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pH-Dependent Conformational Changes in Bisporphyrincalix[4]arene

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Abstract—pH-Dependent conformational changes in bisporphyrincalixarene in which the calix[4]arene core fixes the tetrapyrrole chromophores in the cyclophane orientation relative to each other were studied by spectrophotometric titration and ^{1}H NMR spectroscopy. It was shown that the distance between the reaction centers of the porphyrin fragments of the macrocycle can be controlled by varying the solution acidity. The ranges of reagent concentrations where functionally significant reversible conformational changes of the dimeric porphyrin occur were determined.

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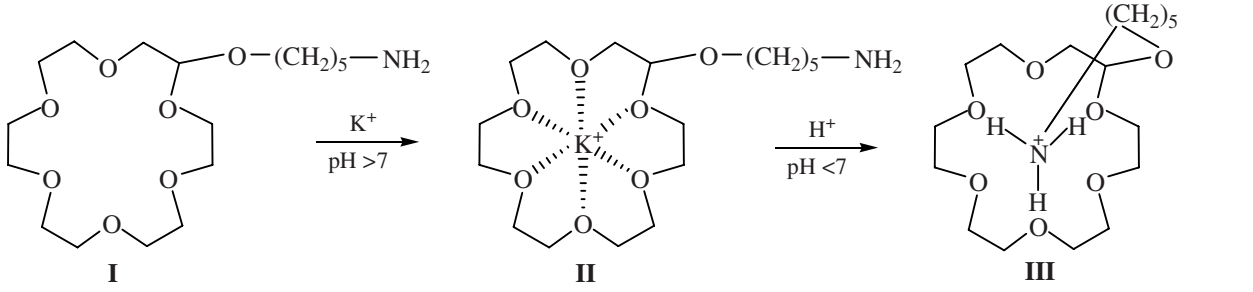
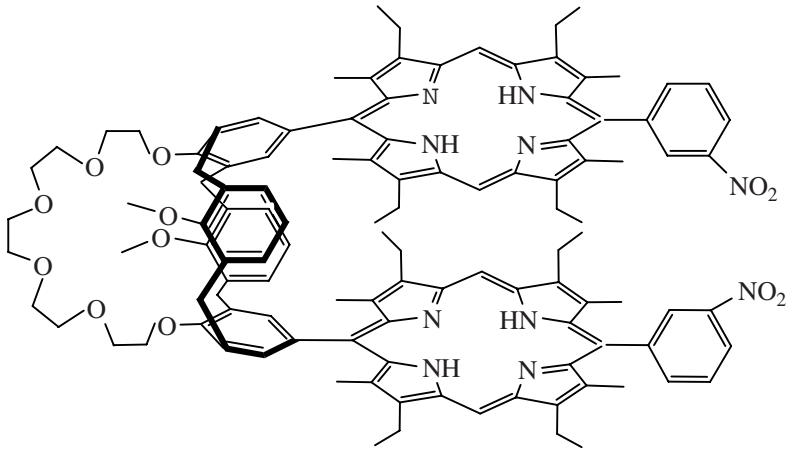
The problem of the development of spatially preorganized molecular devices having practically useful functional properties is extremely urgent for chemistry and biology [1–5]. Depending on whether the components (molecular fragments linked by covalent bonds and partially preserving their properties) are ion-active, photoactive, or electroactive, i.e., on whether they participate in ion exchange, absorption or emission of photons, or donation or acceptance of electrons, ionic, photonic, and electronic devices are distinguished [6]. Incorporation of electronic devices into supramolecular systems allows, in particular, the development of molecular switches, "supramolecules" that reversibly change the steric structure under the action of external factors. For example, 18-crown-6 derivative **I** with a long side chain bearing a terminal NH_2 group is a pH-switchable ionophore [7]. In a neutral or weakly alkaline solution, this crown ether forms with the K^+ ion a common complex **II** (see scheme).



