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ORIGINAL ARTICLE

Synthesis and inclusion properties of a novel double thiacalix[4]arene having (*N,N*-diethylaminocarbonyl)methoxy groups

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Abstract A novel double thicalix[4]arene possessing two amide sites was prepared. The binding behavior with Ag^+ has been examined by ^1H NMR titration experiment. The association constants K_{ass} of the amide sites are quite similar ($K_{ass} = 2.10 \times 10^4$ M^{-1} and $K_{ass} = 2.00 \times 10^4$ M^{-1}), suggesting that the two amide sites work independently.

Keywords Thiacalix[4]arene · *O*-Alkylation · Double calix[4]arene · Conformation · Ionophores · Metal complexation

Introduction

A few groups have been devoting their research efforts towards the molecular designing of higher-order supramolecular systems containing more than one calix[n]arene. For example, Böhmer et al. [1] and Arduini et al. [2] synthesized a few biscalix[4]arenes in which the upper edges confront each other. Ikeda et al. synthesized a multiple calix[4]arene tube which shows a very interesting complexation behavior toward Ag^+ ion [3a]. Ohseto et al. reported a biscalix[4]arene doubly-bridged with oxyethylene chains at the lower rim [3b]. McKervey et al. [4] synthesized a double calix[4]arene in which two calixa[4]arenes are linked by a single chain. Reinhoudt et al. showed the synthesis of ''giant cavities'' consisting of two calix[4]arenes and two calix[4]resorcin- arenes. Asfari et al. [5] succeeded in the isolation of double calix[4]arenes with a 1,3-*alternate* conformation.

Recently Beer et al. reported the synthesis of calix[4]tube base on biscalix[4]arenes which displays exceptional selectivity for potassium over all other group I and II metals but with slow complexation kinetics [6a]. Less rigid ionophores, the calix[4]semitubes, have shown much faster complexation kinetics [6b]. Their complexation behaviors were studied by means of molecular dynamic simulations. These systems have been extended to thiacalix[4]arene which provides a cavity of slightly larger dimensions and may lead to an ionophore with new metal coordination properties. Matthews et al. [7] reported a thiacalix[4]arene dimer, in cone conformation, linked via four ethylene units. However, its arrangement is very rigid reducing its binding ability. On the other hand, Kim et al. [8] reported the synthesis of thiacalix[4]crown trimer linked via oligoethylene glycol units. Recently, Csokai et al. [9a–c] reported the synthesis of thiacalix[4]arene dimers linked by diethylene glycol units under Mitsunobu protocol. Jin et al. [9d] linked two thiacalix[4]arene units by using 2,6-bis(bromomethyl)-4-methylanisole. A number of approaches were carried out in order to synthesis double thiacalix[4]arenes. On the other hand, several groups have demonstrated that calix[4]arene amide derivatives due to their high ionophilicity serve as neutral ionophores [5, 6a, 10, 11].

We report herein the synthesis of the novel double thiacalix[4]arene receptor **3**, in 1,3-*alternate* conformation, having amide moieties as complexation sides. Preliminary studies of complexition behavior of receptor **3** toward Ag^+ ion were carried out due to the

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well known high affinity of amides moieties for such a cation.

Results and discussion

The starting compound, *distal*-5,11,17,23-tetra-*tert*-butyl-25,27-bis-[(*N*,*N*-diethylaminocarbonyl)methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]-arene (*distal*-**1**) was prepared by *O*-alkylation of 5,11,17,23-tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]arene-25,26,27,28-tetraol with *N*,*N*-diethylchloroacetamide in the presence of K_2CO_3 under acetone reflux in 53% yield by according to the reported procedure [12]. The reaction of *distal*-**1** with 2 equiv. of 1,3-dibromopropane in the presence of 2 equiv. of K_2CO_3 or Cs_2CO_3 in acetone under reflux afforded no cyclic products [9, 12] or double thiacalix[4]arene but the compound 1,3-*alternate*-di-[(3-bromopropyl)oxy]thiacalix[4]arene 1,3-*alternate*-**2** in 58 and 68% yields, respectively. However, a similar treatment was carried out in the presence of Na_2CO_3 only afforded the recovery of the starting compound. The same result was obtained in spite of increasing the amount of 1,3-dibromopropane to 10 equiv. Interestingly, when the reaction was carried out in the presence of K_2CO_3 under xylene reflux, the desired double thiacalix[4]arene **3** was obtained in 10% yield as shown in Table 1, run 4. In marked contrast, the reaction in the presence of Cs_2CO_3 under xylene reflux only afforded 1,3-*alternate*-**2**. The larger size of Cs^+ than that of K^+ and the steric hindrance of the *t*Bu groups might not permit the formation of the double thiacalix[4]arene **3**. Under similar reaction conditions in the presence of Na_2CO_3 only a mixture of intractable products was obtained.

