

INTRODUCTION

Introduction:

Calixarene is a macrocycle or cyclic oligomer based on a hydroxyl alkylation product of phenols and aldehydes¹. The word calixarene is derived from calix or chalice since they resemble a pot and from the word arene that refers to the aromatic building block. Calixarenes have hydrophobic cavities that can hold smaller molecules or ions and belong to the class of cavitands known as host-guest chemistry. In 1940s Zinke and Ziegler² discovered base-induced reaction of *p*-alkylphenols with formaldehyde, which yields cyclic oligomers. Then, synthesis of major cyclic oligomers was reported³ comprising original Zinke mixture in good and reproducible yields³.

Calixarenes can be used as ion sensitive electrodes or sensors⁴, optical sensors⁵, chiral recognition devices for solid phase extraction, as a stationary phase and modifiers⁶. Synthesis, properties and applications of calixarenes is the subject of several books⁷⁻¹² and reviews¹³⁻¹⁷. Different structures and properties of calixarene resulted in many studies¹⁸⁻²⁰. The calixarenes are classified in the following categories.

I. HETERO CALIXARENES

Heterocalixarenes or calixhetarenes belong to the family of calixarenes intensively studied due to their interesting chemical and physicochemical properties as well as their application possibilities.

Cone conformers of calix[3]indoles have been synthesised and some of requirements for their formation are discussed²¹. An isomeric series has also been obtained with the combination of an indole with bis (hydroxymethyl)-2, 2'-di-indolylmethane²².

3-substituted 4, 6-dimethoxyindoles possess two reactive sites for electrophilic substitution which can react with aryl aldehydes in the presence of phosphoryl

chloride to give calix[3]indoles. As a part of expanding the range of calixarenes from other activated heterocycles calix[3]benzofurans have been prepared from 3-substituted 4,6-dimethoxybenzofurans and 2-7-hydroxymethylbenzofurans with formaldehyde and aryl- aldehydes in the presence of acetic acid and phosphoryl chloride^{23,24}.

Like indoles and furans the pyridines and pyrroles can play a major role in heterocyclic calixarene chemistry as they exhibit various physical and chemical properties that lead them to vast number of potential applications. Calix(4)pyrroles are effective and selective receptors for anions and neutral guest species which have applications as complexes, catalytic materials, nano-sponges, molecular machines, nano entities and semi conducting materials²⁵. Bipyridyl group containing calixarenes are useful for binding various metal ions.

Calix[4]arene functionalized with two dipyrindyl groups at the lower rim have been synthesized by arena *et al.* and reported its Co(II) and Cu(II) complexes in CH₃CN. Bipyridyl containing calixarenes²⁶ are extensively useful to form complexes with various metal ions²⁷⁻³². Two new meso-indanyl-substituted calix[4]pyrrole receptors have been synthesized³³ using MCM-41 which is a most heterogeneous catalyst to synthesis calix[4]pyrroles. The importance of this class of complexes also stems from the possibility to oxidize or to reduce these systems and thus to exploit these properties at the nano-scale level.

Heterocalixarenes are built from heterocyclic moieties. Another class is heterocalixarenes, i. e. aza, oxa and thia-calixarenes, in which bridges between phenol units contain heteroatoms N, O, or S.

Among these recently thiacalix[4]arenes have been reported as a novel member of the well-known calixarene family. The presence of four sulfur atoms results in many novel features as compared with classical calixarenes, such as

different complexation ability with sulfur contribution, easy chemical modification (oxidation) of bridges and different size and different conformational behavior of this novel macrocycle.

The base-catalyzed condensation of *para*-substituted phenols with formaldehyde gives *t*-butyl thiacalix[4]arene as major product³⁴. Ludwig *et al.*³⁵, Gutsche *et al.*³⁶ & Koni *et al.* have carried out acid catalyst condensation since the numbers of bridging sulfides have a distinct effect on the extractability of sulfur-bridged oligomers of phenol³⁷. A similar procedure has been used for the preparation of the corresponding *tert*-octyl derivative³⁸ but unfortunately the yield of this compound was much lower (14 %).

Recently, thiacalix[4]arenes starting from *p*-(1-adamantyl)phenol³⁹ and biphenyl-4-ol⁴⁰ were prepared under similar reaction conditions. Whereas four-membered thiacalixarenes are now accessible in multi-gram amounts, the higher thiacalixarenes have only been isolated as by-products (trace amounts and 0.03 %, respectively) from a direct condensation procedure⁴¹. Thia-calixarenes have three intrinsic properties, viz. larger cavity, oxidizability of bridging sulfur and coordination to transition metal ions⁴². A similar synthetic strategy based on the sulfur-bridged linear dimer is synthesised⁴³. The starting compound can be prepared in high yield (75 %) in a one step procedure from *p*-*tert*-butylphenol. Cyclization is affected by reaction with elemental sulfur under basic conditions (NaOH) in diphenyl ether. This procedure leads to the even-membered thiacalixarenes in reasonable yields depending on the reaction conditions and the ratios of reactants.

For the systematic study of the thia-calixarenes a series of tetralkylated and partially alkylated compounds were prepared^{44,45}. Derivatives of thia-calixarenes bearing nitro and arylazo group have also been synthesised^{46,47}. Similarly, thiacalix-crowns were synthesized by direct alkylation of 1 with tetra- and pentaethylene

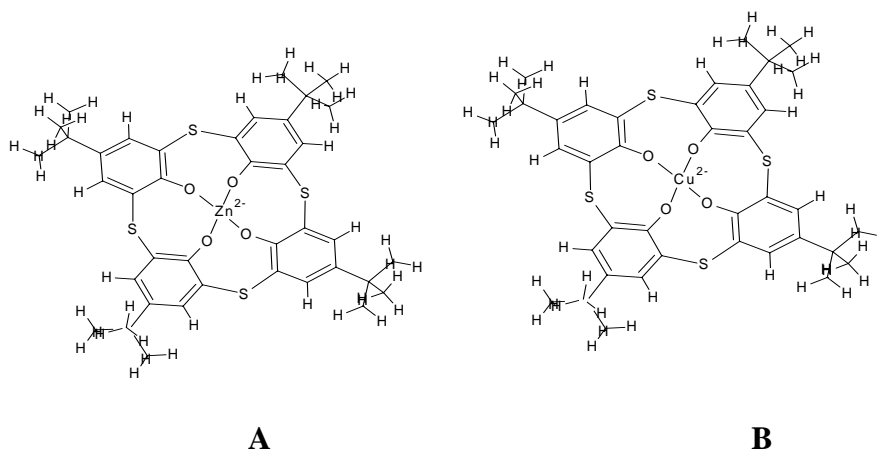
glycolditosylates^{48,49} or diiodides⁵⁰. It was found that depending on the length and the nature of metal carbonates used either mono-crowns or bis-crowns could be obtained in acceptable yield. Recently synthesised thiacalix[4]tube from the starting tetraacetate by reduction and subsequent conversion into the tetratosylate. This precursor was treated with thiacalixarene to give the desired product⁵¹.

Hence, thiacalix[4]arene is a good compound for many applications in supramolecular chemistry⁵²⁻⁶⁰.

Ability of thiacalix[4]arene to bind metal ions have been investigated by solvent extraction method in several studies^{61,62}. Study of its binding ability toward first transition metal ions (Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+}) and Mg^{2+} ion by solvent extraction has been carried out by the dimer method⁶³ thus thiacalixarene shows a high selectivity towards Cu^{2+} at pH 5.5 by coordination of the O^- , S^- , O^- donor sets. Polymeric thiacalix[4]arene derived from terephthaloyldichloride (Merrifield) resin for separation of alkali (Li^+ , Na^+ , K^+ , and Cs^+) and heavy metal (Cu^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , Co^{2+} and Ni^{2+}) cations than the precursor thiacalix[4]arenes. Two new polymeric thiacalix[4]arenes formed by the reaction of 5,11,17,23-tetra-*t*-butyl-25,27-bis[(4-aminobenzyloxy)-26,28-dihydroxy]thiacalix[4]arene with terephthaloyl dichloride and that of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetra-hydroxy-thiacalix[4]arene with chloromethylated polystyrene (Merrifield resin) have been synthesised and applied for complexation using liquid–liquid and solid–liquid extraction procedures⁶⁴. Soluble polymer and the cross-linked polymer derived from Merrifield resin are more efficient for separation and removing transition metals from solution than the precursor thiacalix[4]arene⁶⁴.

The complexation of *p*-*tert*-butylthiacalix[4]arene and its zinc complex have been investigated using quantum chemical calculations⁶⁵. Conformational structures and energies of thiacalix[4]arene and *p*-*tert*-butylthiacalix[4]arene have been

determined and compared with those of sulfonylcalix[4]arene and *p-tert*-butylsulfonylcalix[4]arene molecules⁶⁵. Stabilities of the *p-tert*-butyl thiacalix[4]arene conformers are in the order: cone > partial cone > 1,3-alternate > 1,2-alternate. The stability order of *p-tert*-butyl thiacalix[4]arene conformers is the same as that of calix[4]arene and thiacalix[4]arene conformers but different from that of sulfonylcalix[4]arene and *p-tert*-butylsulfonylcalix[4]arene which have the 1,2-alternate conformer as the most stable species. Comparative studies of the complexation features of thiacalix[4]arene toward the transition-metal ions like Zn²⁺ and Cu²⁺ have also been analyzed in detail. Two and five discrete binding modes have been studied¹⁶³⁻⁶⁶ and the position of the deprotonated phenols seems to influence the structural pattern of binding modes. The most stable of the entire binding mode is predicted in a distorted square planar coordination, using two phenol and two phenolate groups in an opposite pattern. The results point to the stronger binding interaction of Cu²⁺ as compared to Zn²⁺ in all the binding modes, which is consistent with the available experimental data. The results show a higher complexation ability of Cu²⁺ **B** than of Zn²⁺ **A** for all of the binding modes⁶⁶. Further using AMI calculations comparative study on complexation ability with 5, 11, 17, 23-tetra-*tert*-butyl- 25, 27-bis{[4-(methoxycarbonyl)phenyl]methoxy}-2, 8, 14, 20-tetrathiacalix[4]arene towards the transition metal ions Zn²⁺ and Cu²⁺ has also been carried out⁶⁷ to better understand the characteristic host-guest interactions in novel molecular receptors and its parent compound. The complexation ability of Cu⁺² was found to be higher than that of Zn⁺².



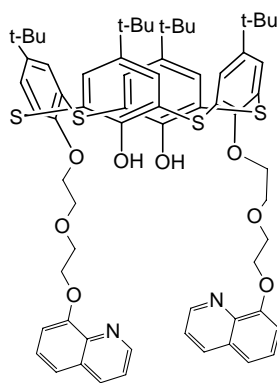
Heteroditopic receptors were synthesized by introducing amide functions at the lower rim of the thiacalix[4]arene as efficient extractants for both cations and anions due to their high stability and hydrophobicity⁶⁸. The presence of acetate functions in the opposite side and the sulphur atoms in the calix framework leads to high affinity towards K^+ and Ag^+ ions respectively. Replacement of diamide by tetraamido derivative of *p-tert* butylthiacalix[4]arene and its cone conformation has been demonstrated through transforming into the tetramethylester derivative, which is known to have a cone conformation. The ability of form complexes with alkali and alkaline earth metal ions and some heavy and transition metal ions (Ag^+ , Cd^{2+} , Pb^{2+} , Cu^{2+} and Zn^{2+}) have been assessed through liquid-liquid extraction of the corresponding picrate salts from water into dichloromethane¹⁶⁶⁻⁶⁹. Results show that sulphur atoms of thiacalixarenes led to a loss of selectivity within the alkali and the alkaline earth series and become selective for Pb^{+2} ions among heavy and transition metal ions⁶⁹.

Ag^+ ions were determined by potentiometric sensors, based on glassy carbon electrode covered with polyaniline and neutral carrier, e.g. thiacalix[4]arene containing pyridine fragments in the substituents at lower rim. The presence of thiacalixarene in the surface layer improves the reversibility and selectivity of the signal towards transition metal ions⁷⁰. The reaction of Ag^+ with thiacalixarene was

proved by extraction of the picrate complexes of transitory metals in the organic phase⁷⁰. Cesium ion-selective electrodes have been fabricated from thiacalix[4]mono and bis(crown-6) ether derivatives which show excellent potentiometric performances with Cs^+/K^+ and Cs^+/Na^+ selectivities comparable with those of the calixcrown-based sensors⁷¹. Among the thiacalix[4]bis(crown-6) ethers studied, the *tert*-butyl derivative has better selectivity for cesium than for the other alkali cations.

Thiacalix[4]crown trimmers incorporating crown-5 and crown-6 have been prepared for separation of Cs^+ and Ag^+ ions⁷². Their conformations and complexation behavior characterized by X-ray diffraction and ¹H NMR spectroscopy shows that the Cs^+ ion is encapsulated in the end-crown rings by the 1:2 complexation ratios while the Ag^+ ion is entrapped in the central thiacalix unit in 1:1 ratio. Extractabilities of the thiacalix[4]crown trimmers for Ag^+ are higher than those of conventional calix[4]crown trimmers.

The effective separation of Am from radioactive waste by a chelating ion-exchange method has been carried out using an octylphenyl-N,N-diisobutylcarbomoyl phosphine oxide (CMPO) or thiacalix[4]arene compound impregnated silica ion-exchanger⁷³. The separation of Cs and Sr can be achieved through a CMPO impregnated silica ion-exchanger. Actinoids and lanthanoids can then be eluted from the CMPO-exchanger, and the resulting solution is recovered from the CMPO-exchanger treated to separate the actinoids with a thiacalix[4]arene compound impregnated silica ion-exchanger in a weak-acid solution⁷³. Separation of actinides from lanthanides involves very difficult procedures. New ion-exchanger, thiacalix[4]arene compounds impregnated with silica ion exchanger (CAPS) or CAPS-SO₂ have been developed for separation of Am from lanthanides⁷⁴ and its efficiency has been comparable with that of Cyanex301 impregnated silica ion-exchanger.



C

A lower rim substitution of diagonal quinolin-8-yloxy pendants via oxyethylene spacer has been synthesized in one step and its coordination properties towards Ni^{2+} , Co^{2+} and Zn^{2+} ions studied by UV-vis, fluorescent spectra and ^1H NMR titration⁷⁵. The results show that **C** forms very stable complexes with the three metal ions, Moreover, anion receptors in the thiacalixarene series bearing four ureido or thioureido functions at the lower rim have been prepared⁷⁶. These compounds can bind anions via hydrogen bonding interactions and represent an ideal example of anion receptor in the thiacalixarene series.

The tetra amino derivative of thiacalix[4]arene has been synthesized and characterized to study its acid-base property in aqueous solution⁷⁷. The nitro-derivative of thiacalix[4]arene was synthesized using glacial acetic acid as regulating agent of acidity and nitric acid as nitrating agent without oxidation of the bridging sulfur. The nitro-groups were then reduced to amino-groups to get the tetra-amino derivative of thiacalix[4]arene.

Thiacalixarene derivatives bearing amide groups effectively extract gold, palladium and platinum from chloride aqueous media via an ion-exchange mechanism⁷⁸ with the thiacalixarene amide, the efficiency for gold separation was much higher than for the two other metal species and the recovery was almost complete. Moreover, thiacalixarene allows the selective extraction of Pd(II) via the

formation of a PdCl_2L_2 complex, where the metal is coordinated through S atoms. These ligands have also shown their effectiveness as carriers to transport gold and palladium from HCl solutions. Gold was selectively recovered from a mixture of Au, Pd and Pt in a supported liquid membrane system containing macrocycle thiacalix[4]arene, while palladium was transported through a plasticized polymeric membrane containing thiacalix[4]arene. Solid phase extraction systems prepared by adsorption of these ligands on activated polymeric cartridges have shown results¹⁷⁵⁻⁷⁸. Thiacalix[4]arene functionalized gold electrodes were also used to determine the optimal experimental conditions in terms of voltage and frequency⁷⁹. The present work is based on the gold electrodes modification by thiacalix[4]arene and *p-tert-butyl* thiacalix[4]arene using the thermal evaporating process. The sensitivity of the TCA-gold sensors is investigated for copper ions detection⁷⁹. The choice of the gold electrode as a substrate for thiacalix[4]arene based sensors is necessary as this material has an inert nature and presents a strong affinity against sulphur derivatives and thiol groups⁷⁹.

