Tetrahedron 64 (2008) 7489–7497

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Solvent extraction and self-assembly of nanosized aggregates of *p-tert*-butyl thiacalix[4]arenes tetrasubstituted at the lower rim by tertiary amide groups and monocharged metal cations in the organic phase

Ivan I. Stoikov [a,*], Elena A. Yushkova [a], Arkadiy Yu. Zhukov [a], Ilya Zharov [b], Igor S. Antipin [a], Alexander I. Konovalov [a]

[a] *Kazan State University, A.M. Butlerov Chemical Institute, 420008 Kazan, Kremlevskaya 18, Department of Chemistry, Russian Federation*
[b] *University of Utah, Salt Lake City, UT 84112, United States*

ARTICLE INFO

Article history:
Received 14 February 2008
Received in revised form 6 May 2008
Accepted 22 May 2008
Available online 27 May 2008

Keywords:
Self-assembly
p-tert-Butyl thiacalix[4]arenes
Molecular recognition
Picrate extraction
Dynamic light scattering (DLS)

ABSTRACT

New *p-tert*-butyl thiacalix[4]arenes functionalized with morpholide and pyrrolidide groups at the lower rim in *cone*, *partial cone*, and *1,3-alternate* conformations were synthesized, and their receptor properties for monocharged cations (alkali metal and silver ions) were studied using the picrate extraction method and dynamic light scattering (DLS). To evaluate the ability of the *p-tert*-butyl thiacalix[4]arene derivatives to recognize metal ions, liquid–liquid extraction of their picrate salts has been carried out in a mutually saturated water–dichloromethane system. The degrees of extraction and the extraction constants for monocharged metal cations (Li^+, Na^+, K^+, Cs^+) have been determined. The ability of the systems, consisting of host and guest molecules, to self-assembly was proved by DLS using a Zetasizer Nano ZS particle size analyzer. It was shown that all the investigated thiacalix[4]arenes are able to form nanoscale particles with silver cations under the experimental conditions. The pyrrolidide derivative in the *cone* conformation showed both self-association and aggregation processes with lithium cations. The degree of extraction for all the investigated systems that formed nanoscale aggregates in the organic phase was more than 67% and the extraction constants, log K_{ex} determined by the picrate extraction method, more than 6.

1. Introduction

The synthesis of nanoscale architectures and appropriate 'smart' materials devoted to creating molecular machines, information coding devices, electromechanical keys and sensors is considered nowadays as one of the perspective tendencies of the investigations into supramolecular chemistry. The development of supramolecular structures and nanoscale elements from single molecules is mainly based on self-assembly principles.[1] They assume spontaneous association of a number of relatively simple subunits, like single molecules, into a highly complex supramolecular product of defined structure. The sedimentation of atoms or molecules onto the surface followed by their self-ordering can be also used for these purposes.[2] It is necessary to mention that self-assembly processes are directed by weak reversible interactions, e.g., hydrogen bonding or van der Waals interactions. They provide thermodynamic control of the reaction with simultaneous correction of the product structural defects. As a result, equilibrium structures are obtained without any intentional control of the process.[2]

Metal based supramolecular structures can be most effectively obtained by non-covalent self-assembly based on specially designed ligands to be spontaneously connected by metal ions.[3–6] This makes it possible to combine the conformation lability of the ligand with the electrostatic interactions of the metal ions. The organic compounds able to form these structures recognize certain types of substrate, and provide the necessary special arrangement of their structural fragments, coordinative centers, and functional groups. Metal ions involved in such interactions act as coordinative centers that definitely direct the ligand surroundings. In addition, metal ion promotion of self-assembling is reversible and allows switching of the direction of the process from assembly to disassembly and vice versa in accordance with outside conditions.

This combination of the properties of the components is favorable for the synthesis of supramolecular structures with a high degree of symmetry, i.e., molecular triangles, squares, pentagons, hexagons, and even a three-dimensional octahedron.[2]

One of the most productive approaches to the development of the above receptor structures designed for the selective interaction with some substrates consists of the modification of the appropriate

* Corresponding author. Tel.: +7 8432 315463; fax: +7 8432 752253.
E-mail address: ivan.stoikov@mail.ru (I.I. Stoikov).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.05.102

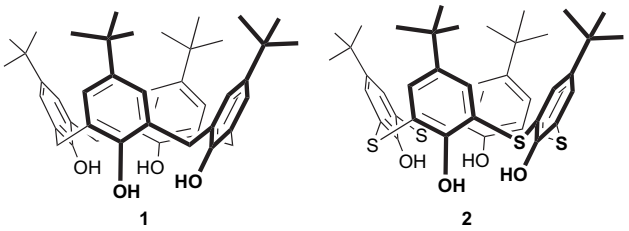


Figure 1. Structures of calixarene and thiacalixarene.

macrocyclic platform by suitable reagents to provide necessary spatial orientation of the binding centers.[7] For this purpose, various platforms are currently used, e.g., crown ethers, calix- and calixrezorcinarenes, and cyclodextrins.[7,8] Now intensive development has produced the chemistry of thiacalix[4]arenes. These are analogs of the classical calix[4]arene in which all four methylene bridges are replaced by sulfur atoms (Fig. 1).[9–11]

The replacement of the original methylene bridges in calixarene **1** by sulfur atoms in thiacalix[4]arene **2** affects conformational mobility of the macrocyclic ring. This facilitates the synthesis of the thiacalix[4]arene derivatives by implementation of various functional groups at their lower rim.[11] As was found, thiacalix[4]arene showed a very high ability to bind transition metal ions, contrary to the rather poor binding ability of precursor calix[4]arene.[11]

The potential of thiacalix[4]arenes functionalized with polar groups at the lower rim of the macrocycle toward self-assembling was explored mainly in aqueous media,[12,13] whereas the ability of other thiacalix[4]arene derivatives to non-covalent self-assembling is still far from being characterized. In this work, we describe the synthesis of novel *p-tert*-butyl thiacalix[4]arenes functionalized with pyrrolidide **6** and morpholide **5** groups at the lower rim in *cone*, *partial cone*, and *1,3-alternate* conformations. Their receptor properties toward alkali (Li^+, Na^+, K^+, Cs^+) and silver ions by picrate extraction and dynamic light scattering (DLS) are also discussed.

2. Results and discussion

2.1. Synthesis of stereoisomers of tetrasubstituted at the lower rim *p-tert*-butyl thiacalix[4]arenes, containing cyclic tertiary amide fragments

In the literature,[14–17] one-step methods of synthesis were described for *cone*, *partial cone*, and *1,3-alternate* (Fig. 2) tetraalkoxythiacalix[4]arene stereoisomers. They can be performed in high yield by alkylation of the hydroxy groups of the lower rim of the macrocycle by α-halogen carbonylic compounds (ethyl bromoacetate, bromoacetone, α-bromoacetophenone, chloro-*N*,*N*′-diethylamide) in the presence of alkali metal carbonates. The size of the metal cation determines the selective formation of the appropriate conformer by template effect.

