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# Synthesis and binding studies of novel thiacalixpodands and bisthiacalixarenes having O,O″-dialkylated thiacalix[4]arene unit(s) of 1,3-alternate conformation

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**Abstract**—A series of thiacalixpodands and bisthiacalixarenes with imine units have been prepared by condensation of *O*,*O*″-bis(2-aminoethyl)-*O*′,*O*‴-dipropyl-*p*-*tert*-butylthiacalix[4]arene of 1,3-alternate conformation with different aromatic (di)aldehydes. The molecules derived from pyridine-2-carbaldehyde and -2,6-dicarbaldehyde quantitatively extract silver ion from aqueous into organic phase with complete selectivity over other metal ions ($Na^+$, $K^+$ and $Cs^+$) under neutral conditions. The former compound forms a 1:2 (L:M) complex with silver ion as proved by NMR spectroscopy, Job's plot and X-ray crystallography.


Calixarenes are one of the most important molecular scaffolds in host–guest supramolecular chemistry.[1] We reported a facile synthesis of thiacalix[4]arene[2] and developed its functions.[3] The presence of sulfur bridges in thiacalix[4]arene resulted in useful properties mostly unknown in the chemistry of classical calixarenes, such as excellent complexing ability towards the transition metal ions[4] in combination with the oxidation of the bridging units[5,6] and different conformational preferences.[7] On the other hand, the strong anti-bacterial activity of the silver ion has been the subject of much interest for the preparation of bio-active materials such as deodorizing clothes and agricultural sterilizing agent. Recently, we prepared a series of bisthiacalix[4]arenes (e.g., **1**) with diimine linkages by condensation of *O*,*O*″-bis(2-aminoethyl)-*p*-*tert*-butylthiacalix[4]arene[8] with aromatic dialdehydes. The bisthiacalixarenes quantitatively extracted silver ion with complete selectivity over other metal ions ($Na^+$, $K^+$ and $Cs^+$) under biologically important neutral conditions regardless of the linking moiety.[9] It was found that they bound a silver ion by an imino nitrogen and a bridging sulfur atom, presumably with the assistance of an adjacent hydroxy oxygen, and that a proper preorganization of these soft binding sites by the restricted cyclic structure of the bisthiacalixarene was necessary for the complexation.[9] In continuation of our research for improving the recognition ability of calixarene-based host molecules for soft metal ions,[9,10] we intended to change the coordination environment by employing *O*,*O*″-bis(2-aminoethyl)-*O*′,*O*‴-dipropyl-*p*-*tert*-butylthiacalix[4]arene **4** of 1,3-alternate conformation as a molecular scaffold for the preparation of thiacalix[4]arene podands **7a**–**c**, as well as bisthiacalix[4]arenes **10a**–**c**. Preliminary studies on the complexation abilities of these host molecules have shown that the modification actually changes the coordination sites and that thiacalixpodand **7a** selectivity and quantitatively extracts silver ion under neutral conditions for the first time as a monocalixarene. Although Kim et al. reported trimeric calix-thiacalix[4]crowns[11] of 1,3-alternate conformation, which extracted silver ion with poor selectivity over sodium and potassium ions, this type of host molecules with imine units at the lower rim have not so far been reported.

