RESEARCH ARTICLE

Calixarene Assembles

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ABSTRACT

An extensive literature work on the numerous calixarene assemblies and their importance has been reviewed. Emphasis has been made on their synthesis, complexation studies and their analytical applications.

KEYWORDS

INTRODUCTION

Supramolecular chemistry focuses on the noncovalent bonding of the molecules having weaker and reversible interactions. These interactions are due to hydrogen bonding, metal coordination, hydrophobic forces, Van der Waals forces, pi-pi interactions and electrostatic effects. Supramolecular chemistry provides molecular self-assembly, folding, molecular recognition, host-guest chemistry, mechanically interlocked molecular architectures and dynamic covalent chemistry. Macrocycles having the cavities can completely surround guest molecules and may be chemically modified to desired application.[1] Calixarene appeared as the third generation of supramolecular host compound after crown ether, cyclodextrins.[2–3]

Calixarenes have been proved to the important building blocks in supramolecular chemistry. Calixarene have received special attention because their easy large scale preparation and ability to undergo further synthetic elaboration.

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The easy chemical transformability of this molecule together with its "tunable" structure make calixarene an attractive candidate for molecular design strategies.[4–9] Calixarenes derived from the Greek calix meaning vase or chalice and arene, which indicate the presence of aryl residues in macrocyclic array. The calixarene exist in a 'cup' like shape with a defined upper-rim, lower-rim and central annulus (Fig.1).

Historically, calixarene can be depended on discovery of phenol-formaldehyde resins investigated by Von Bayer in the 1970s. The polycondensation of phenol and formaldehyde in acid or base proceeds through the ortho and para positions, leading ultimately to the highly cross-linked matrix, such as bakelite. When para position is blocked with alkyl substituents, condensation is restricted to a liner progression and this aspect of phenol-formaldehyde chemistry, led in the 1940s to the discovery of calixarene. Gutsche[10] was the first to draw the attention to their potentiality as molecular receptor or enzyme mimics which are known collectively as "Calixarenes". The calixarenes are synthesized by acid catalyzed condensation of a variety of aromatic compounds. Among these the aldehydes viz. formaldehyde,

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acetaldehyde, propionaldehyde etc. have been reported extensively. Calixarene contains four, six and eight aryl units can easily be prepared in good to excellent yields. Calix(4)arenes are macrocyclic molecules with unique three dimensional structures. Functionalisation of the calix(4)arene is referred to either narrow rim (previously called lower rim) if it occurs at the phenolic oxygen or wide rim (previously called upper rim) if it occurs at the para position after the removal of p-tert-butyl groups. Their controlled synthetic functionalisation and versatile complexation properties[11] allow the use of these compounds in supramolecular chemistry as molecular scaffolds for the construction of various receptors. They are frequently employed as platforms that permit functional groups to be orientated well organized cavities. The great interest in compounds of this type is primarily motivated by the ionophoric property of the narrow rim which leads to applications in the area of cation binding and transport as well as highly selective receptors and novel sensors for polyanionic species. This polyfunctional property stems from the fact that the narrow rim is relatively easy to chemically modify via well established acid-base and nucleophilic reactions. Calixarenes made up of phenol and methylene units have many conformational isomers because of two possible rotational modes of the phenol unit: the oxygen through the annulus rotation and the para substituent through the annulus rotation.
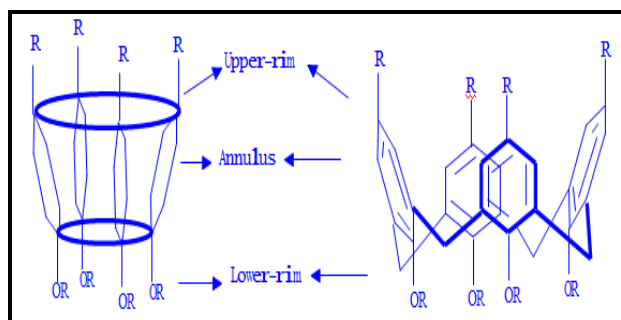

Figure 1.1: Representation of calixarene and designation of the faces

By rotation of phenolic units, calixarene molecules may adopt different conformations: for examples, calix(4)arene compounds have

four limiting conformations are cone, partial cone, 1,2-alternate and 1,3-alternate. Calix(6)arene is constructed by six phenolic units, which results not only in more kinds of derivatives, but also in more conformation mobility than that of calix(4)arene. The conformational interconversion in calix(6)arene can occur not only via the oxygen through the annulus but also by the para substituent through the annulus pathway, even in the case of p-tert-butyl derivatives. Thus, it is difficult to immobilize the conformation of calix(6)arene by introducing bulky substituents onto the lower-rim simply, even if the substituent is as bulky as cholesteryl group.[12] Considering only the relative orientations (syn or anti) of the aromatic nuclei there are eight possible conformations for calix(6)arene i.e., cone, partial cone, 1,2-alternate, 1,3- alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate and 1,3,5-alternate the number increases dramatically if the value of the angles that each aromatic nucleus makes with the average plane of the molecule is taken into account. Recently calixarene family has been extended to the compounds with similar aromatic units due to its conformational flexibility, diverse binding affinity and easiness for the applications.[13−14]