It should be emphasized that the spatial location of substitutes relative to the phenolic oxygen is different for all the stereoisomers. This provides individual orientation of the binding site for each stereoisomer. Thus, *1,3-alternate* has two chelating groups on each

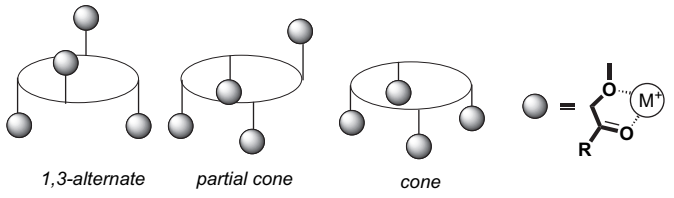


Figure 2. Schematic structures of stereoisomers of tetrasubstituted at the lower rim thiacalix[4]arene.

side of the macrocyclic ring, *partial cone* one and three groups, respectively, and *cone* has all four fragments located on one side of the macrocycle. In accordance with this, *1,3-alternate* is 'double-handed' podande, *partial cone* 'triple-handed', and *cone* is 'four-handed' podande.[18]

It is also important that *1,3-alternate* contains two binding sites. However, binding the first substrate can affect the activity of the second binding site on the opposite side of the macrocycle, due to allosteric effects followed from the flexibility of the thiacalix[4]arene platform.[11]

The differentiation of binding properties of receptors based on *p-tert*-butyl thiacalix[4]arene precursors **3** can be achieved by hydrolysis of tetraesters **3** to the appropriate tetraacids **4** followed by conversion to the acid chlorides and reaction with amines in basic media.[11,19]

In the literature,[11] various methods of hydrolysis of tetraesters **3** to corresponding tetraacids are described for *cone*, *partial cone*, and *1,3-alternate* stereoisomers. The hydrolysis was accomplished by excessive amounts of alkali metal hydroxides in DMF/water and ethyl alcohol/water mixtures. However, the yields of the hydrolysis products were rather low. The isolation of the target compounds was often rather difficult and required several steps.

We have elaborated a general protocol for the synthesis of tetraacid **4** stereoisomers, which gives all the three stereoisomers in good yield. The general route is presented in Scheme 1.

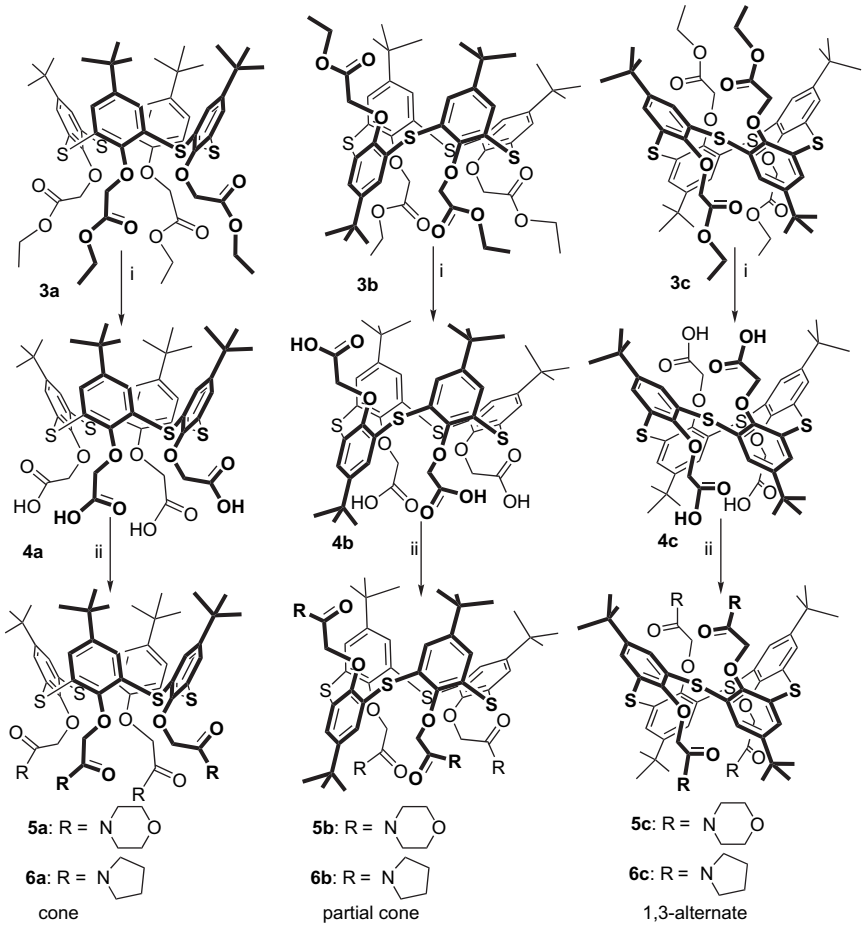
For this purpose, compounds *cone* **3a**, *partial cone* **3b**, and *1,3-alternate* **3c** were mixed with LiOH in THF/water at 60 °C until initial tetraester disappeared from the reaction mixture in accordance with TLC (*cone* **3a** for 5 h, *partial cone* **3b** for 35 h, and *1,3-alternate* **3c** for 40 h). ^{1}H NMR spectra and melting points of compounds **4** correspond to those mentioned in the literature.[20,21] Different reaction times can be explained by different solubilities of the stereoisomers **3** in the THF/water system, which decrease in the range *cone*>*partial cone*>*1,3-alternate*. Also, mutual influence of ethoxycarbonylic groups differently located in the macrocyclic ring plane can affect the reaction rate. All the three isomeric acids were converted to acid chlorides by boiling in thionyl chloride.[19]

In the presence of triethylamine in methylene chloride, tetraamides **5** and **6** were obtained by reaction of the secondary amines (morpholine, pyrrolidine) with the acid chlorides of stereoisomeric tetraacids **4**. Compounds **5** and **6** were purified by recrystallization from EtOH/CH_2Cl_2.

The exchange of the methylene bridges of calix[4]arene **1** by the sulfur atoms of the thiacalix[4]arene **2** leads to the complication of the definition of the macrocycle conformation. Conformer structures of the *1,2-alternate* and *partial cone* can be clearly distinguished by ^{1}H NMR spectroscopy. However, the conformers of the *cone* and *1,3-alternate* have higher symmetry of the structures and hence similar signals in the ^{1}H NMR spectra, i.e., singlets of *tert*-butyl group protons, aromatic ring and oxymethylene protons (see Table 1).

Nevertheless, the conformational differentiation of *cone* and *1,3-alternate* stereoisomers tetrasubstituted at the lower rim can be realized by chemical shifts of the protons mentioned above in the ^{1}H NMR spectra.[15–17] In the *1,3-alternate* conformer, the protons of the $-OCH_2$ group are located in the shielded zone of the neighboring aromatic rings of the macrocycle, and their signals in the ^{1}H NMR spectrum are recorded at stronger fields than those of the *cone* conformer. The chemical shifts of the aromatic macrocycle protons as well as of those of the *tert*-butyl groups depend on the nature of R—substituents near oxymethylene fragments (Fig. 3).