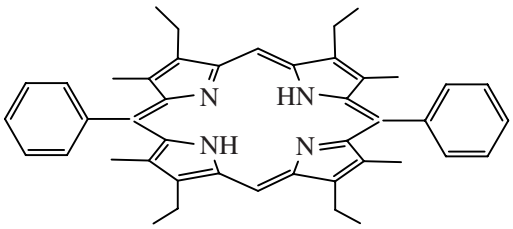
However, in acidic solutions the amino group is protonated, and the ammonium ion, acting like a hand, displaces the potassium ion from the cavity to form an intramolecular complex **III**. The K^+ and NH_4^+ ions have approximately equal size, but the entropy factor associated with the fixation of the alkylammonium group favors its binding in acid solutions. When ammonium complex **III** is returned to a neutral medium containing excess potassium ions, the K^+ ion displaces the ammonium group which is deprotonated in the process. This example demonstrates extreme importance of the steric configuration and relative spatial arrangement of the components of supramolecular systems.

In this study, with the aim to develop controllable tetrapyrrole molecular devices, we examined by spectrophotometric titration and ^{1}H NMR spectroscopy the

pH-dependent conformational changes in bispor-phyrin-calix[4]arene **IV** in which the calix[4]arene core holds the tetrapyrrole chromophores in the cyclophane orientation relative to each other.



IV



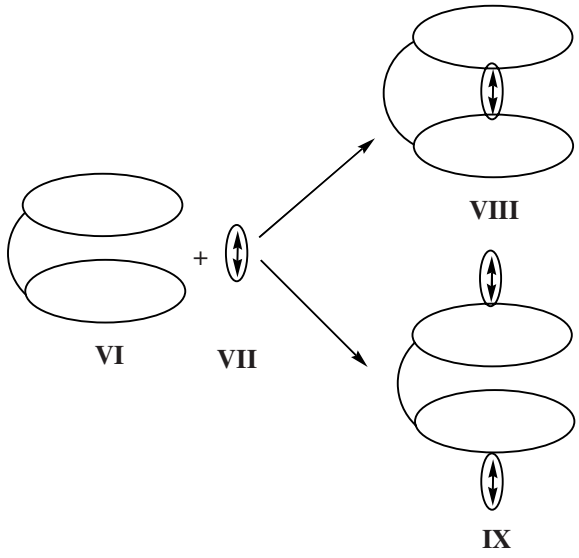
V

It was shown that the distance between the reaction centers of porphyrin fragments of the macroring can be controlled by varying the solution acidity. The ranges of reagent concentrations where functionally significant reversible conformational changes of the dimeric porphyrin occur were determined.

Porphyrins (H_2P) containing four nitrogen atoms in the coordination center (two pyrrole and two pyrrolenine atoms) in proton-acceptor media form mono- (HP^-) and dianions (P^{2-}), and in proton-donor media, mono- (H_3P^+) and dications (H_4P^{2+}). This fact allows the use of this class of tetrapyrrole compounds as pH-controlled ionic and molecular receptors. Of indubitable interest is additional chemical modification of the tetrapyrrole macroring with the aim to introduce into the molecule the fragments that themselves exhibit complexing power toward substrates of definite type [8–10]. Extremely promising in this respect are calix[4]arenes which can form host–guest complexes with small organic molecules retained in the calixarene cavity by hydrophobic interactions [11, 12].

Covalent combination of porphyrin and calix[4]arene fragments gives supramolecules which preserve the electronic and steric structure of their components but, at the same time, exhibit essentially new properties (complexing, acid–base, photochemical, etc.).

The complexing properties of bisporphyrin supramolecules toward small organic molecules have certain features: (1) possibility of "internal" or "external"



VI **VII** **VIII** **IX**

coordination of the substrate; (2) simultaneous addition of two and more substrates to tetrapyrrole fragments. The "internal" coordination is realized in the case the complexing interpor-phyrin cavity of bisporphyrin receptor **VI** and a biden-tate ligand **VII** much in size. The two-center interaction leads to the formation of a stable 1 : 1 complex **VIII**. Without size matching, ligand **VII** is coordinated on the "ex-ternal" side of the tetrapyrrole fragments to form 1 : 2 complex **IX**, less stable than **VIII**.

