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**PAPER**

# *p-tert*-Butyl thiacalix[4]arenes functionalized at the lower rim by amide, hydroxyl and ester groups as anion receptors†

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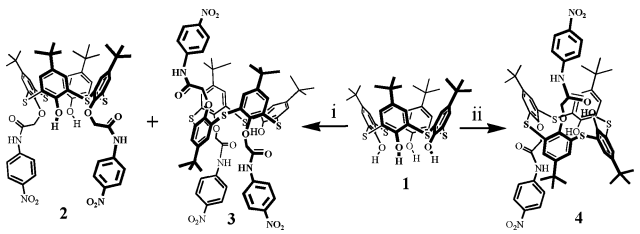
New *p-tert*-butyl thiacalix[4]arenes differently substituted at the lower rim with amide, hydroxyl and ester groups were synthesized. Binding properties of the compounds toward some tetrabutylammonium salts *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $I^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $NO_3^-$) were studied by UV spectroscopy. It was found that the stoichiometry of the complexes, generally, is 1 : 1, and the association constants are in the range of $10^3$–$10^5$ $M^{-1}$. The *p-tert*-butyl thiacalix[4]arenes containing secondary amide groups trisubstituted at the lower rim bind the studied anions most effectively. Selective receptors for fluoride and dihydrogen phosphate salts of tetrabutylammonium were found.

## Introduction

The potential uses of products of supramolecular chemistry and the ability of these products to exhibit properties typical of highly organized biomolecules, *e.g.* molecular recognition, catalysis, active and selective transport, has promoted research in the chemistry of synthetic receptors.[1] Calixarenes[2–7] and thiacalixarenes[8–10] are widely used as building blocks in the design of host molecules[11,12] because of their unique three-dimensional structure and the simplicity of functionalization of the macrocyclic platform.[13] The design and synthesis of systems capable of recognizing anions, continues to be one of the challenging problems in supramolecular chemistry.[14–16] It is well known that proton donor groups, such as amide, hydroxyl or thioureido[11] groups are used for anion binding. The variety in conformations of thiacalix[4]arene isomers (*cone*, *partial cone*, *1,2-alternate*, *1,3-alternate*) and the possibility of variation in the number and nature of substituents allow reaching optimal spatial orientation of binding sites adjusted for specific types of substrates.

Regioselective functionalization of the lower rim of the thia-analog of calixarene is significantly complicated because of the difficulties in selection of the reaction conditions (ratio of reagents, temperature and duration of the synthesis).[10,17] Therefore, synthesis of thiacalix[4]arenes with different substituents at the lower rim is commonly more difficult than that of the other similar macrocycles substituted with identical fragments.[10,17]

Previously, successful selective 1,3-dialkylation of the lower rim of *p-tert*-butyl thiacalix[4]arene with *N*-(*p*-nitrophenyl)-α-bromoacetamide (NPNBA)[18] was performed in the framework of the elaboration of new approaches to the synthesis of synthetic receptors with different substituents. In this respect, it was interesting to investigate the conditions for the further functionalization of the macrocycle **2** (see Scheme 1 below) by ester and amide fragments. Also, the complexation properties of 1,2-di-, 1,3-di-, tri- and tetrasubstituted *p-tert*-butyl thiacalix[4]arenes bearing *N*-(*p*-nitrophenyl)acetamide fragments toward anions were compared.




**Scheme 1** (i) NPNBA/$Na_2CO_3$, $CH_3CN$, reflux;[18] (ii) NPNBA/$Cs_2CO_3$, $CH_3CN$, reflux.[18]

## Results and discussion

### Synthesis of the *p-tert*-butyl thiacalix[4]arene derivatives containing *N*-(*p*-nitrophenyl)-acetamide and ester fragments at the lower rim

Previously it was shown, that NPNBA can be used as a regioselective alkylation reagent for *p-tert*-butyl thiacalix[4]arene. Depending on the nature of alkali metal carbonate and solvent, thiacalix[4]arenes partially substituted at the lower rim, *i.e.* 1,2-di-, 1,3-di- and trisubstituted *p-tert*-butyl thiacalix[4]arenes in the *partial cone* conformation, can be obtained (Scheme 1).[18]

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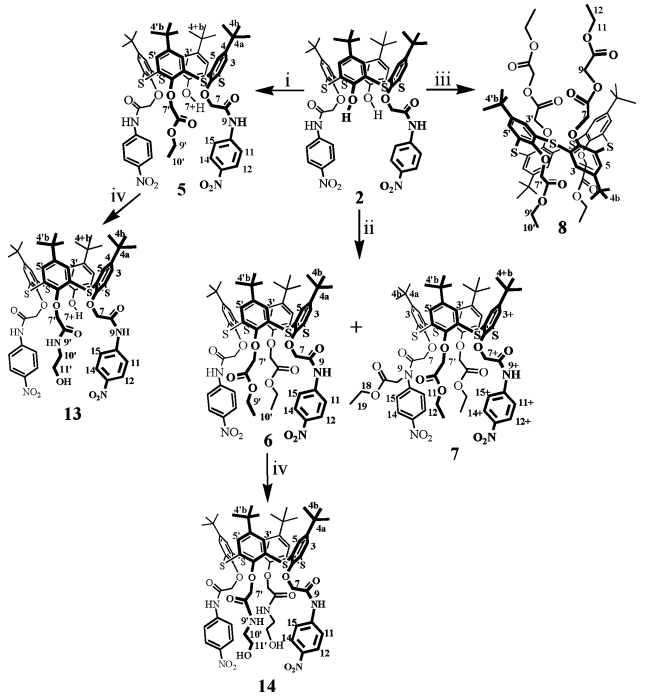
To obtain thiacalix[4]arenes differently substituted at the lower rim, the influence of the conditions of macrocycle **2** alkylation (temperature, time, solvent, a ratio of reagents, the nature of the base) on its stereo- and regiospecificity was studied. Interaction of *p-tert*-butyl thiacalix[4]arene **2** with ethyl bromoacetate in the presence of alkali metal carbonates (sodium, potassium, caesium) in acetone was investigated (Scheme 2). The base and solvent were specified in accordance with their efficiency in alkylation of *p-tert*-butyl thiacalix[4]arene at the lower rim.[19]



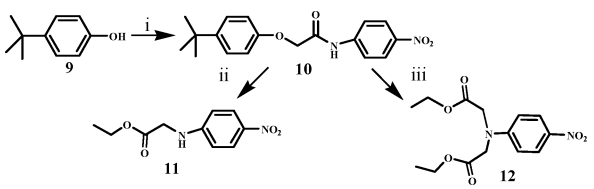
**Scheme 2** (i) $BrCH_2COOEt/Na_2CO_3$, acetone, reflux; (ii) $BrCH_2COOEt/K_2CO_3$, acetone, reflux; (iii) $BrCH_2COOEt/Cs_2CO_3$, acetone, reflux; (iv) $NH_2CH_2CH_2OH$, THF, reflux.

It was found that tri- and tetrasubstituted *p-tert*-butyl thiacalix[4]arenes **5–8** are formed depending on the ratio of reagents (Table 1). In the case of sodium carbonate, a trisubstituted lower rim product *p-tert*-butyl thiacalix[4]arene **5** in the *cone* conformation was isolated as a major product (58% yield). However, a tetrasubstituted lower rim product *p-tert*-butyl thiacalix[4]arene **6** in the *cone* configuration was obtained in the presence of potassium carbonate in 40% yield. As predicted, an increase in the ratio of alkylating reagent and use of potassium carbonate resulted in *N*-alkylation of the amide fragment and formation of a tetrasubstituted lower rim product *p-tert*-butyl thiacalix[4]arene **7** (14% yield). However, in the case of caesium carbonate, compound **8** without the amide group was obtained in 50% yield. It is worth noting that the macrocycles **5–7** formed in the presence of potassium and sodium carbonates are in the *cone* conformation.

To establish the mechanism of the formation of compounds **7** and **8**, model alkylation reactions of 2-(4-*tert*-butylphenoxy)-*N*-(4′-nitrophen-1′-yl)acetamide with ethyl bromoacetate were carried out (Scheme 3). At first, 2-(4-*tert*-butylphenoxy)-*N*-(4′-nitrophen-1′-yl)acetamide **10** was synthesized in acetone by the interaction of *p-tert*-butylphenol **9** with *N*-(*p*-nitrophenyl)-α-bromoacetamide in 73% yield (Scheme 3).

