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Synthesis and Spectrophotometric Study of Acidic and Complexation Properties of 5,15-Bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin and 5,15-Bis(4'-methoxyphenyl)-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin in Acetonitrile

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Abstract—Synthesis of 5,15-bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin and 5,15-bis(4'-methoxyphenyl)-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin is reported. Spectrophotometric study of acidic and complexation properties of these compounds in the DBU–CH_3CN, CH_3CN–$Zn(OAc)_2$ and DBU– CH_3CN– $Zn(OAc)_2$ systems has been carried out. Kinetic parameters of the zinc complexes formation via molecular and ionic routes have been determined. The influence of structural factors on reactivity of the tetrapyrrole macrocycles is discussed.

Keywords: porphyrin, acid–base properties, electronic effect of substituents, structure

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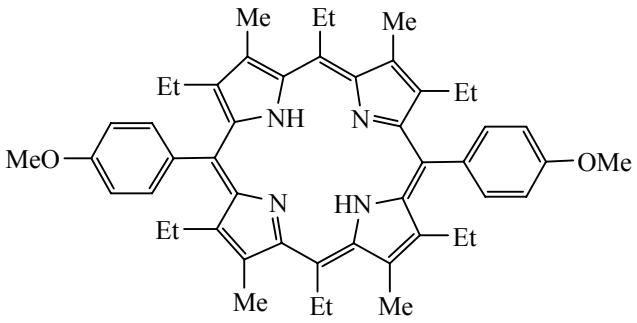
Coordination compounds of porphyrins known for prominent catalytic and biological properties possess diverse structural features [1, 2]. The inner cavity of porphyrin bounded by the nitrogen atoms is able to coordinate metal ions in various oxidation states. The metal location determines the properties of metalloporphyrin: the metal ion can be located either inside the cavity at equatorial plane or above the plane of the nitrogen atoms, thus forming the coordination sites of diverse geometry. The properties of metalloporphyrins are also determined by the nature of the peripheral substituents introduced at the porphyrin cycle via substitution of hydrogen atoms of the macrocycle. Porphyrins and their complexes bearing alkyl and phenyl substituents at *meso*-positions are the most structurally similar to natural porphyrins; importantly, they can be synthesized with sufficiently high yield [3]. Being macrocyclic complexes with unique conjugated π-system, metalloporphyrins can reduce positive and negative charges at the aromatic orbitals facilitating stabilization of cation- and anion-radical ligand forms [2, 4]. Investigation of the complexes formation of the intricately substituted porphyrins existing in the solution in free (molecular) or ionized state allows accounting for the medium (solvent, co-solvent, and titrant) effects changing kinetics of various processes.

In this work we report on preparation and spectrophotometric study of acidic and complexing properties of 5,15-bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin **I** and 5,15-bis(4'-methoxyphenyl)-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin **II** being in molecular and deprotonated forms at 298–318 K.

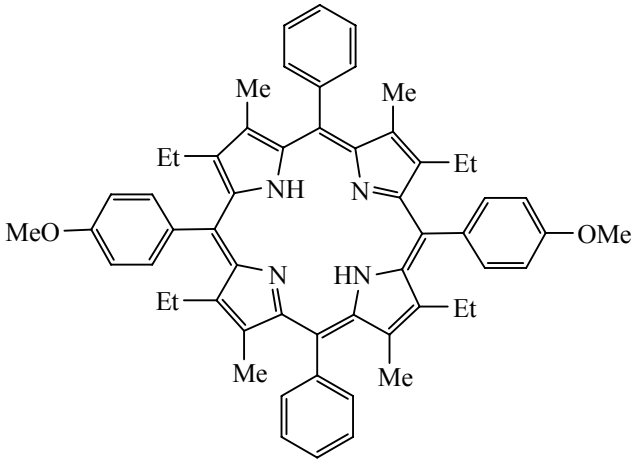
The method of ligands **I** and **II** synthesis is presented in Experimental.

