Novel lariat calix[4]-1,3-aza-crowns with two branched chains — The excellent phase transfer catalysts for nucleophilic substitution reaction

Fafu Yang, Yanhua Wang, Hongyu Guo, Jianwei Xie, and Zhiqiang Liu

Abstract: By reacting calix[4]-1,3-diethoxylaminoethyl derivative (**2**) with phenyl isothiocyanate, novel dendritic calix[4]-arene derivative (**3**) with two different branched chains was synthesized in a yield of 78%. By reacting compound **2** with 1,6-diisocyanatohexane or *N*,*N*′-bis(2-chloracetamide)ethylene in a “1 + 1” intermolecular addition mode, novel lariat calix[4]-1,3-aza-crowns (**4** and **5**, respectively) with two branched ethoxyl chains were prepared in reasonable yields. The composition, structures, and conformations of all new compounds were confirmed by elemental analyses, IR, ESI-MS, ^{1}H NMR, and so forth. The liquid–liquid extraction experiments showed that all new hosts possessed good extraction abilities towards soft and hard metal cations. The liquid membrane transport experiments suggested that they had good transport abilities for K^+ and Ag^+. The experiments of phase transfer catalysis indicated that they possessed excellent catalytic properties of aromatic nucleophilic substitution reaction and benzyl nucleophilic substitution. The optimum yields of products in catalytic reaction were as high as approximately 100%.

Key words: calix[4]crown, lariat, synthesis, liquid membrane transport, phase transfer catalysis.

Résumé : La réaction du dérivé **2** du calix[4]-1,3-diéthoxylaminoéthyle avec l’isothiocyanate d’éthyle a permis de réaliser la synthèse, avec un rendement de 78 %, du nouveau dérivé dendritique du calix[4]arène portant deux chaînes ramifiées différentes. La réaction du composé **2** avec le 1,6-diisocyanatohexane ou le *N*,*N*′-bis(2-chloroacétamide)éthylène dans un mode d’addition intermoléculaire « 1 + 1 », il est aussi possible de préparer avec des rendements raisonnables de nouveaux éthers lariats, des calix[4]-1,3-azacouronnes (**4** et **5**) portant des chaînes ramifiées éthoxyles. La composition, les structures et les conformations de tous les nouveaux produits ont été confirmées par analyse élémentaire, spectrométrie de masse avec ionisation par électronébulisation (SM-IEN), RMN du ^{1}H et autres. Des expériences d’extraction liquide–liquide ont montré que toutes les nouvelles molécules hôtes possèdent de bonnes habilités pour l’extraction des cations métalliques durs et mous. Des expériences de transport dans une membrane liquide suggère qu’elles possèdent de bonnes habilités pour le transport des ions K^+ et Na^+. Les expériences en catalyse de transfert de phase indiquent qu’elles possèdent d’excellentes propriétés catalytiques dans les réactions de substitution nucléophile aromatique et de substitution nucléophile benzylique. Les rendements optimaux de produits dans les réactions catalytiques vont jusqu’à environ 100 %.

Mots-clés : calix[4]couronne, lariat, synthèse, transport dans une membrane liquide, catalyse par transfert de phase.

[Traduit par la Rédaction]

Introduction

The importance of calixarenes in the family of host macrocycles is now well-established.[1–3] Since the first calixcrown was reported in 1983,[4] much research attention had been paid to the synthesis of calixcrowns and the study of their molecular and ion recognition to use them in the design of ion selective electrodes, liquid supported membranes and catalyst, and so forth.[5–7] All kinds of calixcrowns containing only oxygen donor atoms were synthesized and exhibited excellent recognition towards hard metal ions or some soft metal ions, and calixcrowns containing heteroatoms such as aza and sulfur groups usually showed outstanding complexation abilities for soft metal cations.[8–17]

