Calixarenes as sensor materials for recognition and separation of metal ions[‡‡]

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Abstract
Chemical separation and speciation are two fundamental processes that have ushered significant advances in biological and material world. The underlying principles for most innovative separations involve molecular recognition and its subsequent translation to methodologies for detection and separation. Recent advances in the field have demonstrated that calix[n]arenes are attractive sensor materials for recognition of metal ions and small molecules and they can be employed for designing novel molecular filters. An overview of related work on the synthesis and evaluation of calixarene based molecular receptors is presented.

Keywords: Calix[*n*]arenes, ionic recognition, separation, extraction, sensor

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1. Introduction

Chemical separation and speciation are two fundamental processes that entail numerous advances in the biological and material world. From classical precipitation, digestion and filtration, complexation and extraction methods, separation science and technology has revolutionized the world through automation and increased sophistication. Specialized protocols for analysis and spectrometric methodologies are prominent fruits of research in the area of separation science and technology for the target species from the chemical or biological broth of the system under study. Our efforts in the field of separation science concentrate on the design, synthesis and evaluation of novel molecular receptors for the target species and are directed towards development of novel molecular filters for ions and small molecules.

1.1 Recognition, chemical separation and detection of metal ions

The separation of any species from a chemical or biological molecular pool is dependent upon its selective interaction with a molecular receptor (Figure 1a). This interaction can be chemical or physical in nature and basically depends upon the size, charge and shape complementarity of the target species and the receptor. Our current efforts involve utilization of non-covalent intermolecular forces (called molecular or ionic recognition) for designing new methods of detection and separation. We do not intend to use covalent bond formation (or coordination) for this purpose, as that would involve additional energy and material expenditure. Consequently, the below-mentioned steps are followed to gather basic information for translation into molecular filters:

1. Selection and synthesis of suitable molecular receptors
2. Evaluation of intermolecular forces between the target and the molecular receptor
3. Identification of the recognition signal and its amplification
4. Evaluation of molecular aggregation/organization of the target and the molecular receptor
5. Conversion of the recognition event to binding of the target ion or the molecule
6. Diffusion, transport and separation of the bound target from the chemical broth
7. Release of the target and reuse of the receptor molecule.
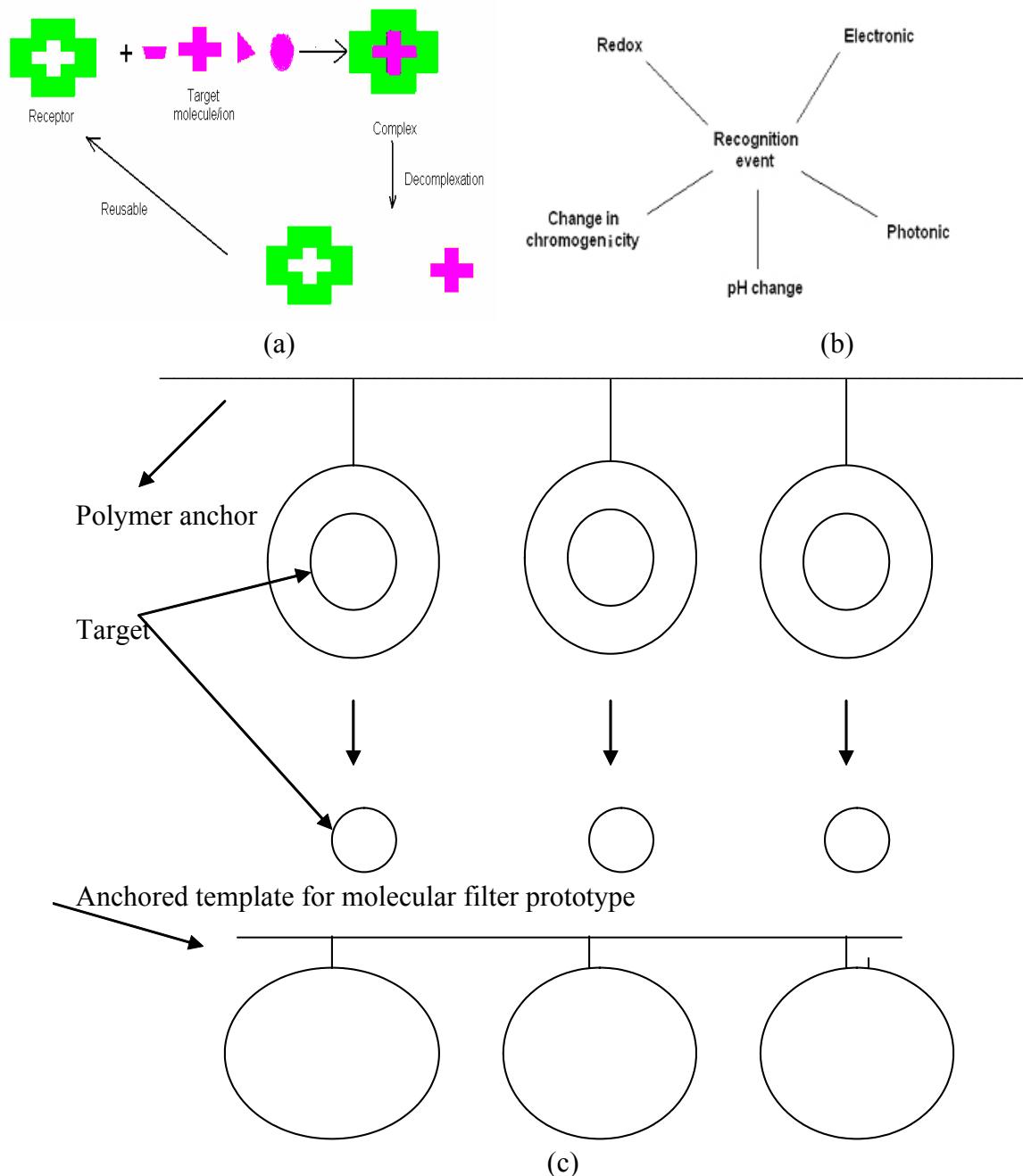
Figure 1. (a) An over-simplified view of recognition and separation; (b) Detection of the recognition event; (c) Anchored molecular receptors on alkoxyorganosilanes or other polymer support systems for separation and detection devices.

Once the molecular receptor and target ion/molecule is identified, the molecular receptor is anchored to the polymer template which can be used for designing separation or detection prototypes of different varieties (Figure 1c). Anchoring of the molecular receptor to an inert surface is normally done through covalent bond formation or impregnation of the receptor

molecules onto the inert surface having a large surface area. Release of the target molecule/ion from the encapsulated polymer template can then be achieved through studies based on binding parameters as well as on the analyte residence time and its release equilibrium.

1.2 General principles

The recognition event is based upon available non-covalent forces between the target and the molecular receptor. The signal for interaction of the molecular receptor and the target ion is usually weak but it can be amplified for measurement. Detection of a recognition event can be achieved directly (through colour change, pH change or spectroscopic change-normally through NMR and UV spectral measurements) or through electronic, photonic, redox or pH perturbation of the weak signal (Figure 1b). Enhancement of the weak signal can also be achieved through the use of a molecular antenna or coupling with large surfaces. The latter can be provided by commercially available materials (alkoxyorganosilanes) or can be generated by self- or induced molecular aggregation, or organization, through intermolecular interactions (micelles, ion pairs, hydrophobic or hydrophilic gels, polymeric surfaces etc).

These principles can be used for detection of metal ions/ organic molecules by translation into ion-selective electrodes, ISFETs or CHEMFETs, etc. The binding of the target ion/molecule by molecular receptors is measured by means of thermodynamic parameters. The binding is also determined by the diffusion and transport of the target ions/molecules through the medium via "symport" or "antiport" mechanisms which have been established in the literature. The release of the target species can be monitored by control of pH, electrochemical, redox or photonic methods to help design separation devices. Though we have results that can lead to development of molecular filters for some ions and molecules of interest, this brief note is restricted to the design, synthesis and evaluation of calix[*n*]arene-based molecular receptors for metal ions in general, and more specifically, for cesium ions.