The electronic absorption spectra and the spectrophotometric titration curve of compound **I** in the DBU–CH_3CN system are shown in Fig. 1 (DBU stands

Scheme 1.



I



II

for 1,8-diazabicyclo[5.4.0]undec-7-ene). The recorded spectra demonstrated formation of two families of the spectral curves with increasing DBU concentration. Each of the sets of the spectral curves corresponded to the own set of isosbestic points, evidencing about the two-stage deprotonation process.

The parameters of the absorption electron spectra of molecular (c_{DBU} 0 mol/L) and the twice deprotonated forms (c_{DBU} 9.95×10^{-5} mol/L) of compound **I** in the DBU–CH_3CN system are summarized in Table 1.

Similar chemical reactions in solutions between organic compounds where one of the compounds is used as proton acceptor have been discussed elsewhere [5].

Two-stage nature of the spectrophotometric titration curve (Fig. 1) confirmed the successive elimination of two electrons upon of the ligand with DBU [Eq. (1)].

$$H_2P \overset{k}{\rightleftarrows} P^{2-} + 2H^+. \quad (1)$$

Here, H_2P and P^{2-} are free (base) and twice deprotonated forms of porphyrin **I**, respectively.

The combined constant of acidic ionization at both steps was calculated using Eq. (2); log k = –9.87 for compound **I** in the DBU–CH_3CN system at 298 K. Accuracy of the constant determination was within ±3–5%.

$$\log k_a = \log Ind + n\log c_{DBU}. \quad (2)$$

Here, k is combined constant of the compound acidity; Ind is indicator ratio of P^{2-}/H_2P; c_{DBU} is analytical value of concentration of DBU in solution, mol/L; and n = 2 is the number of protons detached by DBU.

Taking into account Eq. (2) and the material balance Eq. (3), we concluded that at $c_{DBU} \approx 5.6 \times 10^{-5}$ mol/L almost all the molecules of porphyrin **I** existed in the twice deprotonated form. The calculation methods have been discussed in detail elsewhere [6].

$$c^0 = c(H_2P) + c(P^{2-}). \quad (3)$$

Similarly, behavior of compound **II** in the DBU–CH_3CN system was investigated. Analysis of the spectral data (Fig. 2) again revealed formation of two

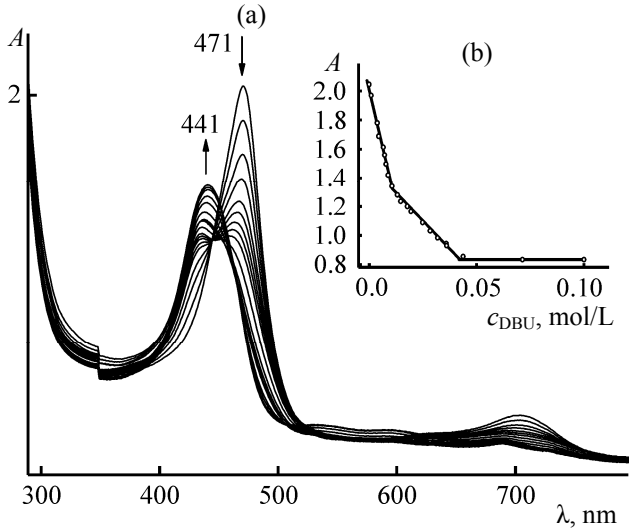


Fig. 1. Changes of the electronic absorption spectra in the course of titration (a) and the spectrophotometric titration curve at λ 472 nm (b) of compound **I** in DBU–CH_3CN. $c_{\mathbf{I}} = 2 \times 10^{-5}$ mol/L, $c_{DBU} = (0–9.95) \times 10^{-5}$ mol/L, 298 K.