Biscalixarenes

Biscalixarenes have attracted great interest because of their peculiar multicavity structure and molecular recognition abilities. In the case of tail-to-tail linkage, the biscalixarenes, providing two diverging cavities have been used as tectons for poly-cap self-assemblies. The detailed synthesis methodologies with various types of spacers of biscalixarene depending upon the nature of the base, stoichiometry of the reactant, complexation and extraction behaviour of these calixarenes are summarized by Agrawal et al.[15] Shinkai et al.[16−17] reported the synthesis of a series of bis[calix(4)arenes] possessing two metal binding sites, each containing four ester or four ether groups. Double and triple calix(4)arenes connected through the oxygen atoms were described,[18] produced by reactions between calix(4)arenes 1,3-difunctionalized at the smaller (lower) rim and difunctional

reagents such as diacid dichlorides or diamines.[19] Double calixarenes linked through one bridge at the smaller (lower) rim and bearing urea groups on the larger (upper) rims have also been reported.[20–21] Rebek et al. described[22] the synthesis and the encapsulation behavior of bis[calix(4)arenes] linked by one bridge at the larger (upper) rims and bearing urea groups in the same rims. The complexation behavior of bis(calixarenes) towards fullerenes C_{60} and C_{70} was studied.[23] A series of bis[calix(4)arenes] derivatives linked through their phenolic oxygens with the aid of a single aliphatic or aromatic chain (tail-to-tail) were obtained by alkylation of 28-hydroxy-25,26,27-tripropoxy calix(4)arenes with a,u-dibromoalkanes in the presence of NaH[24] and by condensation of p-tert-butylcalix(4)arene with methyl 2,6-bis(bromomethyl)benzoate,[25] 2,6-bis(bromo-methyl)-4-methylanisole[26] or with 5,5'-bis(bromomethyl)-2,2'-bipyridine N,N-dioxide.[27] The symmetrical quadruply-linked bis-tBu-calix(4)arene with ethylene linkers has been synthesized, which shows remarkable affinity for potassium ion. The aryl groups radiating from the central core in these tubular receptors are also of importance in the control of metal ion selectivity, behaving as filtering gates by way of cation-π interactions.[28] A series of new biscalixarences consisting of two p-tert-butyl thiacalix(4)arene units linked through lower rims with bridging moieties containing diimine units of different aromatic or heteroaromatic dialdehydes were reported by Kumar et al[29] their complexation behavior was studied towards different metal ions. (Na^+, K^+, Ca^{+2}, Pb^{+2} and Ag^+) Bhalla et al. replaced the conventional calix(4)arene unit of biscalixarences with thiacalixarences which is an attractive host for soft metal ions.[30] To evaluate the binding ability of bisthiacalixarences toward different metal ions, two-phase solvent extraction of metal picrates (Na^+, K^+, Cs^{+2} and Ag^+) was carried out.

Biscalixarene derivatives have been studied for cation complexation, anion recognization, organic, neutral and charged molecular recognization, redox active ionophore, ion selective electrodes and ditopic receptors.[31–39]

Calixcrown

Calix(n)crown ethers compound are macrocycles characterized by possessing two kinds of receptor elements compose of calixarene and crown ether, joined via the phenolic oxygen of calix component. Calix(n)crown in which the calixarene is functionalized at the distal phenolic oxygen with a poly chain have been utilized as the molecular scaffold. The reaction of calix(n)crown with different equivalents of various ditosylates(containing 2,3,4,5,6,7-oxygens) in the weak alkaline medium gives different calix(n)crown ethers. Different calix(n)crown ether and their analytical potentialities are summarized by Agrawal et al.[40]

Calix(n)crown compounds exhibit superior reorganization ability toward alkali, alkaline earth metal, ammonium and transition metal ions due to co operative effect of the calixarene and crown ether moieties.[41,43,44] Mori et al.[45] have reported that structure features and presence of bulkier substituents also play a relevant role in determining the selectivity. Reinhoudt et al.[42] have reported the substituent's at the remaining -OH group for the first time. Study reveals that introduction of four ester, keto, amide or mixed type binding sites on the phenolic groups of the p-tert-butyl calix(4)arene fixes the macrocycle in non-conformation giving a Na^+ selective cation receptor on the other hand the selective 1,3 dialkylation of the calix(n)crown followed by the polyether group attached at two remaining group results in K^+ selective ionophore. Reinhoudt et al.[46] have reported that 1,3 dialkoxy calix(4)arene crown derivative were found to be exceptionally selective ionophore for cesium ion due to the complexation of the cesium ion not only with crown ether moiety but also two rotated aromatic nuclei when fixed in 1,3 alternate conformation. Kim et al. reported that the introduction of benzene rings in to the crown ether loop of calix(4)arene can improve the selectivity for cesium ion due the flattening