In the field of crown ethers, it is well-known that the lariat crown ethers with branched chains usually show outstanding complexation abilities for guest due to the coordinated recognition of crown ether chains and branched chains. However, in the field of calixcrowns, although many calixcrowns were reported, only Bitter and co-workers[18,19] and Bond et al.[20] reported several lariat calix[4]-aza-crowns with one amino-branched chain. These lariat calix[4]-aza-crowns exhibited excellent recognition properties due to the favorable synergistic complexation[18–19] but they were not concerned with their phase catalytic properties. Thus, it is interesting to study the syntheses and properties of novel lariat calixcrowns with other functional groups and more branched chains. In this paper, we report the syntheses of

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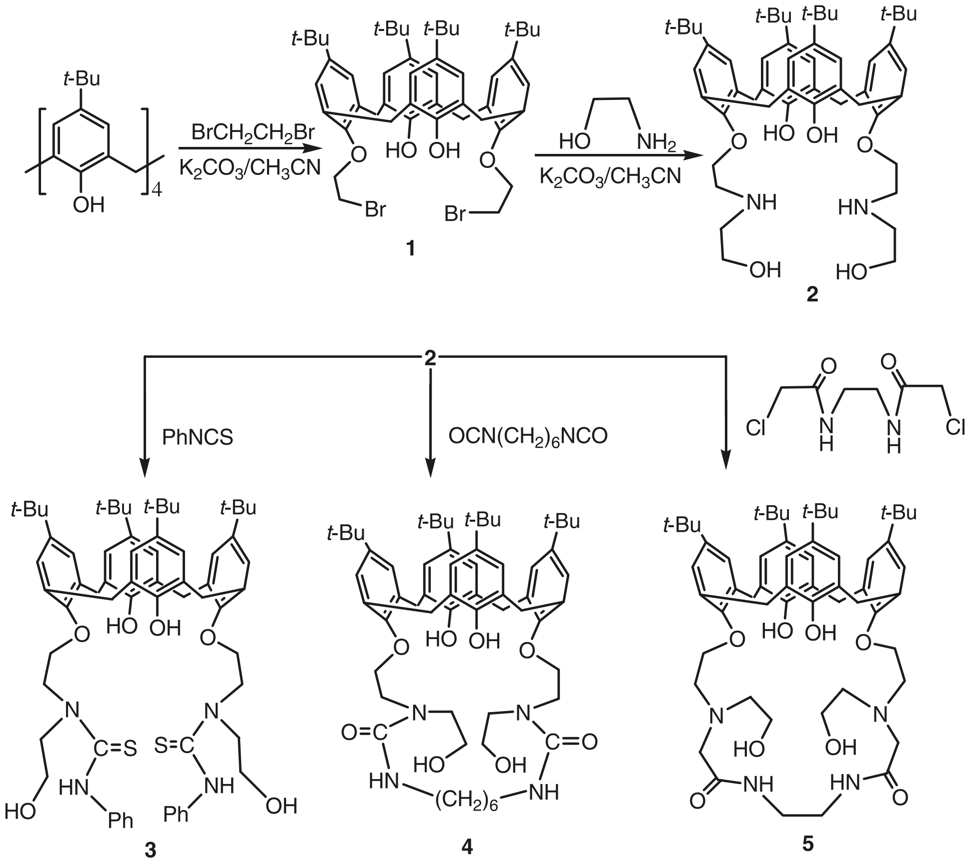
Scheme 1. Synthetic routes for compounds **2**, **3**, **4**, and **5**.



two novel lariat calix[4]-1,3-aza-crowns with two branched ethoxyl chains and a novel dendritic calix[4]arene derivative with two different branched chains. Also, their interesting properties of metal ion extraction, liquid membrane transport, and phase transfer catalysis were studied.

