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REVIEW ARTICLE

Analytical applications of calixarenes from 2005 up-to-date

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Abstract Calixarenes, as nano-baskets, are considered an important group of macrocycles as the third famous host molecules after cyclodextrins and crown ethers have been subject to extensive researches in construction of many extractants, transporters, stationary phases, electrode ionophores and optical and electrochemical sensors over the past four decades. Because of the recent rapid growth in the publications of calixarene applications, this review paper has focused on different analytical applications of calixarenes in the main fields of separation, electroanalysis, spectroscopy and chemometrics. The objectives and the results of about 300 references mainly were published in recent 6 years with emphasis on the analytical applications were reviewed.

Keywords Calixarene · Complexation · Separation · Electroanalysis · Spectroscopy · Chemometrics

Introduction

Supramolecular chemistry is a field of chemistry that studies the multimolecular species formed from complexation of molecular components with relatively similar structures. These systems are bound together reversibly by intermolecular forces, rather than by covalent bonds and shared electrons. Ganjali et al. [1] reported that evolution of macrocycles field comes back to 1987 when Lehn, Cram and Pedersen won the Nobel Prize in chemistry for synthesizing compounds with cavities within which metal ions and other molecules could be bound. After that, crown ethers were synthesized which were capable to form selective complexes with alkali ions, extensive researches were carried out on the selectivity and stability of the resulting complexes.

Calixarenes, were introduced in 1870 for the first time but were ignored until 1940. In 1970s they were studied with uncertainty. During 1990 they were presented in brief out line with an emphasize on the use of these molecules for chemical separations. Gutsche was the first to draw attention to the potential use of them as molecular receptors or enzyme mimics. He proposed that these cyclic oligomers, known as collectively calixarenes in 1978, having recognized in space-filling models of the tetramer a chalice or cup-like shape reminiscent of a Greek crater vase.

Baldini et al. [2] the concept of valency as the number of ligating functionalities of the same or similar types in a supramolecule and connected to each of the guest entities. Calixarenes were obtained by the oligomerisation of phenol and formaldehyde and their valency can be easily varied at least from 1 to 8, while the stereochemical orientation of the ligating arms can be properly tuned by shaping.

Depending upon the relative orientation of the para and phenolic sites, the tetramer (calix[4]arene) can adopt four different conformations [3]. Baldini et al. [2] in their review paper, illustrated these conformations of calixarenes

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including: cone, partial cone, 1,2-alternate, and 1,3-alternate. Various methods for functionalizing calixarenes have been developed and numerous calixarene derivatives have been synthesized during the past two decades. Akkus et al. [4] have referred to Tabakci's paper and reported that the binding properties of calixarenes appear to be highly dependent upon the nature and the number of donor atoms of the calix[4]arene moiety.

Because the three or more lower rim phenolic hydroxyls, they can be easily functionalized to provide variety of donor groups by comparatively straightforward reactions. Calixarenes receiving intensive studies in host–guest chemistry are mainly those that are functionalized on the lower rim with hydrogen or *p*-*tert*-butyl groups on the upper rim. Identities of the para substituents on the upper rim (i.e., substituents in parapositions relative to the phenolic oxygens) also influence the ionophoric propensities of these ligands. However this feature has been much less explored due to the lack of suitable functionalization on the upper rim.

Various applications of calixarenes are used in purification, chromatography, catalysis, enzyme mimics, ion selective electrodes, phase transfer, transport across membranes, ion channels, and self-assembling monolayers [5]. Different complexing groups at the upper rim of calixarenes are able to attract desirable molecules with pre-defined selectivity. The lower rim functional groups of calixarenes are usually responsible for physical properties of calixarene molecules [6].

Calixarenes have demonstrated outstanding complex ability towards ions, neutral molecules, etc., and are considered as the third best host molecules after cyclodextrins and crown ethers [7]. During the last three decades calixarene chromoionophores have long been studied as specific metal ion indicators. Various types of chromogenic calix[4]arene derivatives have recently been synthesized which have shown selective recognition and complexation with metal ions [8]. The analysis without first requiring physical separation is a major driving force for separation techniques, which calixarenes have been used for this purpose [9].