effect. Kurita et al.[47] have reported a platinum complex with calix(4)dithia crown. This platinum complex catalyzed hydroxylation of olefins with $(Eto)_3SiH$. Ungaro and coworkers[48] have carried out an analytical study with a new class of calix(4)crown ether with one of two pyridine appended to the poly ether chain and studied the luminescence properties of europium and terbium. A novel dinuclear gold(I) calix(4)crown acetylide complex has been reported by Yam et al.[49] showing a high K^+/Na^+ selectivity over other alkali cataion. Dodi[50] reported the calix(4)crown displaying and exceptional selectivity towards cesium using high performance liquid chromatography with UV detection. Kim et al.[51] reported a new flurogenic benzothiazolyl ionophore based upon calix(4)crown ether co-determination in aqueous media. In the study, pronounced selective flurogenic behavior toward K^+, Na^+ and Mg^{+2} has also been determined. The effect of crown ether units and Na^+ ion binding towards anion binding ability have been studied by Tongraung et al.[52] Calix(4)arene containing urea and crown/urea moieties formed complexes with Cl^- and Br^- to a different extent. Upon addition of Na^+ the binding ability is increased due to ion-pair enhancement.

Calixresorcinarenes

Resorcinarenes are the analogous of calixarenes with two hydroxyls groups in benzene rings forming a macrocycle. Calixresorcinarenes have been revived considerable attention for the synthesis of the cavitands and (hemi) carcerands etc. Such molecules contain an enforced cavity with the shape of an american football, sufficiently large to accommodate small organic molecules. Calixrescorcinerece play an important role in the field of host molecule, metal ion extraction agents, selective membrance, molecular inclusion and recognition.[53−57] Resorcinarenes have been synthesized from acid-catalyzed condensation reaction of resorcinol and aliphatic aldehyde or aromatic aldehyde. The synthesis, complexation and analytical application are well documented by Agrawal et al.[58] The large number of calixrescorcinerece have formed the complexes with iron, gold, copper, silver, mercury, platinum, lanthanides.[59−63] Calixresorcinarenes also have shown the complexing behavior with a variety of guest molecules such as sugars, steroids, amino acids, triethyl amine and [2.2.2] cryptand.[64−68] The extraction properties of the calix(4)resercinerene resins have been evaluated in competitive extraction and show a selectivity in favor of cesium(I).[69] The extraction of cesium by resorcinol based resin was investigated.[70] The iono selective properties of these new ion-exchange resins are strongly influenced by the nature of the cross linker. The presence of macrocycle lead to an improvement of selectivity towards cesium in the relation with the size of the macrocycles introduced. Binding study of new amino pyridinyl resocene receptors for the recongtions of alkali metal ions have been reported.[71] A new calix(4)rescorcinerece bearing eight hydroxamic acid groups has been synthesized and its analytics properties were investigated and showed high affinity and selectivity toward thorium(IV) and uranium(VI) in the presence of large quantities of associated metal ions.[72−73] A new method for liquid-liquid extraction, separation and pre-concentration of cerium(IV) with a calix(4)resercinerene hydroxamic acid derivative is reported,[74] that was applied for the determination of cerium in standard geological samples, monazite sand and sea water samples. Aminophosphonate calix(4)resorcinarene derivatives extract lanthanum(III) and lutetium(III) ions from aqueous solutions to chloroform much more efficiently than diethyl [(4-nitrophenyl)aminobenzyl]phosphonate does.[75] The alkyl amino menthylated calix(4)-resorcinarene derivatives, modified by dimethyl amino-piperidyl and trimethylamommonium moieties have been synthesized to investigate their extractability towards lanthanide(III) ions and to compare with the extractability of calix(4)resorcinarene.[76] Spectrophotometry and pH measurements were used to study the non-substituted and ortho- substituted calix(4)resorcinarene mediated transport of copper(II) and cobalt(III) complexes with diamine and amino acids from an aqueous source phase to an aqueous receiving phase