**Table 1** Product yields of alkylation of compound **2** by ethyl bromoacetate corrected by the amount of initial thiacalix[4]arene **2** isolated from the reaction media, (R = -$CH_2C(O)OEt$)

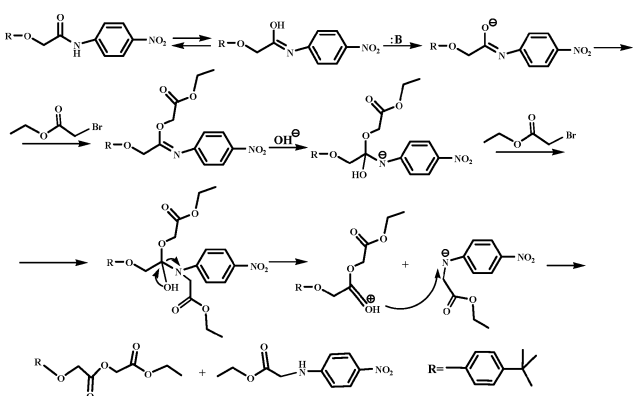
| Base | **2** : RBr : $M_2CO_3$ | Time, h | Yield (%) | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|
| $Na_2CO_3$ | 1 : 4 : 3 | 50 | 58 | 58 | — | — | — |
| $K_2CO_3$ | 1 : 4 : 3 | 60 | 50 | 10 | 40 | — | — |
| $Cs_2CO_3$ | 1 : 4 : 3 | 20 | 6 | — | 3 | 3 | — |
| $Na_2CO_3$ | 1 : 8 : 8 | 60 | 74 | 39 | 35 | — | — |
| $K_2CO_3$ | 1 : 8 : 8 | 60 | 30 | 5 | 25 | — | — |
| $Cs_2CO_3$ | 1 : 8 : 8 | 20 | 50 | — | — | — | 50 |
| $K_2CO_3$ | 1 : 40 : 3 | 60 | 33 | 2 | 17 | 14 | — |



**Scheme 3** (i) NPNBA/$Na_2CO_3$, acetone, reflux; (ii) $BrCH_2COOEt/K_2CO_3$, acetone, reflux; (iii) $BrCH_2COOEt/Cs_2CO_3$, acetone, reflux.

Alkylation of 2-(4-*tert*-butylphenoxy)-*N*-(4′-nitrophen-1′-yl)acetamide **10** by ethyl bromoacetate was performed in similar conditions to the synthesis of thiacalix[4]arenes **7** and **8** in the presence of alkali metal carbonates (sodium, potassium, caesium) in acetone. In the case of sodium carbonate, the reaction did not run and the initial compound **10** was quantitatively isolated. But, compounds **11** (59%) and **12** (32%) were obtained with potassium and caesium carbonates, respectively (Scheme 3).

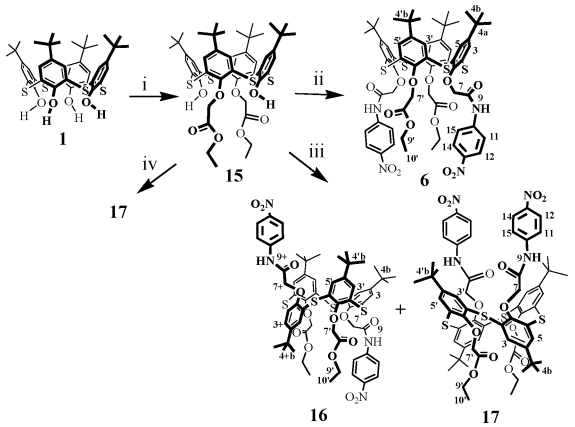
A simple possible mechanism for the formation of compound **8** of hydrolysis of the amide fragment and formation of a diacid, was tested in the alkylation of diacid by ethyl bromoacetate. This reaction did not lead to the formation of the expected compound **8**. Therefore Scheme 4 was suggested based on the results obtained from Schemes 2 and 3. The first stage involves the formation of enol from compound **10** which is followed by deprotonation of the OH group promoted by the base with subsequent nucleophilic substitution with ethyl bromoacetate. The use of caesium carbonate as a base, leads to subsequent deprotonation of compound **11** followed by nucleophilic substitution of ethyl bromoacetate with the formation of compound **12**.



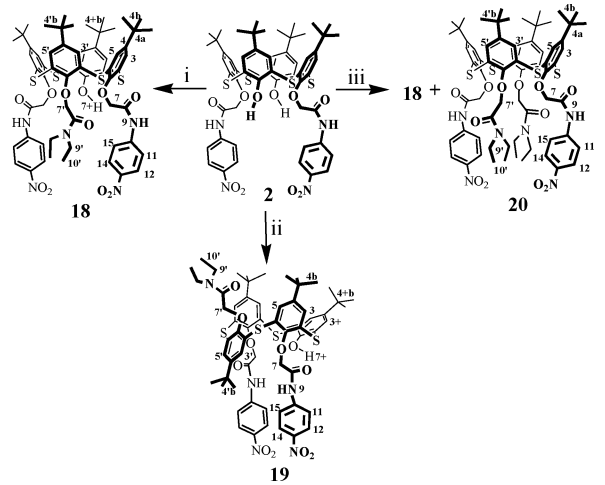
**Scheme 4** Supposed scheme of formation of compound **11**.

Then the chemical properties of the ester groups in thiacalix[4]arenes **5** and **6** were studied using, as an example, their interaction with 2-aminoethanol in THF (Scheme 2). Trisubstituted *p-tert*-butyl thiacalix[4]arene derivative **13** was obtained in 98% yield. The yield of tetrasubstituted analog **14** is significantly lower (48%) probably due to steric hindrance at the reaction centre and possible formation of minor products.

For the synthesis of stereoisomers of thiacalix[4]arene **6** (*cone*, *partial cone*, *1,3-alternate*), alkylation of the di-ether based on *p-tert*-butyl thiacalix[4]arene **15**[20] by NPNBA in the presence of different alkali metal carbonates in acetone was studied. As predicted, in the presence of alkali metal carbonates $M_2CO_3$ (M = Na, K, Cs) the template effect of cations is observed. In the case of sodium carbonate, *cone* stereoisomer **6** was isolated in 60% yield; in the case of potassium carbonate *partial cone* stereoisomer **16** and *1,3-alternate* stereoisomer **17** were isolated in 30% and 49% yields, respectively; and in the case of caesium carbonate *1,3-alternate* stereoisomer **17** was isolated in 50% yield (Scheme 5).



**Scheme 5** (i) $BrCH_2C(O)OEt/Na_2CO_3$, acetone, reflux;[20] (ii) $NPNBA/Na_2CO_3$, acetone, reflux; (iii) $NPNBA/K_2CO_3$, acetone, reflux; (iv) $NPNBA/Cs_2CO_3$, acetone, reflux.



**Scheme 6** (i) $BrCH_2C(O)NEt_2/K_2CO_3$, acetone, reflux; (ii) $BrCH_2C(O)NEt_2/Cs_2CO_3$, acetone, reflux; (iii) $BrCH_2C(O)NEt_2/Na_2CO_3$, acetone, reflux.

**Table 2** Product yields of alkylation of compound **2** by *N*,*N*-diethylbromoacetamide, (R = $-CH_2C(O)NEt_2$)

| Base | **2** : RBr : $M_2CO_3$ | Time, h | Yield (%) | **18** | **19** | **20** |
|---|---|---|---|---|---|---|
| $Na_2CO_3$ | 1 : 4 : 3 | 30 | 93 | 78 | — | 15 |
| $Na_2CO_3$ | 1 : 8 : 8 | 12 | 62 | 62 | — | 11 |
| $K_2CO_3$ | 1 : 4 : 3 | 20 | 81 | 81 | — | — |
| $K_2CO_3$ | 1 : 8 : 8 | 10 | 45 | 45 | — | — |
| $Cs_2CO_3$ | 1 : 4 : 3 | 10 | 40 | — | 40 | — |
| $Cs_2CO_3$ | 1 : 8 : 8 | 10 | 40 | 40 | — | — |

For the purpose of variation in the proton acceptor ability of the carbonyl group in thiacalix[4]arenes, *i.e.* ester groups in compounds **5**, **6**, **16**, **17**, tri- and tetrasubstituted derivatives **18–20** containing *N*,*N*-diethylacetamide group have been synthesized (Scheme 6). Interaction of 1,3-disubstituted *p-tert*-butyl thiacalix[4]arene **2** with *N*,*N*-diethylbromoacetamide with various alkali metal carbonates in acetone has been studied (Table 2).

It appeared that an increase in the ratio of the alkylation reagent doesn't lead to formation of tetrasubstituted products. As a rule, trisubstituted thiacalix[4]arene **18** in the *cone* conformation is formed. However, at the ratio of reagents 1 : 4 : 3 = **2** : RBr : $M_2CO_3$ and using caesium carbonate as the base, trisubstituted thiacalix[4]arene **19** in the *partial cone* conformation is formed. Tetrasubstituted product **20** is formed when the synthesis time was increased to 30 h and sodium carbonate was used as a base.

