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Excellent Ag^+ selective receptors: Syntheses and complexation properties of novel biscalix[4]arene with benzalazine groups

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By reacting mono-substituted or 1,3-bi-substituted [2-(*p*-formylphenyloxy)ethyloxy]-*p-tert*-butylcalix[4]arene (**3** or **4**) with hydrazine hydrate in '1 + 2' or '2 + 2' condensation mode, novel benzalazine-bridging biscalix[4]arenes **5** and **7** were conveniently obtained in the yields of 76 and 81%, respectively. Condensation of compound **4** and salicylide hydrazone gave a novel calix[4]arene benzalazine derivative **6** in the yield of 85%. The structures and conformations of all new compounds were characterised by elemental analyses, ESI-MS, ^{1}H NMR and ^{1}H–^{1}H COSY techniques. Biscalix[4]arene **7** adopts a symmetrical cone conformation with tube cavity. The liquid–liquid extraction experiment showed that all new hosts possessed excellent complexation abilities towards soft metal cations. Compound **7** exhibited high complexation selectivity towards Ag^+. The Ag^+/Na^+ and Ag^+/Hg^{2+} extraction percentages of host **7** were as high as 73.1 and 54.9, respectively. The UV–vis spectra complexation experiments revealed that the complexation constant of receptor **7** with Ag^+ was $1.9 \times 10^5\,M^{-1}$ and the 1:1 stoichiometry of receptor **7**–Ag^+ complex was formed. The ^{1}H NMR spectra complexation experiments suggested that Ag^+ was bound in a cavity composed of two benzalazine groups on bridging chains.

Keywords: biscalix[4]arene; benzalazine; synthesis; complexation; Ag^+

Introduction

Calixarenes and their derivatives are macrocyclic molecules possessing interesting complexation abilities towards target molecules or ions. Many researches were involved in the design and syntheses of different kinds of receptor molecules with defined cavities by using calix[4]arenes as a key structural motif (*1*, *2*). Double calix[4]arenes were prepared as examples of higher order molecular architectures in the recent past (*3–5*). Some biscalix[4]arenes with special structure were synthesised and exhibited interesting complexation for guests. For example, Beer et al. reported a biscalix[4]arene with carboxylic groups that exhibited excellent complexation for UO_2^{4+} (*6*). Budka et al. synthesised a biscalix[4]arene-based ditopic hard/soft receptor for K^+/Ag^+ complexation (*7*). Nabeshima et al. reported biscalix[4]arenes with homotropic and heterotrophic complexation abilities (*8*). Prados et al. reported a biscalix[4]arene with the complexation for fullerene (*9*). Lately, our groups also reported a series of biscalix[4]arenes with interesting complexation properties (*10–13*). From the literature, it can be concluded that the complexation properties of biscalix[4]arene were greatly influenced not only by the structure of biscalix[4]arene, but also by the characteristic of functional groups of bridging chains. Lately, we synthesised a novel biscalix[4]arene with benzalazine groups (*14*). In this paper, we wish to report the full procedures of preparing novel biscalix[4]arene with benzalazine groups as bridging chains in ideal yields, and their excellent complexation abilities for Ag^+.

Results and discussion

Syntheses, structures and conformations

The synthetic route was shown in Scheme 1. Salicylic hydrazone **1** and *p*-tosyloxyethoxyl-benzaldehyde **2** were prepared according to the published procedures (*10*). By refluxing *p-tert*-butylcalix[4]arene with *p*-tosyloxyethoxyl-benzaldehyde (molar ratio = 1:1) in K_2CO_3–MeCN for 48 h, mono-substituted calix[4]arene derivative **3** and 1,3-bis-substituted calix[4]arene derivative **4** were obtained in the yield of 35 and 15% after column chromatography. When the molar ratio of *p-tert*-butylcalix[4]arene and *p*-tosyloxyethoxyl-benzaldehyde was 1:2, only 1,3-bis-substituted calix[4]arene derivative **4** was obtained in the yield of 78% by recrystallisation from $CHCl_3$–MeOH. Reacting compound **4** with salicylic hydrazone gave the calix[4]arene benzalazine derivative **6** under the room temperature in the yield of 85%. It was found that these condensation reactions were sensitive to reaction temperature. Compound **6** could not be obtained under refluxing condition. On the other hand, by refluxing

