1,3-ALTERNATE CALIX[4]ARENE: THE SOPHISTICATED CONFORMER OF CALIX[4]ARENE. A REVIEW

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Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to supramolecular chemistry.

The fascinating calix[4]arene derivatives in 1,3-alternate conformation are reviewed. The review focuses on their molecular construction methodologies, sophisticated properties and applications. A review with 110 references.

Keywords: Calixarenes; Calix[4]arenes; 1,3-Alternate conformation; Conformation analysis; Supramolecular chemistry; Receptors; Nanomachines; Nanotubes; Crown ethers.

1. INTRODUCTION

In supramolecular chemistry, calixarenes show their potential as a "molecular framework" for construction of supermolecules. Among calixarenes, calix[4]arenes are the most popular due to ease of preparation and func-

tionalization. Moreover, it is generally known that calix[4]arenes exist in four main conformations namely: *cone*, *partial cone*, *1,2-alternate* and *1,3-alternate*. By appropriate functionalization of calix[4]arenes, the desired conformer can be obtained[1–3]. Among these four conformers, the 1,3-alternate one is the most powerful building block for construction of well-defined structures directed towards designed properties[4]. This conformation possesses less polarity than the other conformations: cone, partial cone and 1,2-alternate[4–7]. In addition, it provides more topological advantages because it affords two cavities on each side of the calix[4]arene framework (Fig. 1) composed of two phenolic oxygen donor atoms, two aromatic moieties and D_{2h} tube shaped π-base tunnel[8,9]. In 1:1 complexes this molecular tunnel allows cations to switch from one binding site to the other by the so-called "tunneling effect"[10,11] which leads the chemist to elaborate sophisticated structures such as molecular mappemondes[12,13], molecular mills[13,14] and nanotubes[15,16].

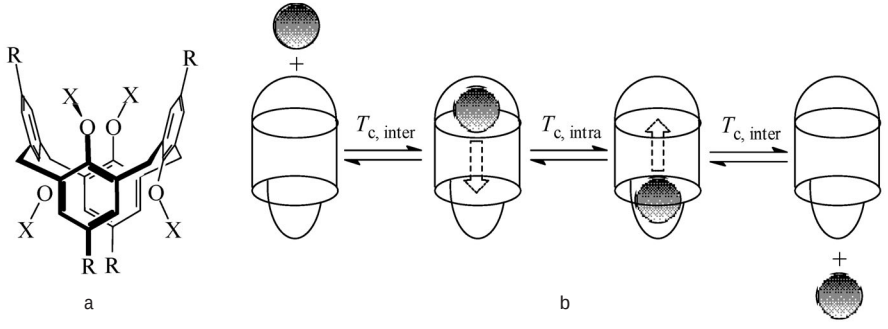


FIG. 1
Two cavities of 1,3-alternate calix[4]arene (a) and cation oscillation in π-base tunnel of 1,3-alternate framework (b) according to investigation by ^{1}H NMR spectroscopy

More specifically, the 1,3-alternate calix[4]arenes composed of two different cavities allow the chemist to build versatile molecules that can provide complex functions such as hard-soft receptors[17,18] capable of binding both hard and soft metal ions simultaneously and molecular syringe[19,20] which can push and pull metal ions passing through π-base tunnel.

Considering the molecular architecture of these 1,3-alternate calix[4]-arenes, they can be categorized into 6 types; open cavities with modified *para*-position, non-identical open cavities, open and bridged cavities, double bridged, identical bridges with modified *para*-position and multi-1,3-alternate calix[4]arenes (Fig. 2).

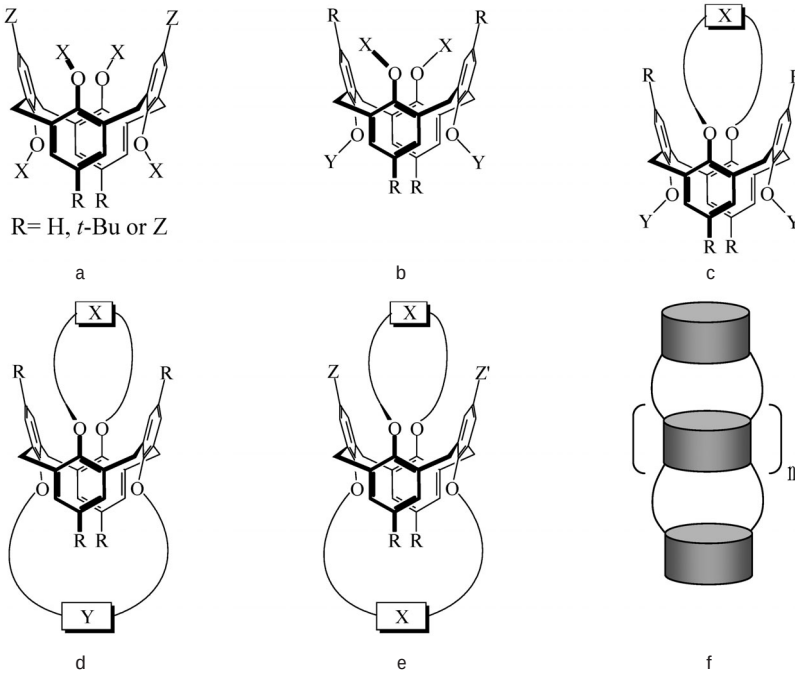


FIG. 2

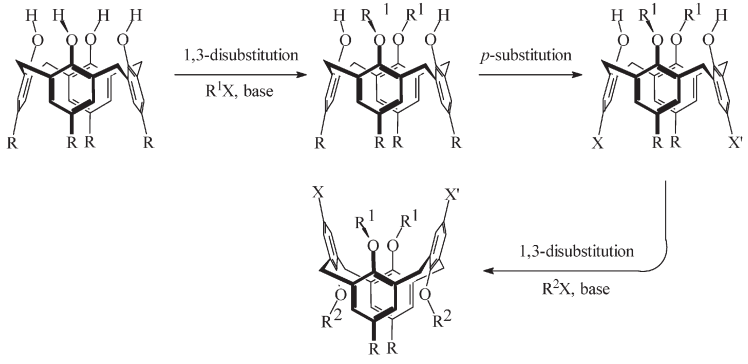
Six types of 1,3-alternate calix[4]arenes: open cavities with modified *para*-position (a), non-identical open cavities (b), open and bridged cavities (c), double bridged cavities (d), double bridged with modified *para*-position cavities (e) and multi-1,3-alternate calix[4]arenes (f)

2. OPEN CAVITIES WITH MODIFIED *para*-POSITION OF 1,3-ALTERNATE CALIX[4]ARENES

This type of 1,3-alternate calix[4]arenes composed of four identical pendant arms and 1,3-phenolic units are modified at the *para*-positions (Fig. 2a). Although this type of 1,3-alternate calix[4]arenes is rare, its synthetical strategy is quite interesting.

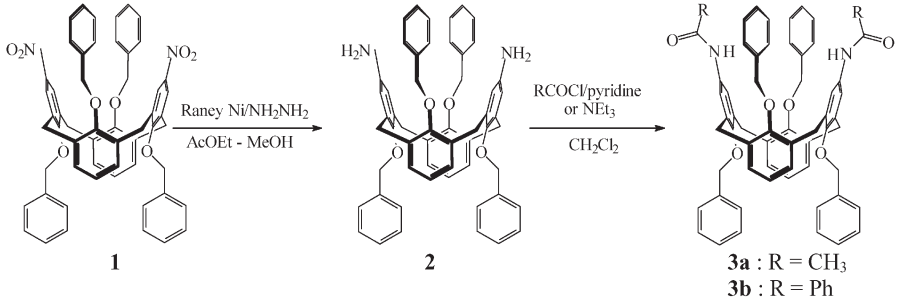
It is well known that the calix[4]arene can be fixed in the 1,3-alternate conformation by functionalization of the hydroxy groups with substituents larger than ethyl group[21]. The general methods for synthesis of symmetrical 1,3-alternate calix[4]arenes are one-pot substitution of calix[4]arene with alkyl tosylate using Cs_2CO_3 as base in DMF at 80 °C [22], in refluxing acetonitrile[23] or acetone[24,25]. The unsymmetrical calix[4]arenes with a modified *para*-position at only one side of the calix[4]arene platform are quite interesting and usually constructed step by step. In the first step, the 1,3-disubstitution is carried out, then, substitution at the *para*-position of free

phenolic units (e.g. bromination[26,27], nitration[28,29]) is performed. Usually the introduced groups are utilized for further functionalization. The last step concerns a second 1,3-disubstitution accompanied with 1,3-alternate conformation inversion (Scheme 1).