The structure and the composition of new thiacalix[4]arene derivatives **5–8**, **13**, **14** and **16–20** were confirmed by $^1H$, $^{13}C$, 2D NOESY NMR and IR spectroscopies, mass spectrometry (EI, ESI, MALDI-TOF) and elemental analysis. Conformations of synthesized macrocycles were established by 2D NOESY NMR spectroscopy.

The occurrence of two singlets of *tert*-butyl protons, two singlets of oxymethylene protons, two singlets of aromatic protons in the $^1H$ NMR spectra of thiacalix[4]arenes differently substituted at the lower rim (**6**, **14**, **17**, **20**) indicates their symmetric structure. However, in the $^1H$ NMR spectra of trisubstituted thiacalix[4]arenes **5**, **13**, **18**, **19**, signals of oxymethylene protons are observed as one singlet and as an AB system due to diastereotopy of -O–$CH_2$- protons of the *N*-*p*-nitrophenylamide substituent. Also, the signal of hydroxyl proton at 7.5–9.5 ppm in the $^1H$ NMR spectra of compounds **5**, **18**, **19** testifies to the incomplete alkylation of the parent thiacalix[4]arene.

The IR spectra of the obtained compounds **5**, **6**, **7**, **8**, **16**, **17** show an ester band ($\nu_{max}$ 1750–1790 $cm^{-1}$), which is absent in the IR spectrum of the parent thiacalix[4]arene **2**. In the IR spectra of trisubstituted thiacalix[4]arenes **5**, **18**, **19**, the absorption band of valence vibrations of the hydroxyl group ($\nu_{max}$ 3456, 3274, 3301 $cm^{-1}$, respectively) is observed which is absent in the IR spectra of tetrasubstituted thiacalix[4]arenes **6** and **20**. Amide, nitro and -C(O)–N- group bands are absent in the IR spectrum of the tetrasubstituted lower rim product thiacalix[4]arene **8**. Also in the IR spectra of stereoisomers of tetrasubstituted thiacalix[4]arenes *cone*, *partial cone*, *1,3-alternate* **6**, **16**, **17**, respectively, the absorption band of valence vibrations of the hydroxyl group is absent, which testifies to the complete substitution of initial di-ether **15**.

**Anion complexation study of the synthesized thiacalix[4]arenes by UV-spectroscopy**

For the design of anionic substrate receptors,[11] positively charged groups, *e.g.* $HN^+$, able to form hydrogen bonds $N^+H \ldots X^-$ and electrostatically interact with anions[21] and also neutral polar fragments, such as amide,[22] urea,[23,24] thiaurea,[25] central ions of metals in metallocenes,[26] are commonly used. Thiacalix[4]arenes substituted on both the upper and lower rims[10,11,17,27–29] and functionalized by corresponding groups also show good potential as synthetic anion receptors.[10]

There are some examples of the synthesis of thiacalix[4]arenes containing secondary amide fragments which can form complexes with anions.[11,27–29] To study the influence of structural factors (the conformation of the macrocycle, the number and the nature of the substituents) on the complexation properties of the lower rim substituted *p-tert*-butyl thiacalix[4]arenes, the receptor properties of the compounds **2–6**, **10**, **13**, **14**, **16–20** toward the tetrabutylammonium salts *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $I^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $NO_3^-$) were investigated by UV spectroscopy. In these compounds, both proton donating secondary amide (*p*-nitrophenylacetamide and monoethanolamide fragments) and hydroxyl (alcoholic and phenolic) groups can participate in anion binding.

The influence of the complexation ability of compounds **2–6**, **10**, **13**, **14**, **16–20** with anions on absorption spectra have been studied in the presence of a 200-fold excess of tetrabutylammonium salts in chloroform. The most significant changes in absorption spectra obtained with *p-tert*-butyl thiacalix[4]arenes in the presence of tetrabutylammonium salts, were observed for the interaction of the studied macrocycles with acetate, dihydrogen phosphate and fluoride tetrabutylammonium, and in the case of macrocycle **19** even when chloride, bromide, nitrate tetrabutylammonium were added. In these spectra, bathochromic shift of the absorption band in the field of 300–340 nm took place. In the case of *p-tert*-butyl thiacalix[4]arenes **16**, **17** and **20** in the presence of studied tetrabutylammonium salts changes in absorption spectra were not observed which testifies to the absence of interactions between these compounds and tetrabutylammonium salts.

Compounds **16** and **17** are in *partial cone* and *1,3-alternate* configuration, respectively, and apparently, the bulky *tert*-butyl groups hinder the complexation with anions.[30,31] It results in sterical hindrance and complexation with anions in the case of thiacalix[4]arenes **16** and **17** is not observed.

The macrocycle **20** contains tertiary amide groups. It is known that the carbonyl group in tertiary amide groups is a stronger electron donor than the carbonyl group of an ester fragment. For quantitative estimation of the donor ability of the investigated ester and *N*,*N*-diethylacetamide groups, the donor number values (DN)[32] of ethyl acetate and *N*,*N*-diethylacetamide were used as model compounds. The DN values of ethyl acetate and *N*,*N*-diethylacetamide are equal to 17.1 and 32.2, respectively. These data indicate that the *N*,*N*-diethylacetamide group interacts more strongly than the ethoxycarbonyl group with Lewis acids. Therefore the carbonyl group of the *N*,*N*-diethylacetamide fragment in macrocycle **20** interacts more strongly with the amide proton of *N*-(*p*-nitrophenyl)acetamide fragment in comparison with thiacalix[4]arene **6**. Undoubtedly, this affects the intramolecular hydrogen bond between the carbonyl group and amide proton. As a result, the interaction between thiacalix[4]arene **20** and anions is not observed.

Complexation properties of thiacalix[4]arenes **2**, **3**, **4**, **5**, **13**, **18**, and **19** were also studied by NMR spectroscopy. In the $^1H$ NMR spectra of the compounds recorded in the presence of anions, a hydroxyl proton signal was observed. Thus, no deprotonation of phenolic hydroxyl took place. For an estimation of the possibility of tetrabutylammonium cations binding with the synthesized thiacalix[4]arenes, solutions of compounds **2–6**, **13**, **14**, **16–20** in the presence of a 10-fold excess of *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $I^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $NO_3^-$) in $CDCl_3$ have been studied by $^1H$ NMR spectroscopy. In $^1H$ NMR spectra, chemical shifts of the protons in *n*-$Bu_4N^+$ do not change indicating the absence of interaction between the thiacalix[4]arenes with tetrabutylammonium cation.

Maximal changes were observed in the case of the interaction of macrocycle **2** with *n*-$Bu_4NF$. Bathochromic shift of the absorption maximum at 306 nm by 8 nm and hyperchromic effect in the fields of 330–380 nm and 270–290 nm occurred in this case. In the case of compound **5**, containing one ester fragment, another characteristic in the changes in absorption spectra was observed. Interaction of thiacalix[4]arene **5** with tetrabutylammonium salts did not induce the shift of the absorption maximum. A hyperchromic effect on absorption bands in the fields of 270–300 nm and 320–380 nm was observed.

The character of the changes in the absorption spectra is identical for complexes of macrocycle **3** with *n*-$Bu_4NX$ (X = $F^-$, $CH_3CO_2^-$, $H_2PO_4^-$). A bathochromic shift and hypochromic effect of the absorption maximum at 306 nm occurred. Also a hyperchromic effect on the absorption band at 310–380 nm was observed.

The character of the changes in the absorption spectra is complicated for the interaction of compound **4** with *n*-$Bu_4NX$. A bathochromic shift and hypochromic effect of the absorption maximum at 306 nm were observed. Also, a new absorption maximum at 325 nm appeared. The fluoride ion caused the strongest changes in the absorption spectrum.

In the case of thiacalix[4]arene **6** containing two ester fragments (which are proton acceptor binding sites) changes in the absorption spectra were observed only in the presence of dihydrogen phosphate ion.

Maximal changes in the absorption spectra of macrocycle **13** were observed in the presence of *n*-$Bu_4NF$ (Fig. 1). In this case, a bathochromic shift at 300 nm by 40 nm, a hyperchromic effect at 350–390 nm and a hypochromic effect at 270–330 nm on the absorption maximum were found.

The most significant changes in the absorption spectra were observed only for the interaction of macrocycle **18** with *n*-$Bu_4NF$. In this case a bathochromic shift by 10 nm of the absorption maximum at 310 nm and a hypochromic effect on the absorption band at 310–340 nm were found.

The character of the changes in the absorption spectra are identical for complexes of thiacalix[4]arene **19** with *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $NO_3^-$). In this case, a bathochromic shift and hypochromic effect of absorption maximum at 303 nm and also a hyperchromic effect on the absorption band at 330–400 nm were observed.