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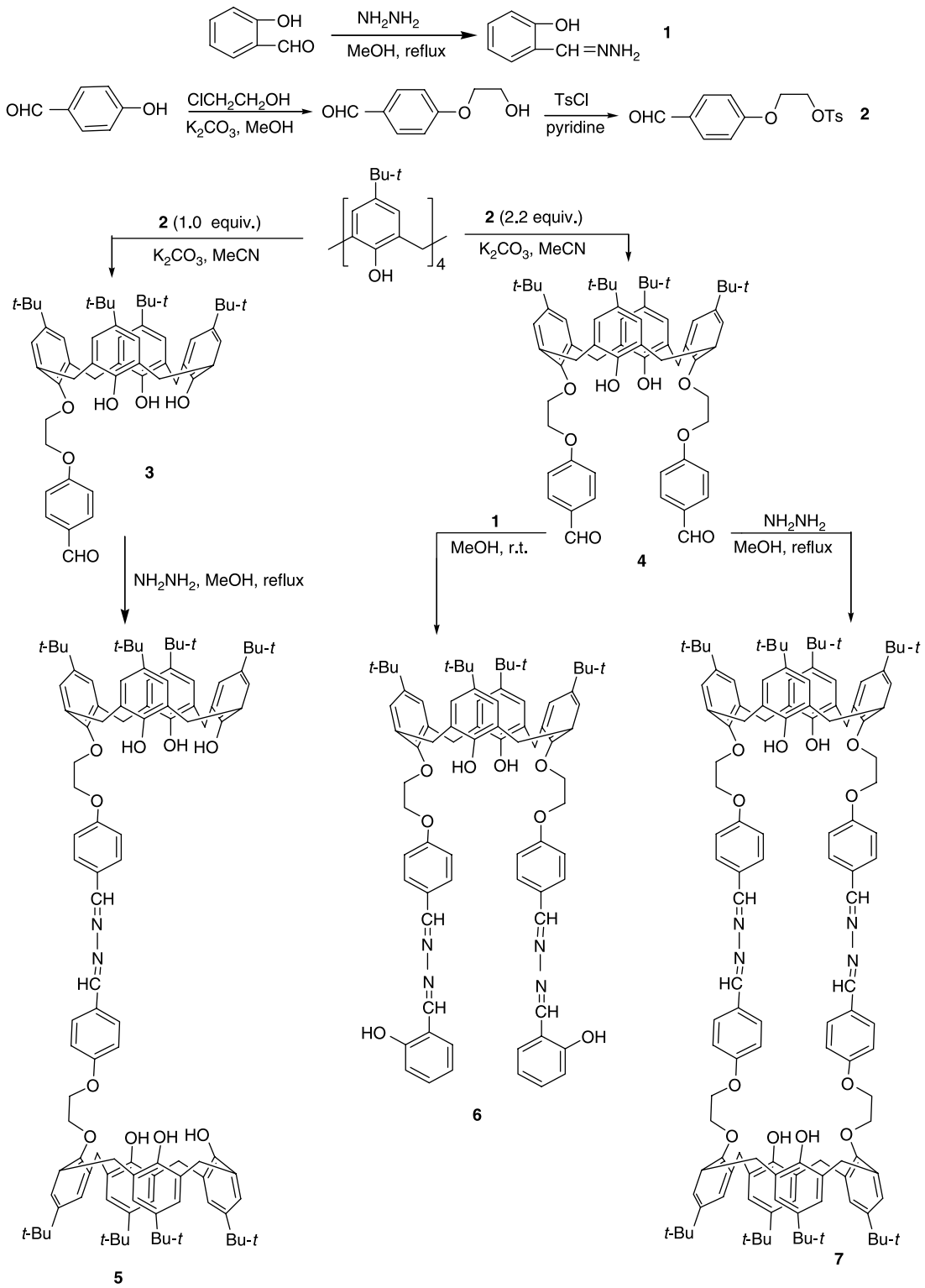

Scheme 1. The synthetic routes of new hosts.

compound **3** or **4** with $N_2H_4{\cdot}H_2O$ (concentration 80%) in $CHCl_3$–MeOH (1:1, v/v) solution for 5 h, the novel biscalix[4]arene with benzalazine chains **5** and **7** were obtained in '2 + 1' or '2 + 2' intermolecular condensation. The separate procedures were simple with recrystallisation and the yields were as high as 76 and 81%, respectively. It was noteworthy that no intramolecular '1 + 1' condensation products or other by-products

were detected in the reaction of synthesising biscalixarene **7**, even under the condition of excess $N_2H_4 \cdot H_2O$. The reason might be attributed to the rigid and stable conjugate structure of benzalazine groups. To the best of our knowledge, compounds **5**, **6** and **7** were the first examples of biscalix[4]arene or calix[4]arene derivatives with benzalazine groups.