Calixarenes are, in fact, ideal 'molecular platforms' for the introduction of specific ligating arms in a preorganized pattern. So, depending on the nature of the ligating groups and on the dimension of the macrocyclic scaffold, these ligands become selective for certain kind of metal ion. Moreover, the ligands to be used in the hydrometallurgic processes associated with radioactive waste treatment, should also operate under harsh chemical and radiolytic conditions. Although several ligands have been well studied in terms of chemical stability in acid conditions, their behavior under irradiation condition has been less explored [10].

In chromatography, calixarenes are often used as mobile phase additives for HPLC and chemically bonded stationary phase for both GC and HPLC. Calixarene-bonded stationary phases are preferable to be used in HPLC, because the UV detection of analytes is hindered by strong absorbance of calixarenes. Furthermore, poor solubility of most calixarenes precludes their applications as additives in aqueous eluents [11].

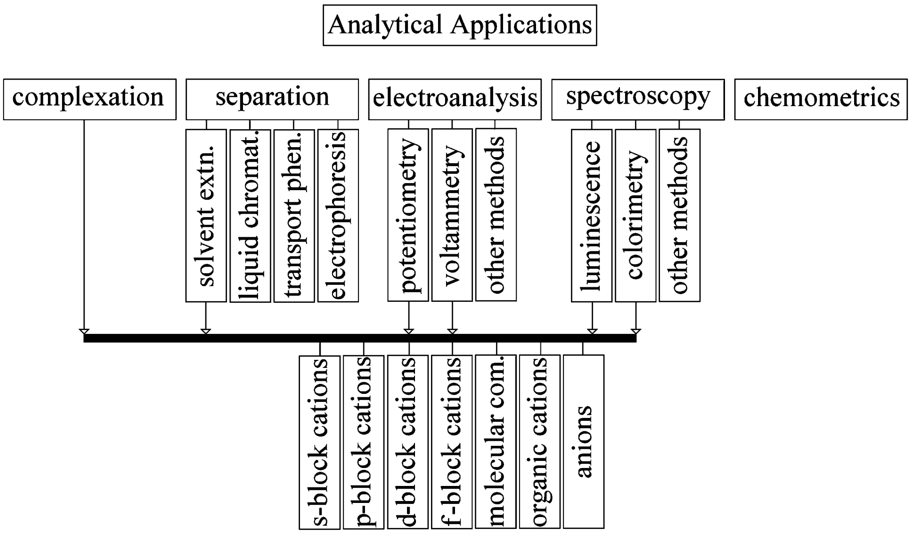
The ionophore properties of calixarenes have been also assessed by using these molecules for fabrication of ion-selective potentiometric sensors [12]. Appropriately functionalized calix[4]arenes have been used as carriers in ion selective membranes. Predominantly, calixarenes containing ester, ether, carboxylic acid and carbamate have been reported for using as ion-selective electrode (ISE) for alkali metal ions [13].

Piezoelectric quartz crystal calixarene sensors have been designed to monitor the volatile organics in the gas phase and in the aqueous solution. Electrochemical sensors based on calixarenes have been shown to be sensitive to various metal ions. It has also been found that the UV–Vis spectra of certain azoderivatives of calixarene changes upon the binding of metal ions or amines. Optical sensors based on these chromogenic calixarenes have been designed to detect various metal ions, gaseous ammonia, and organic amines [14].

Recently, many authors have laid particular stress on the sensitized luminescence of lanthanide ions complexes with calixarene derivatives because these functional complexes show potential applications, such as probes and labels for chemical and biological applications [15]. Most of the research on calix[4]arenes as chromogenic ionophores involves the modification of the lower rim with metal-chelating groups such as acids, amides, esters, ketones, or any ligand that contains lone pair electrons, and then a fluorophore or chromophore is attached on the upper rim [16].