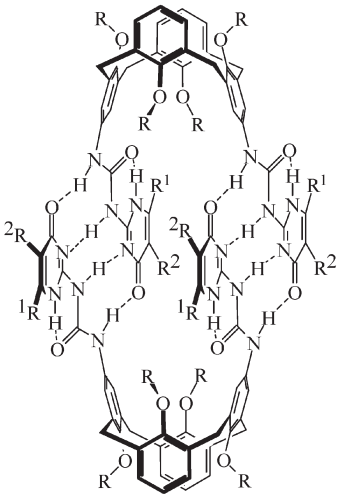
SCHEME 1
Synthetic pathway of open cavities with *para*-modification at only one side of 1,3-alternate calix[4]arenes

This synthetic strategy was employed to synthesize 1,3-alternate dinitrotetrakis(benzyloxy)calix[4]arene **1** [28] which can be further reduced to 1,3-alternate diaminocalix[4]arene **2** and condensed to afford calix[4]arenediamide **3a** and **3b** [29] (Scheme 2).



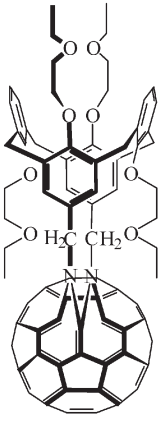
SCHEME 2
Synthetic pathway of 1,3-alternate diamidocalix[4]arenes (**3a**, **3b**)

By the same procedure, 1,3-alternate bis[3-(4-oxo-1-hydropyrimidin-2-yl)-ureido]calix[4]arenes **4a** and **4b** were prepared by passing through 1,3-alternate 5,17-dibromo-25,26,27,28-tetrakis(2-ethoxyethoxy)calix[4]-arene[27]. They form dimers preferentially the *syn*-isomers than the *anti*-isomers (5:1) as revealed by ^{1}H NMR spectroscopy.



4a : R = $EtO(CH_2)_2$, R^1 = *n*-C_9H_{19}, R^2 = H
4b : R = $EtO(CH_2)_2$, R^1 - R^2 = $(CH_2)_4$

This methodology was also used to synthesize "fullerenocalix[4]arene" **5** in which [60]fullerene unit served as a "lid" for the ionophoric cavity. The difference of this architecture from the former examples is a closed cavity made up by cyclization at *para*-position. Upon addition of metal ions, the UV spectrum of **5** scarcely changed but less than that of cone isomer **6**. These 1,3-alternate calix[4]arenes were aimed to serve as "exohedral metallofullerenes"[30].



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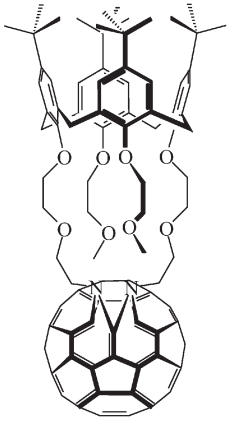

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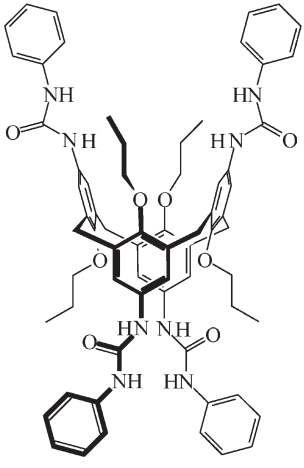
By contrast, the symmetrical 1,3-alternate calix[4]arenes with modified *para*-positions are easier to synthesize than unsymmetrical ones. The functional groups at *para*-position can be introduced either before[25] or after[24] functionalization at phenoxy level.

The 1,3-alternate tetrakis(3-phenylureido)calix[4]arene **7** was synthesized by nitration of 1,3-alternate tetrapropoxycalix[4]arene following by reduction and reaction with phenyl isocyanate[24]. This molecular receptor was aimed to be used as ditopic anion host; however, by ^{1}H NMR titration, it was revealed that this tetraureido derivative showed a very strong negative allosteric effect on the anion binding process in which it could accommodate exclusively one anion instead of two as assumed. Although its binding properties were much similar to the bis(3-phenylureido)calix[4]arene in cone conformation, it provided a distinct size selectivity towards halides, in particular chloride ion[24].



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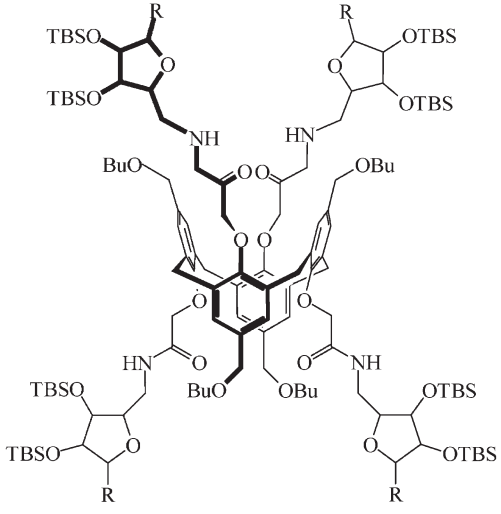
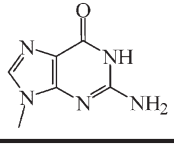
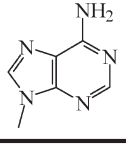


Bu = butyl

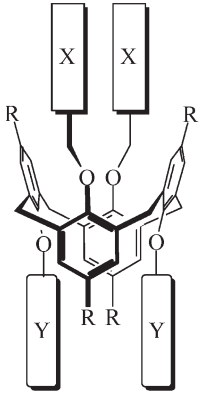
TBS = *tert*-butylsimethylsilyl

8a : R =  **8b : R =** 

Besides the open-cavity 1,3-alternate calix[4]arenes, which can complex solely cation or anion as described, recently, the 1,3-alternate calix[4]arene-guanosine **8a** and 1,3-alternate calix[4]arene-adenosine **8b** were prepared[25]. The water-stabilized dimer of 1,3-alternate calix[4]arene-guanosine conjugate **8a** could act as ion pair receptor which could extract alkali halides from water into organic solution. Both ^{1}H NMR and ion chromatography measurements indicated that a modest selectivities for extracting K^+ over Na^+ and Br^- over Cl^- were obtained[25].

3. NON-IDENTICAL OPEN-CAVITY 1,3-ALTERNATE CALIX[4]ARENES

These calix[4]arenes composed of different kinds of alkyl residues on each side of the 1,3-alternate framework are obtained by two-step alkylation. The first step was carried out using any base but the second one was usually performed using alkyl bromides or alkyl tosylates as alkylating agents and potassium or cesium carbonates as bases[31–37]. Recently, the highly selective preparation of 1,3-alternate **9e** was achieved by using KH in THF at room temperature. This work also showed evidence of the potassium over sodium template effect in the formation of 1,3-alternate conformation[35].



9a R = Bu^t, X = CO_2Et, Y = 

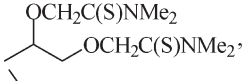
9b R = H, Bu^t, X = CO_2Me, Y = $(CH_2)_nCO_2Et$

9c R = H, X = $C(O)NMe_2$, Y = Pr

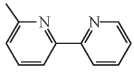
9d R = H, X = $C(S)NMe_2$, Y = Pr

9e R = Bu^t, X = CO_2Me, Y = *n*-Bu

9f R = Bu^t, X = CO_2H, Y = *n*-Bu

9g R = H, X = 

, Y = Pr

9h R = H, X = 

, Y = Pr

From evaluation of lead-selective chemically modified field effect transistors (CHEMFET), it was shown that calix[4]arenedithioamide **9d** in the 1,3-alternate conformation was more selective for Pb^{2+} than the analogous cone conformer. When two pairs of vicinal thioamide moieties were introduced at the same face of 1,3-alternate calix[4]arene **9g**, the highest selectivities were for Cd^{2+} [36]. More recently, the 1,3-alternate calix[4]arene

with dipyridyl pendants **9h** was prepared and its complexation properties towards Cu^{2+} and Co^{2+} were studied. These two cations formed very stable complexes with **9h** with log *K* of about 7, which made the cobalt complex to be a good candidate as dioxygen carrier and the copper complex to be investigated for the catalytic activity of copper enzymes in nonaqueous environment.