*Keywords*: Calixpodand; Bisthiacalixarene; Complexation; Solvent extraction.
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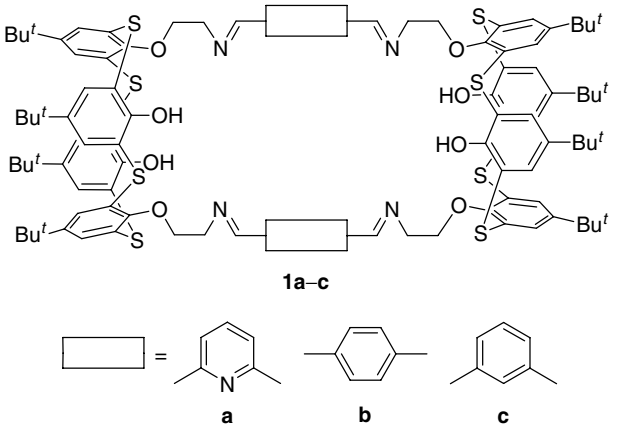
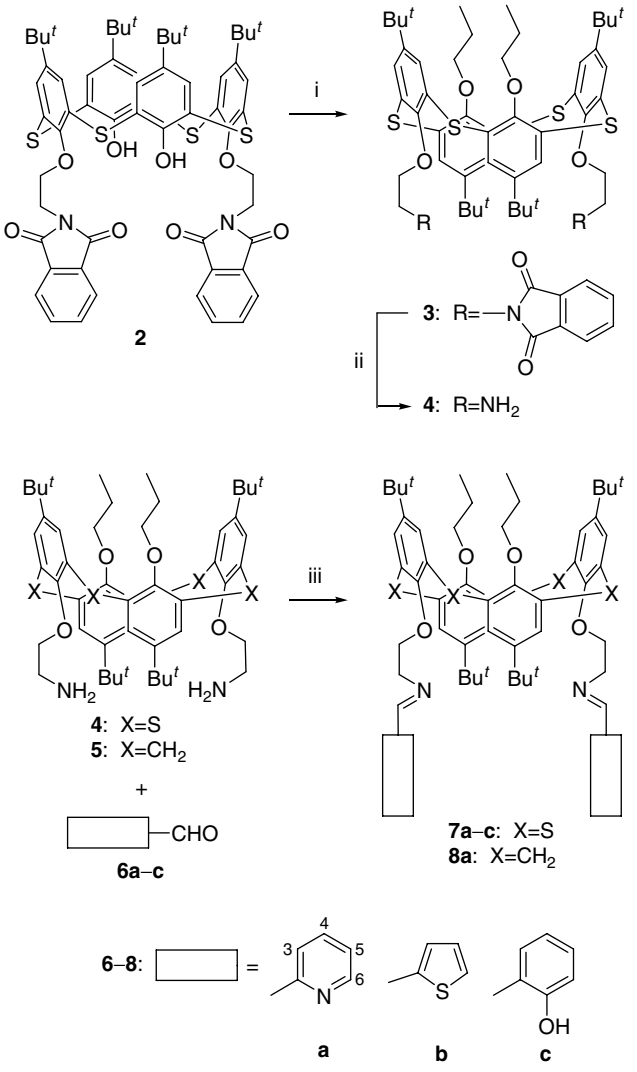