Table 1 Product formation in the reaction of *distal*-**1** with 1,3-dibromopropane

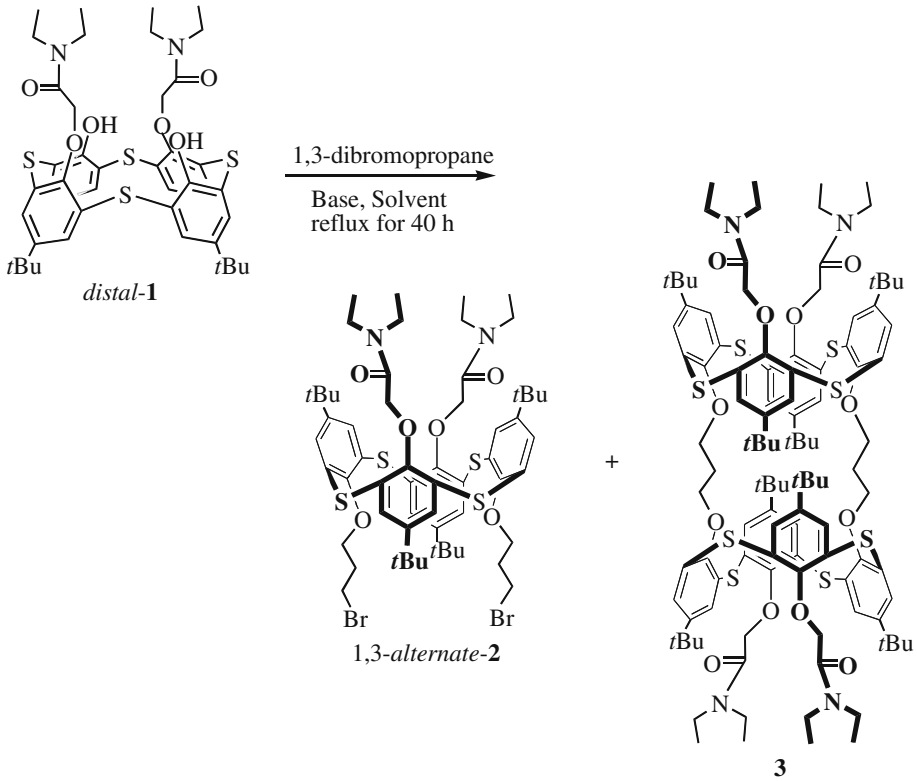
Run	Base	Equiv. of $BrCH_2CH_2CH_2Br$	Solvent	Yield (%)[a] 1,3-*alternate*-**2**	**3**
1	Na_2CO_3[b]	2	Acetone	0	0
2	Na_2CO_3[b]	10	Acetone	0	0
3	K_2CO_3	2	Acetone	58	0
4	K_2CO_3	2	Xylene	30	10
5	Cs_2CO_3	2	Acetone	68	0
6	Cs_2CO_3	2	Xylene	66	0

[a] Isolated yields are shown

[b] The starting compound *distal*-**1** was recovered in quantitative yield

The structure of **2** was reasonably assigned to 1,3-*alternate* on the basis of the chemical shifts of the CH_2CONEt_2 protons and the *t*Bu protons in ^1H NMR spectroscopy [13, 14]. Especially, a singlet signal of the methylene protons of the CH_2CONEt_2 in 1,3-*alternate*-