Table 1. Parameters of electronic absorption spectra of the molecular and twice deprotonated forms of 5,15-bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin **I** and its zinc complexes in the DBU–CH_3CN (λ_1) and CH_3CN–$Zn(OAc)_2$ (λ_2) systems

Form, complex	λ_1 (log ε), nm	λ_2 (log ε), nm
H_2P	471 (5.01)	704 (4.21)
P^{2-}	441 (4.87)	689 (3.99)
$Zn^{2+}P^{2-}$, ZnP	456 (4.87)	650 (4.14)

Table 2. Parameters of electronic absorption spectra of the molecular and twice deprotonated forms of 5,15-bis(4'-methoxyphenyl)-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin **II** and its zinc complexes in the DBU–CH_3CN (λ_1), CH_3CN–$Zn(OAc)_2$ (λ_2), and CH_3CN–DBU–$Zn(OAc)_2$ (λ_3) systems

Form, complex	λ_1 (log ε), nm	λ_2 (log ε), nm	λ_3 (log ε), nm
H_2P	471 (4.87)	642 (4.09)	728 (3.98)
P^{2-}	463 (5.01)	613 (4.26)	710 (3.93)
$Zn^{2+}P^{2-}$, ZnP	478 (4.86)	–	697 (4.04)

types of spectral curves with increasing of concentration of DBU, with own set of the isosbestic points matching each of the curves families. Parameters of the electronic absorption spectra of molecular (c_{DBU} 0 mol/L) and the twice deprotonated (c_{DBU} 2.89 × 10^{-5} mol/L) forms of compound **II** in the DBU–CH_3CN system are summarized in Table 2. The combined constant of acidic ionization for compound **II** in the DBU–CH_3CN system at 298 K was calculated using Eq. (2); log k = –10.41, accuracy of the constant determination was the same as in the case of compound **I**. The calculations analogous to those performed for compound **I** [Eqs. (2) and (3)] revealed that at $c_{DBU} \approx 2.6 \times 10^{-5}$ mol/L practically all the molecules of compound **II** existed in the twice deprotonated form in the DBU–CH_3CN system.

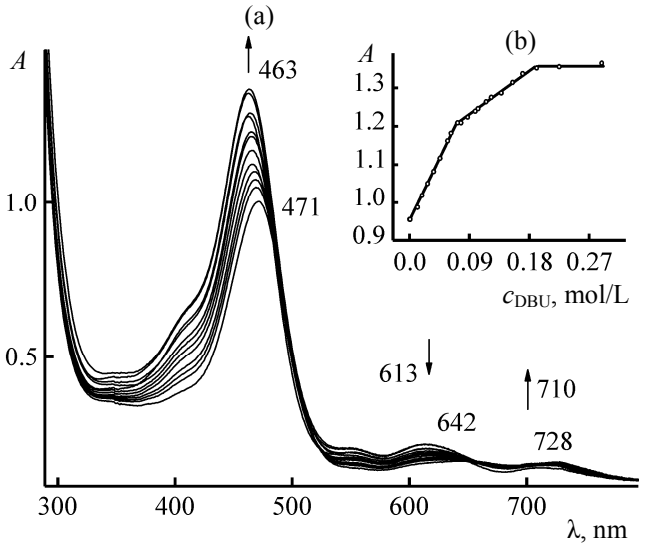


Fig. 2. Changes of the electronic absorption spectra in the course of titration (a) and the spectrophotometric titration curve at λ 472 nm (b) of compound **II** in DBU–CH_3CN. $c_{\mathbf{II}}$ = 1.30 × 10^{-5} mol/L, c_{DBU} = (0–2.89) × 10^{-5} mol/L, 298 K.

Kinetics of formation of zinc complexes with compounds **I** and **II** in the CH_3CN–$Zn(OAc)_2$ and CH_3CN–DBU–$Zn(OAc)_2$ systems was studied by spectrophotometry.

Formation of porphyrins complexes with doubly-charged metal cations in nonaqueous solutions can be presented by Eqs. (4) and (5).

