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Supramolecular systems based on calixarenes

Alexander I. Konovalov[a,b] and Igor S. Antipin[a,b]

[a] *A. E. Arbusov Institute of Organic and Physical Chemistry, Kazan Scentific Center of the Russian Academy of Sceinces, 420088 Kazan, Russian Federation. Fax: +7 843 292 7745; e-mail: konovalov@knc.ru*
[b] *Department of Organic Chemistry, Kazan State University, 420008 Kazan, Russian Federation. Fax: +7 843 231 5416; e-mail: iantipin@ksu.ru*

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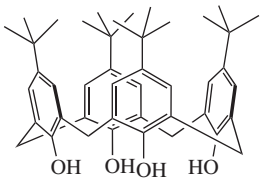
The design, structural characterization and specific properties of (thia)calix[4]arene based supramolecular systems are considered.

The 'bottom-up' technology, in which the higher organized nanosystems are spontaneously formed due to supramolecular self-organization and self-assembly from individual atoms and molecules, is promising for the design of nanomaterials. A key element of supramolecular chemistry, and now nanotechnology, is the principle of molecular recognition. It is well known that molecular recognition (or self-recognition) partners is the reason of a higher specificity of many chemical and biochemical reactions and processes. The result of the recognition is the selective binding of two or more atoms (molecules) with the formation of supramolecular assemblies. From this point of view, an urgent problem of supramolecular chemistry is the molecular design and synthesis of preorganized receptor and amphiphilic molecules, which are capable, on the principles of molecular recognition and multipoint interactions, to form host–guest complexes, as well as self-organized supramolecular assemblies and devices.



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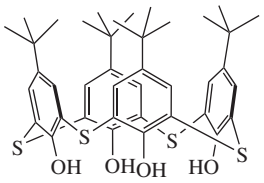

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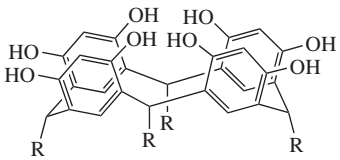

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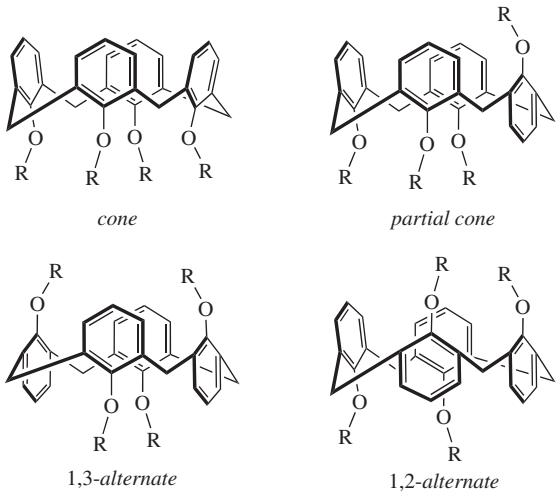
A nanotechnological approach 'bottom-up' can be effectively implemented on the basis of meta-cyclophanes: calix[4]arene **1**, thiacalix[4]arene **2** and calix[4]resorcinarene **3**.[1]

Supramolecular chemistry of calixarenes (phenol and aldehyde cyclic condensation products) has been intensely developed in the last two decades.[2–4] Calix[4]arenes have several attractive properties for the design of receptor molecules, self-organized systems and nanoobjects: (i) the low cost and accessibility of parent macrocycles by one-pot synthesis; (ii) nontoxicity of calixarene platforms; (iii) calixarene ability to incorporate small hydrophobic organic molecules into their molecular cavities with the formation of the stable host–guest complexes; (iv) existence of some macrocycle conformations and ability to fix the required spatial orientation of binding centers (Scheme 1); and (v) a unique possibility to decorate the upper and lower rim of macrocycle by the suitable heteroatom groups and to form the molecular system possessing several binding centers.

Molecular design of receptor structures on the basis of a (thia)calixarene platform. The simplest type of recognition is the selective binding of spherical substrates. To perform this spherical recognition and design of the selective receptors for metal cations, the symmetric pseudo-cavity formed by eight

Professor Alexander I. Konovalov graduated from the Kazan State University (KSU) in 1956, and received his Candidate degree in 1964, Doctor degree – in 1974. In 1990, Professor Konovalov was elected to the Academy of Sciences of the USSR as a corresponding member, and in 1992 he became a full member of the Russian Academy of Sciences. He was an invited speaker in Poland, Germany, France, Italy, Israel, Canada and the United States. Professor Konovalov is a Laureate of the USSR State Prise (1987). Current position: the advisor of the Russian Academy of Sceinces. His research interests include physical organic chemistry, macrocyclic chemistry and supramolecular chemistry.

Professor Igor S. Antipin graduated from the Kazan State University (KSU) in 1976, and received his Candidate degree in 1979, Doctor degree – in 1995. Since 1998, he is the head of Department of Organic Chemistry at KSU, and since 2000 – the head of Calixarene Chemistry laboratory at the A. E. Arbusov Institute of Organic and Physical Chemistry of Kazan Scentific Center of the Russian Academy of Sciences. In 2003, he became a corresponding member of the Russian Academy of Sciences. He was an invited speaker in Poland, Germany, France, Italy, Greece and Czech Republic. His research interests focus on the supramolecular chemistry, nanotechnology and materials science.



Scheme 1

heteroatoms X on the lower rim of thiacalix[4]arene [Figure 1(*a*)] has been simulated.[5,6] The changing of heteroatoms, their hybridization degree and spacer length allows one to construct receptor structures for different cationic substrates.