through a bulky chloroform membrane.[77] Extraction ability of water soluble calix(4)resorcinarene octacarboxylate toward phenol by the assistance of iron(II) ions was investigated in aqueous solutions by photoluminescence (PL) and quantum-chemical methods (QCM).[78] The results showed that water soluble calix(4)resorcinarene octacarboxylate forms stable sandwich type complexes with phenols by 1:2 stoichiometry. Binding properties of resorcinarene- based cavitands functionalized with N-acylthiourea moieties towards different cations are described.[79] Extraction studies with metal (Pb^{+2}, Cu^{+2}, Ag^+, Hg^{+2}, Eu^{+2}, Fe^{+3}, K^+, Na^+ and Ca^{+2}) picrates and the incorporation in the ions selective electrodes (ISEs) show that there is more than a 40% increase of the silver(I) extraction. Tetrathiophosphonate calix(4)-resorcinarene shows excellent extraction properties towards soft metal ions with a better affinity for silver(I) (91%) than thallium(I) (38%) and mercury(II)(16%). The extraction of other picrate salts (Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Pb^{+2}) was not detected.[80] Aminomethylated calix(4)resorcinarene forms the 2:1 complex with copper(II) ions.[81] Resoricnarenes of C_2V symmetry tetrasulfonates are useful as molecular platforms of the design of cation receptor for alkali metals and ammonium(I) ions, containing binding units in the molecule.[82]

Calixnaphalene

Calix(4)naphthalenes are a class of molecules which possess deeper cavities than those of the analogous calix(4)arenes. Over the last several years, Georghiou has pioneered and substantially developed the chemistry of calixarenes derived from naphthalene subunits. The term calix(4)naphthalene was coined to describe these structures, typically prepared from 1 or 2-naphthol or their derivatives.[83]

Condensation of 1-naphthol with formaldehyde produces a mixture of regioisomeric calix(4)naphthalenes. Moreover, each isomer can be individually prepared by a convergent method[84] because the naphthalene units are linked at the C_2 and C_4 positions; this class of calixarenes has the same connectivity as a typical calixarene, yet with a deepened pocket owing to the naphthalene core. The deep binding pocket and the pendant functionality conspire to produce a versatile host that has been used to recognize a range of guests from metal ions[85] to [60] fullerene.[86] Despite the ample precedent for preparation of the 2,4-linked calix(4)naphthalenes, the analogous 3,6-linked isomer cannot be approached in a similar manner. It has been shown that 2,7-dihydroxynaphthalene reacts with electrophiles including formaldehyde, exclusively at the C_1 position[87] thwarting a simple condensation strategy toward its derivatives. Thus, a properly functionalized derivative would be required in order to obtain the desired substitution pat- tern. The complexation of [60]fullerene ('C_{60}') with the C_4-symmetrical endo- calix(4)naphthalene and its tert-butyl-substituted derivative show that they form supramolecular 1:1 complexes with C_{60} in benzene, toluene or CS_2 solution with relatively high association equilibrium constants.

Calixfullerene

Fullerene is a family of carbon allotropes, molecules composed entirely of carbon, in the form of a hollow sphere, ellipsoid or tube. Because of their unique physical and chemical properties, such as efficient singlet oxygen sensing ability, strong electron accepting character, photoinduced charged separation ability and superconductivity upon binding with metals fullerene have attracted intense research interest in various field. In parallel, calixarene may be regarded as third generation of potent host molecule. Since fullerene has globular structure with external-electron surfaces and calixarene have cavity structure with internal-electron surfaces, a marrage of the two third generations by guest host comlexation e.g., through $\pi - \pi$ interaction is an obvious possibility. The ready availability of fullerene has increasingly invited exploration of its outstanding physical and chemical properties of these the superconductivity observed for certain endohedral metallofullerenes has proved a most attractive subject for research.[88] The synthesis

of ionophoric fullerene derivatives in which a metal-binding site is closely situated near the fullerene surface is necessary. Such fullerene derivatives with ionophoric functional groups have been reported by several groups[86–95] but spectroscopic evidence for the direct fullerene-metal interaction was obtained only in a few systems. It is considered that this working hypothesis would be realized most conveniently and most efficiently by using ionophoric calixarenes since they not only provide strong and well characterized ionophoric cavities but also interact with fullerene in the solid state and in solutions. It is known that the highly ion-selective and highly ionophoric cavities can be created by the appropriate modification of the lower rim OH groups while the upper rim p-basic cavities of certain calixarenes can accept fullerene even in solution.[96–103] If fullerene is used as a 'lid' for the ionophoric cavity, a metal cation bound therein would inevitably interact with the fullerene surface. Fullerene[104] which were discovered in 1985 and isolated in microscopic quantities in 1990 can be regarded as the third carbon allotropies after graphite and diamond. Calix(8)arene selectively inclused C_{60} from carbon soot and forms precipate with 1:1 stoichiometry and provides novel and very useful method to obtain C_{60} in very large quantity and high purity. This finding greatly stimulated research into the host guest chemistry of fullrenes. It was found that variety of microcyclic host molecules, such as calixarenes or calixarene analogues form complexes with fullerenes. Williams et al.[105] reported that water soluble calix(8)arene derivatives extract C_{60} fullerenes from an organic into an aqueous phase. Atwood et al.[106] shown that p-benzylcalix(5)arene and p-benzyl-homo-oxacalix(3)arene form 1:2 complex with C_{60} from fullerene solution in toluene. Shinkai et al. reported that p-tertbutylcalix(8)arene can be used to selectively sequester fullerene (C_{60}) from a mixture containing C_{60} and fullerene (C_{70}). This is accomplished by the formation of a 1:1 clathrate in which a C60 guest molecule is bound within the cavity of the host molecule. p-tertbutyl calix(6)arene and calix(6)arene form fullerene rich 1:2 complex with C_{60} or C_{70}.[107–108]

