===== REVIEW =====

Porphyrin–Calix[4]arenes

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Abstract—The review deals with the synthesis, chemical modification, and complexing properties of a new class of molecular receptors, porphyrin–calix[4]arene conjugates.

I. INTRODUCTION

Design and synthesis of nanosize ($1–10^2$ nm) molecules possessing receptor properties constitute an important problem in organic chemistry [1–4]. Porphyrin metal complexes are very promising for this purpose

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Fields of scientific interest: synthetic organic chemistry, supramolecular chemistry, design of molecular receptors selective for definite substrates.

Koifman Oskar Iosifovich was born in 1944 in Saratov. In 1967 he graduated from the Ivanovo Institute of Chemical Technology. Candidate of chemical sciences since 1970, Doctor of chemical sciences since 1983; Head of a laboratory at the Institute of Solution Chemistry, Russian Academy of Sciences. O.I. Koifman is an author of 4 monographs, 150 papers, 23 inventor's certificates, and 3 patents; he had trained 5 Doctors and 15 Candidates of sciences.

Fields of scientific interest: synthesis, physical and chemical properties, and practical applications of porphyrins, their structural analogs, and liquid crystalline compounds.

[5]. Their unique properties originate from unusual geometric and electronic structure of porphyrin ligand (**I**) which is characterized by extended aromatic conjugation system [6, 7]. In the recent years, interest in porphyrin derivatives increases due to their ability to participate in molecular recognition. Molecular recognition is a process where some molecules (host) selectively bind other molecules (guest) to produce a well structurally organized system through intermolecular forces. To ensure a high level of structural organization of the ground state of complexes derived from organic compounds, the presence of several binding centers is usually necessary, for the energy of a single binding center is much lower than the energy of covalent bonds. Therefore, of specific interest is chemical modification of the porphyrin macroring via introduction of fragments capable of forming intercalation compounds with both charged species and nonpolar molecules. From this viewpoint, extremely promising are calix[4]arenes (**II**), cyclic condensation products of phenols with aldehydes [8–10]. Calix[4]-arenes are readily accessible compounds possessing reactive centers which could readily be modified. Calix-[4]arenes are capable of froming guest–host complexes with cations, anions, and small organic molecules.

Calix[4]arene fragments may be used as a molecular scaffold for building up preorganized three-dimensional receptors by combination with porphyrin fragments via covalent bonds [9–13]. Functionalization of the phenolic hydroxy groups, aromatic rings, and bridging fragments in porphyrin–calix[4]arene conjugates could lead to multifold enhancement of their

I   **II**
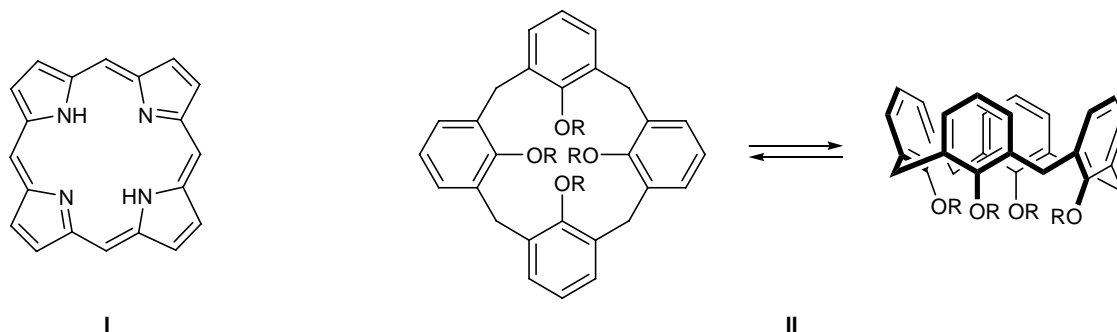
receptor power [10]. The presence in such a supra-molecule of an extended conjugated π-electron system intrinsic to porphyrins makes it possible to success-fully apply a broad range of spectral methods for studying intermolecular interactions.

First studies on receptors containing covalently bound porphyrin and calix[4]arene fragments have been reported in the late 1980s–early 1990s. The present review is the first attempt to systematize, analyze, and generalize published data on the syn-thesis, chemical modification, and complexing pro-perties of a new class of molecular receptors, porphyrin–calix[4]arene conjugates.

II. PORPHYRIN–CALIX[4]ARENES

A large number of compounds containing porphyrin fragments covalently bound to crown ethers [14, 15] and cyclodextrins [16, 17] and possessing specific complexing properties were synthesized in the recent

Scheme 1.

III   **IV**   **V**

(1) CCl₃COOH, MeCN
(2) C₆Cl₄O₂, CH₂Cl₂
(3) Zn(OAc)₂, CH₂Cl₂

VI

VII
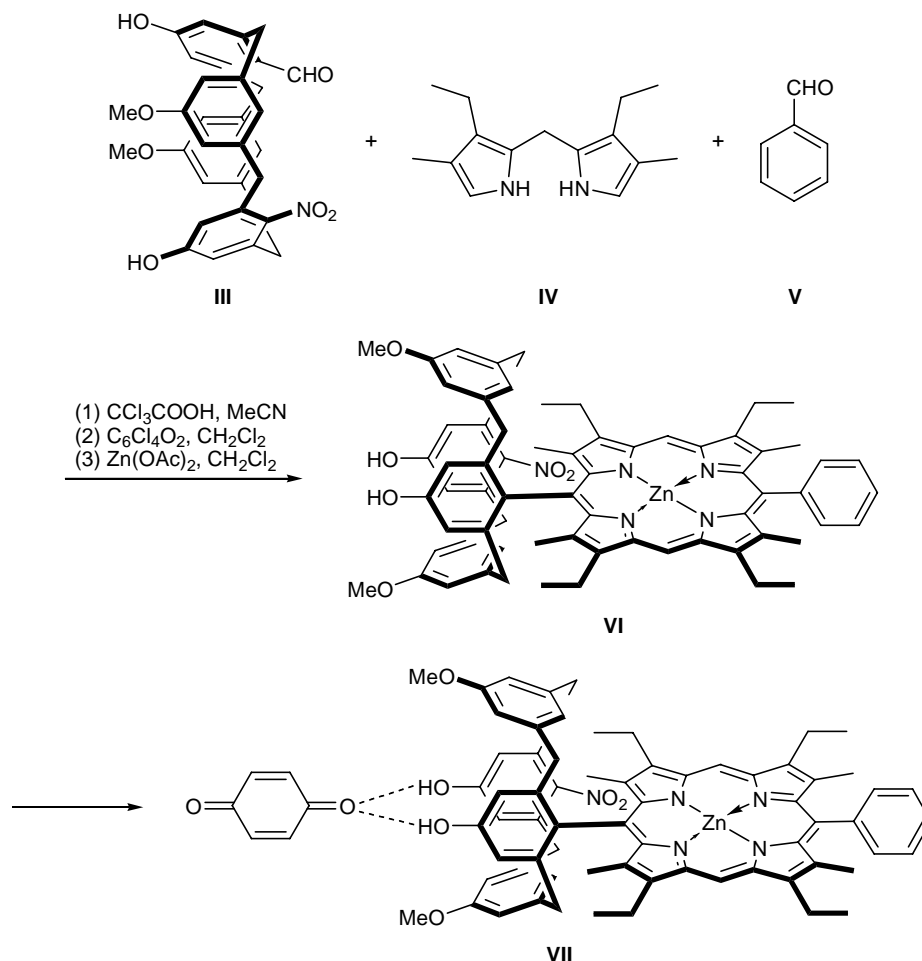
years. Advantages of calix[4]arenes as building blocks were demonstrated for the first time in [18–23].

Porphyrin–calix[4]arene zinc complex **VI** was synthesized in 30% yield by three-component condensation of 26,28-dihydroxy-17-nitro-25,27-dimethoxy-calix[4]arene-5-carbaldehyde (**III**), 2,2'-dipyrrolylmethane **IV**, and benzaldehyde (**V**) (Scheme 1) in two steps according to the procedure for synthesis of porphyrins from α,α'-unsubstituted dipyrrolylmethanes [22]. Compound **VI** is capable of forming guest–host complexes via hydrogen bonding between two phenolic hydroxy groups of the calix[4]arene fragment and carbonyl group of 1,4-benzoquinone. Key calix[4]-arene **III** was prepared as described in [24].

The ^{1}H NMR spectrum of zinc complex **VI** in the absence of benzoquinone contains signals from two nonequivalent hydroxy groups, α-OH and β-OH, at δ 9.03 and 7.97 ppm, respectively. Upon addition of benzoquinone, these signals and those belonging to the *meso* protons in the porphyrin fragment shift upfield. ^{1}H NMR and titrimetric study of the complex formation between **VI** and benzoquinone showed [25, 26]

that the composition of adduct **VII** is 1:1. The low binding constant ($k_{ass} = 70\pm10$ l/mol), as compared to published data for analogous systems, is explained by strong intramolecular hydrogen bonding between the two hydroxy groups in calix[4]arene [22]. A solution of complex **VII** in methylene chloride displayed fluorescence quenching due to two-center binding of benzoquinone by the calix[4]arene fragment. Addition of methanol eliminates noncovalent interactions in **VII** and restores fluorescence of conjugate **VI** to the initial value.

The calix[4]arene moieties in new donor–acceptor systems **VIII** and **IX** [23, 44] adopt different conformations; therefore, the porphyrin (donor) and pyromellitimide fragments (acceptor) appear at different distances from each other (5 and 15 Å, respectively).