Interestingly, the silver complex of 1,3-alternate **10** having two different binding sites showed that, at –85 °C, 8.1% of Ag^+ resided in the cavity composed of two propyl groups and two benzene rings, and 91.9% of Ag^+ was located in the cavity composed of two $EtOCH_2CH_2O$ groups and two benzene rings[38]. This equilibrium was claimed to occur by passing through intramolecular metal vibration inside the π-base tunnel of the 1,3-alternate calix[4]arene (Fig. 3).

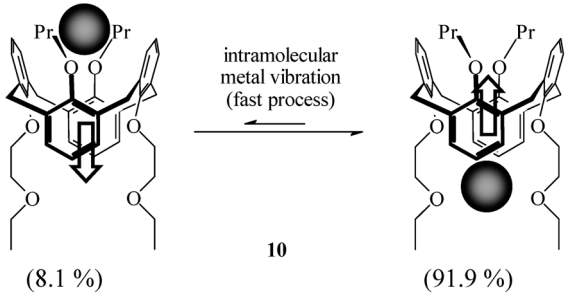


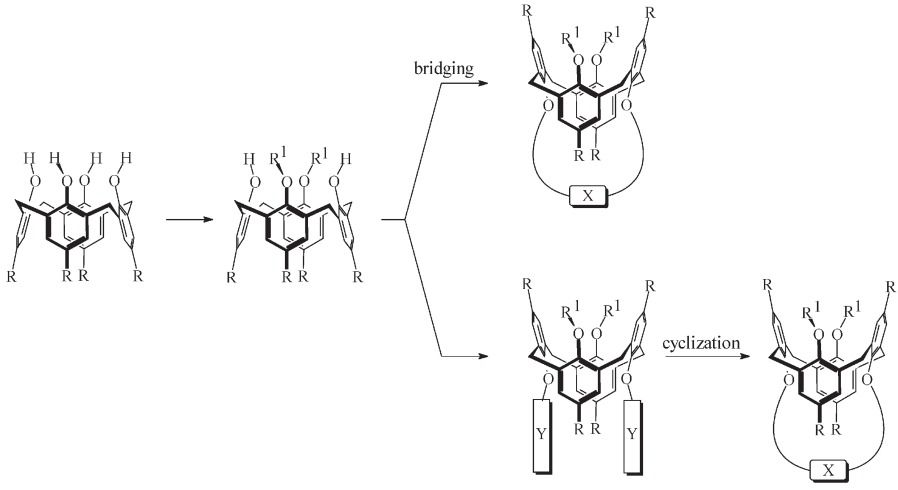
FIG. 3
Different proportions of Ag^+ in the two different cavities of **10**

4. OPEN- AND BRIDGED-CAVITY 1,3-ALTERNATE CALIX[4]ARENES

This architecture is the most popular among unsymmetrical 1,3-alternate calix[4]arenes. They consist of one bridge, usually made of crown ethers, on one side of the 1,3-alternate calix[4]arene framework and two podand arms on the other. The open cavity can provide kinetic properties while the close cavity can offer selectivity of the designed structure.

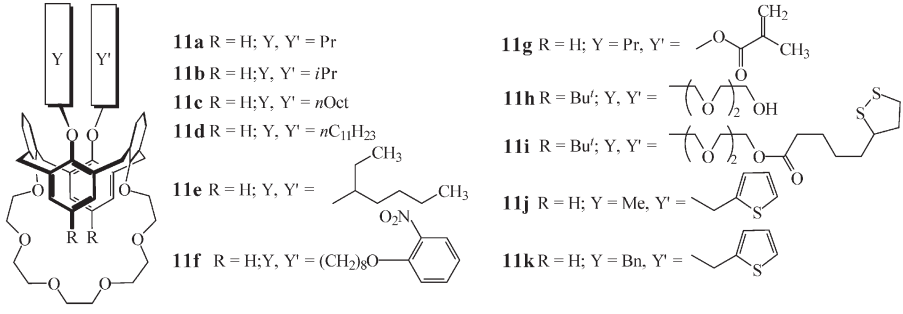
From the synthetic point of view, the 1,3-dialkylation of calix[4]arene was generally carried out first and the close cavity was constructed later in two manners: by bridging or cyclization (Scheme 3).

1,3-Alternate calix[4]crowns were widely synthesized as well as studied for their capabilities as ion-selective receptors. Since it was found, by X-ray crystal structure determination, that 1,3-dimethoxy-*p*-*tert*-butylcalix[4]-arene crown-6 complexes cesium picrate with a very high selectivity by



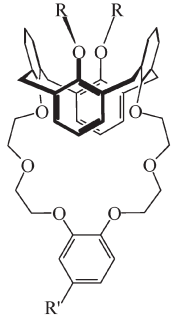
SCHEME 3
Synthetic pathways to open- and closed-cavity 1,3-alternate calix[4]arenes

adopting 1,3-alternate conformation[39,40], many 1,3-alternate calix[4]arene crowns-6 **11a**–**11j** have been synthesized mainly by bridging methodology[39,41–47].



1,3-Alternate calix[4]arene crowns-6 **11a**–**11c** showed much higher efficiency and selectivity for cesium over sodium, which could be explained by the size of the crown ether ring, the less polar 1,3-alternate conformation and the interaction of the cesium ion with π-electron cloud of the arene rings[9,39]. Photophysical properties of 1,3-alternate calix[4]arene crowns-6 were also studied giving evidence of cation–π interactions which played an important role in tuning luminescence properties of the host[48]. Due to their very high selectivities for cesium, the easy removal of cesium cation from the complexes by stripping and their high lipophilicities, these

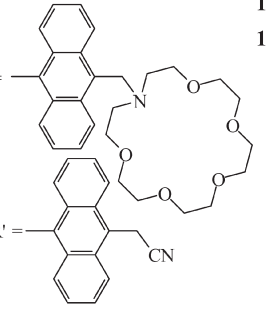
cesium-selective ionophores were highly attractive for treatment of radioactive waste by the supported liquid membrane technique[39,46,49]. Moreover, 1,3-alternate calix[4]arene crown-6 **11g** was attached covalently to polysiloxane to provide durable CHEMFET membranes. The results showed that the sensitivity and selectivity were not affected by this binding and the durability of this CHEMFET membrane was enhanced[42]. An alternative cesium sensor based on self-assembled monolayers (SAM) was made. The 1,3-alternate bis(thioctic ester)-*p*-*tert*-butylcalix[4]crown-6 **11i** was synthesized and self-assembled monolayers were prepared by adsorption on a gold electrode. By impedance spectroscopy and cyclic voltammetry, it was revealed that the SAMs comprising the 1,3-alternate isomer able to recognize cesium ion while that made of its cone conformer had no capability et al.[47] A similar molecular sensor was designed by grafting 1,3-bridged calix[4]-arene crown ether units to position 3 of thiophene (**11j** and **11k**) in order to create conducting polythiophene. These 1,3-alternate calix[4]arene crown ether/polythiophene electropolymers were aimed to selectively recognize and electrochemically respond to alkali metal ions[43].



12a R = *n*-C_8H_{17}, R' = H

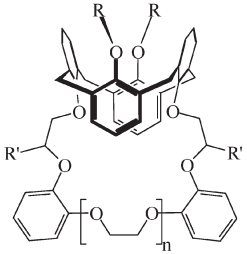
12b R = *n*-C_8H_{17}, R' = CH_2NH_2

12c R = $(CH_2)_3NH_2$, R' = $CH(CH_2CH_3)(CH_2)_3CH_3$



12e R = *i*-C_3H_7, R' =

12f R = , R' =



13a n = 0, R = *n*-C_3H_7, R' = H

13b n = 1, R = *n*-C_3H_7, R' = H

13c n = 1, R = *n*-C_3H_7, R' = C_4H_9

13d n = 1, R = *n*-C_8H_{17}, R' = H

13e n = 1, R = *n*-C_8H_{17}, R' = C_4H_9

13f n = 2, R = *n*-C_3H_7, R' = H

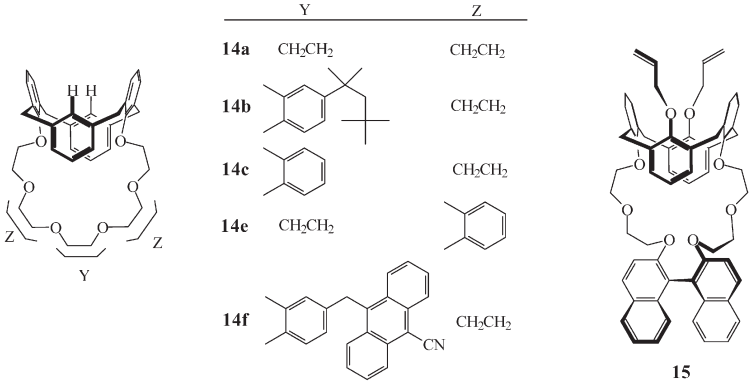
As it was discovered that the replacement of ethylene moieties by phenylene units can greatly improve the Cs^+/Na^+ selectivity in the extraction of cesium from acid radioactive waste[50,51], 1,3-alternate calix[4]arene-monobenzocrown **12a**–**12f** [52–55] and 1,3-alternate calix[4]arene-dibenzocrown **13a**–**13b** [56,57] were synthesized. Although the X-ray crystal structure showed no contribution of benzo units in benzocrown ether loop to cesium complexation, the Cs^+/Na^+ selectivities of these ligands were higher than those of analogous calix[4]arene crowns-6 [56].