2. Molecular receptors based upon Calix[*n*]arenes

Calix[*n*]arenes (*n*=4-20) are phenolic [1]$_n$-metacyclophanes[1] which can be conveniently obtained through acid- or base-catalysed condensation of *p*-substituted phenols and formaldehyde. They possess a distinct hydrophobic upper (or "narrow") rim and a hydrophilic lower (or "wide") rim to encompass a hollow cavity with dimensions that can be varied by varying the number of the phenolic units (*n*) present.[2] The observed diversity of calix[*n*]arenes essentially lies in their conformational isomerism due to restricted rotation of the Ar-CH$_2$-Ar bonds, or complete molecular rotation through the annulus.[3] The molecular rotation through the annulus in case of a calix[4]arene is suppressed if the narrow-rim alkoxy groups are large enough to restrict this flipping motion.[4] Though initial efforts were unsuccessful, increasingly refined synthetic methodologies have enabled the development of procedures for obtaining cone, *partial-cone*,

1,3-alternate and *1,2-alternate* conformations of calix[4]arene derivatives[5] (Fig 2b), which can provide differential capabilities for ionic and molecular recognition.[6]
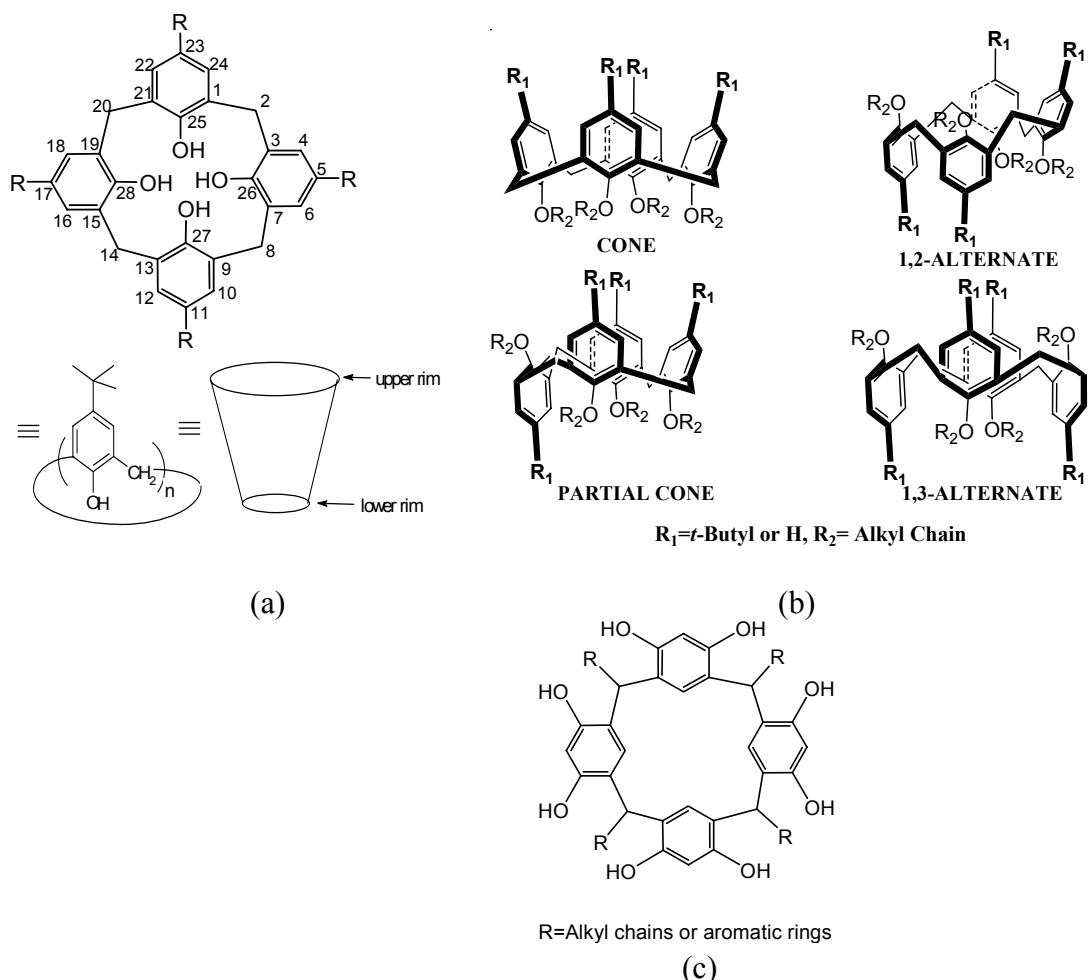

Figure 2. (a) Molecular structure of calix[*n*]arenes; (b) Different conformations of lower- and upper-rim substituted calix[4]arene(s); (c) Molecular structure of resorcinarenes.

Resorcinol derived calix[4]arenes or calix[4]resorcinarenes or resorcinarenes are high melting condensation products of resorcinol and aliphatic or aromatic aldehydes (Fig. 2c). They can be prepared in reasonable to high yields via simple, one step, acid catalyzed condensation between resorcinol and the aldehyde. In contrast to four intraannular OH groups in calix[4]arenes, calix[4]resorcinarene possess eight extraannular OH groups which may involve a 'pair-wise hydrogen bonding'. The absence of intraannular OH groups confers greater flexibility on the system and allows the aryl groups to assume 'out' alignments in addition to the four 'up-down' alignments. These different conformers are called crown, boat, saddle and chair which are equivalent to cone, flattened partial cone, 1,3-alternate and flattened cone conformers of calix[4]arenes. Treatment of parent resorcinarenes with bis-eletrophiles (e.g. ClCH$_2$Br,

TsO(CH$_2$)$_n$OTs, Me$_2$SiCl$_2$, 2,3-dichloro-1,4-diazanaphthalene) in polar aprotic solvents containing a base under high dilution conditions, introduces bridges between each of the four pairs of proximate OH groups. The resulting compounds which are examples of cavitands, show particularly fascinating complexation properties toward small molecules. These bridged resorcinarenes have been functionalized and transformed into closed baskets (carcerands) by Cram and coworkers.[7] However, there are very few literature precedents on the recognition and separation of metal ions by resorcinarene based receptors. The present review is specifically devoted to calix[n]arene based receptors.

Calixarenes generally have high melting points, high chemical and thermal stability, low solubility and low toxicity. Their structure can comparatively be readily modified. These attributes make them attractive materials for exploring their use as molecular receptors for separation and sensing applications.[6]

The design of molecular filters on the other hand requires (1) the conversion of recognition event to binding of the target and the molecular receptor to form a "balanced" target-receptor complex, (2) transport of the target-receptor complex across an appropriate membrane, (3) release of the target molecule/ion, and (4) back-transfer of the molecular receptor for re-use or recycling. A large volume of data has been accumulated on different aspects of these primary separation processes and some general principles have been enumerated. For example, Simon and coworkers[8] have summarized the following set of criteria for evaluation of a molecular receptor:

1. The selected compound should be able to recognize the metal ion(s) of interest.
2. It should lead to selective binding with the target ion/molecule.
3. It should be unresponsive to other accompanying cations and anions.
4. The compound (also called an ionophore) must be retained within the membrane phase.
5. The ion-receptor complex must be able to diffuse freely in the direction of the potential gradient.
6. The stability constant of the ion-receptor complex should not be too large or too small.
7. The kinetics of the ion-transfer and complexation with the ligand should be fast and reversible.