Scheme 2 shows the synthesis of calix[4]arene derivative **VIII** in 1,3-*alternate* (1,3-*alt*) conformation [23]. The presence of bulky propyloxy groups excludes rotation of the aryl fragments with respect to the calix-[4]arene rim, and the 1,3-*alt* conformer is stable (no isomerization occurs even on heating for 12 h in
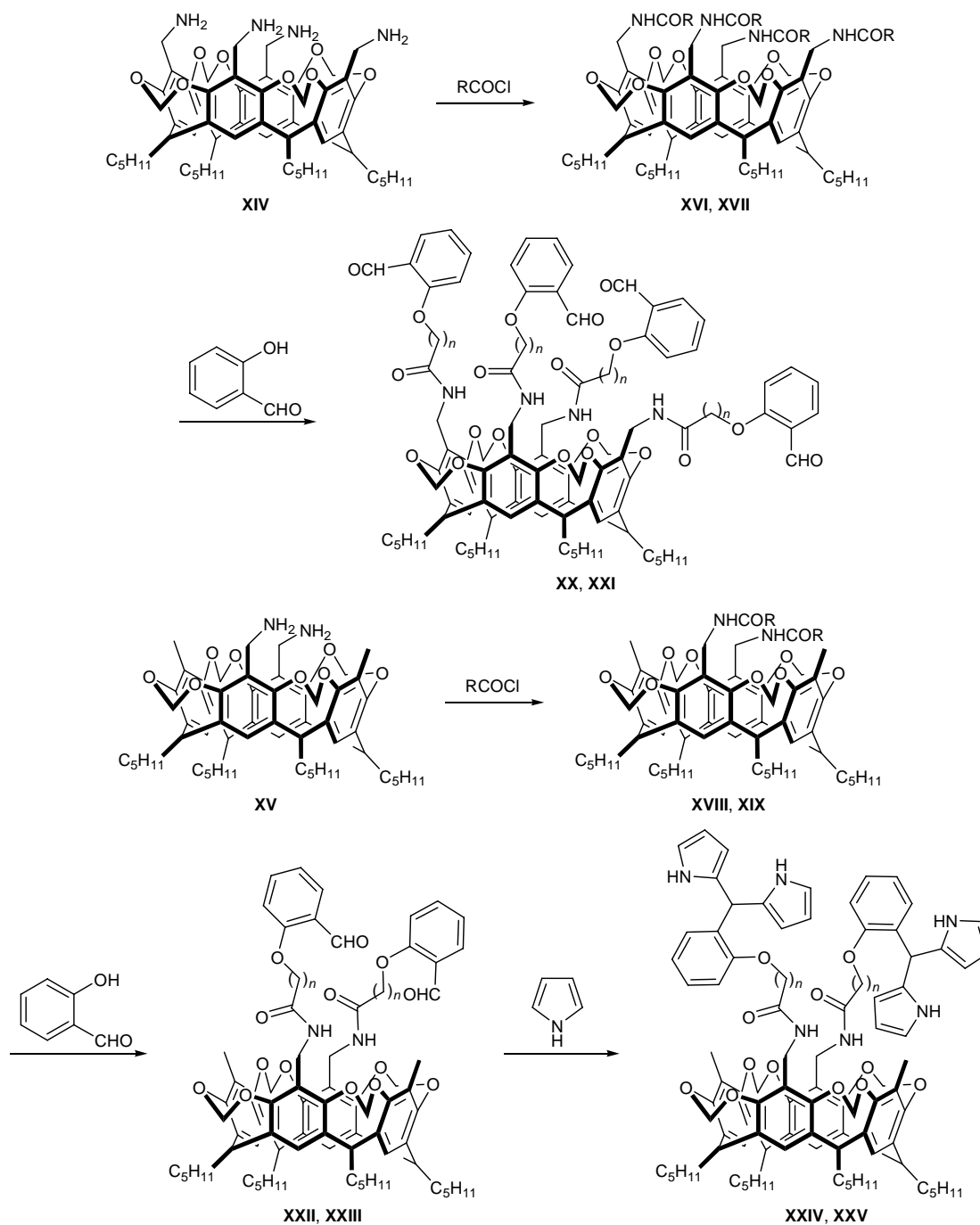

VIII

IX

X
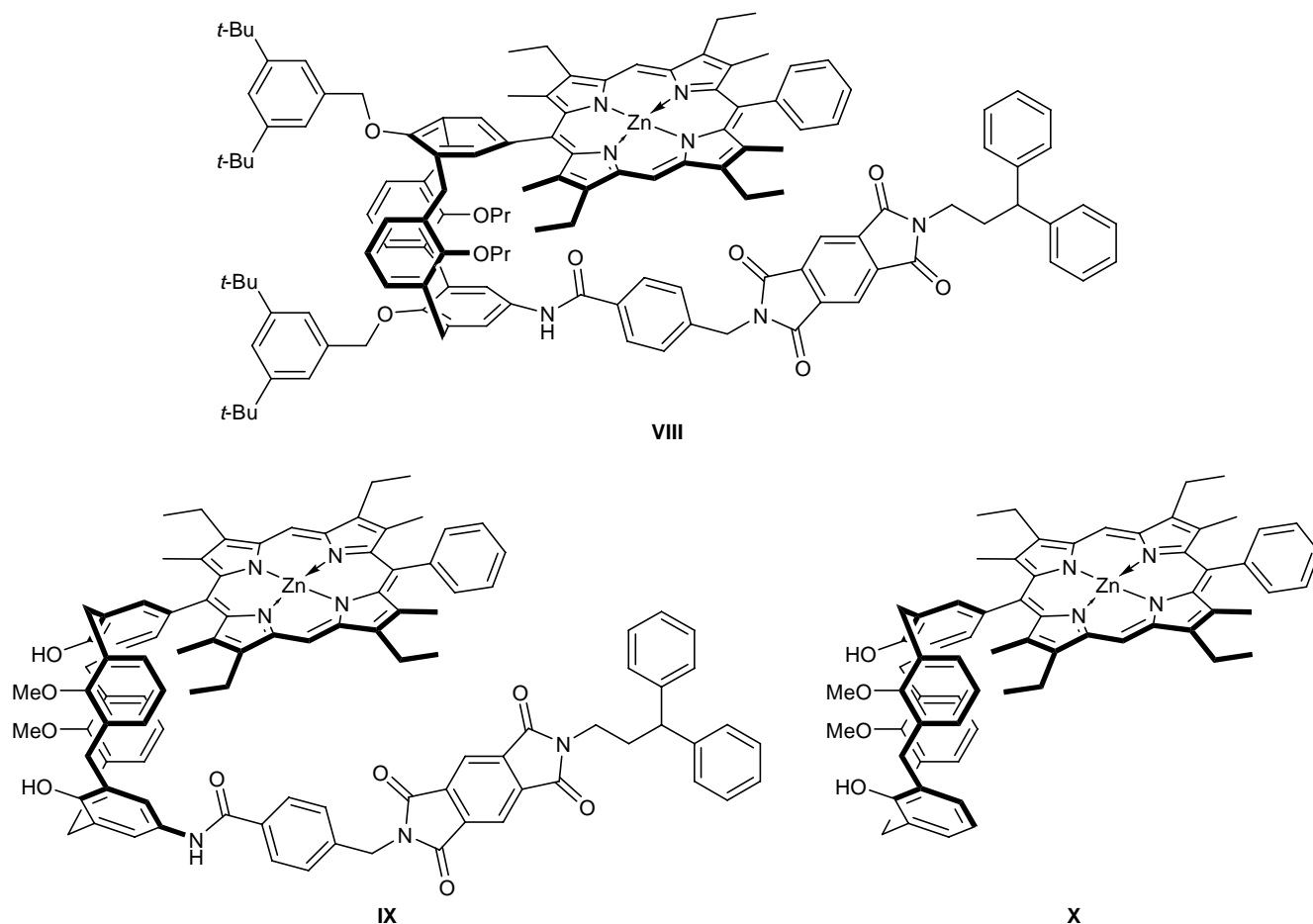
Scheme 2.
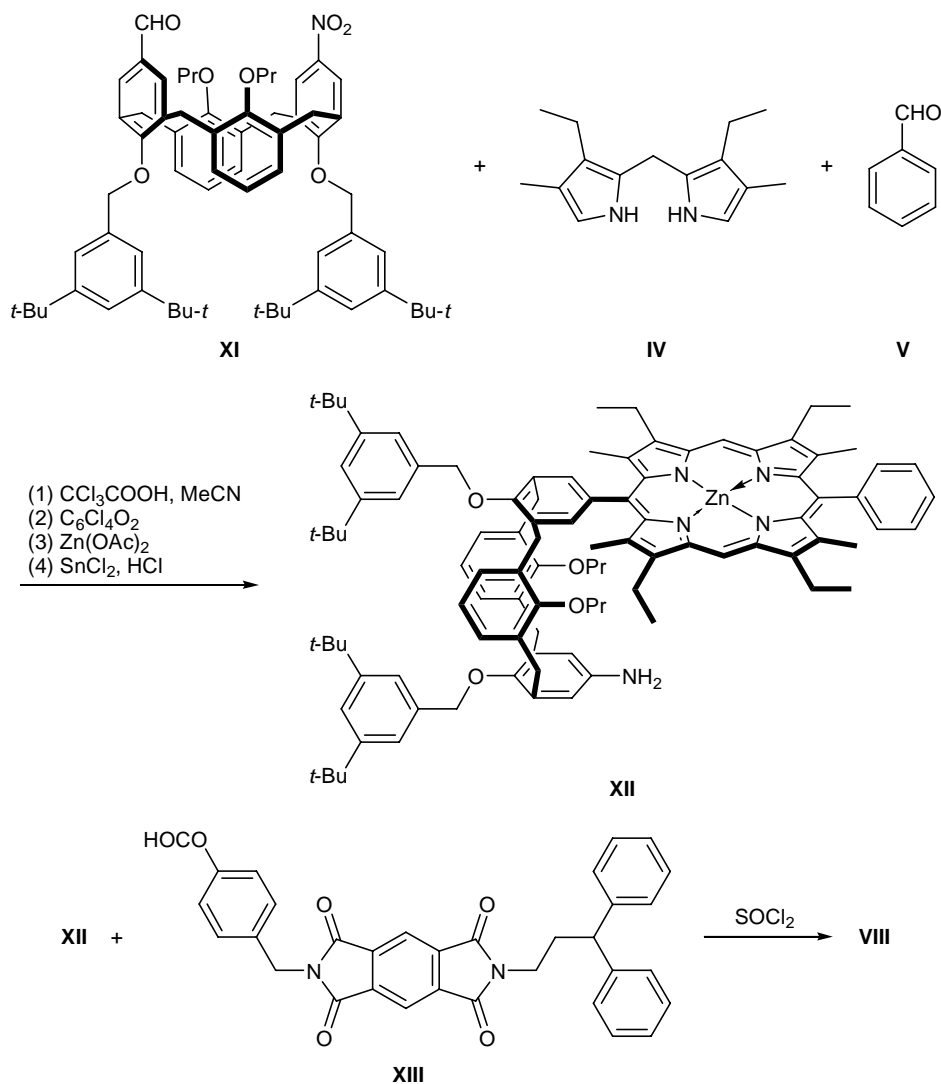
carbon tetrachloride). Likewise, structure **IX** having no bulky substituents on the lower rim (*cone* conformation) and simpler porphyrin–calix[4]arene **X** (as model structure) were synthesized. According to [27], structure **IX** is stabilized by formation of intramolecular hydrogen bond between the two phenolic hydroxy groups; this follows from splitting of the corresponding signals in the ^{1}H NMR spectrum of **IX**.

The fluorescence intensity of complex **VIII** in benzene is as low as 3.5% of the corresponding value for **X**. This means that interaction between spatially close porphyrin and pyromellitimide fragments (distance ~5 Å) leads to effective fluorescence quenching. By contrast, the fluorescence intensity of complex **IX** is 95% as referenced to model structure **X**. Obviously, the pyromellitimide fragment in **IX** is remote from the porphyrin moiety (the distance is ~15 Å), their mutual

interaction is minimal, and no appreciable fluorescence quenching is observed [27].

Middel *et al*. [28] synthesized porphyrin–calix[4]-arenes on the basis of key tetraamine **XIV** and diamine **XV** (Scheme 3). Reactions of the latter with chloroacetyl chloride and 6-bromohexanoyl chloride gave the corresponding tetraamides **XVI** and **XVII** and diamides **XVIII** and **XIX**. Aldehydes **XX–XXIII** were prepared by reaction of **XVI–XIX** with salicylaldehyde. By addition of 10% trifluoroacetic acid to solutions of aldehydes **XXII** and **XXIII** in pyrrole, bis(di-2-pyrrolyl)methane derivatives **XXIV** and **XXV** were obtained. Porphyrin–calix[4]arene **XXVI** was synthesized in 0.9% yield by heating tetraaldehyde **XX** with pyrrole in boiling propionic acid according to Adler [29]. The reaction of tetraaldehyde **XXI** with pyrrole in methylene dichloride in the presence of a catalytic

Scheme 3.

