

Calixarene-Based Molecules for Cation Recognition

Rainer Ludwig* and Nguyen Thi Kim Dzung

Institute of Chemistry/Inorg. and Analyt. Chem., Freie Universitaet Berlin, Fabeckstr. 34-36,
14195 Berlin, Germany, Tel: 30 838 52458, Fax: 30 838 52424.

* Author to whom correspondence should be addressed. E-mail: rludwig@mail.chemie.fu-berlin.de

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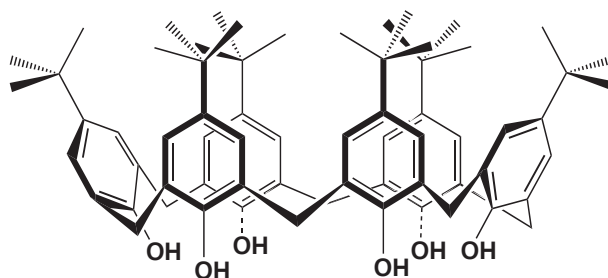
Abstract: This review discusses molecular design principles of calixarene-type macrocycles for ion recognition and gives examples on the relationship between structure and selectivity, however without attempting to cover all the different approaches.

Keywords: Macrocycles, Cyclophanes, Calixarenes, Ion Recognition.

Introduction

Macrocyclic compounds such as crown ethers and cryptands are well-known for their relationship between molecular design and selectivity in complexation of ions. When aromatic subunits are bridged by spacers forming a ring, these macrocycles are called cyclophanes. Phenolic units bridged by methylene spacers in meta-position are called calixarenes, although in recent years macrocycles with related subunits such as resorcin or pyrrol and other spacers such as sulfur are also considered to belong to the same class. Their synthesis, properties and applications are subject of several books, e.g. [1-6] and reviews such as [7-11] and many more as cited in [in 3, p.4-5].

Figure 1. *tert*-Butylcalix[6]arene, comprising 6 CH₂-bridged phenyl rings. The conformation, where substituents at the phenyl rings show into the same direction, is called ‘cone’.



The macrocyclic ring in calixarenes acts as a molecular backbone to which ligating functional groups are attached. There are many examples however where the ring itself engages in binding such as with its π -basic phenolic cavities to class B cations, to class A cations with the phenolic oxygen atoms or to organic molecules by CH- π or π - π -stacking interactions.

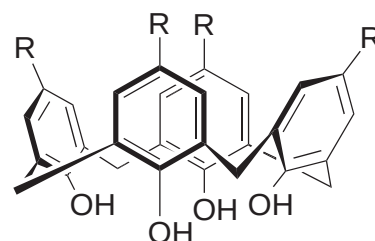
The molecular design allows the rational control of binding properties such as complex stability and selectivity. The main design features are:

- a) The size of the cavity is large enough to accommodate the metal cation. During complexation, the hydration shell is removed from the cation and substituted by the donor atoms of the ligand.
- b) There is a sufficient number of donor atoms in the ligand in order to match the coordination number.
- c) The donor atoms are held by the calixarene backbone with limited flexibility in positions suitable to match the shape of the coordination sphere.
- d) The 'classical' mechanisms of complexation apply to calixarenes as well, ion exchange or ion pairing, with the difference that now several ionizable, chelation or solvating donor groups are combined within one molecule.
- e) Often, synergy is observed if these are different functional groups, e.g. neutral and ionizable.
- f) Using the macrocyclic backbone, an excess of certain ligating groups can be avoided, thus improving the selectivity. E.g. for a divalent cation two ionizable groups are introduced into calix[4]arene which could hold a maximum of four of them. The remaining two neutral binding groups fill up the coordination sphere.
- g) There is a possibility to attach chelating moieties onto calixarenes, thus combining the chelate and the macrocyclic effect. However, the chelating groups increase the flexibility of the ligand and may reduce the overall selectivity. Our own approach is therefore the use of short functional groups.
- h) Branched alkyl groups are attached to the phenyl rings for high hydrophobicity and to avoid crystallized membrane phases.

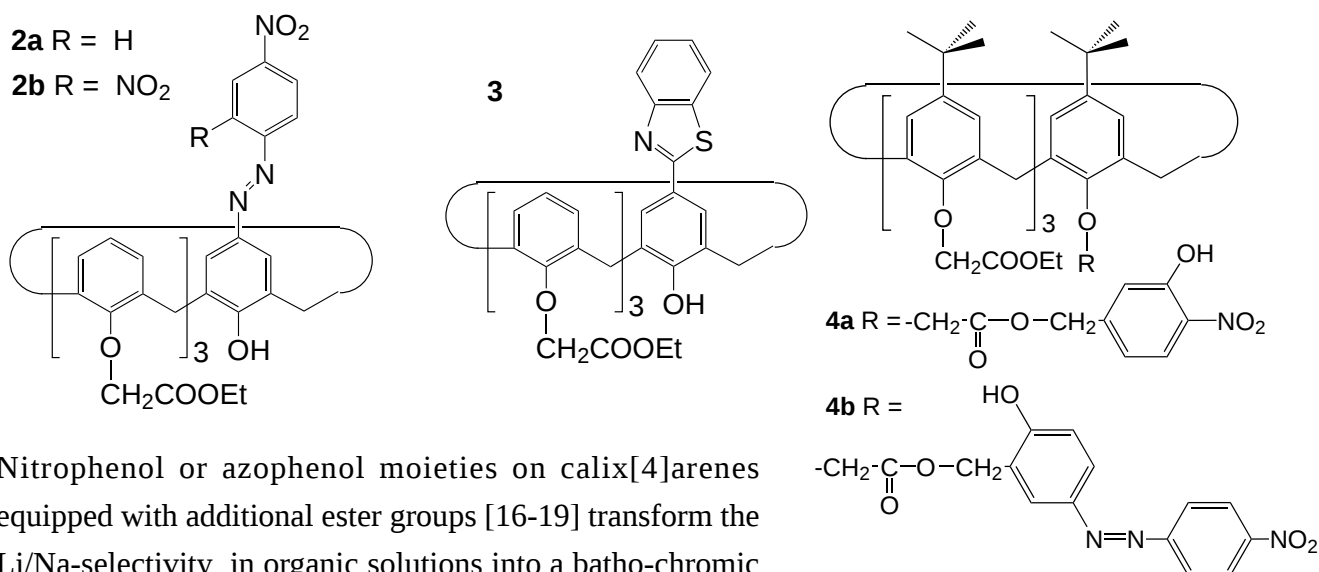
Only a few examples for ion recognition were selected for the following chapters out of the well-over 3000 references on calixarenes so far.

Alkali Ion Recognition

Lithium. As it is the case for crown ethers, calixarenes with oxygen donor atoms turned out to be suitable for selectively binding alkali ions. The ligands are more hydrophobic compared with crown ethers and the membranes therefore are more stable. Although the ring formed by phenolic oxygens in calix[4]arenes (2 Å diameter [12]) is well suited for the diameter of lithium ion (1.36 Å), due to its strong hydration, it is not situated inside the cavity of **1** but at its rim instead [13]. The stronger binding of Li^+ to the phenolate anion compared with the other alkali ions can be visualized by chromo- and fluoroionophores comprised of a calix[4]arene backbone and ligating as well as signalling groups [14,15] such as in ligands **2a** and **3**.