Increase in the binding efficiency of potassium and rubidium cations with increasing lipophilism of substituents in the thiacalixarene fragments of the heterotube is observed. This is because the more hydrophobic and bulky groups offer better protection to the metal cation from the polar methanol molecules, which in turn favors the greater stability of the complex. The comparison of the “lipophilic layer thickness” (the distance from the first atom of the substituent and the plane through the carbons most remote from the first one) shows that this parameter is greater in 1-adamantyl groups than in *tert-butyl* groups⁸⁰. Calix[4]tubes and semitubes comprising two conic calix[4]arene cores connected with alkaline linkers (see Scheme 4) have also been utilized in the preparation of ionophores displaying exceptional cesium, rubidium⁸¹ and potassium selectivities⁸²⁻⁸⁷. Synthetic path is reported⁸⁸.

In addition to the calix-crown chemistry, the reaction of *p*-*tert*-butylthiacalix[4]arene tetrahydrazide derivative in 1,3-alternate conformation with *o*-phthalaldehyde gives thiacalix[4]-1,3-2,4-aza-bis-crown in “1 + 2” condensation mode. Compared with the earlier synthetic methods for preparation of thiacalix[4]-bis-crowns, this synthetic route was simple and the yield was high. Liquid–liquid extraction showed the compound to be an excellent receptor for Zwitterionic amino acids and soft cations such as Ag⁺ and Hg²⁺⁸⁹. The extraction percentage for methionine was 78%. These extraction results indicate that the thiacalix[4]bis-crown are an effective receptors not only for metal cations, but also for bioorganic molecules, such as amino acids.

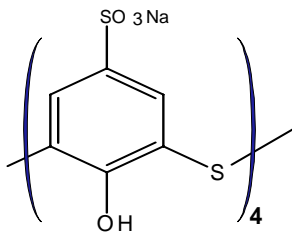
Increase in the cavity size or increase in repeat units leads to better analytical applications in thiacalixarenes. Synthesis of novel hybrid calix[6]arenes by acid-catalyzed condensation between bis(hydroxymethyl) dimer and tetramer of *p*-*tert*-butylphenol bridged by sulfur has been reported in which part of the CH₂ group of calix[6]arene is replaced by sulfur⁹⁰. In order to investigate the effect of bridging sulfur groups on the ability of calix[6]arenes as host molecules, physical properties and inclusion properties toward organic molecules were compared with those of calix[6]arene and *t*-butylcalix[6]arene. The replacement of CH₂ with sulfur has significant effect on conformational properties, strength of intramolecular hydrogen bonding, and inclusion property of calix[6]arene.

A series of new bisalixarenes consisting of two *p*-*tert*-butylcalix[4]arene units linked through their lower rims with bridging moieties containing diimine units of different aromatic or heteroaromatic dialdehydes have been reported by Kumar *et al.*⁹¹. Then complexation behavior was studied towards different metal ions (Na⁺, K⁺, Ca²⁺, Pb²⁺, and Ag⁺) and it was found that these bisalixarenes bind silver ion preferentially but with poor selectivity over the other metal ions.

The strong anti-bacterial activity of silver ion has been the subject of much interest for the preparation of bio-active materials such as deodorizing clothes, agricultural sterilizing agent, etc. Therefore, it is necessary to extract silver ion with higher accuracy in order to fulfill such requirements and also to improving the recognition ability for soft metal ions, especially for silver ion. Bhalla *et al.* replaced the conventional calix[4]arene unit of bis-calixarenes with thiacalixarenes which is an attractive host for soft metal ions⁹². The performance of thiacalix[4]arene analogs of the bis-calixarenes synthesized by using diamine as a molecular scaffold for silver ions were evaluated as a host molecules⁹². To evaluate the binding ability of bithiacalixarenes toward different metal ions, two-phase solvent extraction of metal picrates (Na⁺, K⁺, Cs⁺, and Ag⁺) was carried out. The bithiacalixarenes quantitatively and selectively extract silver ions from the aqueous phase to the organic phase, while with the corresponding conventional bis-calixarenes the extraction was neither selective or quantitative⁹².

Thia-calixarenes have extensive utility in the field of analytical chemistry. Most of these compounds are insoluble in water. Some thiacalixarenes which are soluble in water having sulfonato groups like *p*-sulfonato thiacalixarene and tetra-sulfonatomethylated calix[4]resorcinarene which have been used as chelating agents in cloud point extraction of La(III), Gd(III) and Yb(III) ions with Triton X-100 as non-ionic surfactant⁹³. The study indicates that both complexation ability and structure of calixarenes, govern the extraction efficiency of lanthanides. Thiacalixarene **D** form 1:1 lanthanide complex with similar stability in aqueous media but exhibit different extractability when used as chelating agent in cloud point extraction. Inclusion complexes of two sulfonated calixarene derivatives with C₆₀ fullerene has also been investigated by Kunsagimate *et al.*⁹⁴ both calixarene derivatives show higher photoluminescence intensity in the presence of C₆₀ fullerene.

No considerable emission of C₆₀ fullerene was observed in the absence of calixarenes and the spectral changes were induced by a weak interaction between the calixarene hosts and the C₆₀ guest⁹⁴.



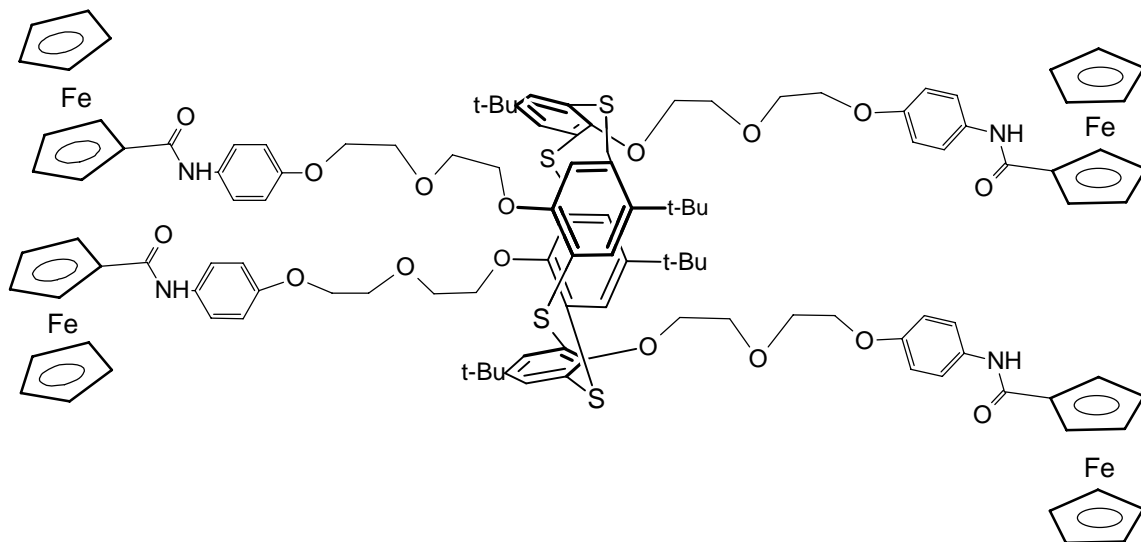
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Thiacalix[4]arene-tetrasulfonate salt have been obtained by the *ipso*-sulfonation of *p-tert*-butylthiacalix[4]arene⁹⁵

The electrochemical study of thiacalix[4]arenes, *p-tert*-butylthiacalix[4]arene and their complexation behavior in the presence of various metal cations has been carried out in order to demonstrate the possibility of voltammetric recognition of metal ions⁹⁶. TCA in pH 8 solution produced different responses to transition metal ions, however, the presence of even high concentration of alkali metal ions and alkaline earth metal ions led only to negligible changes with respect to TCA. Electrochemical properties of thiacalix[4]arenes (TCA) with electro-active phenol functional groups were also investigated through voltammetry and analytical applications using Cd²⁺ ions⁹⁶. Result shows that the anodic peak current of phenol in the presence of Cd²⁺ ion increased as the concentration of the Cd²⁺ ion increased.

Volta metric behavior of the novel ditopic ferrocene-based thiacalix[4]arene receptor **E** was investigated toward the cationic and anionic species to evaluate its potential electrochemical sensing capabilities⁹⁷. This receptor was synthesised to develop new redox-active receptors capable of recognition and sensing of ionic or molecular guests which contains four identical polyether linked ferrocene amide

moieties and exhibits a remarkable selectivity for electrochemical sensing of Eu(III) and dihydrogen phosphate ions, respectively. The present work substantially extends the applications of thiacalixarenes as molecular scaffolds.



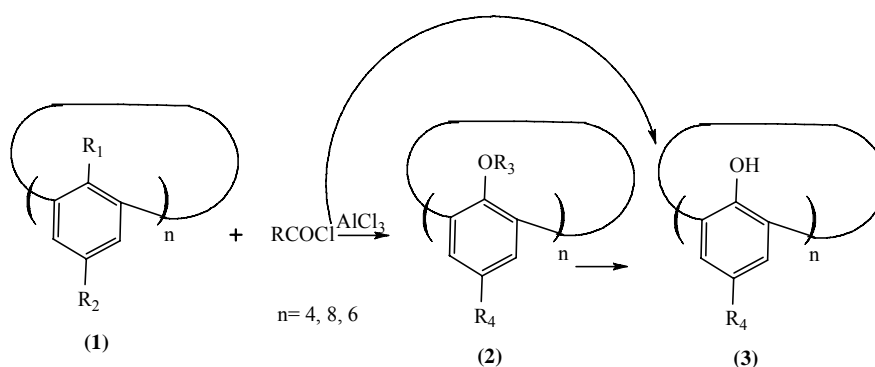
E

II. MODIFIED CALIXARENES

There are two obvious places for modification of calixarenes, such as phenolic hydroxyl groups and *p*-positions. Methylene bridges may be substituted with aromatic system of phenolic units as a whole or may lead to replacement of OH-function by other groups. Functional groups introduced in a first step may be further modified by subsequent reactions including migration.

Usually upper rim substitution of calixarene is carried out by de-*t*-butylation of *p*-*tert*-butyl group followed by subsequent reaction. Substitution of bromination⁹⁸ is reported. Similarly, *p*-bromination of calix[4]arenemethylether⁹⁹ and bromination of tetra-methoxycalix[4]arene is also reported¹⁰⁰. *Ips*o-bromination¹⁰¹ has been carried out under a variety of reaction parameters and optimized conditions give *p*-bromocalixarenes and methylene bridge brominated calix[*n*]arene directly¹⁰¹. Single step, one-pot procedure is also given (Scheme 1) for conversion of *p*-*tert*-

butylcalix[*n*]arenes (Table I) to their *p*-acyl derivatives thus (2) and (3) have been prepared¹⁰².



Scheme 1.

Table: I Substitutions for *p*-acyl derivatives prepared from *p*-*t*-butylcalixarene

R ₁	R ₂	R ₃	R ₄ (3)	R ₄ (4)
OH	H	CO-C ₆ H ₅	CO-C ₆ H ₅	CO-C ₆ H ₅
OH	<i>t</i> -Bu	CO-C(CH ₃) ₃	CO-C(CH ₃) ₃	CO-C(CH ₃) ₃
OMe	<i>t</i> -Bu	CO-CH ₃	<i>t</i> -Bu	CO-4- NO ₂ C ₆ H ₄
		CO-CH ₃ CH ₂	<i>t</i> -Bu	

*Ips*o-substitution is also possible with more than one substitution (Table II)¹⁰³.

Calixarenes having larger cavity size like calix[8]arenes can also be *ip*so substituted¹⁰⁴.

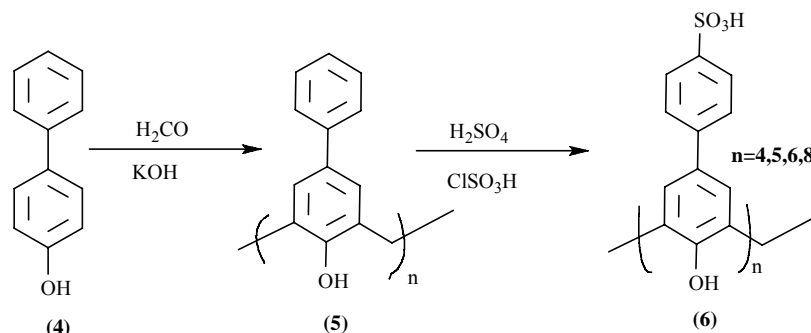
Table: II *ipso*-substitution group for calix[4]arene

Compound	R ₁	R ₂	R ₃	R ₄
1	H	H	H	H
2	H	H	H	Me
3	H	COMe	H	Me
4	H	H	H	COMe
5	Me	COMe	H	H
6	Me	H	H	COMe
7	Me	H	H	CoMe

Calixarenes of varying cavity size can form variety of host-guest type of inclusion complexes similar to cyclodextrins. However, calixarene host molecules have a unique composition that include benzene groups, which provide π - π interaction and hydroxyl groups for hydrogen bonding which is generally water insoluble. Shinkai *et al.* have synthesized water-soluble calixarenes having sulfonate groups¹⁰⁵. The calixarene cavity is capable for molecular recognition in solution, which has an application in the remediation of contaminated groundwater and industrial effluents.

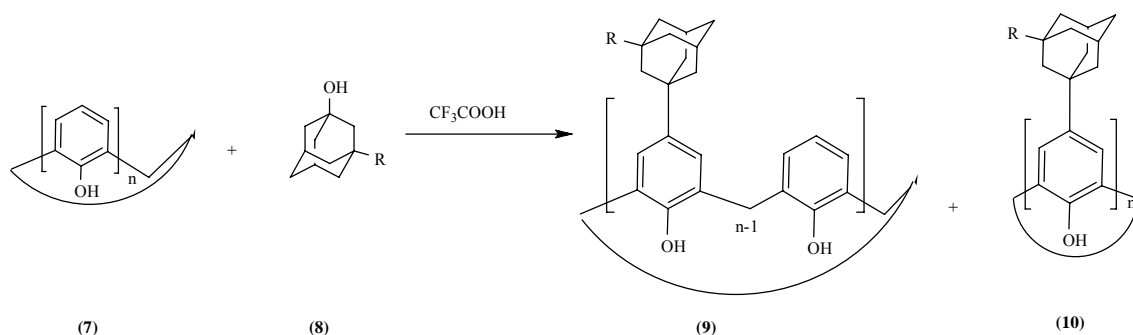
Sasaki *et al.* has carried out intercalation of water-soluble *p*-sulfonated calix[4]arene (CS₄) in interlayer of Mg-Al and Zn-Al (Lactate dehydrogenase) (M₂+/Al = 3) by co-precipitation method¹⁰⁶. Some of the important findings of these studies are the adsorption ability for benzyl alcohol and *p*-nitrophenol (NP) in aqueous solutions which are also larger in Zn-Al/CS₄/LDH than in Mg-Al/CS₄/LDH that is because of effective use of the parallel arranged cavity only in Zn-Al/CS₄/LDH. CS₄/LDHs have considerable possibility as new organic-inorganic hybrid adsorbents for many organic molecules.

Makha and Rasston¹⁰⁷ have synthesized water soluble calixarenes using *p*-phenyl calix[*n*]arene and sulfonate derivatives (Scheme 2), which have exciting possibilities as a phase transfer catalyst in transport processes and more.



Scheme 2.

To increase the size of a hydrophobic cavity calix[*n*]arenes (Scheme 3) consist of different bulky groups. Functional groups present in adamantane fragment (9) and (10) should provide possibility for further modification and conformational organization of the molecule¹⁰⁸⁻¹¹⁰.