XVI, **XVIII**, R = ClCH$_2$; **XVII**, **XIX**, R = Br(CH$_2$)$_5$; **XX**, **XXII**, **XXIV**, n = 1; **XXI**, **XXIII**, **XXV**, n = 5.

amount of boron trifluoride–ether complex, followed by oxidation with excess tetrachlorobenzoquinone (Lindsey procedure), gave 6% of porphyrin–calix[4]-arene **XXVII** [30]. Following an analogous procedure, porphyrin–calix[4]arene **XXVIII** was synthesized in 5% yield by reaction of dipyrrolylmethane derivative **XXIV** with benzaldehyde. Compound **XXIX** was

prepared (yield 3%) according to Lindsey from dipyr-rolylmethane **XXV** and benzaldehyde using trifluoro-acetic acid as catalyst.

Porphyrin–calix[4]arenes **XXVI–XXIX** can readily be identified by signals from the porphyrin NH protons in the ^{1}H NMR spectra ($\delta \approx -2.8$ ppm) and by molecular ion peaks in the mass spectra. Treatment of
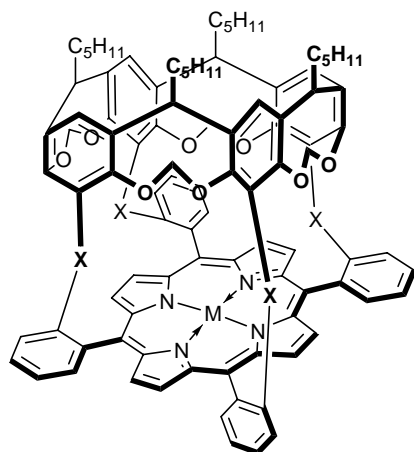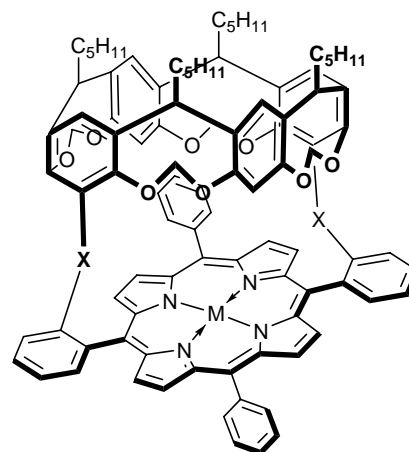
XXVI, XXVII, XXX, XXXI   **XXVIII, XXIX, XXXII, XXXIII**

X = CH₂NHCO(CH₂)ₙ; **XXVI–XXIX**, M = 2H; **XXX–XXXIII**, M = Zn.

compounds **XXVI–XXIX** with excess zinc acetate afforded zinc complexes **XXX–XXXIII** which, unlike the corresponding free ligands, are fairly stable; therefore, they can be purified by column chromatography.

The complex formation of Zn–porphyrin–calix[4]-arene conjugates **XXX–XXXIII** with various organic molecules differing in their size and nature was studied by spectrophotometric titration. The results showed that complex **XXX** in which the distance between the porphyrin and calix[4]arene fragments is the shortest is characterized by the strongest ability to bind *N*-methylimidazole and pyridine in the axial mode (Table 1). Complex **XXX** possesses four bridging units which fix the hydrophobic cavity of the calix[4]arene fragment, and organic molecules are bound in different modes, depending on their size. Large molecules, such as nicotine, nicotinamides, and 4-phenylpyridine, are bound at the outer side of the receptor, and the binding constant is equal to or even less than that found for the tetraphenylporphyrin–zinc complex (Zn–TPP).

Binding of smaller molecules (*N*-methylimidazole, pyridine, methylpyridine) is strongly determined by shielding effect of the calix[4]arene cap and electron density on the donor nitrogen atom. The presence of long and flexible bridging entities in molecule **XXXI** gives rise to a large cavity, and most guest molecules (except for nicotine) bind at the inside. Simultaneously, shielding effect of the calix[4]arene cap weakens. Decrease in the number of bridging groups in going to complex **XXXII** (two bridging units) increases flexibility of the molecule, and hence the distance between the porphyrin and calix[4]arene fragments becomes longer. As a result, 4-phenylpyridine molecule can penetrate into the inner receptor cavity. Porphyrin–calix[4]arene **XXXII** binds nicotinamide 200 times more strongly than does Zn–TPP and is the best receptor among complexes **XXX–XXXII** with respect to nicotinamide, 4-phenylpyridine, and isonicotinamide.

Extension of the bridging groups (compound **XXXIII**) weakens shielding effect of the calixarene cap, as compared to complex **XXXII**. The bridging units in **XXXIII** are sufficiently flexible to ensure their folding with displacement of the porphyrin and calix-[4]arene fragments with respect to each other. As a result, the size of the inner cavity decreases, and the complexing ability of **XXXIII** with respect to small molecules decreases as compared to complexes **XXX–XXXII**. An exception is nicotine; its efficient binding may be rationalized by formation of additional hydrogen bonds with the amide groups in the bridging moieties [31].

¹H NMR study of *N*-methylimidazole binding to **XXXI** in chloroform-*d* showed a very strong shift of

Table 1. Binding constants K ($\times 10^3$, l/mol) for nitrogen-containing ligands and porphyrin–calix[4]arenes **XXX–XXXIII** and Zn–TPP in chloroform ($c_{Zn–TPP} \approx 5 \times 10^{-6}$ M)
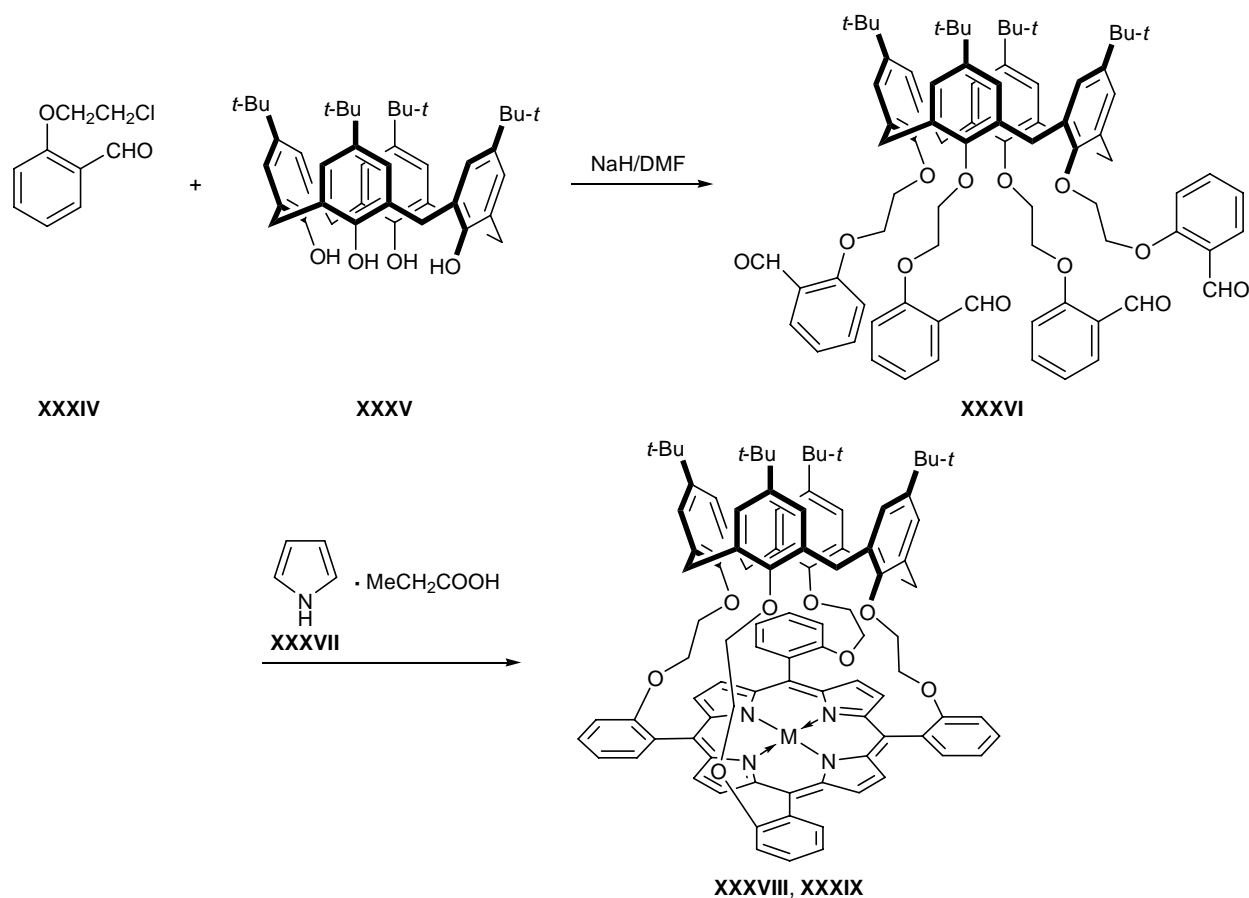
Ligand	**XVII**	**XVIII**	**XIX**	**XX**	Zn–TPP
Pyridine	147	15	18	6.8	0.9
4-Methylpyridine	233	46	80	20	1.6
4-Phenylpyridine	0.4	10	52	13	1.4
1-Methylimidazole	1077	140	290	79	1.5
Nicotinamide	0.7	0.3	62	19	0.3
Isonicotinamide	0.4	13	15	1.6	0.3
Nicotine	0.2	16	20	41	1.4

Scheme 4.

XXXIV + XXXV → XXXVI

XXXVIII, M = 2H; **XXXIX**, M = Fe(II).

the guest proton signals due to shielding effect of ring current in the porphyrin macroring. Signals from the methyl protons shift by 3.6 to –0.9 ppm, while those belonging to protons in the porphyrin fragment and OCH$_2$ groups of the bridging moieties insignificantly change their position.