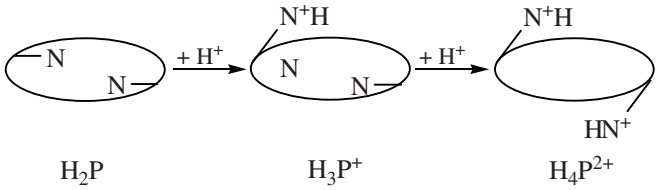
Analysis of the published data [8–10] and our own results [13, 14] indicates that the selectivity of interac-

tions of bisporphyrincalixarene receptors with ions (metal cations and halide anions) and neutral molecules of various nature (alcohols, nitrogen-containing bases, carboxylic acids, amino acids) is largely determined by the steric arrangement of the molecular components of the supramolecule. In this connection, it is extremely topical to examine the possibility of reversibly changing ("controlling") the distance between the porphyrin fragments of porphyrin–calixarene conjugates under the action of external factors:

$$H_2P + H^+ \xrightleftharpoons{k_{b1}} H_3P^+, \quad (1)$$

$$H_3P^+ + H^+ \xrightleftharpoons{k_{b2}} H_4P^{2+}. \quad (2)$$

It is well known [15] that the protonation of the first of the two pyrrolenine nitrogen atoms of the coordination center of the tetrapyrrole macroring [formation of monoprotonated form H_3P^+ from molecular form H_2P, Eq. (1)] is accompanied by distortion of the macroring: The steric hindrance does not allow arrangement of the third hydrogen atom in the coordination cavity, and it is located over the macroring plane. The positively charged nitrogen atom of the pyrrolenine fragment moves with this hydrogen atom out of the macroring plane. Addition of the second hydrogen atom [formation of the double-protonated form H_4P^{2+}, Eq. (2)] leads to additional deformation of the macroring, so that H_4P^{2+} exists in the 1,3-alternate form in which two opposite positively charged pyrrolenine nitrogen atoms, owing to electrostatic repulsion, are placed on different sides of the tetrapyrrole macroring.



H_2P H_3P^+ H_4P^{2+}

According to [16], the formation of H_4P^{2+} from H_2P for monomeric diphenylporphyrin **V** is accompanied by the downfield shift (by ~0.20 ppm) of the ^{1}H NMR signals of NH and meso protons [16]. This trend suggests a significant increase in the intensity of the magnetic field induced by the macrocyclic ring current upon protonation of the porphyrin chromophore. The formation of the monoprotonated form H_3P^+ from the molecular form does not lead to significant changes in the ^{1}H NMR spectrum.

With the aim to obtain mono- (H_6P^{2+}) and diprotonated (H_8P^{4+}) forms of bisporphyrincalixarene **IV**, we performed spectrophotometric titration of the dimeric porphyrin ligand with sulfuric acid in system (3).

$$H_4P - C_2H_5OH - H_2SO_4, \quad (3)$$

$$H_2P + 2H^+ \xrightleftharpoons{k_{b1}} H_6P^{2+}, \quad (4)$$

$$H_6P^{2+} + 2H^+ \xrightleftharpoons{k_{b2}} H_8P^{4+}. \quad (5)$$

A quartz cell was charged with 50 ml of a ~1.5×10^{-5} M solution of a porphyrin ligand. A 0.01 M solution of H_2SO_4 in ethanol was used as titrant. In the titration curve (Fig. 1), there are two steps corresponding to equilibria (4) and (5). Changes in the electronic absorption spectra of system (3) occur with successive formation of two families of curves, with a specific set of isobestic points corresponding to each transition (Fig. 2). Determination of the coordinate of the inflection point (corresponding sulfuric acid concentration) in the titration curve (Fig. 1) allows us to distinguish in the overall pattern (Fig. 2) two sets of curves (Figs. 3, 4) related to the progress of the first and second ionization steps, i.e., to the formation of the mono- (H_6P^{2+}) and diprotonated (H_8P^{4+}) forms of bisporphyrincalixarene **IV**. The threshold concentrations of sulfuric acid in system (3), at which the spectrum of H_4P starts to transform into that of H_6P^{2+}, and the spectrum of H_6P^{2+}, into that of H_8P^{4+} are 2×10^{-5} and 7.5×10^{-5} M, respectively.