Scheme 1



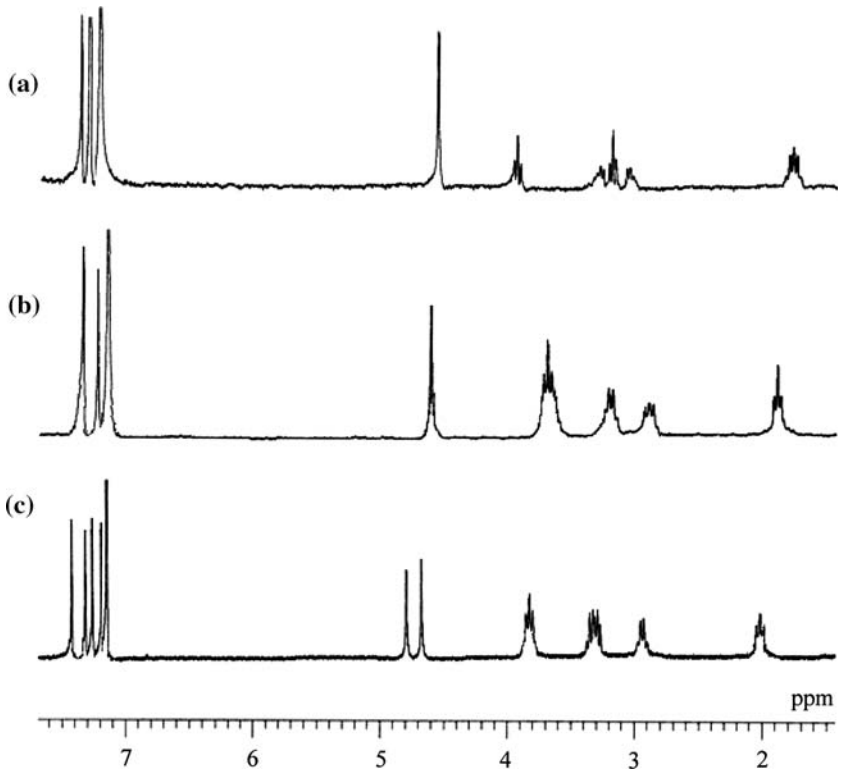


Fig. 1 Partial ^{1}H NMR spectra (300 MHz in $CDCl_3$). (**a**) 1,3-*alternate*-**2**, (**b**) double thiacalix[4]arene **3**, (**c**) 1:1 **3** ⊃ Ag^+ complex

2 was observed at higher field (δ 4.57 ppm) due to the ring current effect arising from the two inverted calixarene benzene rings.

The ^{1}H NMR spectrum of **3** is very simple and symmetrical, showing resonances for the *t*Bu protons at δ 1.16 and 1.19 ppm as singlets in the ratio of 1:1, for the methylene protons at δ 4.61 as a singlet, and for the aromatic protons at δ 7.22 and 7.36 ppm as singlets indicating that the conformation of each thiacalix[4]arene units is 1,3-*alternate*. The presence of a large singlet of 8 protons of the CH_2 at δ 3.69 ppm together with the absence of the signal at δ 3.21 in ^{1}H NMR spectrum strongly suggests the existence of double thiacalix[4]arene **3**, Fig. 1b. The mass spectral data for **3** (M^+ = 1974.90) also strongly supports the dimeric structure.

Complexation studies

The 1,3-*alternate* conformation of each thiacalix[4]arene units is suitable for the formation of 1:1 and 1:2 complex. Besides a high affinity of **3** toward Ag^+ ion, it is expected that the presence of the tertiary amides in the opposite side of the internal cavity of the thiacalix[4]arene should affect partially or totally the preorganization of **3** upon complexation (Fig. 2).

The stoichiometries of 1,3-*alternate*-**2** and **3** complexes with Ag^+ were determined by a two phase-extraction experiment (H_2O/CH_2Cl_2), using the continuous variation method. The percent extractions for 1,3-*alternate*-**2**- and **3**-Ag^+ complexes (Job plots) support the formation of 1:1 and 1:2 complex, respectively, the fact also confirmed by ^{1}H NMR.