The association constants and the stoichiometry (Table 3) of the formed complexes were obtained for quantitative evaluation of the complexation ability of compounds **2–6**, **10**, **13**, **14**, **18**, **19** towards

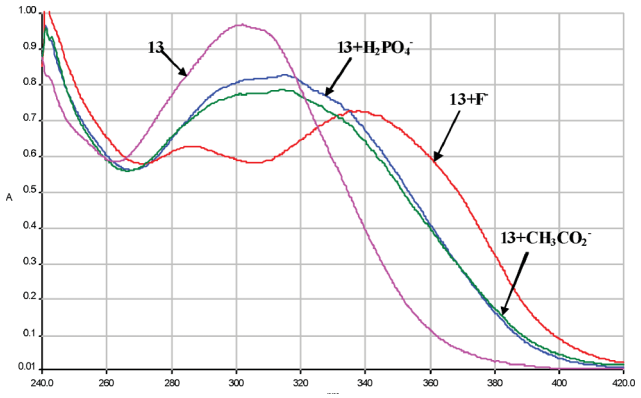



**Fig. 1** Changes in the absorption spectra of compound **13** after adding salts *n*-$Bu_4NX$ (X = $F^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $CHCl_3$, $C_{13} = 2.5 \times 10^{-5}$ M, $C_{n\text{-Bu4NX}} = 5.0 \times 10^{-3}$ M).

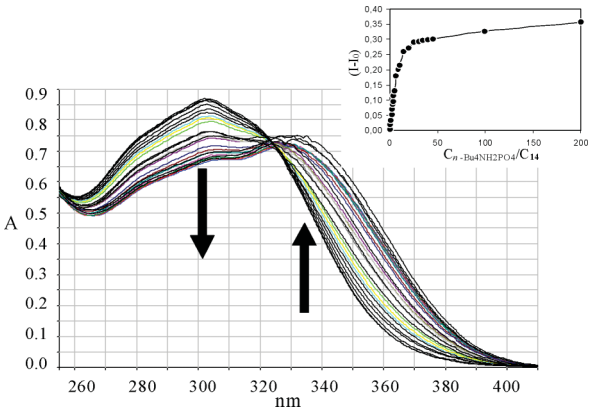



**Fig. 3** UV absorption spectra obtained by titration of the complexed system containing the receptor **14** ($C_{14} = 2.5 \times 10^{-5}$ M) and dihydrogen phosphate ion ($C_{initial} = 2.5 \times 10^{-5}$ M, $C_{final} = 5.0 \times 10^{-3}$ M) in $CHCl_3$. Inset: titration curve ($C_{14} = 2.5 \times 10^{-5}$ M).

some anions ($F^-$, $CH_3CO_2^-$, $H_2PO_4^-$). It was found by using the isomolar series method, that all the studied thiacalix[4]arenes form in $CHCl_3$ 1 : 1 complexes with considered tetrabutylammonium salts (Fig. 2). However, 1,2-disubstituted thiacalix[4]arene **4** forms 1 : 2 complexes. The stoichiometry of the complexation was also confirmed by measuring Job's plots (Fig. 2). The association constants of the studied complexes were estimated in chloroform by the dilution method (Fig. 3). The appropriate complexation constants (Table 3) were calculated using the Benesi–Hildebrand method.[33]

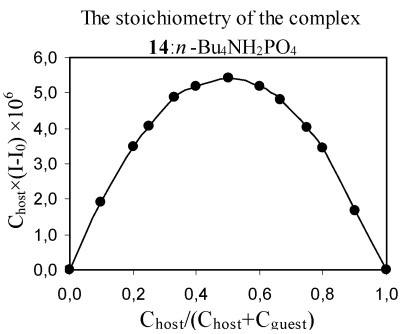



**Fig. 2** Job's plot for the **14** + *n*-$Bu_4NH_2PO_4$ system.

To estimate the contribution of the thiacalix[4]arene platform in anion binding, receptor properties of the model compound **10** were investigated. It was found that the association constants of compound **10** with anions were at least one order of magnitude lower compared with the association constants of all investigated macrocycles with anions (Table 3). In this case a macrocyclic cooperative effect is observed: the groups which have either weak, or no complexation ability form complementary binding sites in the thiacalix[4]arene due to the spatial preorganization.

Introduction of an ester fragment into the lower rim of 1,3-disubstituted thiacalix[4]arene **2** containing *N*-(*p*-nitrophenyl)acetamide groups leads to an increase in preorganization of the molecule and changes in the intramolecular hydrogen bonds between amide protons and the carbonyl group. It results in higher complementarity of the macrocycle towards the anions tested. This was proved by an increase of the association constant by one order of magnitude observed for the complexes of **5** with anions in comparison with those of the parent thiacalix[4]arene **2** (Table 3). Probably, the introduction of a second ester fragment (compound **6**) leads to formation of a pseudo-cavity for the dihydrogen phosphate ion. It should be noted that in the case of tetrasubstituted thiacalix[4]arene **6** the logarithm of the association constant with dihydrogen phosphate

**Table 3** The logarithms of the association constant ($\log K_{ass}$) for complexation of compounds **2–6**, **10**, **13**, **14**, **18**, **19** with *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $H_2PO_4^-$, $CH_3CO_2^-$, $NO_3^-$) in $CHCl_3$ (at 25 °C)

| | | $\log K_{ass}$ | | | | | |
|---|---|---|---|---|---|---|---|
| Compound | Host : Guest | $F^-$ | $Cl^-$ | $Br^-$ | $H_2PO_4^-$ | $CH_3CO_2^-$ | $NO_3^-$ |
| **2** | 1 : 1 | 3.67 ± 0.19 | —[a] | —[a] | 3.41 ± 0.09 | 3.50 ± 0.32 | —[a] |
| **3** | 1 : 1 | 5.25 ± 0.56 | —[a] | —[a] | 4.93 ± 0.21 | 4.85 ± 0.12 | —[a] |
| **4** | 1 : 2 | 7.38 ± 0.17 | —[a] | —[a] | 7.52 ± 0.19 | 7.58 ± 0.26 | —[a] |
| **5** | 1 : 1 | 4.27 ± 0.24 | —[a] | —[a] | 4.43 ± 0.34 | 4.48 ± 0.22 | —[a] |
| **6** | 1 : 1 | —[a] | —[a] | —[a] | 2.98 ± 0.23 | —[a] | —[a] |
| **10** | 1 : 1 | 2.52 ± 0.48 | —[a] | —[a] | 2.81 ± 0.27 | 2.32 ± 0.56 | —[a] |
| **13** | 1 : 1 | 4.55 ± 0.18 | —[a] | —[a] | 3.51 ± 0.02 | 3.48 ± 0.10 | —[a] |
| **14** | 1 : 1 | 3.68 ± 0.22 | —[a] | —[a] | 3.24 ± 0.28 | 3.15 ± 0.05 | —[a] |
| **18** | 1 : 1 | 3.53 ± 0.44 | —[a] | —[a] | —[a] | —[a] | —[a] |
| **19** | 1 : 1 | 3.80 ± 0.32 | 3.36 ± 0.18 | 2.93 ± 0.04 | 3.51 ± 0.10 | 3.37 ± 0.11 | 2.64 ± 0.09 |

[a] No changes in UV spectra.

ion is similar to model compound **10**. It is obvious that the decrease in the efficiency of anion binding due to the formation of hydrogen bonds NH . . . O═C leads to the selective binding of tetrabutylammonium dihydrogen phosphate.

In the case of macrocycles **13** and **14**, the number of proton donating groups increases from the trisubstituted (**13**) to the tetrasubstituted (**14**) compound. Therefore, the increase of the association constant for the studied anions can be expected after introduction of the second monoethanolamide fragment to the lower rim of thiacalix[4]arene.

The association constants of anion binding appear to be similar for compounds **13** and **14** except those for the fluoride ion. It should be noted that the association constant of fluoride binding was higher by one order of magnitude for macrocycle **13** than for thiacalix[4]arene **14**. Probably, the unsubstituted phenolic group at the lower rim of thiacalix[4]arene **13** interacts more effectively with the fluoride ion.

Trisubstituted thiacalix[4]arene **18** in the *cone* conformation with high selectivity binds fluoride ion in comparison with other studied anions. Probably, the presence of the bulky diethylamide group complicates the binding of other anions. However, trisubstituted thiacalix[4]arene **19** in the *partial cone* conformation effectively binds almost all studied anions except the bulky iodide ion.

In the series of trisubstituted thiacalix[4]arenes **3**, **5**, **13**, **18** and **19**, macrocycle **3** in the *partial cone* conformation binds anions more effectively (Table 3). In general, trisubstituted thiacalix[4]arenes bind anions more effectively than tetrasubstituted thiacalix[4]arenes. This might be due to the free phenolic hydroxyl that could participate in anion binding.