To study the deprotonation of the mono- and diprotonated forms of bisporphyrincalixarene **IV**, we examined the reaction of H_6P^{2+} and H_8P^{4+} with piperazine in system (6).

$$H_4P - C_2H_5OH - H_2SO_4 - NHC_4H_8NH \quad (6)$$

A quartz cell was charged with 50 ml of a 7.42×10^{-5} M solution of **IV** in ethanol. The acidity corresponding to the maximal content of the monoprotonated ligand form (according to the previously determined ranges of existence of protonated species) was created by adding a 0.01 M solution of sulfuric acid in ethanol. Then the resulting solution of monocation of bisporphyrincalixarene **IV** was titrated with a 0.001 M solution

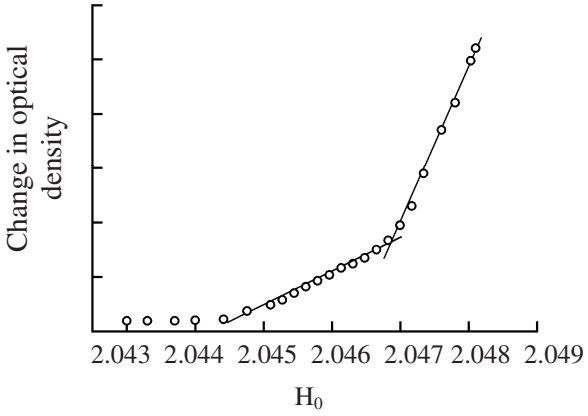


Fig. 1. Spectrophotometric titration curve of compound **IV** (C 1.5×10^{-5} M) with sulfuric acid (C 1×10^{-5}–4×10^{-4} M) at λ 496 nm (descending optical density) in ethanol at 298 K. (H_0) Hammett constant.

of piperazine in ethanol [Eq. (8)]. When the piperazine concentration in the cell reached 4.27×10^{-5} M, the electronic absorption spectrum of the monocationic form H_6P^{2+} transformed into that of the molecular form H_4P (Fig. 5). Similarly we examined the transformation of the diprotonated form of bisporphyrincalixarene **IV** into the monoprotonated form [Eq. (7)]:

$$H_8P^{4+} + NHC_4H_8NH \overset{k_{a1}}{\rightleftharpoons} H_6P^{2+} + N^+H_2C_4H_8N^+H_2, \quad (7)$$

$$H_6P^{2+} + NHC_4H_8NH \overset{k_{a2}}{\rightleftharpoons} H_4P + N^+H_2C_4H_8N^+H_2. \quad (8)$$

The solution acidity corresponding to the maximal (98%) content of the diprotonated ligand form [$C(H_2SO_4)$ 1.5×10^{-4} M) was created by adding a 0.01 M solution of sulfuric acid in ethanol. Then the resulting solution of the bisporphyrincalixarene dication was titrated with a 0.001 M solution of piperazine in ethanol [Eq. (7)]. When the piperazine concentration in the cell reached 3.36×10^{-4} M, the electronic absorption spectrum of the dicationic form H_8P^{4+} transformed into that of the monocationic form H_6P^{2+} (Fig. 5). The threshold piperazine concentrations in system (6), at which the spectrum of H_6P^{2+} transforms into that of H_4P and the spectrum of H_8P^{4+}, into that of H_6P^{2+} are 5×10^{-6} and 5×10^{-7} M, respectively.

In all the cases, the titrant concentration was chosen so that the total change in the solution volume by the end of titration was within 1%. The solution dilution was taken into account with formula (9):