In this paper, a tutorial algorithm was designed to explain the recent applications of calixarenes and its derivatives in analytical chemistry. The applications of calixarene derivatives in five main fields of complexation, separation, electroanalysis, spectroscopy, and chemometrics, are reviewed. Figure 1 presents the flowchart of this manuscript containing a brief discussion from about 300 references in binding and complexation studies, solvent extraction, liquid chromatography, transport phenomena, electrophoresis, potentiometry, voltammetry, conductometry, electrochemical and spectroscopic sensors, luminescence, colorimetry and chemometrics.

Fig. 1 The flowchart of this review



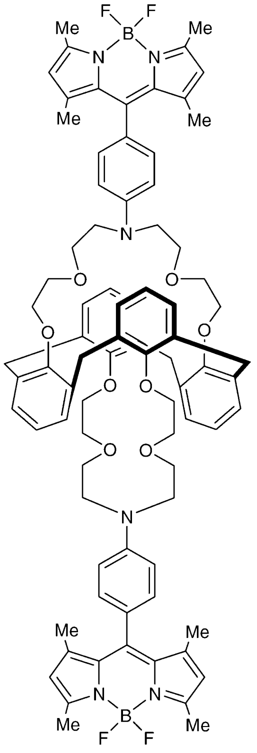
Calixarenes applications in complexation studies

Calixarenes accommodate neutral and ionic species and complexation is their important feature. Complexation studies are reviewed in this section, followed by the abstracted tables, which listed the research works on calixarenes complexation.

s-Block (alkali and alkaline earth) cations

Diamond in 1986 published the first calixarene-sodium complex which were useful in the estimation of sodium cation in blood. After that many researches were conducted on the alkali and alkaline earth cations. Table 1 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and *s*-block cations.

Iranian researchers [3] evaluated the complexation abilities of 26,28-bis-benzyloxy-25,27-dihydroxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene and 25,26,27,28-tetra-benzyloxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene towards alkali metal ions Li^+, Na^+, K^+, Rb^+, and Cs^+ in methanol–chloroform mixture. Yaftian et al. [17] evaluated the complexation ability of a phosphinoymethoxy calix[4]arene towards alkaline earth cations. The stability constants of complexes of boron-dipyrromethene dye 1,3-alt calix-[4]bisazacrown-5 (**01**) with Na^+, K^+, Cs^+, Ca^{2+} and Ba^{2+} ions were determined by Sliwa and Girek [18]. Two aza-crown-5 ether binding sites well fitted the K^+ ion and showed a very high K^+/Na^+ selectivity in acetonitrile, ethanol and ethanol/water mixtures.



01

Finlander chemists reviewed the synthesis and properties of calix[4–8]crowns, calix[4–8]biscrowns and resorcinarenecrowns and concluded that these macrocycles exhibit remarkable ionophoric properties towards alkali and alkaline earth metal cations. Their selectivity has been attributed to their structural features (size of the crown