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n-2)Solv, \quad (4)$$

$$P^{2-} + [MX_2(Solv)_{n-2}] \rightarrow MP + 2X^- + (n-2)Solv, \quad (5)$$

where X, acidoligand; Solv, solvent; and n, coordination number of the metal cation.

Calculation of the other kinetic parameters was performed according to the standard method [Eqs. (6)–(11)]. We start with

$$K_{ef} = (1/t)\log (c^0_{H2P}/c_{H2P}). \quad (6)$$

In terms of the optical density changes Eq. (6) is transformed into Eq. (7):

$$K_{ef} = (1/t)\log [(A_0 - A_\infty)/(A - A_\infty)], \quad (7)$$

where t, time from the reaction start; A_0, A_t, and A_∞, optical density of the solution at time zero, at time t and infinite time (equilibrium), respectively. The actual rate constant of the (n+1) order was calculated using Eq. (8):

$$k_{n+1} = k_{ef}/c^n_{salt}. \quad (8)$$

The activation energy was calculated from the temperature dependence of the rate constant via the Arrhenius equation [Eqs. (9) and (10)]:

$$k = Ae^{-Ea/RT}, \quad (9)$$

$$E = 19.1[T_1T_2/(T_2 - T_1)]\log (k_2/k_1). \quad (10)$$

Finally, entropy of activation $\Delta S^{\neq}$ was calculated using Eq. (11):