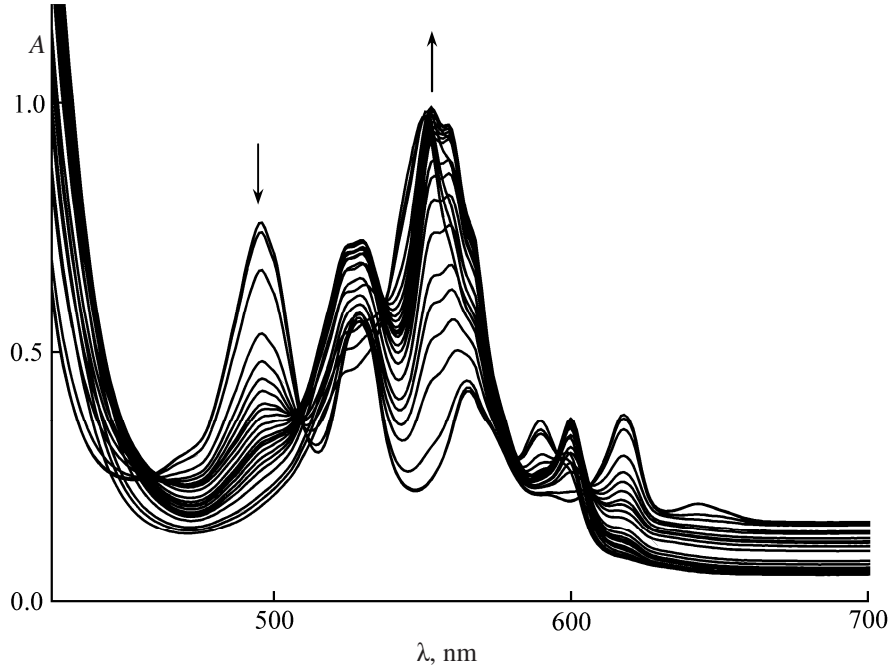


Fig. 2. Evolution of the electronic absorption spectrum of **IV** (1.5×10^{-5} M) in the ethanol–sulfuric acid system with increasing sulfuric acid concentration from 1×10^{-5} to 4×10^{-4} M at 298 K.

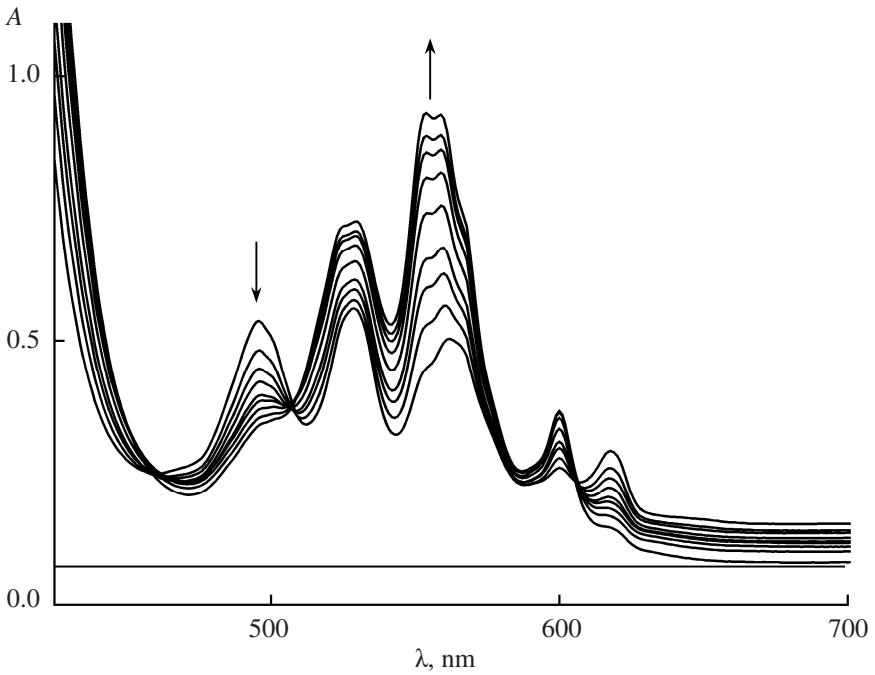


Fig. 3. Evolution of the electronic absorption spectrum of **IV** (1.5×10^{-5} M) in the ethanol–sulfuric acid system with increasing sulfuric acid concentration from 1×10^{-5} to 7×10^{-5} M, which corresponds to the formation of the monoprotonated porphyrin.