Table 1 List of calixarenes used in complexation studies with *s*-block cations

Type of calixarene	Analytes were used	References
Benzyloxy-hydroxycalix[4]arene	Li^+, Na^+, K^+, Rb^+ and Cs^+	[3]
Phosphinoymethoxy calix[4]arene	Li^+, Na^+, K^+, Rb^+ and Cs^+	[17]
1,3-alt Calix[4]bisazacrown-5	K^+	[18]
Calix[4–8]crowns and calix [4–8]biscrowns	Alkali and alkaline earth metal cations	[19]
Calixcrowns, calixbiscrowns	Alkali and alkaline earth metal cations	[20]
C_3-symmetrical *p-tert*-butylhexahomotrithiacalix[3]arene	Alkali metal cations	[21]
Azocalixarenes	Alkali and alkaline earth metal cations	[22]
p-Tetraphenyl tetrahomodioxacalix[4] arene ethylester	Alkali and alkaline earth metal cations	[23]
p-Tetraphenyl tetrahomodioxacalix[4] arene amide	Alkali and alkaline earth metal cations	[24]
Calix[4]arenes bearing hydroxystyryl cyanine dyes	Li^+	[25]
1,3-alternate Thiacalix[4]arene	Li^+	[26]
Tetra-*tert*-butyl-tetrakis(methyl-α-phenylglycylcarbonylmethoxy)calix[4]arene	Alkali metal cations	[27]
Calix[4]arene bearing two ester, polyether, urea, and bipyridine units	Na^+	[28]
Cone and 1,3-alternate tetrakis[(*N*, *N*-diethylaminocarbonyl)methoxy] thiacalix[4]arene	Na^+ and K^+	[29]
Calix[4]pyrroles	Cs_2CO_3	[30]
Calix[4]arene bearing azopyridyl moieties	Radioactive Cs^+	[9]
A cone-shaped calixarene	Mg^{2+} and Ca^{2+}	[31]
1,3-alternate Calix-biscrowns	Cs^+	[18]

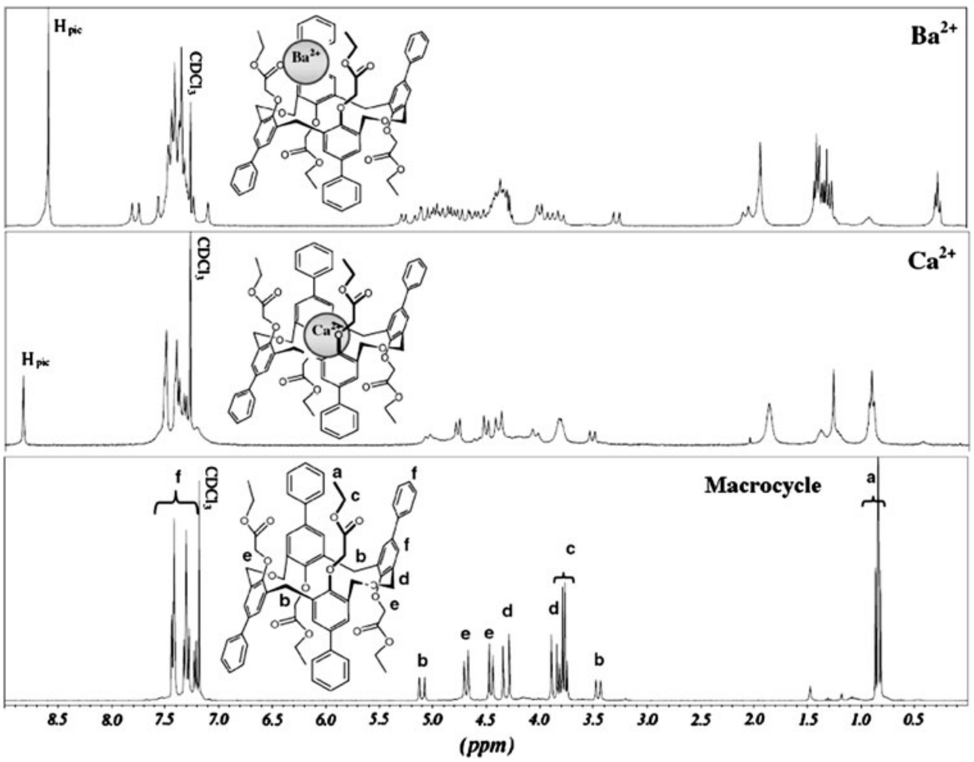
ether moiety) and conformation of the parent calixarene [19]. Kim and Vicens [20] reviewed the complexing properties of calixcrowns, calixbiscrowns and related compounds such as resorcinarene crowns and they reported that calixcrowns exhibit remarkable ionophoric properties towards alkali and alkaline earth metal cations.