In order to enhance the release of cesium ion after complexation, primary amino groups were introduced onto the benzocrown ether loop (**12b**) or onto the open cavity (**12c**). Although the amino groups of both **12b** and **12c** did not enhance the extraction of cesium in alkaline solution, their protonated forms, however, permitted a remarkable pH-switched back-extraction[55].

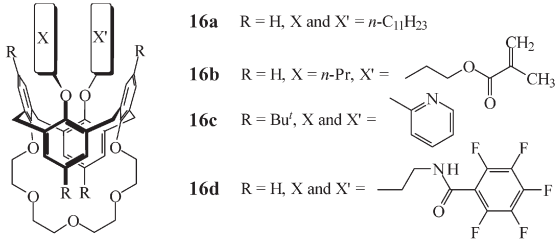
When a fluorophore, anthracene and an azacrown ether, which can influence the emission of the fluorophore by protonation or participation of the nitrogen lone-pair electrons in metal ion complexation, was incorporated in 1,3-alternate calix[4]arene crown ethers, **12e** acted as a supramolecular fluorescent probe: a cesium sensor in acid environment and as a potassium sensor in alkaline environment[52]. In order to increase the Cs/K and Cs/Na selectivity ratios while maintaining fluorescent properties, a cyano group was used instead of the azacrown ether. This cyanoanthracene-modified 1,3-alternate calix[4]benzocrown-6 **12f** represents a new class of Cs^+-selective optical sensors which can bind Cs^+ with a stability constant of 10^7 l/mol [53,54].

By incorporation of two benzo units into crown ether loop (**13a**–**13f**), the 1,3-dipropoxycalix[4]arene-dibenzocrown-6 **13b** gave more efficient and selective extractabilities for cesium over other alkali ions than 1,3-dipropoxycalix[4]arene-dibenzocrown-6 [57].

Very recently, the molecular mechanics calculations performed on the usual 1,3-alternate calix[4]arene crown-6 predicted that the 1,3-alternate 1,3-dihydrocalix[4]arene crown-6 **14a**–**14f** would exhibit greater complementarity for potassium and cesium ions than the parent 1,3-bis(alkoxy)-calix[4]arene crown-6. In experiment, the dihydroxycalix[4]arene crown-6 exhibited enhanced cesium selectivity in the extraction of alkali metal salts due to more bonding interactions between cesium and the two unsubstituted calix[4]arene rings than corresponded to calculations[58]. Besides the use of 1,3-alternate calix[4]arene crown-6 in cesium extraction, a chiral 1,3-alternate 1,1′-binaphthalenecalix[4]arene crown-6 **15** was designed to serve as chemical sensor in detection of ammonium salt enantiomers[59].

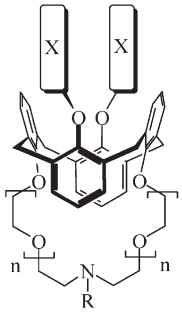


With a smaller crown ether cavities, 1,3-alternate calix[4]arene crown-5 **16a**–**16c** showed high selectivities to potassium ion[42,60,61].



When 1,3-alternate calix[4]arene crown-5 **16b** was covalently bound to CHEMFET membranes, it showed a higher durability compared with **16a** when exposed to a continuous stream of water[42]. By introducing picolyl side arms into the calix[4]arene framework, the 1,3-alternate **16c** showed selectivities for potassium ion similar or even slightly better than valinomycin[60]. By adding pentafluorobenzamide groups as anion binders to the 1,3-alternate calix[4]arene crown-5, the heteroditopic receptor **16d** accommodated both cation and anion simultaneously. Moreover, it self-assembled in a 2:2:2 (calixarene:potassium:acetate) supramolecular structures evidenced by X-ray crystal structure[62].

By replacing the central oxygen atom in crown ether loop by a nitrogen atom, several 1,3-alternate calix[4]azacrown ether, **17a**–**17j**[63–68] and **18**[20], were synthesized to serve as selective extractants for potassium ion[60], ionophores for transition metal-selective polymer-membrane electrodes[66], fluoronophore **17k** with large chelation-enhanced fluorescent (CHEF) effects with Cu^{2+}, K^{+}, Pb^{2+} and Rb^{+} [67] or chromoionophore **17l** for divalent metal ions, in particular Zn^{2+} [68]. These molecular architectures were synthesized by double substitutions followed by cyclization.



17a n = 1, X = *n*-C_3H_7, R = H

17b n = 1, X = *n*-C_3H_7, R = Ts

17c, 17d n = 1, 2; X = *n*-C_3H_7, R =

17e, 17f n = 1, 2; X = *n*-C_3H_7, R =

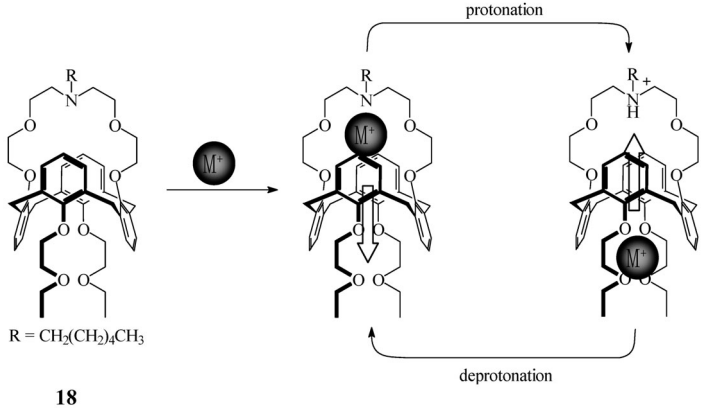
17g, 17h n = 1, 2; X = *n*-C_3H_7, R =

17i, 17j n = 1, 2; X = *n*-C_3H_7, R =

17k n = 1; X = *n*-C_3H_7, R =

17l n = 1; X = *n*-C_3H_7, R =

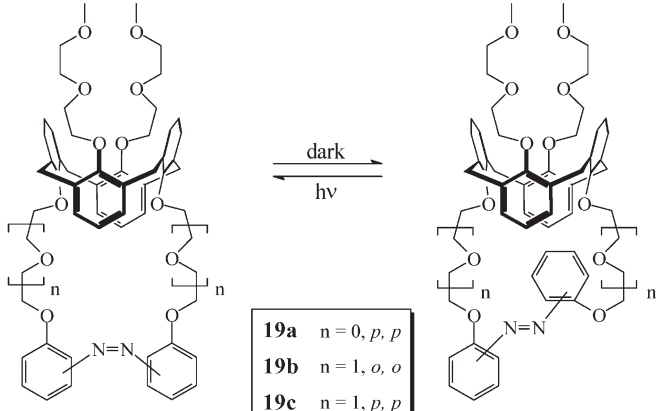
This 1,3-alternate calix[4]arene azacrown ether topology was used to design a "molecular syringe" **18** [20]. In the 1:1 Ag^+ complex, when the nitrogen of the azacrown ether loop was protonated, Ag^+ ion encapsulated in this cavity was pushed out to the bis(ethoxyethoxy) side through the π-base tube of the 1,3-alternate calix[4]arene backbone. These chemically-switchable actions well imitated the function of a syringe, using the π-base tube as a pipette and the crown ring as a rubber cap (Fig. 4)[20].