All new compounds were characterised by elemental analyses, ESI-MS spectra and ^{1}H NMR spectra. The ESI-MS spectra of compounds **3**, **4**, **5**, **6** and **7** showed clearly molecular ion peaks at 796.6, 967.3, 1589.8, 1181.3 and 1905.2, respectively. In the ^{1}H NMR spectra, compounds **3** and **5** showed three singlets (2:1:1) for the *tert*-butyl groups and two pairs of doublets (1:1) for the methylene bridges of the calix[4]arene skeleton. Compounds **4**, **6** and **7** showed two singlets (1:1) for the *tert*-butyl groups, one pair of doublet (1:1) for the methylene bridges of the calix[4]arene skeleton. All the spectral data were in accordance with the assigned structures and certainly indicated that the calix[4]arene units adopt the cone conformation as shown in Scheme 1. Also, the structure and conformation of biscalix[4]arene **7** were further investigated by ^{1}H–^{1}H COSY spectrum as shown in Figure 1. It was found that only one kind of coupling H for $ArCH_2Ar$ on two calixarene-derivative skeletons unambiguously supported the highly symmetrical structure and cone conformation of biscalix[4]arene compound **7**.

Complexation studies for cations

Examination of the CPK molecular models revealed that novel biscalix[4]arene were highly preorganised for binding guests. Benzalazine group was excellent N-donation functional group for binding metal cations. The non-competitive complexation abilities of compounds **5**, **6** and **7** towards a series of metal cations were studied by two phase extraction experiment ($H_2O/CHCl_3$) of metal cation picrate salts. The results were summarised in Figure 2. Compounds **5**, **6** and **7** exhibited higher extraction percentage for soft metal cations than that for hard metal cations. Especially, they showed good extraction selectivity for Ag^+. Compound **7** was excellent Ag^+ receptor with the highest extraction percentage of 51.8%.

On the other hand, to assess the competitive extraction selectivity of new hosts, competitive solvent extraction experiments of new hosts with alkali and transition metallic cations from aqueous solutions into chloroform were performed. The extraction percentages (*E*%) were

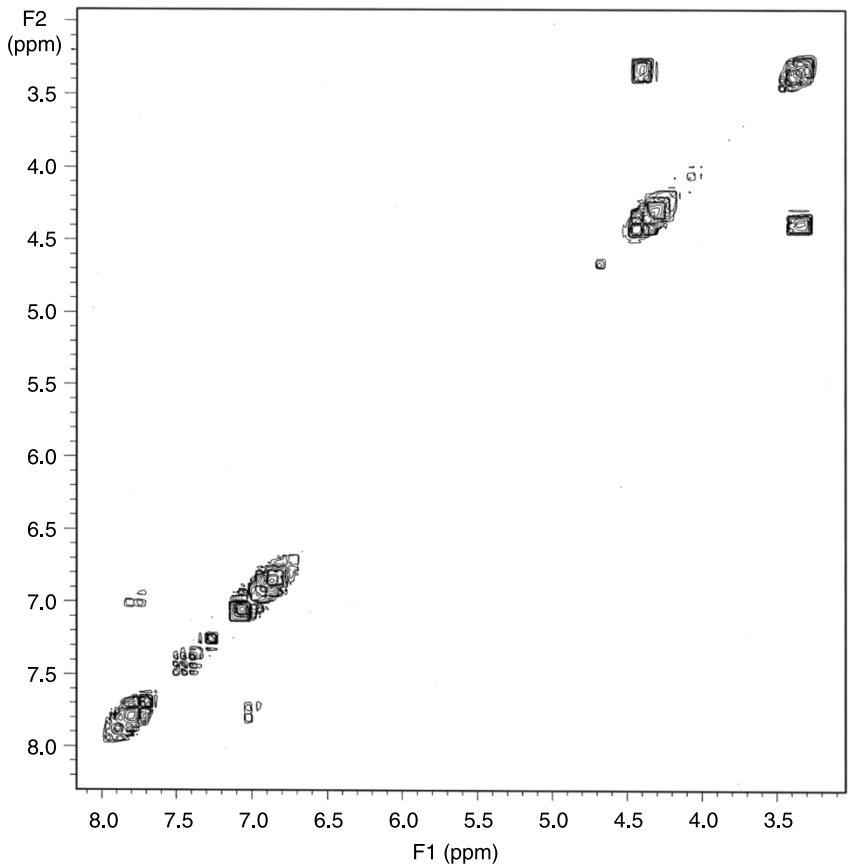

Figure 1. The ^{1}H–^{1}H COSY spectrum of biscalix[4]arene **7**.