Criteria 1-3 are vital in determining the selectivity of the molecular receptors, whereas criteria 4 ensures an adequate lifetime. Criteria 5 is necessary to provide a mechanism for charge-transfer through the membrane while criteria 6 is a requirement for ensuring a constant concentration of free ions in the membrane over the measurement range which forms a prerequisite for Nernstian behaviour. Criterion 7 is necessary to ensure an acceptable response time.

A large number of molecular receptors based upon crown ethers, aza-crown ethers, podands, carcerands and other macrocyclic systems have been investigated for ionic recognition and for their separation and detection. A large body of data has been used for commercial success of several ion-selective electrodes as well as for the development of separation devices and protocols. In this write-up we have restricted ourselves to calixarene-based molecular receptors for ionic separation with emphasis on development of ion-selective electrodes, efficient extractants and sensor materials and for their use in important ion transport systems.[9] The

reviewed literature is generally representative of the phenomena under discussion and is not meant to be exhaustive in nature.

2.1 Calixarene-based receptors for alkali and alkaline earth metal ions

A major driving force for separation techniques is the analysis of metal ions without first requiring their physical separation. Calixarenes have been eminently used for this purpose. For example, alkali and alkaline earth cations have long been attractive targets for developing sensing techniques for blood analysis and for the separation of radionuclides for commercial and military scientific operations. The first publication on calixarene-based sensing agents appeared in 1986 wherein Diamond et al.[10] described **1a** and **1b** as excellent sensors for sodium. These sensors have been found to be useful in the estimation of Na^+ in blood. Recently, Miller et al.[11a] have described a microelectrode based upon calixarene ester **1b** for measuring Na^+ in plant cells with absolutely no interference from K^+ in the 0.1mM – 100mM activity range. Chawla et al.[11b,c] have synthesized calix[4]arene-coumarin conjugates and determined that they can discriminate Na^+ and K^+ sensing through fluorescence techniques. For example, the fluorescence intensity of **2a-c** decreases upon interaction with Na^+ but the fluorescence intensity markedly increases when Na^+ is replaced by K^+. The observation has been found to be useful for translation into development of molecular diagnostics for monitoring Na^+/K^+ balance in biofluids.

1a: R′ = Me**, 1b**: R = Et   **2** R = CH$_2$CO$_2$Et**,**   **3**
        a : R = R′ = H ;
        b : R= NO$_2$, R′ = H **;**
        c : R = H, R′ = NO$_2$
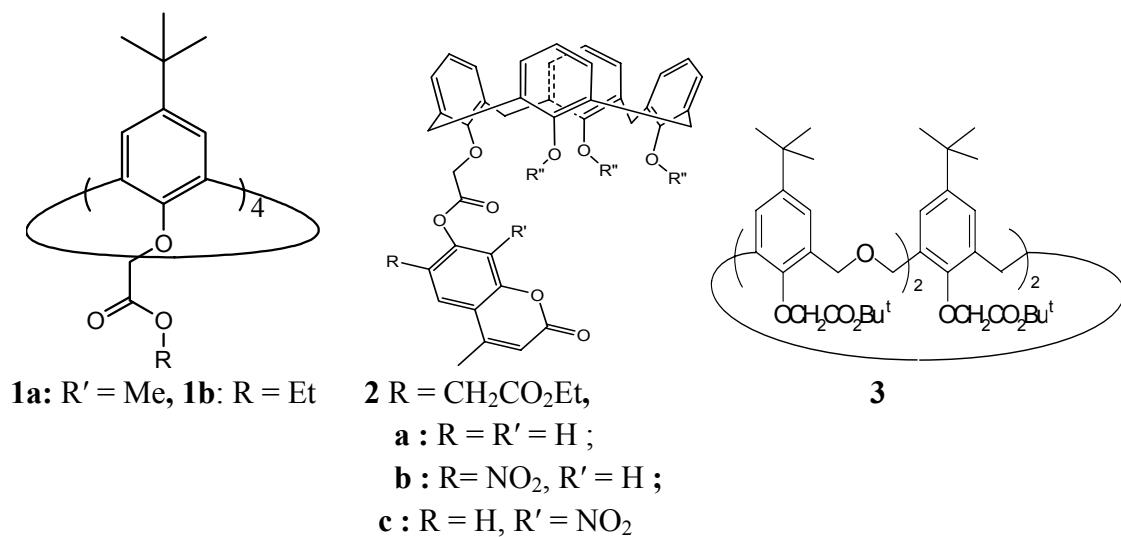
Sensors for ions other than Na^+ require a cavity size larger than that of calix[4]arene. For example, a calixarene **3** with a cavity of size intermediate between that of a calix[4]arene and calix[6]arene has been used for preparing ion selective electrode for K^+.[12] Although this ionophore (**3**) is a tetraester, the dioxacalix[4]arene substructure with two bridging methylene units expanded by additional oxygen atoms has a cavity size larger than that of a normal tetraester derived from small cavity calix[4]arene. Calix[6]arene derivatives show selectivity towards larger alkali cations and this is reflected in their suitability as ionophores for cesium ion.

For example, Jeong *et al.*[13] have determined that an ion-selective electrode (ISE) fabricated from calix[6]arene hexaester **4** exhibits a high selectivity for Cs^+ against other alkali, alkaline earth metal ions and ammonium ions. A linear response in the activity range of $10^{-6} – 10^{-1}M$ of $[Cs^+]$ has been reported. Calix[4]arenes linked to a crown-6 group (e.g. **5**) shows superior Cs^+ selectivity over other alkali metal ions and which is retained after covalent linkage to a polymeric membrane in CHEMFETS.[14]
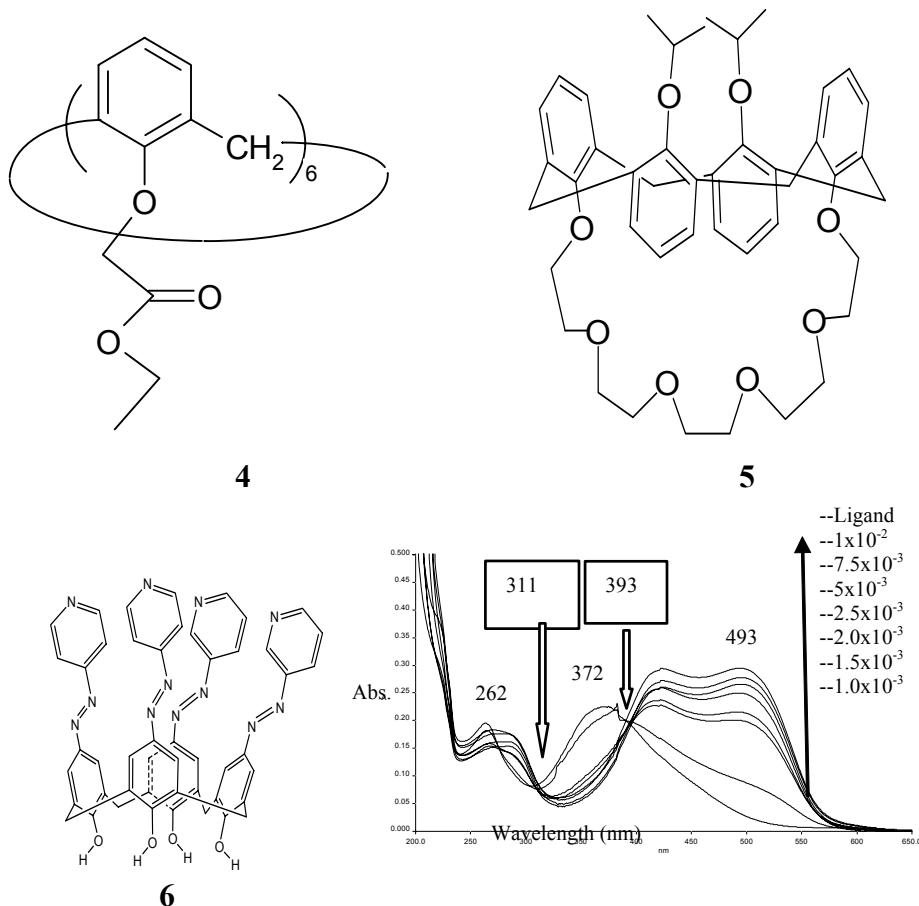
Figure 3. Molecular structure of **6** and Change in the UV/vis spectrum of **6** when titrated by Cs^+ metal salt.