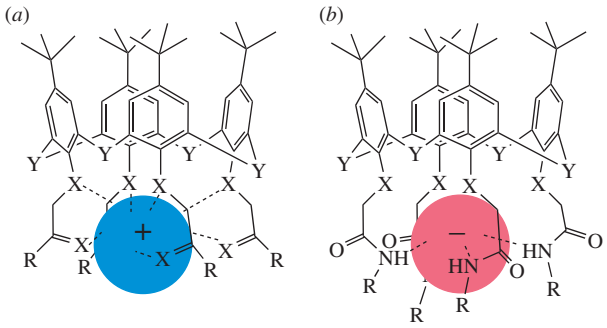


Figure 1 Models of the spherical (*a*) cations and (*b*) anions binding by the lower rim functionalized calix[4]arenes.

This model of spherical substrate recognition can be successfully applied to anion binding.[7–9] But in this case, other types of intermolecular interactions should occur on the lower rim of the macrocycle. It is well known that anions are effectively stabilized by hydrogen bonding with proton-donor solvents. Therefore, the introduction of proton-donor groups in calixarenes [Figure 1(*b*)] permits the construction of effective anion receptors.

A principally different approach based on hydrophobic cavity of calixarenes for the creation of highly effective and selective receptor molecules has been developed.[10–24] The direct incorporation of metal cations into a calixarene cavity effectively occurs only for large cations, for example, silver.[2–4] To enhance the interaction with a calixarene cavity, it was suggested to cover small cations with a 'fur coat' consisting of organic ligands. Such a metallocomplex can more effectively interact with a calixarene cavity with the formation of an outer-sphere inclusion complex (Figure 2).

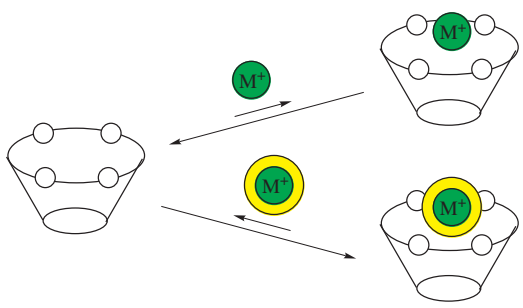


Figure 2 Binding models of the metal ion and metallocomplex by a calixarene cavity.

Unlike spherical recognition of metal ions, the recognition of organic substrates is a much more difficult problem for several reasons. First, the receptor should be complementary to the guest not only in size but also in the spatial orientation of functional groups. Second, the energies of interaction with uncharged substrates are substantially less than in the case of ion particles that reduces the binding efficiency.

We have proposed a new type of receptors to bind substrates containing the carboxyl group (Figure 3).[25–32] Two free hydroxyl groups in the 1,3-disubstituted at lower rim calix[4]arenes are complementary carboxyl groups and carboxylate anions that has given us the basis to assume their effective binding with α-hydroxy, α-amino and dicarboxilyc acids. In this case, two hydrogen bonds can be formed with the substrate carboxyl group. Additional binding may appear due to interactions of the second functional group or/and side-chain of substrate with lateral substituents located on the lower rim of the macrocycle.

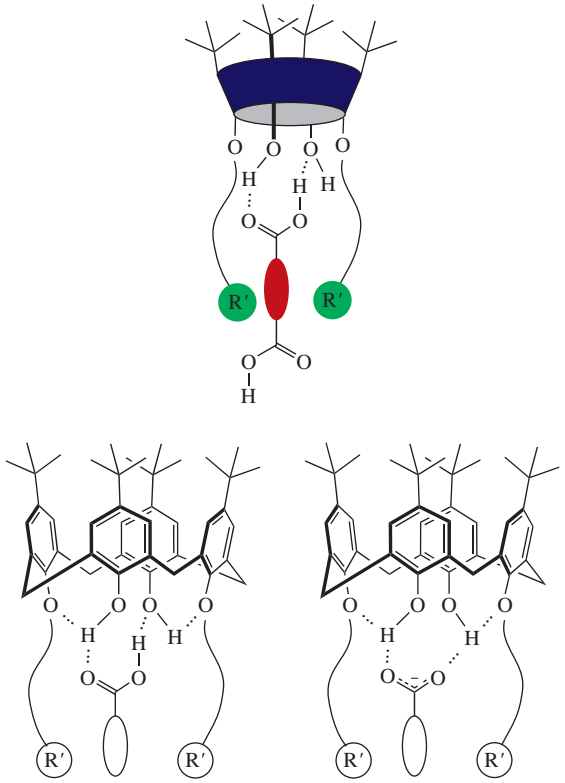
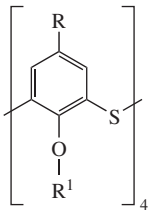


Figure 3 The interaction model of the calix[4]arene based receptors for the substrate containing carboxyl and carboxylate groups.

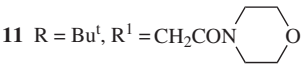
Thus, the directed modification of calixarene platforms allows one to create receptors for various types of substrates. However, the development of methods for chemo- and stereoselective functionalization of both lower and upper rims of (thia)calix[4]arenes and calix[4]resorcinarene are needed. In this direction we have developed approaches to the synthesis of functionalized thiacalix[4]arene stereoisomers,[33–36] partially substituted derivatives[37] and a series of element (B, P, Si) containing calixarenes.[38–54]

Ionophoric properties of functionalized calixarenes and formation of host–guest complexes. To evaluate the ability of thiacalix[4]arene derivatives **4**–**12** to recognize metal ions, liquid–liquid extraction of their picrate salts has been carried out in a mutually saturated water–dichloromethane system.[5,6,33–35,55,56]

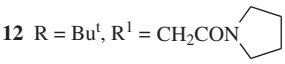
Model compound **13** containing two non-preorganized amido groups was synthesized to estimate the effect of binding site



4 R = Bu^t, R^1 = CH_2COPh
5 R = Bu^t, R^1 = CH_2CONEt_2
6 R = H, R^1 = CH_2COPh
7 R = H, R^1 = CH_2CONEt_2
8 R = Bu^t, R^1 = CH_2COOEt
9 R = H, R^1 = CH_2COOEt
10 R = H, R^1 = CH_2CONBu_2

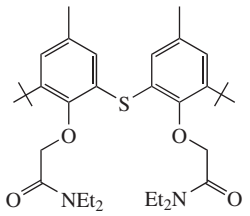


11 R = Bu^t, R^1 = CH_2CON O



12 R = Bu^t, R^1 = CH_2CON

preorganization on calixarene platform. This molecule can be considered as a half of tetrasubstituted calixarene derivative **5**, bearing four preorganized amido groups.