18

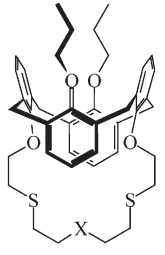
FIG. 4
Molecular syringe **18** derived from 1,3-alternate calix[4]arene azacrown

Besides, a series of 1,3-alternate azacalix[4]crowns **19a**–**19c** was synthesized and their photoisomerization properties were studied on complexations to alkali cations[69,70]. It was found that the two isomers, *Z*- and *E*-, can be switched to each other by UV light or heat in which *Z*-isomer and showed improvement of cesium and rubidium transport through supported liquid membranes (30 to 60%) compared to *E*-isomer[69,70].



19a n = 0, *p*, *p*
19b n = 1, *o*, *o*
19c n = 1, *p*, *p*
19d n = 2, *p*, *p*

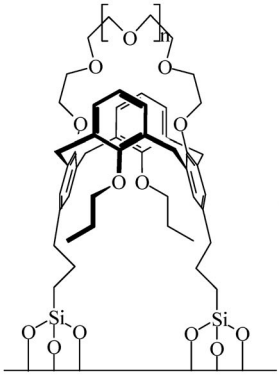
Similarly, the oxygen atoms in crown ether loop of 1,3-alternate calix[4]arene crown were substituted with sulfur atoms in order to increase the silver ion binding ability. The 1,3-alternate dipropoxycalix[4]monothiacrowns **20a**, **20b** were synthesized. These calix[4]thiacrowns showed a very high selectivity for silver ion over other metal ions due to electrostatic interaction between sulfur atoms and silver ion due to π-metal interaction[71].



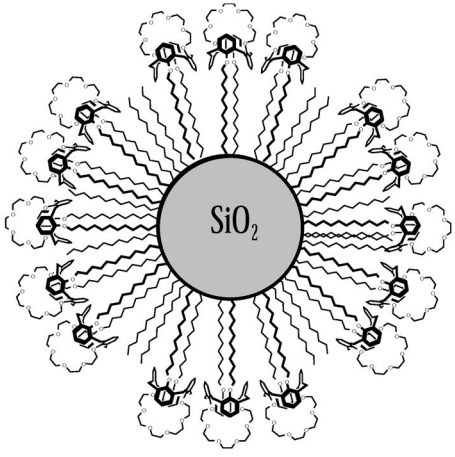
20a X = O
20b X = S

Due to the cesium selectivity potential of 1,3-alternate calix[4]arene crown for separation, they were grafted covalently to the silica gel via hydrosilanization (**21**) and successfully employed for chromatographic sep-

aration of Cs^+ and K^+ from alkali metal ions[72]. In addition, 1,3-bis[1-(11-hydroxyundecyl)oxy]calix[4]arene crown-6 was grafted onto an inorganic silica core to provide a colloid receptor **22**. The NMR and electrophoresis indicated that these calixarene colloids indeed were receptors for cesium ion[73].



21a, b n = 1 or 2



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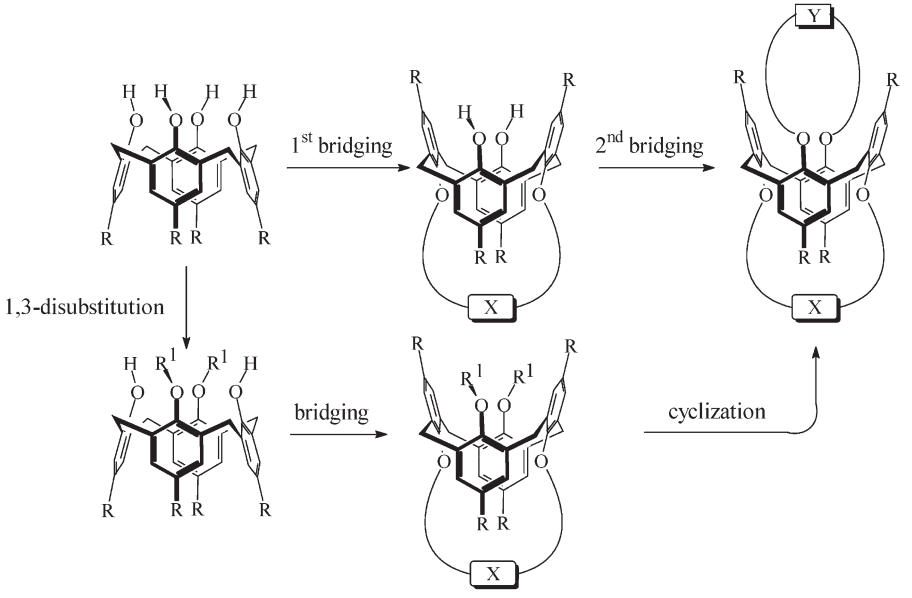
5. DOUBLE BRIDGED 1,3-ALTERNATE CALIX[4]ARENES

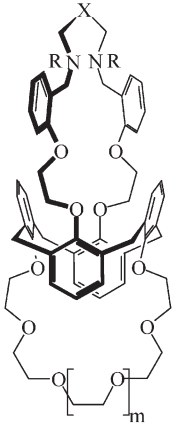
This 1,3-alternate calix[4]arene architecture consists of two identical or different closed cavities on each side of the calix[4]arene framework. For asymmetric bridges, the two cavities can differ in size, shape and/or type of donor atoms providing more sophisticated properties including selectivity and stability.

Regarding the synthetic strategy, symmetric double bridged 1,3-alternate calix[4]arenes can easily be prepared by two-step one-pot reaction[74]. On contrast, asymmetric 1,3-alternate structure can be constructed in two ways as shown in Scheme 4. The first pathway consists of two bridging steps while the other involves three steps: 1,3-disubstitution, bridging and cyclization.

The sequence of construction of the bridges is more or less important for the synthesis of this class of 1,3-alternate calix[4]arenes. It was demonstrated that, in the synthesis of **23f**, the first bridging by a less flexible chain gave a better yield than bridging with a more flexible chain[75,76].



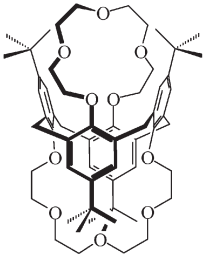
SCHEME 4
Synthetic pathways to asymmetric closed-cavity 1,3-alternate calix[4]arenes



23a X = -, m = 0, R = H
23b X = CH_2, m = 0, R = H
23c X = $(CH_2)_2$, m = 0, R = H
23d X = $(CH_2CH_2)_2NH$, m = 0, R = H
23e X = -, m = 1, R = Ts
23f X = CH_2, m = 1, R = H
23g X = $(CH_2)_2$, m = 1, R = Ts
23h X = $(CH_2CH_2)_2O$, m = 1, R = H

The first symmetrical double bridged 1,3-alternate calix[4]arene reported was 1,3-*p*-*tert*-butylcalix[4]-biscrown-5 **24** [77]. Because these 1,3-alternate crowns can serve as extractants in treatment of nuclear waste containing radioactive ^{137}Cs ion, a series of 1,3-alternate calix[4]arene crown ethers **25a**–**25g** [78–80] was synthesized and used as selective carriers in supported liquid membranes (SLM). Compounds **25c** and **25f** showed high SLM stabil-

ities and high decontamination yields[78]. Recently, 1,3-alternate calix[4]-arene crown ethers **25f** were employed in the complexation and transportation of francium ion for synthesis of radiopharmaceuticals[81]. By incorporation of coumarin as a fluorophore into the crown of 1,3-alternate calix[4]-arene crown-6, a fluorescent molecular sensor **25g** exhibited an excellent selectivity to cesium ion over sodium ion. This calix[4]coumarin derivative showed only a medium selectivity to potassium ion over sodium ion but still quite promising for analytical biochemistry, i.e. for detection of potassium ion in blood and urine which contain high concentrations of sodium ions[80]. The cation oscillation in a π-base tunnel of 1,3-alternate calix[4]-arene, an interesting phenomenon, was observed in this molecular architecture[82,83].



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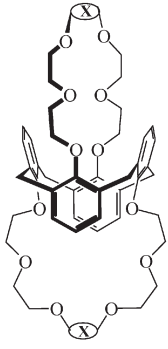
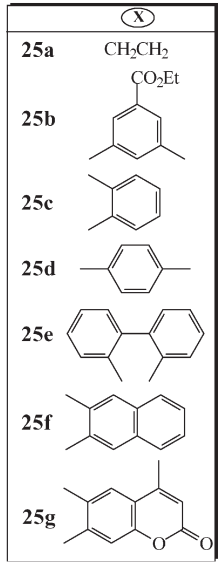
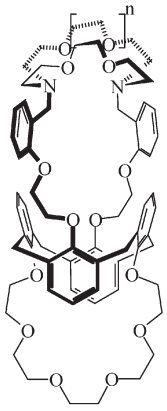




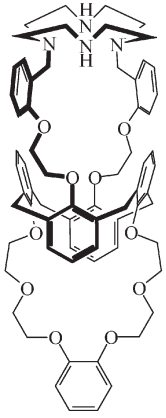
Due to the different cavities of asymmetric double bridged 1,3-alternate calix[4]arene, these ditopic ligands can act as “hard” and “soft” receptors in which the two binding sites can communicate through the 1,3-alternate calix[4]arene unit[75,76,84].