Ashram in Jordan synthesized C_3-symmetrical *p-tert*-butylhexahomotrithiacalix[3]arene and studied its binding properties with alkali cations using biphasic picrate extraction method. The results showed only weak abilities to bind the alkali cations examined [21]. In Turkey, complexation of azocalixarenes towards alkali and alkaline earth metal cations and their applications were reviewed [22]. In Tunisia, the complexation and binding properties of *p*-tetraphenyl tetrahomodioxacalix[4]arene ethylester [23] and *p*-tetraphenyl tetrahomodioxacalix[4]arene amide [24] derivatives towards alkali and alkaline earth metal cations was studied using UV-absorption spectrophotometry and ^{1}H-NMR spectroscopy. Figure 2 presents ^{1}H-NMR spectra of first macrocycle and related complexes.

Calix[4]arene derivatives bearing one or two hydroxystyryl cyanine dyes at the wide rim were synthesized and the influence of Li^+ on its UV–Vis spectra was investigated [25]. In Japan, Perez-Casas et al. [26] examined the binding behaviors of 1,3-alternate thiacalix[4]arene with Li^+ by ^{1}H NMR titration experiment. The exclusive formation of mononuclear complexes of was observed even though the formation of the heterogeneous binuclear complexes was expected. In Croatia [27], the solvent effect on the binding ability of alkali metal cations with 5,11,17,23-tetra-*tert*-butyl-26,28,25,27-tetrakis(*O*-methyl-D-α-phenylglycylcarbonylmethoxy)calix[4]arene was examined in methanol and acetonitrile solutions with different affinities for hydrogen bonding by means of spectrophotometric, conductometric and potentiometric titrations. The intramolecular (NH···O=C) hydrogen bonds in macrocycle need to be disrupted to allow metal ion binding, but it was shown to be an efficient binder for Li^+ and Na^+ cations in acetonitrile and moderately efficient for K^+; Whereas, Rb^+ and Cs^+ did not fit in its cavity. The complex stabilities in methanol were measured to be significantly lower.

Nabeshima et al. [28] synthesized a calix[4]arene framework bearing two ester units, two polyether units, two urea units, and two bipyridine units and used it to recognize Na^+. Casas and Yamato [29] assessed the complexation behaviors of both *cone* and 1,3-alternate tetrakis[(*N*,*N*-diethylaminocarbonyl)methoxy] thiacalix[4]arene by ^{1}H NMR titration experiments. They obtained the evidence of

Fig. 2 ^{1}H-NMR spectra of *p*-tetraphenyl tetrahomodioxacalix[4]arene macrocycle and its complexes towards two alkaline earth metal cations



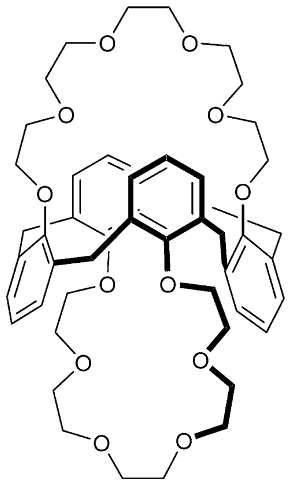
1:2 (homo- and hetero-binuclear) complexes formation of 1,3-alternate derivative with K$^+$ and Na$^+$ cations. Custelcean et al. [30] studied the complexation of calix[4]pyrrole with cesium carbonate. A single anion bridged two calix[4]pyrroles–cesium complexes and formed a crystal structure of Cs_2CO_3 complex.

Arora et al. [9] reported that calix[4]arene bearing azopyridyl moieties at the upper rim can be used as a selective filter for radioactive wastes containing Cs$^+$. *A cone*-shaped calixarene that influenced the Mg^{2+}, ATP-dependent Ca^{2+} accumulation in mitochondria and sarcoplasmatic reticulum of the smooth muscle cells was synthesized and investigated in Ukraine by Klyachina et al. [31]. Polish chemists [18] presented the complexation of 1,3-alt calix-biscrowns with hard cations like Cs$^+$ via π interaction. They reported that 1,3-alternate derivatives have oxygen atoms able to bind hard cations and they have *p*-basic aromatic cavity which may bind soft electron acceptors.

p-Block cations

One of the most interesting properties of the macrocyclic calixarenes is their capacity to recognize *p*-block cations because of their ability to form compounds of high stability with these chemical species. Table 2 presents the complexation studies conducted on calixarene derivatives and *p*-block cations.