13

It was found that diamide **13**, unlike macrocyclic tetraamide **5**, demonstrates extremely low ability to extract alkali metal picrates in the organic phase. The estimation of a macrocyclic cooperative effect for investigated systems gave values of 6–10 log. units depending on the calixarene conformation.[35]

The dependence of effectiveness, stoichiometry and selectivity of metal ion binding on calixarene conformation has been studied.[5,6,33–35,55–58] In particular, it was shown for tetrasubstituted at lower rim macrocycles **4**, **5** that stereoisomers *cone*, *partial cone* (*paco*) and 1,3-*alternate* form complexes of different stoichiometry with alkali metal cations in an organic phase (L:M$^+$): 1:1, 1:2 and 1:4.[6] Macrocycle *cone*-**4** demonstrates the highest ability to extract the sodium cation compared to other alkali metal ions. By contrast, *paco*-**4** and 1,3-*alternate*-**4** extract more effectively larger metal cations such as potassium. The replacement of phenyl for diethylamino group **5** leads to the sharp increase in extraction constants by five to seven orders of magnitude. At the same time, the selectivity of alkali ions binding goes down.[6,34,35] The influence of macrocycle conformation and binding site nature on the complexation ability of functionalized thiacalix[4]arenes with *p*- and *d*-metal cations was also investigated.[56–59]

The effect of *tert*-butyl groups on the binding ability of calixarenes was evaluated.[60] This problem seems curious because *tert*-butyl groups are so far from the binding sites. Calixarenes are typical allosteric systems where changes on the one side lead to changes on the other side of macrocycle. Calixarenes **6**, **7**, **9**, **10** without *tert*-butyl on upper rim demonstrate the drastic changes in extractability and selectivity. No extraction of alkali metal ions by the stereoisomers of macrocycles **6** and **9** was found. The extractability and selectivity of tetraamides **5** and **7** are significantly different (Figure 4). For example, *cone*-**7** unlike *tert*-butyl analogue *cone*-**5** extracts selectively a small lithium cation and its extractability goes down along with increasing ion size.[60]

Observed differences of the extraction capacity were attributed to the preorganization effect of binding centers located on the macrocyclic platform. X-ray pictures of tetraamides **5** and **7** in 1,3-*alternate* conformation (Figure 5) indicate that spatial structures of these compounds are significantly different. *Tert*-butyl groups stabilize the cavity suitable for ion incorporation: the distance between oxygen atoms of carbamoyl groups is 6.65 Å, and as result strong binding properties were observed. In the absence of *tert*-butyl groups the aromatic rings in macrocycle **7** became closely whereas amido groups diverge (8.14 Å). An additional energy for ligand reorganization should be paid at the complexation of calixarene **7**. Obviously, it leads to a decrease of the complex stability.

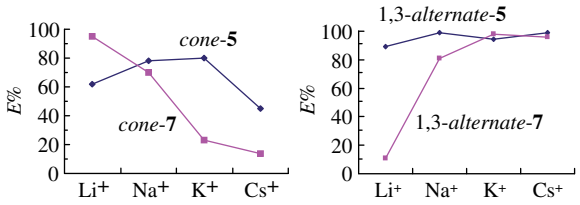


Figure 4 The dependence of extraction degree (*E*%) of alkali metal cations by compounds **5** and **7** in the *cone* and 1,3-*alternate* conformations. Experimental conditions: $[\mathbf{5}]_{org,int} = 3.5\times10^{-4}$ mol dm^{-3}, $[MOH]_{aq,int} = 7.0\times10^{-5}$ mol dm^{-3}, $[HPic]_{aq,int} = 5.0\times10^{-5}$ mol dm^{-3}; $[\mathbf{7}]_{org,int} = 2.5\times10^{-3}$ mol dm^{-3}, $[MOH]_{aq,int} =$ = 0.1 mol dm^{-3}, $[HPic]_{aq,int} = 2.5\times10^{-4}$ mol dm^{-3}.

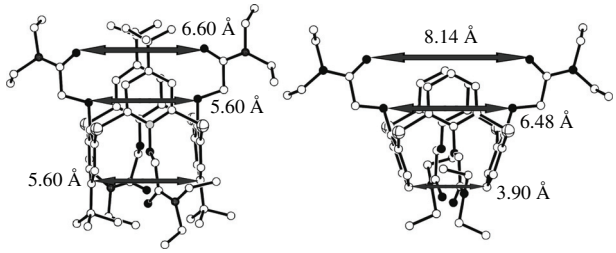
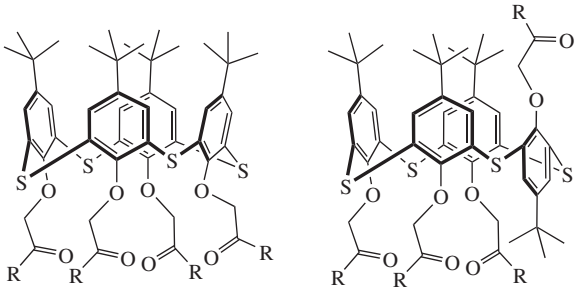
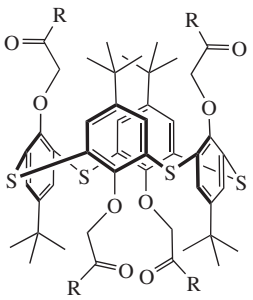


Figure 5 X-ray structure of macrocycles **5** and **7** in the 1,3-*alternate* conformation.