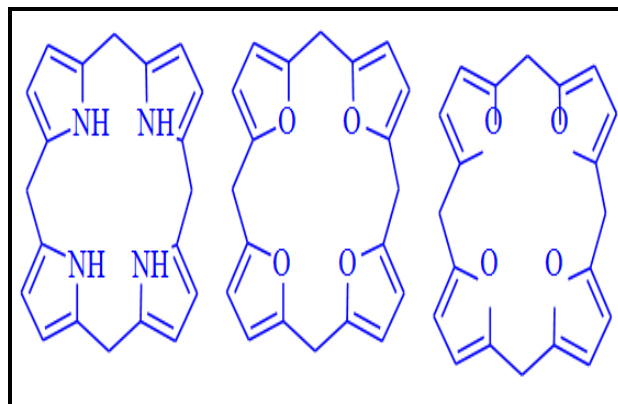The structure of complexes was determined by X-ray diffraction studies.

Figure 1.2: Heterocalixarenes

Heterocalixarene

Heterocalixarene[109–112] constituted by replacement of arylene units of calixarene with heterocyclic moiety and/or attachments of heterocyclic moieties, depending on the electron-rich[109] and electron deficient[110] nature by heterocyclic unit(s), en- compass numerous new opportunities for interaction with electron rich and electron deficient systems. The protonizable hydrogen and hetero atom of the heterocyclic constituent could also induce H-bonding interaction with anionic and acidic

"H" substrates Heterocalix(n)arenes possessing varied heterocycles viz. furan, thiophene, pyridine, imidazole, benzimidazole, indole, benzofuran, benz-1,3- oxazine, pyrimidine-2,4-dione, benzimidazol-2(1H)-one, quinazoline-1,4(1H,3H)- dione etc.[113] Calixpyrrole belongs to the family of heterocalixarene macrocycles, which has four pyrrole units instead of phenolic units. Calixpyrrole, as the name implies, offer a cup-shaped skeleton, in which four pyrrole hydrogen bond donors are ideally pre-organized for anions[114–116] and ion pair binding.[117] This heterocalixarene possesses unique supramolecular characteristics and presents remarkable chemical and physico-chemical properties as well as wide application possibilities. The host properties of calixpyrroles continue to draw research interests due to their potential application as neutral substrates[118–119] optical sensors[120] and an- ion transporting agents.[121] Moreover, they have

been applied in many aspects, such as biologically active species,[122] electroanalytical chemistry,[123] colorimetry[124] as well as they have found novel application as cobalt(II)calix(4)pyrroles complex which was screened for its capability to be used as a catalyst in the epoxidation reaction.[125] The hybrid calixpyrroles are being used for biological applications such as anion sensing and antiviral drug delivery due to their amphiphilic binding characteristics.[126] A hybrid calixpyrrole chelating resin has been used for sorption studies of some noble metals like Au(III), Ag(I), Pt(IV), Pd(II) and other metal cations including Cu(II), Pb(II) and Cd(II).[127−129] Functionalized calix(4)pyrroles are also distinguished as solid supports for the separation of anionic substrates.[130]

They also show promising quality as calix(4)pyrroles modified silica gels for separation of inorganic anions, amino acids, phenols, benzene, carboxylic acids, some medicines[131] and for selective separation and pre-concentration of Ag^+ and Tl^+ by liquid liquidextraction.[132] Calix(4)pyrrole receptor used for uncharged guests species such as simple alcohols, amines and amides. Colorimetric and electrochemical sensor for anion, in addition to new support capable of separating mixture of anion. Octa-alkyl porphrinogens which was renaming as octa-alkyl calix(4)pyrrole by sessler and co-worker adopted four extreme conformation like cone, partial cone, 1,2-alternate and 1,3-alternate like calix(4)arene used for binding neutral substrates like methanol, ethanol benzyl alcohol, DMF, isopropyl alcohol, sec-butanol, N, N-dimethylacetamide and N-formylglycine ethyl ester. Selective anion complexation with octamethyl calix(4)pyrrole and 2,5-dimethylpyrrole has been investigated by Monte Carlo (MC) simulations in CH_2Cl_2 and their gas-phase calculation shown that they adopt the 1,3-alternate conformation in the absence of halide-anions and cone conformers was not stable in the presence of halide-anions due to the formation of four NH-halidehydrogen bonds[133] and octa-methyl calix(4)pyrrole-anion