In Table 2, the chemical shifts and the splitting of the proton signals of the *tert*-butyl groups, oxymethylene fragments, and aromatic rings in the ^{1}H NMR spectra of *cone* **5**, **6** and *1,3-alternate* **5**, **6** isomers are summarized. For all the compounds, the oxymethylene proton signals of the *cone* stereoisomer were found at a weaker



Scheme 1. Reagents and conditions: (i) LiOH, H_2O/THF, HCl; (ii) $SOCl_2$, reflux, RH, NEt_3, CH_2Cl_2, rt.

Table 1
Multiplicity and intensity of the signals in the ^{1}H NMR spectra of stereoisomers of *p-tert*-butyl thiacalix[4]arene tetrasubstituted at the lower rim

	cone	*partial cone*	*1,3-alternate*	*1,2-alternate*
$-OCH_2-$	s (8H)	s (2H), s (2H), AB-qv (4H)	s (8H)	AB-qv (8H)
$C(CH_3)_3$	s (36H)	s (18H), 2 s (9H)	s (36H)	s (36H)
Ar–H	s (8H)	s (2H), s (2H), AB-qv (4H)	s (8H)	AB-qv (8H)

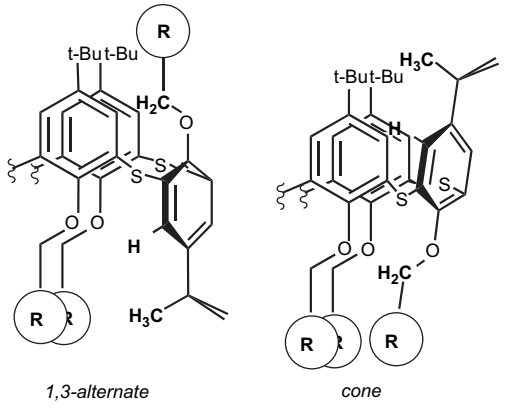


Figure 3. Fragments of the stereoisomers: *1,3-alternate* and *cone* structures.

field in comparison with those of the *1,3-alternate*. Changes in the chemical shifts of about 0.66–0.85 ppm were observed.

The chemical shifts of the aromatic protons depend less on the conformation of the macrocyclic ring, they drift by only 0.02–0.26 ppm upfield from *cone* to *1,3-alternate* stereoisomer. This is evidence of the screening effect of the neighboring aryl fragments in the *cone* stereoisomer on the aryl protons of macrocycle ring. The protons of the *tert*-butyl groups of the *cone* stereoisomer were found at a stronger field as compared to the corresponding proton signals of the *1,3-alternate* stereoisomer. This effect is probably due to the spatial location of the *tert*-butyl groups of the *cone* stereoisomer, shielded by the neighboring fragments of the marocycle.

Table 2
Proton chemical shifts of *cone* and *1,3-alternate* conformers of compounds **5** and **6** in the ^{1}H NMR spectra (300 MHz, $CDCl_3$)

Compound	$C(CH_3)_3$	OCH_2O	Ar–H
cone (**5a**)	1.08	5.34	7.30
1,3-alternate (**5c**)	1.26	4.68	7.51
cone (**6a**)	1.07	5.21	7.27
1,3-alternate (**6c**)	1.24	4.56	7.53

The changes in chemical shifts of the *tert*-butyl protons and those of the aromatic rings of the macrocycle observed for *cone* and *1,3-alternate* conformers depend not only on the shielding influence of the aromatic fragments of the macrocycle, but also on the nature of the functional substituents at the phenolic oxygens. Meanwhile, the oxymethylene protons of the substituted *cone* stereoisomer were found at weaker fields than those of the *1,3-alternate* stereoisomer.

2.2. The degrees of extraction

The two-phase extraction of alkali metals and silver picrates with *p-tert*-butyl thiacalix[4]arenes functionalized with diethylamide

groups at the lower rim in *cone*, *partial cone*, and *1,3-alternate* conformations was investigated earlier.[11,22] As was shown, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-[(*N*,*N*-diethylacetyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene efficiently extracted alkali metal ions but showed poor extraction selectivity.[22]

Compounds **5**(**a**–**c**) and **6**(**a**–**c**) seemed promising for extraction investigation. The substitution of the diethylamide groups with pyrrolidide **6** and morpholide **5** resulted in a change in the electronic and the spatial structure of the macrocyclic receptors. It is known that the constants of basicity of the compounds decrease in the range: pyrrolidide[25]>diathylamide[24]>morpholide[23] (pK_{BH}^{+}=11.27, 10.93, and 8.70, respectively). The replacement of conformationally mobile diethylamide groups with pyrrolidide **6** and morpholide **5** cycles should also change 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. This will result in changes of the receptor properties toward metal cations for all the conformers of *p-tert*-butyl thiacalix[4]arenes.

The receptor properties of the *p-tert*-butyl thiacalix[4]arene derivatives **6** and **5** in three conformations toward alkali metal and silver cations were studied using the picrate extraction method (Table 3).

One can see (Table 3) that all the investigated compounds **5** and **6** 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.[27,28] 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 group. The extraction efficiency decreases in the range **5**<**6** for macrocycles with the morpholide group that showed the least electron donation properties and with the pyrrolidide group, respectively. Compound **5a** (*cone*) is very poor extractant for alkali metal cations as compared to compound **6a** (*cone*) under the conditions investigated. Meanwhile, compound **6a** shows effective extraction of Li^+, Na^+, and Ag^+ ions. The replacement of the amide-containing substituent changed the electrostatic properties of thiacalix[4]arene derivatives **5b** and **6b** (*partial cone*). The pyrrolidide derivative **6b** (*partial cone*) selectively bonded to K^+. Conformational isomer **5b** (*partial cone*), as well as compound **5a** (*cone*) is poor extractant for alkali metal ions under the conditions investigated. The variation of the substituents with an amide essentially influences the efficiency but not the selectivity of linkage for macrocycles in the *1,3-alternate* conformation. Both macrocycles **5c** (*1,3-alternate*) and **6c** (*1,3-alternate*) are selective extractants for K^+, but the first one showed higher efficiency and the second one higher selectivity for a K^+/Na^+ mixture.

Thus, the variation of the cyclic fragments in the structure of thiacalix[4]arenes tetrasubstituted with amide-containing groups at the lower rim, affects not only the efficiency of alkali metal ion binding but also the selectivity of receptors. The influence of the electronic nature of the amide groups on the efficiency of the cation binding, as well as steric effects of the substituents, provides the necessary conformation for interaction with the guest molecules.

Table 3
Percent of extraction (%*E*) of alkali and silver metal ions by conformational isomers of the thiacalix[4]arene derivatives **5** and **6**[a]

	Li^+	Na^+	K^+	Cs^+	Ag^+
Absorption with CH_2Cl_2	1±1	2±1	1±1	1±1	4±1
cone (**5a**)	10±3	12±1	5±1	6±3	79±1
cone (**6a**)	78±2	78±2	60±2	51±2	99±1
partial cone (**5b**)	5±3	8±2	14±2	9±2	68±3
partial cone (**6b**)	18±1	38±1	55±1	19±1	100±1
1,3-alternate (**5c**)	16±1	40±1	77±2	40±3	98±1
1,3-alternate (**6c**)	18±1	74±1	97±2	79±2	100±1

'±' standard deviation for four experiments.
[a] Extraction condition: $[L]_{org,init}=2.5\times10^{-3}$ M, $[MPic]_{aq,\ init}=2.32\times10^{-4}$ M.[26]

2.3. Extraction constants log K_{ex} and complex stoichiometry

To quantify the ability of the *p-tert*-butyl thiacalix[4]arene derivatives **6** and **5** in three conformations to recognize metal ions, the extraction constants, and the stoichiometry of the cation–calixarene complexes formed in the organic phase have been determined using the picrate extraction method (Table 4).