Recently, a series of Cs^+-selective chromoionophore (an ionophore which change colour on recognition of target species) based on calix[4]arene bearing azo-pyridyl moieties at the upper rim has been reported by Chawla *et al.*[15a,b] The synthesized compounds possessing at least one 4-azopyridyl group at the upper rim have been found to exhibit a red shift of about 50 nm upon addition of excess of Cs^+ with concurrent appearance of a new absorption band near 500 nm. The change is prominently accompanied by a significant color change which is not observed in the case of interference from other ions. Since to-date, no azo calixarene without a crown ether

loop has been reported to be used as a selective filter for radioactive wastes containing Cs^+, these compounds have been examined as selective ionic filters. For example, changes in the $\lambda_{max}$ of **6** in their UV/vis spectra upon addition of alkali metal salts in methanol are depicted in Figure 3. Two isobestic points at 311 nm and 393 nm have also been identified in the case of **6** when titrated with Cs_2CO_3 solution in methanol.

In a very recent publication, Chawla *et al*[15c] have examined the tetrathiacalix[4]arene-based receptor, **7a**, for Cs^+ and Rb^+ selectivity over other alkali and alkaline earth metal ions. The study reveals selective bathochromic shifts in UV–visible spectroscopy on interaction with these ions. Similarly, **7b**[15d] has been used for the detection of alkali metal cations by the same group of researchers.

7a   **7b**   **8**
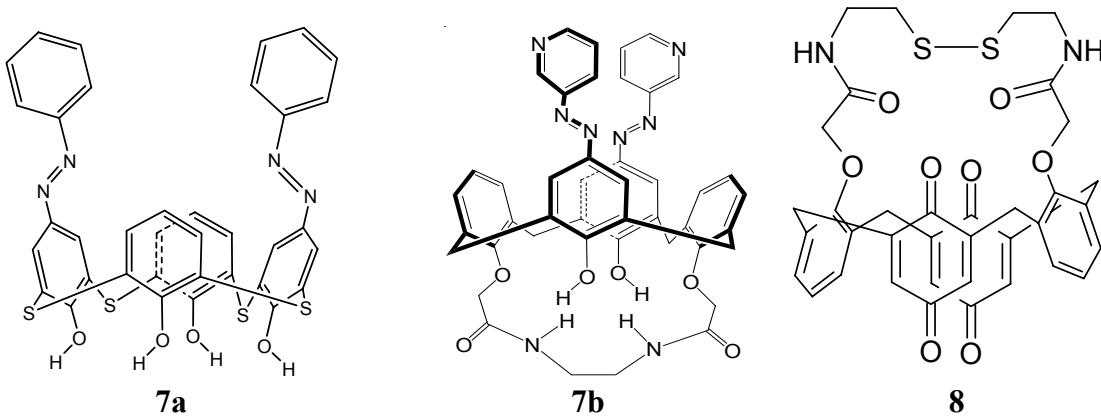
A new methodology to detect two metal ions using a single electrode (tunable chemical sensors) has been described by Shinkai *et al.*[16] wherein a photo-responsive ionophoric calix[4]arene is immobilized on a PVC membrane. The resultant product has been shown to possess selectivity that can be switched from one target ion to another by external light irradiation. It has been demonstrated that an electrode based on this ionophore shows an affinity for Li^+ as against other alkali and alkaline earth metal ions in the dark whereas it functions as an excellent Na^+ sensor when irradiated at 365nm.

A redox-active voltametric sensor based on a self-assembled monolayer of calix[4]arene disulfide-diquinone **8** has been shown to selectively recognize Ba^{2+} in aqueous media (activity range $10^{-6}M – 10^{-4}M$) with no significant interference from alkali and alkaline earth metal ions except for Sr^{2+} and Ca^{2+}. Only 100- and 500-fold concentrations of Sr^{2+} and Ca^{2+} ions, respectively, can lead to voltametric responses comparable to that of Ba^{2+}.[17a] Similarly, a diformyl calix[4]arene derivative **9** has shown remarkable selectivity for Ba^{2+}.[17b]

9 (R= Alkyl chain)   **10**
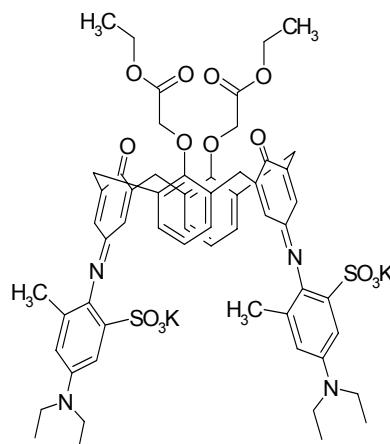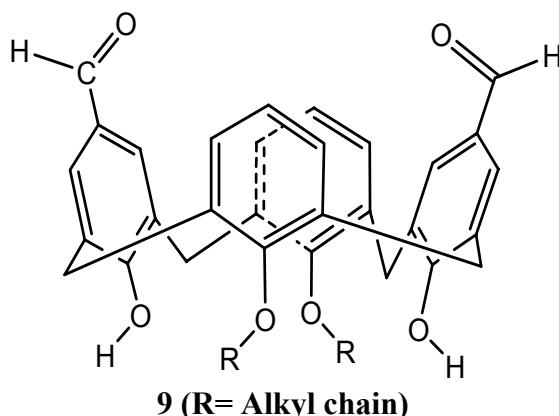
Although a number of publications have appeared on calixarene-based electrochemical sensors for metal ions, not much work has been reported on calixarene- based optodes. It is only recently that Kürner and Werner[18] have published their work on Ca^{2+}-selective optode membranes based on 1,3-bis(indoaniline) derived 2,4-bis[(ethylcarbonyl)-methoxy]calix[4]arene **10**. The resulting optode has been shown to have a potential to determine Ca^{2+} ion concentration in physiological samples just by monitoring a wavelength shift.

A PVC membrane incorporating the parent *p-tert*-butyl calix[8]arene has been evaluated as a sensor material for a Sr^{2+}-selective ISE.[19] It has been observed that this electrode shows the best response with a working concentration range of $2x10^{-5} – 1x10^{-1}M$ and a near-Nernstian slope in the pH range 2.4 – 4.8. The selectivity data shows that the electrode is sufficiently selective over a number of interfering ions including alkaline earth metals with a fast response time of 15s.

Apart from the above-mentioned sensor materials, calixarene derivatives have also been used as extractants for alkali [$Li^{+ 20a,b,p}$, $Na^{+ 21s}$, $K^{+ 22k}$, $Cs^{+ 24e,y}$, $Fr^{+ 25}$] and alkaline earth metal ion [$Ca^{2+ 26c-e}$, Sr^{2+27a}, Ra^{2+28}].

Extensive research work published during the past decade on calixarene-based receptors for metal ions is difficult to enumerate in this brief note but key references for use of calixarenes for alkali [$Li^{+ 20}$, $Na^{+ 21}$, $K^{+ 22}$, $Rb^{+ 23}$, $Cs^{+ 24}$, $Fr^{+ 25}$] and alkaline earth metal ions [$Ca^{2+ 26}$, $Sr^{2+ 27}$, $Ba^{2+ 17}$, $Ra^{2+ 28}$] are provided in Tables 1and 2.