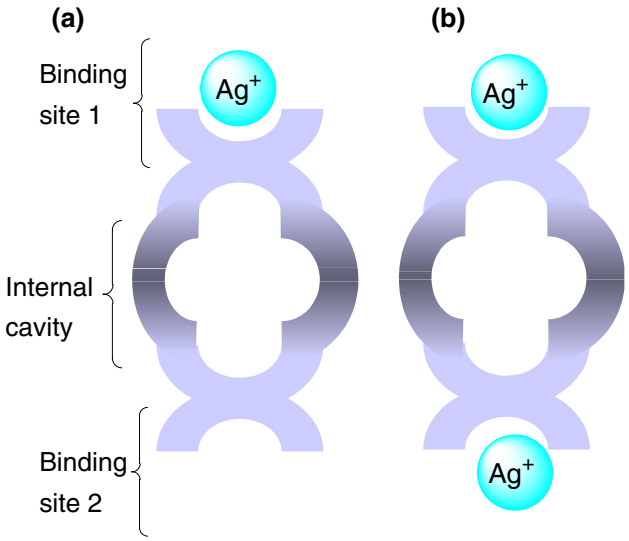


Fig. 2 Schematic representation of **3** and its complexes with Ag^+ (**a**) 1:1 complex, (**b**) 1:2 complex

Titration ^{1}H NMR studies of 1,3-*alternate*-**2** with an equiv. of $AgSO_3CF_3$ new peaks appeared. The chemical shifts of the amide protons were the most affected

(1,3-*alternate*-**2** ⊃ Ag^+; $K_{ass} = 2.14 \times 10^4$ M^{-1}), indicating the cation complex in the amide site [14a] and the formation of 1:1 complex. Addition of an equiv. of $AgSO_3CF_3$ into **3** caused the appearance of new peaks and similar chemical shift changes. The addition of an extra equiv. of Ag^+ ion into the solution containing the 1:1 complex of 1,3-*alternate*-**2**, afforded negligible chemical shift in the spectrum of 1,3-*alternate*-**2** ⊃ Ag^+ complex. In contrast, new signals were observed in the spectrum of **3** ⊃ Ag^+ caused by the formation of Ag^+⊂ **3** ⊃ Ag^+ complex. The total simplification of the spectrum of the 1:2 complex, due to the symetrization of the **3**, took a day. The value of the association constants K_{ass} for the 1:1 and 1:2 complexes of **3** are quite similar ($K_{ass1} = 2.10 \times 10^4$ M^{-1} and $K_{ass2} = 2.00 \times 10^4$ M^{-1}), suggesting that the two amide sites work independently. Contrary to our expectation, each thiacalix[4]arene unit formed only 1:1 complex. The signals belong to internal cavity composed by the 1,3-propylene units scarcely shifted which indicates not only this cavity is not suitable for complex formation with Ag^+ but also the preorganization of **3** upon complexation slightly changed upon complexation of Ag^+ by the amide sites.

Conclusion

Treatment of *distal*-**1** with 1,3-dibromopropane in xylene in the presence of K_2CO_3 afforded a novel double thiacalix[4]arene **3** possessing amide moieties at one edge of each thiacalix[4]arene unit, for which the calixarene unit adopts the 1,3-*alternate* conformation. The formation of 1:1 and 1:2 complexes of **3** with Ag^+ ion was observed. The original C_{2V}-symmetry has been remained after complexation of **3** with Ag^+. The formation of 1:2 complex of **3** with Ag^+ ion indicates the 1,3-propylene linked does not affect the binding ability of the amide moieties. Now we are studying the modification of the length of linked group between the calixarene units and their complex formation toward different cations.

Experimental

All mps (Yanagimoto MP-S_1) are uncorrected. ^{1}H NMR spectra were determined 300 MHz with a Nippon Denshi JEOL FT-300 NMR spectrometer with $SiMe_4$ as an internal reference: *J*-values are given in Hz. IR spectra were measured for samples as KBr pellets in a Nippon Denshi JIR-AQ2OM spectrophotometer. UV spectra were measured by Shimadzu 240 spectrophotometer. Elemental analyses were performed by Yanaco MT-5.