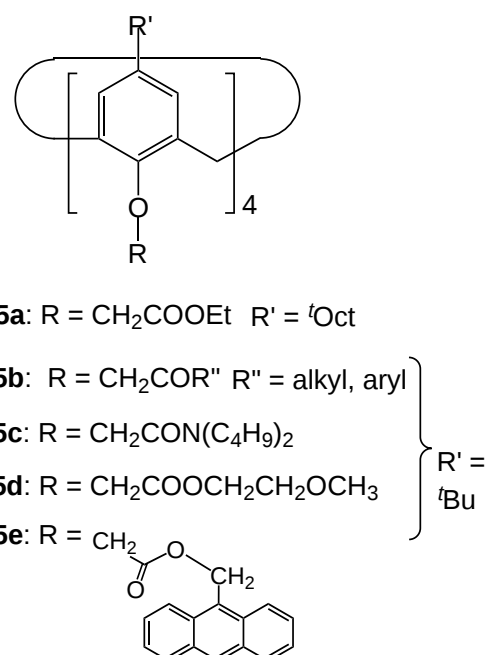
1 R = *tert*-Butyl, *tert*-Octyl



Nitrophenol or azophenol moieties on calix[4]arenes equipped with additional ester groups [16-19] transform the Li/Na-selectivity in organic solutions into a batho-chromic shift from 350 to 425 nm with the help of an auxiliary base to support deprotonation. Ligand **4a** as example is characterized by a sensitivity of 10^{-5} M Li⁺ and selectivity of $\log K_{\text{Li,Na}} = -1.5$. This value improves to $\log K_{\text{Li,Na}} = -1.9$ (THF/H₂O) with the related ligand **4b** [17]. PVC-optodes, which apply the 520 nm absorbance, retain this selectivity [20]. The calixarene with a nitrophenylazophenol group is rather versatile: It not only detects lithium ions in the presence of an weak base, but in turn detects weak bases such as volatile amines when Li⁺ is already present in the membrane [20-22].

Despite the ligand structure, the solute-solvent interactions are an important factor contributing to the alkali ion selectivity [23]. For example, the selectivity of ligand **2b** for Li⁺ in solution changes towards Na⁺ in optode membranes due to solvent effects ($\log K_{\text{Na,Li}} = -2.8$) [24].

Sodium. There are many different, successful approaches to Na⁺-binding by calixarenes and only a few can be mentioned here. In calix[4]arenes bearing carboxymethoxy-groups such as in ligand **5** the carbonyl and ether oxygens form a cavity with a size suitable for Na⁺. Earlier reviews [25-27] deal with these structures and a good example is **5a** with $\log K_{\text{Na,M}} = -3.1$ (K⁺), -4.6 (Li⁺), -5.1 (Rb⁺), -5.8 (Cs⁺) (SSM) [28,29]. Covalently attaching calixarenes to polysiloxane in the membrane further improves the long-term stability while retaining the selectivity ($\log K_{\text{Na,M}} = -2.6$ (K), -3.5 (Li), -3.8 (Mg), -3.4 (Ca), FIM) [30,31]. Copolymerizing Na⁺-selective, ester and methacrylamide groups containing calixarenes also increases the lifetime without a negative impact on selectivity compared with the monomer ($\log K_{\text{Na,M}} = -2.4$ (K), -3.4 (Ca), -4.3 (Mg)) [32].



In recent years we observe the development of optical sensors and the current goal is to improve their properties so that they can compete with potentiometric sensors. A straightforward way is the mixing of a neutral ligand and an ionizable dye in a membrane which responds to cations with the release of protons. Sodium ions can be detected selectively by ligand **5d** as change of the 660 nm absorption of ETH 5294 ($\log K_{\text{Na,K}} = -3.06$; Li, NH_4 and group II: no response) [33,34] under pH-controlled conditions, or by **5a-c** and various other ligands.

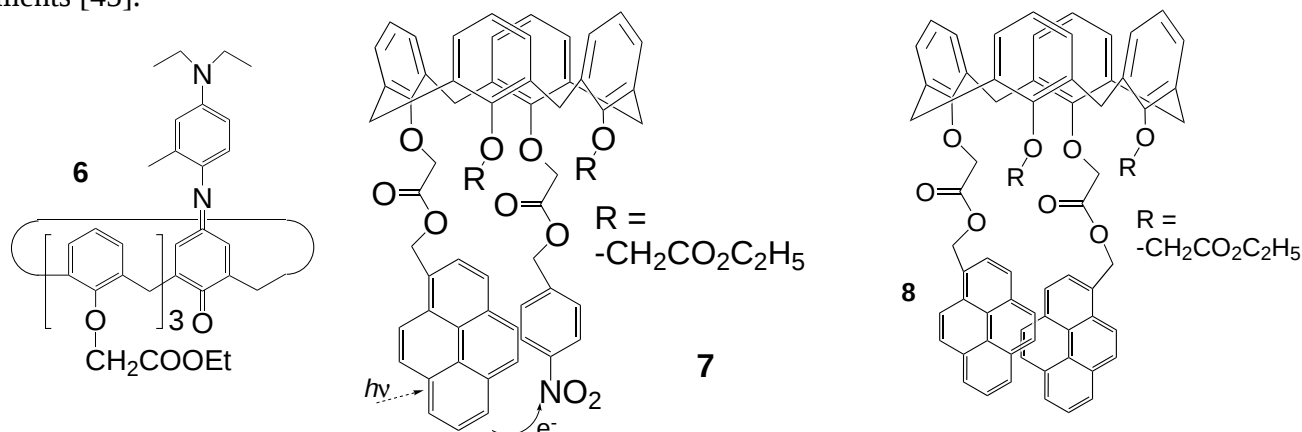
Calixarenes with azophenol [24] or indoaniline [35] as chromogenic groups or acylmethoxynaphthalene [36] as fluorogenic group as part of the macrocyclic ring transform the binding of Na^+ to the calixarene into an optical signal, such as a 42 nm bathochromic shift in case of ligand **6** [35].

The fluorescence emission of pyrene is quenched by an adjacent nitrophenol in **7**, but the emission intensifies 8 times when Na^+ is complexed, which widens the distance between the carbonyl oxygens and separates both groups ($\log K_{\text{ass}}$ for MSCN = 4.3 (Na), 2.9 (K), 2.2 (Cs), 1.9 (NH_4), 1.2 (Li), $\text{Et}_2\text{O}:\text{MeCN}$ 97:3) [37].

Various other mechanisms involving fluorescence were applied to calix[4]arenes for sodium sensing, e.g.:

- Intramolecular energy transfer from a pyrene donor to an anthroyloxy acceptor pair ($S_{\text{fNa,K}} = 59$, $\text{MeOH}:\text{THF}$) [38];
- the intersystem crossing from the lowest excited singlet to the triplet state in acyl-methoxynaphthalene groups, which is prevented by Na^+ binding to the acyl group because the energy level of the $n\pi^*$ excited state increases [36];
- the decrease of fluorescence emission in **5e**, when Na^+ is bound [39,40]; or
- the increase of monomer:excimer emission ratio (30 times) in ligand **8** due to a larger distance upon complexation (Na/K selectivity = 154) [41].