Almog *et al*. [32] synthesized a conjugate consisting of covalently bonded porphyrin and calix[4]arene fragments by the procedure widely used for the preparation of capped porphyrins [33, 34]. The reaction of aldehyde **XXXIV** with calix[4]arene **XXXV** gave tetraaldehyde **XXXVI** in which the four aldehyde groups are equidistant from the lower rim (Scheme 4). It is known that addition of long alkyl groups (longer than propyl) fixes the calixarene structure so that the molecule cannot change its conformation [34]. The ^{1}H NMR spectra of tetraaldehyde **XXXVI** showed that addition of four bulky substituents, such as **XXXIV**, anchors the calix[4]arene fragment exclusively in the *cone* conformation (two doublets from the ArCH$_2$Ar protons at δ 3.31 and 4.60 ppm). Porphyrin–calix[4]-

arene conjugate **XXXVII** was obtained by condensation of tetraaldehyde **XXXVI** with pyrrole (**XXXVII**) in boiling propionic acid (overall yield 25%). The upfield shift (Δδ = 0.24 and 0.40 ppm) of the ArCH$_2$Ar signals in the ^{1}H NMR spectrum of adduct **XXXVII** as compared to **XXXVI** indicates that the calix[4]arene fragment in the porphyrin–calixarene conjugate is located over the porphyrin macroring and that it suffers from shielding by the porphyrin π-electron ring current. The complexing power of conjugate **XXXVII** was estimated by studying fluorescence quenching of the latter with benzoquinone in methylene chloride [32]. This process has been studied in detail for *meso*-tetraphenylporphyrin (TPP) [35]. Enhancement of fluorescence quenching of **XXXVII** by a factor of ~3.5 relative to TPP indicates that the hydrophobic cavity in the calix[4]arene fragment is an effective trap for benzoquinone. It was found that, like five-coordinate capped porphyrin complexes, iron(II)–porphyrin–calix-[4]arene complex **XXXVIII** in the presence of 1-tri-phenylmethylimidazole is capable of reversibly bind-

ing oxygen with formation of a stable 1:1 μ-superoxo complex and that complex **XXXVIII** can be used as molecular oxygen carrier.

Milbradt and Weiss [36] synthesized a porphyrin–calix[4]arene conjugate containing two calixarene fragments in the opposite *meso* positions of the tetrapyrrole macroring. Two approaches were applied. The first of these (Scheme 5) is based on a very convenient procedure for the synthesis of porphyrins from dipyrrolylmethanes having no substituents in both α-positions [37]. Monoalkylation of 4-*tert*-butylcalix[4]arene (**XXXV**) with 4-(2-bromoethoxy)benzaldehyde (**XL**) in dimethylformamide in the presence of Ba(OH)$_2$/ BaO gave aldehyde **XLI** which was brought into acid-catalyzed condensation with 2,2'-dipyrrolylmethane (**XLII**) in methylene chloride. The subsequent oxidation with dichlorodicyanobenzoquinone afforded porphyrin–calix[4]arene **XLIII** in 35% yield calculated on aldehyde **XLI**. The second approach (Scheme 6) involves chemical modification of preliminarily prepared *meso*-bis[4-(2-bromoethoxy)phenyl]porphyrin **XLV** which was synthesized by condensation of dipyrrolylmethane **XLII** with aldehyde **XL**. The reaction of

XLV with 2 equiv of calix[4]arene **XXXV** in dimethylformamide in the presence of Ba(OH)$_2$ gave the target porphyrin–calix[4]arene conjugate **XLIII** as a result of monoalkylation of two calix[4]arene molecules. The yield of **XLIII** was 66%, calculated on **XXXV**. Likewise, using *meso*-diphenylporphyrinato-zinc (**XLVI**) as key compound, zinc complex of porphyrin–calix[4]arene **XLIV** was obtained. Fluorescence study of complexes **XLIII** and **XLIV** in the presence of benzoquinone has confirmed the ability of the calix[4]arene fragments in conjugates **XLIII** and **XLIV** to form guest–host complexes with neutral organic molecules.

Porphyrin–calix[4]arene conjugates were synthesized by condensation of pyrrole with diformyl derivatives of appropriate calix[4]arenes [2]. Dialdehyde **XLVII** containing two formyl groups on the upper rim reacted with pyrrole in boiling propionic acid to produce 3–5% of porphyrin–calix[4]arene **XLVIII** (Scheme 7). Key compound **XLVII** was synthesized by alkylation of the two opposite hydroxy groups in 4-*tert*-butylcalix[4]arene with 2-(4-bromobutoxy)benzaldehyde in boiling acetone using K$_2$CO$_3$ as base.
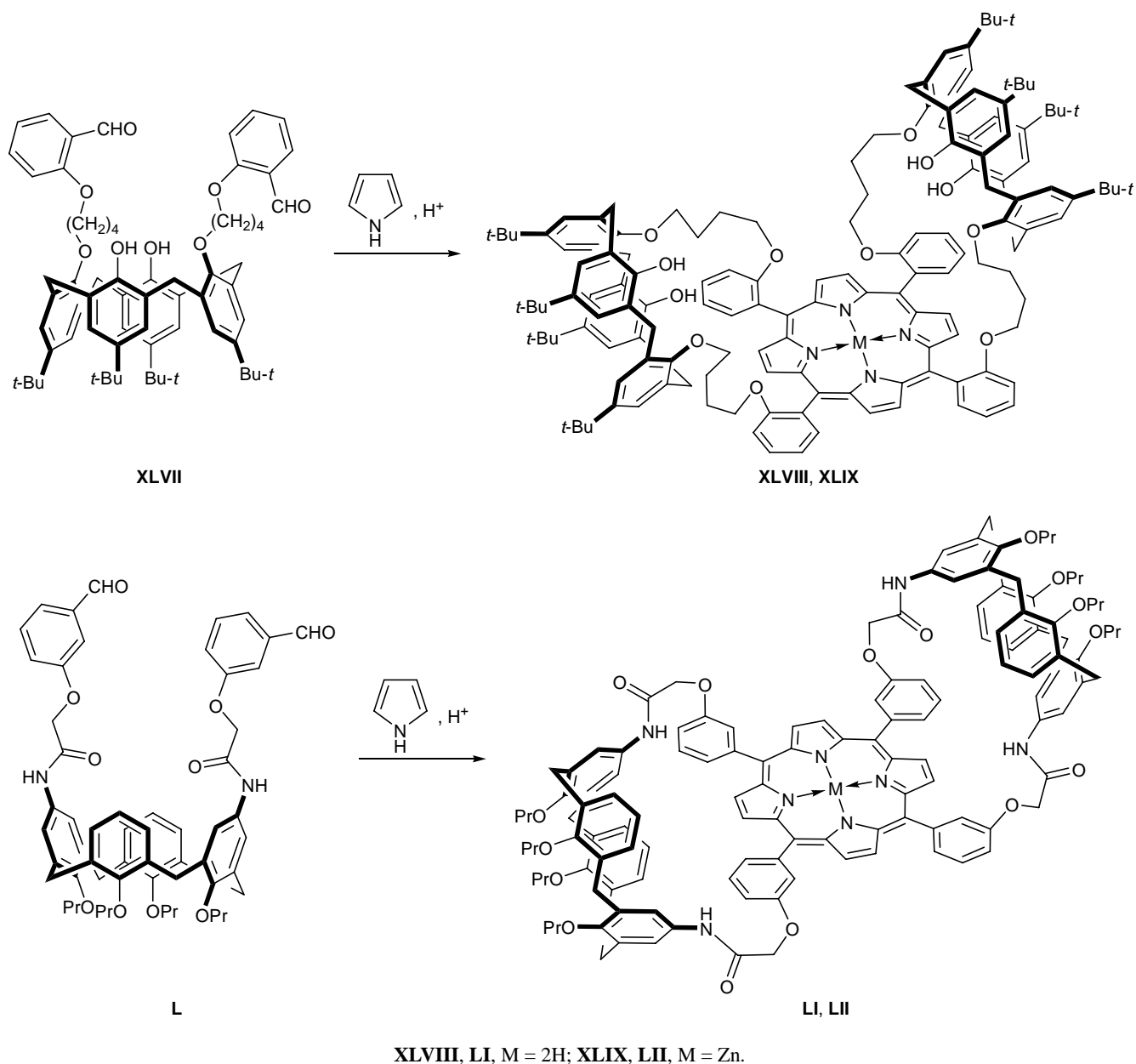
Scheme 5.

Scheme 6.

Scheme 7.

XLVII

XLVIII, XLIX

L

LI, LII

XLVIII, **LI**, M = 2H; **XLIX**, **LII**, M = Zn.
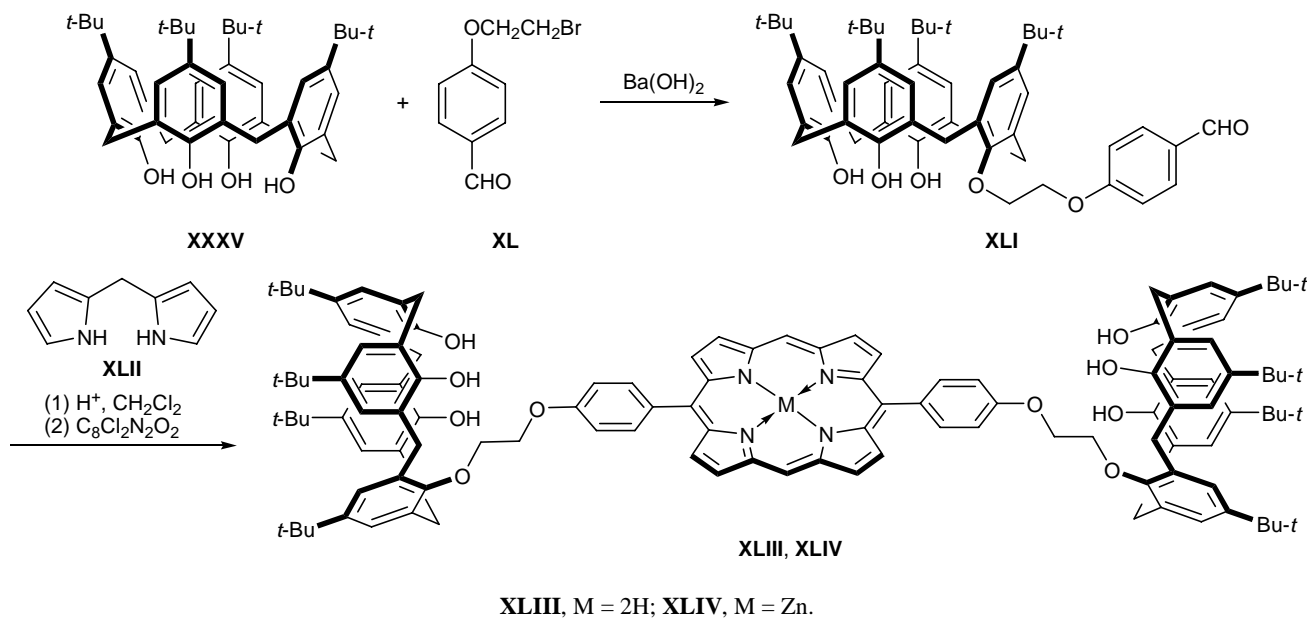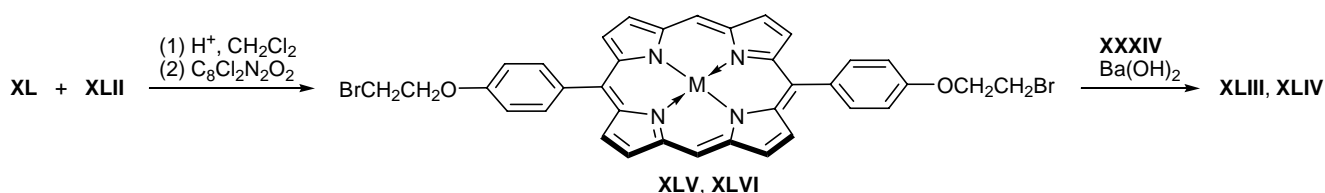
Theoretically, conjugate **XLVIII** can exist as three different isomers due to restricted rotation of the benzene rings in the *meso* positions of the porphyrin fragment; however, only one isomer was isolated from the reaction mixture [38–40]. Its ¹H NMR spectrum contained two singlets from the β-pyrrole protons at δ 8.84 and 8.70 ppm and four singlets with similar intensities due to protons in the aromatic part of the calix[4]arene scaffold. Zinc complex **XLIX** was obtained by heating ligand **XLVIII** with zinc acetate in a boiling chloroform–methanol mixture (1:1). Analysis of the ¹H NMR spectra of complex **XLIX** in the presence of pyridine indicated formation of a guest–host complex in which both calix[4]arene fragments are equivalent with respect to the bound pyridine molecule [38].