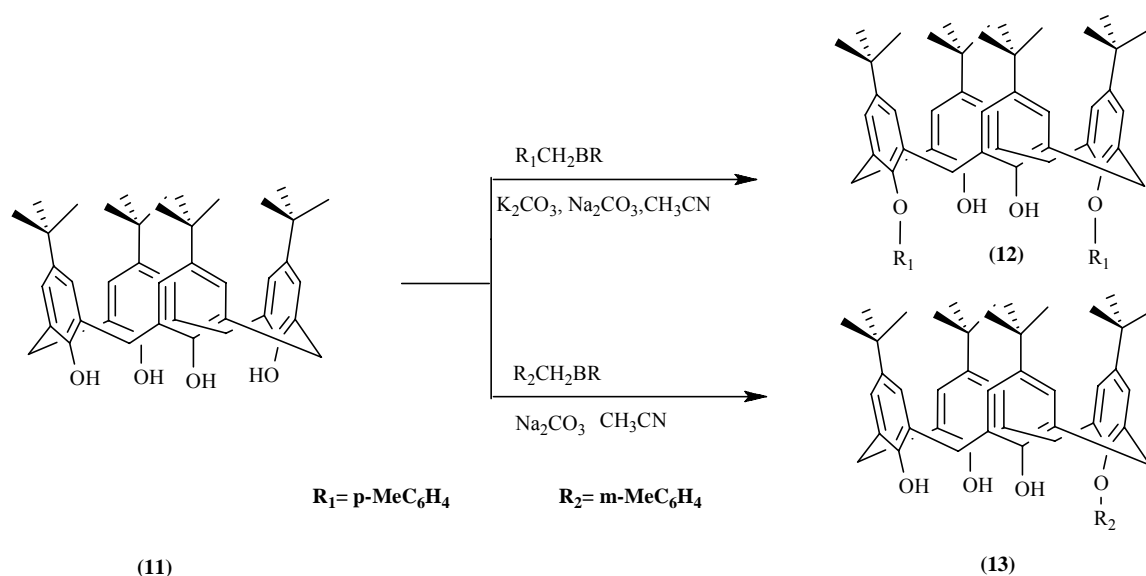


Scheme 3.

Self-assembly of tetradentate ligand 5,5-bipyrimidine with *c*-methyl calix[4]resorcinarene is reported^{111,112}. It modulates volume and periphery of cavity in a predictable fashion by changing size, flexibility and composition of spacer between pyrimidyl units.

Introduction of bulky substituents as *m*-methyl benzyl groups incorporate and remove protective groups in synthesis of calixarenes with three different substituents in the molecule. In presence of sodium and potassium carbonates reaction of

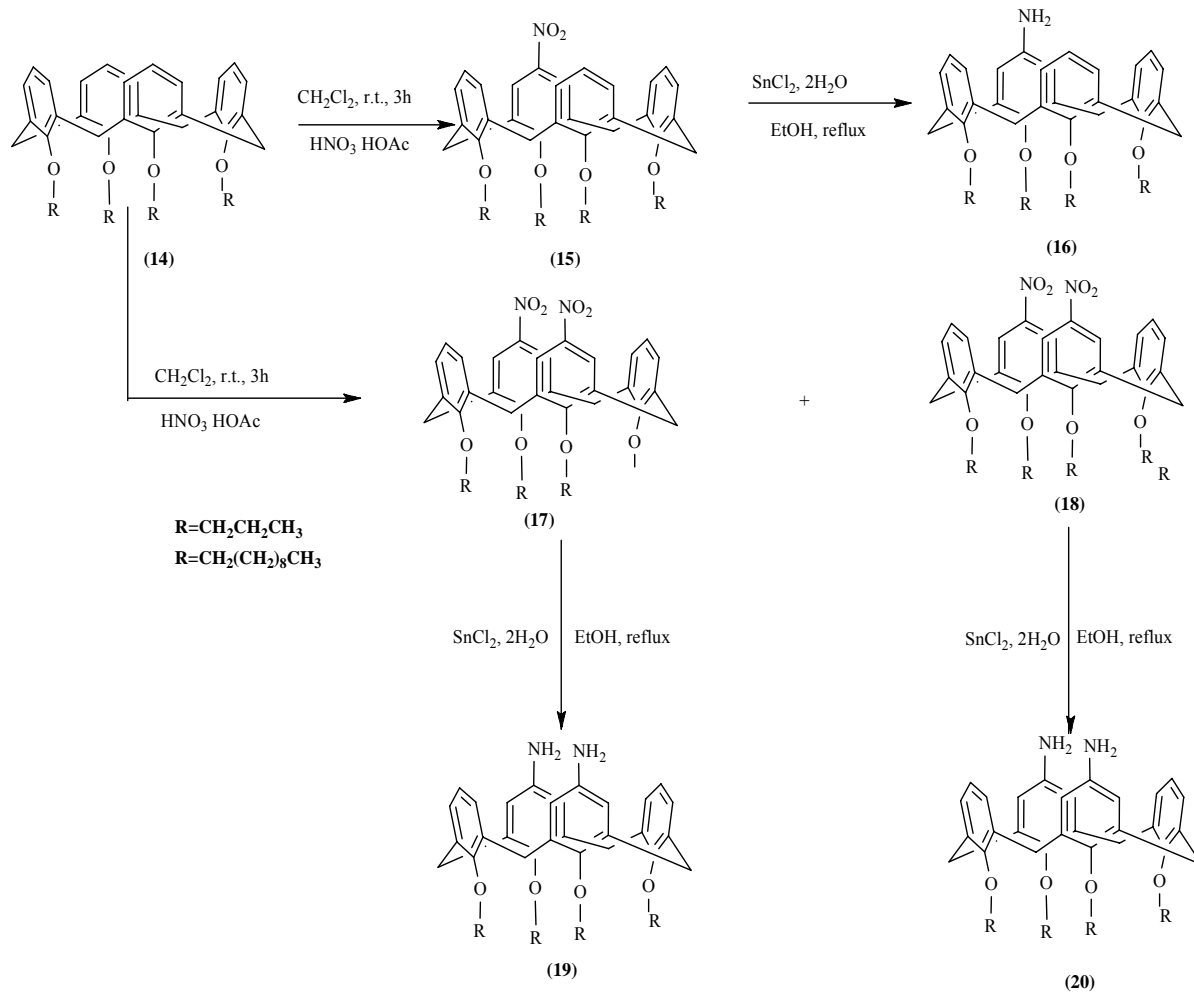
calixarene with *p* and *m*-methyl benzyl bromides gives compounds **(12)** and **(13)** that affect composition, current conformations, and yield of products (Scheme 4)¹¹³⁻¹¹⁶.



Scheme 4.

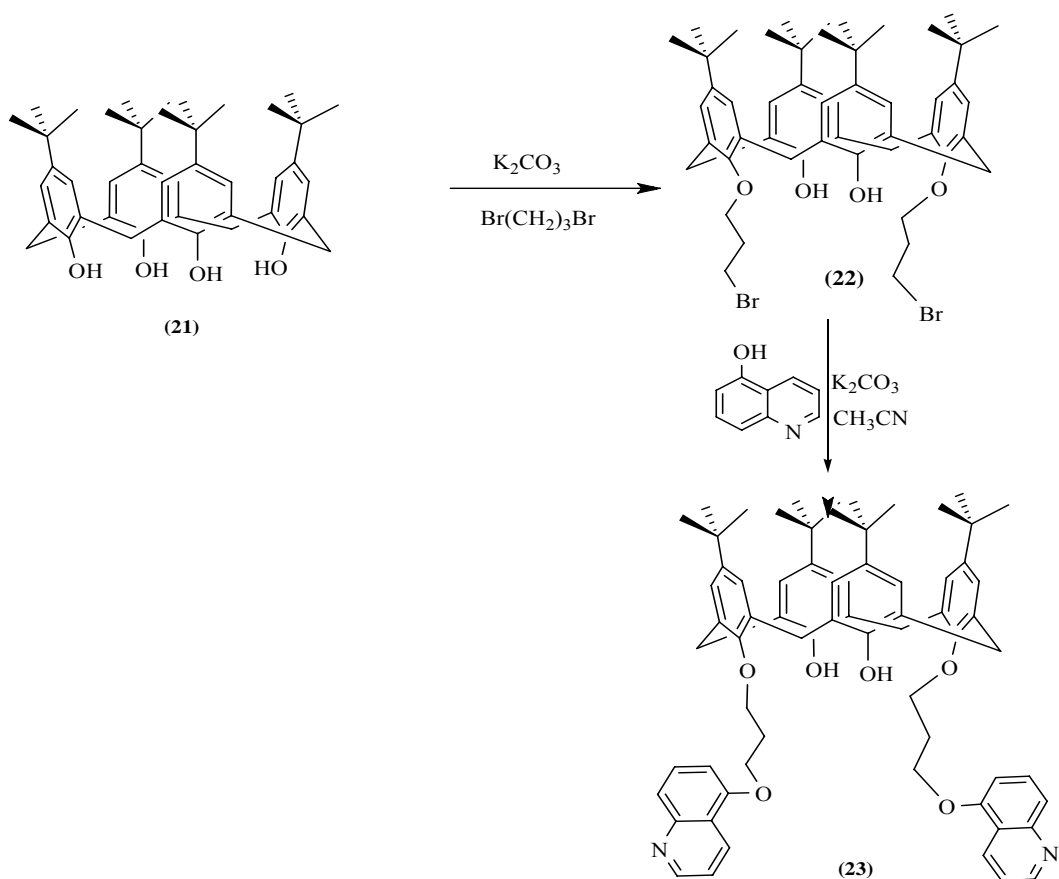
Mono- and bis-nucleoside base **(19)** and **(20)** derived calix[4]arene receptors provide chemical and biological insight into fundamental base-pairing processes.

Means of constructing complex is given in Scheme 5¹¹⁷.



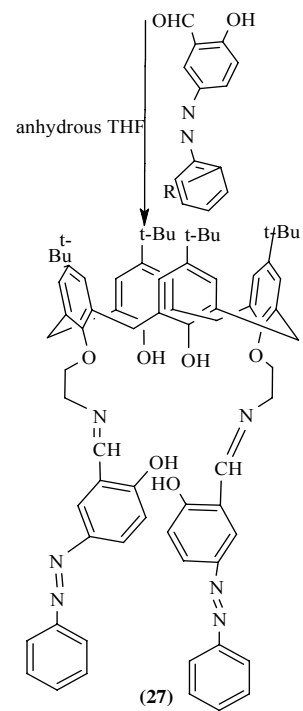
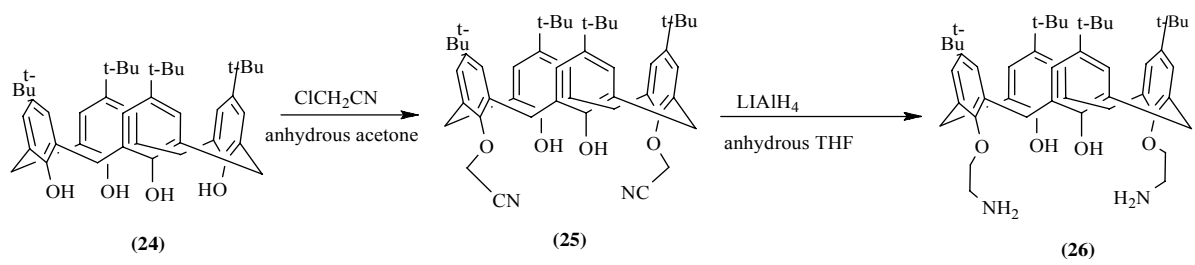
Scheme 5.

Novel bis(8-hydroxyquinoline)calix[4]arene (**23**) has been prepared according to Scheme 6. It is a versatile building block of supramolecular chemistry. This ligand is specially designed for photo physical applications in metallo-supramolecular chemistry¹¹⁸⁻¹²⁰.

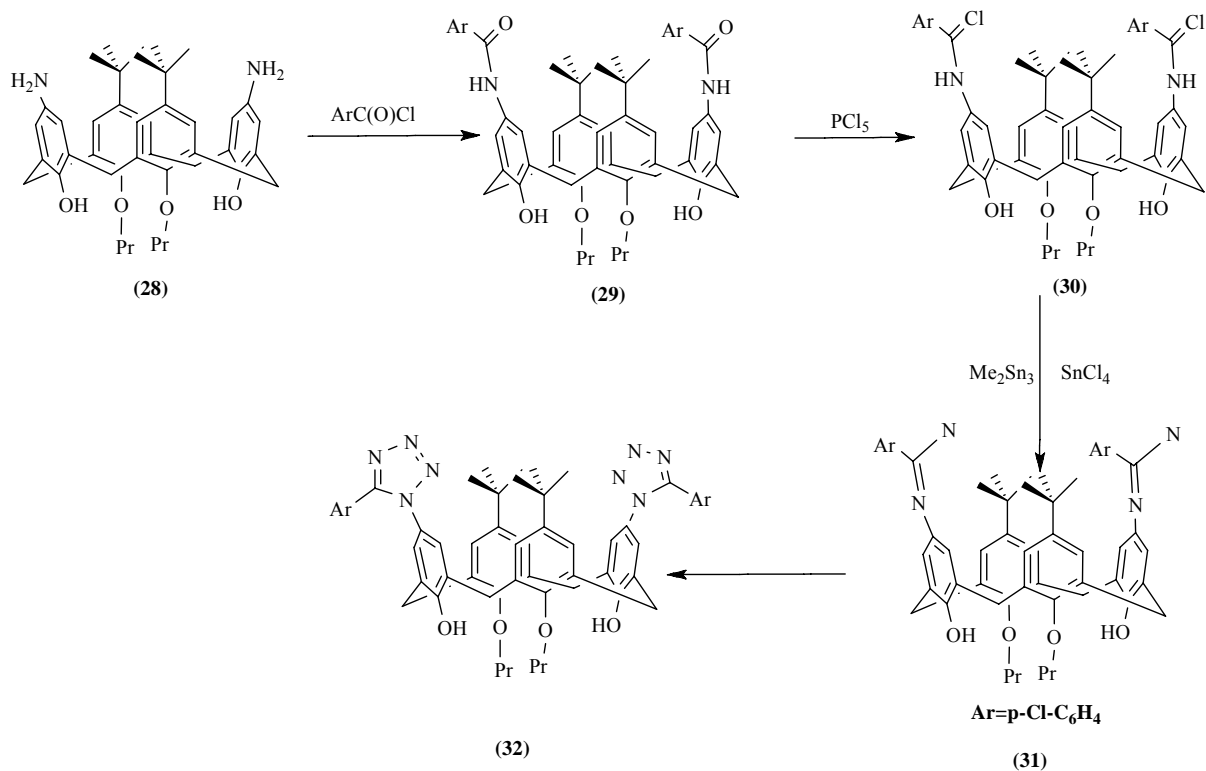


Scheme 6.

Synthesis of bis(azo-phenol)calix[4]arenes (27) possessing multiple chromogenic donors have been prepared by Liu *et al.*(Scheme 7)¹²¹. It is useful for alkali metal ions Na^+ , K^+ , Rb^+ and Cs^+ . Bis and tetrakis-tetrazole derivatives of calix[4]arene (32) have ability to bind cations of transition metals (Scheme 8). Result of structural investigation of macrocycle and its complex with palladium dichloride is also reported¹²²⁻¹²⁴.