It was shown that the complex stoichiometry depended on the receptor configuration that allowed one ligand molecule to bind two or more cations. It was established that complex stoichiometry of Li^+, Na^+, K^+ ions with **5a** (*cone*) and complex stoichiometry of K^+ with **6a** (*cone*) were practically 1:1 (Table 4). Thus, four ligating groups located on the same side of macrocycle plane can participate in the binding of these cations (Fig. 4). The stoichiometry of **5b** (*partial cone*), **6b** (*partial cone*), **5c** (*1,3-alternate*), **6c** (*1,3-alternate*) complexes is either 2:1 or 1:1. Small Li^+ ion forms 2:1 complexes in the organic phase with **5b** (*partial cone*) and **5c** (*1,3-alternate*) (Table 4). It means that in this case, both pairs of functional groups interact with the guest ion independent of each other, and structural changes caused by ion complexation on one side of *1,3-alternate* and *partial cone* do not cause significant hindrance for binding on the other side (Fig. 4).

Unusual stoichiometry of *p-tert*-butyl thiacalix[4]arenes tetrasubstituted at the lower rim by morpholide **5** and pyrrolidide **6** groups with some cations was observed. Rather high reliability of the linear fitting (R^2=0.995–0.999) can be considered as evidence in favor of the preferable formation of the single complex. The stoichiometry of the complexes depended on some factors, i.e., allosteric effect and self-assembly. Complex stoichiometry of Na^+ ion with **6a** (*cone*), K^+ ion with **5c** (*1,3-alternate*), and Na^+, K^+, and Cs^+ ions with **6c** (*1,3-alternate*) are practically equal to 1:2 (Table 4). Thus, two receptor molecules can participate in the binding of one cation. Such behavior could be rationalized for *1,3-alternate* in terms of a negative allosteric effect induced by the changes in the conformers' spatial structure. In order to bind the first cation, the molecular cleft formed by two ligating groups can expand to achieve the ideal inter-atomic distance necessary for complexation of large alkali cations. As a result, two other ligating groups on the opposite side of *1,3-alternate* move closer to each other, and thus the binding of the second cation becomes impossible.[18] The formation of 1:1 complexes of *p-tert*-butyl thiacalix[4]arenes **5c** (*1,3-alternate*) and **6c** (*1,3-alternate*) with Na^+ and Li^+, correspondingly, is probably due to the negative allosteric effect (Table 4). Complex stoichiometry of Na^+ and K^+ ions with **6b** (*partial cone*) and Cs^+ ions with **5c** (*1,3-alternate*) are equal to about 2:3 (Table 4). Thus, three receptor molecules can participate in the binding of two cations. The formation of the complexes with a 3:2 guest–host ratio was observed for **5b** (*partial cone*) with sodium and cesium cations.

As a rule, the necessary criterion for a spontaneous process at constant temperature and pressure is negative Gibbs free energy, as a combination of enthalpy, temperature, and entropy. This change in entropy of the majority complexation processes in solution is the determining factor.[27] It is very difficult, however, to predict the change in the entropy of complexation ΔS, because the solvent can influence this process. The decrease in particle number and conformational flexibility of receptor structures due to the complexation processes leads to a positive entropy of complexation and, hence, the system is ordered. However, a positive change in entropy increases the disorder of the system, due to the increase in particles number, and it may explain the desolvation of the interacting sites that lead to form new aggregates and therefore solvatation. The newly formed associative interaction, however, gives rise to

Table 4
Percent extraction (%*E*), extraction constants log K_{ex} and stoichiometry complexes of **6**, **5** forming in the organic phase[a]

	Li^+			Na^+			K^+			Cs^+			Ag^+		
	n	log K_{ex}	*E*%	*n*	log K_{ex}	*E*%	*n*	log K_{ex}	*E*%	*n*	log K_{ex}	*E*%	*n*	log K_{ex}	*E*%
cone (**5a**)	0.78±0.01	3.23±0.04	61±3	0.92±0.02	4.03±0.06	74±3	0.80±0.07	3.05±0.19	41±3	—	—	8±2	0.73±0.03	4.20±0.10	79±1
cone (**6a**)	1.91±0.13	8.43±0.52	98±1	1.79±0.10	8.03±0.41	98±1	1.15±0.03	5.43±0.10	82±3	0.62±0.01	2.27±0.04	37±1	1.06±0.12	6.08±0.49	99±1
partial cone (**5b**)	0.62±0.01	1.97±0.02	22±2	0.82±0.01	3.53±0.04	61±2	0.65±0.02	3.35± 0.05	82±3	0.73±0.01	2.45±0.02	17±2	1.56±0.06	8.37±0.23	68±3
partial cone (**6b**)	0.98±0.03	4.51±0.08	81±2	1.36±0.02	6.44±0.09	97±1	1.57±0.07	7.32±0.28	96±2	0.91±0.01	3.95±0.04	69±2	1.57±0.13	8.18±0.55	100±1
1,3-alternate (**5c**)	0.64±0.03	1.99±0.06	16±2	1.22±0.03	5.74±0.10	93±2	2.14±0.12	9.47±0.47	97±2	1.35±0.18	6.28±0.18	94±3	2.01±0.11	9.93±0.42	98±1
1,3-alternate (**6c**)	0.80±0.03	3.28±0.09	53±2	1.87±0.12	8.33±0.46	74±1	1.99±0.16	9.06±0.63	100±3	1.93±0.14	8.52±0.53	100±2	1.87±0.22	9.83±0.92	100±1

'±' standard deviation.
[a] Extraction condition: $[L]_{org,init}=10^{-4}$ to 2.5×10^{-3} M, $[MPic]_{aq,\ init}=2.32\times10^{-4}$ M.[26]

molecular vibrations, which in principle add a positive entropy again. The high values of extraction constant can testify to the ability of these systems to form nanoscale aggregates in the organic phase. Thus, these association processes accompany the increase of the entropy, and the resulting positive value in the change in the ΔG contribution. According to the equation of the chemical reaction isotherm, the more negative the value of Gibbs free energy, the more the equilibrium constant is shifted to formation of the reaction products.

For the investigated systems consisting of *p-tert*-butyl thiacalix[4]arenes molecules and silver cations, the high values of extraction constants may be explained by increase of entropy of these systems due to formation of nanoscale particles. We have offered a hypothesis that silver cations, which form nanoscale aggregates with 'host' molecules, are able to be simultaneously coordinated at the four bridging sulfur atoms of the *p-tert*-butyl thiacalix[4]arene molecule and the oxygen atoms of the amide carbonyl groups. Thus, the increase in the number of linkage centers leads to an increase in the disorder of the system. At the same time, this circuit cannot be realized for more 'rigid' alkali metal cations, which are, apparently, coordinated only at the tertiary amide fragments located at the lower rim of the receptor molecules. Thus the aggregation of the synthesized *p-tert*-butyl thiacalix[4]arenes with and without metal cations was investigated.