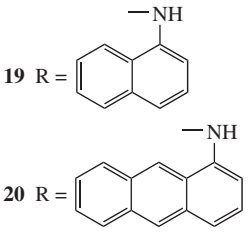
The replacement of conformationally mobile diethylamide groups with morpholide **11** and pyrrolidide **12** cycles changes significantly the geometry of the cation binding center, *i.e.*, the cavity formed by the oxygen atoms of the phenyl and amide groups at the lower rim, as well as their ionophoric properties.[55] Compounds **11** and **12** in *cone*, *partial cone* and 1,3-*alternate* conformations extract silver cations effectively due to the coordination of the bridging sulfur atom of the macrocycle with this metal ion. The binding effectiveness toward alkali metal cations by *p*-*tert*-butyl thiacalix[4]arene tetrasubstituted with carbonyl-containing groups at the lower rim is determined by the donor ability of the substituted carbonyl groups. The extraction efficiency decreases in the order **11** < **12** in accordance with their electron donation properties.

p-*tert*-Butyl thiacalix[4]arenes functionalized with the secondary amide groups at the lower rim in *cone*, *partial cone* and 1,3-*alternate* conformations are poor extractants for the ions of *s* (Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}), *p* (Al^{3+}, Pb^{2+}), and *d* (Fe^{3+}, Co^{3+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}) elements. The low binding efficiency of **14**–**18** is related to the poor donor ability of the substituted carbonyl group and strong hydrogen bonding between the protons of NH groups and carbonyl fragments of the amide groups, which leads to the formation of mainly dimeric associates of similar size (1.1–2.7 nm).[61] For systems **17** and **18**, the hydrodynamic size of nanoscaled particles tends to increase in the order *cone*, *partial cone*, 1,3-*alternate*, whereas for amides **15** and **16** this order is changed in the opposite direction. These results coincide well with picrate extraction characteristics, *i.e.*, an increase of extraction constants is accompanied by a decrease in the hydrodynamic size of particles.





14 R = $NHCH_2Ph$
15 R = NHPh
16 R = $NH(CH_2)_7Me$
17 R = $NH(CH_2)_{11}Me$
18 R = $NH(CH_2)_{17}Me$



Aggregation processes with the formation of nanoparticles are more characteristic of the complexes of metal cations with functionalized thiacalixarene. In particular, tetraamides **11** and **12** in different conformations form monodisperse nanoparticles (130–150 nm) with the silver cations in dichloromethane solution (Figure 6).[55] A similar behaviour was observed for secondary tetraamides **14**–**18**[61] and tetrahydrozides.[62] One-dimensional coordination polymers were formed in the system of ω-alkoxynitrile derivatives of thiacalix[4]arene in 1,3-*alternate* conformation and silver cation.[63]

In accordance with the approach presented in Figure 1(*b*), thiacalix[4]arenes containing secondary amides on the lower rim can bind anions through hydrogen bonds with the NH group. To control the process of complexation with anions, a fluorescence group was introduced into the amido fragment (compounds **19**, **20**).[64] Receptor properties of new fluorescent sensors showed that 1,3-*alternate*-**19** recognizes F^-, *cone* stereoisomer gives specific signal to F^- and Cl^-, whereas a *partial cone* stereoisomer distinguishes between F^- and Cl^- from Br^-. Thus, tetranaphthyl thiacalix[4]arene **19** can be used to design fluorescent sensors for halogen anion recognition in a physiological (millimolar) range of concentrations.

For the extraction of technetium(VII), which exists as the pertechnetate anion TcO_4^- in aqueous solutions, ligands **21** and **22** were synthesized on the calixarene platform (X = CH_2) in *cone* conformation. Both synthesized ligands demonstrated high extraction capacity in relation to the pertechnetate ion in acidic and alkaline media.[65,66]

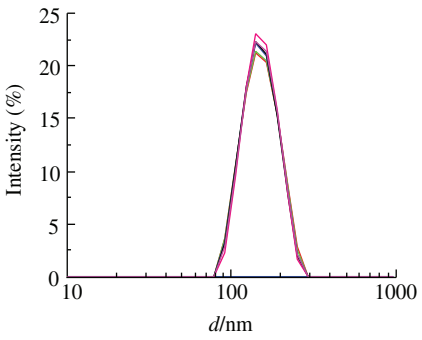
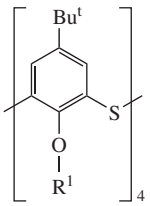
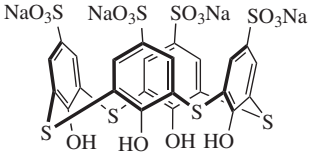


Figure 6 The size distribution of the particles formed in the system *cone*-**12**/Ag^+ in dichloromethane.



21 $R^1 = CH_2COPh$
22 $R^1 = CH_2COOEt$

The regularities of the formation of supramolecular metal-containing systems on the basis of outer-sphere association of metallocomplexes with calixarene derivatives were established.[11–13,15–22] In these systems, the calixarene cavity can be considered as the molecular container providing a specific microenvironment for the guest binding.



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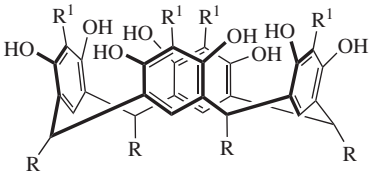


24 R = Me, $R^1 = CH_2SO_3Na$
25 $R = C_5H_{11}$, $R^1 = CH_2SO_3Na$
26 R = Me, $R^1 = CH_2NMe_2$
27 R = Me, R^1 = H

The formation of outer-sphere complexes by calix[4]arenes has been shown by X-ray analysis in solid phase[15,22,24] and NMR spectroscopy in solution by the example of complexes of *p*-sulfonatothiacalix[4]arene **23** and sulfonatomethylated calix[4]resorcinarenes **24**, **25** with positively charged and kinetically inert metallocomplexes: tris(ethylenediaminate), bis(gistidinate), bis(ethylenediaminate)oxalate complexes of Co^{III}, tris(dipyridyl) complexes of Co^{III} and Ru^{II}, as well as a potassium complex with 18-crown-6.[18–23] The outer-sphere association leads to the inclusion of chelate cycles (Figure 7) or chelate cycle fragments (Figure 8) into the cavity of a macrocyclic tetraanion.