Table 1. Calix[4]arene receptors for alkali metal ions

Selectivity for	Application	Selectivity over	Ref.
Li^+	Extraction	Na^+, K^+, Cs^+, NH_4^+	20a
Li^+	Extraction	Na^+, K^+, Cs^+, Rb^+	20b
Li^+	Chromoionophore	Na^+	20c,d
Li^+	Chromoionophore	Na^+	20e
Li^+	Redox switch	Na^+, K^+	20f,g
Li^+	Membrane transport	Na^+, K^+, Cs^+, Rb^+	20h
Li^+	Receptor	Na^+	20i-o
Li^+	Extractant	Na^+	20p
Li^+	Ion transport	Na, K^+, Rb^+, Cs^+	20q
Li^+	Transport	Na^+	20r
Li^+ & Na^+	Ionophore	Cs^+, Rb^+, K^+	20s
Na^+	ISE	K^+	21a-d
Na^+	Potentiometric sensor	--	21e,f
Na^+	Potentiometric sensor	---	21e,g
Na^+	Fluorescent sensor	$Li^+, K^+, Ca^{2+}Mg^{2+}$	21h
Na^+	ISE	$Li^+, NH_4^+,$ Group II	21i
Na^+	Fluorescent optode	$Li^+, K^+, Rb^+, NH_4^+, Mg^{2+}, Ca^{2+}, H^+$	21j
Na^+	Fluorescent sensor	K^+	21k
Na^+	Fluorescent receptor	Li^+, K^+, Ca^{2+}	21l
Na^+	Fluorescent optode	K^+	21m
Na^+	ISE	K^+	21n
Na^+	HPLC separation	Li^+, Cs^+, K^+	21o
Na^+	Nanotubes	---	21p
Na^+	ISE, Ion-sensing films and light transmitting or optical wave guide type ion sensors	---	21q
Na^+	Fluorescent sensor based on intramolecular energy transfer	Other Group I ions	21r
Na^+	Extractant (self co-extraction)	---	21s
Na^+	Ionophore	Li^+, K^+, Ca^{2+}	21t
Na^+	Optode membrane material	Other Group I	21u
Na^+	Chromoionophores	Li^+, K^+, TMA^+	21v
Na^+	ISE	Other group I ions	21w,x

Na^+	ISE in serum determination	Other group I ions	21y
Na^+	Colorimetric reagents for solvent extraction	---	21z
Na^+	Chromatographic separation	Other group I ions	$21z_1$
Na^+	ISE for analysis of blood sodium	Other common interferants, K^+	$21z_2,z_3$
Na^+	Sensor	Li^+, K^+	$21z_4$
Na^+	Fluorescent sensor	Li^+	$21z_5$
K^+	Ionophore	Li^+, Na^+, Cs^+, Rb^+, Ba^{2+}	22a,b
K^+	Chromatographic separation	Na^+, Mg^{2+}, Ca^{2+}	22c
K^+	Fluoroionophore	Na^+, Li^+, Rb^+, Cs^+	22d
K^+	Ionophore (calix-tubes)	Na^+, Li^+, Rb^+, Cs^+	22e
K^+	Ditopic receptor	Na^+, Li^+, Rb^+, Cs^+	22f
K^+	Ionophore (calix-tubes)	Na^+, Li^+, Rb^+, Cs^+	22g
K^+	Liquid membrane transport	Li^+, Na^+, NH_4^+	22h
K^+	Chromoionophore	Other Group I ions	22i
K^+	Chemically modified electrode	Na^+	22j
K^+	Extraction and transport	Other metal ions	22k
K^+	Ionophore	---	22l
K^+	Ionophore	Other alkali metal ions	22m
Rb^+	Ionophore	Na^+, K^+, Li^+	23a, b
Cs^+ and Rb^+	Redox active ionophore	Na^+, K^+, Li^+	23c
Cs^+	ISE	Other group I, Group II, NH_4^+, some transition metal ions	24a
Cs^+	Transport	---	24b
Cs^+	Receptor	Na^+	24c
Cs^+	ISE	Li^+, K^+, Na^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}	24d
Cs^+	Extraction	Li^+, Na^+, K^+, Rb^+	24e
Cs^+	Fluorescent probe	K^+, Rb^+	24f-h
Cs^+	Extraction from radioactive wastes	Na^+	24i,j
Cs^+	Ionophore	Na^+, K^+, Li^+, Rb^+	24k
Cs^+	Ion-pair extraction	Other Group I ions	24l
Cs^+	Extraction through thin sheet supported liquid membrane, ISE	Na^+, Li^+, K^+, Rb^+	24m-p

Cs^+	Ionophore	Na^+	24q
Cs^+	Ionophore	Na^+, K^+, Rb^+	24r
Cs^+	Sensor material	---	24s
Cs^+	Ionophore	Na^+	24t
Cs^+	Optode	Na^+, K^+, Li^+, Rb^+	24u
Cs^+	Transport	Na^+, K^+, Li^+, Rb^+	24v
Cs^+	Transport	Na^+	24w
Cs^+	PVC membrane electrode	Group I, Group II, H^+, NH_4^+	24x
Cs^+	Extractant, Membrane transport	Other Group I ions	24y
Cs^+	Ionophore	Na^+, Li^+, Rb^+	24z
Cs^+	Membrane transport	Na^+, K^+	$24z_1$
Cs^+	Ionophore	---	$24z_2$
Fr^+	Extraction	$^{225}Ac, Na^+$	25

Table 2. Calixarene receptors for alkaline earth metal ions

| Selectivity for	Application	Selectivity over	Ref.
Ca^{2+}	Chromoionophore	Na, K, Mg^{2+}	26a
Ca^{2+}	Chromoionophore	Other Group II cations	26b
Ca^{2+}	Extractant	Na, Sr^{2+}, Mg^{2+}	26c
Ca^{2+}	Extractant	$Sr^{2+}, Ba^{2+} Mg^{2+}$	26d
Ca^{2+}	Extractant	$Sr^{2+}, Ba^{2+}, Mg^{2+}$	26e
Ca^{2+}	ISE	Na, K, NH_4, Li, Mg^{2+}	26f,g
Ca^{2+}	Chromogenic receptor	Li, K, Rb, Na, Cs, Ag, Mg^{2+}, Sr^{2+}	26h
Ca^{2+}	Fluorescent probe	NH_4, Li, Na, K, Cs, $Mg^{2+}, Sr^{2+}, Ba^{2+}$	26i
Ca^{2+}	Optode membrane material	Other Group I, Group II cations	26j,k
Ca^{2+}	Redox active receptor	---	26l, m
Ca^{2+}	Voltametric or redox active ionophore	Ag and Other Group I ions	26n
Ca^{2+}	Extractant	Sr^{2+}, Ba^{2+}	26o
Ca^{2+}	Optical sensor	---	26p
Sr^{2+}	ISE	$Ca^{2+}, Ba^{2+}, Mg^{2+}$, Li, K, Na, Pb^{2+}	19
Sr^{2+}	Ionophore for removal of ^{90}Sr from radioactive wastes	Group I cations as well as Ca^{2+} and Ba^{2+} ions	27a
Sr^{2+}	Transport	Na^+	27b
Ba^{2+}	Voltametric sensor	Group I and Group II cations	17
Ra^{2+}	Extractant	Light earth metal ions	28

2.2 Calixarene based receptors for transition and heavy metal ions

It has been reported that the introduction of soft donor atoms in a calixarene framework promotes their complexation with transition and heavy metal ions. For example, O'Connor *et al.*[29] have established that calix[4]arene derivatives **11a-c** with S and N groups, in ISEs, are extremely sensitive to Ag^+, Cu^{2+} and Pb^{2+} ions. With an appropriate number and disposition of soft donor atoms, it is possible to achieve selectivity for heavy metal ions over alkali metal cations. For example, He *et al.*[30] have reported a Ag^+-selective electrode based upon a pyridyl unit-containing calix[4]arene derivative, **12**. This electrode gives a good Nernstian response for Ag^+ in the activity range $5 \times 10^{-6} – 10^{-2} M$ and exhibits a high selectivity for Ag^+ against alkali, alkaline earth and transition metal ions. Similarly, Sun *et al.*[31] have described the evaluation of 25,27-dihydroxy-26,28-bis(3-phenyl-thiapropoxy)-calix[4]arene and 25,27-dihydroxy-26,28-bis(3-phenylthia-propoxy)-5,11,17,23-tetra-*tert*-butylcalix[4]arene for Ag^+ selectivity in ISEs against alkali metals, alkaline earth metals, Al^{3+}, Tl^+, Pb^{2+} and some transition metal ions. These ISEs have promised excellent Ag^+ selectivity over most of the interfering cations examined except for Hg^{2+} and Fe^{2+} which show a relatively smaller interference.