2.4. Self-assembly of aggregates consisting of *p-tert*-butyl thiacalix[4]arenes derivatives and metal cations in the organic phase

At the present time, the study of non-covalent self-assembly processes based on precisely designed ligands spontaneously connected to metal ions has received increasing attention. The interest in these products is stimulated by their size, since nanoscale materials show unique features often quite different from traditional materials. For example, nanoscaled silver particles have a most powerful bactericidal effect.[28–30] Variation of the form, size, and structure of nanoparticles affects their physical and chemical properties. This offers new opportunities for directional changes of the nanoparticle properties, taking advantage of already existing applications in the field of lithography, catalysis, biomedicine, electronics, and optical sensors.[28–30] Dynamic light scattering (DLS) is one of the methods used for the particles size determination.

The ability of the systems consisting of *p-tert*-butyl thiacalix[4]arenes **5**, **6** and metal nitrates to self-assemble has been investigated under the same conditions as picrate extraction. DLS was also used for determination of the hydrodynamic diameter and polydispersity index of host–guest systems in CH_2Cl_2 (Table 5). Figure 5 shows the intensity size distributions for the complex of the thiacalix[4]arene functionalized with pyrrolidide units in the *cone* conformation with silver cations.

One can see (Table 5) that all the investigated compounds **5** and **6** form nanoscale particles with silver cations due to the coordination of the bridging sulfur atom and the oxygen atoms of the carbonyl groups with this metal ion (c.n.=4) (Fig. 6).[31,32]

It was shown that the systems with *p-tert*-butyl thiacalix[4]arenes **5**, **6** in three conformations and silver cations with identical values of extraction constants and the same stoichiometry determined by the picrate extraction method, formed aggregates of the same size with identical hydrodynamic diameters (**5b**, **6b** (*partial cone*)—134, 131 nm, and **5c**, **6c** (*1,3-alternate*)—141 and 140 nm, respectively). It should be mentioned that the increase in the values of extraction constants leads to the increase in the hydrodynamic size of the particles.

Only the pyrrolidide derivative in the *cone* conformation has an abnormal value of particle size (153 nm); this could be related to its

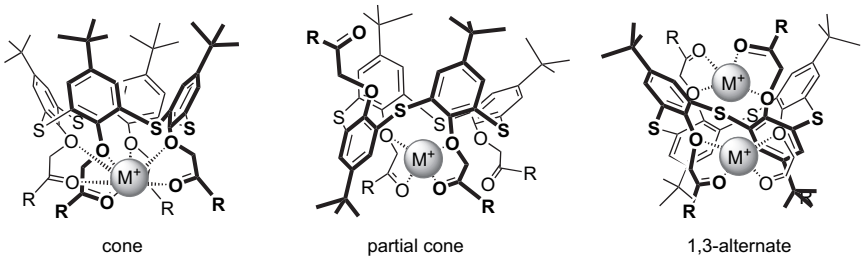


Figure 4. The possible structures of *p-tert*-butyl thiacalix[4]arene conformer complexes with alkali metal cations.

Table 5
Hydrodynamic diameter, (nm), polydispersity index

	Size/polydispersity index					
		Li^+	Na^+	K^+	Cs^+	Ag^+
cone (**5a**)	—	—	—	—	—	84±2/0.18±0.03
cone (**6a**)	195±71/ 0.71±0.29	143±3/ 0.19±0.14	—	—	—	153±3/0.08±0.02
partial cone (**5b**)	—	—	—	—	—	134±1/0.16±0.03
partial cone (**6b**)	—	—	—	—	—	131±19/0.17±0.04
1,3-alternate (**5c**)	—	—	—	—	—	140±2/0.19±0.03
1,3-alternate (**6c**)	—	—	—	—	—	141±7/0.23±0.06

'±' standard deviation of three experiments.
'—' the systems do not form any aggregates.

low value (0.08), while the polydispersity index of other systems was in between 0.16 and 0.23, i.e., the pyrrolidide derivative in the *cone* conformation forms the most stable nanoscale particles. It was established that the pyrrolidide derivative in the *cone* conformation is able to self-associate (d=195 nm) (Table 5), however, the high polydispersity index, 0.71, can be explained by the instability of the aggregates formed under experimental conditions (20 °C). The aggregation is promoted by dipole–dipole interaction of tertiary amide groups (Fig. 7).[33,34] The experiments with this system carried out at lower temperature (2 °C) gave particles with hydrodynamic diameter of 624 nm and polydispersity index of 0.29. It should be emphasized that the system consisting of the self-associated pyrrolidide substituted thiacalix[4]arene in the *cone* conformation can be stabilized at 20 °C by the introduction of small lithium cations, so that the size of the aggregates decreased (d=143 nm). As was shown, only this system had abnormally high values of extraction constant and stoichiometry ratio (cation–thiacalix[4]arene 1:2) determined by the picrate extraction method.

The hydrodynamic diameter of these particles was the same (143 nm) as that of conformation isomers—**5c**, **6c** (*1,3-alternate*) coupled with silver cations. Presumably, the lithium cation (c.n.=4) is coordinated at the carbonyl and phenolic oxygen atoms, whereas similar silver coordination assumes participation of bridging sulfur atoms of the macrocycle.

3. Conclusion

Thus, new *p-tert*-butyl thiacalix[4]arenes functionalized with morpholide and pyrrolidide groups at the lower rim in *cone*, *partial cone*, and *1,3-alternate* conformations were synthesized and their receptor properties for monocharged cations (Li^+, Na^+, K^+, Cs^+, and Ag^+) were studied using the picrate extraction method and dynamic light scattering (DLS). The study of the ability of similar receptor structures to form nanoscale aggregates with metal cations in organic phase has recently received increasing attention.

For the first time it was shown that thiacalix[4]arenes investigated are able to form nanoscale (80–160 nm) particles with silver cations in organic media. Meanwhile, this aggregation cannot be realized for more 'rigid' alkali metal cations, which are probably coordinated at the tertiary amide fragments located at the lower rim of the receptor molecules only. Thus, it was determined by DLS that the thiacalix[4]arenes investigated are not able to form aggregates with alkali metal cations. The pyrrolidide derivative in the *cone* conformation only forms nanoscale particles with a lithium cation. It was established that the pyrrolidide derivative in the *cone* conformation is able to self-associate. Lithium cations, being rather smaller in size in comparison with other alkali metals, probably stabilize this process contrary to other metal cations investigated.

In the case of alkali metal cations, only the system consisting of the pyrrolidide substituted thiacalix[4]arene in the *cone* conformation and lithium cations had abnormally high values for extraction constant, and its ability to aggregate with this substratum was determined. Similar results for all investigated *p-tert*-butyl thiacalix[4]arenes and silver cations were observed.