Starting from the protocols **23a**–**23h**, many sophisticated 1,3-alternate calix[4]arenes **26**–**29** were synthesized[17,18,76,85–87].

To increase the binding ability, 1,3-alternate calix[4]arene-cryptand-crown-6, **26a** and **26b**, were designed. By complexation studies, it was demonstrated that **26b** can accommodate Na^+, K^+, NH_4^+ and Rb^+ in the cryptand cavity whereas Rb^+ and Cs^+ resided in the crown-6 cavity. More-



26a n = 0
26b n = 1



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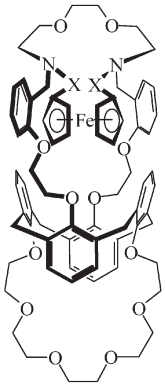
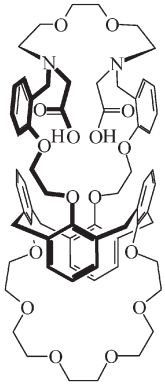
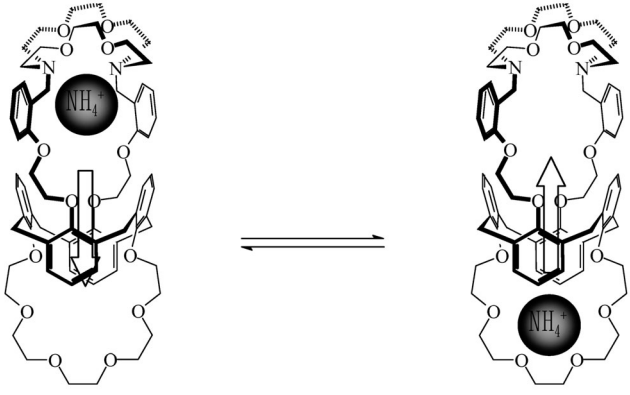


28a X = C=O
28b X = CH_2



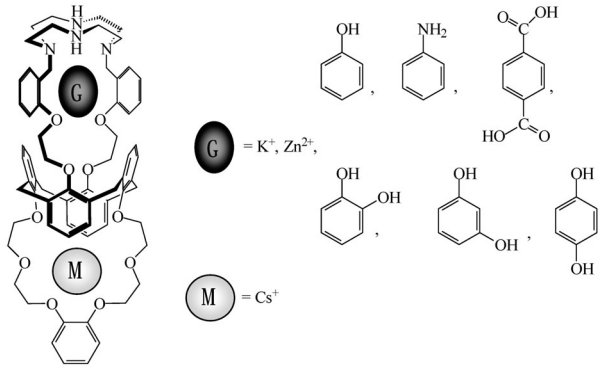
29

over, $Na^+ \cdot Cs^+ \cdot$**26b** and $K^+ \cdot Cs^+ \cdot$**26b** heterodinuclear complexes were prepared[76]. As a "hard-soft" receptor, **26b** showed complexation abilities with Ni^{2+} and Zn^{2+} also with Cs^+ [88]. In the NH_4^+ complex, the NH_4^+ cation can travel from the cryptand cavity to the crown ether one by passing through a π-base 1,3-alternate calix[4]arene channel with an exchange velocity (k_c) of 169 s^{-1} and activation Gibbs energy ($\Delta G_c^{\#}$) 12 kcal/mol [76]. This is the first evidence of cation oscillation for an unsymmetrical-bridge-cavity 1,3-alternate calix[4]arene.



26b **26b**

In order to increase its binding abilities to transition metals for serving as Cs^+ sensor, 1,3-alternate calix[4]arene-cyclen-benzocrown-6 **27** was synthesized[85]. Its cyclen unit can accommodate transition ions such as Zn^{2+} as well as some organic molecules possessing hydrogen bond donors, for example phenol, aniline, catechol, resorcinol, hydroquinone and terephthalic acid while its benzocrown moiety showed its ability to complex Cs^+ [85].



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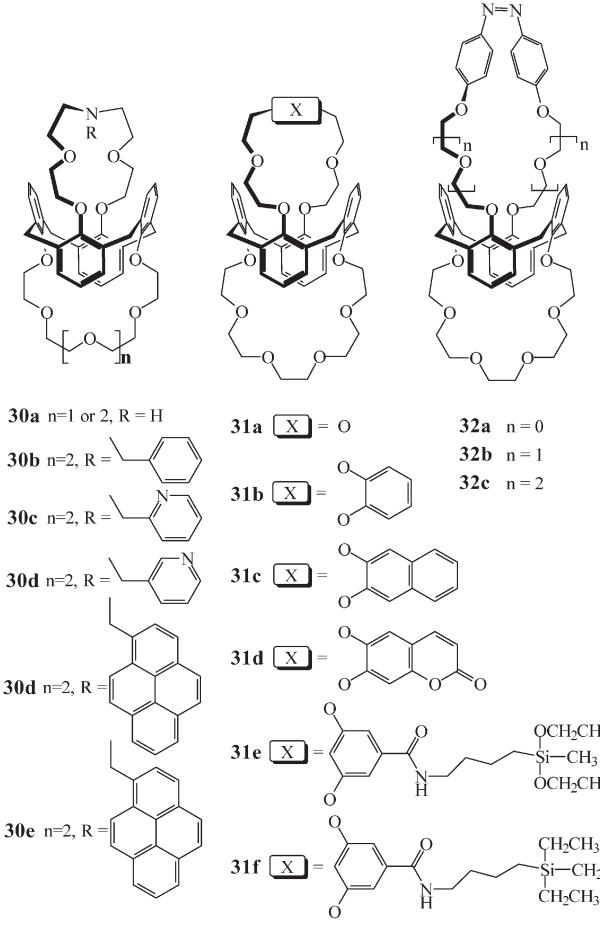
With the intention to find molecular sensors and/or catalysts, a redox-active center, ferrocene, was incorporated into the 1,3-alternate calix[4]-arene framework[86]. Complexation properties of these two redox-active calixarenes **28a** and **28b** to alkali and alkaline earth cations were studied by cyclic votammetry. **28a** and **28b** were shown to possess pseudo-reversible redox properties[86].

By incorporating ionizable moieties into the 1,3-alternate calix[4]arene skeleton, calix[4]arene-amino acid-crown-6 **29** was synthesized and studied for its complexation of alkali, alkaline earth, heavy and transition metal ions as well as some lanthanide ions by pH-metry and UV spectrophotometry. The results suggested that alkali metal ions were located only near the glycol chain, and other cations in the crown unit bearing the amino acid moieties. The results showed that the two crown units behave independently and the ligand is capable of binding two cations of different nature (e.g. alkali cation and transition metal ion) simultaneously[87]. The effect of nitrogen donor atoms in enhancing the binding ability was confirmed by a comparison with complexation of 1,3-alternate calix[4]azacrown-5 **30a** and 1,3-alternate calix[4]-biscrown-5. The results lead to the conclusion that the replacement of the central O atom by NH group in the crown ether cavity provided a better binding[89]. Moreover, the silver ion oscillation through the calix[4]azacrown tube of **30a** and its corresponding

symmetrical 1,3-alternate calix[4]-bisazacrown-5 was detected. The latter exhibited an intramolecular metal ion tunneling but not the former[90].

Considering the substituents on nitrogen atom, the picolyl groups in **30c** and **30d** participated in silver ion complexation while the benzyl group (**30b**) did not[91]. When a fluorescent moiety, pyrene, was attached to nitrogen atom, "molecular Taekowndo" processes between Ag^+–K^+, Cu^{2+}–K^+ and Ag^+–Cs^+ pairs were easily monitored via fluorescence change[67]. These phenomena between Cu^{2+}–Cs^+ and Ag^+–Cs^+ pairs were also observed in 1,3-alternate calix[4]cyanoanthracenylcrown-azacrown[92].