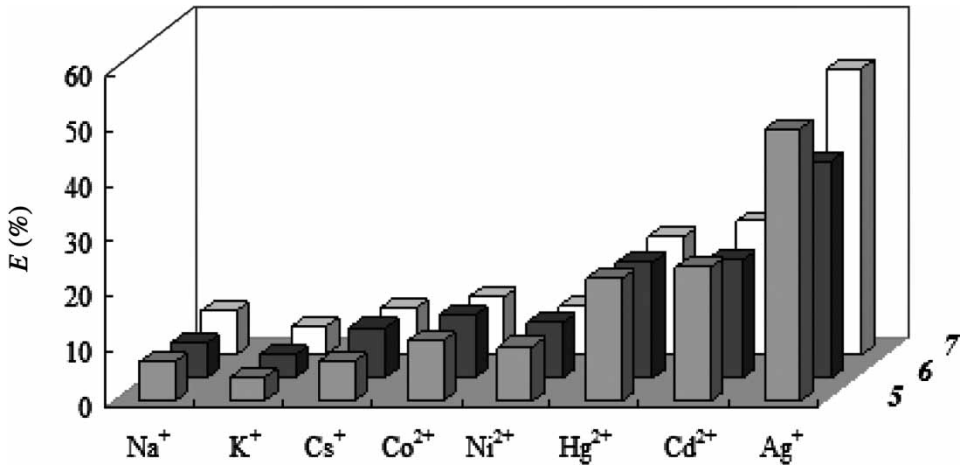

Figure 2. Percentage extraction of **5**, **6** and **7** towards picrate salts.

summarised in Table 1. It can be seen that, in the competition experiments, the extractabilities towards the competing metallic ions showed similar capability order of non-competitive extraction experiment: soft metallic cations ⩾ hard metallic cations. Although the extraction percentages were lower than that of the non-competitive extraction experiment in some cases, however, the extraction selectivities in competition experiments were far higher than that of the non-competitive experiment. For example, the Ag^+/Na^+ and Ag^+/Hg^{2+} extraction percentages of host **7** were as high as 73.1 and 54.9, respectively.

Because biscalixarene **7** was the most excellent receptor in the extraction experiments, the complexation behaviours of receptor **7** for cations were further studied by UV–vis spectra. The UV–vis spectra changes in compound **7** with metal cations perchlorate salts were investigated, as shown in Figure 3. Little shift of the maximal absorption wavelength of receptor **7** with alkali metal cations Na^+, K^+ and Cs^+ can be seen, although the maximal absorbance decreased obviously. However, the maximal absorption wavelength of receptor **7** with soft metal cations Ag^+, Hg^{2+}, Cd^{2+}, Co^{2+} and Ni^{2+} made strong red shift and the maximal absorbance changed greatly. Similar to the results of extraction experiments, Ag^+ was the most effective cations for the complexation of receptor **7**. The wavelength of receptor **7** with Ag^+ shifted from 356.5 to 498.4 nm and the maximal absorbance decreased from 0.72 to 0.36.

Figure 4 showed the absorption spectra of receptor **7** with different concentrations of Ag^+ cation. It can be seen that the maximal absorbance at 356.5 nm decreased and new absorption at 498.4 nm increased gradually. These phenomena obviously indicated that the complexation occurred between host and guest. Also, from the UV–vis spectra titration, the association constant of complex **7** with Ag^+ was calculated to be $1.9 \times 10^5\,M^{-1}$ by the nonlinear curve fitting procedure (*15*).

In order to investigate the stoichiometry of receptor **7**–Ag^+ complex, the method of continuous variations was used. The Job plot experiment showed that the maxima of receptor **7** with Ag^+ at the mole fraction of 0.5 indicated the formation of approximate 1:1 host–guest complex (Figure 5).

To investigate the complex sites of compound **7** for Ag^+, the complex ^1H NMR spectra of compound **7** for Ag^+ were studied. Figure 6 showed the partial ^1H NMR spectra of compound **7** and compound **7** with Ag^+. The protons shift of HC═N moved from 8.55 to 8.60 ppm and the other protons signals almost kept immovability. These results suggested that Ag^+ was bound in the cavity composed of two benzalazine groups on bridging chains, not in the cavities of calixarene skeleton. The signals of OH, confirmed by the disappearance with D_2O exchange, made little shifts from 8.63 to 8.64 ppm, which might be attributed to the influences of ClO_4^- anions. Obviously, due to Ag^+ bound in the cavity composed of two benzalazine

Table 1. Competitive extracting percentages (*E*%) of picrate salts from water into $CHCl_3$.