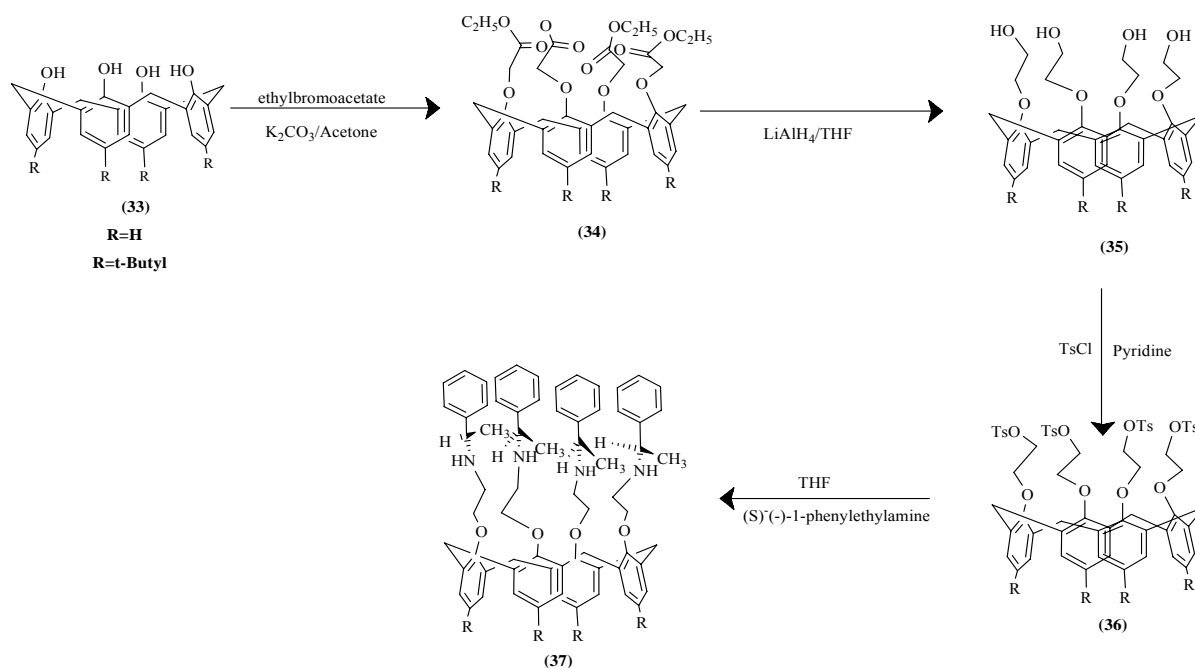


THF: Tetrahydrofuran
Scheme 7.



Scheme 8.

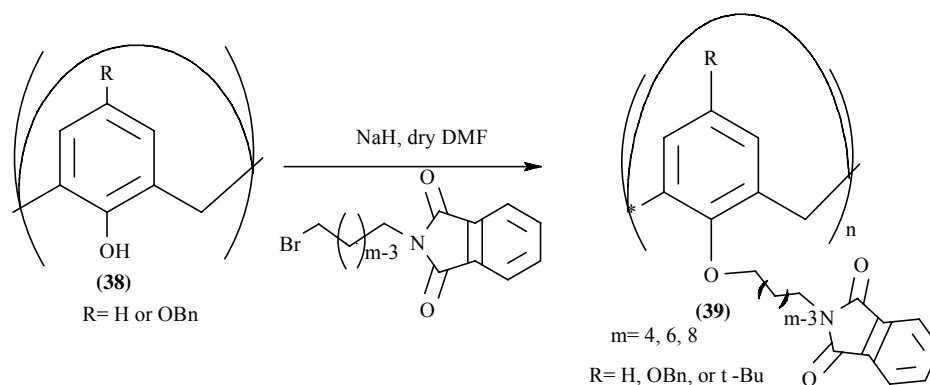
Separation of amino acids is a key technology for downstream processing in bio-industrial complex. To know amino acid extraction ability of a cyclic ligand, Tabaksi *et al*¹²⁵. have carried out a reaction of *p*-tert-butylcalix[4]arene and *p-h*-calix[4]arene with (S)-(-)-1-phenylethylamine (**37**) (Scheme 9). It forms useful host molecule for quantitative extraction α -amino acid methyl esters and α -phenylethylamines in a liquid–liquid extraction system.



THF: Tetrahydrofuran

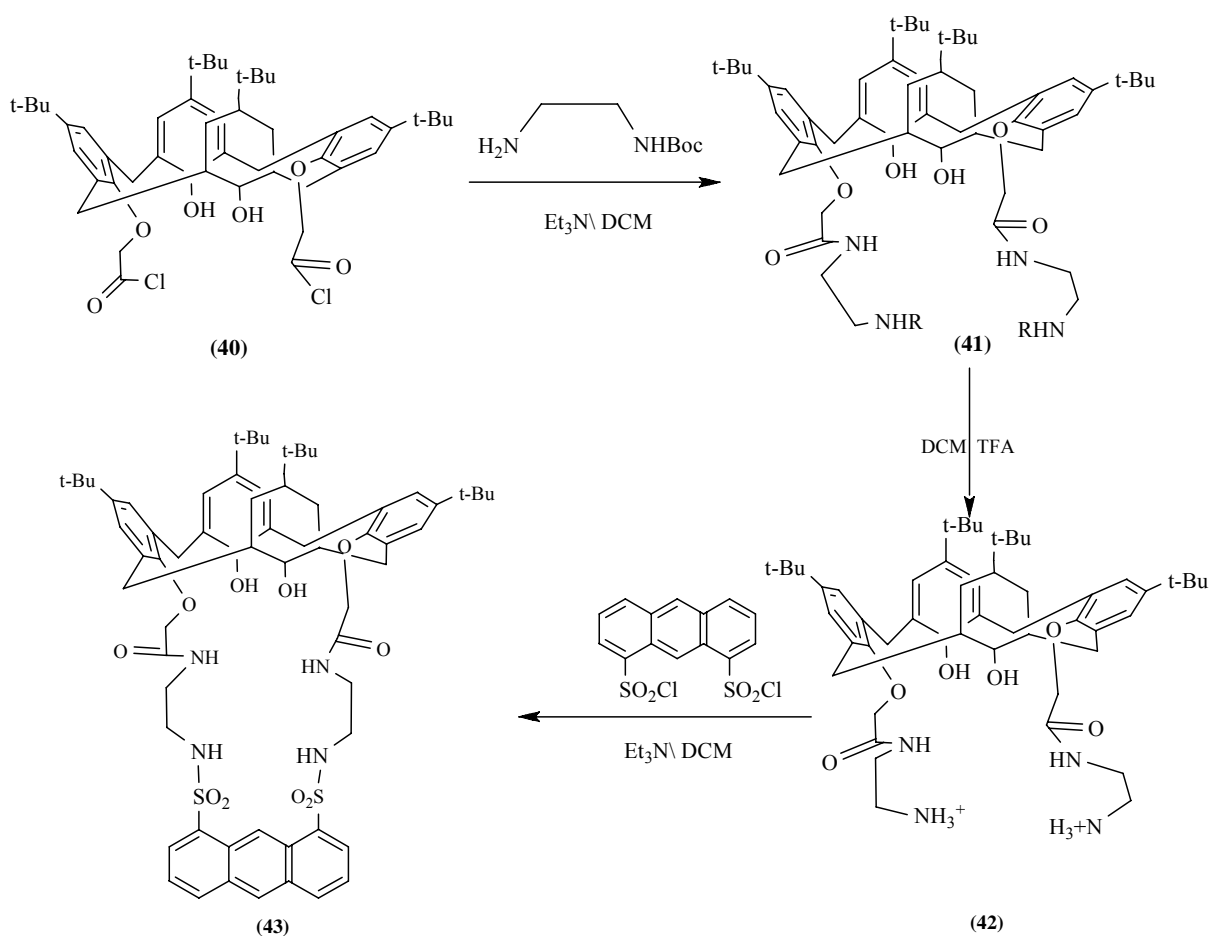
Scheme 9.

Specified applications of calixarenes can be possible by substitution of selected groups either on upper or lower rim. Several picolinamide binding groups at upper or lower rim of calix[*n*]arenes (**39**) (*n* = 4, 6, 8) have been synthesized for extraction of actinides (Scheme 10)¹²⁶. Fluorescence chemosensors, calix[4]arene containing tetraamide derivative (**43**) (Scheme 11)¹²⁷, exhibit high selectivity for H₂PO₄⁻ over a wide range of anions, selectivity for H₂PO₄⁻ is more than 2700-fold higher than for F⁻.



DMF: Dimethyl formamide

Scheme 10.

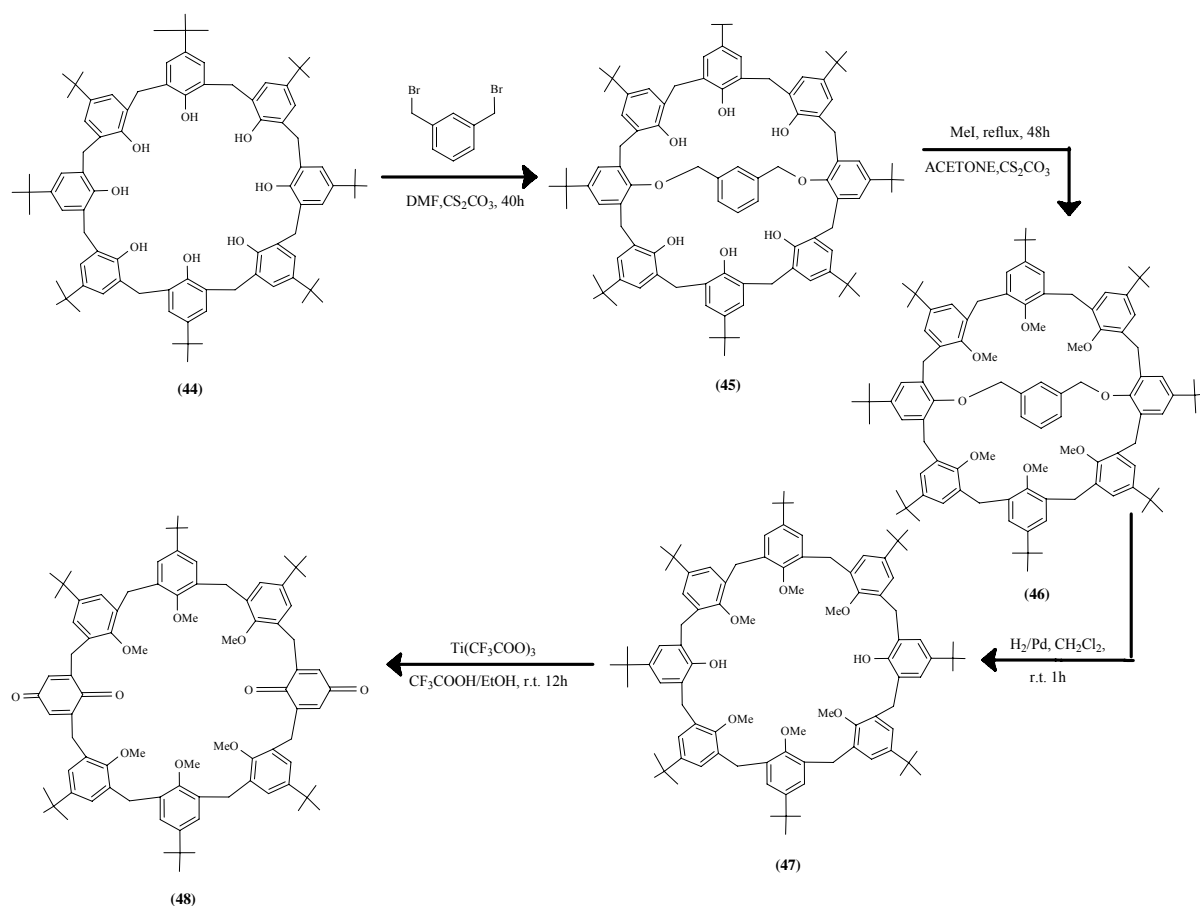


DCM: Dichloromethane TFA: Trifluoroacetic acid

Scheme 11.

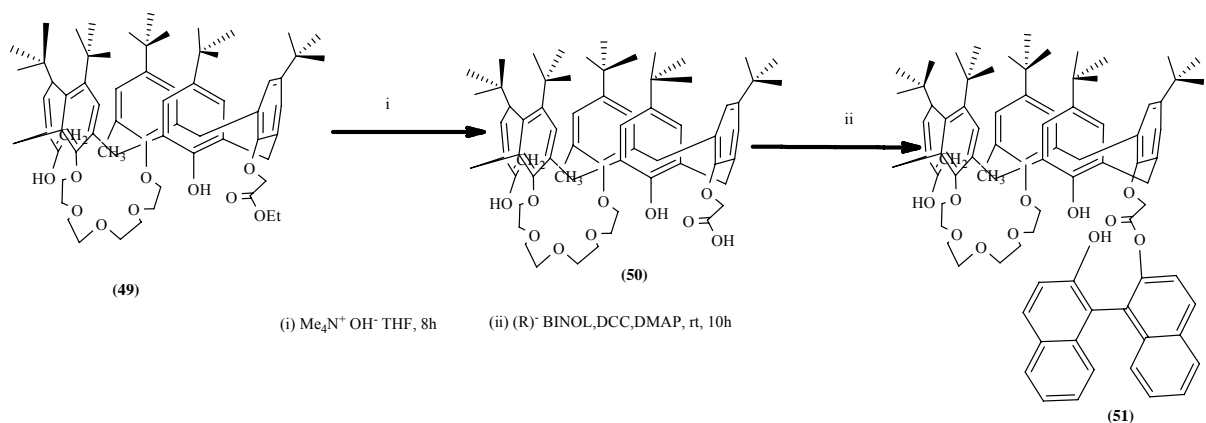
Fluorescence-labeled calix[4]arene substituted with peptides serve as a useful platform to produce artificial receptors using peptides and various types of other building blocks¹²⁸. Upper rim, c-linked and cbz-protected cone calix[4]arene bis-1-

alanyl derivative and have been synthesized to prepare self-assembled nanotubes in the solid state through a two-dimensional network of hydrogen bonds between the amide chains of adjacent conformers¹²⁹. A new type of inherently chiral calix[5]arene has been obtained from significant inherently chiral calix[5]arene derivatives using (R)-BINOL and their racemates (Scheme 13)¹³⁰⁻¹³². Calix[8]quinone derivative (**48**) has also been synthesized in Scheme 12 through a protection-deprotection procedure for the same purpose¹³³.



DMF: Dimethyl formamide
MeI: Methyl iodide

Scheme 12.

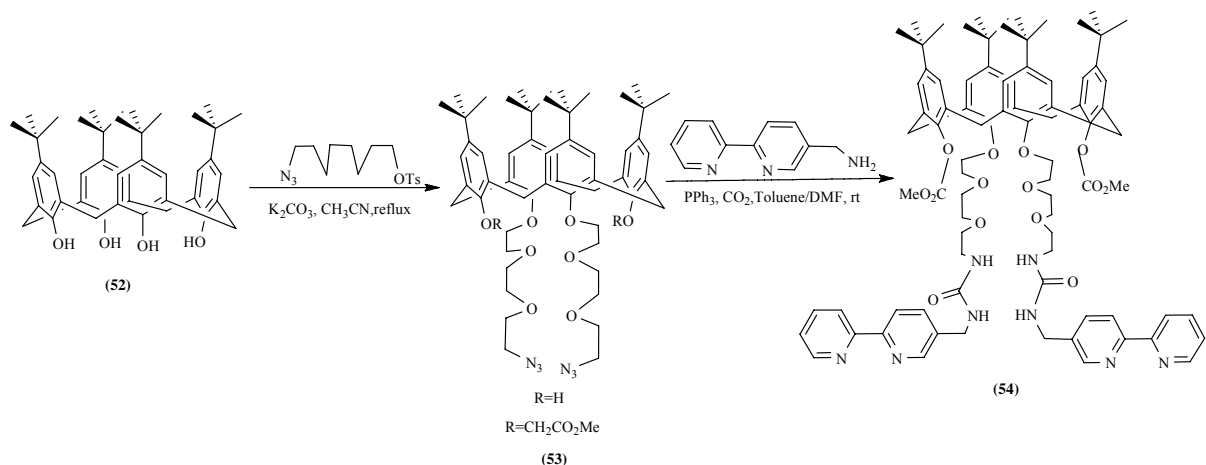


DCC: Dicyclohexyl carbodiimide

DMAP: 4-Dimethylaminopyridine

Scheme 13.