Results and discussion

Syntheses and characterization of products

The synthetic routes are shown in Scheme 1. 1,3-Broethoxylcalix[4]arene (**1**) was prepared according to the published procedures.[21] By refluxing compound **1** with excess ethanolamine (molar ratio = 1:10) in K_2CO_3/MeCN for 48 h, the calix[4]-1,3-diethoxylaminoethyl derivative (**2**) was obtained in a yield of 73% after recrystallization in CH_3OH/H_2O. By further reacting compound **2** with phenyl isothiocyanate under room temperature, novel dendritic calix[4]arene derivative (**3**) with two different branched chains was obtained in a yield of 78% after recrystallization in $CHCl_3$/petroleum ether (60 ~ 90 °C). On the other hand, by refluxing compound **2** with 1,6-diisocyanatohexane in high diluted $CHCl_3$ solution over night, novel lariat calix[4]-1,3-aza-crown (**4**) with two branched ethoxyl chains was prepared with a yield of 62% in a "1 + 1" addition mode after recrystallization in $CHCl_3$/petroleum ether (60 ~ 90 °C). Also, by refluxing compound **2** with *N*,*N′*-bis(2-chloracetamide)ethylene in K_2CO_3/MeCN for 72 h, novel lariat calix[4]-1,3-aza-crown (**5**) with two branched ethoxyl chains was obtained in a yield of 42% in a "1 + 1" condensation mode after column chromatography. In this condensation reaction, no catalyst, such as KI, was added to avoid the reaction of *N*,*N′*-bis(2-chloracetamide)ethylene with the phenolic hydroxyl groups of compound **2**. Moreover, to test the reaction activity of phenolic hydroxyl groups of compound **2** in this reaction, compound **1** was refluxed with *N*,*N′*-bis(2-chloracetamide)ethylene with the same reaction conditions, but no materials took part in the reaction in 72 h (if KI was added, materials took part in reaction). This result certainly suggested that it was not the phenolic hydroxyl groups but the amino groups of compound **2** taking part in the condensation reaction as showed in Scheme 1. To the best of our knowledge, compound **3** was the novel dendritic calix[4]arene derivative with two different branched chains, and compounds **4** and **5** were the first examples of lariat calix[4]-1,3-aza-crowns with two branched ethoxyl chains.

All new compounds were tested by elemental analyses, IR, ESI-MS, and ^{1}H NMR spectra. The ESI-MS spectra of compounds **2**, **3**, **4**, and **5** clearly showed molecular ion peaks (M^+, MH^+, or MNa^+) at 824.0, 1116.0, 990.3, and 985.8, respectively. In the ^{1}H NMR spectra, all of the compounds showed two singlets (1:1) for the *tert*-butyl groups and one pair of doublets (1:1) for the methylene bridges of the calix[4]arene skeleton. Comparing with the similar ^{1}H NMR spectra of the other calix[4]arene 1,3-bisubstituted or 1,3-bridged derivatives in cone conformation,[8–11] all these ^{1}H NMR spectra data of the new compounds **2**–**5** were in accordance with the assigned structures and indicated that the calix[4]arene units adopted cone conformation as shown in Scheme1.

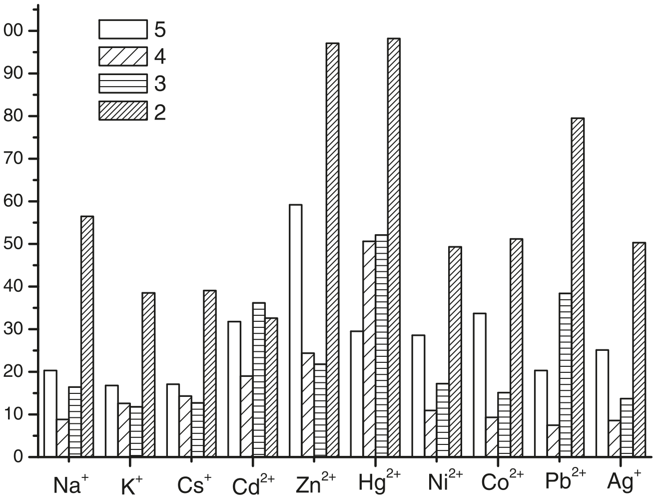
Liquid–liquid extraction for metal cations