Cation	Na^+	K^+	Cs^+	Co^{2+}	Ni^{2+}	Hg^{2+}	Cd^{2+}	Ag^+
5	1.2	0.5	0.4	2.4	2.9	6.2	1.8	22.8
6	2.1	1.1	2.0	3.8	4.1	8.5	4.3	26.6
7	0.6	1.2	0.9	2.3	1.6	0.8	1.9	43.9

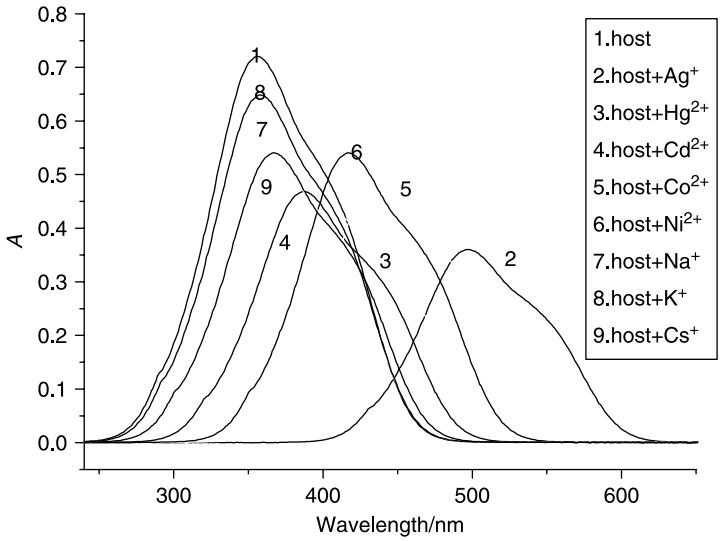

Figure 3. The UV–vis spectra changes in receptor **7** (2×10^{-5} M) with metal cations (6×10^{-5} M).

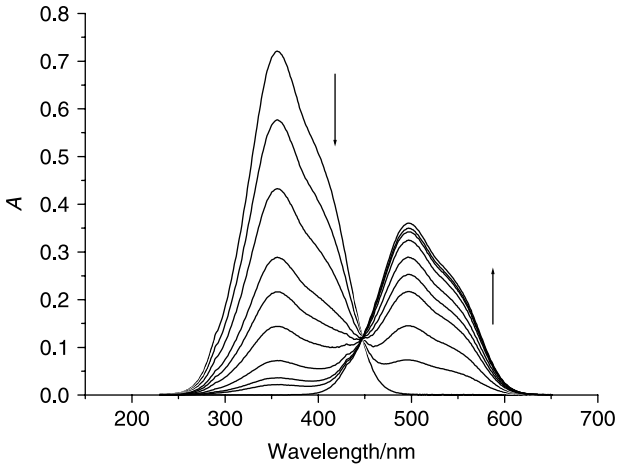

Figure 4. Absorption spectra of receptor **7** (2×10^{-5} M) with different concentrations of Ag^+ [Ag^+]/[compound **7**]: 0, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0,1.5, 2.0 and 3.0.

groups, compound **7**–Ag^+ preferred to form 1:1 complex, which was in accordance with the above-mentioned UV–vis spectra titration.

Conclusions

Novel calix[4]arene benzalazine derivative **6** and benzalazine-bridging biscalix[4]arenes **5** and **7** were conveniently synthesised in ideal yields. Biscalix[4]arene **7** adopts a symmetrical cone conformation with tube cavity. The liquid–liquid extraction experiment showed that all new hosts possessed excellent complexation abilities towards soft metal cations. Compound **7** exhibited high complexation selectivity towards Ag^+. The Ag^+/Na^+ and Ag^+/Hg^{2+} extraction percentages of host **7** were as high as 73.1 and 54.9, respectively. UV–vis spectra complexation experiments revealed that the complexation constant of receptor **7** with Ag^+ was $1.9 \times 10^5\,M^{-1}$ and the 1:1 stoichiometry of receptor **7**–Ag^+ complex was formed. The ^1H NMR spectra complexation experiments suggested the Ag^+ was bound in cavity composed of two benzalazine groups on bridging chains.