Bochenska et al. [32] synthesized a number of *p-tert*-butylcalix[4]arene thioamides and presented the X-ray structures of the macrocycle towards $Pb(ClO_4)_2$. Its slightly distorted *cone* conformation was established. Sliwa and Girek [18] reported that the 1,3-alt-calixbiscrowns are able to coordinate metal ions via π interaction. They contain π-basic aromatic cavity that may bind soft electron acceptors and they have oxygen atoms able to bind hard cations. Therefore **02** may serve as a receptor for Tl$^+$.



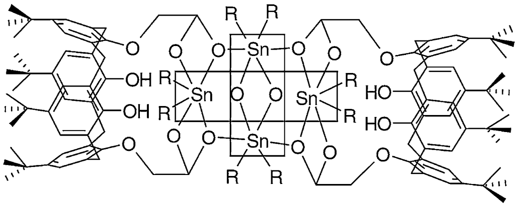
02

Konishi et al. [33] used electrospray-ionization mass spectrometry to study the complexation of π-coordinate calix[4]arene derivatives toward Tl$^+$. Competitive

Table 2 List of calixarenes used in complexation studies with *p*-block cations

Type of calixarene	Analytes were used	References
p-*tert*-Butylcalix[4]arene thioamides	$Pb(ClO_4)_2$	[32]
1,3-alt-Calixbiscrowns	Tl^+	[18]
Calix[4]arene derivatives	Tl^+	[33]
p-Sulfonatothiacalix[4]arene	Tl^+	[34]
Calix[4]arene diethers	Germanium and tin	[35]
Calix[4]arene-1,3-di-acid derivative	Sn^{4+}	[36]

complexation of three calix[4]arene derivatives demonstrated no effect of olefinic substituents and their location on the Tl^+ complexation. They also determined the stability constants for the complexes in methanol using 18-crown-6 as the reference ligand. Guo et al. [34] reported that Tl^+ is particularly favorable to be included into the cavity of *p*-sulfonatothiacalix[4]arene due to the cation polarizability. American chemists [35] prepared germanium and tin complexes of calix[4]arene diethers and demonstrated that the produced complex exist as *exo* and *endo* isomers in which the metal is located either outside or inside the calixarene cavity. The *exo* isomer was considered to be the kinetic product, whereas the *endo* isomer was thermodynamically more stable. Amjad et al. [36] synthesized Sn^{4+} complexes (**03** and **04**) with a calix[4]-arene-1,3-di-acid derivative to investigate the ability of Sn^{4+} complexes in preventing absorption of lead.



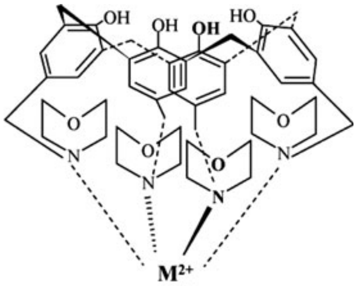
$R_1=CH_3$ $R_2=CH_2CH_2CH_2CH_3$

03 and 04

d-Block (transition and heavy) cations

The selective interaction process between calixarenes and transition metal ions requires among other conditions, structural characteristics and dimensions of the cavity formed by the calixarene ring so that it can be capable to fit suitably to a specific cation. The efficiency of interaction may also be affected by the nature of the metal ion and by the number, distance and orientation of the donor atoms of calixarene that are structurally accessible to the complexed cation. The ability of the solvent molecules to compete with the donor atoms of the calixarene towards the coordination sites of the cation, is another factor that can thermodynamically influence the complexation process. Table 3 presented the content of this sub-section including the complexation studies conducted on calixarene derivatives and *d*-block cations.