Two polyether moieties, two urea sites, and two bipyridine units containing novel multi-responsive host (**54**) has been synthesized and its ion binding sites are arranged on calix[4]arene skeleton¹³⁴. Compound (**54**) recognizes Na^+ and Ag^+ simultaneously as well as quantitatively and captures an anionic guest. The ability of (**54**) to recognize anions including CF_3SO_3^- and BF_4^- remarkably increases using Na^+ and Ag^+ .

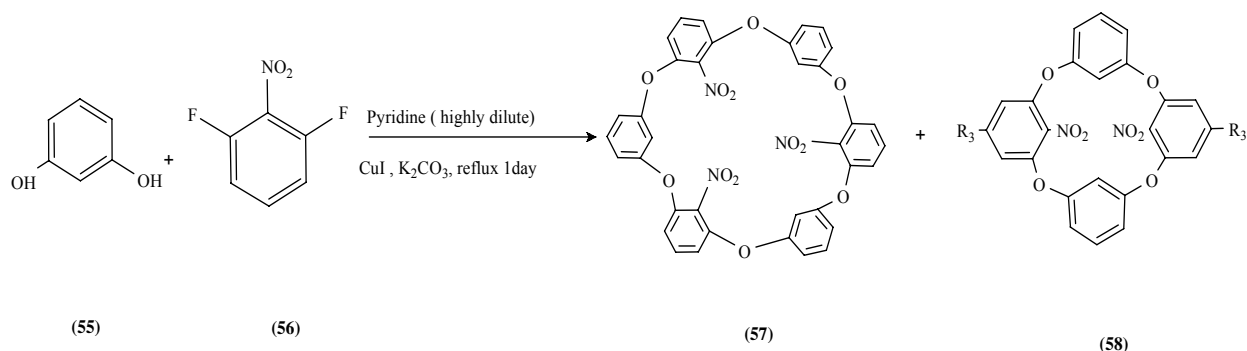


DMF: Dimethyl formamide

Scheme 14.

Yang *et al.*¹³⁵ and Tilki *et al.*¹³⁶ have synthesized oxo-calixarenes (**57**), (**58**) (Scheme 15), which are having unique applications in molecular recognition studies and for enhancement of Ag^+ and Hg^+ ion selectivity by minimizing side arm effect.

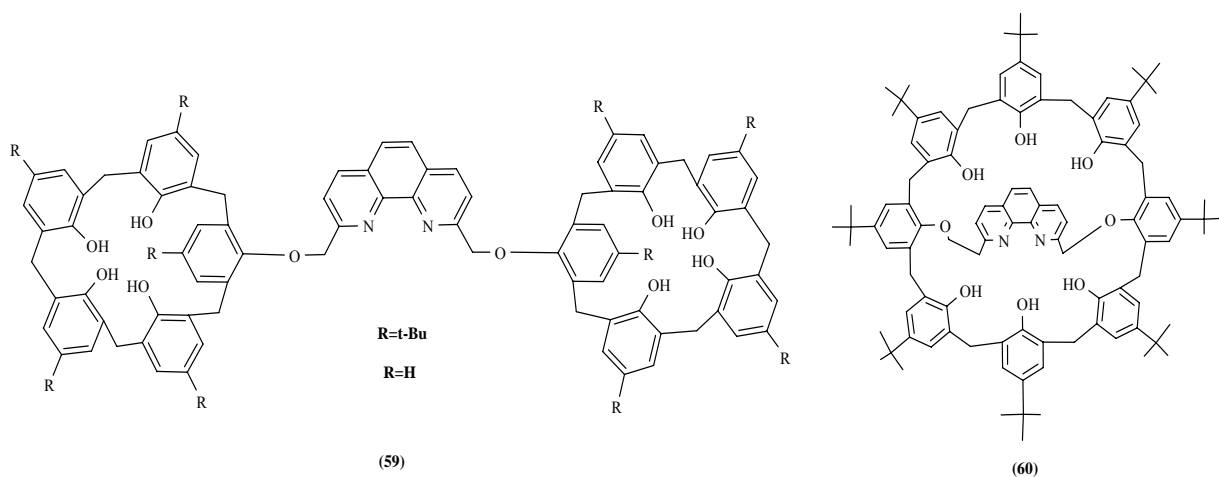
However, extraction results of bisazocalix[4]arenes show no selectivity toward heavy metal ions but effect of bis-structure on color and selectivity of bisazocalix[4]arenes have been discussed, their dyeing behavior, performance on solvent and framework effect are assessed¹³⁶⁻¹³⁸.



Scheme 15.

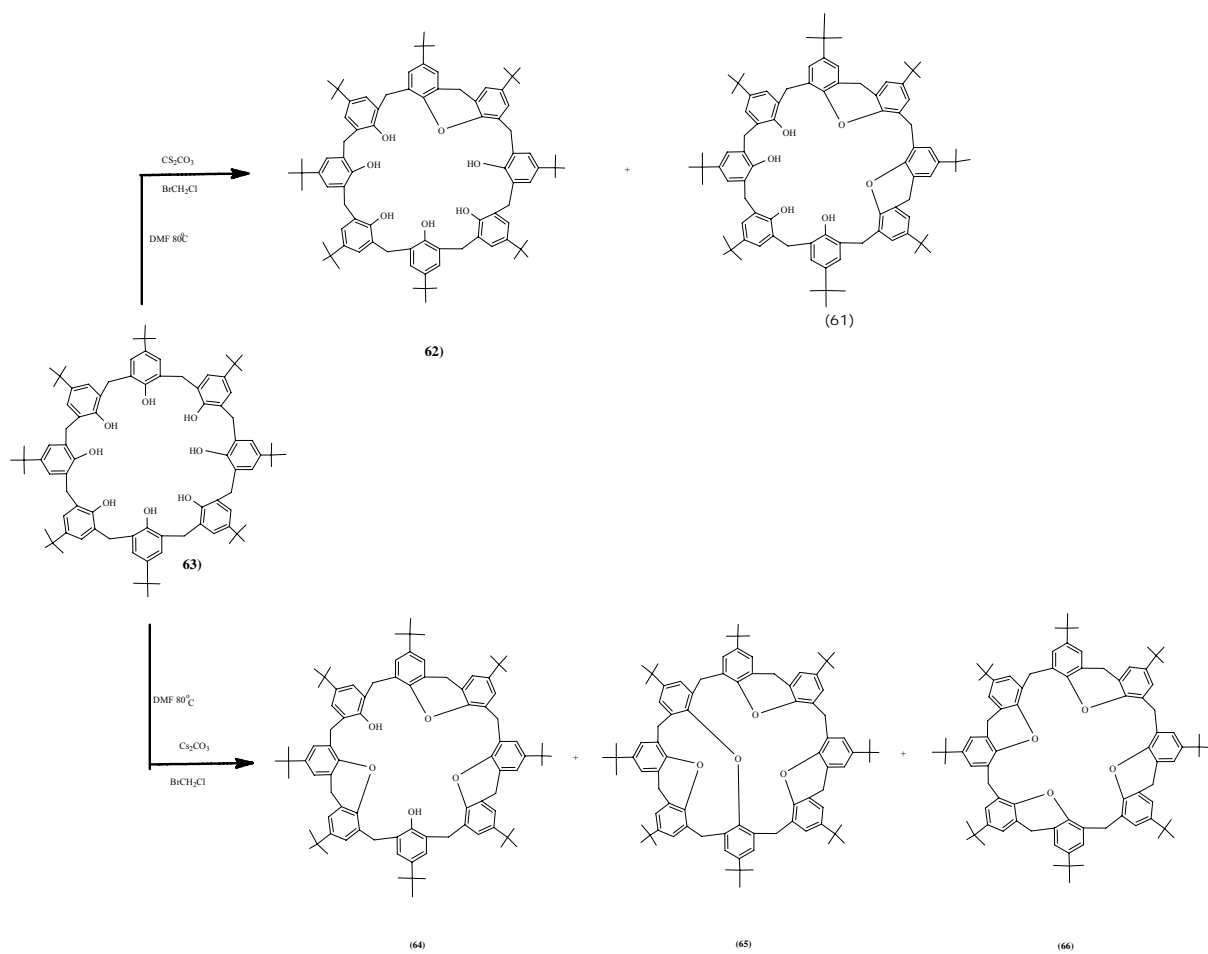
III. BRIDGED CALIXARENES

Remarkable regio-selectivities have been observed in bridging reactions of calixarenes. If a bridge contains functional groups like S, N, O, then it is easy to get sterically shielded reagents. Size of macrocycles affects selectivity towards metal ions. Bigger cavity size calixarenes are more selective to heavy metal ions other calixarenes. Calix[5]arene and calix[8]arene react with bis(bromomethyl)-substituted heterocycles such as 1,10-phenanthroline to give [1+1] condensation products (60) and [2+1] dicalixarenes (59). Resulting heterocycles are selective ligand for copper(I) ions and also show remarkable synthetic selectivity¹³⁹⁻¹⁴¹.

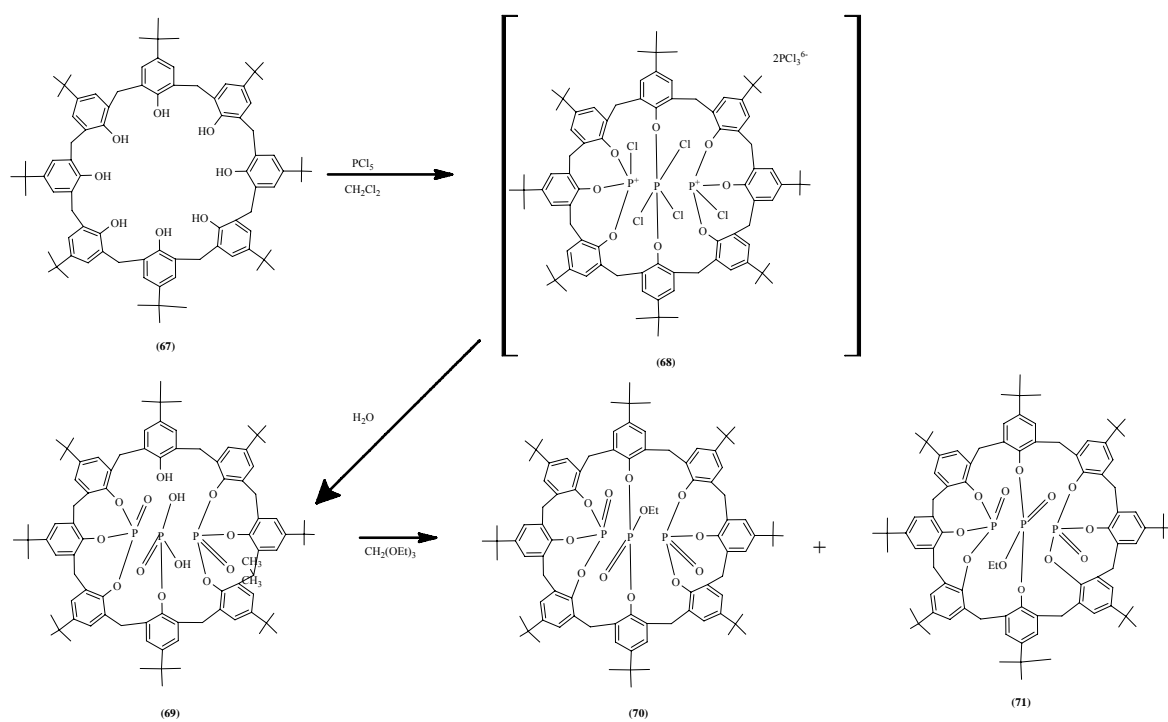


Above compounds due to bulky group inside cavity could not be much elongated but elongation of calix[8]arenes could be possible by bridging such calixarenes with ethers, phosphoryls and aza groups. Depending on length and nature of bridges, they possess better encapsulating properties toward alkali metal ions, Rare earths and heavy metal ions. Such calixarenes have been prepared from *p-tert*-butylcalix[8]arenes and using two step alkylation procedure¹⁴²⁻¹⁴⁷.

Mono to tetra-dioxamethylene bridged calix[8]arene derivatives¹⁴⁸ (**64**), (**65**), (**66**) have been synthesized (Scheme 16) and *p-tert*-butylcalix[8]arene (**67**) with 5 equiv. of PCl_5 in CH_2Cl_2 gives compound (**68**) whose subsequent hydrolysis gives compound (**69**) (Scheme 17)¹⁴⁹.

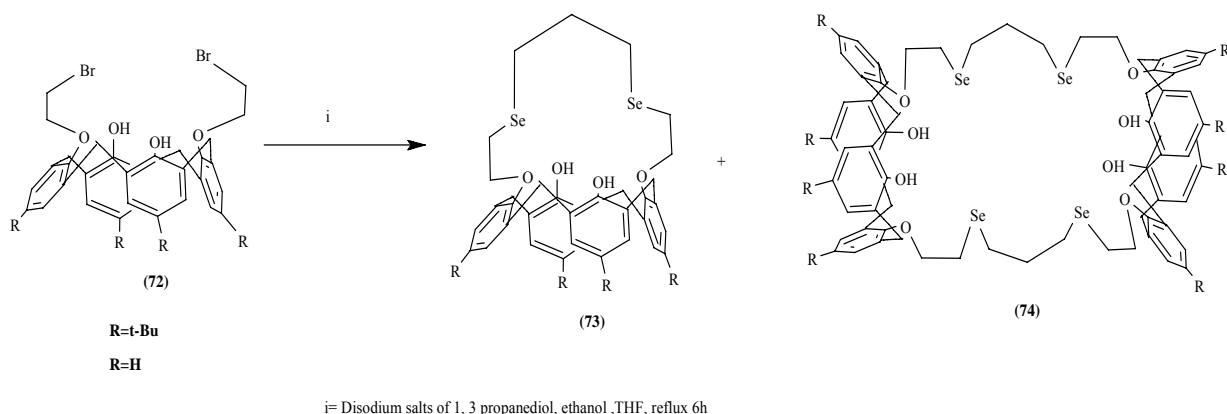


DMF: Dimethyl formamide
Scheme 16.



Scheme 17.

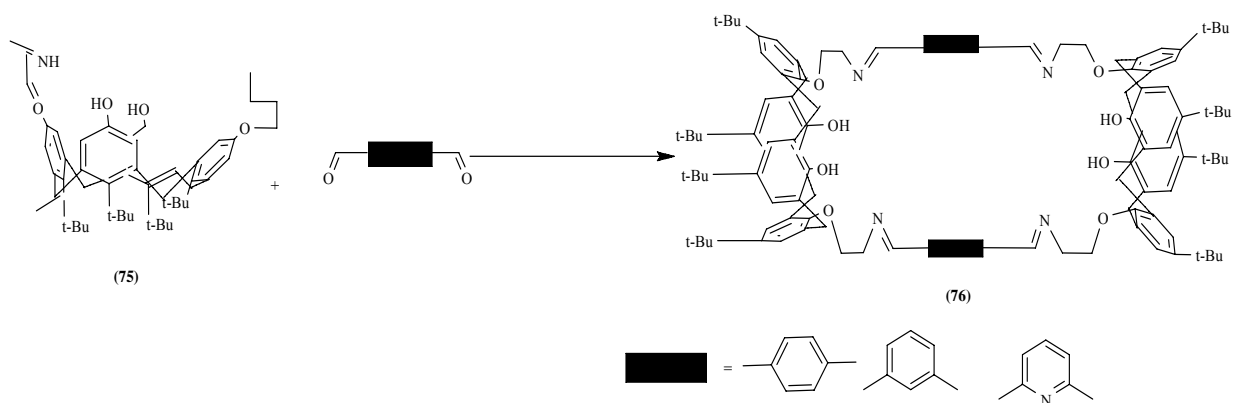
Series of tweezer-like calix[4]arene derivatives containing sulfur, nitrogen and oxygen atoms exhibit a good Ag^+ selectivity against interfering ions. These results encourage to investigate some novel ionophores containing other soft donors such as selenium. With this consideration, Zeng *et al.* have been synthesized two calix[4](diseleno)crown ethers (**74**) from compound (**72**) and (**73**) (Scheme 18) ¹⁵⁰⁻¹⁵².