Experimental

Melting points are uncorrected. The ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 500 instrument, using TMS as reference. ESI-MS spectra were obtained from DECAX-30000 LCQ Deca XP mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. The UV–vis measurements were performed on Varian UV–vis spectrometer. Cation concentrations in competitive extracting experiments were measured with Thermo Intrepid XSP Radial ICP-OES. All solvents were purified by standard procedures. The picrate salts were prepared according to the literature (*16*, *17*).

Syntheses of p-tert-*butylcalix[4]arene derivatives 3 and 4*

A mixture of *p-tert*-butylcalix[4]arene (2 mmol, 1.48 g), *p*-tosyloxyethoxyl-benzaldehyde (2 mmol, 0.64 g) and K_2CO_3 (2 mmol, 0.28 g) was stirred in refluxing acetonitrile (100 ml) for 2 days under N_2 atmosphere. After distilling off the solvent under reduced pressure, the residue was treated with 30 ml HCl (10%) and extracted with 40 ml $CHCl_3$. The organic layer was separated, dried over anhydrous $MgSO_4$ and then filtered and concentrated.

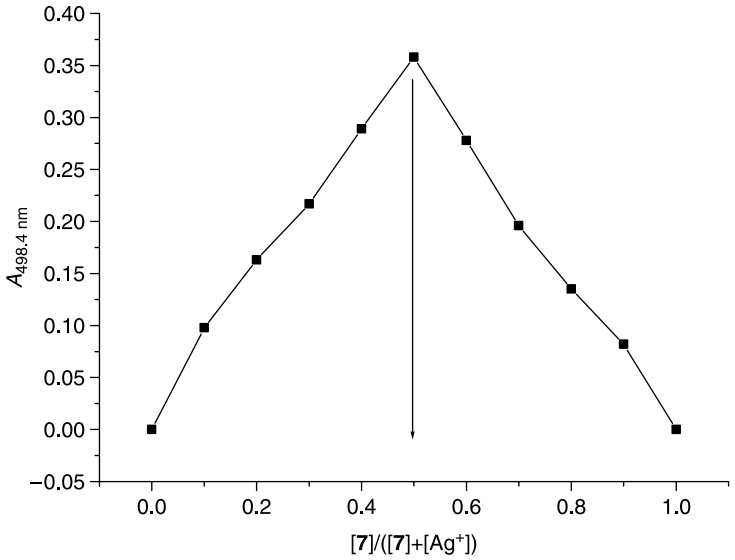

Figure 5. The Job plot documenting the stoichiometry of 1:1 for the complexation of Ag^+ by receptor **7** in DMF. The plot was constructed from absorbance changes at 498.4 nm using the sum of concentrations 4×10^{-5} M.

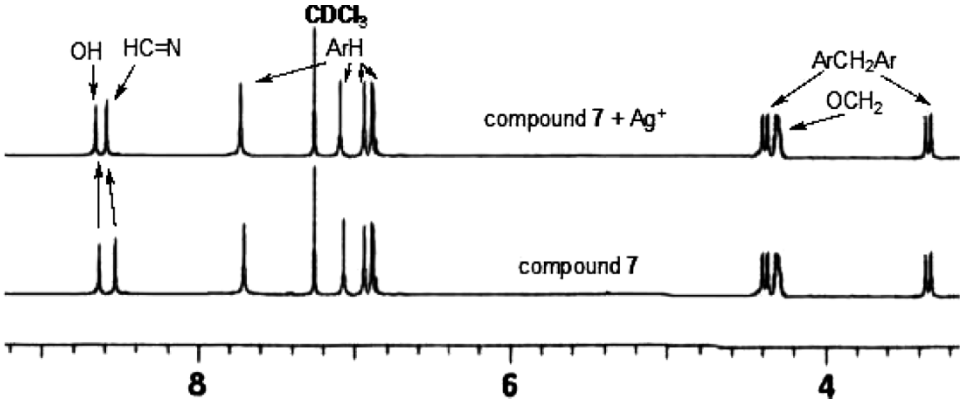

Figure 6. Partial ^{1}H NMR spectra of compound **7** and compound **7** with Ag^+.