Materials

5,11,17,23-Tetra-*tert*-butyl-2,8,14,20-tetrathiacalix[4]-arene-25,26,27,28-tetraol [15] and *distal*-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(*N,N*-diethylaminocarbonyl) methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene *distal*-**1** were prepared according to the reported procedure [14b].

*O-Alkylation of distal-***1** *with 1,3-dibromopropane in the presence of K_2CO_3 in acetone*

A mixture of *distal*-5,11,17,23-tetra-*tert*-butyl-25,27-bis[(*N,N*-diethylaminocarbonyl) methoxy]-26,28-dihydroxy-2,8,14,20-tetrathiacalix[4]arene *distal*-**1** (100 mg, 0.106 mmol), K_2CO_3 (29 mg, 0.21 mmol) in dry acetone (30 mL) was refluxed for 1 h under nitrogen. Then a solution of 1,3-dibromopropane (42 mg, 0.21 mmol) in acetone (5 mL) was added at room temperature. The mixture was refluxed for 40 h under argon, cooled at room temperature and concentrated under reduced pressure. The residue was dissolved in dichlormethane (2 × 15 mL), washed with 1 N HCl. The organic layer was separated, washed with brine (2 × 15 mL) and dried over $MgSO_4$. After filtration, the solvent was evaporated to dryness to obtained crude product, which was subjected to column chromatography (silica gel, 1:1 hexane–chloroform) to give a pure compound 1,3-*alternate*-**2** (72 mg, 58%) as colorless prisms. Mp 201–204 °C. IR *v* (KBr)/cm^{-1} 1666 (C=O). ^{1}H NMR δ ($CDCl_3$) 0.84 (6H, m, NCH_2CH_3), 1.09 (6H, m, NCH_2CH_3), 1.20 (18H, s, *t*-Bu), 1.30 (18H, s, *t*-Bu), 1.78 (4H, m, $CH_2CH_2CH_2$), 3.05 (4H, m, NCH_2CH_3), 3.21 (4H, t, *J* = 7.0, $CH_2CH_2CH_2Br$), 3.28 (4H, m, NCH_2CH_3), 3.93 (4H, t, *J* = 7.0, $CH_2CH_2CH_2Br$), 4.57 (4H, s, CH_2CO), 7.31 (4H, s, Ar-*H*), 7.37 (4H, s, Ar-*H*). MS *m/z* 1186.33 (M^+). Anal. Calcd. For $C_{58}H_{80}Br_2N_2O_6S_4$ (1189.32): C, 58.57; H, 6.78. Found: C, 58.55; H, 6.76%.

*O-Alkylation of distal-***1** *with 1,3-dibromopropane in the presence of K_2CO_3 in xylene*

A mixture of *distal*-**1** (200 mg, 0.21 mmol), K_2CO_3 (58 mg, 0.42 mmol) in dry xylene (35 ml) was refluxed for 1 h under nitrogen. Then a solution of 1,3-dibromopropane (44 mg, 0.42 mmol) in xylene (10 ml) was added at room temperature. The mixture was refluxed for 40 h under argon, cooled at room temperature and concentrated under reduced pressure. The residue was dissolved in dichlormethane (2 × 30 ml), washed with 1 N HCl. The organic layer