Likewise, the reaction of dialdehyde **L** with pyrrole in propionic acid leads to porphyrin–calix[4]arene conjugate **LI** where both calix[4]arene cavities are opened toward the porphyrin fragment. The yield of **LI** isolated by column chromatography was 4%. Key compound **L** possessing two aldehyde groups on the upper rim was prepared by reaction of 1,3-bis(chloroacetylamino)tetrapropoxycalix[4]arene with 3-hydroxybenzaldehyde [2]. Treatment of ligand **LI** with

zinc acetate quantitatively afforded zinc complex **LII**. Zinc complexes **XLIX** and **LII** derived from porphyrin–calix[4]arenes are promising as models for multipoint recognition of various species. Apart from the reactive metal–porphyrin center capable of forming complexes with anions and neutral molecules, they possess two lipophilic calix[4]arene cavities with a size of ~1.0–1.5 nm [2]. The presence of such functional groups as OH and C(O)NH endows conjugates **XLIX** and **LII** with additional receptor properties due to hydrogen bonding or dipole–dipole interactions with organic anions or polar neutral molecules.

III. BIS-PORPHYRIN–CALIX[4]ARENES

Of specific interest are bis-porphyrin–calix[4]-arenes in which the porphyrin fragments are fixed by the calix[4]arene scaffold in a certain orientation with respect to each other. A combination of these structural fragments in a single molecule via covalent bonds opens unique possibilities for building up cavities (traps) to bind both ionic [13, 41–46] and neutral species [47–50].

The first cyclophane-like dimeric porphyrin in which the porphyrin macrorings are linked through calix[4]arene fragments [51] was synthesized according to the two-step procedure for the porphyrin synthesis from α,α'-unsubstituted dipyrrolylmethanes [37] (Scheme 8). The reaction of dialdehyde **LIII** with dipyrrolylmethane **XLII** in methylene chloride in the presence of trifluoroacetic acid, followed by oxidation with dichlorodicyanobenzoquinone gave 0.4% of bis-porphyrin–calix[4]arene **LIV**. The presence in the ^{1}H NMR spectrum of **LIV** of well defined doublets at δ 4.83 and 3.85 ppm from protons of the bridging CH$_2$ groups clearly indicates that the calix[4]arene fragments adopt a *cone* conformation.

Calix[4]arene **LV** and thiacalix[4]arene **LVI** [52] were also used as molecular spacers. These compounds can be regarded as fairly accessible [53, 54]. By treatment with ethyl bromoacetate in boiling acetone in the presence of potassium carbonate, key compounds **LV** and **LVI** were converted into the corresponding di- and tetraesters which were subjected to alkaline hydrolysis to obtain carboxylic acids. These acids were brought into reactions with monoamino-substituted *meso*-tetraphenylporphyrin to obtain diamides **LVII** and **LVIII** in 78 and 72% yield, respectively (Scheme 9); tetraamides **LIX** and **LX** were synthesized through the corresponding acid chlorides (yield 45 and 71%, respectively) [55]. Complex formation of bis(porphyrin)–calix[4]arene ligands with zinc acetate in dry methylene chloride afforded zinc complexes **LXI**–**LXIV**. According to the ^{1}H and ^{13}C NMR data, the calix[4]arene fragments in **LXI**–**LXIV** occur in the *cone* conformation. The ^{1}H NMR spectrum of bis(porphyrinatozinc)–thiacalix[4]arene **LXII** contains two groups of signals from protons of the *tert*-butyl groups (δ 1.25 and 1.36 ppm), which corresponds to the C_{2v} symmetry typical of calix[4]arenes in the *cone* conformation substituted at the opposite positions. The position of signals from the corresponding protons in the ^{1}H NMR spectra of zinc complexes **LXIII** and **LXIV** also indicates *cone* conformation of the calix-[4]arene fragment (C_{4v} symmetry).

The electron absorption spectra of zinc complexes **LXII** and **LXIV** displayed maxima at λ 550 and 588 nm corresponding to the $Q(1.0)$ and $Q(0.0)$ bands; the zinc complex of *meso*-tetraphenylporphyrin is characterized by absorption maxima at λ 548 and 586 nm [56, 57]. However, unlike the latter, the Soret bands in the spectra of the dimers are considerably broadened and split, indicating strong exciton interaction between π-elecron systems of the neighboring
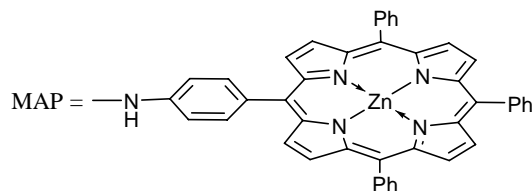
Scheme 8.

LIII   XLII   LIV

Scheme 9.
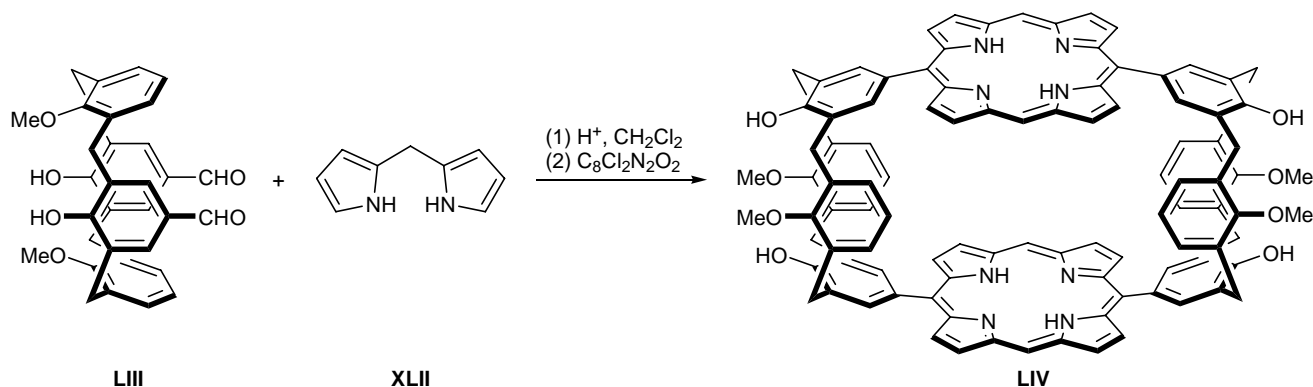
LV, LVI   LVII–LX
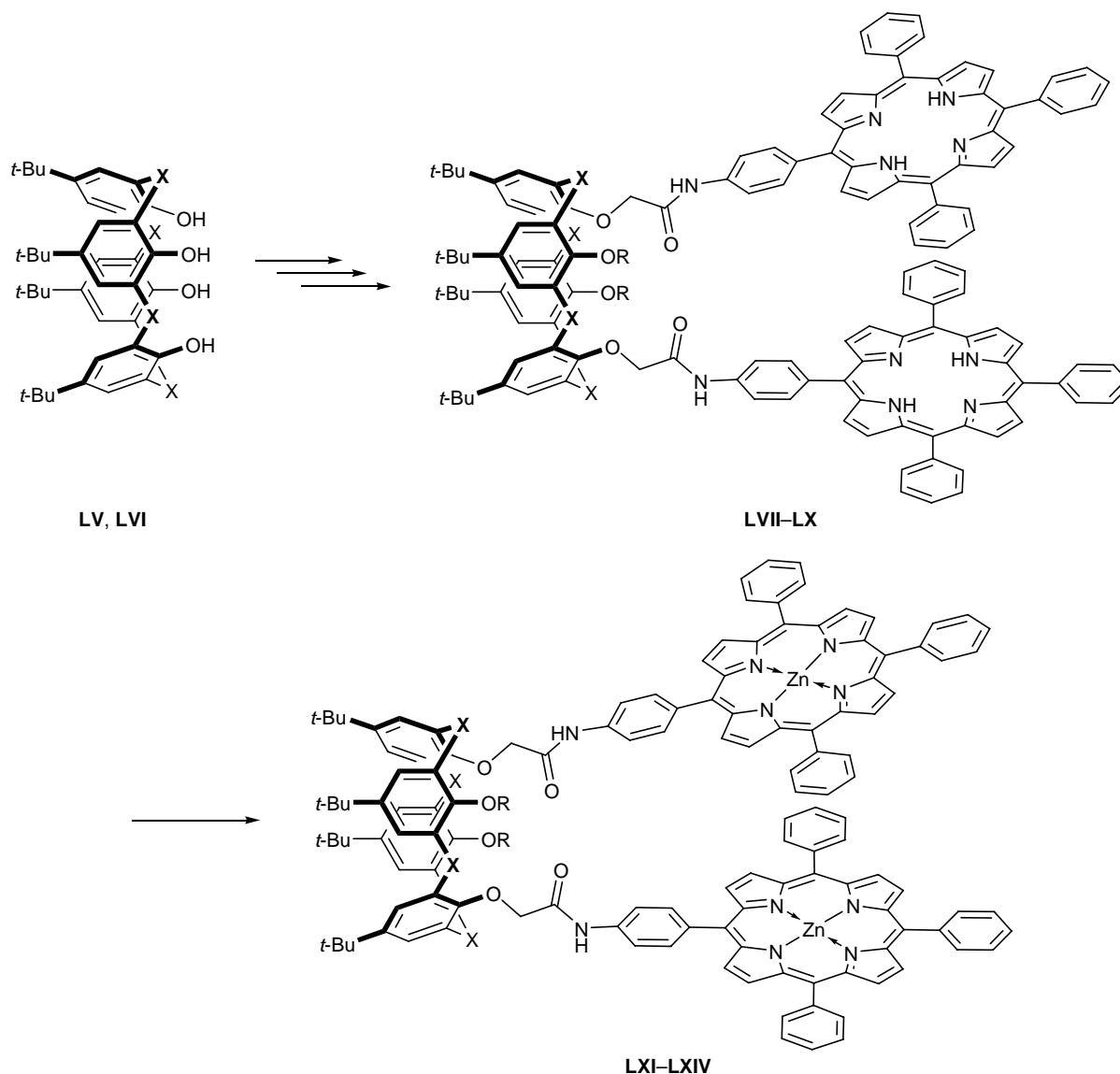
LXI–LXIV

LVII, LVIII, LXI, LXII, R = H; **LIX, LX**, R = CH₂CO-MAP; **LXIII, LXIV**, R = CH₂CO-MAP-Zn; **LV, LVII, LIX, LXI, LXIII**, X = CH₂; **LVI, LVIII, LX, LXII, LXIV**, X = S;

MAP =

porphyrin fragments. Analogous variations were also observed in the electron absorption spectra of porphyrin–calix[4]arenes [55], covalently bound dimeric porphyrins [58, 59], and porphyrin oligomers [60, 61]. In keeping with the Kasha exciton model [62], red shift of the Soret band corresponds to the head-to-tail orientation of the porphyrin fragments in a dimer while blue shift of that band is typical of the face-to-face orientation of the macrorings. The observed splitting of the Soret band in the spectra of complexes **LXII** and **LXIV** indicates that one porphyrin fragment is located above the other. Analogous pattern was observed in the electron absorption spectra of complexes **XLI** and **LXIII** having methylene bridges in the rim.