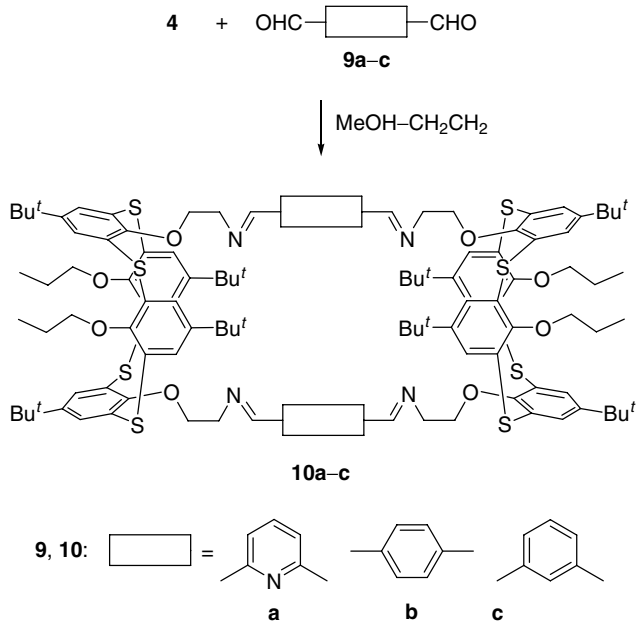

Thiacalixpodands **7a–c** were prepared from a known precursor **2**[8] as shown in Scheme 1. Treatment of compound **2** with propanol under Mitsunubo conditions[12] using diethyl azodicarboxylate (DEAD) and triphenylphosphine in THF gave dipropyl ether **3** in 90% yield. The hydrazinolysis of compound **3** in ethanol gave diamine **4** in 80% yield.[13] The 1,3-alternate conformation of both compounds **3** and **4** was deduced from an X-ray crystallographic analysis of a silver complex of thiacalixpodand **7a** prepared from compound **4** (vide infra). Condensation of diamine **4** with 2.0 mol equiv of dialdehydes **6a–c** in a mixture of refluxing dichloromethane and methanol (1:1) gave thiacalixpodands **7a–c** in high yields.[14] The products were virtually insoluble in the mixed solvent to separate out as pure solids, which gave satisfactory elemental analysis after one recrystallization from chloroform and methanol (9:1). Using the same procedure, we prepared calixpodand **8a** with a conventional calix[4]arene unit by condensing **5** with **6a**. Bisthiacalix[4]arenes **10a–c** were also prepared by condensation of diamine **4** with 1.0 mol equiv of dialdehydes **9a–c** (Scheme 2).[15] The structures of calixpodands **7a–c** and **8a** and bisthiacalixarenes **10a–c** were confirmed from their spectroscopic and analytical data. The IR spectra of **7a–c**, **8a** and **10a–c** showed a C=N stretching band at 1634–1645 $cm^{-1}$ and no absorption bands characteristic to free formyl and amino groups, indicating that the condensation had taken place. This was confirmed by the FAB mass spectra that showed a parent ion peak corresponding to the 1:2 or 2:2 condensation products.

To evaluate the binding ability of these host molecules towards different metal ions, two-phase solvent extraction of metal picrates ($Na^+$, $K^+$, $Cs^+$ and $Ag^+$) was carried out. A chloroform solution of an extractant (0.1 mM) was equilibrated with an aqueous solution of a metal picrate (0.1 mM) under neutral conditions. The ion extractability ($E$) was calculated from the picrate concentration in the organic phase, which was determined by UV spectroscopy. The results are summarized in Figure 1. Bisthiacalixarene **10a** having a pyridine-2,6-diyl group on the linking moiety quantitatively extracted silver ion with complete selectivity over other metal ions, while the other bisthiacalixarenes **10b** and **10c** did not extract any of the metal ions examined. This observation, combined with the fact that bisthiacalixarenes **1a–c** with free hydroxy groups on the thiacalixarene unit extracted silver ion regardless of the linking moiety,[9] indicates that the coordination environment has changed by the etherification of the hydroxy groups and that the heteroatom on the aromatic ring of the linking moiety is important for binding silver ion. This is also the case for the thiacalixpodands. Thiacalixpodands **7a–c** selectively extracted silver ion with different efficiencies depending on the side chain, the extractability being 100%, 29% and 4% for **7a**, **7b** and **7c**, respectively. It should be noted that non-O-propylated counterpart of **7b** did not extract any of the metal ions under the same conditions.[9] A comparison of the binding ability of thiacalixpodand **7a** with that of calixpodand **8a** shows that the presence of the bridging sulfur atoms is also important both for the metal selectivity and the extractability (Fig. 1).