complexes with colored species such as 4-nitrophenolate anion would perturb the electronic properties of the anion sufficiently to produce color change and calorimetric properties studied using UV/VIS spectroscopic techniques in CH_2Cl_2 at 25^0C.[134] Dansyl, Lissamine-rhodamine B and Fluorescien use as fluorescent labels with spacer elements contain sulfonamide or thiourea moieties provided additional H-bonding donor sites in calix(4)pyrrole which was tested as potential receptor for F^- and Cl^- . These anion studied in the form of their tetrabutyl ammonium (TBA^+) salts were chosen because of their biological importance.[135]

Calixfurans

Calixfurans are the earliest entries amongst heterocalixarenes. Calixfurans appear to be a tactful supporting actor in the chemistry of calixarenes. Regardless of their rather modest intrinsic binding abilities, the weak coordination by the furan units of calixfurans or hybrid systems plays a crucial role in certain cases. More importantly, calixfurans can be converted into a wide variety of macrocycles including those otherwise difficult to access since the furan unit serves as a versatile functional group. Further development of the synthetic strategy of calixfurans as well as the novel methods for their transformation to other functional molecules is highly anticipated. Since the conformational behavior of calixfurans has not been sufficiently clarified yet, the more sophisticated strategy for regulation of their conformational dynamics should be explored for the ready construction of the desired molecular framework. Calix(4)furan, methylene bridged cyclic oligomer of furan was first taken as the product of furan condensation reaction in the presence of ketones and HCl catalysis.[136] After the first synthesis, many other methods to make calix(4)furan and extended calix(n)furan (n = 6,8 and 10) have been reported.[137−143] Calix(4)furan also allows four main conformations and the predominant conformer is the 1,3-alternate determined by X-ray[139] and theoretical methods. Since the oxygen atom in a furan ring provides the electron abundant

nature, calix(4)furan is expected to bind cationic guest molecules.[140−141] As receptors, calix(n)furans and hybrid C_4 systems reveal some unique metal cation binding modes. As compared with calix(n)furans, calix(n)tetra-hydrofurans, show better cation binding abilities which are influenced by the cavity size and bridge substituents. Calix(n)furans constitute precursors for many otherwise inaccessible cyclic entities including heterocalix(n)arenes. The reactions of calix(4)furan (n =1, R = Me) with H_2S and H_2Se constitute the only synthesis of calix(4)thiophene and its selena analog.

Calixthiophene

Calixthiophene can be obtained by introducing a sulfur atom instead of an O or NH in a heterocycle. Calix(4)thiophene, constituting four thiophene rings in the macrocycle has been scarcely synthesized compared to the other members in the family due to its synthetic difficulty. The first synthesis was reported from calix(4)furan in the presence of H_2S and HCl.[144] Among various conformations of calix(4)thiophene, 1,3-alternate was found to be the most stable conformer by theoretical method. It was suggested that the sulfur atom in a thiophene ring acts as a soft donor and consequently interacts with soft metal cations.[145] Thiophene bearing substituents at the bridged carbon, due to steric strain, undergo facile acid catalyzed condensations with carbonyl compounds to form calix(4)thiophenes. The chemical transformation mode involving sodium sulphide induced conversion of 1,4-butadyne chromophores provides a structurally intriguing category of calix(4)thiophenes possessing cyclopropylidene bridges.

Heteracalixarenes

Heteracalixarenes i.e., thia calixarene, azacalixarene and oxacalixarene, in which bridges between phenol unit contain hetero atoms S, N or O.

Thiacalixarenes

Thiacalixarenes, the calixarene analogs having sulfide bridges instead of methylene bridges, are recent members of the calixarene family.[146]

Analytical application of various thia calixarene with their derivatives have been discussed and their metal binding affinities have been summarized by Agrawal et al.[147], Miyano et al.[148] reported a facile procedure which involved heating a mixture of p-tert-butylphenol, elemental sulfur (S_8) and NaOH in tetraethylene glycol dimethylether to afford p-tert-butylthiacalix(4)arene, accompanied by traces of p-tertbutylthiacalix(5)arene and p-tert-butylthiacalix(6)arene. The latter have also reported a high yield synthetic procedure[149−150] starting from the sulfur-bridged dimer of p-tert-butylphenol, yielding predominantly p-tert-butylthiacalix(4)arene with p-tert-butylthia-calix(6)arene and p-tert-butylthiacalix(8)arene in synthetically useful yields. Thiacalix(4)arene prepared from p-tert-octylphenol padmantyl-pheno and biphenyl-4-o have also been reported. Thiacalixarene chemistry dates back to 1997, with the first report of p-tert-butylthiacalix(4)arene, achieved through a stepwise procedure in 4% yield by Sone et al further, an intuitive strategy has been put forward for synthesis of p-tert-butylthiacalix(8)aren by terephthalate induced cyclization of a mixture of acyclic oligomers obtained by reacting a mixture of p-tert-butylphenol and sulfur in ethylene glycol/diphenyl ether in the presence of CaO. Recently, the same strategy has been extended to improve the yields of p-tert-butylthiacalix(4)arene, p-tert-butylthiacalix(6)-arene and p-tert-butylthiacalix(4)arene using different organic acids as templates.[156]