was separated and dried over $MgSO_4$ anhydrous. After filtration, the solvent was evaporated to dryness to obtained crude product, which was triturated with MeOH to give **3** (41 mg, 10%) as a colorless solid. Recrystallization from $CHCl_3$–MeOH (3:1) afforded **3** as colorless prisms. Mp 289–292 °C. IR ν (KBr)/cm^{-1} 1664 (C=O). ^{1}H NMR δ ($CDCl_3$) 0.87 (12H, t, J = 7.0, NCH_2CH_3), 0.98 (12H, t, J = 7.0, NCH_2CH_3), 1.16 (36H, s, *t*Bu), 1.19 (36H, s, *t*Bu), 1.89 (4H, s, $CH_2CH_2CH_2$), 2.91 (8H, q, J = 7.0, NCH_2CH_3), 3.23 (8H, q, J = 7.0, NCH_2CH_3), 3.69 (8H, t, J = 7.0, $CH_2CH_2CH_2$), 4.61 (8H, s, CH_2CO), 7.22 (8H, s, Ar-*H*), 7.36 (8H, s, Ar-*H*). MS *m/z* 1974.90 (M^+). Anal. Calcd. For $C_{110}H_{148}N_4O_{12}S_8$ (1974.90): C, 66.90; H, 7.55. Found: C, 66.49; H, 7.50%.

^{1}H NMR Complexation experiments

To a $CDCl_3$ solution (4×10^{-3} M) of **3** in the NMR tube was added 1–2 molar solution of $AgSO_3CF_3$. The spectrum was measured after addition and the temperature of NMR probe kept constant at 27 °C. The ^{1}H NMR data of the complexes is given below.

3⊃Ag^+: δ_H ($CDCl_3$) 0.88 (6H, t, J = 7.0, NCH_2CH_3), 0.92 (6H, t, J = 7.0, NCH_2CH_3), 0.96 (6H, t, J = 7.0, NCH_2CH_3), 0.99 (6H, t, J = 7.0, NCH_2CH_3), 1.15 (18H, s, *t*-Bu), 1.17 (18H, s, *t*-Bu), 1.21 (18H, s, *t*-Bu), 1.23 (18H, s, *t*-Bu), 2.00 (4H, s, $CH_2CH_2CH_2$), 2.95 (8H, q, J = 7.0, NCH_2CH_3), 3.31 (8H, m, NCH_2CH_3), 3.82 (8H, t, J = 7.0, $CH_2CH_2CH_2$), 4.69 (4H, s, CH_2CO), 4.81 (4H, s, CH_2CO), 7.20 (4H, s, Ar-*H*), 7.28 (4H, s, Ar-*H*), 7.31 (4H, s, Ar-*H*), 7.42 (4H, s, Ar-*H*).

Ag^+⊂**3**⊃Ag^+: δ_H ($CDCl_3$) 0.90 (12H, t, J = 7.0, NCH_2CH_3), 0.10 (12H, t, J = 7.0, NCH_2CH_3), 1.18 (36H, s, *t*-Bu), 1.22 (36H, s, *t*-Bu), 2.04 (4H, s, $CH_2CH_2CH_2$), 3.10 (8H, q, J = 7.0, NCH_2CH_3), 3.51 (8H, q, J = 7.0, NCH_2CH_3), 3.87 (8H, t, J = 7.0, $CH_2CH_2CH_2$), 4.95 (8H, s, CH_2CO), 7.22 (8H, s, Ar-*H*), 7.36 (8H, s, Ar-*H*).

Stoichiometry of metal complexation

The method of continuous variation [16] was employed to determine the stoichiometry of 1,3-*alternate*-**2** and **3** complexes. Two-phase solvent extraction was carried out between aqueous picrates (5 mL, [metal picrate] = 2×10^{-4} M, $AgNO_3$) and **3** (5 mL, [**3**] = 2×10^{-4} M in CH_2Cl_2). The molar ratios of the both **3** and metal picrate were varied from 0 to 1, while the total concentration was kept at several constant levels. The two-phase mixture in a glass tube immersed in a thermostated water bath at 25 °C was shaken at 300 strokes per min for 1 h and then kept, at the same temperature, for 2 h, allowing the complete separation of the two phases. The absorbance of each solution was determined by UV spectroscopy (λ = 290 nm). Job plots were generated by plotting the extracted [Ag^+] versus the mole fraction of metal.

Determination of association constants

^{1}H NMR Titrations. Solutions of the receptor 1,3-*alternate*-**2** and **3** were prepared at a concentration typically on the order of 0.01 mol dm^{-3} in $CDCl_3$. The initial ^{1}H NMR spectrum was recorded, and aliquots of cation ($AgSO_3CF_3$), in the same solvent, were added by a microsyringe from a solution made such that from 1 molar equiv to 2 molar equiv were added in 20 µl. The association constant values were calculated by the integral intensity of CH_2CON methylene protons in the complex and free host molecules.