$$\Delta S^{\neq} = 19.1\log k^{298} + E/(298 - 253). \quad (11)$$

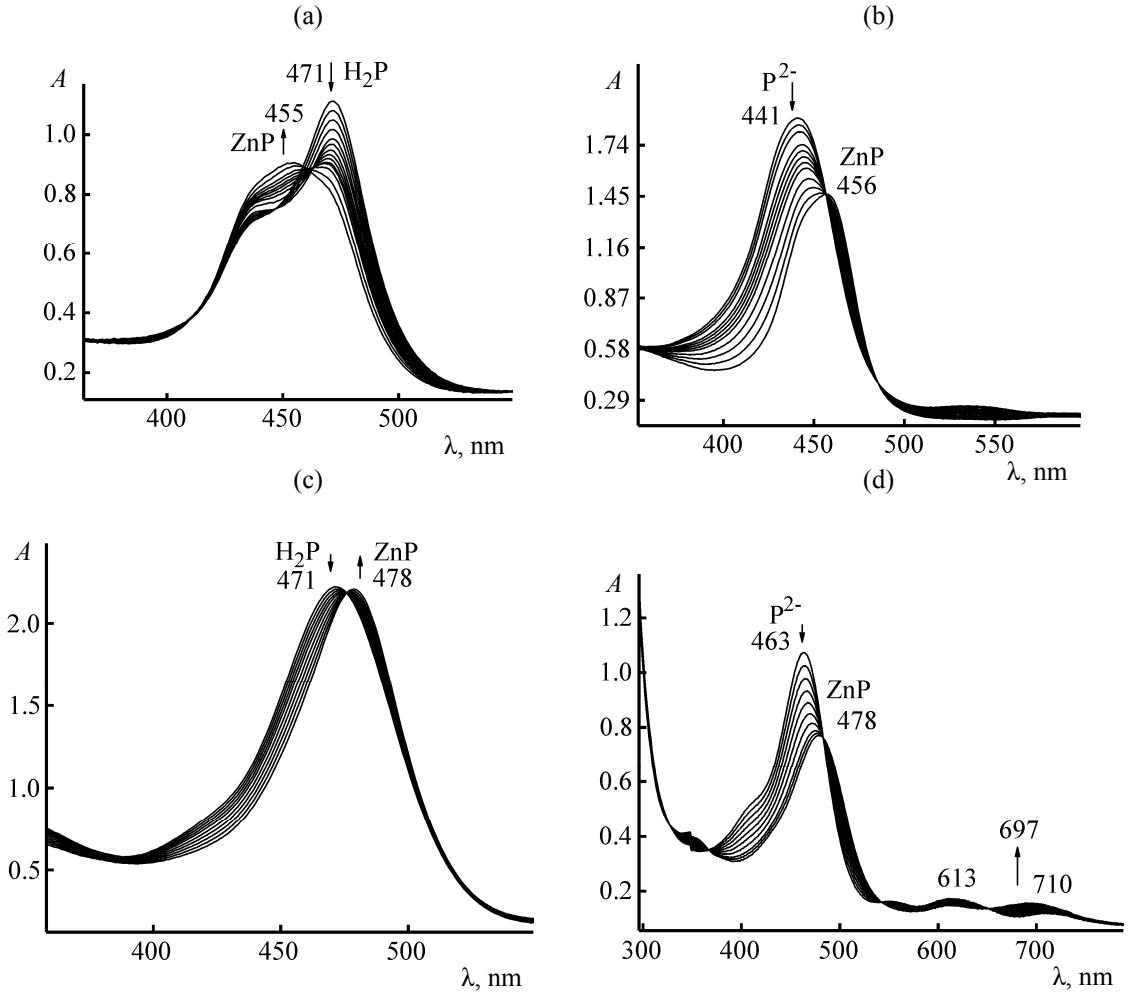


Fig. 3. Change of the electronic absorption spectra in the course of the complexation reaction of compounds **I** and **II** with zinc acetate in acetonitrile at 298 K. For compound **I**: (a) in CH_3CN–$Zn(OAc)_2$, $c_{\mathbf{I}} = 1.08 \times 10^{-5}$ mol/L, $[Zn(OAc)_2] = 3.13 \times 10^{-3}$ mol/L; (b) in CH_3CN–DBU–$Zn(OAc)_2$ ($c_{\mathbf{I}} = = 2.55 \times 10^{-5}$ mol/L, $[Zn(OAc)_2] = 2.55 \times 10^{-4}$ mol/L, $c_{DBU} = 5.6 \times 10^{-5}$ mol/L; for compound **II**: (c) in CH_3CN–$Zn(OAc)_2$, $c_{\mathbf{II}} = = 3.01 \times 10^{-5}$ mol/L, $[Zn(OAc)_2] = 3.13 \times 10^{-3}$ mol/L; and (d) in CH_3CN–DBU–$Zn(OAc)_2$, $c_{\mathbf{II}} = 1.05 \times 10^{-5}$ mol/L, $[Zn(OAc)_2] = 1.55 \times 10^{-4}$ mol/L, $c_{DBU} = 2.6 \times 10^{-5}$ mol/L.

At each of the three temperatures, the experiment was reproduced at least in triplicate.

Changes of the electronic absorption spectra in the course of the reaction of compounds **I** and **II** with zinc acetate in the CH_3CN–$Zn(OAc)_2$ and CH_3CN–DBU systems at 298 K are shown in Fig. 3. The reaction order with respect to the porphyrin was determined from dependences log (c^0_{H2P}/c_{H2P}) versus time (Fig. 4); the reaction order was equal to unity. The reaction order with respect to the salt was determined from the slope of the linear plot of log k_{eff} vs log $c[Zn(OAc)_2]$ (Fig. 5).

Kinetic parameters of the reaction of zinc complexes formation with the porphyrins are listed in Table 3. The data suggested similarity of the kinetic and acidic properties in the case of compounds **I** and **II** under the examined conditions. The final complexation products in the both studied systems CH_3CN–$Zn(OAc)_2$ and CH_3CN–DBU–$Zn(OAc)_2$ were the same, suggesting no extra coordination of the zinc complexes with DBU. Replacement of ethyl substituents in the macrocycle with phenyl ones led to slight reduction of acidic and complexation properties; the change of kinetic parameters was observed independently of the presence of the organic base in the system.