Crowned calixarenes are characterized by a high degree of molecular preorganization and therefore achieve even higher selectivities, especially among alkali ions. The crown moiety and the calixarene restrict each others molecular flexibility, leading to a better discrimination by ion size. Examples are **9a** ($\log K_{\text{Na,M}} = -5.0$ (K^+), -2.8 (Li^+), -4.8 (Rb^+), -4.4 (NH_4^+), -4.5 (Mg^{2+}), -4.4 (Ca^{2+}), -5.4 (H^+), FIM) [42,43] and a similar ligand [44] with a narrow cavity for maximum Na/K-selectivity. Mixing it with fluorophore ETH 5294 renders **9a** to become an optode (detection limit 10^{-7} M Na^+ , $\log K_{\text{Na,M}} < -3.06$ (K), < -2.4 (Ca), < -3.9 (Mg), response time 10s) which can be miniaturized for intracellular measurements [45].



Another mechanism for fluorescence detection applied in **9b**, where the phenyl groups contribute to the selectivity, is reduced molecular motion upon Na^+ binding, increasing the emission intensity [46]. On the other hand, the monomer/excimer ratio increases in case of pyrene-derivative **9c** ($\log K_{\text{ass}} = 5.48(\text{Na}^+)$, $4.84(\text{Li}^+)$, < detection limit(K^+), MeCN, MClO_4) [47]. This crowned calixarene skeleton can be converted into a chromoionophore as demonstrated for the ligand **9d** (Na/K -selectivity $10^{3.1}$ in extraction) [48].

The fluorescence emission wavelength of a conjugated poly(phenylene bithiophene) with calix[4]arene-crown-4 moieties as selective binding sites switches by 50 nm above 1 mM Na^+ [49].

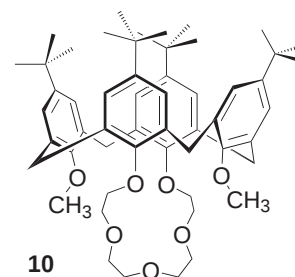
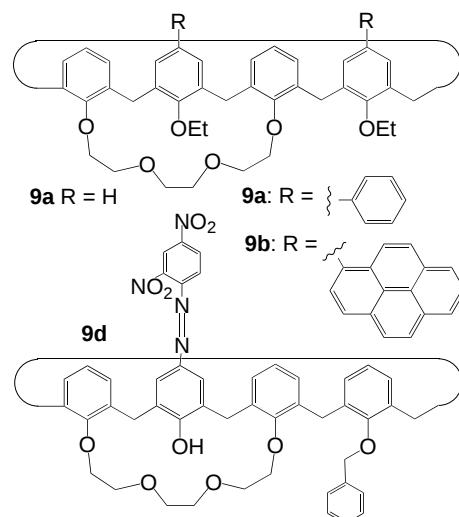
Potassium. The same idea of a crowned calix[4]arene can be applied for K^+ recognition. For example, ligand **10** is a *t*-butylcalix[4]arene bearing a crown-5 group and has a K/Na selectivity of $10^{3.1}$ in chemically modified field effect transistors [50].

In combination with a nitrophenolazophenol moiety, the extraction of K^+ by such a crowned calixarene can be observed photometrically (selectivity as $\log(K_{\text{ex,K}}/K_{\text{ex,Na}}) = 3$) [51].

However, these are *cone* (or distorted *cone*) conformers, where the four phenyl rings look into the same direction, so the ligating groups are on one side of the molecule and the hydrophobic groups form the other side. Changing the conformation to partial *cone* (one phenyl ring inverted) or alternating (phenyl rings look up and down, alternating), the ligand becomes even better pre-organized for binding K^+ . Alkyl groups larger than methyl are required as substituents at the phenolic oxygens, otherwise the high selectivity ($\log K_{\text{K,Na}} = -3.7$, SSM) [52] decreases with time due to conformational isomerism. In addition, removal of sterically bulky *t*-butyl groups improves the selectivity and the highly selective ligands **11a, b** [53] were characterized by various methods (e.g. **11a**, $\log(K_{\text{ex,K}}/K_{\text{ex,Na}}) = 5.5$, CHCl_3 , picrate extr.; $\log K_{\text{K,M}} = -4.4$ (Na), -4 (Mg), -3.9 (Ca), FIM) [31,53,54].

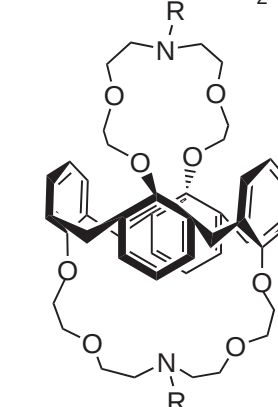
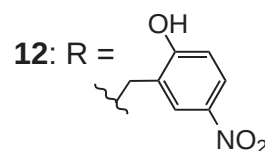
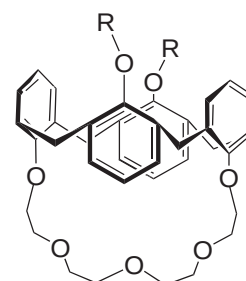
The same alternate conformer but with azacrown-5 moieties, ligand **12** and its monocrown relatives show K^+ -selectivity in transport as well as in ISEs, which translates into an optical signal with the help of the nitrophenol chromophoric group [55-57].

Rubidium and Caesium. There are two main approaches for Rb^+ and Cs^+ recognition by calixarenes. The first one applies calix[6]- or calix[8]-arenes bearing mono- or bidentate groups. Examples are ligand **13** ($\log K_{\text{Cs,M}} = -3.9$



11a: R = *i*Pr

11b: R = Et



(Na), -2.7 (K), -1.9 (Rb), -2.8 (NH_4), SSM) and related structures [58-61], with improved selectivity at the expense of hydrophobicity upon removal of the *p-t*-butyl groups [62].

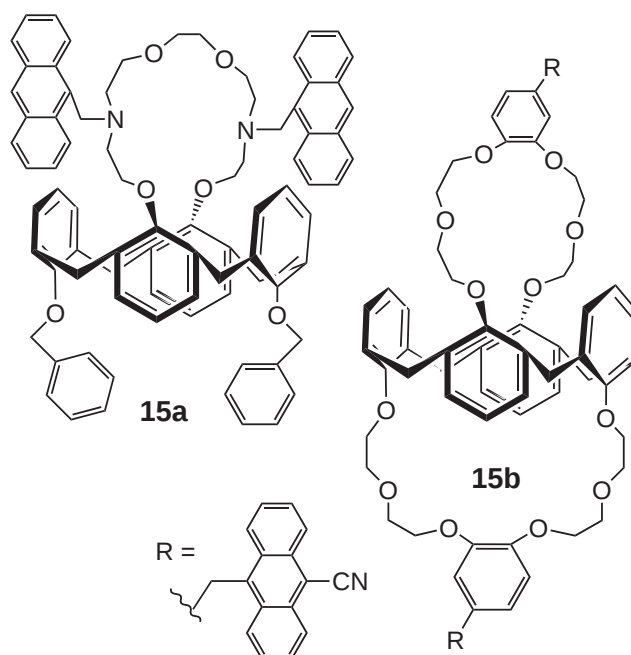
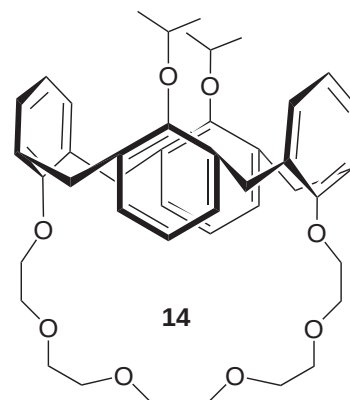
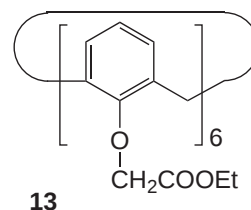
The second approach utilizes crowned calixarenes such as **14** in 1,3-*alternate* conformation [63-69] which provide high Cs/K-selectivity (e.g. $\log K_{\text{Cs,M}} = -4.5$ (Na), -2.2 (K)). The selectivity is still reasonably high after covalent linking to polymeric membranes in CHEMFETs ($\log K_{\text{Cs,M}} = -3.2$ (Na), -2.3 (K), -4 (Ca), -2 (NH_4), FIM) [31]. The absence of *t*-butyl groups is important for a good Cs^+ -selectivity because it enables cation- π -interaction. This type of interaction is also responsible for a strong decrease of $^1\pi\pi^*$ fluorescence emission of **14** upon complexation with Cs^+ [70].