The examination of stability constants of the outer-sphere associates on the basis of **23** and **24** indicated that their structure, in particular, the degree of metallocomplex incorporation into the cavity is defined by the electrostatic interactions on the macrocycle rim and CH–π interactions with the macrocycle cavity.[18–22] These regulatities gave a possibility for the develop-

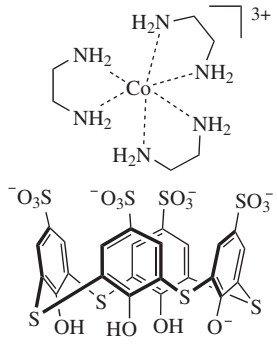


Figure 7 The structure of outer-sphere associate of tris(ethylenediaminate) Co^{III} with **23** according to ^1H NMR data.

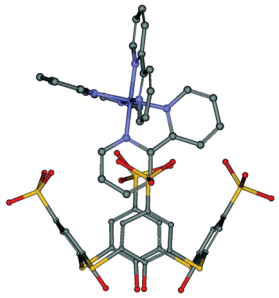


Figure 8 The structure of outer-sphere associate of tris(dipyridyl) Ru^{II} with *p*-sulfonatothiacalix[4]arene according to X-ray diffraction data.

ment of a pH-switchable host–guest complexation machine using anionic calixarenes and positively charged metallocomplexes[24] or organic cations.[67] In Figure 9, a pH-switchable system based on the *N*-methylpyridinium cation and macrocycle **24** is presented. Due to the deprotonation of the phenolic hydroxyls of calix[4]-resorcinarene platform, the reorientation of the organic cation in the macrocyclic cavity can be reached.

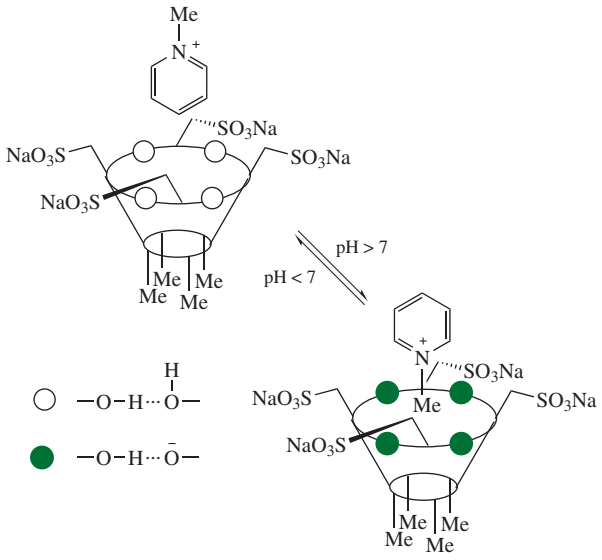


Figure 9 Schematic diagram of the pH-dependent orientation of the *N*-methylpyridinium cation in the macrocycle **24** cavity.

Protonated N,N-dialkylaminomethylated derivative **26** is a receptor on the anionic metallocomplexes.[15] It was shown that macrocycle **26** stabilizes negatively charged tetrachloride zinc and cadmium complexes $[MCl_4]^{2-}$. The structure of the outer-sphere complex of $2(\mathbf{26})^{4+}(ZnCl_4)^{2-}\cdot 6Cl^-\cdot 4H_2O$, crystallized from solution, in which zinc tetrachloride anions are not the dominant form, is presented in Figure 10. The outer-sphere association is the cause of stabilizing the unstable form $[ZnCl_4]^{2-}$ and $[CdCl_4]^{2-}$.

A similar picture is observed in the case of labile organic metallocomplexes. For the unstable bis(dipyridyl) and bis(phenanthrolinate) complexes of lanthanides,[10–12] as well as phenanthrolinate Cu^{II} complexes,[11,13] it was shown that outer-sphere association of these charged complexes with the anions of calixarenes **26**, **27** in weakly alkaline media is thermodynamically favourable.

Thus, the study of ionophoric properties of some new classes of ligands based on functionalized calix[4]arenes demonstrated that they are efficient and selective complexons and reveal a number of important effects: (i) macrocyclic cooperative effect; (ii) allosteric effect; (iii) effect of macrocycle conformation on the ion binding selectivity; (iv) formation of outer-sphere complexes; and (v) stabilization of unstable ion structures.

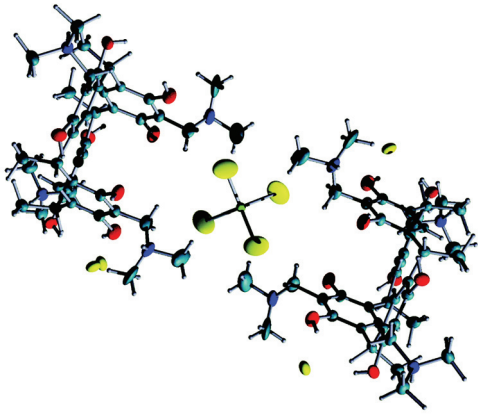
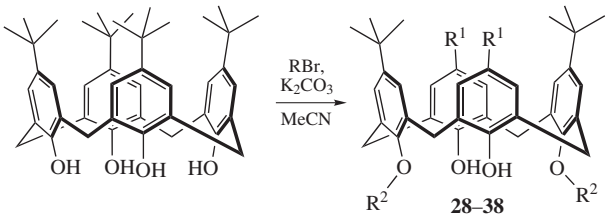


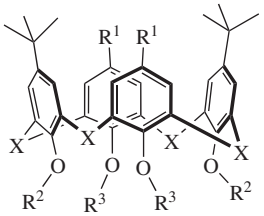
Figure 10 X-ray structure of the outer-sphere associate of $2(\mathbf{26})^{4+}(ZnCl_4)^{2-}\cdot 6Cl^-\cdot 4H_2O$.