**Scheme 1.** Reagents: (i) PrOH, DEAD, $PPh_3$, THF; (ii) $H_2NNH_2 \cdot H_2O$, EtOH; (iii) $MeOH–CH_2Cl_2$.

To elucidate the binding mode of these host molecules with silver ion, the $^1H$ NMR spectra of their complexes were recorded. Addition of 1.0 mol equiv of silver triflate to thiacalixpodand **7a** did not cause the appearance




**Scheme 2.**

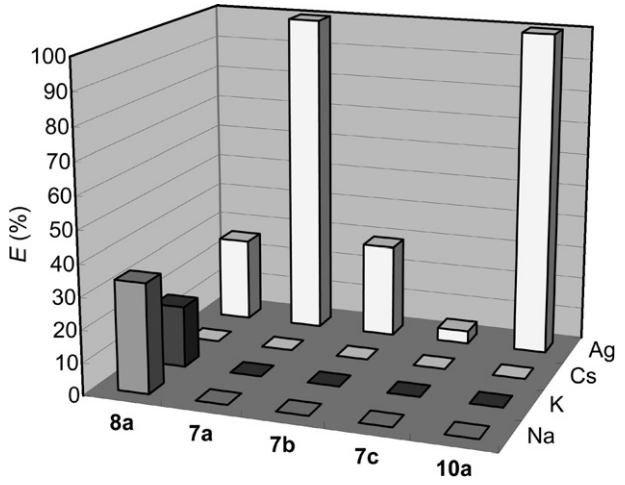



**Figure 1.** Extractability of metal picrates with host molecules **7a–c**, **8a** and **10**. Source phases: aqueous phase, 2 mL, [metal picrate] = 0.1 mM; organic phase, $CHCl_3$, 2 mL, [host] = 0.1 mM. The data are the average values of three independent runs.

of new signals but led to the distinct change in the chemical shifts to indicate fast metal exchange between complexed and uncomplexed species on the NMR time scale (Table 1). The signals of the H-5 and H-4 protons of the pyridine rings, the imino protons and $NCH_2$ protons shifted to lower fields by $\Delta\delta$ +0.30, +0.28, +0.12 and +0.11 ppm, respectively, suggesting that the host molecule bound silver triflate by an imino and pyridyl nitrogen, as well as a bridging sulfur atom (vide supra). On addition of another equiv of silver triflate, the signals of most of the protons moved downfield. This was attributed to conformational change of the thiacalixarene moiety rather than an electronic effect induced by the complexation. Thus, the two types of side chains seemingly moved away from the anisotropic shielding effects of the facing benzene rings. This is quite evident from the chemical shifts of the propoxy groups ($OCH_2$, $CH_2$, $CH_3$), which underwent a dramatic downfield shift by $\Delta\delta$ +0.58, +0.73 and +0.41 ppm, respectively. The $OCH_2$, $NCH_2$ and imino protons of the other side chains were also shifted downfield by $\Delta\delta$ +0.20, +0.66, +0.37 ppm, respectively. A Job's plot revealed that the stoichiometry of the complex was 1:2 (L:M) (Fig. 2). It should be noted that bisthiacalixarene **1b** forms a 1:1 complex with silver ion as evidenced by $^1$H NMR titration experiment.[9,16] This means that the O-propylation bore an efficient host which can accommodate quadruple amount of silver ions by a thiacalixarene unit as compared with bisthiacalixarene **1b**.[17] To our pleasure, recrystallization of a complex prepared from **7a** and 2.0 mol equiv of silver nitrate gave single crystals suitable for X-ray crystallographic analysis (Fig. 3).[18] The X-ray structure clearly showed that the two silver ions were trapped in the two compartments of **7a**, each being composed of two $sp^2$ nitrogen atoms of a side chain and an adjacent sulfur atom of the thiacalixarene, which well agreed with the structure in the solution deduced from the solvent extraction experiments and the $^1$H NMR analyses.

On addition of 1.0 mol equiv of silver triflate to **10a**, the signals of the imino protons and the H-3 and H-4 protons of pyridine rings were shifted downfield by $\Delta\delta$ 0.49, 0.55 and 0.30 ppm, respectively, indicating that the imino and pyridyl nitrogens were interacting with silver ion. However, the addition of 2.0 or more than 2.0 mol equiv of silver triflate caused a considerable broadening of the NMR spectrum and hence the stoichiometry of the silver complex of **10a** in the solution could not be determined. On the other hand, we observed a slow metal exchange between complexed and uncomplexed species on the addition of 0.5 mol equiv of silver triflate to **10a**, from which the association constant was calculated to be $5.66 \times 10^2\ M^{-1}$.