The complexation abilities of compounds **2**, **3**, **4**, and **5** towards a series of metal cations were studied by two-phase extraction experiments ($H_2O/CHCl_3$) of metal cation picrate salts. The results were summarized in Fig. 1. Compounds **2**, **3**, **4**, and **5** exhibited good extraction abilities for both soft and hard metal cations. These results were in accordance with the "soft and hard acids and bases" concept, i.e., amino groups and hydroxyl groups were favorable for binding soft and hard metal cations, respectively. It is worthy to note that the extraction percentage of compound **2** for Zn^{2+} and Hg^{2+} were as high as 100%. On the other hand, hosts **4** and **5** showed lower extraction percentages but higher extraction selectivities than that of hosts **2** and **3**. For example, the extraction selectivity of host **4** for Hg^{2+}/Ag^+ was 6.75 (extraction percentage of Hg^{2+}/extraction percentage of Ag^+ = 50.6/7.5). These extraction results might suggest that the crown structures of compounds **4** and **5** were more favorable for producing the complexation selectivity than that of the open-chain structures of compounds **2** and **3**.

Liquid membrane transport for K^+, Zn^{2+}, and Ag^+

To investigate the potential application of new hosts **2**, **3**, **4**, and **5**, they were studied by liquid membrane transport experiments. Based on the extraction experiments, the K^+, Zn^{2+}, and Ag^+ were chosen as representative usual metal cations of hard and soft cations, and representative extraction abilities with variational extraction percentages (from 10% to 100%) in extraction experiments. The fluorinion was chosen as the anion of these metal salts because F^- plays an important role in the nucleophilic substitution reaction of preparing fluorine compounds. The transport results were summarized in Table 1. It could be seen that the salt concentration in the receiving phase increased with prolonging the running times. It was interesting that hosts **2**, **3**, **4**, and **5** possessed transport abilities for cations in the similar order of $K^+ \approx Ag^+ > Zn^{2+}$. For example, in compound **5**, the salts concentrations in the receiving phase of K^+ and Ag^+ in 20 h were 8.9×10^{-3} mol/L and 7.8×10^{-3} mol/L, respectively. However, the salt concentration of Zn^{2+} was as low as 4.3×10^{-3} mol/L under the same transport conditions. On the other hand, hosts **4** and **5** showed far higher transport amounts than that of hosts **2** and **3** in the running times over 20 h. For example, the concentrations of K^+ in the receiving phase using hosts **4** and **5** as carriers in 20 h were 6.8×10^{-3} mol/L and 8.9×10^{-3} mol/L, respectively. However, the concentrations of K^+ in jthe receiving phase using hosts **2** and **3** were as low as 1.8×10^{-3} mol/L and 1.7×10^{-3} mol/L, respectively, under the same transport conditions. These results of liquid membrane transport were utterly different from the results of two phase extraction experiments. It was known that the liquid membrane transport ability relied on the balance of the complexation ability of the host for guest and the decomplexing ability of the complexes.[22,23] These results of liquid membrane transport might suggest that complex **2**M^+(and **2**M^{2+}, **3**M^+, **3**M^{2+}) possessed stronger stabilities and lower decomplexing abilities in comparison with the corresponding complexes with hosts **4** and **5**. Thus, although the two phase extraction abilities of hosts **4** and **5** were lower than that of hosts **2** and **3**, the lower stabilities of the complexes with **4** and **5** led to higher decomplexing abilities and then higher speeds of liquid membrane transport than that of **2** and **3**.

Fig. 1. Percentage extraction (%) of **2**, **3**, **4**, and **5** towards picrate salts.



The phase transfer catalysis of the nucleophilic substitution reaction

Based on the experiment results of liquid membrane transport, the phase transfer catalytic properties of aromatic nucleophilic substitution reactions were studied. Aromatic fluorine compounds have important applications in insecticidal and refined chemicals.[24] The replacement of aromatic Cl by F in nucleophilic substitution reactions was chosen as a reaction system to evaluate the phase transfer catalytic abilities of new hosts **2**, **3**, **4**, and **5**. The experiment results are shown in Table 2. It can be seen that the yield of the product was as low as 8.5% when the reaction was performed without a catalyst (Table 2, entry 1). As catalysts were added, the yields greatly increased. Under the same reaction conditions, hosts **4** and **5** showed higher catalytic activity than that of hosts **2** and **3** (Table 2, entries 2–5). These results were in accordance with the results of the liquid membrane transport experiment. Using AgF instead of KF, hosts **4** and **5** still keep the high catalytic activity, although the yields of the product decreased a little (Table 2, entries 6–7). On the other hand, the yields of the products were over 90% when the reaction time was prolonged to 24 h and 36 h (Table 2, entries 8–11). Also, *p*-nitrochlorobenzene, having an electron withdrawing group (1,2-dichloro-4-nitrobenzene or 2,4-dinitrochlorobenzene), offered higher yields (Table 2, entries 12–13), which were attributed to the favorable influence of the electron withdrawing group for an aromatic nucleophilic substitution reaction. The yields were as high as 100% when using 2,4-dinitrochlorobenzene as material.