Molecular recognition of carboxylic acids by the functionalized (thia)calix[4]arenes. According to the molecular modeling, the phenolic hydroxyls of 1,3-disubstituted at lower rim calixarenes are complementary to carboxyl groups and carboxylate anions and can effectively bind α-hydroxy, α-amino and dicarboxylic acids. A series of compounds **28–48** has been obtained by selective alkylation of *p-tert*-butylcalix[4]arene. To evaluate the binding ability of synthesized macrocycles, the kinetic experiments on the membrane transport of α-hydroxy and α-amino acids (*d*,*l*-tartaric, glycolic, *d*,*l*-mandelic and *d*,*l*-glutamic acids) and dicarboxylic acids (oxalic, malonic and succinic acids) were carried out.[25–32] The addition of macrocycles **28–48** to the membrane phase accelerates substrate transport across the membrane to indicate carrier–substrate complex formation.

Two models (**A**, 'docking') and (**B**, 'tweezers') of molecular recognition of α-hydroxy, α-amino and dicarboxylic acids by



28–38



39–48

28 $R^1 = Bu^t$, $R^2 = CH_2Ph$
29 $R^1 = Bu^t$, $R^2 = CH_2$-β-naphthyl
30 $R^1 = Bu^t$, R^2 = fluoren-9-yl
31 $R^1 = Bu^t$, $R^2 = CH_2CH{=}CHPh$
32 $R^1 = Bu^t$, $R^2 = CH_2{-}C_6H_4{-}NO_2$-*p*
33 $R^1 = Bu^t$, $R^2 = CH_2{-}C_6H_4{-}CN$-*p*
34 $R^1 = Bu^t$, $R^2 = CH_2{-}C_6H_4{-}COOEt$-*p*
35 $R^1 = Bu^t$, $R^2 = CH_2{-}C_6H_4{-}O{-}C_6H_4{-}NO_2$-*p*
36 $R^1 = Bu^t$, $R^2 = CH_2C_6F_5$
37 $R^1 = Bu^t$, $R^2 = CH_2{-}C_6H_4{-}COOH$-*p*
38 $R^1 = NO_2$, $R^2 = CH_2Ph$
39 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2COOEt$, R^3 = H
40 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2COOH$, R^3 = H
41 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2CH_2NHCOPh$, R^3 = H
42 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2C(O)NH(CH_2)_7Me$, R^3 = H
43 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2C(O)NHPh$, R^3 = H
44 X = CH_2, $R^1 = NO_2$, $R^2 = CH_2CH_2NHCOPh$, R^3 = H
45 X = CH_2, $R^1 = Bu^t$, $R^2 = CH_2$-4-pyridyl, R^3 = H
46 X = CH_2, $R^1 = Bu^t$, $R^2 = R^3 = CH_2COMe$
47 X = CH_2, $R^1 = Bu^t$, $R^2 = R^3 = CH_2COOEt$
48 X = S, $R^1 = Bu^t$, $R^2 = R^3 = CH_2COOEt$

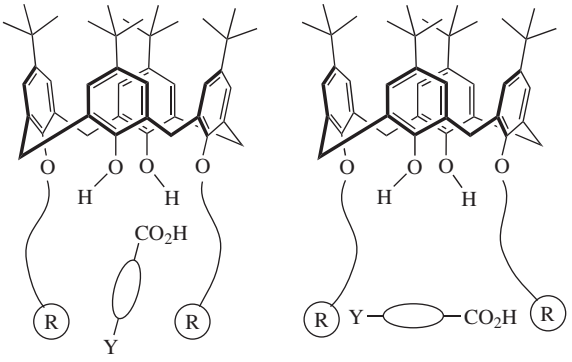


Figure 11 Models of the organic acids binding by 1,3-disubstituted at the lower rim calix[4]arenes: (**A**) 'docking' and (**B**) 'tweezers'.

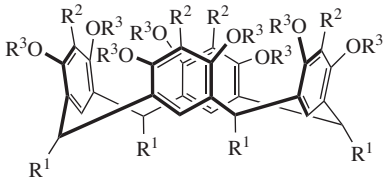
1,3-disubstituted at the lower rim calixarenes were established (Figure 11). The fundamental difference between these models consists in a different substrate orientation relatively to the host molecule. In the first model (**A**, Figure 11), the recognition occurs at both phenolic hydroxyls of macrocycle and additional binding sites located on the lateral substituents (R). In another binding scheme (**B**, Figure 11) substituents (R) on the calix[4]arene lower rim act as a 'tweezers' or 'two-arms' podand.

The examination of membrane transport and ^{1}H NMR spectroscopy data for dicarboxylic acids showed that substrates with a minimal length of carbon chain form preferably the complexes of 'tweezers' type, but with the increase of its length the formation of 'docking' type complexes is more likely. The receptor ability of 1,3-disubstituted (at the lower rim) calix[4]arenes can be significantly changed by variation of some factors: π-area of aromatic system (efficiency of π–π interactions), donor–acceptor characteristics and acid–base properties of calixarene phenolic groups.