Solvent dependence of spectral variations originates from conformational mobility of the fragment connecting the porphyrin macrorings and calix[4]arene moiety. Polar solvents induce more complex exciton interactions [55]. As shown in [63–67], the hydrophobic cavity in thiacalix[4]arene is larger than in calix[4]-arene with methylene bridging groups. The distances between two contiguous (*cis*) and two opposite (*trans*) sulfur atoms in 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-2,8,14,20-tetrathiacalix[4]arene (**LXII**) in the *cone* conformation are 5.48 and 7.67 Å, respectively, while the distances between the corresponding CH$_2$ groups in analog **LXI** are 5.11 and 7.16 Å [63]. Appreciable differences in conformational behavior of thiacalix[4]arene derivatives were observed both in solution [66, 67] and in the solid state [64, 65], and strong effect on their reactivity was also found [68].

Study of the complex formation of bis(porphyrinatozinc)–calix[4]arenes **LXI** and **LXII** with 1,4-diazabicyclo[2.2.2]octane (DABCO) revealed considerable differences between these compounds, which originate from different sizes of the calix[4]arene cavities therein [52]. The larger cavity in **LXII** better fits the structure of the bidentate ligand with oppositely located nitrogen atoms; as a result, a 1:1 complex is formed with a constant K_{as} of $(1.0\pm0.1)\times10^7$ l/mol (chloroform, 294 K). Complex formation with conjugate **LXI** containing a conventional calix[4]arene fragment involves independent coordination of two DABCO molecules to two tetrapyrrole macrorings to give a 2:1 complex.

X-Ray analysis of calixarene diesters **LXV**–**LXVIII** revealed an unusual mode of hydrogen bonding at the lower rim of thiacalix[4]arenes **LXVII** and **LXVIII** which are intermediate compounds in the synthesis of bis(porphyrinatozinc)–calix[4]arene conjugates **LXI** and **LXII**. It is well known [11, 12, 69–72] that hydroxy groups in the lower rim of classical
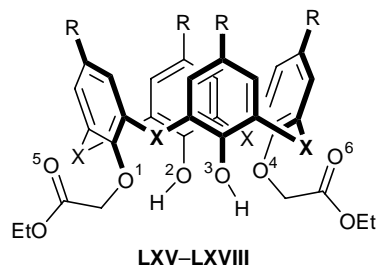
LXV, **LXVII**, R = H; **LXVI**, **LXVIII**, R = *t*-Bu;
LXV, **LXVI**, X = CH$_2$; **LXVII**, **LXVIII**, X = S.

oppositely substituted calix[4]arenes in the *cone* conformation are involved in H-bonding with both neighboring substituents (see figure, *a*). Such arrangement of substituents makes the molecular symmetry close to C_2. By contrast, thiacalix[4]arenes **LXVII** and **LXVIII** give rise to very unusual structures in which both oppositely located hydroxy groups form hydrogen bonds with the same group OR in the lower rim (see figure, *b*).

Compound **LXV** exists in the *cone* conformation where two hydrogen bonds are arranged almost symmetrically. The distances $O^1\cdots H^1$ and $H^2\cdots O^4$ are 1.92 and 2.06 Å, respectively. Such arrangement gives rise to a cavity having a C_4 symmetry with respect to phenolic fragments. Both OR substituents in the lower rim are turned out from the calix[4]arene cavity, and the distance between the ester oxygen atoms O^5 and O^6 is 7.10 Å. Thiacalix[4]arene molecules **LXVII** and **LXVIII** adopt a different conformation which is not typical of "classical" calix[4]arenes. Protons of both hydroxy groups in **LXVII** are involved in hydrogen bonds with the same oxygen atom with the following distances: $O^1\cdots O^2$ 2.98, $O^1\cdots O^3$ 2.94, $O^2\cdots O^4$ 3.80, $O^3\cdots O^4$ 3.92 Å. The conformation of diester **LXVIII** is similar. The distances $O^1\cdots O^2$ (2.90 Å) and $O^1\cdots O^3$ (3.08 Å) as compared to $O^2\cdots O^4$ and $O^3\cdots O^4$ (3.84 Å) clearly indicate unsymmetrical arrangement of hydrogen bonds [52]. As a result, the molecular symmetry is
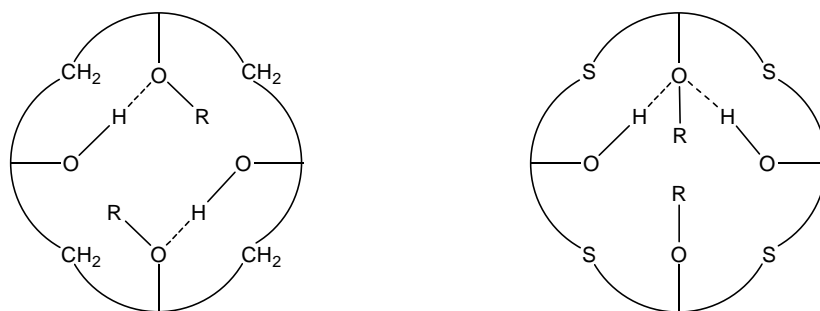
Hydrogen bonds in disubstituted (a) calix[4]arene **LXV** and (b) thiacalix[4]arene **LXVII**.

reduced, and the distance between the two ester oxygen atoms becomes equal to 4.66 Å, i.e., it is considerably shorter than in calix[4]arene **LXV**.

Although selective complex formation between various cations and calixarene derivatives has been extensively studied in the past two decades [11, 12], creation of calix[4]arene receptors capable of recognizing anions is a relatively new scientific problem [73].

LXIX, LXX

LXIX, X = H;

LXX, X =
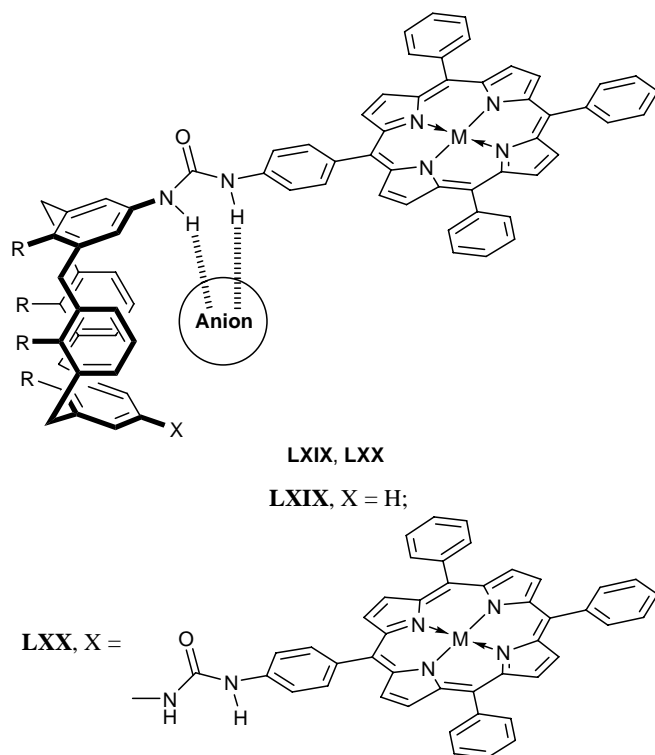
Calix[4]arenes having "activated" amide groups, capable of binding anions via formation of hydrogen bonds with the NH groups [74–82], as well as porphyrin–calix[4]arenes **LXIX** and **LXX** which are selective for various anions [83], were synthesized. Initial amino-substituted porphyrin **LXXI** and calix[4]-arenes **LXXII–LXXVI** in a *cone* or 1,3-*alt* conformation were prepared by reduction of the corresponding nitro derivatives [84–86]. Heating of amine **LXXI** with bis(trichloromethyl) carbonate in dichloroethane in the presence of triethylamine gave unstable isocyanate **LXXVII** [87], and reactions of the latter with amino-calix[4]arenes **LXXII–LXXVI** afforded porphyrin–calix[4]arenes **LXXVIII–LXXXII** in 33–68% yield (Scheme 10).

Study of interaction between conjugates **LXXVIII–LXXXII** with I^-, Br^-, Cl^-, and NO_3^- ions by spectrophotometric titration showed that the complex formation is accompanied by a small red shift (by 0.5 nm)

Table 2. Binding constants K (l/mol) for porphyrin–calix[4]-arenes **LXXVIII–LXXXII** and various anions in methylene chloride at 24°C ($c_{\text{receptor}} \approx 1.5 \times 10^{-6}$ M)

Anion	LXXVIII	LXXIX	LXXX	LXXXI	LXXXII
Cl^-	6.3×10^3	5.8×10^5	6.9×10^5	1.4×10^6	6.6×10^5
Br^-	1.2×10^3	7.8×10^4	6.9×10^4	2.2×10^5	6.5×10^4
I^-	240	8×10^3	2.4×10^3	2.9×10^4	4.8×10^3
NO_3^-	820	3×10^4	1.3×10^4	–	4.5×10^3

and broadening of the Soret band in the electron absorption spectrum [83]. More essential variations were observed in the ^{1}H NMR spectra. Signals from aromatic protons shift upfield, the maximal shift being observed in the spectrum of **LXXX** upon interaction with Cl^-. The changes in proton chemical shits, induced by complex formation, indicate that the porphyrin fragments in the bisporphyrin–calix[4]arene conjugate become closer to each other due to interaction between the anion and hydrogen atoms in the bridging groups.

Analysis of the binding constants (Table 2) shows that, regardless of the conformation of the calix[4]-arene fragment (*cone* in **LXXX** or 1,3-*alt* in **LXXXII**), compounds **LXXIX**, **LXXX**, and **LXXXII** effectively bind small spherical anions. The bridging groups connecting the calix[4]arene and porphyrin fragments are sufficiently flexible to accommodate Cl^- and Br^- ions, irrespective of whether the porphyrin fragments are arranged *cis* (**LXXIX**) or *trans* (**LXXX**, **LXXXII**) on the upper rim of calix[4]arene. Moreover, the propoxy groups located between the porphyrin fragments in 1,3-*alt* conformers do not hamper complex formation with anions. On the other hand, considerable differences in the binding constants found for larger anions (such as I^- and NO_3^-) suggest the existence of some steric hindrances to complex formation. The binding constants decrease as the size of the anion increases (for porphyrin–calix[4]arene **LXXX**, $K_{Cl} = 6.9 \times 10^5 > K_{Br} = 6.9 \times 10^4 > K_I = 2.4 \times 10^3$ l/mol). Receptor **LXXX** is a better complexing agent with respect to Cl^- than its analog possessing the same calix[4]arene scaffold but having phenyl groups instead of porphyrin fragments ($K_{Cl} = 4.6 \times 10^3$ l/mol) [79]. A twofold decrease in the binding constant in going from porphyrin–calix[4]-arene receptor **LXXVII** ($K_{Cl} = 6.3 \times 10^3$ l/mol) to bis-(porphyrin)–calix[4]arene **LXXX** ($K_{Cl} = 6.9 \times 10^5$ l/mol) may be regarded as an additional support to the assumption that anion is held in the complex via interaction with NH groups in the bridges.