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References

1. Böhmer, V., Goldmann, H., Vogt, W., Vicens, J., Asfari, Z.: The synthesis of double-calixarenes. Tetrahedron Lett.. **30**, 1391–1394, (1989)
2. Arduini, A., Manfredi, G., Pochini, A., Sicuri, A.R., Ungaro, R.: Selective formylation of calix[4]arenes at the 'upper rim' and synthesis of new cavitands. J. Chem. Soc., Chem. Commun. 936–937 (1991)
3. (a) Ikeda, A., Shinkai, S.: Multiple connection of 1,3-alternate-calix[4]arenes. An approach to synthetic 'nano-tubes'. J. Chem. Soc., Chem. Commun. 2375–2376 (1994); (b) Ohseto, F., Shinkai, S.: Syntheses of and metal cation oscillation in ionophoric biscalix[4]arenes. J. Chem. Soc. Perkin Trans. 2. 1103–1109 (1995)
4. McKervey, M.A., Owens, M., Schulten, H.R., Vogt, W., Böhmer, V.: A new type of double calix[4]arenes by linkage via the phenolic Hydroxy groups. Angew. Chem. Int. Ed. Engl. **29**, 280–282 (1990)
5. Asfari, Z., Abidi, R., Arnaud, F., Vicens, J.: Synthesis and complexing properties of a double-calix[4]arene crown ether. J. Inc. Phenom. **13**, 163–169 (1992)
6. (a) Matthews, S.E., Schmitt, P., Felix, V., Drew, M.G.B., Beer, P.D.: Calix[4]tubes: A new Class of Potassium-Selective Ionophore. J. Am. Chem. Soc. **124**, 1341–1353 (2002); (b) Felix, V., Matthews, S.E., Beer, P.D., Drew, M.G.B.: Selectivity of calix[4]tubes towards metal ions: A molecular dynamics study. Phys. Chem. Chem. Phys. **4**, 3849–3858 (2002); (c) Webber, P.R.A., Beer, P.D., Chen, G.Z., Felix, V., Drew, M.G.B.: Bis(calix[4]diquinone) Receptors: Cesiumand Rubidium-Selective Redox-Active Ionophores. J. Am. Chem. Soc. **125**, 5774–5785 (2003). (d) Webber, P.R.A., Cowley, A., Drew, M.G.B., Beer, P.D.: Potassium Selective Calix[4]semitubes. J. Chem. Eur. 2439–2446 (2003)
7. Matthews, S.E., Felix, V., Drew, M.G.B., Beer, P.D.: Thiacalix[4]tube: synthesis, X-ray crystal structure and