11a: R = CH₂CO₂CH₂N(CH₂)₃C=O   **12**   **13**
11b: R = CH₂C(S)NEt₂
11c: R = CH₂CO₂CH₂CH₂SMe
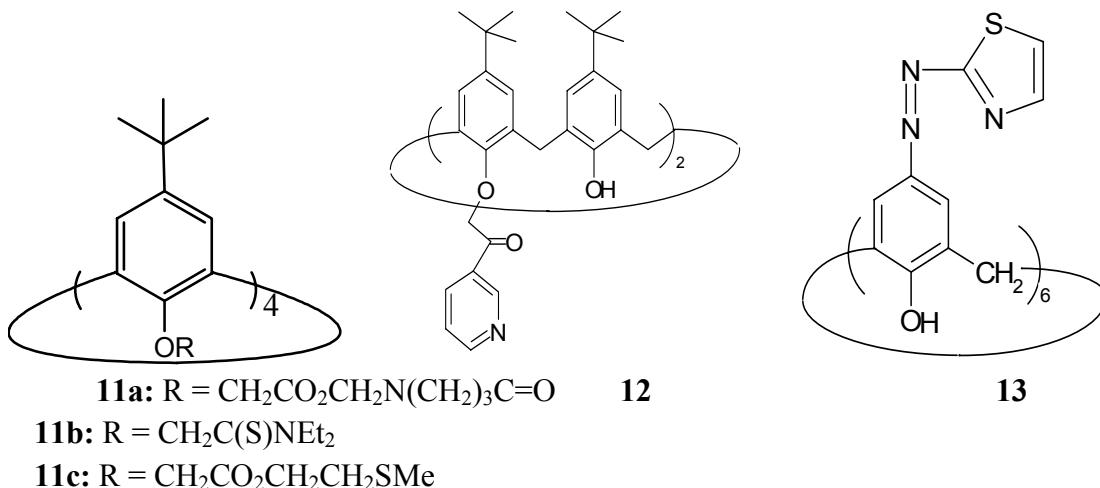
The use of ISEs for the detection of soft heavy metal ions such as Hg^{2+} and Pb^{2+} have received much interest due to their importance in controlling the levels of environmental pollutants in natural waterways and potable water. Considerable efforts have been directed towards the design of calixarene-based ISEs for these soft heavy metal ions. A mercury ion-selective electrode has been reported by Jianquan *et al.*[32a] who have prepared a polymeric membrane based on a calixarene derivative **13**, containing a thiazole azo group as the ionophore. The ISE obtained exhibits a stable detection reproducibility and high selectivity against alkali, alkaline earth and transition metal ions, except Ag^+. This Hg^{2+}-ISE has been successfully applied to determine mercury in real samples. The same group of workers[32b] have described a lead ion-selective electrode prepared with a polymeric membrane based on a calixarene derivative **14**, containing carboxyphenyl azo groups. This electrode gives a good Nernstian response in the

range 10^{-6} -10^{-2} M and exhibits a high selectivity towards alkali, alkaline earth and transition metal ions. Molecular modeling experiments reveal that the ion-calixarene complex exists in the cone conformation with lead ion bound by the azo group (N=N) on the upper rim of the molecular receptors. Malinowska and coworkers[33] have also prepared lead selective PVC electrodes based on di- and tetra-thioamide-functionalized calix[4]arenes and have determined that the electrodes have good selectivity against alkali metals and Cu^{2+}, Zn^{2+} and Cd^{2+}.

14   **15**   **16**
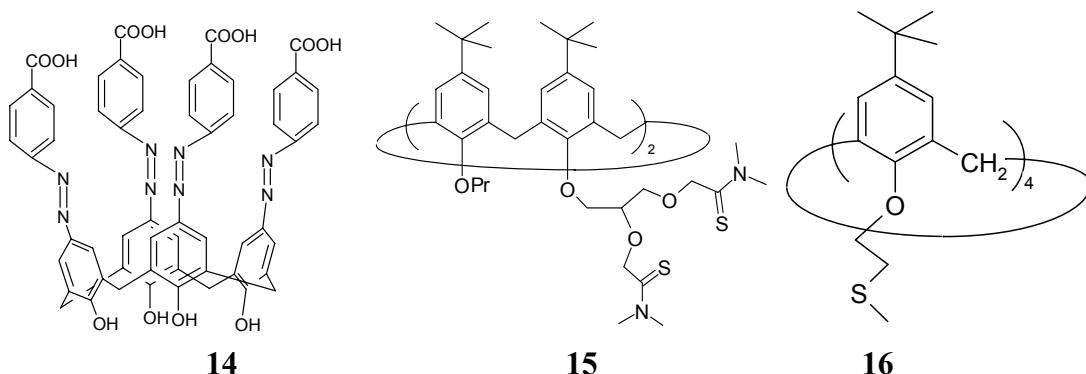
Reinhoudt *et al.*[34] have described an ISE based on a calixarene derivative **15** in its 1,3-alternate conformation for Cd^{2+}. This derivative has been claimed to be a highly selective sensor material for Cd^{2+} with selectivity over Pb^{2+} and Cu^{2+}.

Likewise, Cobben *et al.*[37] have described calixarene-based ISFETs targeted at Ag^+, Cu^{2+}, Cd^{2+} and Pb^{2+} using 29 different calixarene derivatives. ISFETs employing thioethers **16** and **17** have been determined to exhibit excellent Ag^+ sensitivity and good selectivity though no mention is made of its selectivity over Na^+ ions. Ligand **17** has resulted in devices that are more selective for Cu^{2+} against Ag^+ and Hg^{2+} ions, both of which would probably interfere in this type of membrane sensors. Preliminary data have also been reported for Cd^{2+} and Pb^{2+} selective ISFETs.

Recently, Kimura *et al.*[36] have described a remarkable Tl^+ selectivity for ion sensors based on calix[4]arene tetrapropyl ether derivatives by taking advantage of the π-coordination possible with their skeletal aromatic rings. The reported ISE has also been successfully applied to Tl^+ assays in human urine for monitoring thallium poisoning.[36] A near-Nernstian response has been observed in the activity range of 1×10^{-1} – 3×10^{-6}M with a very high selectivity with almost no interference from related alkali metal ions.