Using the established regularities, selective carriers for some acids were constructed. In particular, the most effective and selective carriers of oxalic acid was 1,3-disubstituted calix[4]arene **45** bearing pyridine fragments on substituents R. This macrocycle transports oxalic acid across a lipophilic membrane with the flux acceleration coefficient of 277, while these values are no more than 5 for other investigated acids. This is consistent with the stability constants of calixarene **45** with oxalic $(1.2\pm0.15)\times10^5$ M^{-1} and glycolic $(2.8\pm0.4)\times10^4$ M^{-1} acids determined by UV-VIS spectroscopy in dichloromethane. Macrocycle **44**, in which two free hydroxyl groups have higher acidic properties, interacts selectively with glutamic acid.

Calixarene self-organization and the design of functional supramolecular systems in a liquid phase. The ability of calix[4]resorcinarene derivatives to self-association in solutions through hydrophobic factor, as shown previously,[68–72] is one of the fundamental properties of these compounds, which only recently has been actively used for the creating of nanosized particles in solution and on the surface.[73,74] Amphiphilic calix[4]resorcinarenes depending on the structure of functional groups may demonstrate the surface-active properties, forming direct or reverse micelles at low concentrations or do not show surface activity, forming in water stable nanoparticles of different size.[75,76]

An aggregation study was carried out using calix[4]resorcinarene **49**, functionalized calix[4]resorcinarenes with the aminomethyl **50**, aminoacetal **51**, tris(hydromethyl)methylamido **52** and alkylphosphonate **53** groups, as well as calix[4]resorcinarene **54** containing simultaneously aminomethyl and alkylphosphonate groups.



49 R^1 = Me–$C_{11}H_{23}$, R^2 = R^3 = H
50 R^1 = C_9H_{19}, R^2 = CH_2NMe_2, R^3 = H
51 R^1 = $C_{11}H_{23}$, R^2 = $CH_2N(Me)CH_2CH(OMe)_2$, R^3 = H
52 R^1 = C_8H_{17}, R^2 = H, R^3 = $CH_2C(O)NHC(CH_2OH)_3$
53 R^1 = $CH_2P(O)(OH)Bu$, R^2 = R^3 = H
54 R^1 = $CH_2P(O)(OH)Bu$, R^2 = CH_2NMe_2, R^3 = H

The critical micelle concentrations (CMC) of aminomethylated calix[4]resorcinarenes **50**, **54** demonstrate a high ability of the macrocycle to micelle formation in water or water–organic solvent mixtures, in particular, water–dimethylformamide (DMF) solutions. It desreases the surface tension (σ) to ~40 mN m^{-1}, which is comparable with the similar characteristics of traditional surfactants.[74] But CMC values in all studied solutions are reduced by one to three orders of magnitude.[70,71]

The macrocyclic effect on aggregation behaviour was evaluated by comparing with 2-(*N*,*N*-dimethylaminomethyl)-4-nonylphenol **55**, which can be considered as a structural unit of aminomethylated calix[4]resorcinarene **50**. The CMC of macrocycle **50** in water is one order of magnitude lower than for model phenol **55** at similar pH. Moreover, calixarene **50** forms micelles in water–DMF mixtures in a wide range of DMF concentrations from 10 to 75 vol%, whereas compound **55**, at 10–30 vol% only.

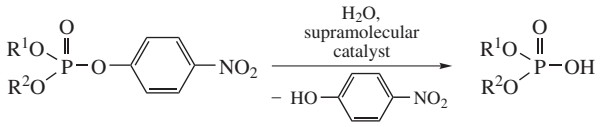
The effective way to regulate receptor properties and size of nanoparticles and micelles on the basis of calix[4]resorcinarenes was developed.[71,72,76–87] It includes co-surfactant addition and/or solvent composition variation. Mixed micelle formation has been established for nonionic and anionic co-surfactants (TX100, Brij35, TX405 and sodium dodecylsulfate) and calix[4]resorcinarenes **49** (R = Me–$C_{11}H_{23}$).[77–79] It should be noted that these calixarenes are insoluble in water, and thus mixed micellar aggregate formation can be used for their solubilization. This property, as well as the ability of micellar solutions to pseudophase temperature-induced separation, became the basis for the development of an ecologically safe (not required organic solvents) method of lanthanide ion concentration by micellar extraction or cloud point extraction.[88]

The formation of mixed micelles on the basis of amphiphilic calix[4]resorcinarenes and cetyltrimethylammonium bromide (CTAB) leads to both CMC values decrease and the micelles size increase in comparison with CTAB individual micelles.[71,72] For example, the diameter of CTAB nanoparticles (10^{-2} mol dm^{-3}) is increased with additives of **52** (10^{-3}–10^{-2} mol dm^{-3}) from 4 to 49 nm in water and from 1.5 to 3.2 nm in aqueous DMF. Thus, the solvent can affect the size of individual and mixed micelles.

The study of the amphiphilic calix[4]resorcinarenes aggregation[49–54] in nonpolar chloroform showed that the aggregates like reverse micelles are formed at 2×10^{-5}–1×10^{-4} mol dm^{-3}. CMC values depend on the structure and number of the polar groups.[89–91] These amphiphilic macrocycles and natural or synthetic surfactants can form mixed micelles, as confirmed by dielcometric titration, IR and 2D NMR spectroscopy. It is interesting that aggregates with ionic surfactant contain several surfactant molecules per one calixarene molecule. In the case of the nonionic surfactants or zwitter-ionic phosphatidylcholine the mixed aggregates are the capsules formed by amphiphilic calixarenes containing one surfactant molecule.

The directed formation of nanoparticles having a different structure and size (2–190 nm) based on amphiphilic calixarenes and surface-active substances allows one to construct chemical nanoreactors, where the principles of supramolecular, metallocomplex and enzymatic catalysis can be realized.

Indeed, for the fist time, we found[92–96] that the micelles and nanoparticles formed by calix[4]resorcinarenes have catalytic activity in the hydrolysis of phosphorus acid esters. This reaction, playing an important role in the processes of life, is one of the most studied in physical and supramolecular chemistry.