They offer new opportunities both in selection of new materials with extended antibacterial properties, 'smart' materials in nanolithography (formation of nano- and microscale pictures of given geometry and relief onto a semiconductor layer[1,2]), and nanochip technologies (multiple analyte detection). The variation of binding abilities and directional control of binding selectivity can provide new synthetic receptors which are more stable and more selective than natural biological receptors for synthetic and natural guest species. These supramolecular architectures can also find application in catalysis, quantum dots formation, nanotube, and more complicated nanostructure synthesis.[2]

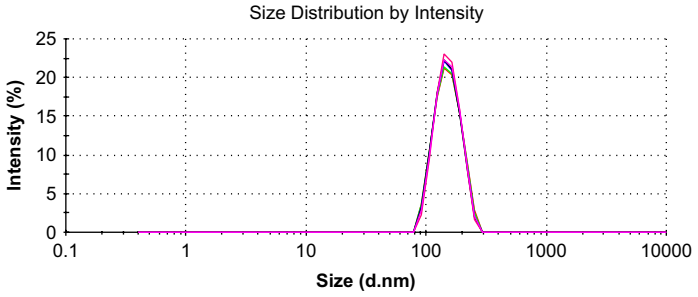


Figure 5. Intensity size distributions for the system consisting of molecular thiacalix[4]arenes functionalized with pyrrolidide units in the *cone* conformation and silver cations in CH_2Cl_2 (HPLC).

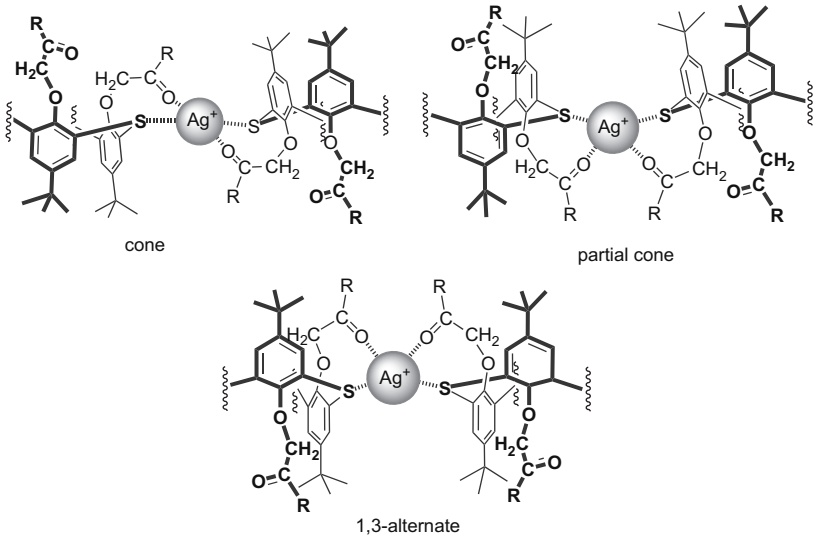


Figure 6. The possible coordination patterns of the 'soft' acid (silver cation) with conformational isomers of thiacalix[4]arenes.

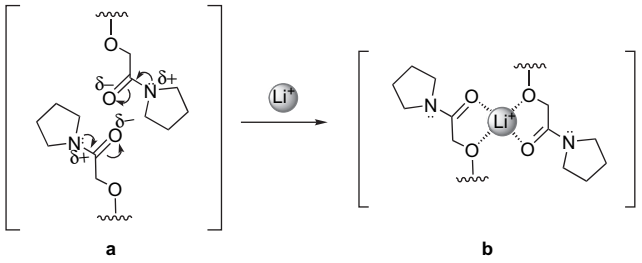


Figure 7. The possible scheme of coordination units: (a) the dipole–dipole interaction of tertiary amide groups; (b) the interactions of tertiary amide groups with lithium cation.

4. Experimental

4.1. General

Melting points were determined using Boetius Block apparatus. Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified by standard procedures. The ^{1}H and ^{13}C NMR spectra were recorded with 300 MHz Varian XL-300 spectrometer. IR spectra (KBr pellets) were recorded with Vector 22 (Bruker) IR spectrometer. ESI mass spectra were recorded with Bruker Esquire MS. Elemental analysis was performed with Perkin–Elmer 2400 Series II instruments.

4.2. General procedure of hydrolysis of tetraesters 3(a–c)

Esters **3**(**a**–**c**) (5 g, 4.70×10^{-3} mol) were put into a round-bottom flask and THF (872 mL) was added; solution of lithium hydroxide monohydrate (2.7 g, 7.00×10^{-2} mol) in water (280 mL) was added, mixed at 60 °C for *cone* **3a**—5 h, for *partial cone* **3b**—35 h, for *1,3-alternate* **3c**—40 h. Then the reaction mixture was evaporated, the sediment was filtered, and dried at lower pressure.

cone **4a**: 4.14 g (98%); *partial cone* **4b**: 4.14 g (98%); *1,3-alternate* **4c**: 4.14 g (98%).[20]

4.3. General procedure of the synthesis of compounds 5(a–c) and 6(a–c)

Acids **4**(**a**–**c**) (1 g, 1.05×10^{-3} mol) were put into a round-bottom flask and then $SOCl_2$ (10 mL, 0.084 mol) was added. The mixture was heated at reflux for 1.5 h, then the excess $SOCl_2$ removed. The residue was dried under reduced pressure for 2 h. A solution of amine (pyrrolidine or morpholine) (33.6×10^{-3} mol) and triethylamine (5 mL, 0.04 mol) in methylene chloride (50 mL) was added. The mixture was stirred at rt overnight. The reaction was quenched by addition of 2 M HCl (30 mL). Organic layer was separated, dried (mol. sieves, 3 Å) and evaporated in vacuo. The remainder was crystallized from ethyl alcohol/methylene chloride.

*4.3.1. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-morpholidocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene cone (**5a**)*

White powder, yield: 1.20 g (93%). Mp: 258 °C. ^{1}H NMR (300 MHz, 373 *K*, $CDCl_3$) δ 7.30 (s, 8H, ArH), 5.34 (s, 8H, OCH_2CO), 3.71–3.68 (m, 16H, $-CH_2OCH_2-$), 3.60–3.57 (m, 16H, $-N(CH_2CH_2)_2O$), 1.08 (s, 36H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 156.8, 146.4, 132.2, 127.4, 67.8, 66.6, 45.90, 41.9, 34.2, 31.9. IR (KBr) ν_{max} 1253, 1662, 2857, 2961. MS (ESI): calcd for $[M^{+}Na]^{+}$ m/z=1251.5, found m/z=1251.4. El. Anal. Calcd for $C_{64}H_{84}N_4O_{12}S_4$: C, 62.52; H, 6.89; N, 4.56; S, 10.43. Found: C, 62.42; H, 6.99; N, 4.56; S, 10.26.