In conclusion, we prepared novel thiacalix[4]arene-based host molecules with imine units by condensation of O′,O‴-dipropylated *O*,*O*″-bis(2-aminoethyl)-*p*-*tert*-butylthiacalix[4]arene with aromatic (di)aldehydes. The

**Table 1.** Change in the chemical shifts of compound **7a** on complexation with silver triflate in $CDCl_3/CD_3OD$ (9:1)

| | Calixarene | | | | –$OCH_2CH_2N$=CH–pyridyl | | | | | | | –OPr | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ArH | ArH | $Bu^t$ | $Bu^t$ | $OCH_2$ | $NCH_2$ | CH=N | H-3 | H-4 | H-5 | H-6 | $OCH_2$ | $CH_2$ | $CH_3$ |
| **7a** | 7.33 | 7.47 | 1.26 | 1.28 | 3.86 | 3.34 | 8.30 | 7.97 | 7.76 | 7.35 | 8.60 | 4.22 | 1.11 | 0.65 |
| **7a** + Ag | 7.27 | 7.38 | 0.99 | 1.26 | 3.80 | 3.45 | 8.42 | 7.78 | 8.04 | 7.65 | 8.59 | 4.20 | 1.08 | 0.65 |
| $\Delta\delta$ | −0.06 | −0.09 | −0.27 | −0.02 | −0.06 | +0.11 | +0.12 | −0.19 | +0.28 | +0.30 | −0.01 | −0.02 | −0.03 | 0.00 |
| **7a** + 2Ag | 7.60 | 7.62 | 1.04 | 1.27 | 4.06 | 4.00 | 8.67 | 7.78 | 8.07 | 7.67 | 8.80 | 4.80 | 1.84 | 1.06 |
| $\Delta\delta$ | +0.27 | 0.15 | −0.22 | −0.01 | +0.20 | +0.66 | +0.37 | −0.19 | +0.31 | +0.32 | +0.20 | +0.58 | +0.73 | +0.41 |

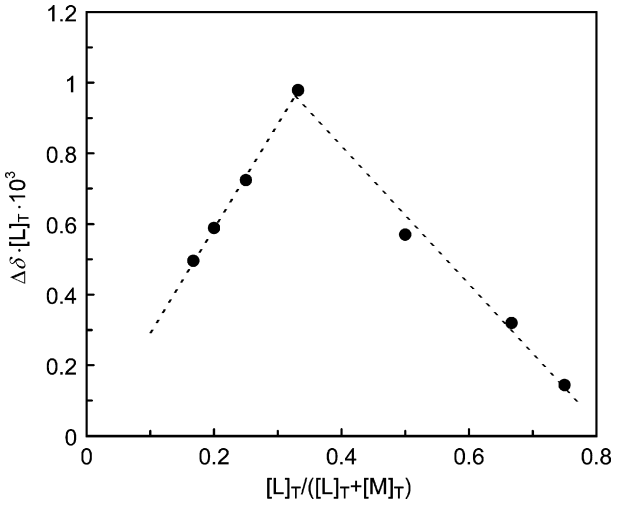



**Figure 2.** Job's plot of compound **7a** with $Ag^{+}$. The sum of total concentration $[L]_T + [M]_T$ was $8.0 \times 10^{-3}$ M in $CDCl_3/CD_3OD$ (9:1). $\Delta\delta$ denotes change in chemical shift of the imino protons of **7a** upon complexation with silver triflate.