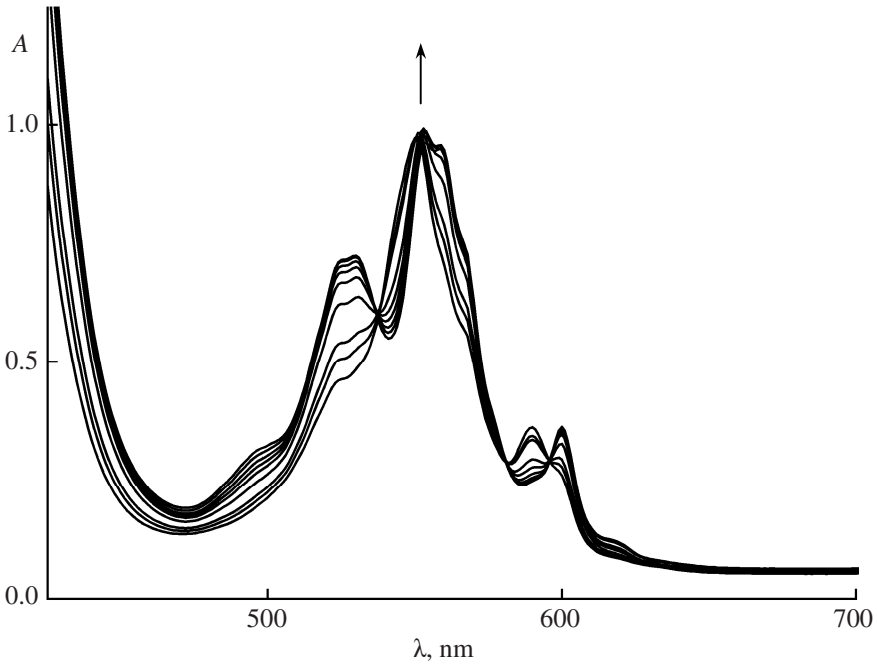
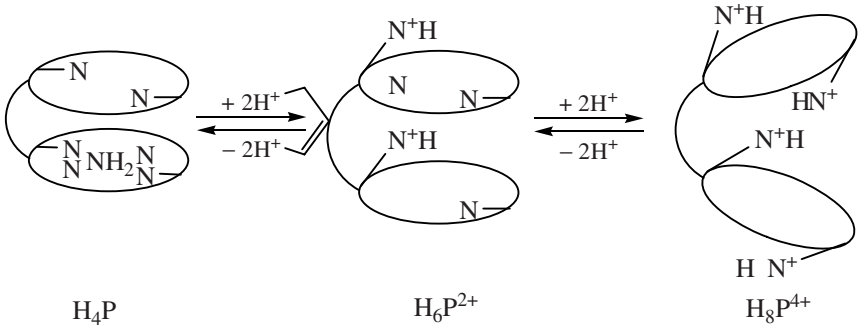


Fig. 4. Evolution of the electronic absorption spectrum of **IV** (1.5×10^{-5} M) in the ethanol–sulfuric acid system with increasing sulfuric acid concentration from 7×10^{-5} to 4×10^{-4} M, which corresponds to the formation of the diprotonated porphyrin.

$$A_t = A_t^0/(1 + V_\Sigma/V_0), \quad (9)$$

where A_t is the running optical density after adding the titrant; A_t^0, running optical density corresponding to the solution volume before adding the titrant; V_Σ, total volume of the titrant added; and V_0, initial volume of the ligand solution in the cell.

The ^{1}H NMR spectra of the molecular (H_4P) and double-protonated (H_8P^{4+}) forms of **IV** show that protonation of the nitrogen atoms in the tetrapyrrole fragments is accompanied by their moving apart from each other. Whereas in the spectrum of H_4P the mutual shielding of the porphyrin fragments arranged in the cyclophane fashion relative to each other causes an upfield (compared to the H_2P form of monomeric analog **V**) shift of the signals of the NH and meso protons (by ~0.15 ppm), electrostatic repulsion of the double-protonated porphyrin fragments in H_8P^{4+} bearing the positive charge leads to disappearance of their mutual shielding effect owing to maximal separation from each other (the chemical shifts of the NH and *meso* protons of H_4P and H_6P^{2+} virtually coincide). Thus, conformational changes in the molecule, caused by protonation of the tetrapyrrole fragments of the dimer in going from H_4P to H_8P^{4+}, are accompanied by a downfield shift of the signals of the NH and *meso* protons by ~0.35 ppm.



In the ^{1}H NMR spectrum of the monodeprotonated form (H_6L^{2+}), the upfield shift (~0.15 ppm) of the signals of these protons compared to the spectrum of the molecular form (H_2P) of monomeric porphyrin **V** is preserved. Apparently, in H_6P^{2+} the protonated nitrogen atoms of the porphyrin fragments bearing a positive charge (one charged atom per macroring) are arranged apart from each other, with no significant mutual repulsion. Therefore, transformation of the molecular form H_4P into the monoprotonated form H_6P^{2+} is not accompanied by significant conformational changes.