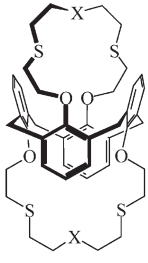


In the family of crown ethers, 1,3-alternate calix[4]arenes with unsymmetrical cavities **31a**–**31f** were synthesized[80,93–98]. Recently, 1,3-alternate calix[4]crown-5-crown-6 **31a** was synthesized and the $2K^+$·**31a** homo-

dinuclear and $K^+ \cdot Cs^+ \cdot$**31a** heterodinuclear complexes were prepared[93]. In these complexes, the potassium ion can be accommodated by both crown-5 and crown-6 cavities whereas cesium ion was encapsulated only in the crown-6 loop. This was evidenced by the X-ray structure determination[94]. The introduction of 1,2-phenylene (**31b**) or naphthylene-2,3-diyl (**31c**) groups into the crown-6 cavities improved the Cs^+/Na^+ selectivities[95]. The ^1H NMR spectra and X-ray crystal structure of their cesium complexes showed that cesium ion preferred to be complexed in the polyether loop containing aromatic units[95]. The coumarin unit (**31d**) also increased the Cs^+/Na^+ (4.0×10^4) and K^+/Na^+ (540) selectivities[80]. In order to reduce the loss of calix[4]arene crown-6 in the removal of cesium from high-sodium liquid wastes, 1,3-alternate calix[4]arenes **31e** and **31f** were prepared and grafted onto a polysiloxane backbone by a sol-gel process[96]. From solid–liquid extraction studies, it was found that the performance, efficiency and selectivity decreased compared with liquid–liquid extraction. This was due to steric hindrance, cavity deformation and micro-environmental polarity resulting from the grafting of the carrier[96].

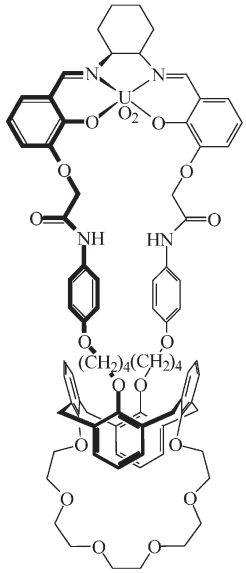
Allosteric systems based on 1,3-alternate calix[4]arenes were designed and synthesized by incorporating azobenzene unit into crown ether loop **32a**–**32c** [97,98]. In the case of **32b**, preliminary complexation studies of alkali and ammonium cations showed that these cations are located in unmodified crown-6 cavity of 1:1 complexes. The complexation can also induce the changes in the *cis*/*trans* ratio of azobenzene unit which resulted from the conformational changes of 1,3-alternate calix[4]arene platform[97]. The X-ray crystallographic evidence, for **32a** and its cesium complex, of reorganizations of **32a** prior to complexation was also given[98].

By integrating sulfur atoms into crown ether bridges, the 1,3-alternate calix[4]-bisthiacrowns **33a**, **33b** exhibited very high selectivities for silver ion over alkali and other transition metal ions. However, these selectivities were much less than those of their monocrown analogues[71].



33a X = O
33b X = S

In order to complex simultaneously both cation and anion, 1,3-alternate uranylcalix[4]arene-salophen-crown-6 **34** was synthesized and used to study the transportation of CsCl and $CsNO_3$ from aqueous phase to acetonitrile across supported liquid membranes[99].



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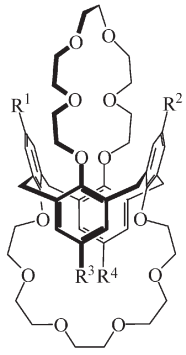
6. IDENTICAL BRIDGES WITH *PARA*-MODIFIED 1,3-ALTERNATE CALIX[4]ARENES

This molecular structure can be prepared starting from double bridged 1,3-alternate calix[4]arene. Many substituents, bromo[100,101], nitro[102], carboxylic[100,101], aldehyde[101] and hydroxy groups[102], can be selectively introduced at *para*-positions of benzene ring of the 1,3-alternate calix[4]arene framework to provide desired properties. The bromo derivatives **35a** and **35k** were very useful for replacement by other functional groups[100,101].

Proton-ionizable calix[4]arenes, **35c**, **35h** and **35i**, were used to study their affinity to alkali cations and to determine the cesium/sodium selectivity. The results revealed that all 1,3-alternate calix[4]arene crown-6 containing ionizable groups at *para*-position possessed higher Cs^+ extraction efficiency than the conventional 1,3-alternate calix[4]arene crown-6 [100,101]. Moreover, the dihydroxycalix[4]arene-biscrown-6 **35i** exhibited a higher Cs^+/Na^+ selectivity than dicarboxylate **35h** but lower than tetrahydroxycalix[4]arene-biscrown-6 **35l** [101].



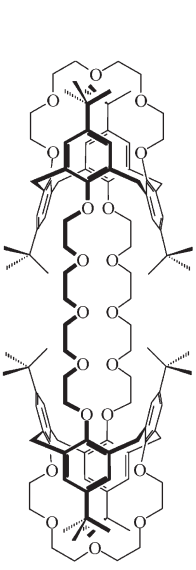
	R^1	R^2	R^3	R^4
35a	H	H	H	Br
35b	H	H	H	NO_2
35c	H	H	H	CO_2H
35d	H	H	H	$CONHSO_2CF_3$
35e	H	NO_2	H	NO_2
35f	H	H	NO_2	NO_2
35g	H	H	CHO	CHO
35h	H	H	CO_2H	CO_2H
35i	H	H	OH	OH
35j	H	NO_2	NO_2	NO_2
35k	Br	Br	Br	Br
35l	OH	OH	OH	OH
35m	NO_2	NO_2	NO_2	NO_2

The participation in Cs^+ complexation of nitro group in mononitro ligand **35b** was observed; however, tetranitro one **35m** did not extract cesium ions[102].

7. MULTI-1,3-ALTERNATE CALIX[4]ARENES: AN APPROACH TO CALIX[4]ARENE NANOTUBES

By linking 1,3-alternate calix[4]arene framework together at the phenoxy group or *para*-positions, calix[4]arene nanotubes have been achieved. A first double 1,3-alternate calix[4]arene **36** was prepared in 1992 [103]. From complexation studies, it was found that K^+ and Rb^+ reside only in the central crown ether cavity of **36** but not in crown-5 loops at the extremities due to the steric hindrance of *tert*-butyl groups[103]. Analogous debutylated dimers were synthesized and their complexation studies proved, by X-ray investigation of crystal structures, that the alkali ions are preferably located in two extreme cavities[104]. Furthermore, the corresponding trimer **37a** and pentamer **37b** were also prepared; it formed homodinuclear complexes as found in the dimers[104].

The calix[4]arene nanotube **38** containing three 1,3-alternate calix[4]arene units was prepared but no metal (Ag^+) oscillation in the 1,3-alternate calix[4]arene tunnel of the silver complex was observed[105]. Nevertheless, the tubular configuration of multi-1,3-alternate calix[4]arene was confirmed by the X-ray crystal structure of double calix[4]arene **39**. This nanotube possessed a cross-section of 12 Å and a length of 28 Å. Its inside diameter varied between 4.1–4.5 Å and the two terephthaloyl units were parallel and separated by 3.3–3.9 Å [106].