By the purification of column chromatography on silica gel (100–200 mesh) using petroleum ether (60–90°C)–CH_2Cl_2 (1:1) as an eluent, compound **3** was obtained as white powder in the yield of 35% and compound **4** was obtained as by-product in the yield of 15%. When *p*-tosyloxyethoxyl-benzaldehyde was in quantity of 4.4 mmol (1.28 g) and K_2CO_3 was 10 mmol (1.40 g) in the above reaction, only compound **3** was obtained in the yield of 78% by recrystallisation from $CHCl_3$/MeOH. Compound **3**: mp 186–188°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.04 [s, 9H, $C(CH_3)_3$], 1.10 [s, 18H, $C(CH_2)_3$], 1.20 [s, 9H, $C(CH_2)_3$], 3.37 (d, $J = 13.0$ Hz, 2H, $ArCH_2Ar$), 3.42 (d, $J = 13.0$ Hz, 2H, $ArCH_2Ar$), 4.27–4.30 (m, 6H, OCH_2 and $ArCH_2Ar$), 4.33 (d, $J = 13.0$ Hz, 2H, $ArCH_2Ar$), 6.86–7.34 (m, 12H, ArH), 7.33 (s, 1H, ArCHO), 9.42 (s, 2H, OH) and 9.64 (s, 1H, OH); MS *m/z* (%): 796.6 (M^+, 70). Anal. calcd for $C_{53}H_{64}O_6$: C, 79.86; H, 8.09; found: C, 79.80; H, 8.14. Compound **4**: mp 199–202°C; ^{1}H NMR (500 MHz, $CDCl_3$): 1.00 [s, 18H, $C(CH_3)_3$], 1.27 [s, 18H, $C(CH_2)_3$], 3.31 (d, $J = 13.0$ Hz, 4H, $ArCH_2Ar$), 4.32–4.36 (m, 12H, OCH_2 and $ArCH_2Ar$), 6.84 (s, 4H, ArH), 7.02 (d, $J = 8.5$ Hz, 4H, ArH), 7.26 (s, 4H, ArH), 7.32 (s, 2H, ArCHO), 7.82 (d, $J = 8.5$ Hz, 4H, ArH) and 9.89 (s, 2H, OH); MS *m/z* (%): 967.3 ($M - Na^+$, 100). Anal. calcd for $C_{62}H_{72}O_8$: C, 78.78; H, 7.68; found: C, 78.72; H, 7.71.

Synthesis of biscalix[4]arene benzalazine derivative 5

A mixture of compound **3** (0.10 g, 0.126 mmol) and 80% hydrazine hydrate solution (0.065 mmol) was refluxed in $CHCl_3$–MeOH (1:1, v/v) solution (10 ml) for 5 h. TLC detection indicated the disappearance of compound **3**. The solvent was removed under reduced pressure and the residue was treated with methanol to give crude product, followed by crystallising from $CHCl_3$/MeOH; compound **5** was obtained as white powder in the yield of 76%. Compound **5**: mp 156–157°C. ^{1}H NMR (500 MHz, $CDCl_3$)

δ: 1.14 [br s, 18H, $C(CH_3)_3$], 1.16 [br s, 36H, $C(CH_3)_3$], 1.21 [s, 18H, $C(CH_3)_3$], 3.40 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$), 3.44 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$), 4.21 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$), 4.48 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$), 4.45–4.56 (m, 8H, $ArOCH_2$), 6.98–7.11 (m, 16H, ArH), 7.85 (br s, 8H, ArH), 8.66 (s, 2H, CH═N), 9.35 (s, 4H, ArOH) and 10.12 (s, 2H, ArOH); MS *m/z* (%): 1589.8 (M^+, 98). Anal. calcd for $C_{106}H_{128}N_2O_{10}$: C, 80.07; H, 8.10; N, 1.76; found: C, 79.92; H, 8.14; N, 1.73.

Synthesis of calix[4]arene benzalazine derivative 6

A mixture of compounds **4** (0.20 g, 0.21 mmol) and **1** (0.0634 g, 0.46 mmol) was stirred in MeOH–$CHCl_3$ (1:1, v/v, 10 ml) solution under room temperature. TLC detection indicated the disappearance of compound **4** in 3 h. The solvent was removed under reduced pressure in room temperature. The residue was treated with MeOH to give crude product, following by crystallising from EtOH, compound **6** as white powder in the yield of 85%. Compound **6**: mp 158–160°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.02 [s, 18H, $C(CH_3)_3$], 1.28 [s, 18H, $C(CH_3)_3$], 3.32 (d, $J = 12.5$ Hz, 4H, $ArCH_2Ar$), 4.30 (s, 8H, OCH_2), 4.39 (d, $J = 12.5$ Hz, 4H, $ArCH_2Ar$), 6.87–7.76 (m, 24H, ArH), 8.52 (br s, 4H, N═CH), 8.71 (s, 2H, ArOH) and 11.79 (s, 2H, OH); MS *m/z* (%): 1181.3 (M^+, 100). Anal. calcd for $C_{76}H_{84}N_4O_8$: C, 77.26; H, 7.17; N, 4.74; found: C, 77.19; H, 7.23; N, 4.66.