Attaching benzo or naphto groups to the crown moiety increases the Cs/Na-selectivity [71]. The Cs/K-selectivity on the other hand improves to over 4000 after removal of the two phenolic oxygens outside the crown cavity [72].

Photo-induced electron transfer (PET) is a common mechanism in nature which can also be applied for sensitive detection such as in ligand **15a** ($\Phi = 0.03$ (Cs^+ added), $\Phi = 0.003$ (no M^+), $\log(\beta_{\text{Cs}}/\beta_{\text{K}}) = 1.3$, detection limit 10^{-5} M, $\text{CH}_2\text{Cl}_2:\text{MeOH}$) and the related biscrown-calix[4]arene **15b** [73-75]. The crown moiety is rigidified by the calixarene and contributes to the Cs^+ -selectivity, while PET from benzocrown oxygens or aza-crown nitrogens to the excited singlet state of anthracene or cyanoanthracene groups quenches the fluorescence emission in the uncomplexed state. Complexation triggers an increase in fluorescence emission. This can be detected with more accuracy and sensitivity compared to a fluorescence ‘switch-off’ mechanism.

Instead of calix[4]arene, the larger calix[5]arene can be used as molecular platform. Then, the smaller crown-5 ring is suitable for Cs^+ -binding. With azophe-nol as chromophoric groups it responds selectively to Cs^+ with a new absorption at 475 nm due to deprotonation ($\log K_{\text{Cs,M}} = -2.2$ (K), -0.8 (Rb), Li and Na no effect, detection limit 10^{-5} M, methoxyethanol/ H_2O 9:1) [76].

Doubly crowned calix[4]arene such as **16** avoid the need for protective groups during synthesis and can bind two metal ions in one molecule. The selectivity of **14** and similar ligands having aromatic or aliphatic groups on the crown moiety towards Cs^+ was shown in extraction and transport experiments [77-87] and in ISEs ($\log K_{\text{Cs,M}} = -4.88$



(Na), -2.2 (K), -1.94 (NH_4), -0.9 (Rb), <-5 (group II), FIM, lin. range $0.1\text{-}10^{-6}$ M) [88].

An optode composed of **17** and chromophore ETH5294 is stable and selective ($\log K_{\text{Cs,M}} = -2.1(\text{Na})$, -2.3(K), -2.5(Ca), -3.2(Li), -2.8(Mg), SSM, lin. range 10^{-2} - 10^{-6} M), but has a long response time of 5 min [89].

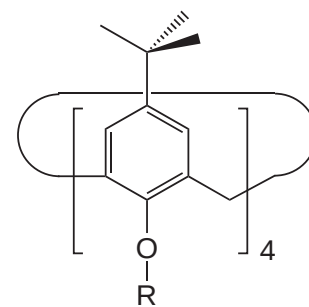
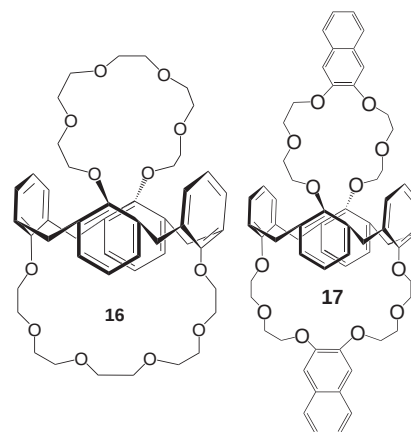
Alkaline Earth Ion Recognition

Among ester, acid or amide groups anchored to calixarenes, the latter turned out to form most stable complexes with alkaline earth ions due to the high carbonyl group polarity, e.g. [62,90]. A good selectivity for Ca^{2+} over Mg^{2+} is achieved with tertiary amides such as **18a** in electrodes ($\log K_{\text{Ca,Mg}} = -1.9$, FIM) [91] and with **18b** in complexation ($\log(K_{\text{Ca}}/K_{\text{Mg}}) > 7.8$, MeOH) [92,93]. Ca and Sr cannot be discriminated by these ligands due to the enthalpy-entropy compensation. As far as complexation is concerned, the carboxylic acid groups in **18c** provide also a good Ca/Mg-selectivity ($\log K = 22.44$ (Ca), 20.92 (Sr), 17.96 (Ba), 11.02 (Mg), 9.94 (Na), 9.05 (K), MeOH) [94].

With phosphine oxide groups appended to the lower rim in **18d**, good $\text{Ca}^{2+}/\text{Na}^{+}$ -selectivity and membrane durability (>7 weeks) is achieved in ISEs ($\log K_{\text{Ca,M}} = -2.2$ (Na), -2.7 (K), -2 (NH_4), -1.6 (Li), -2.6 (Mg), SSM) [95]. In an optode comprising a mixture of **18d** and the acidochromic dye ETH 5294 even higher selectivity coefficients were reported ($\log K_{\text{Ca,M}} = -4.77$ (Na), -3.84 (K), -3.65 (NH_4), -2.3 (Li), -1.4 (Mg), -1.1 (Ba)) [33,34].

Several papers were published about chromoionophoric calixarenes for Ca^{2+} . The ligand **19** [96] for example contains indoaniline groups the polar quinone carbonyl oxygens of which coordinate divalent cations well. The large bathochromic shift (110 nm) and the higher association constants $\log(K_{\text{ass,Ca}}/K_{\text{ass,Mg}}) = 4.9$, $\log(K_{\text{ass,Ca}}/K_{\text{ass,K}}) = 1.4$, K^+ : 28 nm shift, EtOH) reflect the Ca-selectivity, which is a result of the size matching between host and guest. Even a logical switch using Ca^{2+} and K^+ has been designed based on ditopic recognition [97].