preliminary binding studies. New J. Chem. **25**, 1355–1358 (2001)
8. Kim, S.K., Lee, J.K., Lee, S.H., Lim, M.S., Lee, S.W., Sim, W., Kim, J.S.: Silver ion shuttling in the Trimer-Mimic Thiacalix[4]crown tube. J. Org. Chem. **69**, 2877–2880 (2004)
9. (a) Csokai, V., Grun, A., Balázs, B., Toth, G., Horváth, G., Bitter, I.: Unprecedented cyclizations of Calix[4]arenes with glycols under the Mitsunobu protocol, Part 2. O,O-and O,S-Bridged Calixarenes. Org. Lett. **6**, 477–480 (2004); (b) Csokai, V., Balázs, B., Toth, G., Horváth, G., Bitter, I.: Unprecedented cyclisations of calix[4]arenes under the Mitsunobu protocol. Part 3: Thiacalix[4]crowns versus dimmers. Tetrahedron **60**, 12059–12066 (2004); (c) Csokai, V., Grün, A., Bitter, I.: Unprecedented cyclisations of calix[4]-arenes with glycols under the Mitsunobu protocol. Part 1: A new perspective for the synthesis of calixcrowns. Tetrahedron Lett. **44**, 4681–4684 (2003); (d) Jin, Y., Liu, Q., Gong, S., Chen, Y.: An Approach to Double Thiacalixarene. Synth. Commun. **35**, 589–593 (2005)
10. (a) Arduini, A., Ghidini, E., Pochini, A., Ungaro, R., Andreetti, G.D., Calestani, G., Ugozzoli, F.: *p-t*-Butylcalix[4]arene tetraacetamide: a new strong receptor for alkali cations [1]. J. Incl. Phenom. **6**, 119–134 (1988); (b) Matsumoto, H., Nishino, S., Takeshita, M., Shinkai, S.: Synthesis and ion selectivities of triamide derivatives of Hexahomotrioxacalix[3]arene. Remarkably large metal template effect on the ratio of cone vs. partial-cone conformers. Tetrahedron **51**, 4647–4654 (1995); (c) Wolf, N.J., Georgiev, E.M., Yordanov, A.T., Whittlesey, B.R., Kock, H.F., Roundhill, D.M.: Synthesis and crystal structures of lower rim amine and carbamoyl substituted calixarenes as transfer agents for oxyanions between an aqueous and a chloroform phase. Polyhedron **18**, 885–896 (1999)
11. Sabbatinim, N., Guardigli, M., Mecati, A., Balzani, V., Ungaro, R., Ghidini, E., Casnati, A., Pochini, A.: Encapsulation of lanthanide ions in calixarene receptors. A strongly luminescent terbium(3+) complex. J. Chem. Soc., Chem. Commun. 878–879 (1990)
12. Akdas, H., Bringel, L., Bulach, V., Graf, E., Hosseini, M.W., De Cian, A.: Molecular baskets based on tetramercaptotetrathiacalix[4]arene and tetrathiacalix[4]arene. Tetrahedron Lett. **43**, 8975–8979 (2002)
13. (a) Iki, N., Marumi, F., Fujimoto, T., Morohashi, N., Miyano, S.: Selective synthesis of three conformational isomers of tetrakis[(ethoxycarbonyl)methoxy]thiacalix[4]arene and their complexation properties towards alkali metal ions. J. Chem. Soc. Perkin Trans. **2**, 2745–2750 (1998); (b) Lang, J., Vlach, J., Dvorakova, H., Lhotak, P., Himl, M., Habal, R., Stibor, I.: Thermal isomerisation of 25,26,27,28-tetrapropoxy-2,8,14,20-tetrathiacalix[4]arene: isolation of all four conformers. J. Chem. Soc. Perkin Trans. **2**, 576–580 (2001)
14. (a) Pérez-Casas, C., Yamato, T.: Hard-soft receptors, tetrakis[(N,N-diethylaminocarbonyl)methoxy] thiacalix[4]arene derivatives with cone and 1,3-alternate conformation. J. Incl. Phenom. **53**, 1–8 (2005); (b) Yamato, T., Pérez-Casas, C., Rahman, S., Tae-Gil, J., Elsegood, M.R.J., Redshaw, C.: Synthesis, structures and inclusion properties of distal-bis[(2-pyridylmethyl)oxy]tetrathiacalix[4]arenes. J. Chem. Res., 270–273 (2006)
15. (a) Kumagai, J., Hasegawa, M., Miyanari, S., Sugawa, Y., Sato, Y., Hori, T., Ueda, S., Kamiyama, H., Miyano, S.: Facile synthesis of *p-tert*-butylthiacalix[4]arene by the reaction of p-tert-butylphenol with elemental sulfur in the presence of a base. Tetrahedron Lett. **38**, 3971–3972 (1997); (b) Iki, N., Kabuto, C., Fukushima, T., Kumagai, H., Takeya, H., Miyanari, S., Miyashi, T., Miyano, S.: Synthesis of *p-tert*-Butylthiacalix[4]arene and its inclusion property. Tetrahedron **56**, 1437–1443 (2000)
16. Pedersen, C.J.: Cyclic polyethers and their complexes with metal salts. J. Am. Chem. Soc. **89**, 2495–2496 (1967)