Also, the replacement of aliphatic Cl by a nitrile group in a benzyl nucleophilic reaction was studied by using new hosts **2**, **3**, **4**, and **5** as phase transfer catalysts. The experiment results are shown in Table 3, which are similar to the results in Table 2. The yields of products were greatly increased from 6.4% to approximately 90% when catalysts were added. Although hosts **4** and **5** showed higher catalytic activities than that of hosts **2** and **3**, the differences in yields were not remarkable. The yields were as high as almost

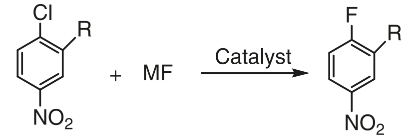
Table 1. Salts concentrations (in the receiving phase) change with running times for different carriers in cation transport.

	$K^+(10^{-3}$ mol/L)				$Zn^{2+}(10^{-3}$ mol/L)				$Ag^+(10^{-3}$ mol/L)			
Carriers[a]	2 h	5 h	10 h	20 h	2 h	5 h	10 h	20 h	2 h	5 h	10 h	20 h
2	0.5	1.1	1.5	1.8	0.2	0.6	0.9	1.1	0.4	1.0	1.6	1.9
3	0.4	0.8	1.4	1.7	0.5	1.0	1.4	1.6	0.4	0.9	1.5	1.7
4	2.3	4.5	5.8	6.3	1.4	3.1	4.5	5.5	2.0	4.1	5.3	6.5
5	3.0	5.6	7.2	8.9	0.8	1.8	3.2	4.3	2.6	4.9	6.6	7.8

Note: The source aqueous solution: 0.05 mol/L of each salt.

[a] Membrane: 5.0×10^{-4} mol/L carrier in $CHCl_3$. For a blank experiment, no transport rate was detected in the absence of carriers during more than 12 h of continuous running.

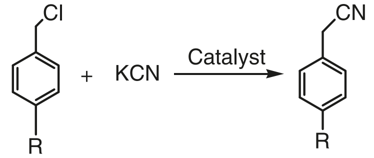
Table 2. Catalytic investigation of compounds **2**, **3**, **4**, and **5** in aromatic nucleophilic reactions.



Entry	R	M^+	Catalyst	Run time (h)	Yield (%)
1	H	K^+	None	12	8.5
2	H	K^+	**2**	12	72.5
3	H	K^+	**3**	12	79.3
4	H	K^+	**4**	12	88.2
5	H	K^+	**5**	12	90.5
6	H	Ag^+	**4**	12	86.4
7	H	Ag^+	**5**	12	88.6
8	H	K^+	**4**	24	94.3
9	H	K^+	**5**	24	96.7
10	H	K^+	**4**	36	97.8
11	H	K^+	**5**	36	98.2
12	Cl	K^+	**5**	24	98.8
13	NO_2	K^+	**5**	24	99.2

Note: Reaction conditions: *p*-nitrochlorobenzene or its derivatives (5 mmol), potassium fluoride or silver fluoride (10 mmol), catalyst (3.0 mol%), DMSO as solvent (12 mL), reaction temperature (40 °C).

Table 3. Catalytic investigation of compounds **2**, **3**, **4**, and **5** in benzyl nucleophilic substitution.