Scheme 10.

LXXI   **LXXVII**

LXXVIII

LXXXII   **LXXX, LXXXI**   **LXXIX**
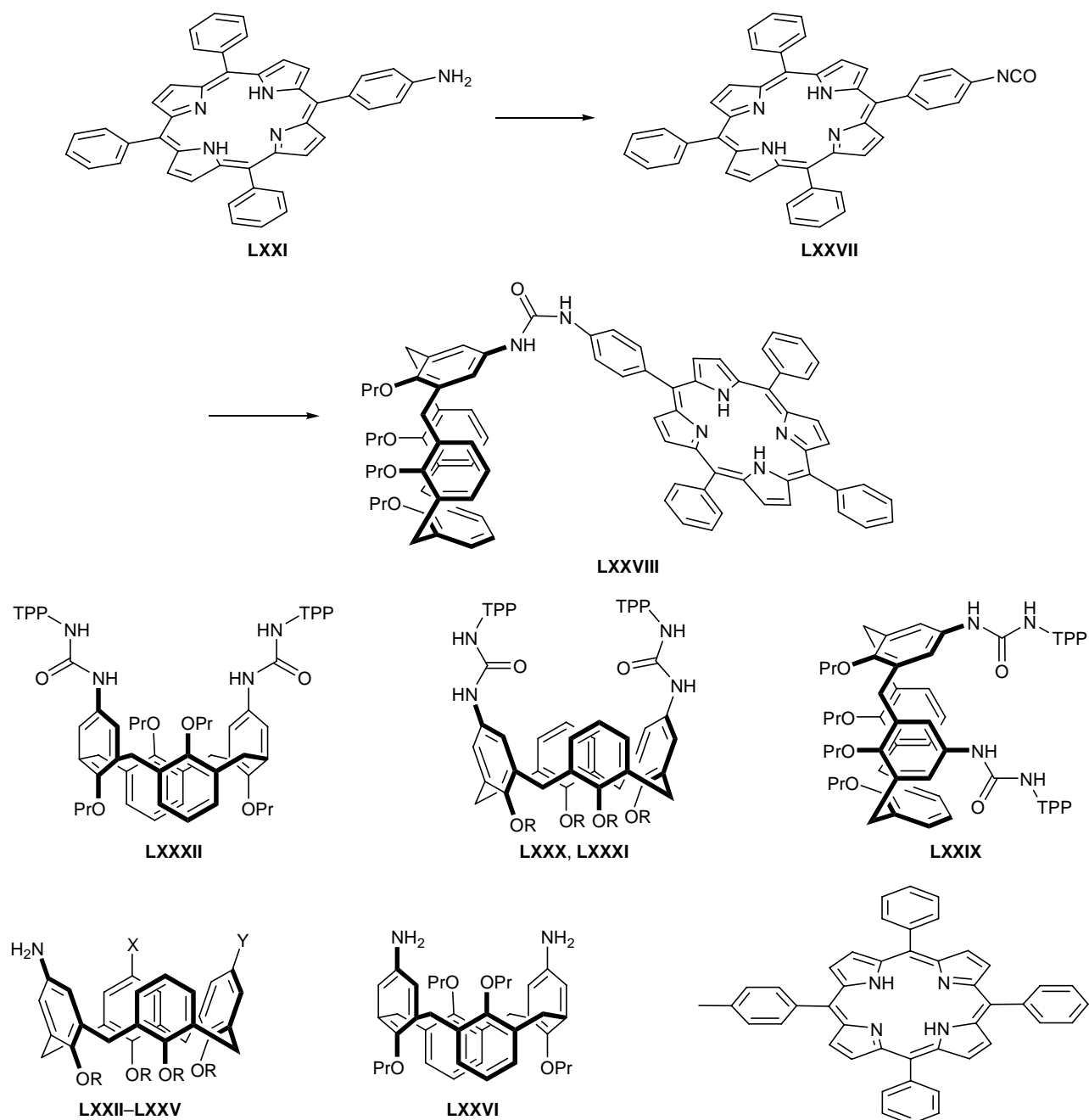
LXXII–LXXV   **LXXVI**

LXXII–LXXIV, LXXX, R = CH₃CH₂CH₂; **LXXVI, LXXXI**, R = EtOCOCH₂; **LXXII, LXXIII, LXXV**, X = H; **LXXIV**, X = NH₂;
LXXII, LXXIV, Y = H; **LXXIII, LXXV**, Y = NH₂.

Bis(porphyrin)–calix[4]arene **LXXX** represents a specific kind of receptors, for it possesses another cavity at the lower rim of the calix[4]arene scaffold, which is formed by four ester groups capable of binding alkali metal cations. Conjugate **LXXX** showed a high sensitivity to Cl⁻ with binding constants of $1.4{\times}10^6$ and $1.5{\times}10^5$ l/mol in methylene chloride and acetonitrile, respectively. After addition of LiClO₄ or

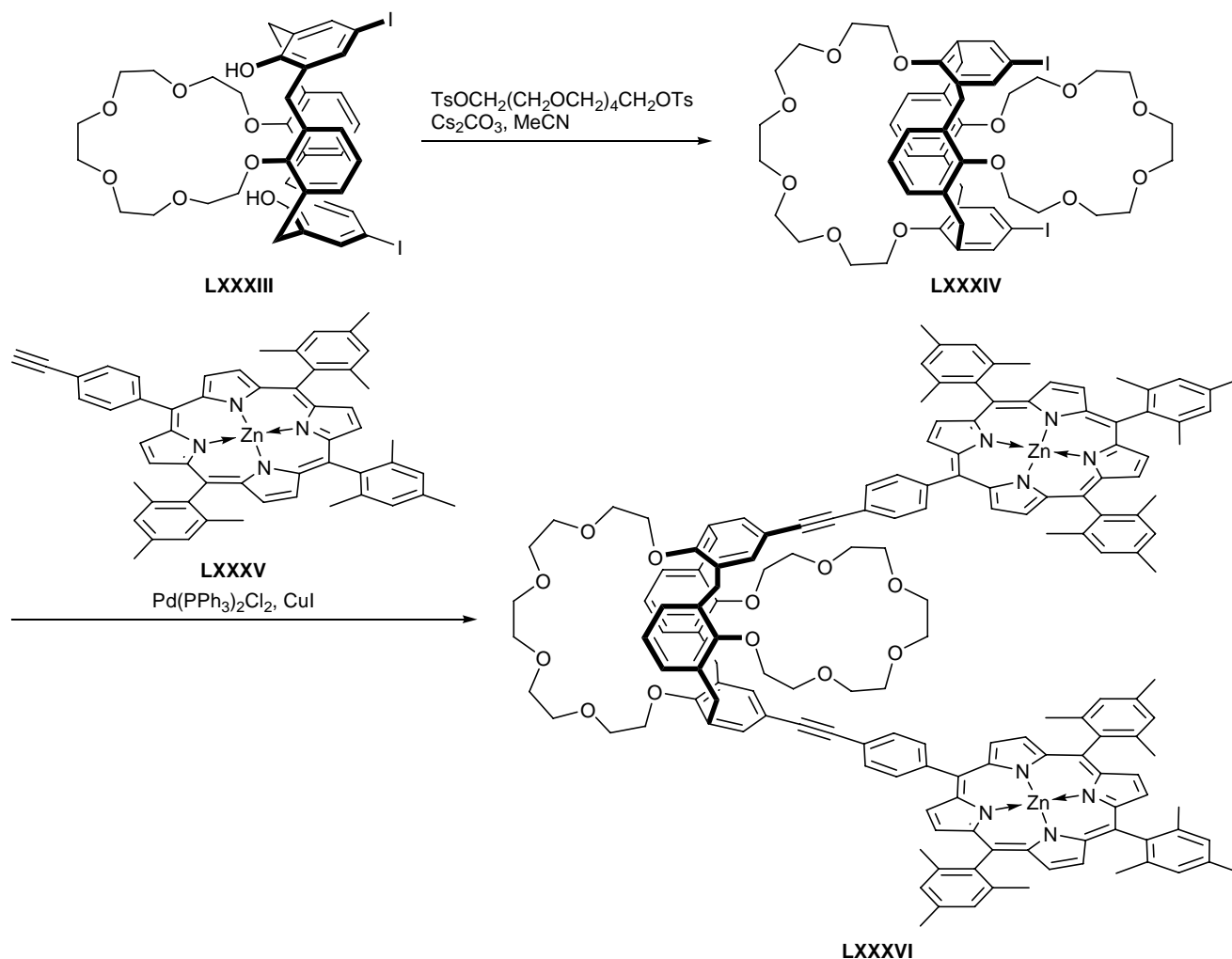NaClO₄ to a solution of conjugate **LXXX** in acetonitrile, the Soret band in the electron absorption spectrum of the system becomes narrower, and its intensity sharply increases. These variations originate from binding of the metal cation by the ester groups in **LXXX**. Obviously, binding of metal cation at the lower rim is accompanied by strengthening of the calix[4]arene scaffold structure. Narrowing of the