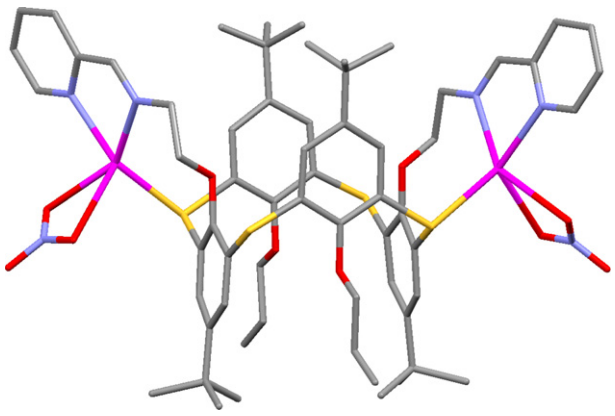


**Figure 3.** X-ray structure of a silver complex prepared from **7a** and 2.0 mol equiv of silver nitrate. Hydrogen atoms are omitted for clarity.

solvent extraction experiments showed that thiacalixpodand **7a** and bisthiacalixarene **10a** with pyridine units quantitatively extracted silver ion with a complete selectivity over the other metal ions. The complexation experiments, together with the comparison of the binding ability among different host molecules, suggested that thiacalixpodand **7a** ligated to a silver ion by the imino and pyridyl nitrogen of a side chain with the assistance of an adjacent bridging sulfur atom, the stoichiometry of the complex being 1:2 (L:M). These structural features of the silver complex in the solution well agreed with those in the crystal proved by an X-ray analysis.

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12. *Preparation of dipropyl ether* **3**: To a mixture of compound **2** (1.07 g, 1.00 mmol), propanol (0.79 mL, $d = 0.80$ g mL$^{-1}$, 11 mmol), triphenylphosphine (1.16 g, 4.42 mmol) in dry THF (70 mL) was added dropwise in 40% solution of DEAD in toluene (1.80 g, 4.13 mmol). The mixture was stirred for 48 h and then the solvent was removed under reduced pressure to leave a residue, which was crystallized from methanol to give dipropyl ether **3** in 90% yield, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.69 (t, $J = 7.6$ Hz, 6H, $CH_3$), 1.12–1.18 (m, 4H, $CH_2$), 1.24 (s, 18H, $C(CH_3)_3$), 1.37 (s, 18H, $C(CH_3)_3$), 3.60 (t, $J = 8.0$ Hz, 4H, $NCH_2$), 3.87 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 4.13 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 7.35 (s, 4H, ArH), 7.73 (s, 4H, ArH), 7.62–7.69 (m, 4H, Phth), 7.83–7.86 (m, 4H, Phth); FAB-MS $m/z$ 1150 ($M^+$).
13. *Preparation of diamine* **4**: A solution of compound **3** (1.15 g, 0.999 mmol) and hydrazine monohydrate (1.00 g, 20.0 mmol) in ethanol (20 mL) was refluxed for 24 h and then cooled. During this time, a solid was separated. It was filtered, dissolved in 20% ammonium hydroxide solution and extracted with chloroform. The chloroform layer was dried and distilled under reduced pressure to

give diamine **4** in 80% yield, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.63 (t, $J = 7.6$ Hz, 6H, $CH_3$), 0.86–0.92 (m, 4H, $CH_2$), 1.26 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 2.42 (t, $J = 5.2$ Hz, 4H, $NCH_2$), 3.74 (t, $J = 7.6$ Hz, 4H, $OCH_2$), 3.95 (t, $J = 5.2$ Hz, 4H, $OCH_2$), 7.29 (s, 4H, ArH), 7.36 (s, 4H, ArH); FAB-MS $m/z$ 890 [$(M)^+$].