Another chromoionophore, ligand **20**, utilizes azophenol groups and works well at neutral pH. Upon binding of Ca^{2+} a 168 nm bathochromic shift is induced as determined by extraction into CHCl_3 (detection limit 10^{-4} M, $\log K_{\text{Ca,M}} = -2.3(\text{Sr})$, -2.9(Mg), -2.8(Na)) [98]. Sr^{2+} can be detected by ISEs containing underivatized *t*-butylcalix[8]arene ($\log K_{\text{Sr,M}} = -1.2$ (Ca), -1.3

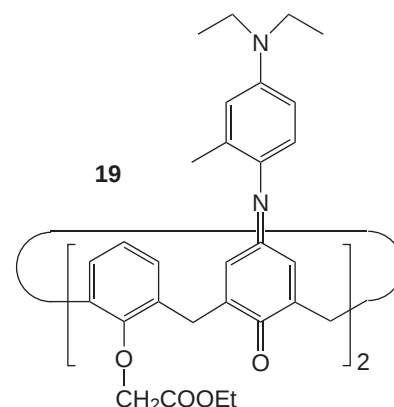


18a: R = $\text{CH}_2\text{CON}(\text{C}_4\text{H}_9)_2$

18b: R = $\text{CH}_2\text{CON}(\text{Et})_2$

18c: R = $\text{CH}_2\text{-COOH}$

18d: R = $\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{ph})_2$

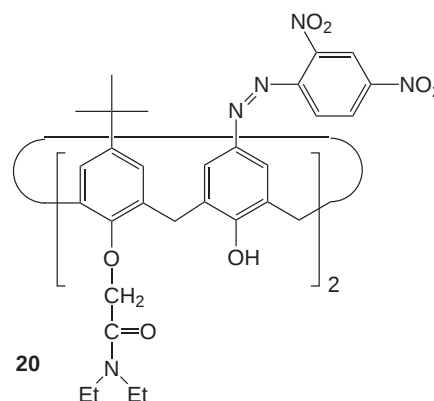


(Ba), -1.4 (Mg, Li), -1.5 (K), -0.3 (Na), -1.3 (Pb), FIM, linear range $2 \cdot 10^{-5}$ - 0.1 M [99].

Expanding the calix[n]arene cavity from $n = 4$ over 5 to 6 changes the Sr/Na-selectivity of the amide derivatives from 0.09 over 2.8 to 760 in extraction ($D_{\text{Sr}}/D_{\text{Na}}$), which further improves with alkylether instead of *t*-butyl groups in 4-position of the phenyl rings [100].

Amide derivatives of calixarenes have also been used for Sr^{2+} -separation in synergistic mixtures with hydrophobic anions [101,102], which should work in ISE membranes as well.

Calix[4]diquinone-based ionophores were proposed for amperometric sensors for Ba^{2+} due to the selectivity over alkali and ammonium complexes as shown by the largest anodic shift in voltammetry [103,104].



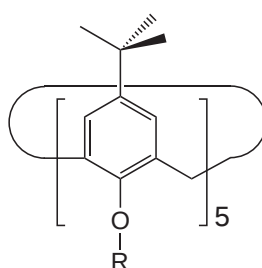
Ammonium, Guanidium Ion and Amino Acid Recognition

Ammonium ions can be included in the cavity of calixarenes and discriminated by size and steric reasons. A phenolic OH-group can transfer a proton [105] to primary, secondary or tertiary amines and complexation occurs due to electrostatic, dispersive, H-bonding, $\text{CH}_3\text{-}\pi$ and for aromatic amines also $\pi\text{-}\pi$ interaction. $\text{N}^+\text{-}\pi$ -interactions were proven to take part as well, e.g. [106-109]. Alternatively, deprotonated calixarenes can bind quaternary amines [110].

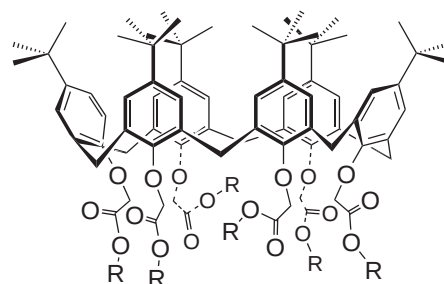
The phenolic OH-groups in the water-soluble calix[6]arene with *p*-sulphonato instead of *t*-butyl groups were employed for fluorimetric sensing [111]: The ligand is selective for acetylcholine over primary and secondary amines and was mixed with an auxiliary fluorescent cation which competes for binding. Binding of acetylcholine releases the fluorophore, the emission of which is quenched only in the complexed state by the phenolate anions (detection limit 10^{-6} M acetylcholine, $\text{H}_2\text{O}/\text{MeOH}$ 1:1).

Hydrophobic ether derivatives such as ligand **21** discriminate between structural isomers such as butylammonium ions in ISEs ($\log K_{n,x} = -1.20$ (*i*), -1.31 (*s*), -1.65 (*t*), $\alpha\text{-BuNH}_3^+$, FIM) and in their complex stabilities [112].

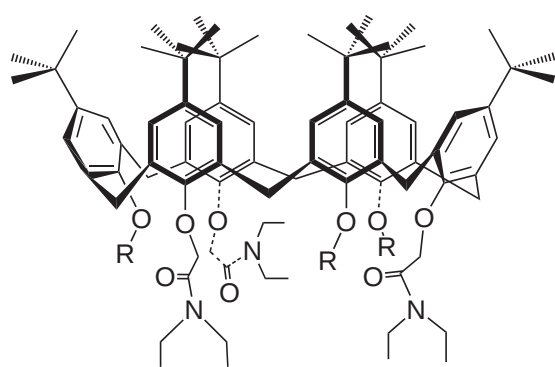
Ester derivatives such as **22**, the synthesis of which can be accomplished smoothly, bind amines in the order $n > s$ -, $i > t$ -butylamine and have a preference for shorter amines [113-116]. The ligand discriminates according to guest hydrophobicity and shows selectivity for Phe- and Tyr-esters over Gly, Ala and 4-aminobutyric acid. The analogous decylester derivative in ISEs responds to primary amines due to tripodal $\text{NH}_3^+ \cdots \text{O}=\text{C}$ hydrogen bonding. Selectivity is observed for amines without bulky substituents in α -position, such as to



21: R = $(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$

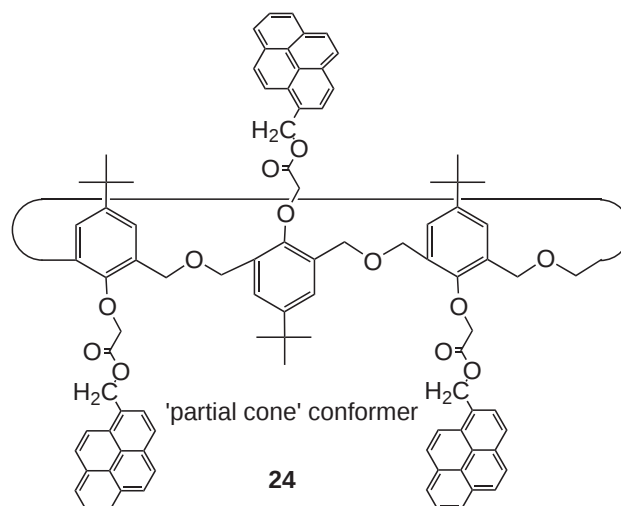


22: R = Ethyl



23a: R = CH₂C(O)N(C₂H₅)₂

23b: R = CH₃



24

dopamine ($\log K_{(\text{dopamin/adrenalin})} = -1.55$, SSM) [117].