Results of simulation of geometry of molecules **I** and **II** using the PM3 semi-empirical quantum-chemical method (HyperChem) (Fig. 6) matched well the

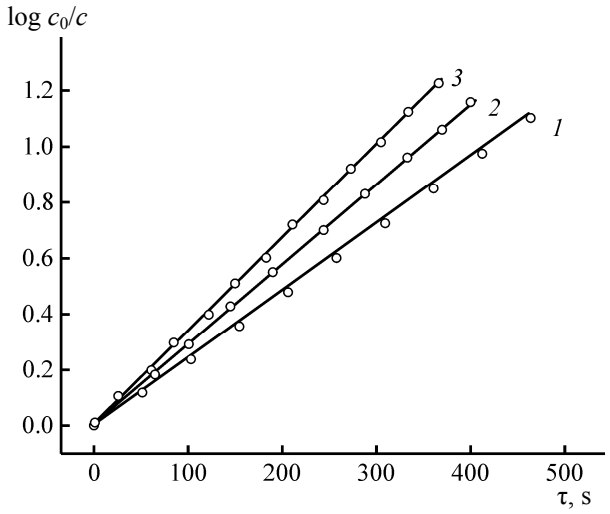


Fig. 4. log (c^0/c) as function of t for formation of zinc complex with compound **I** in CH_3CN–$Zn(OAc)_2$ at (*1*) 298, (*2*) 308, and (*3*) 318 K. $c_{\mathbf{I}} = 1.08 \times 10^{-5}$ mol/L, $[Zn(OAc)_2] = 3.13 \times 10^{-3}$ mol/L.

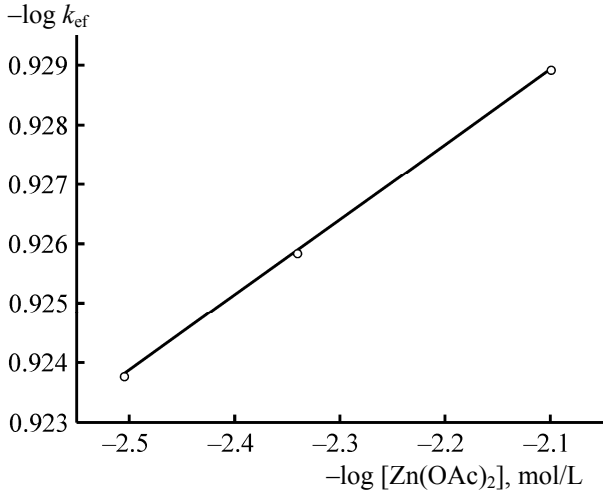


Fig. 5. log k_{ef} on as function of log [$Zn(OAc)_2$] for formation of zinc complex with compound **I** in acetonitrile at 298 K (tan α = 1.02, R = 0.9998).

experiment data. The simulation results suggested that the weak effect of the methoxyphenyl groups located at *meso*-positions of the macrocycle was due to rotation of the substituents out of the macrocycle plane by 70–85°C. Therefore, the effect of methoxy groups at the phenyl fragment could be transmitted exclusively via the σ-bonds, and variation of the peripheral substituents likely caused only minor distortion of the macrocycle (Fig. 6). The reference data indicate the effect of the macrocycle distortion on the porphyrin macrocycle acidic properties [3]; in the case studied here that was confirmed by similarity of the deprotonation constants. Complex formation with anionic forms of porphyrins **I** and **II** was ≈22–26 faster,