*4.3.2. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-morpholidocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene partial cone (**5b**)*

White powder, yield: 1.06 g (82%). Mp: 149 °C. ^{1}H NMR (300 MHz, 373 K, $CDCl_3$) δ 7.76 (s, 2H, ArH), 7.60 (d, J=2.5 Hz, 2H, ArH), 7.59 (s, 2H, ArH), 7.06 (d, J=2.5 Hz, 2H, ArH), 5.24 (s, 2H, OCH_2CO), 4.80 (d, J=12.5 Hz, 2H, OCH_2CO), 4.78 (s, 2H, OCH_2CO), 4.55(d, J=12.5 Hz, 2H, OCH_2CO), 3.82–3.22 (m, 32H, $-N(CH_2CH_2)_2O$), 1.38 (s, 9H, $(CH_3)_3C$), 1.31 (s, 9H, $(CH_3)_3C$), 1.06 (s, 18H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 156.8, 146.3, 132.1, 127.4, 67.7, 66.5, 45.9, 41.9, 34.2, 31.1. IR (KBr) ν_{max} 1260, 1654, 2859, 2904, 2960. MS (ESI): calcd for $[M^{+}Na]^{+}$ m/z=1251.5, found m/z=1251.3. El. Anal. Calcd for $C_{64}H_{84}N_4O_{12}S_4$: C, 62.52; H, 6.89; N, 4.56; S, 10.43. Found: C, 62.11; H, 6.95; N, 4.36; S, 10.58.

*4.3.3. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-morpholidocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene 1,3-alternate (**5c**)*

White powder, yield: 0.98 g (76%). Mp: 255 °C. ^{1}H NMR (300 MHz, 373 K, $CDCl_3$) δ 7.51 (s, 8H, ArH), 4.68 (s, 8H, OCH_2CO), 3.62 (m, 16H, $-CH_2OCH_2-$), 3.35–3.22 (m, 16H, $-N(CH_2CH_2)_2O$), 1.26 (s, 36H; $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 156.8, 146.3, 132.1, 127.4, 67.7, 66.5, 45.9, 41.9, 34.2, 31.1. IR (KBr) ν_{max} 1265, 1651,

2860, 2905, 2959. MS (ESI): calcd for $[M^+Na]^+$ m/z=1251.5, found m/z=1251.3. El. Anal. Calcd for $C_{64}H_{84}N_4O_{12}S_4$: C, 62.52; H, 6.89; N, 4.56; S, 10.43. Found: C, 62.34; H, 6.98; N, 4.49; S, 10.29.

*4.3.4. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-pyrrolididocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene cone (**6a**)*

White powder, yield: 1.03 g (84%). Mp: 248 °C. ^{1}H NMR (300 MHz, 373 K, $CDCl_3$) δ 7.27 (s, 8H, ArH), 5.21 (s, 8H, OCH_2CO), 3.62 (t, J=6.8 Hz, 8H, –$N(CH_2CH_2)_2$), 3.44 (t, J=7.0 Hz, 8H, –$N(CH_2CH_2)_2$), 2.00–1.79 (m, 16H, –$N(CH_2CH_2)_2$), 1.07 (s, 36H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.8, 157.9, 145.3, 133.9, 128.7, 72.0, 45.4, 33.7, 30.9, 26.0, 23.8. IR (KBr) ν_{max} 1268, 1653, 2871, 2963. MS (ESI): calcd for $[M^+Na]^+$ m/z=1187.5, found m/z=1187.4. El. Anal. Calcd for $C_{64}H_{84}N_4O_8S_4$: C, 65.82; H, 7.01; N, 4.87; S, 11.16. Found: C, 65.49; H, 7.38; N, 4.65; S, 11.03.

*4.3.5. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-pyrrolididocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene partial cone (**6b**)*

White powder, yield: 1.16 g (95%). Mp: 255 °C. ^{1}H NMR (300 MHz, 373 K, $CDCl_3$) δ 7.85 (s, 2H, ArH), 7.62 (d, J=2.4 Hz, 2H, ArH), 7.55 (s, 2H, ArH), 7.02 (d, J=2.4 Hz, 2H, ArH), 4.95 (s, 2H, OCH_2CO), 4.70 (s, 2H, OCH_2CO), 4.71 (d, J=14.5 Hz, 2H, OCH_2CO), 4.65 (d, J=14.5 Hz, 2H, OCH_2CO), 3.57–3.42 (m, 12H, –$N(CH_2CH_2)_2$), 3.31–3.24 (m, 4H, –$N(CH_2CH_2)_2$), 1.94–1.73 (m, 16H, –$N(CH_2CH_2)_2$), 1.39 (s, 9H, $(CH_3)_3C$), 1.29 (s, 9H, $(CH_3)_3C$), 1.05 (s, 18H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.5, 165.5, 165.7, 159.1, 157.8, 157.7, 146.1, 146.0, 144.1, 134.8, 134.6, 134.2, 133.9, 128.3, 128.1, 126.7, 72.9, 70.6, 67.5, 46.2, 45.8, 45.6, 45.4, 45.2, 34.2, 33.9, 33.9, 31.2, 31.1, 31.0, 26.1, 24.0, 23.9, 23.8. IR (KBr) ν_{max} 1260, 1653, 2871, 2961. MS (ESI): calcd for $[M^+Na]^+$ m/z=1187.5, found m/z=1187.3. El. Anal. Calcd for $C_{64}H_{84}N_4O_8S_4$: C, 65.82; H, 7.01; N, 4.87; S, 11.16. Found: C, 65.80; H, 7.26; N, 4.76; S, 11.39.

*4.3.6. 5,11,17,23-Tetra-tert-butyl-25,26,27,28-tetrakis-[(N-pyrrolididocarbonyl)-methoxy]-2,8,14,20-tetrathiacalix[4]arene 1,3-alternate (**6c**)*

White powder, yield: 1.10 g (90%). Mp: 272 °C. ^{1}H NMR (300 MHz, 373 K, $CDCl_3$) δ 7.53 (s, 8H, ArH), 4.56 (s, 8H, OCH_2CO), 3.47 (t, J=6.0 Hz, 8H, –$N(CH_2CH_2)_2$), 3.03 (t, J=6.0 Hz, 8H, –$N(CH_2CH_2)_2$), 1.82–1.68 (m, 16H, –$N(CH_2CH_2)_2$), 1.24 (s, 36H, $(CH_3)_3C$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9, 157.6, 146.0, 132.4, 127.9, 69.9, 45.8, 34.1, 31.1, 26.2, 23.9. IR (KBr) ν_{max} 1260, 1653, 2872, 2953. MS (ESI): calcd for $[M^+Na]^+$ m/z=1187.5, found m/z=1187.3. El. Anal. Calcd for $C_{64}H_{84}N_4O_8S_4$: C, 65.82; H, 7.01; N, 4.87; S, 11.16. Found: C, 65.64; H, 7.36; N, 4.65; S, 11.29.

4.4. Determination of extraction parameters

4.4.1. The degree of extraction

The alkali metal picrates were prepared by stepwise addition of a 2.32×10^{-4} M aqueous picric acid solution to a 0.1 M aqueous solution of metal hydroxide (LiOH, NaOH, KOH, CsOH) until neutralization, which was checked by pH control with a glass electrode. Silver picrate were prepared by stepwise addition of a 1.6×10^{-2} M of $AgNO_3$ to 2.32×10^{-4} M aqueous picric acid solution; in this case, the solutions were weakly acidic (pH 4). Distilled water was used for preparation of all aqueous solutions. Aqueous picrate solution (3 mL, 2.32×10^{-4} M) and 3 mL of 2.32×10^{-4} M solution of thiacalix[4]arene derivatives in CH_2Cl_2 (chemical pure) were shaken for 30 min at room temperature (22 °C). The absorbance A_i of the aqueous phase after extraction, and that of the aqueous phase before extraction, A_0, were measured at the wavelength of maximum absorption of the picrate ion, λ_{max}=355 nm. The percentage of the cation extracted was calculated as the ratio $100\times(A_0-A_i)/A_0$. Five independent experiments were carried out for each combination of ligand and metal picrate.