## Conclusion

New thiacalix[4]arenes containing amide, hydroxyl and ester fragments, differently substituted at the lower rim were synthesized. For the synthesis of stereoisomers of *p-tert*-butyl thiacalix[4]arene with ester and amide fragments at the lower rim, the template effect of alkali metal cations was used. Receptor properties of the newly synthesized thiacalix[4]arene derivatives toward some tetrabutylammonium salts *n*-$Bu_4NX$ (X = $F^-$, $Cl^-$, $Br^-$, $I^-$, $CH_3CO_2^-$, $H_2PO_4^-$, $NO_3^-$) were studied by UV spectroscopy. The values of the association constants ($10^3$–$10^5$ $M^{-1}$) of complexes obtained from derivatives of *p-tert*-butyl thiacalix[4]arene with tetrabutylammonium salts with 1 : 1 stoichiometry were determined by electron spectroscopy. It was shown that trisubstituted *p-tert*-butyl thiacalix[4]arenes containing secondary amide groups bind anions more effectively. On an example of *p-tert*-butyl thiacalix[4]arenes differently substituted at the lower rim, significant influence of the number and nature of substituents on the complexation properties of synthetic receptors was shown. Selective receptors for fluoride ion and dihydrogen phosphate ion were found. The newly synthesized compounds can be used to develop sensors for anions and in the development of systems like an "electronic tongue".

## Experimental

### General

Melting points were determined using the Boetius Block apparatus. Most chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified by standard procedures. $^1$H NMR spectra were recorded at room temperature with a 300 MHz Varian XL-300 spectrometer in $CDCl_3$ as a solvent; chemical shifts are reported in ppm. The 2D and $^{13}$C NMR spectra were recorded on a Bruker-500 MHz instrument in $CDCl_3$ at room temperature. IR spectra (nujol) were recorded with a Vector 22 (Bruker) IR spectrometer. Mass spectra were recorded with a Bruker Esquire MS, MALDI-TOF Dynamo Finnigan (with 1,8,9-trihydroxyanthracene or 4-nitroaniline matrices), Varian MAT 312. Elemental analysis was performed with a Perkin–Elmer 2400 Series II instruments.

### General procedure for the preparation of thiacalix[4]arenes 5–8

5,11,17,23-Tetra-*tert*-butyl-25,27-bis-hydroxy-26,28-bis[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-thiacalix[4]arene **2** (1 g, 1.39 mmol) was suspended in 30 mL of dry acetone containing a 3-fold (or a 8-fold) excess of an anhydrous alkali metal carbonates. Then a 4-, 8- or 40-fold excess of ethyl bromoacetate and 40 mL of dry acetone was added. The mixture was refluxed for several hours. The reaction was monitored by TLC. After cooling, the solid residue was removed by filtration. The filtrate was evaporated to dryness. Then, both solids were treated separately using the same procedure. Solid was dissolved in 30 ml of chloroform and washed with 30 mL of 2 M HCl. The organic layer was dried over molecular sieves, filtered and evaporated under reduced pressure. Crystallization of the resulting solid from chloroform–ethanol or dichloromethane–ethanol mixture gave pure samples of **5–8**. In the case of compound **8**, the compounds **11** and **12** were also isolated.

**5,11,17,23-Tetra-*tert*-butyl-25-hydroxy-27-[(ethoxycarbonyl)-methoxy]-26,28-bis[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-thiacalix[4]arene (5).** Yield 0.41 g (58%). Mp: 275 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.84 (s, 9H, $(CH_3)_3C$), 1.13 (s, 9H, $(CH_3)_3C$), 1.22 (s, 18H, $(CH_3)_3C$), 1.31 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.27 (q, 2H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.64 (d, 2H,-O–$CH_2$–CONH, $^2J_{HH}$ = 15.8 Hz), 4.71 (s, 4H, -O–$CH_2$-), 5.86 (d, 2H,-O–$CH_2$–CONH, $^2J_{HH}$ = 15.8 Hz), 6.98 (s, 2H, Ar–H), 7.40 (s, 2H, Ar–H), 7.56, 7.58 AB system (4H, Ar–$H_A$, Ar–$H_B$, $^4J_{HH}$ = 2.6 Hz), 7.76 (m, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 7.99 (m, 4H, Ar′–H, $^3J_{AB}$+$^5J_{AB'}$ = 9.1 Hz), 9.07 s (1H, OH), 10.40 s (2H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.02, 30.80, 31.19, 34.06, 34.38, 62.10, 72.02, 74.32, 119.34, 120.53, 124.57, 127.80, 128.98, 129.08, 133.39, 134.80, 135.11, 136.00, 143.24, 143.33, 143.60, 147.67, 148.75, 155.26, 155.49, 158.71, 168.47, 169.89. Spectrum $^1$H-$^1$H NOESY: $H^{4b}/H^3$, $H^{4'b}/H^{3'}$, $H^{4+b}/H^{3+}$, $H^7/H^{7'}$, $H^{7'a}/H^{7'b}$, $H^{15}/H^9$, $H^9/H^{11}$, $H^7/H^9$, $H^3/H^{5'}$, $H^{7+}/H^9$, $H^5/H^{3+}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3456, 3319, 3271, 1766, 1698, 1611, 1596, 1555, 1505, 1383, 1340. MS (ESI) $m/z$ = 1162 [$M^+$]. El. Anal. Calcd for $C_{60}H_{66}N_4O_{12}S_4$: C, 59.27; H, 5.29; N, 4.50. Found: C, 60.21; H, 5.72; N, 4.82.

**5,11,17,23-Tetra-*tert*-butyl-25,-27-bis-[(ethoxycarbonyl)-methoxy]-26,28-bis-[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-thiacalix[4]arene (6).** Yield 0.46 g (40%). Mp: 220 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.93 (s, 18H, $(CH_3)_3C$); 1.31 (s, 18H, $(CH_3)_3C$); 1.19 (t, 6H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.2 Hz); 4.09 (q, 4H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.2 Hz); 4.53 (s, 4H, -O–$CH_2$–COOEt); 5.35 (s, 4H, -O–$CH_2$–C(O)–NH); 7.01 (s, 4H, Ar–H); 7.74 (s,

4H, Ar–H); 8.15 (AA′BB′ system, 8H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.3 Hz); 10.95 (s, 2H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.01, 18.45, 30.90, 31.27, 34.40, 61.49, 72.43, 74.01, 120.71, 124.66, 127.81, 133.17, 136.72, 143.72, 143.99, 147.39, 147.88, 156.13, 158.62, 168.09, 168.65. Spectrum $^1$H-$^1$H NOESY: $H^{4b}/H^3$, $H^{4'b}/H^{3'}$, $H^9/H^{11}$, $H^9/H^{15}$, $H^{9'}/H^{10'}$, $H^7/H^{7'}$, $H^9/H^{7'}$, $H^3/H^{5'}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3261, 1753, 1699, 1611, 1596, 1543, 1518, 1378, 1341. MS (ESI) $m/z$ = 1248 [M$^+$]. El. Anal. Calcd for $C_{64}H_{72}N_4O_{14}S_4$: C, 60.39; H, 5.49; N, 4.23. Found: C, 61.52; H, 5.81; N, 4.48.

**5,11,17,23-Tetra-*tert*-butyl-25,-27-bis-[(ethoxycarbonyl)methoxy]-26-[*N*-(4′-nitrophenyl)aminocarbonylmethoxy]-28-[*N*-(4″-nitrophenyl),-*N*-(ethoxycarbonylmethyl)-aminocarbonylmethoxy]-thiacalix[4]arene (7).** Yield 0.16 g (14%). Mp: 300 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.95 (s, 18H, $(CH_3)_3C$), 1.19 (s, 9H, $(CH_3)_3C$), 1.25 (s, 9H, $(CH_3)_3C$), 1.21 (m, 9H, -$CH_2$–$CH_3$), 4.12 (m, 6H, -$CH_2$–$CH_3$), 4.39 (s, 2H, -N–$CH_2$–C(O)OEt), 5.17 (s, 2H, -O–$CH_2$–C(O)–N–$CH_2$–C(O)OEt), 5.38 (s, 2H, -O–$CH_2$–C(O)–NH), 4.73, 4.78 (AB system, 2H, $H_A$, $H_B$, -O–$CH_2$–COOEt, $^2J_{HH}$ = 16.5 Hz), 7.07, 7.08 (AB system, 4H, Ar–$H_A$, Ar–$H_B$, $^4J_{HH}$ = 2.6 Hz), 7.42 (s, 2H, Ar–H), 7.63 (s, 2H, Ar–H), 7.62 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 8.4 Hz), 8.28 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 8.4 Hz), 8.21 (AA′BB′ system, 4H, Ar″–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.5 Hz), 11.00 (s, 1H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 13.75, 29.09, 29.34, 29.70, 30.61, 30.91, 33.73, 33.88, 34.01, 60.70, 61.15, 71.17, 119.47, 124.48, 124.89, 127.76, 128.04, 132.72, 134.09, 136.13, 136.53, 136.69, 146.71, 146.96, 156.41, 156.80, 168.71, 169.53. Spectrum $^1$H-$^1$H NOESY: $H^{4b}/H^3$, $H^{4'b}/H^{3'}$, $H^{4+b}/H^{3+}$, $H^{15}/H^{11+}$, $H^{14}/H^{12+}$, $H^{9+}/H^{15+}$, $H^{9+}/H^{11+}$, $H^7/H^{7'}$, $H^{7'}/H^{7+}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3267, 1747, 1698, 1608, 1596, 1543, 1513, 1377, 1341. MALDI-TOF MS $m/z$ = 1358 [M+Na]$^+$, 1375 [M+K]$^+$. El. Anal. Calcd for $C_{68}H_{78}N_4O_{16}S_4$: C, 61.15; H, 5.89; N, 4.19; Found: C, 60.65; H, 5.59; N, 4.04.