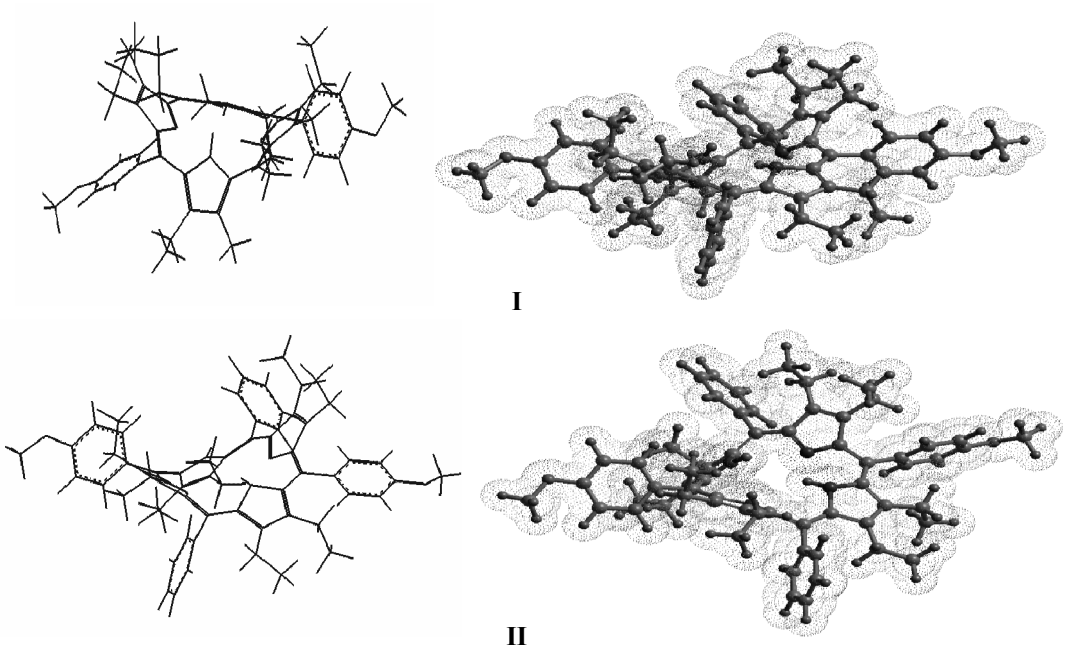


Fig. 6. Spatial structures of porphyrins **I** and **II** simulated with PM3 method (HyperChem).

Table 3. Kinetic parameters of the coordination of compounds **I** and **II** with zinc acetate in the $CH_3CN–Zn(OAc)_2$ and $CH_3CN–DBU–Zn(OAc)_2$ systems

Porphyrin, system	$[Zn(OAc)_2]$, mol/L	$k_v \times 10^{-2}$, L mol s^{-1}	ΔE, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
I				
$CH_3CN–Zn(OAc)_2$	3.13×10^{-3}	74	14	–212
$CH_3CN–DBU–Zn(OAc)_2$	2.55×10^{-4}	1660	9	–169
II				
$CH_3CN–Zn(OAc)_2$	3.13×10^{-3}	59	17	–206
$CH_3CN–DBU–Zn(OAc)_2$	1.06×10^{-4}	1560	10	–167

and the $E^{\neq}$ values were 5–7 kJ mol^{-1} lower as compared with the neutral molecules; likely due to elimination of energy losses on deformation and rupture of the N−H bonds at the reaction site.

The obtained results aids in targeted variation of the rate various processes involving tetrapyrrole macrocycles by changing pH of the reaction medium; that is essential for synthesis of complex tetrapyrrole species as well as for deeper investigation of catalytic acceleration of slow chemical reactions.

EXPERIMENTAL

Spectrophotometric titration with 1,8-diazabicyclo [5.4.0]undec-7-ene DBU in acetonitrile was performed using a Cary 100 Varian spectrophotometer. The measurement and data processing procedures were described elsewhere [7, 8]. Electronic absorption spectra were registered with Shimadzu UV1800, Hitachi U2000, and Cary 100 Varian spectrophotometers.

Acetonitrile ("highly pure" grade, less than 0.03% of water) was used as a solvent. 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) was used as a deprotonating reagent; constant of ionization of its conjugated acid pK_a 13.2. Zinc acetate ("analytical pure" grade) was further purified via recrystallization from aqueous acetic acid followed by drying of water at 380–390 K [9].