Entry	R	Catalyst	Run time (h)	Yield (%)
1	H	None	12	6.4
2	H	**2**	12	84.2
3	H	**3**	12	88.5
4	H	**4**	12	93.6
5	H	**5**	12	97.4
6	H	**4**	24	98.6
7	H	**5**	24	98.9
8	CH_3	**4**	12	92.1
9	CH_3	**5**	12	88.4
10	CH_3	**4**	24	98.5
11	CH_3	**5**	24	98.2

Note: Reaction conditions: benzyl chloride or *p*-methylbenzyl chloride (5 mmol), potassium cyanide (10 mmol), catalyst (3.0 mol%), DMSO as solvent (12 mL), reaction temperature (40 °C).

100% when the reaction time was prolonged to 24 h. All these catalytic results in Table 2 and Table 3 indicate that novel lariat calix[4]-1,3-aza-crowns (**4** and **5**) are excellent phase transfer catalysts for nucleophilic substitution reactions.

Conclusion

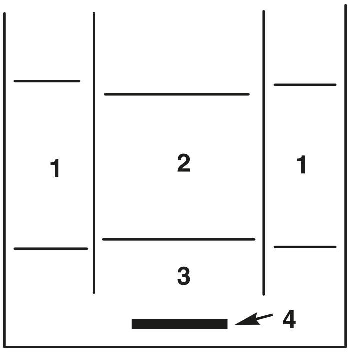
Novel dendritic calix[4]arene derivative (**3**) with two different branched chains was prepared by reacting calix[4]-1,3-diethoxylaminoethyl derivative (**2**) with phenyl isothiocyanate. Novel lariat calix[4]-1,3-aza-crowns (**4** and **5**) with two branched ethoxyl chains were prepared by reacting compound **2** with 1,6-diisocyanatohexane or *N*,*N*′-bis(2-chloracetamide)ethylene in a "1 + 1" intermolecular addition mode. The composition, structures, and conformations of all new compounds were confirmed by elemental analyses, IR, ESI-MS, ^{1}H NMR, and so forth. The liquid–liquid extraction experiment showed that all new hosts possessed good complexation abilities towards soft metal cations and hard metal cations. The liquid membrane transport experiments suggested that they had good transport abilities for both K^+ and Ag^+. The experiments of phase transfer catalysis exhibited that they possessed excellent catalytic properties of aromatic nucleophilic substitution reaction and benzyl nucleophilic substitution. The yields of products in catalytic reaction were as high as approximately 100%.

Experimental section

Instruments

Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker-ARX 500 instrument, using TMS as a reference. ESI-MS spectra were obtained from a DECAX-30000 LCQ Deca XP mass spectrometer in MeCN, setting the ESI capillary at 3.5 kV and the cone voltage at 40 V. Elemental analyses were performed at a Vario EL III elemental analyzer. The UV–vis measurements were performed on a Varian UV–vis spectrometer. The gas chromatography was performed on a Varian 450-GC/240-MS instrument. Atomic absorption was measured on a WFX-II spectrograph. All solvents were purified by standard procedures. 1,3-Broethoxyl-calix[4]arene (**1**) was prepared according to the published procedures.[21] The picrate salts were prepared according to literature.[25,26]

Fig. 2. Liquid membrane cell: (**1**) source phase, (**2**) receiving phase, (**3**) membrane phase, and (**4**) magnetic stirring bar.



Syntheses of calix[4]-1,3-diethoxylaminoethyl derivative (2)

Under N_2 atmosphere, a mixture of compound **1** (0.430 g, 0.5 mmol), ethanolamine (0.30 mL, 5 mmol), and K_2CO_3 (0.280 g, 2 mmol) was stirred in refluxing dry acetonitrile (30 mL) for 48 h. Thin layer chromatography (TLC) detection showed the disappearance of compound **1**. After distilling off the solvent under reduced pressure, the residue was treated with 30 mL HCl (10%) and a white precipitate separated out. The precipitate was filtered and recrystallized by $MeOH/H_2O$. Compound **2** was obtained as a white powder in a yield of 73%; mp 204–206 °C. IR (KBr, cm^{-1}) ν: 3421 (OH and NH). ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.97 (s, 18H, $C(CH_3)_3$), 1.23 (s, 18H, $C(CH_3)_3$), 3.28 (bs, 8H, $ArCH_2Ar$ and OCH_2), 3.49 ~ 3.53 (bs, 8H, NH_2 and OCH_2), 3.88 ~ 3.92 (bs, 4H, NCH_2), 4.16 (s, 4H, OH and NH), 4.24 (d, 4H, J = 13.5 Hz, $ArCH_2Ar$), 6.85 (s, 4H, ArH), 7.01 (s, 4H, ArH), 7.24 (s, 2H, ArOH). ESI-MS m/z (%): 824.0 (MH^+, 100). Anal. calcd. for $C_{52}H_{74}N_2O_6$: C 75.87, H 9.06, N 3.40; found: C 75.77, H 9.15, N 3.29.