Thiacalixarenes have three intrinsic properties, viz. larger cavity, oxidizability of bridging sulfur and coordination to transition metal ions. Their ability to bind metal ions has been investigated by solvent extraction method in several studies.[157−158] 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 method. This thiacalixarene shows a high selectivity towards Cu^{+2} at pH 5.5 by coordination of the O and S donor sets. Polymeric thiacalix(4)arene derived from terephthaloyldichloride (Merrifield) resin

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is better at removing alkali (Li$^+$, Na$^+$, K$^+$, Cs$^+$) and heavy metal (Cu^{+2}, Cd^{+2}, Hg^{+2}, Pb^{+2}, Co^{+2} and Ni^{+2}) cations than the precursor thiacalix(4)arenes. 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 hydrophobicity.[159] 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. The ability of tetra(diethyl)-amide-p-   tert-butylthiacalix-(4)arene to bind 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 dichloromethane.[160] Results show that replacement of the bridging $-CH_2$ units by sulphur atoms in thiacalixarences led to a loss of selectivity within the alkali and the alkaline earth series. The thiacalixarene became selective for Pb^{+2} ion among heavy and transition metal ions. The reaction of Ag$^+$ with thiacalixarene was proved by extraction of the picrate complexes of transitory metals in the organic phase.[161] Cesium ion-selective electrodes have been fabricated from thiacalix(4)arene mono and bis(crown-6) ether derivatives which show excellent potentimetric performances with Cs$^+$/K$^+$ and Cs$^+$/Na$^+$ selectivities comparable with those of the calixcrown-based sensors.[162] Among the thiacalix(4)bis (crown-6) ethers studied, the tert-butyl derivative has better selectivity for cesium than for the other alkali cations. The effective separation of americium from radioactive waste by a chelating ionexchange method has been carried out using an octylphenyl-N,^{3} N-diisobutylcarbomoyl phosphine oxide (CMPO) or thiacalix(4)arene compound impregnated silica ionexchanger.[163] Thiacalixarence derivatives bearing amide groups effectively extract gold, palladium and platinum from chloride aqueous media via an ion-exchange mechanism.[164] With the thiacalixarene amide, the efficiency for gold separation was much higher than for the other two metal species and the recovery was almost complete. Moreover, thiacalixarene allows the selective extraction of Pd (II) via the formation of a PdCl$_2$l$_2$ 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 membrance containing thiacalix(4)arene. Solid phase extraction systems prepared by adsorption of these ligands on activated polymeric cartridges have shown good results. Thiacalix(4)arene functionalized gold electrodes have also been used as sensors,[165] since these materials present a strong affinity against sulphur derivatives and thiol groups which has an inert nature. Some thiacalixarences which are soluble in water having sulfonato groups like p-sulfonato thiacalixarence and tetra-sulfonatomethylated calix(4)resorcinarene 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 surfactant.[166]

Oxacalixarene

Homooxacalixarenes represent a new class of macrocyclic receptors analogous to calixarenes[167−169] where some or all methylene bridges between the aromatic rings are replaced by CH$_2$OCH$_2$ moieties. The oxygen atoms in the ring are potencial binding sites and this prompted study of comlexatation and liquid-liquid extraction of metal ions. The parent compound hexa homo tri oxacalix(3)arenedonot bind alkali metal ions,[170] while tri o-sustituted derivatives hexa homo tri oxa-calix(3)arene are effective but do not show marked selectivity in the extraction of Na$^+$, K$^+$ and Cs$^+$ ions.[171] Among the o-substituted derivatives with additional binding sites on the lower rim in the fixed cone conformation appears to be particularly strong and selective ligand with association constants in THF/CHCl$_3$ 1:1 at 25^{0}C larger than 107 M^{-1} for Na$^+$, Ca^{+2} and Ba^{+2} ions. Inclusion in the cage, with four cation and several cation oxygen dipole interactions,

