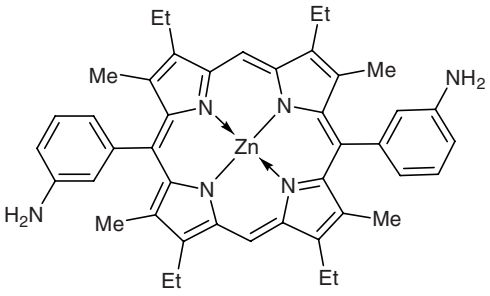


V, M = H_2; **VI**, M = Zn.

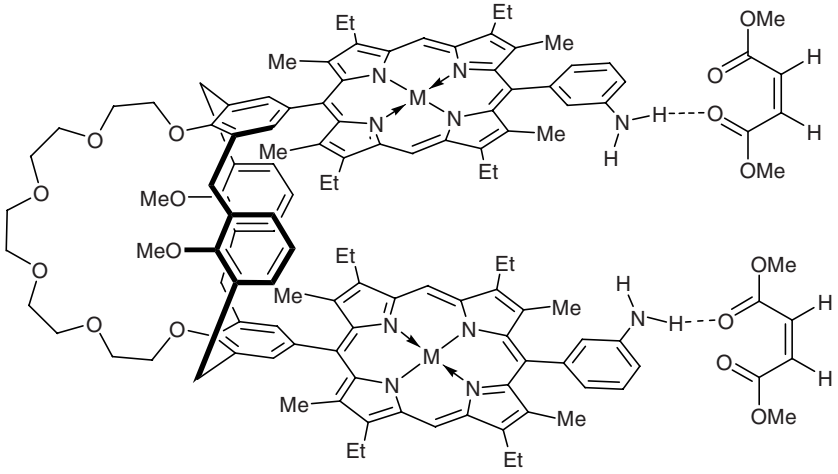
occurs in one step to give complex **IX**. Only one step is observed on the titration curve (Fig. 1), and an isosbestic point is present in the electronic absorption spectra (Fig. 2). On the basis of the titration data, the stability constant K_s of complex **IX** was estimated at ~177445 l/mol.

$$K_s = \frac{[\mathrm{ZnP \cdot L}]}{[\mathrm{ZnP}][\mathrm{L}]} = \frac{1}{[\mathrm{L}]}\left(\frac{\Delta D_{i,\lambda_1}}{\Delta D_{0,\lambda_1}}\frac{\Delta D_{0,\lambda_2}}{\Delta D_{i,\lambda_2}}\right).$$

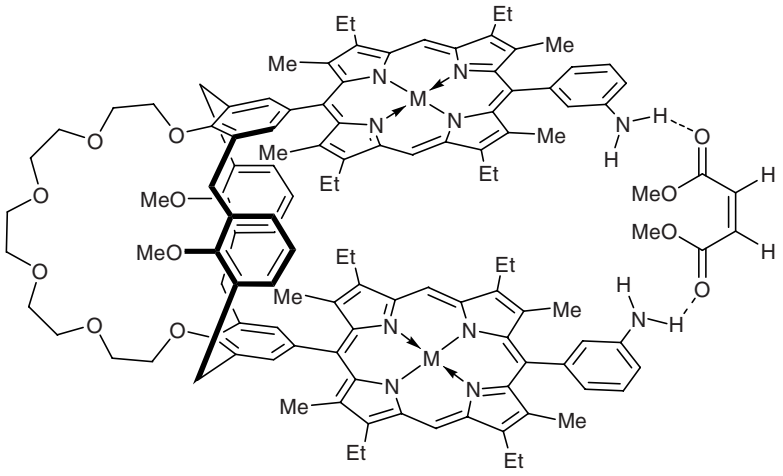
Here, λ_1 is the descending wavelength, λ_2 is the ascending wavelength, [L] is the concentration of dimethyl maleate, ΔD_0 is the maximal change in the



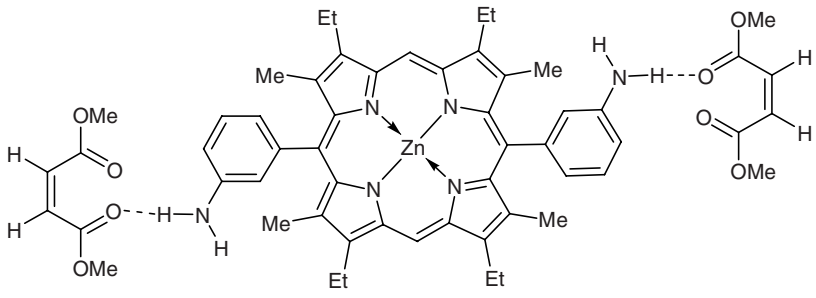
VII



VIII



IX



X

optical density at a given wavelength, and ΔD_i is the change in the optical density at a given wavelength at a given concentration [9]. The error in the determination of K_s was 7–10%.