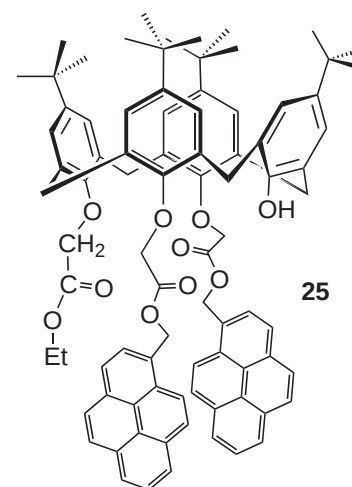
The more hydrophobic and larger p-adamantylcalix[8]arene is characterized by higher sensitivity (0.1 µg/ml L-Phe compared with 2.8 µg/ml (**22**)) and complex stability [118]. Steric effects are discussed to cause the selectivity for L-Leu over L-Phe ester [119,120].

Ligand **23a** is a stronger H-bond acceptor as compared with **22** and binds guanidinium as shown in transport [121] and at interfaces [122]. The suitable cavity size and binding geometry contribute to the selectivity over alkali ions. Having excessive binding sites removed while retaining C₃-symmetry, **23b** has a higher selectivity in CHEMFETs ($\log K_{\text{gu,M}} = -1.8$ (K), -1.85 (Na), -1.8 (NH₄), -2.8 (Ca), FIM) [123] and in transport across liquid membranes [124]. Another approach towards favourite gu⁺-binding ($\log K_{\text{ass}} = 3.4$) utilizes a 'cap' for rigidifying calix[6]arenes [125] or homotrioxacalix[3]arene [126], although in the first case it slows down the dissociation rate. The calix[6]arene and the homotrioxacalix[3]arene were also used as molecular backbones to anchor fluorophoric groups such as in **24**, where the binding of gu⁺ changes the monomer-excimer intensity ratio [127,128].

Chirality can be introduced into calix[4]arene by 3 or more different substituents such as in **25** [129], where the excimer emission intensifies upon amino acid binding.

Combined hydrogen bond donors and acceptors, such as α-aminophosphonate groups held by the calix[4]arene molecular platform allow the binding of hydrophilic amino acid zwitter ions with a selectivity order His > Phe, Tyr, Typ, which can slightly be influenced by the substituent in para-position [130,131].

Ammonium and alkylammonium ions can be sensed by calixarenes where diquinone is part of the macrocycle together with ligating sites such as ester or amide for hydrogen bonding [132,133].



25

Crowned Calixarenes for Ammonium Recognition.

Crowned calix[4]arenes retain the capability of hydrogen bonding to guests while discriminating better according to steric reasons such as bulkiness due to the rigidified cavity. Examples are the preference for n-butyl over tert-butylamines in transport and extraction [134,135] and

the selectivity for primary over tertiary ones [136]. The crown also contributes to the complex stability [137] as it forms a more closed cavity shielding the ion from its hydration shell. Modifying the crown moiety with hydrophobic groups and attaching it to the ‘upper rim’ rather than to the phenolic oxygens also improves the selectivity for primary ammonium over alkali ions [138,139].

With inherently chiral, crowned calix[4]arenes the chiral recognition of ammonium ions may be possible [140]. An interesting example for the design of a chiral host is seen in the structures **26a** and **b**. The symmetrical ligand discriminates among butylamines due to steric and electrostatic reasons of the binaphthyl hinge ($\log K_{\text{ass}} = 3.0(t-)$, $2.8(s-)$, $2.5(i-)$, $2(n\text{-butylamine})$, EtOH) [141]. Compared with ligand **22** before, this order is nearly reversed. R-isomers of amines and amino acids are preferably bound by the unsymmetrical ligand **26b** [142,143]. In both cases sensing is easily accomplished by a bathochromic shift (red to blue colour change) and a new absorption, mainly due to proton transfer.

Crowned calixarene **27** interacts with amines primarily by means of H-bonding, while bulkiness and hydrophobicity also contribute to the observed selectivity $n- \gg s- \rightarrow t-$ [144]. The proton transfer is sensed as a 93 nm bathochromic shift.

Host-guest proton transfer also cause the colour change from yellow to orange (monoamines) or to red (di-, triamines) in bisazobiphenyl-bridged calix[n]arenes ($n = 4, 8$) [145-147]. However, the mechanism of proton transfer cannot be applied to aromatic amines due to their lower basicity.

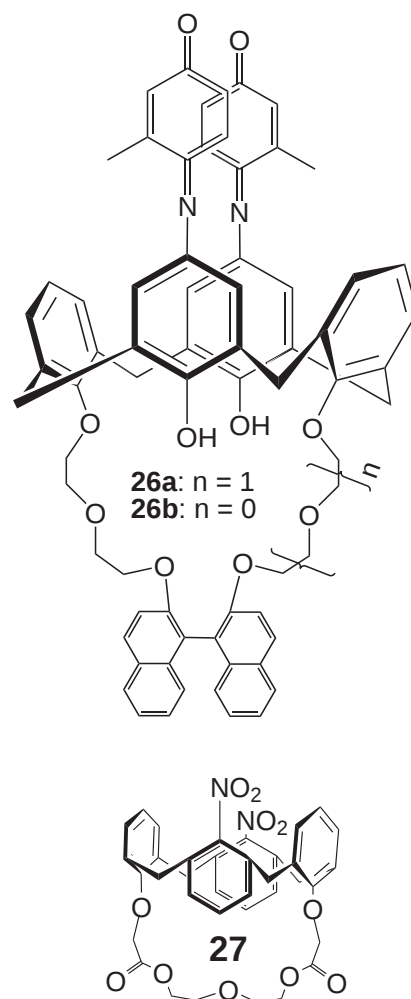
Silver Ion recognition

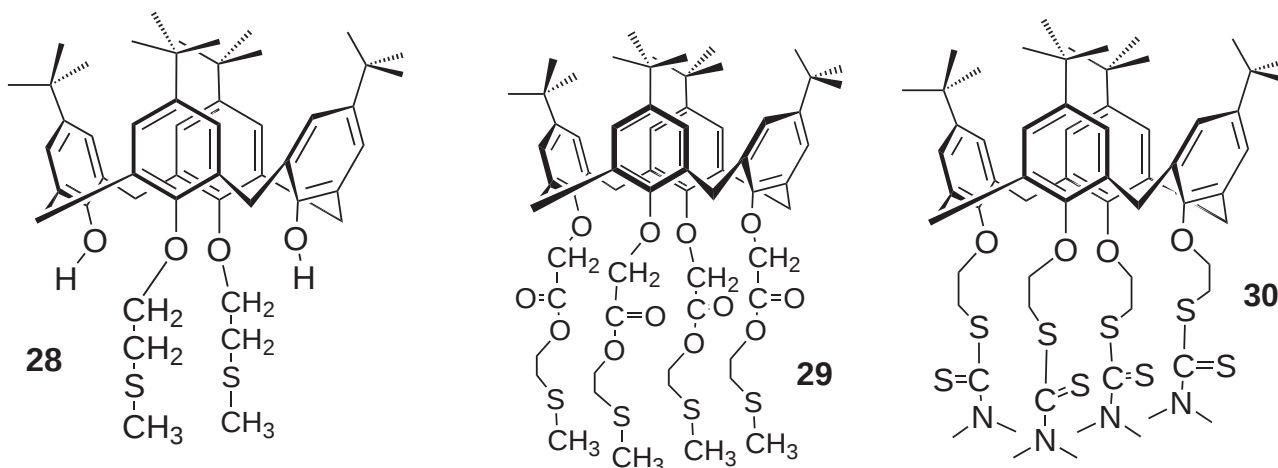
Although good Ag^+ -sensitive electrodes are well-established, also calixarenes were investigated for this purpose. One reason is the specific interaction between the π -clouds and ‘soft’ cations [148-150] which leads to selective complexation without the need for other donor groups.