THF: Tetrahydrofuran

Scheme 18.

Selenium schiff base¹⁵⁴ and hydroxamic acid¹⁵³ containing bis-calixarenes are also versatile compounds in calixarene chemistry as these are useful to show silver-ion selectivity by two-phase extraction and transportation. Bis-calix[4]arene (**76**) forms silver-selective pvc membrane due to electrostatic interaction between metal ion and aza crown cavity composed of oxygen and nitrogen atoms as donors (Scheme 19) ¹⁵⁴.

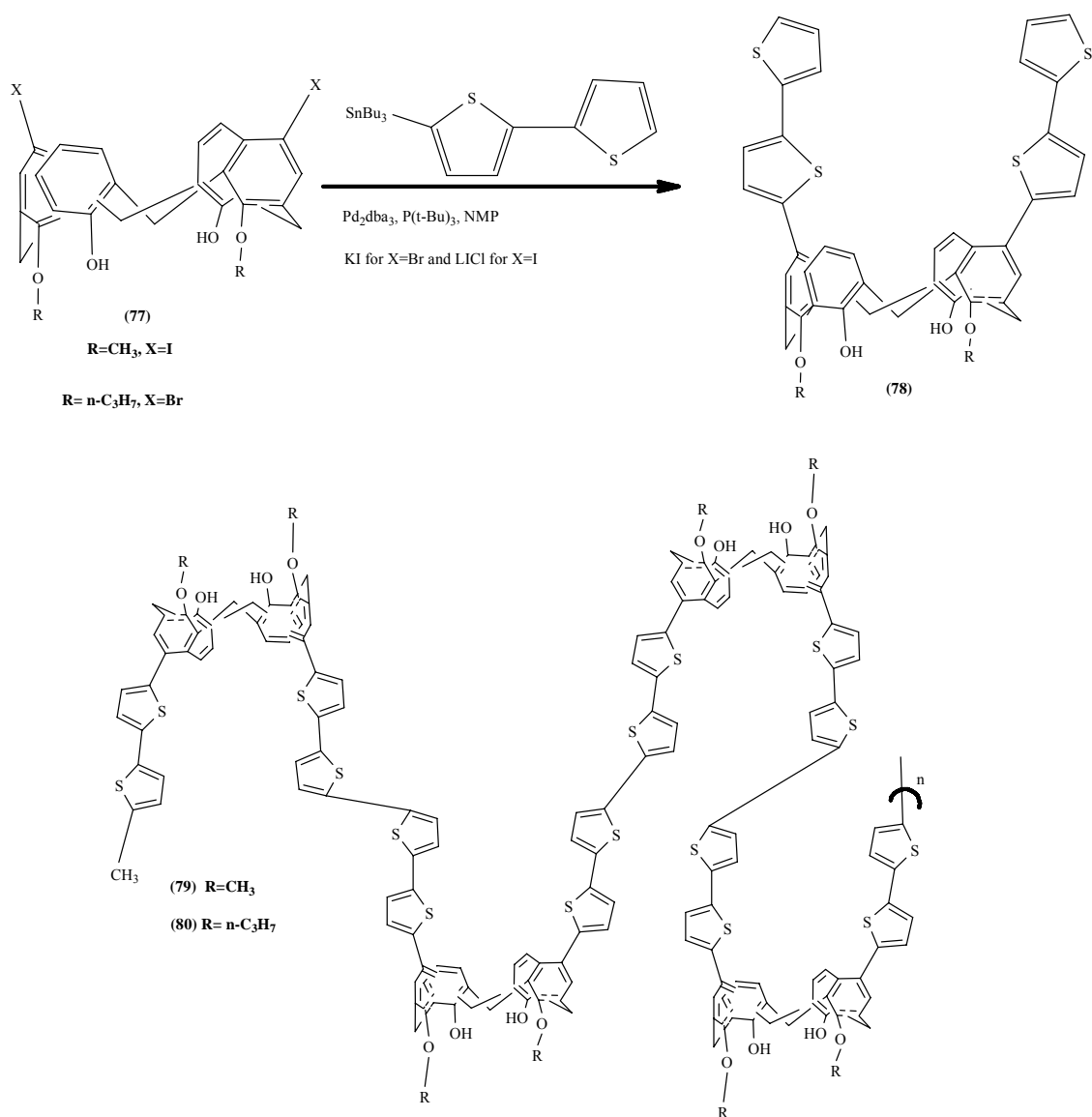


Scheme 19.

IV. POLYMERIC CALIXARENES

A variety of polymer supported calixarenes have variety of applications, Polyethyleneimine supported calix[6]arenes can extract uranium from seawater¹⁵⁵, polyacryloyl chloride and chloromethyl polystyrene supported calix[4]arenes have been used to extract iron¹⁵⁶ and lead¹⁵⁷, methacrylate¹⁵⁸ acrylonitrile and styrene¹⁵⁹ derived calix[4]arenes have been polymerized to make calixarene oligomers. Because of such a wide extraction and analytical ability, use of polymer supported calixarenes are increasing.

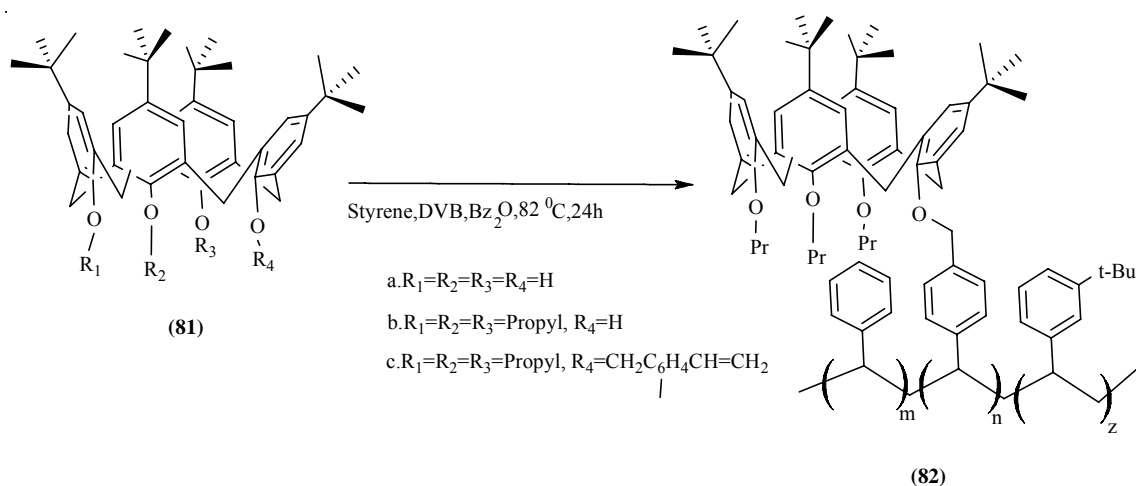
Proton-doped segmented polymers Poly(**79**) and Poly(**80**) are based upon a calix[4]arene scaffold increases conductivity of these calixarene polymers(Scheme 20)¹⁶⁰. These active compounds are attractive candidates for design of sensing and actuating materials¹⁶¹.



NMP: N-methylpyrrolidine

Scheme 20.

Utility of calix[4]arenes for phase transfer reactions, adsorbents or for fabricating membranes and sensors, copolymer and homopolymer containing calix[4]arene moieties on polymer backbone were successfully synthesized from monomer and styrene¹⁶². Both polymers show good selectivity towards Hg^+ ion. In a related study¹⁶³, radical polymerization of styrene has been carried out in the presence of a novel calix[4]arene derivative bearing two distal benzyl–vinyl groups in the lower rim. Such terpolymer (**82**) exhibits good thermal stability and good yield (Scheme 21)¹⁶⁴.



DVB: Divinylbutyl
Scheme 21.

Nitrile functionality at lower rim of calix[4]arenes that have been synthesized via nucleophilic substitution reactions have an effective binding character for particular set of cations and can be useful for laboratory, clinical, environmental, and industrial process analysis¹⁶⁵.

A novel benzyl-terminated dendron based sol-gel coating has been developed for Capillary micro extraction. Characteristic branched design of dendron makes them structurally superior extraction media compared to their traditional linear polymeric counterparts¹⁶⁶. Other higher molecular weight moieties that are also useful for many specialized applications like new polymer-supported calix[6]arene hydroxamic acid have been synthesized¹⁶⁷. Resin was used for chromatographic separation of U (VI), Th (IV) and Ce (IV).

Versatile starting materials for synthesis of polymerizable calixarene derivatives (**85a-c**) have been synthesized for extraction of cations as well as for anions. (Table III, (Scheme 22)). Depending on oxidative stability it is observed that ionophore (**95a**) is selective for Hg²⁺, whereas ionophores (**85b**) and (**85c**) are selective for both Cd²⁺ and Hg²⁺¹⁶⁸.

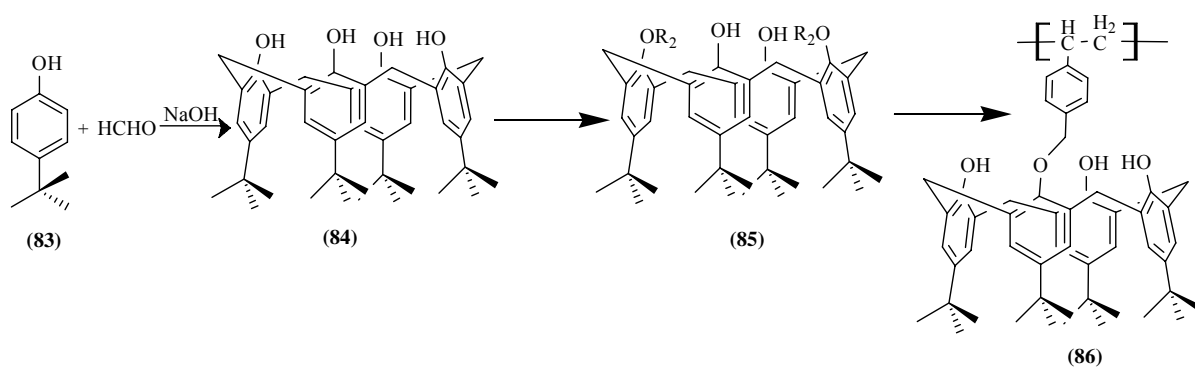
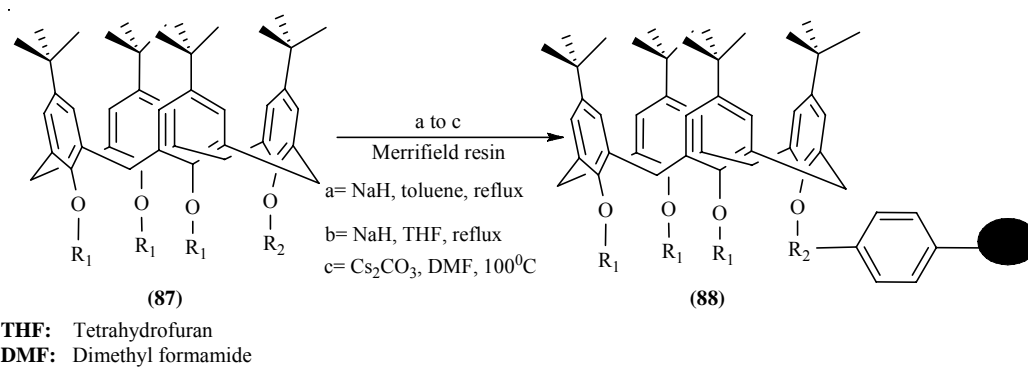


Table III Substitution groups to prepare polymerizable calixarene derivatives

Sample No.	R ₁	R ₂
85a	CH ₂ CN	CH ₂ CN
86a	CH ₂ CN	CH ₂ CN
85b	H	CNC ₆ H ₄ NH ₂
86b	CNC ₆ H ₅ NH ₂	CNC ₆ H ₄ NH ₂
85c	H	CNC ₆ H ₄ NH ₂
86c	CNC ₆ H ₅ NH ₂	CNC ₆ H ₄ NH ₂

Scheme 22.

Immobilized calix[4]arene (**88**) containing merrifield resin is a very useful polymeric scaffold for synthesis of various lower rim derivatives (Table IV) (Scheme 23). It was demonstrated here with the preparation of triacid¹⁶⁹.

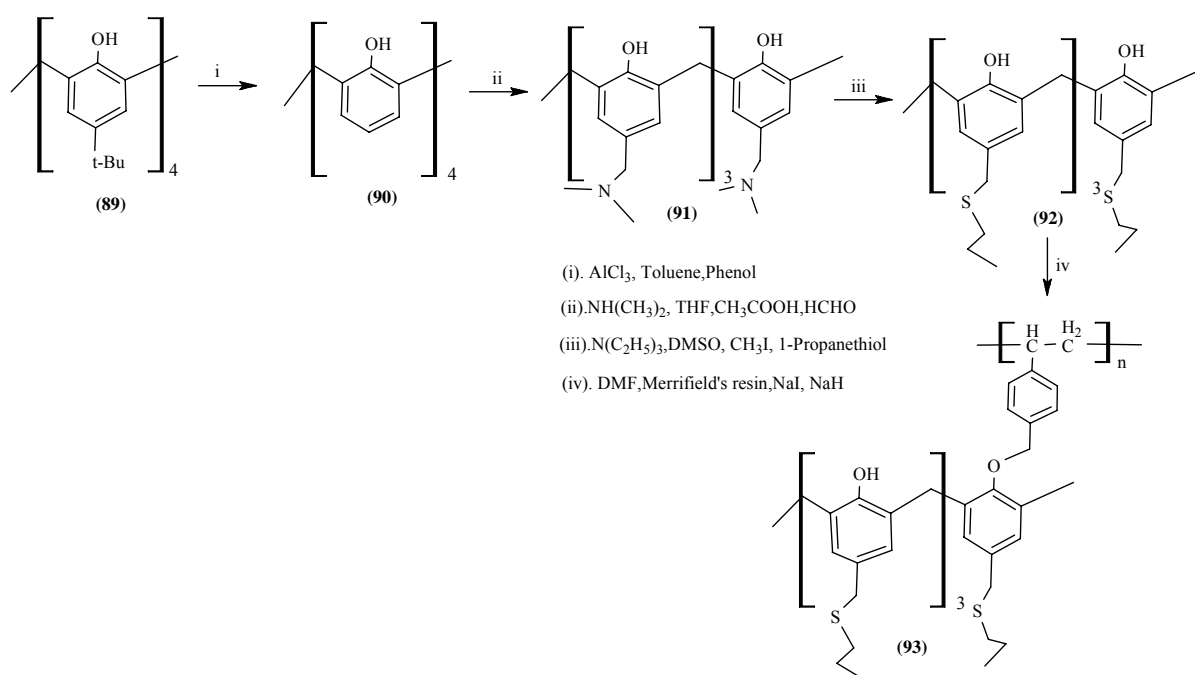


Scheme 23.

Table: IV Substitution groups for Merrifield resin containing calixarene

R ₁	R ₂	R ₁	R ₂
H	CH ₂	H	H
CH ₂ CO ₂ Et	CH ₂	Propyl	H
CH ₂ CO ₂ H	CH ₂	CH ₂ CO ₂ Et	CH ₂ CO ₂ Et
CH ₂ CO ₂ Na	CH ₂	CH ₂ CO ₂ H	CH ₂ CO ₂ H
CH ₂ CO ₂ H	C(O)OCH ₂	Propyl	H

Thio-ether functionalized calix[4]arene based polymeric resin compounds (**92**) that are versatile starting materials for synthesis of polymerizable calixarene derivatives¹⁷⁰. They are suitable for extraction of toxic heavy metal cations as well as for dichromate anions (Scheme 24).