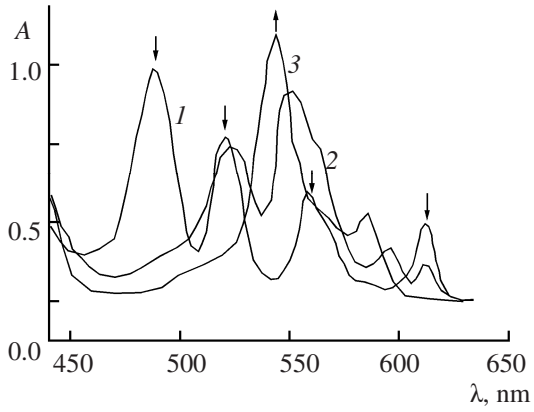


Fig. 5. Electronic absorption spectrum of **IV** (7.42×10^{-5} M) in the system **VI:** (*1*) H_4P, $C(NHC_4H_8NH)$ 0 M, (*2*) H_6P^{2+} $C(NHC_4H_8NH)$ 3×10^{-7}–4.27×10^{-5} M, (*3*) H_8P^{4+} $C(NHC_4H_8NH)$ 4.27×10^{-5} M–3.36×10^{-4} M.

The ^{1}H NMR monitoring of transformations of the mono- and diprotonated forms of bisporphyrincalixarene in system (6) shows that the first step of the deprotonation of the porphyrin fragments [Eq. (7)] is accompanied by their mutual approach: The signals of the NH and meso protons of H_6P^{2+} are shifted upfield by ~0.35 ppm relative to H_8P^{4+}, i.e., in the H_6P^{2+} molecule, as in H_4P, the porphyrin fragments arranged in the cyclophane fashion exert a shielding effect on each other. The lack of significant changes in the ^{1}H NMR spectrum in going from H_6P^{2+} to H_4P indicates that the molecule of **IV** upon transition from the H_6P^{2+} to H_4P form [Eq. (8)] does not undergo significant conformational changes involving a change in the distance between the porphyrin fragments.

Our results show that the distance between the tetrapyrrole fragments in **IV** can be controlled by varying the solution acidity. The prospects opened by this phenomenon are determined by the possibility of developing molecular switches based on porphyrin–calixarene conjugates, i.e., "controllable" supramolecules capable of reversibly changing the steric structure, properties, and functions under external actions. Achievements in this field open vast prospects for the development of new molecular technologies.