Allyl ethers of calix[4]arene utilize the same type of interaction, this time between the allyl and phenyl π -clouds and Ag^+ [151]. The selectivity over ‘hard’ cations is excellent ($\log K_{\text{Ag,M}} = -3.3(\text{H})$, $-3.6(\text{Pb})$, $-1.8(\text{Hg})$, $-0.6(\text{Tl})$, <-4 (group I+II, NH_4), FIM, lin. range $10^{-4} - 10^{-1} \text{ M Ag}^+$).

The selectivity was also confirmed by extraction using various allyl and benzyl ether derivatives [152].

The second approach to Ag^+ -selectivity consists of the introduction of ‘soft’ donor atoms such as sulfur and nitrogen. As an example, thioether **28** was used in ISEs ($\log K_{\text{Ag,M}} = -2.5(\text{Hg})$, $-4.7(\text{K, Pb})$, $-5(\text{Na, Ni})$, <-5 (group II, NH_4 , Cu, Cd, Zn), FIM, response time 10 s, linear range $10^{-4.5} \text{ M Ag}^+$) [153,154] as well as in CHEMFETs with a polysiloxane matrix ($\log K_{\text{Ag,M}} = -4.3(\text{Ca})$, $-4.4(\text{Cu})$, -4.7





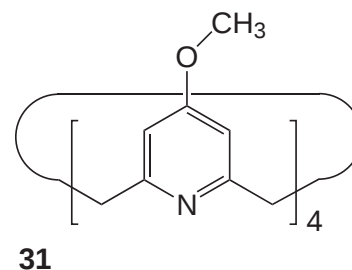
(K), -2.5 (H), -2.4 (Hg), -4 (Cd), FIM, lin. range above $10^{-4.2}$ M) [155]. The membrane conditioning can further increase the selectivity [156].

Thioester groups in calix[4]arenes such as **29** lower the selectivity over sodium ions to some extent due to their carbonyl oxygens ($\log K_{\text{Ag,Na}} = -1.2$ in ISE, lin. range 10^{-4} to 10^{-1} M) [157,158].

Thiocarbamoyl groups [159,160] or dithiocarbamoyl groups when attached to the calixarene skeleton such as in ligand **30** [161,162] provide selectivity for Ag^+ , Pd^{2+} , Hg^{2+} and other 'soft' metal ions over 'hard' ones.

Alternatively, nitrogen as donor atom for Ag^+ -complexation was successfully applied to avoid interference by alkali and ammonium ions. The pyridinophane **31** resembles a calixarene, selected $\log K_{\text{Ag,M}}$ values are -2.7 (K), -3.1 (Pb), -3.4 (Cd) (SSM) [163].

The Ag^+ -complex of **28** acts as reversible electron-transfer agent and by this way stabilizes the phase boundary potential in solid-state sensors for polyanions [164]. Thioether-substituted calixarenes self-assemble on surfaces of Au or Ag, allowing mono- or multilayered structures with recognition sites such as the molecular cavity.

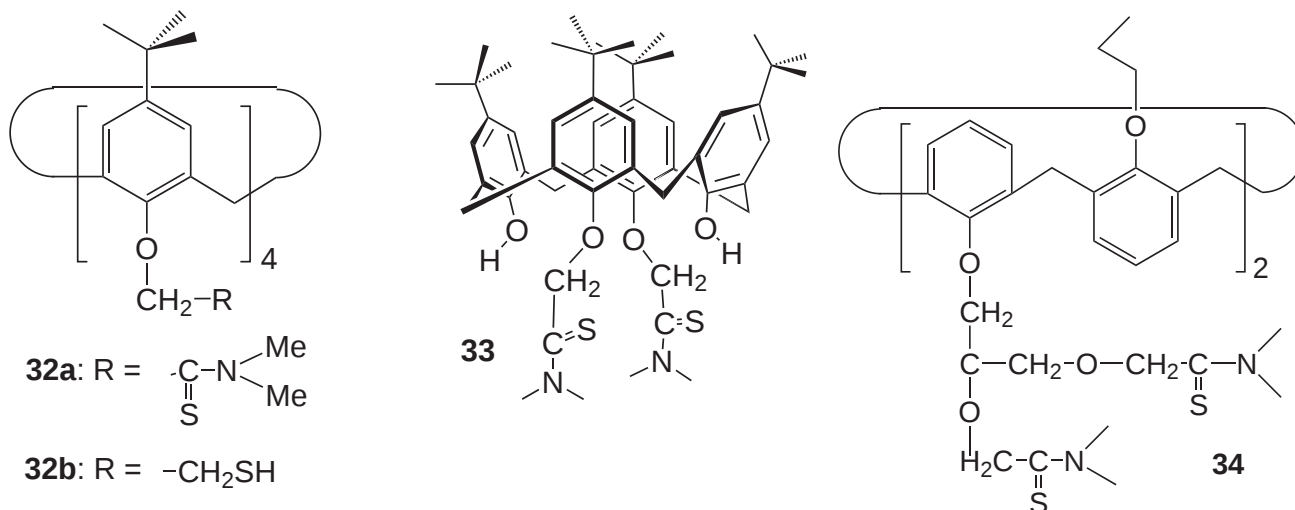


Other Heavy Metal Ion Recognition

Although many calixarene derivatives were characterized by solvent extraction and membrane transport with respect to their heavy metal selectivity [1,7,165,166], limited data are available for sensors.

Examples are the determination of Hg^{2+} , Pb^{2+} and Cu^{2+} by anodic stripping voltammetry [167] and with CHEMFETs [153] utilizing thioamide groups on a calixarene skeleton. For Pb^{2+} , thioamides such as ligand **32a** was investigated in CHEMFETs ($\log K_{\text{Pb,M}} = -4.2$ (Cd), -3.4 (Cu), -5.2 (K), -4.3 (Ca), detection limit 10^{-6} M, FIM) [153], in CHEMFETs with polysiloxane membranes which avoid the need for a plasticizer ($\log K_{\text{Pb,M}} = -3.3$ to -3.7 (K), -3.0 to -3.3 (Cu), -3.8 (Cd), -4.2 (Ca), FIM) and linear range (above 10^{-5} M) [31,155,168], and in ISEs ($\log K_{\text{Pb,M}} < -3$, pH-range 3-6) [169].

Similar ligands were applied in anodic stripping voltammetry for Pb^{2+} -determination [167,170]. The thiol **32b**, also based on the calix[4]arene frame, was successfully used for analyzing Pb^{2+} by the same



method using screen-printed carbon electrodes. The detection limit of 5 ng per ml after preconcentration is sufficient for water quality control [171].