5,15-Bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin (I). A mixture of 1.0 g (2.36 mmol) of 5,5'-dicarbethoxy-*ms*-(4'-methoxyphenyl)-4,4'-dimethyl-3,3'-diethyldipyrrolylmethane and 1.0 g (17.80 mmol) of potassium hydroxide in 6 mL of water was heated in a sealed ampoule at 180°C for 4 h. Then the ampoule was opened, the precipitated *ms*-(4'-methoxyphenyl)-4,4'-dimethyl-3,3'-diethyldipyrrolylmethane was filtered off and dissolved in 20 mL of methanol. Propionic aldehyde, 0.2 mL (2.78 mmol), was added to the solution; then 0.5 mL of hydrobromic acid was added upon stirring, under inert. The obtained mixture was stirred at room temperature for 2 h. The precipitated porphyrinogen was filtered off and dissolved in 20 mL of THF. 0.87 g (3.54 mmol) of chloranil, 0.5 g (2.50 mmol) of copper(II) acetate hydrate, and 0.6 mL (4.28 mmol) of triethylamine were added to the obtained solution. The mixture was refluxed during 0.5 h and then evaporated to dryness. The residue was dissolved in methylene chloride and purified via column chromatography on aluminum oxide (Brockmann III grade) eluting the first red-colored zone of the copper complex with methylene chloride. Solvent was removed from the eluate; the complex was precipitated with methanol, filtered off, washed with methanol, and dried in air at 70°C. Yield 0.14 g (14.6%), R_f 0.13 (benzene–hexane, 1 : 1). Electronic absorption spectrum, λ_{max}, nm (log ε): 569 (4.15), 434 (5.14).

A mixture of 0.1 g (0.12 mmol) of the copper complex, 1.0 mL (10.9 mmol) of phosphoryl chloride, and 1 drop of conc. hydrochloric acid in 50 mL of methylene chloride was refluxed for 0.5 h, cooled, and sequentially washed with 5% hydrochloric acid, 5% ammonia, and water. Solution of the porphyrin in methylene chloride was dried over sodium sulfate and passed through the short chromatographic column with alumina (Brockmann III grade) eluting the first green-colored zone of the porphyrin with methylene chloride. The solvent was removed from the eluate; 5,15-bis(4'-methoxyphenyl)-2,8,12,18-tetramethyl-3,7,10,13,17,20-hexaethylporphyrin was precipitated with methanol, filtered off, washed with methanol, and dried in air at

70°C. Yield 0.045 g (50.1%), R_f 0.26 (benzene–methanol, 10 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.99 d (4H, 2',6'-H, *J* 8.1 Hz), 7.23 d (4H, 3',5'-H, *J* 8.1 Hz), 5.05 q (4H, 5,15-CH_2, *J* 7.5 Hz), 4.13 s (6H, OCH_3), 3.62 s (12H, 3,7,13,17-CH_3), 2.81 q (8H, 2,8,12,18-CH_2, *J* 7.4 Hz), 1.81 t (6H, 5,15-CH_2, *J* 75 Hz), 1.21 t (12H, 2,8,12,18-CH_3). Electronic absorption spectrum ($CHCl_3$), λ_{max}, nm (log ε): 693 (3.68); 545 (3.80); 450 (4.83).

5,15-Bis(4'-methoxyphenyl)-10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin (II) was prepared similarly. Yield 0.061 g (65.8%). R_f 0.24 (benzene–methanol, 10 : 1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8.20–8.29 m (4H, *o*-H, Ph), 8.19 d (4H, 2',6'-H, Ar, *J* 8.0 Hz), 7.68–7.75 m (6H, *m,p*-H, Ph), 7.22 d (4H, 3',5'-H, Ar, *J* 8.0 Hz), 4.12 s (6H, OCH_3), 1.80 br.s (12H, CH_3), 2.52 br.s (8H, CH_2), 0.47 br.s (12H, CH_3).

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