EXPERIMENTAL

5,17-Biszinc[2,8,12,18-tetramethyl-3,7,13,17-tetraethyl-10-(3-nitrophenyl)porphyrin]-25,27-dimethoxy-26,28-crown[6]calix[4]arene IV and 5,15-diphenyl-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin V were prepared according to [16, 17]. Spectroscopic studies were performed with a Varian Cary 100 spectrometer at 298 K. The solvents were purified and dried by standard procedures [18, 19]. The ^{1}H NMR spectra were recorded on a Bruker VC-200 spectrometer with a working frequency of 200 MHz in $CDCl_3$, internal reference TMS. Bisporphyrincalixarene **IV**: R_f 0.53 (Al_2O_3, eluent CH_2Cl_2–C_6H_{14}, 1 : 2). Electronic absorption spectrum (ethanol), λ_{max}, nm (log ε): 403.3 (4.91), 505.6 (4.03), 541.5 (3.60), 572.1 (3.73), 629.4 (3.21). ^{1}H NMR spectrum (H_4P), δ, ppm: 10.13 s (4H, *ms*-H), 7.92–7.82 m (4H, $Ar_{ortho,\ porph}$ + 4H, $Ar_{calixarene}$), 7.63–7.41 m (2H, $Ar_{meta,\ porph}$ + 4H, $Ar_{calixarene}$), 7.26 d (2H, $Ar_{para,\ porph}$), 7.01 t (2H, $Ar_{para,\ calixarene}$), 4.40 s (6H, OCH_3), 4.31 d (4H, $ArCH_2Ar$), 3.83 q (8H, CH_2CH_3), 3.77 m (8H, CH_2CH_3), 3.70 s (4H, OCH_2CH_2O), 3.64 m (16H, OCH_2CH_2O), 3.00 d (4H, $ArCH_2Ar$), 2.03 s (12H, CH_3), 2.12 s (12H, CH_3), 0.89 t (12H, CH_2CH_3), 0.86 t (12H, CH_2CH_3), –3.17 s (4H, NH). ^{1}H NMR spectrum (H_6P^{2+}), δ, ppm: 10.16 s (4H, *ms*-H), 7.95–7.80 m (4H, $Ar_{ortho,\ porph}$ + 4H, $Ar_{calixarene}$), 7.64 –7.40 m (2H, $Ar_{meta,\ porph}$ + 4H, $Ar_{calixarene}$), 7.27 d (2H, $Ar_{para,\ porph}$), 7.05 t (2H, $Ar_{para,\ calixarene}$), 4.40 s (6H, OCH_3), 4.31 d (4H, $ArCH_2Ar$), 3.83 q (8H, CH_2CH_3), 3.76 m (8H, CH_2CH_3), 3.70 s (4H, OCH_2CH_2O), 3.63 m (16H, OCH_2CH_2O), 3.01 d (4H, $ArCH_2Ar$), 2.02 s (12H, CH_3), 2.11 s (12H, CH_3), 0.91 t (12H, CH_2CH_3), 0.87 t (12H, CH_2CH_3), –3.18 s (4H, NH). ^{1}H NMR spectrum (H_8P^{4+}), δ, ppm: 10.47 s (4H, *ms*-H), 7.94–7.81 m (4H, $Ar_{ortho,\ porph}$ + 4H, $Ar_{calixarene}$), 7.65–7.42 m (2H, $Ar_{meta,\ porph}$ + 4H, $Ar_{calixarene}$), 7.28 d (2H, $Ar_{para,\ porph}$), 7.03 t (2H, $Ar_{para,\ calixarene}$), 4.41 s (6H, OCH_3), 4.33 d (4H, $ArCH_2Ar$), 3.85 q (8H, CH_2CH_3), 3.78 m (8H, CH_2CH_3), 3.72 s (4H, OCH_2CH_2O), 3.65 m (16H, OCH_2CH_2O), 3.03 d (4H, $ArCH_2Ar$), 2.05 s (12H, CH_3), 2.14 s (12H, CH_3), 0.90 t (12H, CH_2CH_3), 0.85 t (12H, CH_2CH_3), –2.79 s (4H, NH).

Porphyrin V. R_f 0.71 (Al_2O_3, eluent CH_2Cl_2–C_6H_{14}, 1 : 2). Electronic absorption spectrum (ethanol), λ_{max}, nm (log ε): 408.1 (5.20), 511.6 (4.17), 545.7 (3.70), 578.2 (3.87), 631.4 (3.64). ^{1}H NMR spectrum (H_2P), δ, ppm: 10.28 s (2H, *ms*-H), 7.94 d (4H, Ar_{ortho}), 7.70 t (4H, Ar_{meta}), 7.26 d (2H, Ar_{para}), 3.85 q (8H, CH_2CH_3), 2.15 s (12H, CH_3), 0.91 t (12H, CH_2CH_3), –3.02 s (2H, NH). ^{1}H NMR spectrum (H_3P^+), δ, ppm: 10.29 s (2H, *ms*-H), 7.94 d (4H, Ar_{ortho}), 7.71 t (4H, Ar_{meta}), 7.27 d (2H, Ar_{para}), 3.88 q (8H, CH_2CH_3), 2.15 s (12H, CH_3), 0.90 t (12H, CH_2CH_3), –3.03 s (2H, NH). ^{1}H NMR spectrum (H_4P^{2+}), δ, ppm: 10.49 s (2H, *ms*-H), 7.95 d (4H, Ar_{ortho}), 7.72 t (4H, Ar_{meta}), 7.27 d (2H, Ar_{para}), 3.87 q (8H, CH_2CH_3), 2.16 s (12H, CH_3), 0.92 t (12H, CH_2CH_3), –2.81 s (2H, NH).

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