Thioamides based on the resorc[4]arene skeleton instead work in CHEMFETs for Pb^{2+} , although with reduced selectivities compared with some of the above-mentioned calixarenes ($\log K_{\text{Pb,M}} = -1.9$ (K), -2.1 (Cu), -2.4 (Cd), -4.3 (Ca), FIM) [172].

The selectivity of thiophosphate derivatized calix[6]arenes ($\log K_{\text{Pb,M}} = -2.65$ (Cd), -2.4 (Cu), -1.4 (Ca), sensitivity (10^{-4} M Pb, FIM) depend also on the ligand's substitution pattern [173]. A wider linear range (10^{-5} M Pb^{2+}) was demonstrated with ethyleneoxydiphenyl phosphine oxide groups, the interference by Ca^{2+} can be avoided by expanding the calixarene ring size [174].

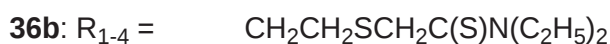
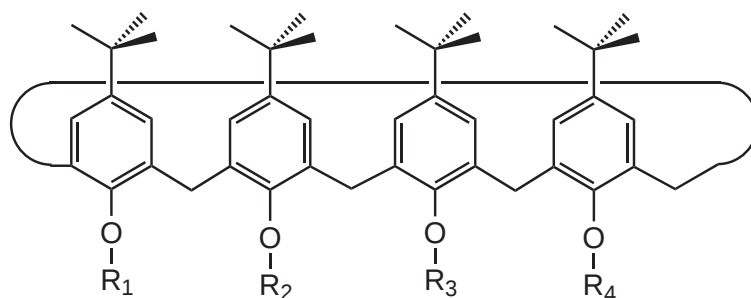
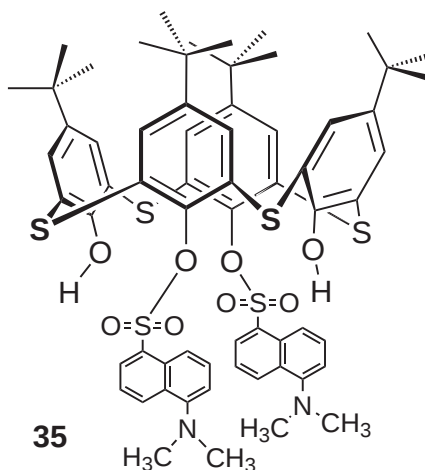
Calixarene **33** contains two thioamide groups and was used for the preparation of Cd-selective CHEMFETs ($\log K_{\text{Cd,M}} = -3.2$ (Ca), -0.6 (Cu), >0 (K, Pb), FIM) [153]. Adding two more amide groups improves the selectivity over K^+ at the expense of Cu^{2+} ($\log K_{\text{Cd,K}} = -2.6$, detection limit $10^{-5.5}$ M Cd). With polysiloxane membranes, the interference by Pb^{2+} could be avoided ($\log K_{\text{Cd,M}} = -4.1$ (Ca), -2.6 (K), -2.0 (Pb), >0 (Cu), FIM) [155]. To achieve selectivity over Pb^{2+} and Cu^{2+} in PVC or polysiloxane-based membranes, the ligand **34** with an alternating conformation was developed ($\log K_{\text{Cd,M}} = -0.7$ (Pb), -4.2 (Ca), -3.0 (K), -1.6 (Cu), lin. range 10^{-5} M, Nernstian slope, polysiloxane, FIM) [168].

The dansyl-groups render **35** a fluorophore which responds to Cd^{2+} with increased emission intensity when the dansyl groups are inside the hydrophobic cavity ($\Delta I/I^0 = 0.42$, Cd, $0.23(\text{Al}^{3+})$, $0.2(\text{Cr}^{3+})$, $0.17(\text{Zn}^{2+}$, $\text{Cu}^{2+})$, <0 (for alkali, Co, Ni ions), H_2O , 489nm, 3×10^{-4} M metal, pH 7) [175].

1,2-Diquinone containing calixarenes were proposed for the voltammetric detection of transition metal ions due to their interaction with them as exemplified by Ag^+ [176].

Dithioamide groups on the calix[4]arene backbone, represented by ligands **36a** and **b** were applied for Cu^{2+} -selective CHEMFETs, although an interference by K^+ occurs ($\log K_{\text{Cu,M}} = -1.9$ (Ca), -2.1 (Cd), -1.7 (Pb), >0 (K), linear range to 10^{-4} M Cu^{2+} , FIM, **36a**) [153].

From N-(X)sulfonyl carboxamide derivatized calix[4]-arene, which is selective for Hg^{2+} in extraction [177] the fluorophore **37** was derived, the 520 nm emission of which is quenched upon complexation due to electron transfer [178].



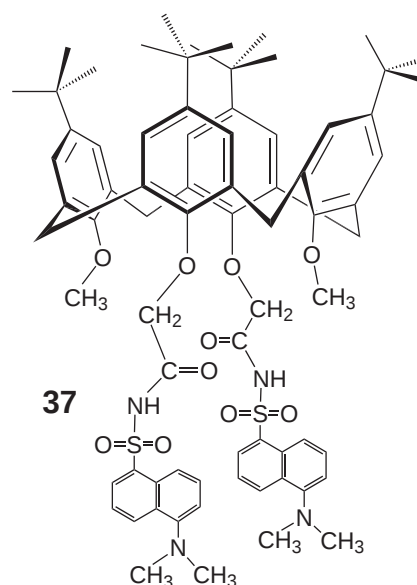
Utilizing the cation- π -interaction of the phenyl rings, Tl^+ could be selectively sensed by the propyl ether of de-*t*-butylated calix[4]arene in an ISE with $\log K_{\text{Tl,M}} = -1.35$ (Ag), -2.7 (Hg), <-4.0 (K, NH_4 , H, Pb), <-5 (Ca, Na, Mg), lin. range $0.1 - 3 \cdot 10^{-6}$ M, FIM) [179].

Calix[4]arenes can be bridged with a dioxotetraaza group having an anthracene group appended [180]. The complexation is monitored by means of the fluorescence emission, depending on whether quenching (Ni^{2+}) or emission-enhancing cations (Zn^{2+}) are present.

f-Elements. For f-element ions, a large amount of data has been accumulated in the area of extraction and transport, and rather selective ligands were developed [1]. These molecular designs are based on calixarenes bearing (i) bidentate groups such as carbamoylphosphine oxide, (ii) monodentate groups such as phosphine oxide, esters of phosphoric, phosphonic or phosphinic acids, or (iii) different monodentate groups such as acid and amide within the same molecule.

Of special interest are the luminescent properties of lanthanide ions encapsulated in calixarenes, because they are shielded from the hydration shell by the macrocyclic cavity. If the energy levels match each other, energy transfer from excited ligand energy state to a lanthanide ion energy level or between two different lanthanide ions occurs with high efficiency. FIAs could be based on this approach. Data on luminescence properties of Tb^{3+} and Eu^{3+} [181-193] and also other lanthanides [194-199] with quantum yields of up to 30% show that the design of the functional group acting as molecular 'antenna' to absorb the energy is very important.

The pentahydroxycalix[6]arene acts as a pseudoplanar pentadentate ligand, for UO_2^{2+} and with the indoaniline group introduced responds selectively with a bathochromic shift (59 nm) in the presence of a base [200].



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