Synthesis of novel dendritic calix[4]arene derivative (3)

A mixture of compound **2** (0.205 g, 0.25 mmol) and phenyl isothiocyanate (0.3 mL, 2 mmol) was stirred in 10 mL $CHCl_3$ for 4 h under room temperature. TLC detection indicated the disappearance of compound **2**. The solvent was removed under reduced pressure at room temperature. The residue was treated with 10 mL petroleum ether (60 ~ 90 °C) and a white precipitate separated out. The precipitate was filtered and recrystallized by $CHCl_3$/petroleum ether (60 ~ 90 °C). Compound **3** was obtained as a white powder in a yield of 78%; mp 213–216 °C. IR (KBr, cm^{-1}) ν: 1239 (C=S). ^1H NMR (500 MHz, $CDCl_3$) δ: 0.95 (s, 18H, $C(CH_3)_3$), 1.21 (s, 18H, $C(CH_3)_3$), 3.22 (t, 4H, OCH_2), 3.38 (d, 4H, J = 14.5 Hz, $ArCH_2Ar$), 3.57 (t, 4H, OCH_2), 3.82 (t, 4H, NCH_2), 3.96 ~ 4.01 (m, 4H, NCH_2), 4.28 (d, 4H, J = 14.5 Hz, $ArCH_2Ar$), 6.79 (s, 2H, ArH), 6.96 (d, 4H, J = 7.5 Hz, ArH), 7.15 (s, 4H, ArH), 7.32 (m, 8H, ArH), 7.18, 7.40, 9.48 (s, each, 2H, each, OH and NH). MS m/z (%): 1116.0 (MNa^+, 100). Anal. calcd. for $C_{66}H_{84}N_4S_2O_6$: C 72.50, H 7.74, N 5.12; found: C 72.33, H 7.83, N 5.01.

Synthesis of novel lariat calix[4]-1,3-aza-crown (4)

A mixture of compound **2** (0.205 g, 0.25 mmol) and 1,6-diisocyanatohexane (0.048 mL, 0.3 mmol) was refluxed in 100 mL $CHCl_3$ for 12 h. TLC detection indicated the disappearance of compound **2**. The solvent was removed under reduced pressure. The residue was treated with 10 mL petroleum ether (60 °C ~ 90 °C) and a white precipitate separated out. The precipitate was filtered and recrystallized by $CHCl_3$/petroleum ether (60 ~ 90 °C). Compound **4** was obtained as a white powder in a yield of 62%; mp 232–234 °C. IR (KBr, cm^{-1}) ν: 1703 (C=O). ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (s, 18H, $C(CH_3)_3$), 1.31 (s, 18H, $C(CH_3)_3$), 1.42 (bs, 4H, CH_2), 1.86 (bs, 4H, CH_2), 3.16 ~ 3.30 (m, 8H, NCH_2 and OCH_2), 3.32 (d, 4H, J = 12.5 Hz, $ArCH_2Ar$), 3.49 ~ 4.11 (m, 12H, NH_2 and OCH_2), 4.18 (d, 4H, J = 12.5 Hz, $ArCH_2Ar$), 4.90, 6.34, 6.54 (s, each, 2H, each, OH and NH), 6.66 (s, 4H, ArH), 7.08 (s, 4H, ArH). ESI-MS m/z (%): 990.3 (M^+, 100). Anal. calcd. for $C_{60}H_{86}N_4O_8$: C 72.69, H 8.74, N 5.65; found: C 72.58, H 8.82, N 5.55.