17   **18a (R= C₆H₁₃),**
           18b (R= -CH₂CH=CH₂)   **19a**   **19b**
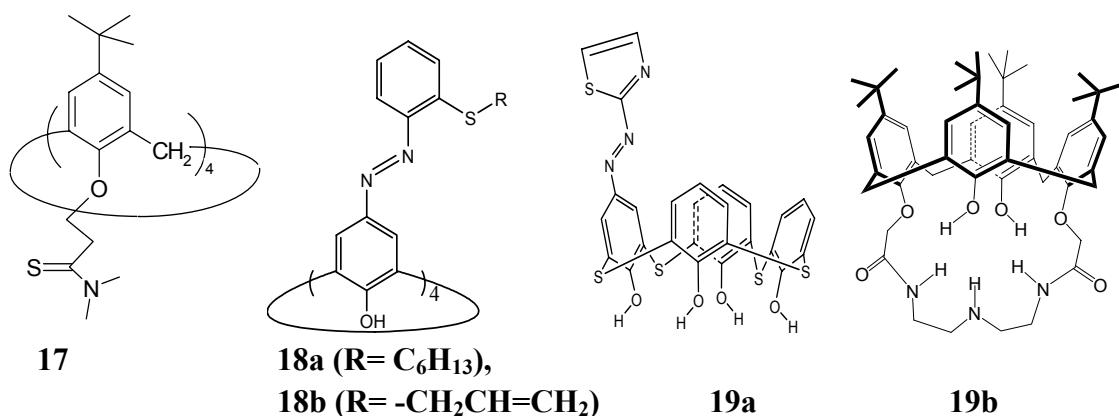
Chawla *et al.*[35b] have determined that **18a** and 1**8b** have the potential of detecting ppm quantities of soft metal ions like Hg^{2+} and Pd^{2+} through a visual change which is being further investigated. Similarly, **19a**[15c] and 19**b**[15d] have been used for the detection of Pd^{2+} and Hg^{2+}respectively by the same group.

**20**   **21** R=H, **a:** n=4, **b:** n=8
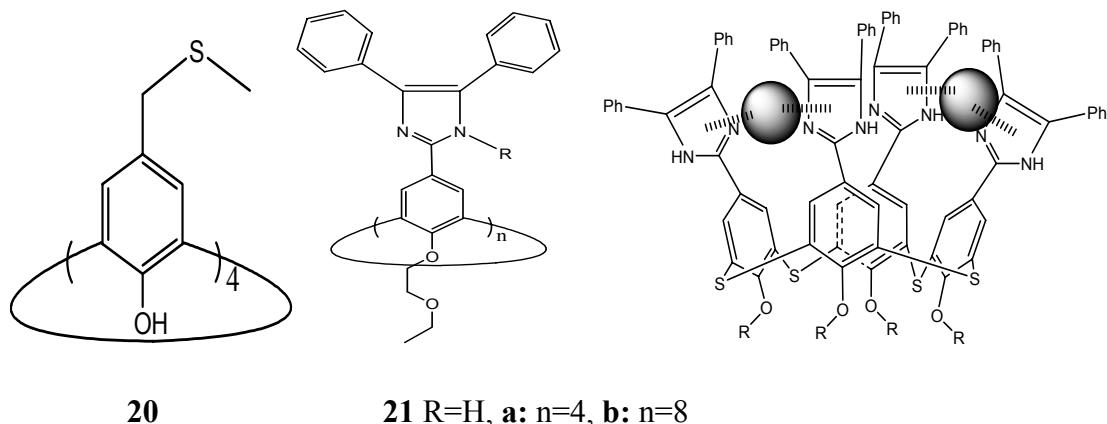
Figure 4. A plausible structure of **21a-Ag$^+$** complex.

Chawla *et al.*[35] have reported the extraction studies of soft metal ions by using calix[4]arene with sulphur atoms in its framework. Highly efficient extraction (>99%) of Cd^{2+} and Pb^{2+} ions from an aqueous solution into organic layer with (**20**) has been described.,[35a] Chawla *et al.*[67] have also reported the synthesis of calix[n]arenes (**21a** *n*=4, **21b** n=8) with imidazole moieties directly atached to the upper rims. These heterocyclic calix[*n*]arenes have been shown to be highly selective extractants (>98%) for Ag$^+$ ions. Though the crystal structure of the silver complex has so far been not possible to be recorded, spectroscopic study (IR, NMR) strongly suggests that silver ions are interacting through the upper rim and the hydrogen atoms attached to the nitrogens of the imidazole rings do not take part in the complexation process. A comparative study with its acyclic (*n*=1) derivative also suggests that the size and nature of the macrocyclic

structure of calixarene has a major role to play in the recognition process. A plausible structure of **21a.Ag$^+$** complex has been shown in Fig 4.

Extensive studies on calix[*n*]arene based as molecular receptors for transition metal ions [Fe(III)[38], Cu(II)[39], Zn(II)[40], Pb(II)[41], Ag(I)[42], Au(I)[43], Cd(II) [36], Hg(II)[44], Tl(I)[36]] have been carried during the past decade (Table 3).

**Table 3.** Calixarene-based molecular receptors for transition metal ions

Selectivity for	Application	Selectivity over	Ref.
Fe^{3+}	Extractant	---	38a
Fe^{3+}	Microsensors	Heavy metals, Ag^+ etc.	38b
Fe^{3+}	Extractant	Cu^{2+}, Ni^{2+}, Co^{2+}	38c
Cu^{2+}	ISE	K^+, Na^+, Cs^+, Rb^+, Li^+, Cd^{2+}, Ni^{2+}, Fe^{3+}	39a
Cu^{2+}	Extractant	---	39b
Zn^{2+}	Chromoinophore	Sr^{2+}, Ca^{2+}, Mg^{2+}, Na^+	40
Pb^{2+}	Chromatographic separation (C_4 is impregnated on a resin)	Zn^{2+}	41a
Pb^{2+}	Extractant	---	41b
Pb^{2+}	ISE	---	41c
Pb^{2+}	Separation of Pb by calix[4]arene derivative adsorbed in resin	Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}	41d
Pb^{2+}	Adsorption agents for separating Pb	Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}	41e,f
Pb^{2+}	ISE	Group I, Group II, T.M. ions	41g
Pb^{2+}	ISE	Ca^{2+} and common interferants	41h
Pb^{2+}	Ion selective membrane electrode	Group I, group II and some transition metal ions	41i
Pb^{2+} & Ag^+	Extractant	Zn^{2+}, Cd^{2+}, Co^{2+}	42a
Ag^+ & Pb^{2+}	Ionophores	Cu^{2+} and Hg^{2+}	42b
Pb^{2+} & Hg^{2+}	Ionophore	Cd^{2+}, Na^+	42c
Hg^{2+} & Pb^{2+}	Liquid membrane transport	---	42d
Ag^+	ISE	NH_4^+, H^+, Group I & II	42e,f
Ag^+	Extractant & ISE	Group I, group II and some transition metal ions	42g

Ag^+	ISE	Group I, group II and some transition metal ions	42h,i
Ag^+	Ionophore	---	42j
Ag^+	ISE	Na^+	42k
Ag^+	Extractant	$Mn^{2+}, Fe^{2+}, Hg^+, K^+, Co^{2+}, Cd^{2+}, Tl^+,$ $Cu^{2+}, Ca^{2+}, Zn^{2+}$	42l
Ag^+	ISE	$K^+, Co^{2+}, Ba^{2+}, Na^+, Cu^{2+}, NH_4^+, Ni^{2+},$ Hg^{2+}, Pb^{2+}	42m
Ag^+	ISE	$Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+},$ $Ni^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}$	42n
Ag^+	Ionophore	$Cd^{2+}, Co^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}$	42o
Ag^+	ISE	Group I, Pb^{2+}, Hg^{2+}	42p
Ag^+	ISE	Group I, group II and some transition metal ions	42q
Ag^+	Sensor	Na^+	42r
Ag^+	Extractant	---	42s
Ag^+	Molecular syringe	---	42t
Ag^+	ISE	Group I, group II, heavy metals eg. Hg^{2+}, Pb^{2+}	42u
Ag^+	Extractant	Pd^{2+}	42v
Ag^+	Ionophore	---	42w
Ag^+	Ionophore	---	42x
Ag^+ & Hg^+	Membrane transport, ion-selective electrode for Ag	Group I, Group II, $Zn^{2+}, Cu^{2+}, Cd^{2+},$ Ni^{2+}, Pb^{2+}	42y
Ag^+ & Au^+	Extractant	Pd^{2+}, Pt^{2+}	43
Cd^{2+}	CHEMFETs	$Ca^{2+}, Cu^{2+}, K^+, Pb^{2+}$	36
Hg^{2+}	Extractant	Group I, Group II, $Co^{2+}, Ni^{2+}, Cu^{2+},$ Zn^{2+}, Pb^{2+}	44a
Hg^{2+}	Fluorophore	$Pt^{2+}, Ag^+, Cd^{2+}, Pb^{2+}, Pd^{2+}$	44b
Tl^+	ISE for Tl(I) assay in human urine	---	36