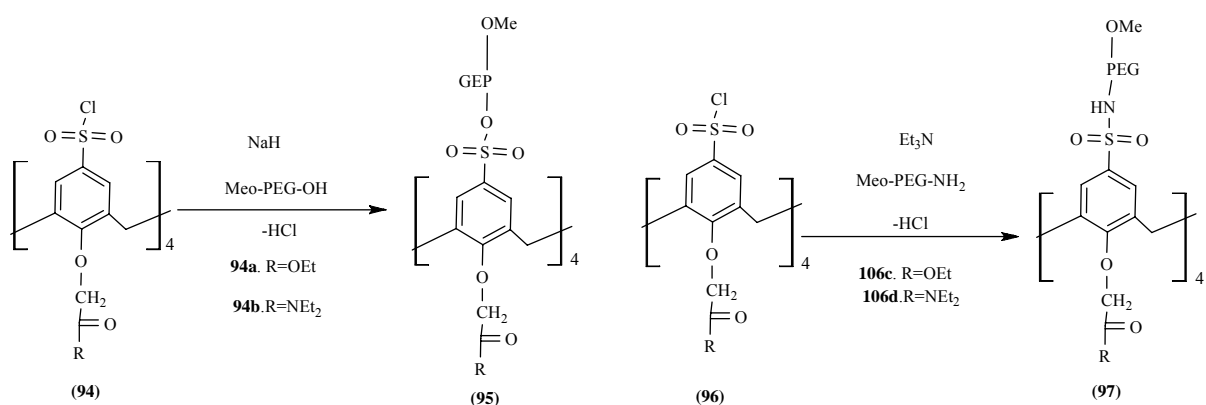


DMSO: Dimethylsulfoxide

DMF: Dimethyl formamide

Scheme 24.

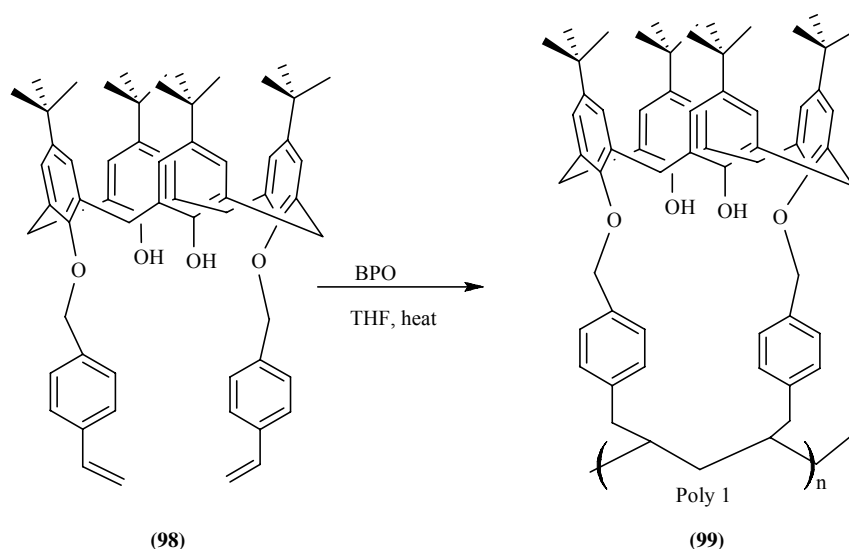
In case of more than one functionalization of polymeric groups on calix[4]arenes (**97**) both ligating and methoxy poly(ethylene glycol) groups are introduced for formation of sulfonyl ester groups on wide rim (Scheme 25), schiff base derivatives on narrow rim, and thioether groups on both wide and narrow rims¹⁷¹, which are non-toxic, non-flammable, biphasic and hydrophilic. It can also be potentially useful for simultaneous extraction of both metals and organics that are commonly present in soil and water.



PEG: Polyethyleneglycol

Scheme 25.

Cyclo-polymerizability of calix[4]arene monomer is also a favorable interaction that occurs between two vinyl benzyl units due to constrained conformation generated by calixarene moiety, which in turn drive intermolecular cyclization. Poly1 (**99**) represents a new type of highly organized macromolecule useful for widespread applications associated with single-handed helical polymers¹⁷² (Scheme 26).

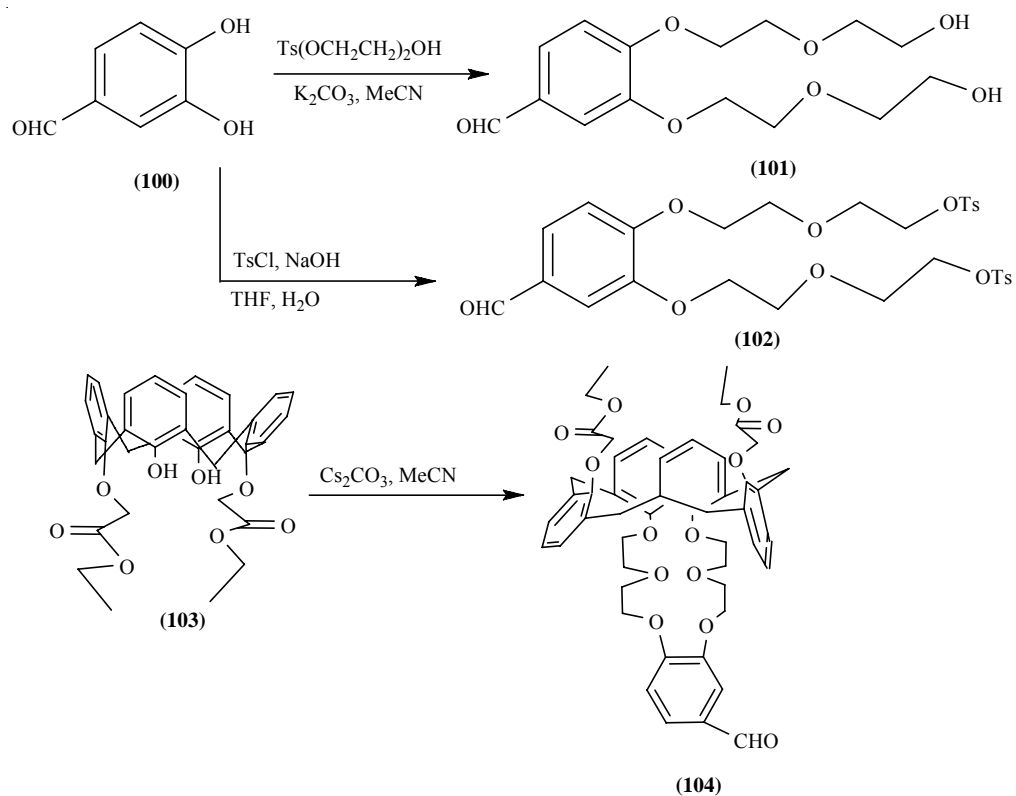


BPO: Benzoyl Peroxide

Scheme 26.

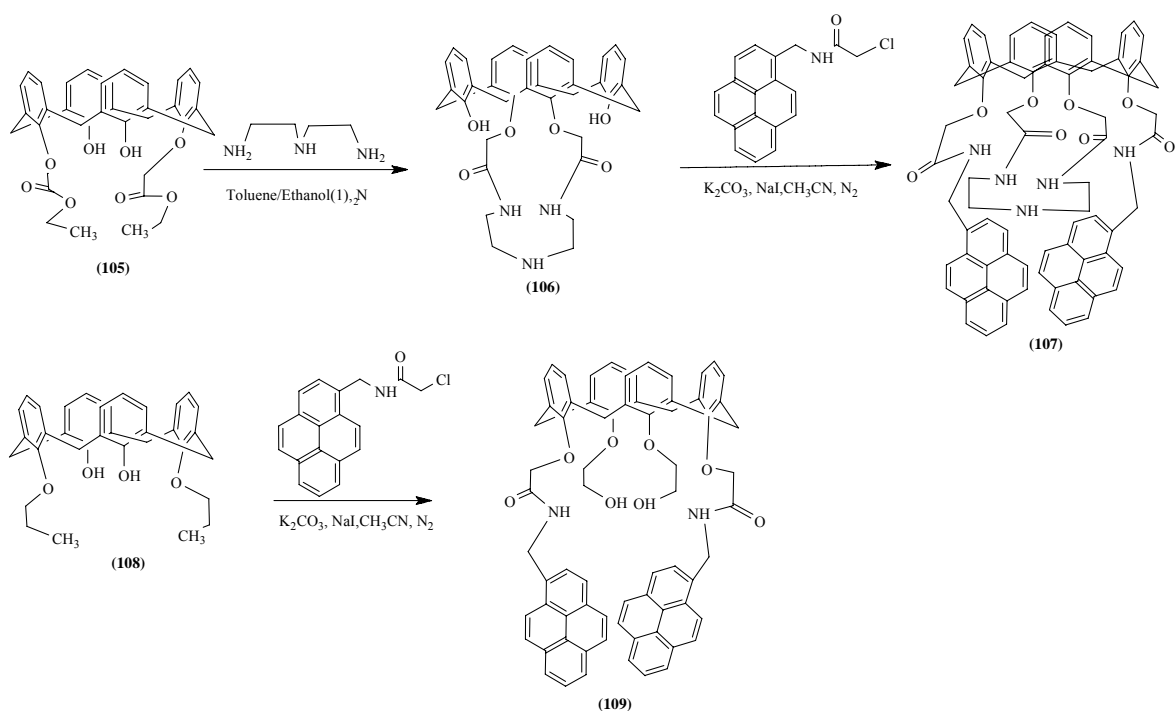
V. CROWN AND FULLERENE BEARING CALIXARENES

Calix[*n*]crowns are macrocycles composed of subunits of a calix[*n*]arene and crown ether joined via phenolic oxygen of calix component. Chen *et al.*¹⁷³ have synthesized dendrimers from an excellent ionophore 1, 3 calix[4]crown that gives multi metal recognition central dendrimer (Scheme 27). Moreover, 2nd generation dendrimers have also been synthesized from 1,3 calix[4]benzocrown-6 as repeat units¹⁷⁴. The 1,3-calix[4]arene bis-crown-6 containing six oxygen donor atoms are also potential extractant for selective removal of cesium cation from radioactive liquid nuclear waste¹⁷⁵.



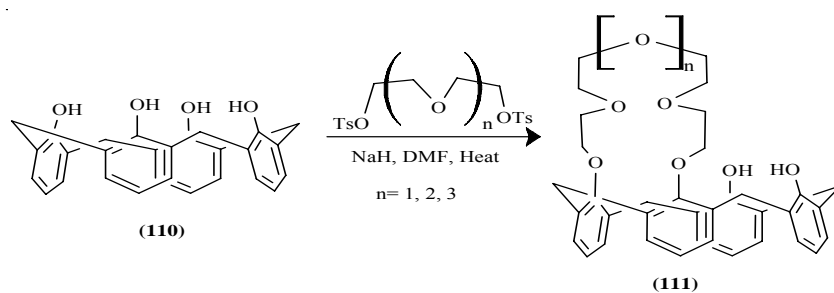
Scheme 27.

To increase complexation ability and for better analytical applications, one has to substitute calix[n]crown with different hetero or bulky groups. A new fluorogenic cone calix[4]triazacrown-5 (**107**) bearing two pyrene amide groups and its structural analogues (**109**) have been prepared by Lee *et al.*¹⁷⁶ (Scheme 28). Such fluorescent chemosensors are effective useful tool to analyze and clarify roles of charged chemical species in living system as well as to measure amount of metal ions from sources contaminated with them^{177,178}.



Scheme 28.

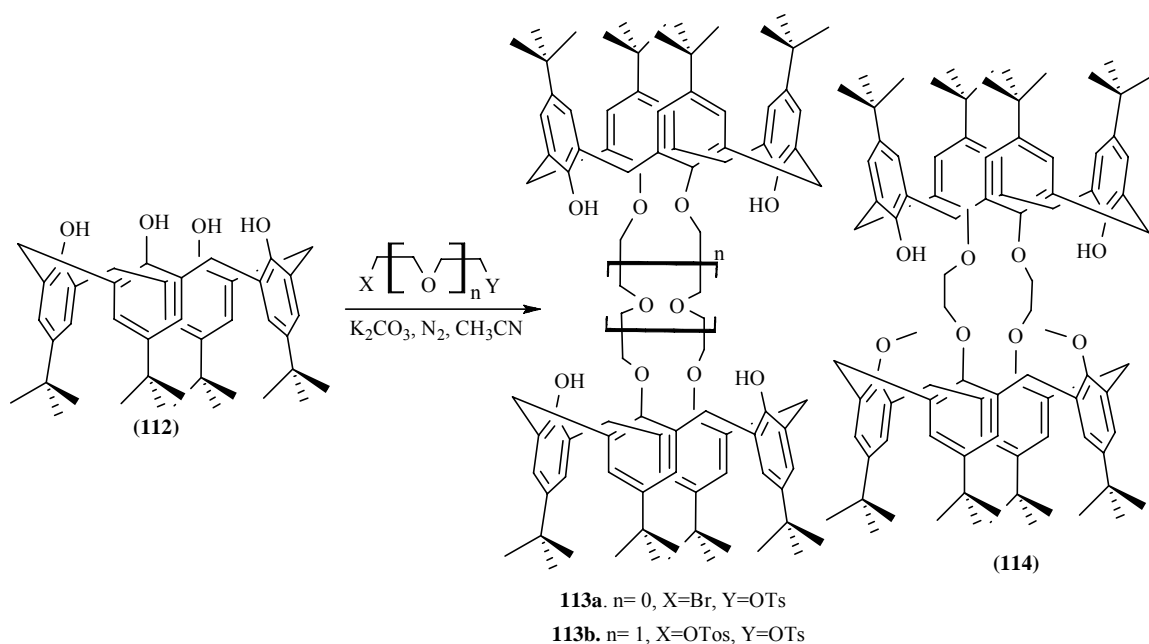
To perform selective extraction of metals, preparation of a series of *p*-sulfonated 1,2,3,4-calix[4]arene-biscrowns (**111**) are reported¹⁷⁹ for Cs^+/Na^+ selectivity (Scheme 29).



DMF: Dimethyl formamide

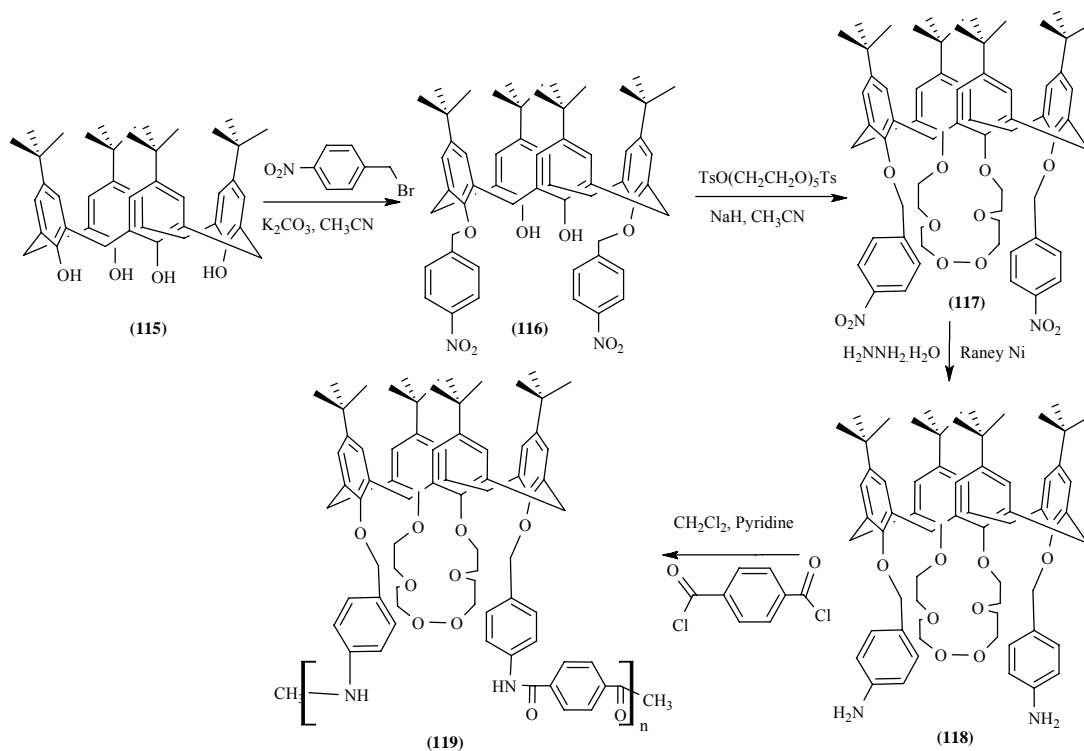
Scheme 29.