Synthesis of novel lariat calix[4]-1,3-aza-crown (5)

Under N_2 atmosphere, a mixture of compound **2** (0.205 g, 0.25 mmol), *N*,*N*′-bis(2-chloracetamide)ethylene (0.064 g, 0.3 mmol), and K_2CO_3 (0.280 g, 2 mmol) was stirred in refluxing dry acetonitrile (30 mL) for 72 h. The TLC detection indicated the disappearance of compound **2**. After distilling off the solvent under reduced pressure, the residue was purified by column chromatography (50 cm × 3 cm, SiO_2 100–200 mesh, acetone/CH_2Cl_2 (3:2, v/v) as eluant, 500 mL). Compound **5** was then obtained as a white powder in a yield of 42%; mp 241–244 °C. IR (KBr, cm^{-1}) ν: 1653 (C=O). ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.89 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$), 3.26 ~ 3.36 (m, 12H, $ArCH_2Ar$, NCH_2, and OCH_2), 3.65 ~ 4.06 (m, 8H, NH_2 and OCH_2), 4.12 (d, 4H, J = 12.5 Hz, $ArCH_2Ar$), 4.14 ~ 4.33 (m, 8H, OCH_2CO and NCH_2), 6.61 (s, 4H, ArH), 7.08 (s, 4H, ArH), 6.82, 7.01, 8.52 (s, each, 2H, each, OH and NH). ESI-MS m/z (%): 985.8 (MNa^+, 100). Anal. calcd. for $C_{58}H_{82}N_4O_8$: C 72.31, H 8.58, N 5.81; found: C 72.21, H 8.66, N 5.70.

Procedures for two phase extraction experiments of metallic picrates

According to the reported method,[25] 3 mL of chloroform solution containing calixarene derivatives (2.0×10^{-5} mol/L) and 3 mL of aqueous solution containing metallic picrate (2.0×10^{-5} mol/L) were placed in a flask (Caution: metallic picrates are hazardous materials; avoid fire, extrusion, high temperature, and so forth). The pH of 6.9 ~ 7.1 of these aqueous solutions suggests that little hydrolysis happened. 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 of 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. The average of the twice-independent experiments was carried out. Control experiments showed that no picrate extraction occurred in the absence of the calixarene derivatives.

Procedures for metal ion transport experiments

According to the reported method,[27] liquid membrane transport experiments were conducted using the bulk liquid membrane apparatus presented in Fig. 2. The membrane phase was the $CHCl_3$ solution of new host with a concentration of 5.0×10^{-4} mol/L. The membrane phase (25.0 mL) was added to the bottom of the vessel and stirred magnetically at 200 rpm. An aqueous salt solution (15 mL) with a concentration of 0.05 mol/L (source phase, fluorides) and 15 mL of doubly distilled deionized water (receiving phase) were poured on top of the organic phase. The two water phases were separated by a cylindrical glass cell holding a glass tube. The interface between the membrane phase and the source phase (or the receiving phase) was 7.5 cm^2. The measurements were performed at a constant temperature of 25 °C. The concentration of salt in the receiving phase was determined by atomic absorption spectrography. The pH value of the source phase and receiving phase changed in the scope of $6.9 \sim 7.2$, which indicated that little hydrolysis happened in the metal ion transport experiments. Blank experiment showed that no transport was detected in the absence of host during more than 12 h of continuous running. Each experiment was repeated three times. The cation concentration in the receiving phase was reported as the mean of the determination and the relative standard deviation from the mean was less than 5%.

The procedures of phase transfer catalysis of a nucleophilic substitution reaction

A typical nucleophilic substitution reaction was conducted by mixing reactant (5 mmol) and corresponding inorganic salt (10 mmol) in 12 mL of DMSO. The catalyst (3.0 mol%) was added and the reaction was stirred (800 rpm) for a stipulated time period (Table 2 and Table 3) at 40 °C. The yields of product were analyzed by gas chromatography (Varian 450-GC/240-MS).

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