Porphyrinate **VII** reacted with dimethyl maleate to form 1:2 complex **X**. The complex formation occurred in one step (Fig. 3), and an isosbestic point was observed in the electronic absorption spectra of the system **VII**–L. The stability constant of complex **X** was estimated at ~61089 l/mol.

Our results showed that dimethyl maleate with zinc porphyrinates **VI** and **VII** forms complexes characterized by different stabilities. The 1:1 complex with bisporphyrine **VI** is more stable by a factor of ~3 than the 2:1 complex with porphyrine **VII**. The mode of coordination is determined by the size of the receptor cavity.

EXPERIMENTAL

Calixarene **I**, dipyrrolylmethane **II**, and porphyrin complex **VII** were synthesized according to the procedures described in [2, 10]. The products were isolated by column chromatography on neutral aluminum oxide using methylene chloride–hexane (1:1) as eluent. Organic solvents were purified by standard procedures [11]. The progress of reactions was monitored by TLC on Silufol UV-254 plates.

The ^{1}H NMR spectra of compounds **IV**–**VII** were recorded on a Bruker VC-200 spectrometer (200 MHz) from solutions in benzene-d_6 using 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 on a Varian Cary 100 spectrophotometer.

5,5′-[3^2,7^2-Dimethoxy-1^2,5^2-(3,6,9,12-tetraoxatetradecamethylenedioxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1^5,5^5-diyl]bis{[2,8,12,18-tetraethyl-3,7,13,17-tetramethyl-15-(3-nitrophenyl)porphyrinato]zinc(II)} (IV). A solution of 95.4 mg (0.59 mmol) of trichloroacetic acid in 10 ml of acetonitrile was added to a solution of 0.27 g (0.37 mmol) of diformylcalix[4]arene **I**, 0.36 g (1.48 mmol) of bis(3-ethyl-4-methyl-1*H*-pyrrol-2-yl)methane (**II**), and 0.11 g (0.74 mmol) of 3-nitrobenzaldehyde (**III**) in a mixture of 60 ml of acetonitrile and 100 ml of methylene chloride. The mixture was stirred for 3 h under argon, treated with a solution of 1.46 g (6.1 mmol) of tetrachloro-1,2-benzoquinone in 20 ml of methylene chloride, stirred for 2 h, and evaporated to a volume of 30 ml. The residue was washed with a 10% solution of ammonia, the precipitate was dried and dissolved in 100 ml of methylene chloride, a saturated solution of zinc(II) acetate in 10 ml of methanol was added, and the mixture was stirred for 30 min and

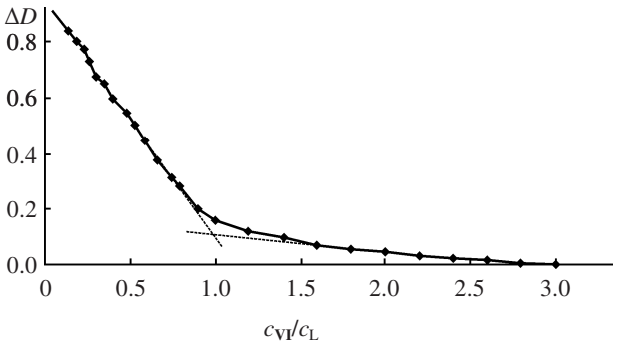


Fig. 1. Spectrophotometric titration of zinc complex **VI** with dimethyl maleate in toluene at the descending wavelength (λ = 404 nm, 298 K, $c^0_{VI} = 0.35\times10^{-5}$ M).