Kerdpaiboon *et al*¹⁸⁰ have synthesized three new calix[4]quinines from their corresponding double calix[4]arenes (**113a**)¹⁸¹, (**113b**)¹⁸², (**114**)¹⁸³. Their complexation studies have been carried out with alkali metal ions such as Li^+ , Na^+ , K^+ , and Cs^+ (Scheme 30).



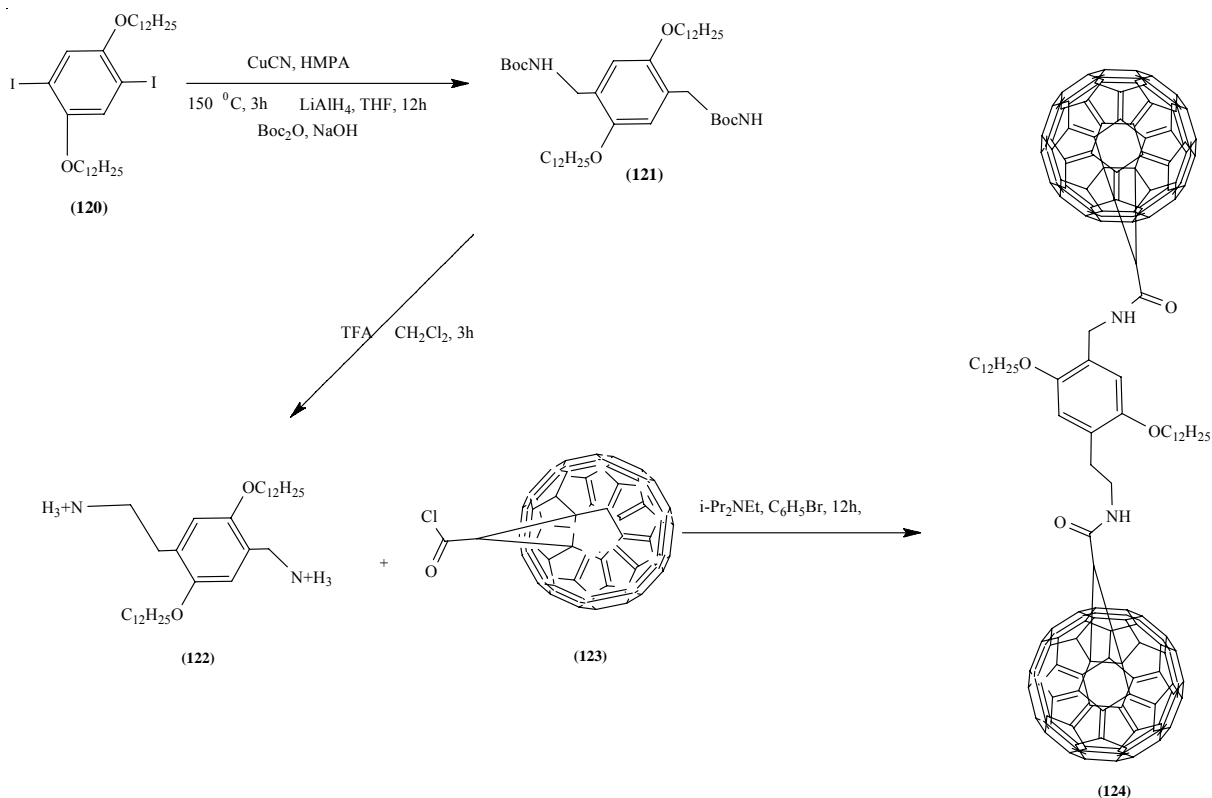
Scheme 30.

Substitution of oligomers increases liquid liquid extraction ability for calix[4]crown-6 monomers **(118)** and **(119)** (Scheme 31)¹⁸⁴ while aza crown based two new calix[4]arene ionophores increases complexation ability with metal ions¹⁸⁵.

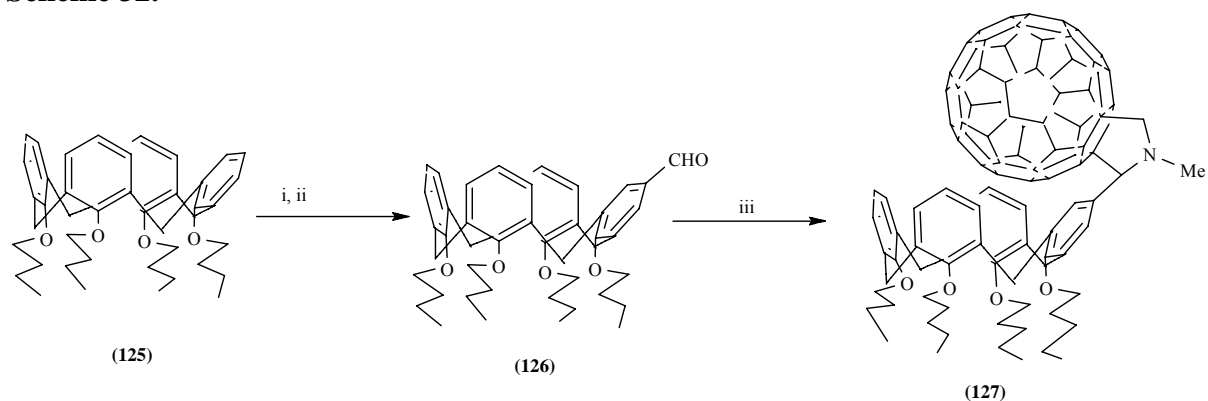


Scheme 31.

Apart from crown ethers, covalent assemblies of fullerene and calixarenes have also been investigated thoroughly to study polymeric nature appeared in solid phase^{186,187} using calix[5]arenes (Scheme 32)¹⁸⁸. Intramolecular association, self complexation and de-complexation properties using tetra-*o*-alkylated cone calix[4]arene (**127**) skeleton have also been examined (Scheme 33)^{189,190}.



TFA: Trifluoroacetic acid
Scheme 32.



(i) NBS, acetone, rt, 24 h; (ii) *n*-Bu-Li, THF, -78 °C, 1 h, then DMF, -78 °C to rt, (iii) C₆₀, *N*-methylglycine, toluene, 16 h.

Scheme 33.

VI. CALIXARENE HYDROXAMIC ACID

The general method for the synthesis of hydroxamic acids is based on the treatment of the acid chloride, amide, ester or anhydride with suitable hydroxylamines under weak alkaline condition. Many reviews and papers on hydroxamic acids as well as on calix hydroxamic acids have been published so far¹⁹¹⁻¹⁹⁶. Moreover, the hydroxamic acid has upper and lower rim calix[4]arene¹⁹⁷⁻²⁰¹ and calix[6]arene²⁰²⁻²⁰⁶ have been synthesized and their analytical applications are reported²⁰⁷⁻²⁰⁹.. It has been observed that the change in the substituents in the hydroxamate moiety alters the selectivity and sensitivity of the reagent towards the metal ions. With this in view, Polymer-based calixarene hydroxamic acids have been reported for the separation and recovery of iron(III), cobalt(II), lead(II), manganese(II)²¹⁰. Chromatography separation of gallium(III), indium(III) and thallium(III) using polycalixarene hydroxamic acid has been investigated²¹¹. 25, 26, 27, 28-tetrahydroxy-5, 11, 17, 23-tetrakis (N-*p*-chlorophenyl) calix[4]arene hydroxamic acid has been synthesized by agrawal *et al* and applied for the trace determination of thorium (iv) in geological samples at low ppb level²¹² which was later on synthesised for the extraction and determination of zirconium(IV) and uranium(VI)^{213,214}. A calix[6]arene bearing three hydroxamic acid groups has been synthesised to study extraction properties towards transition metal ions and compared with other proton-ionizable related calix[6]arenes and with a monomeric hydroxamic acid analog²¹⁵. Incorporation of two hydroxamic acids on calixarene base receptor has been synthesized for the optical detection of Cu⁺² and Ni⁺² in solution²¹⁶. For determination of Uranium in environmental samples and to understand its transport mechanism, Incorporation of eight hydroxamic acid groups on calix[4]resorcinarene have been synthesized²¹⁷. Calixarene hydroxamic acids have also been used for the sequestration of calcium(II), potassium(I),

manganese(II), aluminium(III)²¹⁸. A bispyrenyl calix[4]arene-based receptor, incorporating two hydroxamic acid functionalities has been designed for the optical detection of copper(II) and nickel(II) metal ions in solution²¹⁹. Moreover, theoretical study on such hydroxamic acid functionality on calixarene is carried out using density functional theory calculations. In which interaction energies between the metals and functional group have been determined. Calculation of interaction energies have pointed out clearly a better affinity with the hydroxamic acid group of these calixarenes²²⁰.

Little work has been reported on the acid catalyzed reaction for the synthesis of calix[n]arene, however, there are some evidences of calixarenes, obtained by the acid catalyzed reaction of phenol and formaldehyde and functionalization of these calixarenes improves their complexation ability and selectivity towards metal ions²²¹⁻²²⁶. Introducing hydroxamic acid functionality on the upper rim of the calixarene have been reported for the complexation and extraction of metal ions²²⁷⁻²³⁰ and sensor devices^{231,232}. Calix[n]arene-based uranophiles bearing hydroxamic groups on the lower rim (2n; n= 4 and 6) have been synthesized and the extractability and the selectivity towards uranyl ion estimated in a two-phase (water–chloroform) solvent-extraction system.²³³ Likewise 4-tert-butylcalix[4]arene tetrahydroxamate chelators have been synthesized using short synthetic rout with moderate yield, on which some extraction studies have been accomplished to estimate the metal ion selectivity and extraction efficacy of these chelators. Study proves that these have been identified as selective solvent extractant for actinide(IV) ions²³⁴.

AIM AND SCOPE

The increase in industrial activity in recent years has resulted in contamination of ground and surface water by toxic metal ions²³⁵. In developing countries, water pollution generated by industrial effluents has been a serious issue²³⁶. For ecologically sustainable growth, monitoring of metal ions such as Cr⁶⁺, Cu²⁺, Cd²⁺, Pb²⁺, Hg²⁺, Co²⁺, and Ni²⁺ in natural water as well as in bio-fluid samples is required. Toxic heavy metals such as cadmium, mercury, copper and lead are hazardous to human health²³⁷ as well as to the environment because of their accumulative and persistent character. The importance of detection of heavy metals²³⁸⁻²⁴¹ and controlling the level of such pollutants has generated increasing interest in the development of novel sensors, such as calixarene-based ionophores, ion selective electrodes or chemically modified field effect transistors. These macrocycles have been used for catalysis, molecular recognition or ion separation, and sensors²⁴²⁻²⁴⁴.

Reviews of past seven years reveal that there is very less research has been carried out on thia-calixarenes and negligible research on complexation of them with metal ions. Chemists usually prefer the reproduction of nature, which constructs the large and complex systems with high degree of efficiency. One of the vehicles used for this research are thia-calix and thiacalix-crown ethers. The introduction of chelating group, such as hydroxamic acid may further enhance the complexing ability for transition metals in particular.

With this in view, it was thought desirable to introduce hydroxamic acid group in thia-calixarenes to synthesis a new series of thia-calixarene hydroxamic acids to study the extraction, complexation and preconcentration of selected transition metal ions²⁴⁵.

PRESENT INVESTIGATION

Herein, conventional as well as microwave irradiated synthesis of thia-calix[4]arene, biphenylthia-calix[4]arene, thia-calixcrown and their nitro and hydroxamic acid derivatives is described. Previously synthesised thiacalix[4]arene, biphenylthiacalix[4]arene and thia-crowns are nitrated by refluxing them with KNO_3 and AlCl_3 which is further partially reduced by hydrazine hydrate at $0-10^\circ\text{C}$. and its hydroxamic acids have been prepared by corresponding acid chloride. These derivatives were characterized by FT-IR, ^1H NMR, ^{13}C NMR and C, H, N analysis.

These compounds have been applied to different analytical techniques for the extraction and transport of Zn(II), Cu(II), Ag(I) and Hg(II). Selection of the ligand for particular metal ion has been done on the basis of properties, cavity size, metal ion affinity and previous work.

Here advanced analytical techniques have been selected which are eco-friendly, rapid, sensitive and simpler than traditional liquid-liquid extraction.

Determinations of such methods have been done by spectrophotometrically and ICP-MS. Results reveal that the metals formed colored and colorless complexes with reagents which are extracted in organic solvents. The organic solvent was then measured spectrophotometrically.

A simple and selective preconcentration method using cloud point approach is proposed for the extraction and separation of Zn(II). The analyte in the initial aqueous solution is complexed with BPTC4HA at optimum pH 8.5, Triton X-100 is added as a surfactant and Na_2SO_4 was added to reduce cloud point temperature. After phase separation at 45°C based on cloud point of the mixture and dilution of the surfactant-rich phase with acetonitrile-ethanol, the analyte is determined by spectrophotometrically at λ_{max} 327nm and also by ICP-MS. The variables (viz. pH, Temperature, Pressure, Surfactant concentration)

were affecting the complexation and extraction steps were optimized. The selectivity of method towards Zn(II) in the presence of other foreign ions are also investigated. Moreover, Transportation study through membrane in the presence of 0.1N HNO₃ stripping agent was investigated and 99.9% ± 0.5% transport of Zn(II) was found with $t_{1/2}$ = 9.8 min. The method affords recoveries in the range of 96-101%. The determination of Zn(II) for the detection at µg level in environmental and food samples was successfully applied.

A rapid and reproducible method has been developed to measure trace amount of copper using supercritical fluid extraction (SFE). Copper is extracted with Thiacalix[4]arene hydroxamic acid (TC4HA) in dichloromethane by Supercritical carbon dioxide (SF-CO₂) –dichloromethane (modifier) medium. The copper is extracted at pH 4.0 and directly measured at λ_{max} 317nm by spectrophotometry and also by ICP-MS. The distribution ratio of copper was determined and the slope of log D_M Vs TC4HA concentration plot was found to be 1.0 which shows that extracted species in SF-CO₂ extraction (SFE) give 1:1 Cu²⁺ and TC4HA complex. The extracted species both in SF-CO₂ extraction and solvent extraction were determined to be as [Cu(TC4HA)] complexes. The copper is determined as low as nanogram level in presence of several cations and anions. The effect of diluents, modifier concentration, temperature and pressure on the extraction and separation of copper was discussed. The TC4HA has been successfully used as carrier for efficient transport of Cu(II). Maximum transportation of Cu(II) was observed for 20 min with $t_{1/2}$ equal to 10.4 min.

A new functionalized biphenyl thiacalix[4]crown hydroxamic acid is reported for the liquid-liquid extraction, separation, preconcentration and trace determination of Ag(I) and Hg(II). The various extraction parameters viz. optimum pH, choice of solvent, effect of the reagent concentration etc. have been studied. Ag(I) gives the

colorless complex having molar absorptivity $6.13 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at pH 6.0 and Hg(II) gives light coloured complex having molar absorptivity $3.7 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at pH 9.0. For the trace determination the extracts were directly inserted into plasma for ICP-MS measurements which enhances the sensitivity and obeys Beer's Law $0.024\text{-}25.0 \text{ }\mu\text{g ml}^{-1}$ for Ag(I) and $0.034\text{-}20.0 \text{ }\mu\text{g ml}^{-1}$ for Hg(II). Membrane transportation study is carried out of metals where maximum transport is observed with $t_{1/2} = 17.8 \text{ min.}$ for Hg(II), and $t_{1/2} = 11.5 \text{ min.}$ for Ag(I). Finally, the method is applied for the trace determination and the separation of Ag(I) and Hg(II) in the biological and environmental samples.

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