4.4.2. Extraction constants log K_{ex} and stoichiometry of the complexes

Extraction experiments were performed at ligand concentration (10^{-4} to 2.5×10^{-4}). The alkali metal picrates were prepared from 2.32×10^{-4} M aqueous solutions of picric acid and a 0.1 M aqueous solution of metal hydroxides. The log K_{ex} and n values were determined from the plot of $\log(a/1-a)$ versus $\log[L]_{org}$. as described elsewhere.[17] Three independent experiments were carried out for each system.

4.5. Dynamic light scattering (DLS)

The particle sizes were determined by Zetasizer Nano ZS instrument at 2 °C and 20 °C. The instrument contains a 4 mW He–Ne laser operating at a wavelength of 633 nm and incorporates non-invasive backscatter optics (NIBS). The measurements were performed at a detection angle of 173° and the measurement position within the quartz cuvette was automatically determined by the software. The solutions of the systems investigated were prepared by addition of metal nitrate to 10 mL of 10^{-4} M solution of thiacalixarene derivatives in CH_2Cl_2 (HPLC). The mixture was mechanically shaked for 2 h and then magnetically stirred in thermostated water bath at 20 °C for 1 h. The final concentration of metal nitrates in 10 mL CH_2Cl_2 (HPLC) was 2.32×10^{-4} M. Three independent experiments were carried out for each combination of a ligand and metal nitrate.

Acknowledgements

The financial support from RFBR (06-03-32160), CRDF (RUC1-2825-KA-06), joint program of CRDF and Ministry of Science and Education of Russian Federation 'Fundamental Researches and Higher Education' (REC-007) is gratefully acknowledged.

References and notes

1. Bhushan, B. *Springer Handbook of Nanotechnology*; Springer: Heidelberg, Germany, 2004.
2. Poole, C. P., Jr.; Owens, F. J. *Introduction to Nanotechnology*; John Wiley and Sons: Hoboken, NJ, 2003, Chapter 10.
3. Leninger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853–908.
4. Lawrence, D. S.; Jiang, T.; Levett, M. *Chem. Rev.* **1995**, *95*, 2229–2260.
5. MacGillivray, L. R.; Atwood, J. L. *Angew. Chem., Int. Ed* **1999**, *38*, 1018–1033.
6. Fujita, M.; Tominaga, M.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371–380.
7. Atwood, J. L.; Davies, J. E. R.; McNicol, D. D.; Vogtle, F.; Gokel, G. W.; Lehn, J.-M. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996.
8. Gutsche, C. D. *Calixarenes Revisited. Monographs in Supramolecular Chemistry*; RSC: London, 1998.
9. Iki, N.; Miyano, S. *J. Inclusion Phenom. Macrocyclic Chem.* **2001**, *41*, 99–105.
10. Lhotak, P. *Eur. J. Org. Chem.* **2004**, 1675–1692.
11. Morohashi, N.; Narumi, F.; Iki, N.; Hattori, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291–5316.
12. Martin, O. M.; Mecozzi, S. *Supramol. Chem.* **2005**, *17*, 9–15.
13. Orr, G. W.; Barbour, L. J.; Atwood, J. L. *Science* **1999**, *285*, 1049–1052.
14. Morohashi, N.; Katagiri, H.; Iki, N.; Yamane, Y.; Kabuto, C.; Hattori, T.; Miyano, S. *J. Org. Chem.* **2003**, *68*, 2324–2333.
15. Iki, N.; Narumi, F.; Fujimoto, T.; Morohashi, N.; Miyano, S. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2745–2750.
16. Gafiullina, L. I.; Vershinina, I. S.; Stoikov, I. I.; Antipin, I. S.; Konovalov, A. I. *J. Struct. Chem.* **2005**, *46*, 25–29.
17. Stoikov, I. I.; Omran, O. A.; Solovieva, S. E.; Latypov, S. K.; Enikeev, K. M.; Gubaidullin, A. T.; Antipin, I. S.; Konovalov, A. I. *Tetrahedron* **2003**, *59*, 1469–1476.
18. Araki, T.; Tsukube, H. *Liquid Membranes: Chemical Application*; CRC: Boca Raton, FL, 1990; p 213.
19. Zlatuskova, P.; Stibor, I.; Tkadlecova, M.; Lhotak, P. *Tetrahedron Lett.* **2004**, *60*, 11383–11390.
20. Iki, N.; Morohashi, N.; Narumi, F.; Fujimoto, T.; Suzuki, T.; Miyano, S. *Tetrahedron Lett.* **1999**, *40*, 7337–7341.
21. Stastny, V.; Stibor, I.; Dvorakova, H.; Lhotak, P. *Tetrahedron* **2004**, *60*, 3383–3391.
22. Solovieva, S. E.; Grüner, M.; Omran, A. O.; Gubaidullin, A. T.; Litvinov, I. A.; Habicher, W. D.; Antipin, I. S.; Konovalov, A. I. *Russ. Chem. Bull., Int. Ed.* **2005**, *9*, 2104–2112.

23. Brucheman, R. V.; Verhoek, F. H. *J. Am. Chem. Soc.* **1948**, *70*, 1401–1404.
24. Evans, H. *Trans. Faraday Soc.* **1951**, *47*, 25–49.
25. Searies, T.; Blok, Q. *J. Am. Chem. Soc.* **1956**, *78*, 4917–4920.
26. Lamartine, R.; Bavoux, C.; Vocanson, F.; Martin, A.; Senlisb, G.; Perrinb, M. *Tetrahedron Lett.* **2001**, *42*, 1021–1024.
27. Stibor, I. *Anion Sensing*; Springer: Berlin, Heidelberg, 2005.
28. Caruso, F. *Adv. Mater.* **2001**, *13*, 11–22.
29. Kaltenpoth, G.; Himmelhaus, M.; Slansky, L.; Caruso, F.; Grunze, M. *Adv. Mater.* **2003**, *15*, 1113–1118.
30. Lauhon, L. J.; Gudiksen, M. S.; Wang, D.; Lieber, C. M. *Nature* **2002**, *420*, 57–61.
31. Singh, N.; Kumar, M.; Hundal, G. *Tetrahedron* **2004**, *60*, 5393–5405.
32. Sykora, J.; Himl, M.; Stibor, I.; Cisarova, I.; Lhotak, P. *Tetrahedron* **2007**, *63*, 2244–2248.
33. Venkatesu, P.; Grandra Sekhar, G.; Prabhakara Rao, M. V.; Tadeusz, H. *Thermochim. Acta* **2006**, *443*, 62–71.
34. Garcia Martinez, A.; Teso Vilar, E.; Garcia Fraile, A.; Martinez-Ruiz, P. *J. Chem. Phys.* **2006**, *124*, 234305–234309.