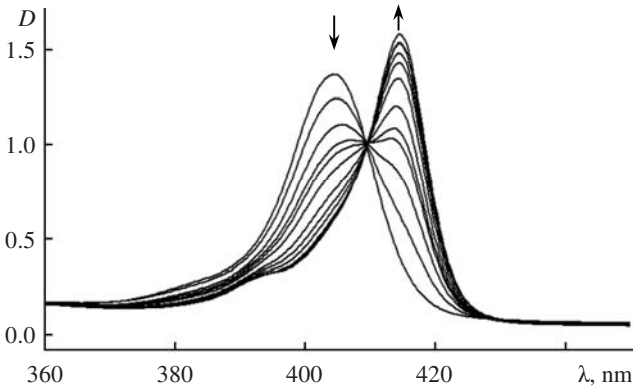


Fig. 2. Variations of the spectral pattern of zinc complex **VI** in the Soret band region upon addition of dimethyl maleate (0 to 6.3×10^{-5} M, toluene, 298 K).

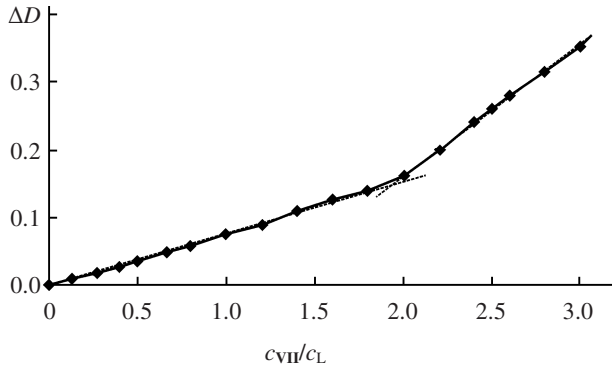


Fig. 3. Spectrophotometric titration of zinc complex **VII** with dimethyl maleate in toluene at the descending wavelength (λ = 404 nm, 298 K, $c^0_{VII} = 0.35\times10^{-5}$ M).

filtered. The filtrate was evaporated to a volume of 10 ml, and the residue was subjected to chromatography on aluminum oxide using methylene chloride–hexane (1:1) as eluent. Yield 46.5 mg (4.5%). R_f 0.50 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (logε): 410.5 (5.01), 539.1 (4.26), 573.2 (3.93). ^{1}H NMR spectrum, δ, ppm: 10.09 s (4H, *meso*-H), 7.91–7.80 m (4H, *o*-H in $C_6H_4NO_2$, and 4H, H_{arom} in calixarene), 7.65–7.45 m (2H, *m*-H in $C_6H_4NO_2$, and 4H, H_{arom} in calixarene), 7.25 d (2H, *p*-H in $C_6H_4NO_2$), 7.03 t (2H, *p*-H, calixarene), 4.41 s (6H, OCH_3), 4.02 d (4H, ArC**H**$_2$Ar), 3.84 q (8H, C**H**$_2$CH$_3$), 3.78 m (8H, C**H**$_2$CH$_3$), 3.69 s (4H, OCH_2CH_2O), 3.66 m (16H, OCH_2CH_2O), 3.37 d (4H, ArC**H**$_2$Ar), 2.06 s (12H, CH_3), 2.18 s (12H, CH_3), 1.04 t (12H, CH_2C**H**$_3$), 0.91 t (12H, CH_2C**H**$_3$). Mass spectrum, *m*/*z* (I_{rel}, %): 2066.91 (76) $[M]^+$. Found, %: C 70.77; H 6.78; N 6.74. $C_{122}H_{141}N_{10}O_{12}Zn_2$. Calculated, %: C 70.80; H 6.82; N 6.77.