Soret band and increase in its intensity in the spectrum of **LXXX** in the presence of a metal cation is explained by weakening of the exciton interaction between π-electron systems of nearby tetrapyrrole macrorings, i.e., by increase in the distance between the porphyrin fragments. Thus the recognizing ability of a receptor toward anions can be controlled via complex formation with metal cation.
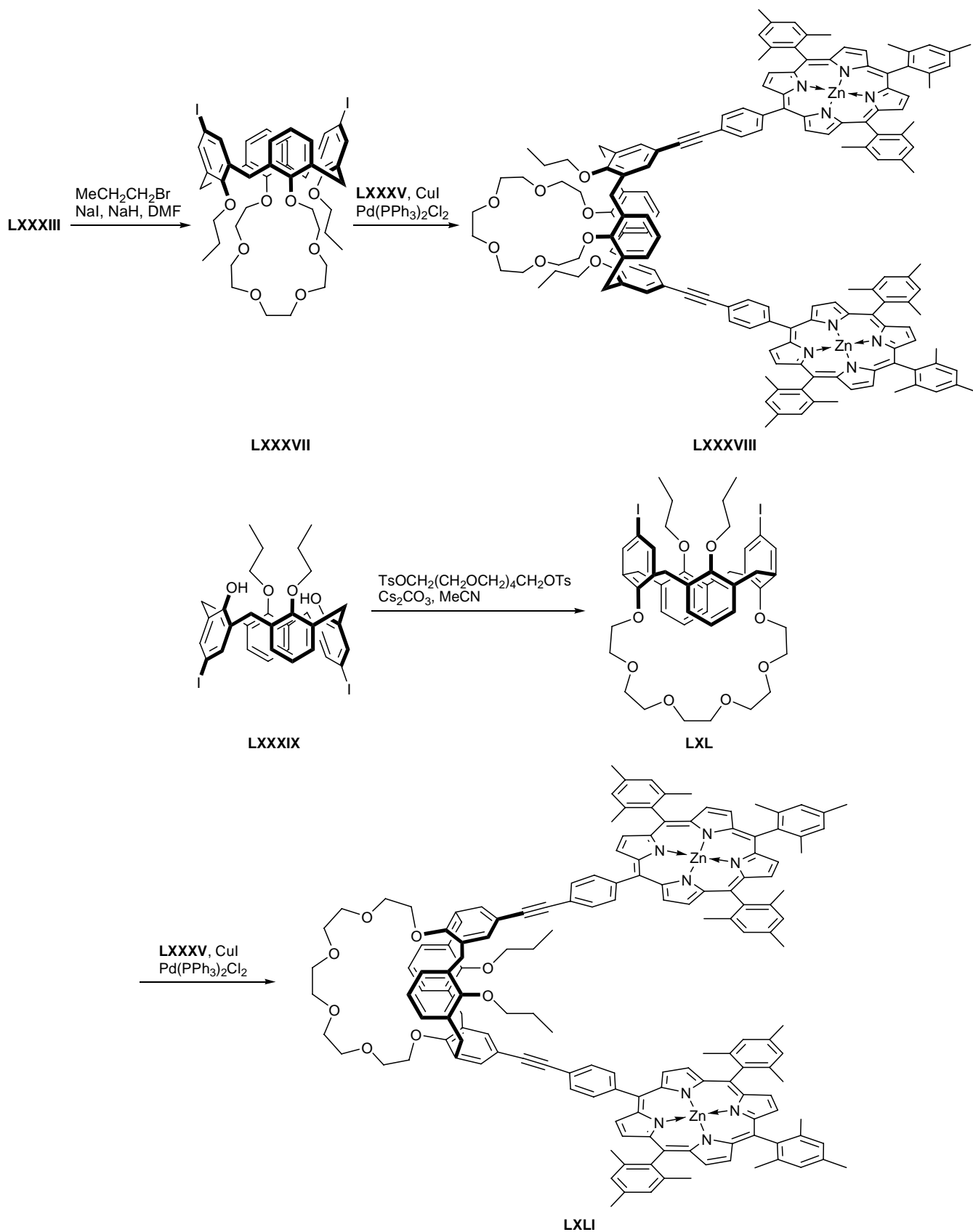
Jokic *et al.* [88] synthesized bis-porphyrins whose cyclophane structure is fixed by calix[4]arene bridges occurring in various conformations (Scheme 11). Key diiodo derivatives **LXXXIII** and **LXXXIX** were prepared by selective halogenation of crown[6]–calix[4]-arene and dipropoxycalix[4]arene [89, 90]. Alkylation of compounds **LXXXIII** and **LXXXIX** gave derivatives **LXXXIV**, **LXXXVII**, and **LXL** in which the calix[4]arene fragments adopt either *cone* or 1,3-*alt* conformation. The propoxy groups hamper rotation of the aryl fragments, so that no transformation of calix-

[4]arene from one conformation into another is possible. Reactions of 5,10,15-trimesityl-20-(4-ethynyl-phenyl)porphyrinatozinc (**LXXXV**) with calixarenes **LXXXIV**, **LXXXVII**, and **LXL** in toluene in the presence of Pd(PPh$_3$)$_2$Cl$_2$, CuI, and Et$_3$N resulted in formation of bis(porphyrin)–calix[4]arene conjugates **LXXXVI**, **LXXXVIII**, and **LXLI** in 35, 45, and 40% yield, respectively. Compounds **LXXXVI**, **LXXXVIII**, and **LXLI** showed in the ^{1}H NMR spectra small upfield shifts of the β-pyrrole and *meso*-phenyl proton signals relative to the corresponding signals of porphyrin–calix[4]arene **LXXXV**. These shifts, in combination with variation in the signal multiplicity, indicate face-to-face orientation of the tetrapyrrole macrorings. A small upield shift of proton signals upon "replacement" of the polyether change in conjugate **LXXXVI** by propyl groups in complex **LXLI** suggests shortening of the distance between the porphyrin fragments. Compound **LXXXVIII** is characterized by
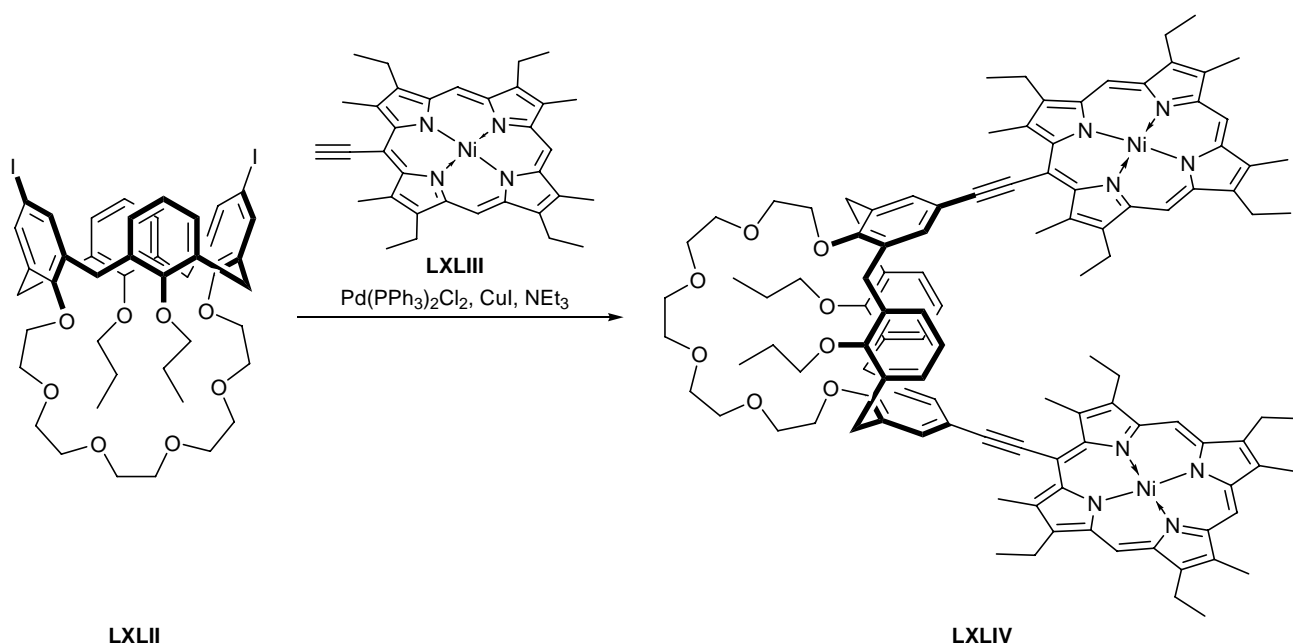
Scheme 11.

Scheme 11 (contd.)**.**

LXXXIII → MeCH₂CH₂Br, NaI, NaH, DMF → **LXXXVII** → **LXXXV**, CuI, Pd(PPh₃)₂Cl₂ → **LXXXVIII**

LXXXIX → TsOCH₂(CH₂OCH₂)₄CH₂OTs, Cs₂CO₃, MeCN → **LXL**

→ **LXXXV**, CuI, Pd(PPh₃)₂Cl₂ → **LXLI**

Scheme 12.

LXLIII
Pd(PPh₃)₂Cl₂, CuI, NEt₃

LXLII   **LXLIV**

enhanced mutual shielding of the neighboring tetrapyr-role macrorings. The maximal shift ($\Delta\delta = 0.15$ ppm) is observed for the nearby β-pyrrole protons and *ortho* protons in the phenyl groups.

Study of the interaction between bis(porphyrin)–calix[4]arenes **LXXXVI**, **LXXXVIII**, and **LXLI** and DABCO showed that the cyclophane structure of these dimers favors formation of complexes where the ligand is located inside the cavity formed by the porphyrin fragments. Protons of the bidentate ligand suffer a stronger shielding effect of the tetrapyrrole macrorings, and they appear as an intense singlet at δ –5 ppm.

Cyclophane-like bis-porphyrin **LXLIV** in which the calix[4]arene fragment is linked through a triple carbon–carbon bond to the *meso* position of porphyrin [91] was synthesized by the Sonogashira reaction [92–94] of diiodocalix[4]arene **LXLII** with 5-ethynyl-octaethylporphyrinatonickel (**LXLIII**) (Scheme 12). The reaction was carried out in thoroughly dehydrated toluene in the presence of CuI, Pd(PPh₃)₂Cl₂, and tri-ethylamine. The product was isolated in 52% yield by chromatography on aluminum oxide, followed by recrystallization from methylene chloride–methanol (1:1). Bis-porphyrin derivative **LXLIV** was charac-terized by considerable broadening of the Soret band and decrease in its intensity, as compared to initial complex **LXLIII**. A strong red shift ($\Delta\lambda \approx 10$ nm) of the Soret band in going from polar methanol to weakly polar toluene should be noted. Presumably, effective

solvation of the aromatic fragments in **LXLIV** by toluene molecules is accompanied by increase of the distance between the tetrapyrrole macrorings and hence weakening of interaction between their π-elec-tron systems. The ¹H NMR spectrum of **LXLIV** con-tains signals from protons in the calixarene and por-phyrin fragments. The bridging methylene groups give rise to two symmetric doublets in the regions δ 3.1–3.5 and 4.0 ppm, indicating *cone* conformation of the calix-arene fragment in **LXLIV**. In the electron absorption spectrum of bis(porphyrinatonickel)–calix[4]arene in toluene–methanol (2:1) containing potassium cations, the Soret band is appreciably displaced toward shorter wavelengths. Therefore, such porphyrin–calix[4]arene conjugates may be promising from the viewpoint of development of sensors for alkali metal cations.

IV. CONCLUSION

The data considered in the present review suggest that connection of porphyrin and calix[4]arene frag-ments through covalent bonds gives rise to a new generation of receptors. Tetrapyrrole macrorings in the resulting structures are capable of coordinating nitrogen-containing bases, calix[4]arene fragments are selective for cations, and bridging units which combine the porphyrin and calixarene fragments into a single *supramolecule* form complexes with anions. Porphy-rin–calix[4]arene conjugates provide the possibility for variation of recognizing ability with respect to anions via complex formation with metal cations. The pres-

ence in their molecules of porphyrin π-electron system makes it possible to use a broad range of spectral methods to analyze intermolecular interactions with their participation. Studies in the field of porphyrin–calix[4]arene receptors are now in the earliest stage of their development; however, the obtained results indicate wide prospects in the design of selective receptors and supersensitive sensors on the basis of porphyrin–calix[4]arene conjugates.

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