2.3 Calixarene-based receptors for *f*-block elements

Although a number of calixarene derivatives containing N, S, O and P groups have been described in the literature for extraction of various *f*-block metal ions, only a few reports have been described which utilize calixarene based ISEs for this class of elements. Recently,

McKervey et al.[45] have constructed a Eu^{3+}-ISE based on a diphenyl-phosphinoylethyl substituted calix[4]arene **22** in a cone conformation. A high selectivity over Na$^+$ has been described.[45]
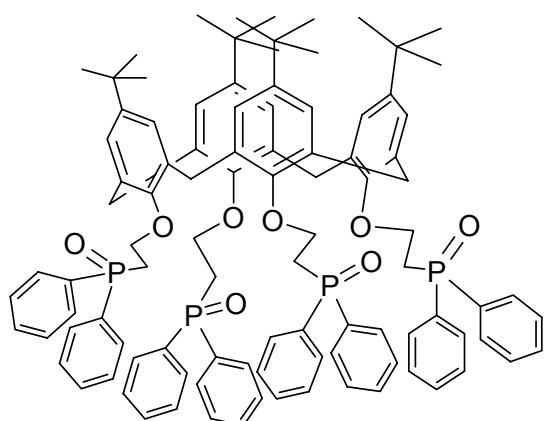
22

Extraction of UO$_2^{2+}$ from nuclear wastes has been an important practical application of calixarenes. Since the first experiments in 1986 on the use of p-*tert*- butylcalix[6]arene hexasulphonate, various calix[*n*]arene derivatives have been explored for a similar purpose. For instance, Gupta et al.[46] have described an ISE based on *tert*-butylcalix[6]arene hexasulphonate in an optimized membrane composition in PVC for extraction of UO$_2^{2+}$. A moderate selectivity over competing cations (linear range: $4x10^{-5}$ – 0.1M) has been achieved. The performance of this ISE has been shown to be comparable with radiochemical determinations.[46]

Utilization of calixarenes as molecular receptors for *f*-block elements is an emerging field with potential applications in nuclear waste management [La(III), Eu(III), Er(III), Y(III)[47], Lu(III), Ho(III), Pr(III), Yb(III), La(III)[48], Tb(III)[49], Th(IV)[50], UO$_2$(II)[51], U(VI) [52], Am(III) [53]) (Table 4).

Table 4. Calixarene receptors for *f*- block elements

Selectivity for	Application	Selectivity over	Ref.
La^{3+}, Eu^{3+}, Er^{3+}, Y^{3+}	Extractant	Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, Yb^{3+}	47
Lu^{3+}, Ho^{3+}, Pr^{3+}, Yb^{3+}, La^{3+}	Extractant	---	48
Tb^{3+}	Receptor	---	49
Th^{4+}	Extractant	UO$_2^{2+}$	50a
Th^{4+}	Extractant	Eu^{3+}	50b
UO$_2^{2+}$	Extractant	---	51a
UO$_2^{2+}$	ISE	---	51b
UO$_2^{2+}$	Extractant	Na$^+$	51c,d

UO_2^{2+}	Modified Electrodes	PO_4^{3-}, Fe^{3+}, $Mo_7O_{246}^{-}$, VO_2^{+}, Cr^{3+}	51e,f, g
UO_2^{2+}	Extractant	Bi^{3+}, Lu^{3+}, Cd^{2+}, Y^{3+}, Sr^{2+}, La^{3+}, Ag^{+}, Hg^{2+}, Pb^{2+}	51h,i
UO_2^{2+}	Receptor	---	51j
UO_2^{2+}	Optical sensor	---	51h
U(VI)	Extractant	---	52
Am^{3+}	Extractant	Nd^{3+}, Er^{3+}, Yb^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+}	53

2.4 Receptors based on polymeric calixarenes

Calixarene-based polymers have just begun to receive attention as the new polymers may be processed into materials suitable for molecular devices (ion-selective electrodes, molecular filtration or extraction membranes).[54] Recently, Yilmaz *et al.*[55] have described the synthesis of two new polymers, **23a** and **23b**, containing pendant calix[4]arene units with nitrile functionalities at their lower rim via radical-initiated reactions. It has been deduced that both polymers show a good selectivity towards Hg^{2+} which support their utility as adsorbents or potential candidate materials for fabricating membranes and sensors to detect and separate Hg^{+} with high selectivity. Selective complexation of Na^{+} by polymeric calix[4]arene tetraesters has been reported by Hasalettin and coworkers.[56] Arrigan and coworkers[57] have examined the use of polymeric calixarene ester **24** as a chemically-modified electrode for voltametric analysis of Pb^{2+}, Cu^{2+} and Hg^{2+} ions in dilute solutions.

23a: R = CH₂CN   **23b:** R = CH₂CN ; X = Ph   **24: R** = CH₂CO₂Et ;
X=CH₂CO₂CH₂CH₂OCO
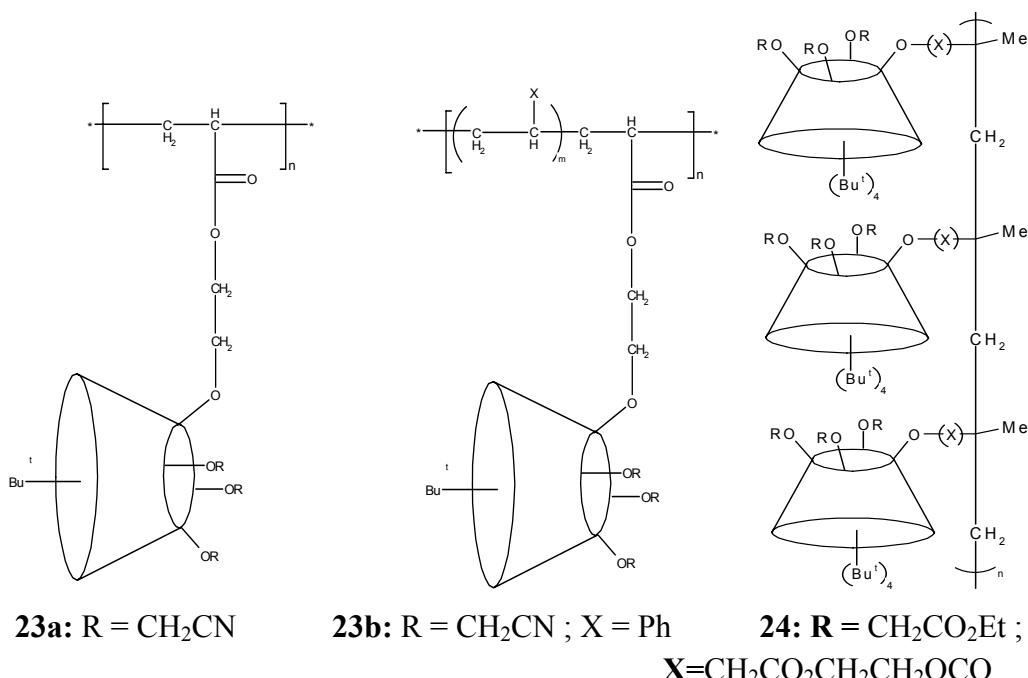
3. Conclusions

In summary, design, synthesis and evaluation of calix[4]arene-based molecular receptors for improved selectivity towards target molecule/metal ions and their separation is one of the most important goals of supramolecular science and technology. As the separation factor increases, the application of calixarene derivatives in selective binding and transport will become imperative with commercial consequences and far reaching ramifications.

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5. References

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