5,5′-[3^2,7^2-Dimethoxy-1^2,5^2-(3,6,9,12-tetraoxatetradecamethylenedioxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1^5,5^5-diyl]bis[15-(3-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin] (V). A suspension of 0.03 g (0.01 mmol) of bis-porphyrin complex **IV**, 10 ml of hydrochloric acid, and 0.02 g (0.10 mmol) of tin(II) chloride dihydrate was stirred for 30 min at 60°C. The mixture was cooled and filtered, and the filtrate was diluted with 30 ml of water. The precipitate of bis-porphyrin **V** hydrochloride was filtered off and washed in succession with dilute (1:1) hydrochloric acid, an ammonia solution, and hot water. Yield 20.1 mg (61%), R_f 0.63 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (logε): 406.1 (4.96), 505.9 (4.09), 541.7 (3.59), 572.5 (3.79), 629.8 (3.24). ^{1}H NMR spectrum, δ, ppm: 10.05 s (4H, *meso*-H), 7.89–7.75 m (4H, *o*-H in $C_6H_4NH_2$, and 4H, H_{arom} in calixarene), 7.61–7.40 m (2H, *m*-H in $C_6H_4NH_2$, and 4H, H_{arom} in calixarene), 7.23 d (2H, *p*-H in $C_6H_4NH_2$), 7.00 t (2H, *p*-H, calixarene), 4.43 s (6H, OCH_3), 4.05 d (4H, ArC**H**$_2$Ar), 3.87 q (8H, C**H**$_2$CH$_3$), 3.81 m (8H, C**H**$_2$CH$_3$), 3.72 s (4H, OCH_2CH_2O), 3.68 m (16H, OCH_2CH_2O), 3.39 d (4H, ArC**H**$_2$Ar), 3.03 br.s (4H, NH_2), 2.09 s (12H, CH_3), 2.21 s (12H, CH_3), 1.07 t (12H, CH_2C**H**$_3$), 0.93 t (12H, CH_2C**H**$_3$), –2.81 s (4H, NH). Mass spectrum, *m*/*z* (I_{rel}, %): 1876.1 (62) $[M]^+$. Found, %: C 79.97; H 7.68; N 7.43. $C_{122}H_{145}N_{10}O_8$. Calculated, %: C 80.00; H 7.72; N 7.46.

5,5′-[3^2,7^2-Dimethoxy-1^2,5^2-(3,6,9,12-tetraoxatetradecamethylenedioxy)-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1^5,5^5-diyl]bis{[15-(3-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato]zinc(II)} (VI). Bis-porphyrin **V**, 30 mg, was dissolved in 70 ml of *N*,*N*-dimethylformamide, 10 equiv of zinc(II) acetate was added, and the mixture was heated for 30 min at the boiling point. The mixture was cooled and diluted with an equal volume of water, and the precipitate was filtered off and subjected to chromatography on aluminum oxide using methylene chloride–hexane (1:1) as eluent. The product was additionally recrystallized from methylene chloride–methanol (1:1). Yield 27.52 mg (86%), R_f 0.72 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (logε): 408.5 (5.01), 538.1 (4.24), 572.1 (3.91). ^{1}H NMR spectrum, δ, ppm: 10.07 s (4H, *meso*-H), 7.85–7.73 m (4H, *o*-H in $C_6H_4NH_2$, and 4H, H_{arom} in calixarene), 7.60–7.35 m (2H, *m*-H in $C_6H_4NH_2$, and 4H, H_{arom} in calixarene), 7.21 d (2H, *p*-H in $C_6H_4NH_2$), 7.05 t (2H, *p*-H, calixarene), 4.44 s (6H, OCH_3), 4.02 d (4H, ArC**H**$_2$Ar), 3.83 q (8H, C**H**$_2$CH$_3$), 3.74 m (8H, C**H**$_2$CH$_3$), 3.66 s (4H, OCH_2CH_2O), 3.61 m (16H, OCH_2CH_2O), 3.32 d (4H, ArC**H**$_2$Ar), 3.00 br.s (4H, NH_2), 2.06 s (12H, CH_3), 2.19 s (12H, CH_3), 1.06 t (12H, CH_2C**H**$_3$), 0.91 t (12H, CH_2C**H**$_3$). Mass spectrum, *m*/*z* (I_{rel}, %): 2003.8 (81) $[M]^+$. Found, %: C 73.02; H 7.01; N 6.95. $C_{122}H_{141}N_{10}O_8Zn_2$. Calculated, %: C 73.06; H 7.04; N 6.99.

[5,15-Bis(3-aminophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato]zinc(II) (VII). R_f 0.51 (Al_2O_3, CH_2Cl_2–C_6H_{14}, 1:2). Electronic absorption spectrum (toluene), λ_{max}, nm (logε): 413.3 (5.14), 535.1 (4.46), 570.3 (3.97). ^{1}H NMR spectrum, δ, ppm: 10.19 s (2H, *meso*-H), 7.89 d (2H, *o*-H), 7.73 s (2H, *o*-H), 7.36 t (2H, *m*-H), 7.25 d (2H, *p*-H), 3.89 q (8H, C**H**$_2$CH$_3$), 3.09 br.s (4H, NH_2), 2.28 s (12H, CH_3), 1.16 t (12H, CH_2C**H**$_3$).

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