Synthesis of benzalazine-bridged biscalix[4]arene derivative 7

A mixture of compound **4** (0.4 g, 0.42 mmol) and 80% hydrazine hydrate solution (0.02 ml, 0.42 mmol) was refluxed in $CHCl_3$–MeOH (1:1, v/v) solution (20 ml). TLC detection indicated the disappearance of compound **4** in 5 h. The solvent was removed under reduced pressure and the residue was treated with methanol to give crude product, followed by crystallising from $CHCl_3$–MeOH; compound **5** was obtained as white powder in the yield of 81%; mp 298–300°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.04 [s, 36H, $C(CH_3)_3$], 1.28 [s, 36H, $C(CH_3)_3$], 3.37 (d, $J = 12.0$ Hz, 8H, $ArCH_2Ar$), 4.32 (br s, 16H, OCH_2), 4.39 (s, $J = 12.0$ Hz, 8H, $ArCH_2Ar$), 6.88 (s, 8H, ArH), 6.92 (s, 8H, ArH), 7.07 (br s, 8H, ArH), 7.70 (br s, 8H, ArH), 8.55 (s, 4H, N═CH) and 8.63 (br s, 4H, OH); MS *m/z* (%): 1905.2 ($M-Na^+$, 95). Anal. calcd for $C_{124}H_{144}N_4O_{12}$: C, 79.11; H, 7.71; N, 2.98; found: C, 79.03; H, 7.80; N, 2.89.

Non-competitive extracting experiment of metallic picrates

According to the reported method (*16*), 3 ml of chloroform solution containing calixarene derivatives (2.0×10^{-5} M) and 3 ml of aqueous solution containing a metallic picrate (2.0×10^{-5} M) were placed in a flask. The mixture was shaken for 5 min and stored for 2 h at room temperature. The extraction ability was not affected by further shaking, indicating that the equilibrium had been attained within 2 h. The aqueous phase was separated and subjected to the analysis by UV absorption spectrometry in near 357 nm. The extracting percentage ($E\%$) was determined by the decrease in the picrate concentration in the aqueous phase: $E\% = \{([Pic]_{blank} - [Pic]_{water})/[Pic]_{blank}\} \times 100$, where $[Pic]_{blank}$ denoted the picrate concentrations in the aqueous phase after extraction with pure chloroform and $[Pic]_{water}$ denoted the picrate concentrations in the aqueous phase after extraction with chloroform solution containing calixarene derivatives as extractants. Average of twice independent experiments was taken. Control experiments showed that no picrate extraction occurred in the absence of the calixarene derivatives.

Competitive extracting experiments of metallic cations

Competitive extraction experiments were performed with equal volumes (10 ml) of an aqueous solution of an equimolar mixture of picrate salts (Na^+, K^+, Cs^+, Co^{2+}, Ni^{2+}, Hg^{2+}, Cd^{2+} and Ag^+, 2.0×10^{-5} M each) and a $CHCl_3$ solution (10 ml) of the hosts (2.0×10^{-5} M) were mixed in a stoppered flask and vigorously shaken for 15 min. The solution was stored for 2 h. This was repeated three times, and then the solutions were left standing for 24 h until phase separation was complete. The relative concentrations of the cations in the aqueous phase were determined by ICP-OES. Quantification was made by using a standard solution containing a mixture of picrate salts (Na^+, K^+, Cs^+, Co^{2+}, Ni^{2+}, Hg^{2+}, Hg^{2+}, Cd^{2+} and Ag^+). A blank experiment without added hosts was carried out under similar experimental conditions.

UV–vis spectra studies of complexation experiments

All UV–vis experiments were performed in DMF solution by adding a stock solution of respective cations perchlorates. The stoichiometry of the complexes was determined by the Job method of continuous variations. The association constant was calculated by the Benesi–Hildebrand formula with nonlinear curve fitting procedure (*15*).

^{1}H NMR complexation experiments

A $CDCl_3$ solution (2×10^{-3} M) of compound **7** in the NMR tube was added 1 M solution of $AgClO_4$. The spectrum was measured before and after addition, and the temperature of NMR probe kept constant at 27°C.

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