**5,11,17,23-Tetra-*tert*-butyl-25,27-bis-[(ethoxycarbonyl)-methoxy]-26,28-bis[3′-(ethoxycarbonyl)-2′-oxopropoxy]-thiacalix[4]arene (8).** Yield 0.52 g (50%). Mp: 197 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.21 (s, 18H, $(CH_3)_3C$), 1.25 (s, 18H, $(CH_3)_3C$), 1.28 (t, 6H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 1.32 (t, 6H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.3 Hz), 4.23 (q, 4H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.25 (q, 4H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.3 Hz), 4.62 (s, 4H, -O–$CH_2$-), 4.70 (s, 4H, -O–$CH_2$-), 4.75 (s, 4H, -O–$CH_2$-), 7.47 (s, 4H, Ar–H), 7.52 (s, 4H, Ar–H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.21, 14.26, 31.02, 31.05, 31.09, 34.17, 34.18, 34.20, 34.23, 60.58, 60.64, 61.51, 67.71, 67.77, 68.19, 68.23, 68.26, 127.63, 127.66, 127.70, 133.49, 133.52, 133.71, 146.22, 146.50, 157.16, 167.25, 167.70, 167.95. Spectrum $^1$H-$^1$H NOESY: $H^{4b}/H^3$, $H^{4'b}/H^{3'}$, $H^7/H^{5'}$, $H^3/H^{7''}$, $H^{4b}/H^{9''}$, $H^7/H^{5'}$, $H^3/H^{7''}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 1784, 1766, 1761, 1093. MS (EI) $m/z$ = 1180 [M$^+$]. El. Anal. Calcd for $C_{60}H_{76}O_{16}S_4$: C, 61.00; H, 6.48. Found: C, 61.22; H, 6.56.

***N*-(4′-Nitrophenyl)-2-amino-ethylacetate (11).** Yield 0.22 g (13%). Mp: 130 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.31 (t, 3H, -$CH_3$, $^3J_{HH}$ = 7.1 Hz), 3.96 (d, 2H, -$CH_2$-), 4.26 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 5.13 (s, 1H, NH), 6.53 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.0 Hz), 8.08 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.0 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.16, 44.93, 34.40, 61.94, 111.48, 126.32, 138.92, 151.97, 169.70. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3356, 1723, 1597, 1542, 1506, 1377, 1336, 1112, 1023. MS (EI) $m/z$ = 224 [M$^+$]. El. Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39; N, 12.49. Found: C, 53.53; H, 5.37; N, 12.09.

***N*-(4′-Nitrophenyl)-2-amino-diethylacetate (12).** Yield 0.23 g (10%). Mp: 128 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.28 (t, 6H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.2 Hz), 4.19 (s, 4H, -$CH_2$-), 4.23 (q, 4H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.2 Hz), 6.58 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$+$^5J_{AB'}$ = 9.2 Hz), 8.11 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$+$^5J_{AB'}$ = 9.2 Hz). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.04, 14.14, 14.36, 53.37, 53.48, 61.17, 61.64, 61.74, 62.31, 117.37, 125.97, 126.04, 139.03, 152.68, 169.30. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 1748, 1597, 1515, 1486, 1376, 1342, 1116, 1025. MS (EI) $m/z$ = 310 [M$^+$]. El. Anal. Calcd for $C_{14}H_{18}N_2O_6$: C, 54.19; H, 5.85; N, 9.03. Found: C, 53.78; H, 5.65; N, 8.85.

### General procedure for the preparation of compound 10

*p-tert*-Butylphenol (6 g, 0.04 mol) was suspended in 100 mL of dry acetone containing a 2.5-fold excess of anhydrous sodium carbonate. The mixture was refluxed for 2 h. Then *N*-(*p*-nitrophenyl)-$\alpha$-bromacetamide (8.3 g, 0.03 mol) and 100 mL of dry acetone were added. The mixture was refluxed for 33 h. The reaction was monitored by TLC. After cooling, the solid residue was removed by filtration. The filtrate was evaporated to dryness. Then, both solids were treated separately using the same procedure. Solid was dissolved in 100 ml of chloroform and washed with 50 mL of 2 M HCl. The organic layer was dried over molecular sieves, filtered and evaporated under reduced pressure. Crystallization of the resulting solid from dichloromethane–ethanol mixture gave a pure sample of **10**.

**2-(4-*tert*-Butylphenoxy)-*N*-(4′-nitrophen-1′-yl)acetamide (10).** Yield 7.71 g (73%). Mp: 156 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.30 (s, 9H, $(CH_3)_3C$), 4.63 (s, 2H, -$CH_2$-), 6.92 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$ + $^5J_{AB'}$ = 8.9 Hz), 7.35 (AA′BB′ system, 2H, Ar–H, $^3J_{AB}$ + $^5J_{AB'}$ = 8.9 Hz), 7.82 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.2 Hz), 8.21 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.2 Hz), 8.68 (s, 1H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 31.45, 34.26, 67.83, 114.42, 119.52, 125.09, 126.81, 142.68, 143.99, 145.74, 154.55, 167.07. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3344, 1691, 1612, 1596, 1543, 1508, 1377, 1338, 1112, 1070. MS (EI) $m/z$ = 328 [M$^+$]. El. Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.75; H, 6.07; N, 9.00.

### General procedure for the preparation of compounds 11 and 12

2-(4-*tert*-Butylphenoxy)-*N*-(4′-nitrophen-1′-yl)acetamide (1 g, 3.05 mmol) was suspended in 30 mL of dry acetone containing a 4-fold excess of anhydrous potassium or caesium carbonates. Then a 4-fold excess of ethyl bromoacetate and 40 mL of dry acetone were added. The mixture was refluxed for 40 or 13 h. The reaction was monitored by TLC. After cooling, the solid residue was removed by filtration. The filtrate was evaporated to dryness. Then, the residue was dissolved in 30 ml of chloroform and was washed with 30 mL of distilled water. The organic layer was dried over molecular sieves, filtered and evaporated under reduced pressure. Crystallization of the resulting solid from ethanol or diethyl ether gave pure samples of **11** and **12** with 59% and 32% yields, respectively.

**General procedure for the preparation of thiacalix[4]arenes 13–14**

Thiacalix[4]arene **5** (0.50 g, 0.43 mmol) or **6** (0.50 g, 0.40 mmol) was suspended in 30 mL of dry tetrahydrofuran. Then a 4-fold (or an 8-fold) excess of 2-aminoethanol were added. The mixture was refluxed for 12 or 30 h. The reaction was monitored by TLC. After cooling, the solvent of reaction mixture was evaporated to dryness under reduced pressure. Then crystallization of the resulting solid from methanol or ethanol gave pure samples of **13–14**.

**5,11,17,23-Tetra-*tert*-butyl-25-hydroxy-27-[*N*-(2-hydroxyethyl)-carbamoylmethoxy]-26,28-bis[*N*-(4′-nitrophenyl)aminocarbonyl-methoxy]thiacalix[4]arene (13).** Yield 0.42 g (98%). Mp: 188 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.00 (s, 9H, $(CH_3)_3C$), 1.07 (s, 18H, $(CH_3)_3C$), 1.24 (s, 9H, $(CH_3)_3C$), 3.74 (m, 2H, -$CH_2$–$CH_2$-), 3.94 (m, 2H, -$CH_2$–$CH_2$-), 4.19 (s, 1H, -$CH_2$–$OH$), 4.69 (s, 2H, –O–$CH_2$–C(O)NH$(CH_2)_2$OH, 4.75 (d, 4H, -O–$CH_2$-, $^2J_{HH}$ = 15.3 Hz), 5.24 (d, 4H, -O–$CH_2$-, $^2J_{HH}$ = 15.3 Hz), 7.20 (s, 2H, Ar–H), 7.34 (d, 2H, Ar–H, $^4J_{HH}$ = 2.6 Hz), 7.37 (d, 2H, Ar–H, $^4J_{HH}$ = 2.6 Hz), 7.54 (s, 2H, Ar–H), 7.83 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 7.97 (t, 1H, -NH–$CH_2$-, $^3J_{HH}$ = 5.6 Hz), 8.05 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 8.51 (s, 1H, -OH), 10.43 (s, 1H, -$NH$–$C_6H_4$–$NO_2$). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 12.97, 13.89, 30.84, 31.29, 34.33, 40.30, 40.54, 73.04, 73.82, 76.75, 77.26, 120.82, 124.49, 128.24, 132.38, 136.82, 143.45, 144.32, 146.97, 147.18, 156.50, 159.07, 166.58, 168.37. Spectrum $^1$H-$^1$H NOESY: $H^3/H^{4b}$, $H^5/H^{4b}$, $H^{3'}/H^{4'b}$, $H^{3+}/H^{4+b}$, $H^3/H^{5'}$, $H^{3'}/H^5$, $H^5/H^{3+}$, $H^9/H^{11}$, $H^{11}/H^{12}$, $H^{10'}/H^{11'}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3600, 3371, 3278, 1662, 1552, 1512, 1377, 1342, 1303. MALDI-TOF MS $m/z$ = 1178 $[M+H]^+$, 1200 $[M+Na]^+$, 1216 $[M+K]^+$. El. Anal. Calcd for $C_{60}H_{67}N_5O_{12}S_4$: C, 61.15; H, 5.73; N, 5.94. Found: C, 60.84; H, 5.74; N, 5.94.