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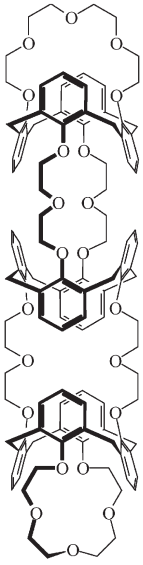

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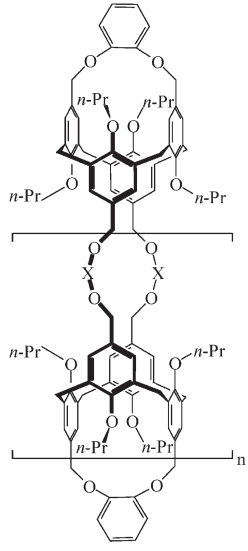

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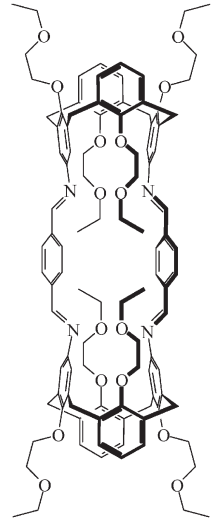

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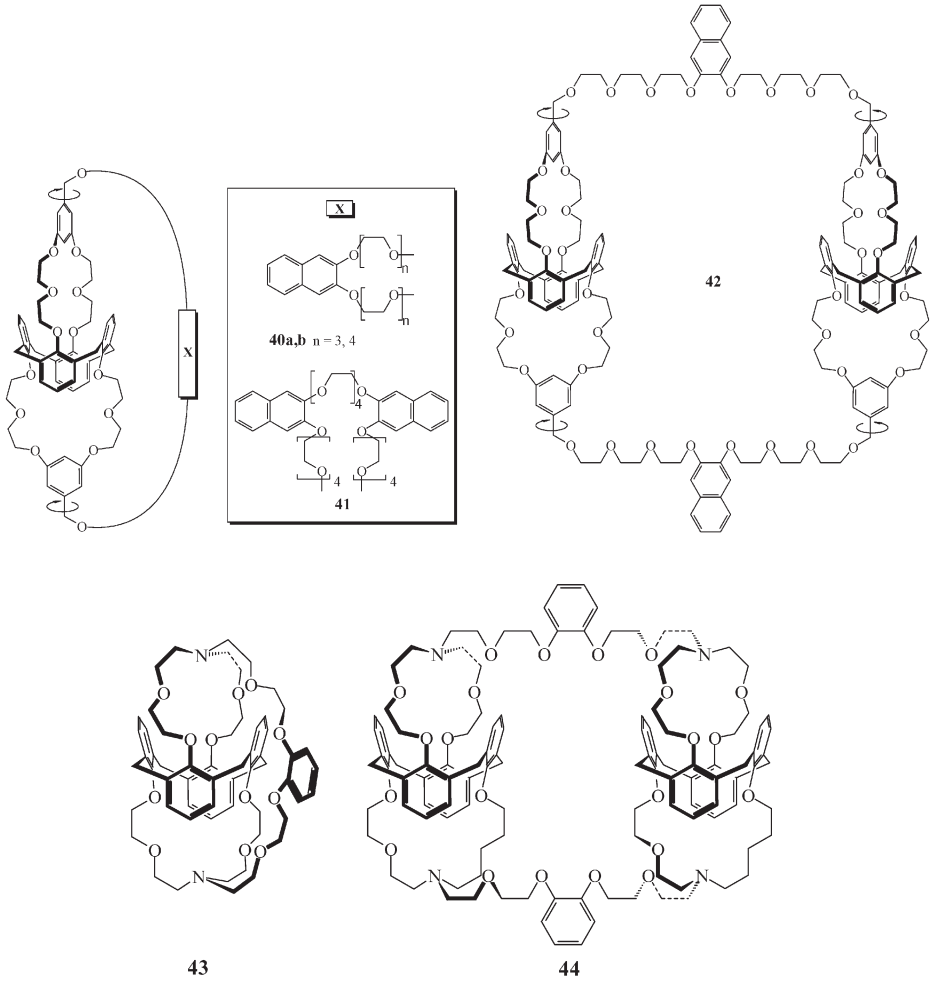
8. STRAPPED 1,3-ALTERNATE CALIX[4]-BISCROWNS: AN APPROACH TO CALIX[4]ARENE MOTORS

Attempts to integrate mechanical properties into the 1,3-alternate calix[4]-biscrown to elaborate calix[4]arene-based motors were performed[12–14]. The "mappemonde" **40a**, **40b** and **41** were designed by computer assistance and synthesized[12]. By ^{1}H NMR spectroscopy, it was demonstrated that these globular calix[4]crowns spinned about the axis both in the free and complexed forms[12].

A molecular "mill" **42** was also constructed. The rotation of calix[4]arene units was observed[14].

The second generation of molecular "mappemonde" and "mill" was accomplished with 1,3-alternate calix[4]-bisazacrown. In these molecular architectures **43** and **44**, no spinning about the axis was observed[13].



9. CONCLUSIONS

Out of different conformers of calix[4]arene, we confine ourselves in reviewing calix[4]arene chemistry only to the 1,3-alternate conformation due to its sophisticated structure which provides two well-defined cavities linked by π-base channel. Regarding to synthetic strategies and applications, 1,3-alternate calix[4]arene derivatives are classed into six types: open cavities with modified *para*-position, non-identical open cavities, open and bridged cavities, double bridged cavities, double bridged with modified *para*-position cavities and multi-1,3-alternate calix[4]arenes. The open-

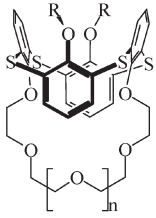
cavity 1,3-alternate calix[4]arenes that have the kinetic advantage are used as molecular sensors in CHEMFET and SAM sensors. More selectivities are obtained when open-cavity 1,3-alternate calix[4]arenes are replaced with open- and bridged-cavity 1,3-alternate calix[4]arenes. During the last ten years, many developments have been realized, from simple ditopic receptors, two open-cavity 1,3-alternate calix[4]arenes, to molecular nanotubes, molecular motors and beyond.

10. PERSPECTIVES

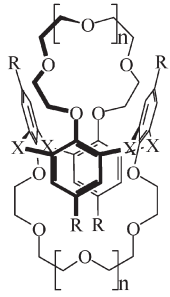
One of the most potential applications of 1,3-alternate calix[4]arenes which should be emphasized here is their use in selective extractions of cesium from radioactive waste treatment as for example the grafting of by covalently linking asymmetric 1,3-alternate calix[4]arene by one crown loop to support material or simply adsorbed on a stationary phase. Biological systems are sophisticated molecular machines giving rise to never-seen phenomena and calix[4]arenes in the 1,3-alternate conformation offer the possibility of mimicking such biological systems. One can envisage that metal oscillation through the calix[4]arene unit is similar to channel-movement of cations and anions in natural polymers. The synthesis of nanotubes constructed with several calix[4]arene unit open the road to the creation of ion channels to be incorporated in natural membranes. The STM technique used to look at macromolecules as simple object allows the chemists to think that, as an example, the complexation of a cation in a macrocycle can be “touched and revealed as a real image” at the molecular level.

Continuous developments of this calixarene family extend to the analogous platform that contains sulfide, sulfoxide or sulfone bridges, thiacalix[4]arene, sulfinylcalix[4]arenes and sulfonylcalix[4]arenes. These molecular frameworks are different from the conventional calix[4]arenes in terms of cavity sizes, e.g. 5.5 Å in case of thiacalix[4]crowns and 5.1 Å in case of conventional calix[4]crowns[107], and electronic densities[107,108]. Some interesting phenomena were found such as complexation and metal oscillation behaviors. Some examples that demonstrate these mentioned phenomena belong to 1,3-alternate thiacalix[4]arene-monocrowns **45a**–**45c** [108,109] and 1,3-alternate thiacalix[4]arene-biscrowns **46a**–**46f** [109,110]. From extraction studies, it was found that the extraction abilities of 1,3-alternate thiacalix[4]arene-monocrowns **45a**–**45c** were lower than those of the conventional 1,3-alternate calix[4]arene-monocrowns. This was explained by weaker electrostatic interaction of polyether ring oxygen atoms with metal ions and diminished π-metal interaction between metal ions

and the aromatic rings of thiacalix[4]arene evidenced by X-ray crystal structure and ^{1}H NMR spectroscopy[109]. The metal ion shuttling was found in 1,3-alternate thiacalix[4]arene-biscrowns **46a**–**46d** [109]. It was revealed that the metal ion exchange was more facile than in the conventional 1,3-alternate calix[4]arene-biscrowns which was described by same effects that were found in 1,3-alternate thiacalix[4]arene-monocrowns[109].



45a n = 1, R = Me
45b n = 2, R = Me
45c n = 1, R = Pr
45d n = 2, R = Pr
45e n = 3, R = Pr



	R	X	n
46a	Bu^t	S	1
46b	H	S	1
46c	Bu^t	S	2
46d	H	S	2
46e	Bu^t	SO_2	1
46f	H	SO_2	1

In case of sulfone bridge, 1,3-alternate sulfonylcalix[4]arene-biscrowns **46e**, **46f** possessed the extraction abilities for alkali ions slightly inferior than the calix[4]arene-biscrown but provided slightly superior selectivities[110].

These sulfur-containing bridge calix[4]arene families open more opportunity for the chemists to create more realistic ion channels, nanotubes as well as molecular devices. Within this cylindrical framework, ones can expand the utilization of calix[4]arenes to specific applications that may meet needs of technologies for 21st century.

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