The kinetic study of the hydrolysis of phosphorus acid *p*-nitrophenyl esters showed that amphiphilic calixarenes are effective catalysts for these reactions in water–organic and micellar media. The reactivity of the micelles formed by macrocycles **49** and **50** is four to nine times higher than that of micelles of aminomethylated phenol **55**. The main difference in terms of supramolecular catalysis is that the CMC of calix[4]resorcinarenes aggregates is lower and the binding constant K_S is higher than that in the case of aminomethylated phenols by a factor of 10. Thus, the more 'rigid' micelles of the macrocyclic amphiphiles (calix[4]resorcinarenes) containing four aromatic nuclei and preorganized hydroxyl and amino groups are formed more easily. They bind substrates stronger than amphiphilic phenol micelles and demonstrate high hydrolytic activity at low concentrations.

To increase the supramolecular system reactivity, the composition on the basis of calix[4]resorcinarenes and cationic surfactant – cetyltrimethylammonium bromide (CTAB) was designed. The mixed aggregates of CTAB–**50** in the water–DMF mixture, as well as the mixed micelles of CTAB–**52** in water, demonstrate a high catalytic activity (Figure 12). It was found that the catalytic activity changes can be assigned to the formation and reorganization of mixed micelles of CTAB–**52**. The greatest catalytic activity at pH 8 was shown by the mixed micelles with a size of 49 nm at a ratio of **52**:CTAB ~ 1:5 (Figure 12).

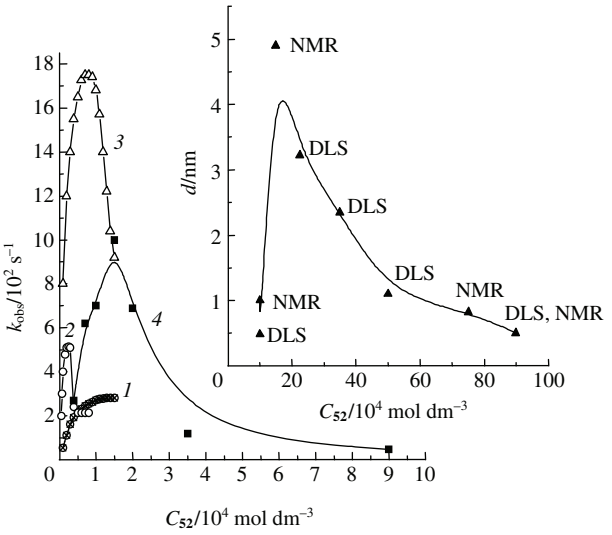


Figure 12 The dependence of observed hydrolysis constants (k_{obs}) of *p*-nitrophenyl-bis(chloromethyl) phosphonate *vs.* its concentration (*1*) in the absence and (*2*)–(*4*) presence of CTAB in water: (*2*) $C_{CTAB} = 1\times10^{-3}$, (*3*) 5×10^{-3}, (*4*) 1×10^{-2} mol dm^{-3}; (*1*)–(*3*) pH 9.0 and (*4*) pH 8.0, 30 °C. Inset: concentration dependence of mixed micelles size (*d*) for the system **52**–CTAB ($C_{CTAB} = 1\times10^{-2}$ mol dm^{-3}).

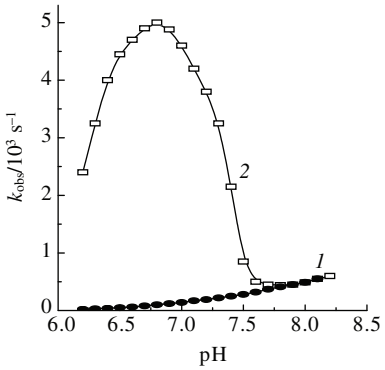


Figure 13 The pH dependence of observed hydrolysis constants (k_{obs}) for the system on the basis of **50** (*1*) in the absence and (*2*) presence of La^{III}: $C_{\mathbf{50}} = C_{La^{III}} = 4\times10^{-4}$ mol dm^{-3}, $C_{T\text{-}X\text{-}100} = 5\times10^{-3}$ mol dm^{-3}, solvent: DMF (10 vol%)–H_2O, 25 °C.

The synergetic effect of mixed micelles and metallocomplexes on the catalytic activity has been established for metallomicelles La^{III}–**50**–Triton X-100. It leads to a shift in the catalytic activity maximum in the area of reagent low concentrations and neutral pH (Figure 13), as well as to an increase of hydrolysis rate of unreactive *p*-nitrophenyldiphenylphosphate in 170000 times in comparision with noncatalytic reaction.

Metallomicelles of La^{III}–**50**–Triton X-100 demonstrated a 60 times higher catalytic activity than that of mixed micelles of **50**–Triton X-100 due to several factors. Most important ones are the decrease of the dissociation constants of aminomethylated calixarene nucleophilic groups due to the coordination with La^{III} and the effective binding of phosphorus acid esters ($K_S = 41000$ dm^3 mol^{-1}) in comparison with the micelles of **50**–Triton X-100 ($K_S = 4600$ dm^3 mol^{-1}).

In conclusion, note that 2008 is a jubilee for supramolecular chemistry. In 1978, J.-M. Lehn introduced the term 'supramolecular systems'. Today, it became apparent that they have their own niche in the hierarchy of matter in accordance with its growing: atoms–molecules–supramolecular systems–biological systems (Figure 14).

Atoms	a b c	
Molecules	A (a–a) B (a–b) C (b–c) covalent bonds	
Supramolecular systems	A···A A···B A···B···C C···A noncovalent bonds (intermolecular)	supermolecules supramolecular assemblies
Biological systems	interdependent community of functional supramolecular systems (self-reproduction)	

Figure 14 The hierarchy of matter.

Supramolecular systems based on calixarenes having fundamental properties such as molecular recognition, membrane transport, supramolecular self-organization (aggregation) and supramolecular catalysis, are an excellent illustration of this provision.

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