14. *General procedure for the preparation of thiacalixpodands* **7a**–**c**: To a solution of diamine **4** (89.0 mg, 0.10 mmol) in a 1:1 mixture of dichloromethane and methanol (20 mL) was added a solution of aldehyde **6a**–**c** (0.20 mmol) in methanol (5.0 mL). The mixture was stirred for 2 days to separate a solid, which was filtered, washed and recrystallized from chloroform and methanol (9:1). Compound **7a**: Yield 75%, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.64 (t, $J = 7.6$ Hz, 6H, $CH_3$), 1.06–1.12 (m, 4H, $CH_2$), 1.26 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 3.29 (t, $J = 8.0$ Hz, 4H, $NCH_2$), 3.85 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 4.20 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 7.30 (s, 4H, ArH), 7.33 (t, $J = 8.0$ Hz, 2H, PyH), 7.46 (s, 4H, ArH), 7.72 (t, $J = 4.0$ Hz, 2H, PyH), 7.94 (d, $J = 8.0$ Hz, 2H, PyH), 8.29 (s, 2H, HC=N), 8.62 (d, $J = 4.0$ Hz, 2H, PyH); FAB-MS $m/z$ 1068.3 ($M^+$). Anal. Calcd for $C_{62}H_{76}N_4O_4S_4$: C, 69.62; H, 7.16; N, 5.24; S, 11.99. Found: C, 69.37; H, 6.96; N, 5.17; S, 11.68. Compound **7b**: Yield 70%, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.62 (t, $J = 7.6$ Hz, 6H, $CH_3$), 1.05 (m, 4H, $CH_2$), 1.26 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 3.13 (t, $J = 8.0$ Hz, 4H, $NCH_2$), 3.83 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 4.13 (t, $J = 8.0$ Hz, 4H, $OCH_2$), 7.03 (t, $J = 4.0$ Hz, 2H, ThH), 7.21 (d, $J = 4.0$ Hz, 2H, ThH), 7.31 (s, 4H, ArH), 7.43 (s, 4H, ArH), 7.37 (d, $J = 4.0$ Hz, 2H, ThH), 8.24 (s, 2H, HC=N); FAB-MS $m/z$ 1078.7 ($M^+$). Anal. Calcd for $C_{60}H_{74}N_2O_4S_6$: C, 66.75; H, 6.91; N, 2.59; S, 17.82. Found: C, 66.38; H, 6.76; N, 2.49; S, 17.68. Compound **7c**: Yield 85%, $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.62 (t, $J = 7.6$ Hz, 6H, $CH_3$), 1.03–1.06 (m, 4H, $CH_2$), 1.26 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 3.17 (t, $J = 7.8$ Hz, 4H, $NCH_2$), 3.83 (t, $J = 7.8$ Hz, 4H, $OCH_2$), 4.15 (t, $J = 7.8$ Hz, 4H, $OCH_2$), 6.87 (t, $J = 7.8$ Hz, 2H, hydroxyphenyl-H), 6.94 (d, $J = 8.1$ Hz, 2H, hydroxyphenyl-H), 7.16 (d, $J = 7.8$ Hz, 2H, hydroxyphenyl-H), 7.28–7.30 (m, 2H, hydroxyphenyl-H), 7.32 (s, 4H, ArH), 7.42 (s, 4H, ArH), 8.25 (s, 2H, HC=N), 13.00 (s, 2H, ArOH); FAB-MS $m/z$ 1098 ($M^+$). Anal. Calcd for $C_{64}H_{78}N_2O_6S_4$: C, 69.91; H, 7.15; N, 2.55; S, 11.66. Found: C, 69.61; H, 6.83; N, 2.53; S, 12.01.