probably occurs in the complex with Cs^+ ion for which a high extraction from water into dicholoromethane and a high selectivity are observed.[172] The shallow nest of hexa homo tri oxacalix(3)arene, both as the simple ligand and sub units in capsular hosts has proved to be particularly effective in complexation of fullerenes. The C_3 symmetry of the oxygen atoms array in the derivatives of hexa homo tri oxacalix(3)arene is suitable for complexation of primary ammonium ions. The cone form tri butyl ether of hexa homo tri oxacalix(3)arene showed a high affinity for $Bu-NH_3^+$ ions.[173−176] Homo oxacalixarene strongly binds quaternary ammonium ions in lipophilic in the absence of such relatively strong interaction as hydrophobic forces, hydrogen bonding and ion paring with the ligand, this binding essentially relies on the cation-π inter action.[177] Homooxacalix(3)arene forms 1:1 complex with C_{60} in the solid state having ball and socket structure in which host molecule are perfect in the cone conformation with C_3V symmetry. The study of complexing ability of oxacalix(3)arenes by extraction from water solution of Li, Na or K picrates into CH_2Cl_2 and by 1_H NMR spectroscopic membrane showed that oxacalixarene selectively measurements during titration with metal triflates.

Azacalixarene

Azacalixarenes, which are generated by the insertion of nitrogen atoms into the bridging ethylene unit of the calixarene structure, have several isomers based on the position of the nitrogen atoms and the ring size. Azacalixarenes can be easily synthesized by heating bis(hydroxymethyl)phenol derivatives and benzylamines in refluxing toluene or xylene for 3 days. The desired cyclic compounds are obtained selectively in moderate to high yields. The choice of non-polar solvents is essential in this reaction because the template effect by OH-OH, OH-N hydrogen bonds play an important role in the cyclization.[178] Thus, the high dilution technique is not required in this reaction. Several reports support this phenomenon i.e., a phenol cyclic trimer was observed in supersonic jets.[179] Generally, condensation reactions

between alcohol and amines require drastic reaction conditions and catalysts.[180] However, in the case of hydroxyl methylphenols, C-N bond formation occurs under relatively mild conditions. In particular, in spite of their potential richness and versatility as ligands, the structural studies of their complexes are scarce compared to those of calixarenes and even oxacalixarenes, which are another closely related family of expanded calixarenes. The presence of a soft nitrogen atom in azacalixarenes is envisioned to bind soft cations like ion metals according to hard soft acid and base principle (HSAB) as well as other specific features such as building sophisticated receptors, metal ligand systemsetc. The triaza[3.3.3] N-benzyl-triaza[3.3.3] extracted UO_2^{+2} efficiently even in the presence of a high concentration of NaCl. The extraction ability has a high pH dependency; uranyl ion is most effectively extracted in the neutral region. Since azacalixarenes have nitrogen atoms as a base, they form metal complexes under neutral conditions. Lanthanide extraction experiments were carried out by using N-(2-picolyl)-triaza[3.3.3] derivatives as a ligand in order to investigate the metal selectivities among lanthanide ions. It was showed that triaza[3.3.3] derivatives as a ligand extracted alkali metal ions efficiently, but the selectivity was very poor because of the flexibility of the picolyl side arms. In the case of lanthanide ions, extraction occurred very efficiently, however, the extraction is very sensitive to the pH of the aqueous phase. Thury etal. prepared UO_2^{+2}, Nd^{+3} and Yb^{+3} complexes of azacalixarenes without using any bases and succeeded in obtaining complexes suitable for crystallographic analysis.[181] Interestingly, in the crystal structures, OH protons are not located on the oxygen atoms but are transferred to nitrogen atoms and form intramolecular zwitter ionic structures. The metal ions are placed out of the plane of the $O–NH^+–O$ linkage this is ascribed to the $NH^+–M^+$ repulsion. A review by Thury et al. described the complexes of element ions of oxa and azacalixarenes.[182] Since azacalixarenes have nitrogen and oxygen atoms in the cyclic structure and if nitrogen atoms have a positive

charge, generation of an intramolecular betaine compound is expected by the dissociation of OH protons similar to the metal complexes.[183] Calix(aza)crown ether refers to the molecules combining calixarene elements and azacrown units. The first calix(aza)crown were prepared by the reactions of either calix dimethyl ester with the appropriate diamine -NH_2NH_2 and were shown to complex with divalent (Be^{+2}, Mg^{+2}, Ca^{+2}, Sr^{+2} and Ba^{+2}) and trivalent (Sc^{+3}, Y^{+3}, In^{+3}, Gd^{+3} and Bi^{+3}) metal ions.[184] Complexes with NH_4^+ with calixazacrown have been reported by Kim et al.[185] by synthesizing 1,3 alternate calix(4)azacrown. Yb^{+3}, Nd^{+3} and alkali metal binding properties of homoazacalix(n)arene have been reported.[186−188]

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