**5,11,17,23-Tetra-*tert*-butyl-25,27-bis[*N*-(2-hydroxyethyl)carbamoylmethoxy]-26,28-bis[*N*-(4′-nitrophenyl)aminocarbonyl-methoxy]thiacalix[4]arene (14).** Yield 0.25 g (48%). Mp: 148 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 1.09 (s, 18H, $(CH_3)_3C$), 1.14 (s, 18H, $(CH_3)_3C$), 3.38 (m, 4H, -$CH_2$–$CH_2$-), 3.84 (m, 4H, -$CH_2$–$CH_2$-), 4.84 (s, 4H, -O–$CH_2$–C(O)NH$(CH_2)_2$OH), 4.99 (t, 2H, -OH, $^3J_{HH}$ = 5.0 Hz), 5.23 (s, 4H, -O–$CH_2$-), 7.34 (s, 4H, Ar–H), 7.40 (s, 4H, Ar–H), 7.90 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 8.21 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 8.28 (t, 2H, -$NH$–$CH_2$-, $^3J_{HH}$ = 5.3 Hz), 10.49 (s, 2H, -$NH$–$C_6H_4$–$NO_2$). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 31.03, 31.11, 34.40, 42.18, 60.58, 74.88, 76.75, 77.26, 119.42, 125.10, 127.73, 135.10, 136.25, 143.86, 148.22, 168.16. Spectrum $^1$H-$^1$H NOESY: $H^3/H^{4b}$, $H^{3'}/H^{4'b}$, $H^3/H^{5'}$, $H^7/H^{7'}$, $H^7/H^9$, $H^{10'}/H^{11'}$, $H^{11}/H^{12}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3400, 3346, 1651, 1544, 1515, 1302, 1377, 1342, 1056. MALDI-TOF MS $m/z$ = 1279 $[M+H]^+$, 1301 $[M+Na]^+$, 1317 $[M+K]^+$. El. Anal. Calcd for $C_{64}H_{74}N_6O_{14}S_4$: C, 60.08; H, 5.83; N, 6.57. Found: C, 59.80; H, 5.80; N, 6.54.

**General procedure for the preparation of thiacalix[4]arenes 6, 16–17**

Thiacalix[4]arene **15** (1 g, 1.12 mmol) was suspended in 40 mL of dry acetone containing a 4-fold excess of an anhydrous alkali carbonate. Then *N*-(*p*-nitrophenyl)-$\alpha$-bromacetamide (1.2 g, 4.48 mmol) and 20 mL of dry acetone were added. The mixture was refluxed for 60 h. The reaction was monitored by TLC. After cooling, the solid residue was removed by filtration. The filtrate was evaporated to dryness. Then, both solids were treated separately using the same procedure. Solid was dissolved in 30 mL of chloroform and was washed with 30 mL of 2 M HCl. The organic layer was dried over molecular sieves, filtered and evaporated under reduced pressure. Crystallization of the resulting solid from chloroform–ethanol or dichloromethane–ethanol mixture gave pure samples of **6**, **16**, **17** with 60%, 30% and 49% or 50% yield, respectively.

**5,11,17,23-Tetra-*tert*-butyl-25,27-bis-[(ethoxycarbonyl)methoxy]-26,28-bis[*N*-(4′-nitrophenyl) aminocarbonylmethoxy]-thiacalix[4]arene (16).** Yield 0.41 g (30%). Mp: 287 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.94 (s, 18H, $(CH_3)_3C$), 1.34 (s, 9H, $(CH_3)_3C$), 1.37 (s, 9H, $(CH_3)_3C$), 1.25 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.17 (m, 4H, -O–$CH_2$–$CH_3$), 4.67, 5.01 (AB quadruplet, 4H,-O–$CH_2$–COOEt, $^2J_{AB}$ = 15.7 Hz), 5.11 (s, 4H, -O–$CH_2$–C(O)NH$C_6H_4NO_2$), 7.08 (d, 2H, Ar–H, $^4J_{HH}$ = 2.5 Hz), 7.42 (d, 2H, Ar–H, $^4J_{HH}$ = 2.5 Hz), 7.43 (s, 2H Ar–H), 7.86 (s, 2H Ar–H), 7.89 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.4 Hz), 7.97 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.4 Hz), 8.15 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$+$^5J_{AB'}$ = 9.4 Hz), 8.21 (AA′BB′ system, 2H, Ar′–H, $^3J_{AB}$+$^5J_{AB'}$ = 9.4 Hz), 10.63 (s, 1H, NH), 10.70 (s, 1H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 18.89, 35.67, 36.04, 38.84, 39.08, 44.30, 44.64, 44.81, 44.97, 45.31, 65.83, 74.76, 123.92, 124.24, 130.65, 130.94, 132.51, 133.42, 147.70, 147.96, 151.63, 152.16, 161.40, 171.67, 173.05, 173.46. Spectrum $^1$H-$^1$H NOESY: $H^{4'b}/H^{9+}$, $H^{9'}/H^{10'}$, $H^{5'}/H^{7+}$, $H^{4'b}/H^{3'}$, $H^{4'b}/H^{5'}$, $H^{4+b}/H^{3+}$, $H^{4b}/H^3$, $H^{5'}/H^{9+}$, $H^{9'}/H^{3+}$, $H^{7'}/H^{3+}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3271, 1750, 1706, 1611, 1596, 1548, 1511, 1376, 1341. MALDI-TOF MS $m/z$ = 1249.5 $[M+H]^+$, 1271.5 $[M+Na]^+$, 1287.5 $[M+K]^+$. El. Anal. Calcd for $C_{64}H_{72}N_4O_{14}S_4$: C, 61.40; H, 6.01; N, 4.46; S, 10.32. Found: C, 61.59; H, 6.34; N, 4.36; S, 10.62.

**5,11,17,23-Tetra-*tert*-butyl-25,-27-bis-[(ethoxycarbonyl)methoxy]-26,28-bis[*N*-(4′-nitrophenyl) aminocarbonylmethoxy]-thiacalix[4]arene (17).** Yield 0.67 g (50%). Mp: 234 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.66 (s, 18H, $(CH_3)_3C$), 1.29 (s, 18H, $(CH_3)_3C$), 1.25 (t, 6H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.19 (q, 4H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.62 (s, 4H,-O–$CH_2$–COOEt), 4.79 (s, 4 H, -O–$CH_2$–C(O)–NH), 7.24 (s, 4H, Ar–H), 7.58 (s, 4H, Ar–H), 7.74 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.4 Hz), 8.19 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.4 Hz), 9.08 (s, 2H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 14.18; 30.37; 30.54; 30.72; 30.85; 30.95; 31.06; 33.97; 34.35; 60.78; 65.85; 70.46; 119.49; 124.96; 125.03; 125.78; 128.31; 128.44; 128.60; 133.04; 133.26; 143.08; 143.83; 147.67; 147.85; 155.61; 155.99; 167.17; 167.47. Spectrum $^1$H-$^1$H NOESY: $H^{4b'}/H^9$, $H^{4b'}/H^7$, $H^{4b}/H^{9'}$, $H^{4b'}/H^{11}$, $H^{4b}/H^{7'}$, $H^{4b}/H^{7'}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3259, 1766, 1697, 1613, 1598, 1541, 1513, 1377, 1343. MALDI-TOF MS $m/z$ = 1249.8 $[M+H]^+$, 1271.7 $[M+Na]^+$, 1287.7 $[M+K]^+$. El. Anal. Calcd for $C_{64}H_{72}N_4O_{14}S_4$: C, 61.40; H, 6.01; N, 4.46; S, 10.32. Found: C, 61.59; H, 6.34; N, 4.36; S, 10.62.