15. *General procedure for the preparation of bisthiacalixarenes* **10a**–**c**:To a solution of diamine **4** (89.0 mg, 0.10 mmol) in a 1:1 mixture of dichloromethane and methanol (20 mL) was added a solution of dialdehyde **9a**–**d** (0.10 mmol) in methanol (5.0 mL). The mixture was refluxed for the indicated period to separate a solid, which was filtered, washed, dried and recrystallized from a mixture of dichloromethane and methanol. Compound **10a**: Refluxed for 4 days (yield 78%), $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.61 (t, $J = 7.6$ Hz, 12H, $CH_3$), 0.97–1.03 (m, 8H, $CH_2$), 1.22 (s, 36H, $C(CH_3)_3$), 1.29 (s, 36H, $C(CH_3)_3$), 3.07 (t, $J = 8.0$ Hz, 8H, $NCH_2$), 3.83 (t, $J = 7.2$ Hz, 8H, $OCH_2$), 4.30 (t, $J = 8.0$ Hz, 8H, $OCH_2$), 7.33 (s, 8H, ArH), 7.40 (s, 8H, ArH), 7.74 (t, $J = 7.6$ Hz, 2H, PyH), 7.99 (d, $J = 7.6$ Hz, 4H, PyH), 8.30 (s, 4H, HC=N); FAB-MS ($m/z$):1978 [$(M)^+$]. Anal. Calcd for $C_{114}H_{142}N_6O_8S_8$: C, 69.12; H, 7.23; N, 4.24; S, 12.95. Found:C, 68.86; H, 6.98; N, 4.17; S, 12.57. Compound **10b**: Refluxed for 5 days (yield 75%); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.61 (t, $J = 8.0$ Hz, 12H, $CH_3$), 0.98–1.04 (m, 8H, $CH_2$), 1.27 (s, 36H, $C(CH_3)_3$), 1.29 (s, 36H, $C(CH_3)_3$), 3.04 (t, $J = 8.0$ Hz, 8H, $NCH_2$), 3.84 (t, $J = 8.0$ Hz, 8H, $OCH_2$), 4.17 (t, $J = 8.0$ Hz, 8H, $OCH_2$), 7.31 (s, 8H, ArH), 7.44 (s, 8H, ArH), 7.65 (s, 8H, ArH), 8.13 (s, 4H, HC=N); FAB-MS $m/z$ 1978 [$(M+1)^+$]. Anal. Calcd for $C_{116}H_{144}N_4O_8S_8$: C, 70.40; H, 7.33; N, 2.83; S, 12.96. Found: C, 70.05; H, 7.10; N, 2.69; S, 12.73. Compound **10c**: Refluxed for 2 days (yield 75%), $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 0.59–0.65 (m, 12H, $CH_3$), 0.97–1.11 (m, 8H, $CH_2$), 1.23 (s, 36H, $C(CH_3)_3$), 1.27 (s, 36H, $C(CH_3)_3$), 3.04 (t, $J = 8$ Hz, 8H, $NCH_2$), 3.84 (t, $J = 8$ Hz, 8H, $OCH_2$), 4.17 (t, $J = 8$ Hz, 8H, $OCH_2$), 7.31 (s, 8H, ArH), 7.44 (s, 8H, ArH), 7.67 (t, $J = 7.6$ Hz, 2H, ArH), 7.94 (d, $J = 7.6$ Hz, 4H, ArH), 8.02 (s, 2H, ArH), 8.13 (s, 4H, HC=N); FAB-MS $m/z$ 1977 ($M^+$). Anal. Calcd for $C_{116}H_{144}N_4O_8S_8{\cdot}2H_2O$: C, 69.14; H, 7.40; N, 2.78; S, 12.73. Found: C, 69.42; H, 7.10; N, 2.69; S, 12.43.

16. Stoichiometry of silver complexes with compounds **1a** and **1c** could not be determined by $^1$H NMR spectroscopy because of severe peak broadening.[9]

17. Apparently, the propylation changes both the coordination ability of the phenolic oxygen and the conformation of the thiacalixarene unit. To evaluate which change decisively affects the binding ability of the host molecule, we tried in vain to prepare the stereoisomer of diamine **4** of cone conformation.

18. Crystal data: triclinic, space group $P\bar{1}$, $a = 13.404(3)$ Å, $b = 14.1880(16)$ Å, $c = 22.894(3)$ Å, $\alpha = 72.874(11)°$, $\beta = 90.022(14)°$, $\gamma = 61.794(16)°$, $V = 3616.1(10)$ Å$^3$, $Z = 2$. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 629867.