**General procedure for the preparation of thiacalix[4]arenes 18–20**

Thiacalix[4]arene **2** (1 g, 0.93 mmol) was suspended in 30 mL of dry acetone containing a 3-fold (or a 8-fold) excess of an anhydrous alkali carbonate. Then a 4-fold (or a 8-fold) excess of *N*,*N*-diethylbromoacetamide and 40 mL of dry acetone were added.

The mixture was refluxed for several hours. The reaction was monitored by TLC. After cooling, the solid residue was removed by filtration. The filtrate was evaporated to dryness. Then, both solids were treated separately using the same procedure. Solid was dissolved in 30 ml of chloroform and was washed with 30 mL of 2 M HCl. The organic layer was dried over molecular sieves, filtered and evaporated under reduced pressure. Crystallization of the resulting solid from chloroform–ethanol or dichloromethane–ethanol mixture gave pure samples of **18–20**.

**5,11,17,23-Tetra-*tert*-butyl-25-hydroxy-26,28-bis[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-27-[*N*,*N*-diethylcarbamoylmethoxy]-thiacalix[4]arene (18).** Yield 0.86 g (78%). Mp: 256 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.68 (s, 9H, $(CH_3)_3C$), 1.05 (s, 9H, $(CH_3)_3C$-), 1.30 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 1.31 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 1.34 (s, 18H, $(CH_3)_3C$), 3.27 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 3.58 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.63 (d, 2H, -O$CH_2$CONH-, $^2J_{HH}$ = 16.0 Hz), 4.74 (s, 2H, -O$CH_2$CONEt$_2$), 6.36 (d, 2H, -O$CH_2$CONH-, $^2J_{HH}$ = 16.0 Hz), 6.76 (s, 2H, Ar–H), 7.27 (s, 2H, Ar–H), 7.71 and 7.80 (AB quadruplet, 4H, Ar–$H_A$, Ar–$H_B$, $^4J_{HH}$ = 2.5 Hz), 7.76 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 7.93 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 9.47 (s, 1H, -OH), 10.97 (s, 2H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 13.00, 14.22, 30.67, 31.35, 34.43, 41.17, 73.51, 74.52, 119.39, 124.34, 128.43, 129.80, 132.79, 135.05, 135.39, 136.91, 143.01, 144.11, 147.25, 148.51, 155.26, 155.62, 159.67, 166.47, 169.18. Spectrum $^1$H-$^1$H NOESY: $H^7/H^{9'}$, $H^7/H^{7'}$, $H^7/H^{10'}$, $H^3/H^{4b}$, $H^{3'}/H^{4'b}$, $H^{3+}/H^{4+b}$, $H^7/H^9$, $H^{7+}/H^9$, $H^3/H^{5'}$, $H^5/H^{3+}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3274, 3397, 1717, 1641, 1597, 1738, 1545, 1511, 1330, 1378, 1110, 1096. MALDI-TOF MS $m/z$ = 1190.56 $[M+H]^+$, 1212.55 $[M+Na]^+$, 1228.57 $[M+K]^+$. El. Anal. Calcd for $C_{62}H_{71}N_5O_{11}S_4$: C, 62.55; H, 6.01; N, 5.88. Found: C, 62.42; H, 5.87; N, 5.83.

**5,11,17,23-Tetra-*tert*-butyl-25-hydroxy-26,28-bis[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-27-[*N*,*N*-diethylcarbamoylmethoxy]-thiacalix[4]arene (19).** Yield 0.44 g (40%). Mp: 168 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.35 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.0 Hz), 1.04 (s, 9H, $(CH_3)_3C$-), 1.07 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.0 Hz), 1.15 (s, 18H, $(CH_3)_3C$), 1.31 (s, 9H, $(CH_3)_3C$), 2.91 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.0 Hz), 3.27 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.0 Hz), 4.43 (d, 2H, -O$CH_2$CONH-, $^2J_{HH}$ = 15.1 Hz), 4.70 (s, 2H, -O$CH_2$CONEt$_2$), 5.11 (d, 2H, -O$CH_2$CONH-, $^2J_{HH}$ = 15.1 Hz), 7.65 (s, 2H, Ar–H), 7.71 (s, 2H, Ar–H), 7.41 and 7.55 (AB quadruplet, 4H, Ar–$H_A$, Ar–$H_B$, $^4J_{HH}$ = 2.5 Hz), 7.46 (s, 1H, -OH), 7.68 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 8.07 (AA′BB′ system, 4H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.1 Hz), 9.80 (s, 2H, -NH-). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 30.83, 30.94, 31.37, 34.25, 34.44, 69.61, 72.93, 119.20, 121.31, 124.92, 127.10, 128.20, 132.37, 133.38, 134.88, 135.00, 143.14, 143.75, 144.53, 147.88, 148.91, 155.00, 156.45, 158.08, 165.65, 166.73. Spectrum $^1$H-$^1$H NOESY: $H^{7'}/H^{4b}$, $H^7/H^{4'b}$, $H^{9'}/H^{4b}$, $H^7/H^{5'}$, $H^7/H^9$, $H^{10'}/H^{4b}$, $H^{9'}/H^{10'}$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3301, 3404, 1730, 1616, 1622, 1733, 1512, 1549, 1378, 1340, 1111; 1075. MALDI-TOF MS $m/z$ = 1190.58 $[M+H]^+$, 1212.57 $[M+Na]^+$, 1228.55 $[M+K]^+$. El. Anal. Calcd for $C_{62}H_{71}N_5O_{11}S_4$: C, 62.55; H, 6.01; N, 5.88. Found: C, 61.84; H, 6.03; N, 5.78.

**5,11,17,23-Tetra-*tert*-butyl-25,27-bis[*N*-(4′-nitrophenyl)-aminocarbonylmethoxy]-26,28-bis[*N*,*N*-diethylcarbamoylmethoxy]-thiacalix[4]arene (20).** Yield 0.18 g (15%). Mp: 183 °C. $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ (ppm): 0.86 (s, 18H, $(CH_3)_3C$), 0.98 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 1.14 (t, 3H, -O–$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 1.34 (s, 18H, $(CH_3)_3C$), 3.00 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 3.36 (q, 2H, -$CH_2$–$CH_3$, $^3J_{HH}$ = 7.1 Hz), 4.74 (s, 4H, -O$CH_2$CONEt$_2$), 5.43 (s, 4H, -O$CH_2$CONH-), 6.90 (s, 4H, Ar–H), 7.81 (s, 4H, Ar–H), 8.16 (AA′BB′system, 8H, Ar′–H, $^3J_{AB}$ + $^5J_{AB'}$ = 9.6 Hz), 11.30 (s, 2H, NH). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ (ppm): 30.98, 31.27, 34.32, 42.03, 61.99, 73.91, 75.60, 119.55, 120.92, 124.76, 127.98, 128.50, 134.16, 134.33, 135.21, 135.50, 143.42, 143.67, 148.41, 149.03, 155.40, 157.49, 167.65, 169.59. Spectrum $^1$H-$^1$H NOESY: $H^7/H^{7'}$, $H^{9'}/H^{10'}$, $H^3/H^{4b}$, $H^{3'}/H^{4'b}$, $H^{11}/H^{10'}$, $H^{12}/H^{10'}$, $H^{11}/H^{9'}$, $H^{12}/H^{9'}$, $H^9/H^{11}$, $H^7/H^9$, $H^{7'}/H^9$. IR (Nujol) $\nu_{max}$ cm$^{-1}$: 3373, 1656, 1638, 1546, 1735, 1509, 1545, 1330, 1378, 1112, 1096. MALDI-TOF MS $m/z$ = 1325.66 $[M+Na]^+$. El. Anal. Calcd for $C_{68}H_{82}N_6O_{12}S_4$: C, 62.65; H, 6.34; N, 6.45. Found: C, 62.53; H, 6.14; N, 6.45.

### Materials and general methods

The studies of the receptor properties of thiacalix[4]arene derivatives **2–6**, **10**, **13**, **14**, **16–20** were carried out in $CHCl_3$ (analytical grade). UV spectra were obtained on a Perkin Elmer spectrophotometer Lambda 35.

### Determination of the stoichiometry by isomolar series method

The series of experiments with the constant total concentration of guest and host molecules (0.02 M) and various guest/host ratio was prepared and processed as described earlier.[33]

### Experimental methods of determination of the association constant

Absorption properties of compounds were studied in chloroform solution ($2.5 \times 10^{-5}$ M). The efficiency of anion binding was estimated by addition of a 200-fold excess of tetrabutylammonium salt in chloroform. The concentration of the anion in titration experiment was varied from $2.5 \times 10^{-5}$ M to $5.0 \times 10^{-3}$ M. The association constants were determined as described earlier.[33]

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