Mewis and Archibald [37] outlined recent advances towards biomedical applications of calixarene complexes with transition metals. Seigle-Ferrand et al. [38] synthesized a calixarenic ditopic podand incorporating at the lower and upper rims two bipyridine and two dipyrrolyl groups, respectively. This calixarene fixed in cone conformation formed complexes with Cu^+ but with different stoichiometries. Qureshi et al. [8] studied complexation behavior of *p*-morpholinomethylcalix[4]arene (**05**) toward Cu^{2+}, Co^{2+} and Ni^{2+} by UV–Vis and fluorescence techniques.



05

Gaetano et al. [39] synthesized a calix[4]arene derivative incorporating two bipyridyl groups and one primary amino attachment function at the lower rim. They coupled it to Wang benzaldehyde resin and displayed its complexation abilities towards Cu^+ and Zn^{2+} cations. Arena et al. [40] introduced sulfonato groups into the backbone of a bipyridyl-based calixarene to obtain a novel water-soluble compound able to complex Cu^{2+} and Co^{2+} and showed the different stoichiometries and stabilities of new complexes from the analogous water insoluble calixarene by spectrophotometric titration. Creaven et al. [41] synthesized two novel calix[4]arene:Schiff base receptors, one had prepared by two pendant aldimines, while the other had two-point attachment of a calixarene:dialdehyde onto a calixarene:diamine to form a calix-tube. Its binding with $AgClO_4$ showed large complexation-induced shifts in H NMR positions.

Korean chemists [42] synthesized two calix[4]arene derivatives containing four alkyl thiol linkages, which that allow the calixarenes to attach onto the gold surface. The silver ion had affinity only to one of the monolayers, which had hydrophobic polarity. O'Dwyer and Cunnane [43] investigated the stoichiometry of *O*,*O*″-bis[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene-silver complex in water|1, 2-dichloroethane interface and they found that the

Table 3 List of calixarenes used in complexation studies with *d*-block cations

Type of calixarene	Analytes were used	References
–	Transition metals	[37]
Bipyridine-dipyrrolyl calixarene	Cu^+	[38]
p-Morpholinomethylcalix[4]arene	Cu^{2+}, Co^{2+} and Ni^{2+}	[8]
Bipyridyl-amino calixarene	Cu^+ and Zn^{2+}	[39]
Sulfonato dipyridylcalixarene	Cu^{2+} and Co^{2+}	[40]
Aldimines calix[4]arene-Schiff base	$AgClO_4$	[41]
Alkyl thiol calix[4]arene	Ag^+	[42]
O,*O*″-bis[2-(Methylthio)-ethyl]-*tert*-butylcalix[4]arene	Ag^+	[43]
Calix[4]pyrrole Schiff base	Cu^+ and Cu^{2+}	[44]
Tetraalkyl(tolyl)thiomethylcalix[4]arenes	Pd^{2+} and Ag^+	[45]
1,3-alternate Thiacalix[4]arene bearing two rhodamine B lactams	Cr^{3+} and Fe^{3+}	[46]
1,3-alternate Thiacalix[4]arene	Ag^+	[26]
Tetramethyl-tetra(4-hydroxy phenyl) calix[4]pyrrole and tetramethyl-tetra(dihydroxy phenyl) calix[4]pyrrole	Cu^{2+}	[47]
Azocalix[4]arenes	Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^+, Hg^+ and Hg^{2+}	[48]
Azocalixarenes	Transition metal cations	[22]
Tetraphosphineoxide calix[4]arene	Co^{2+} and Ni^{2+}	[49]
Thiacalix[4]arene	Ag^+	[50]
p-*tert*-Butyl-*thia*calix[4]arenes and *p*-*tert*-butylcalix[4]arenes	Transition metal cations	[51]
Calix[4]arenes	Ag^+	[33]
Calixarenes bearing *β*-ketoimine groups	Cu^{2+}, Ag^+ and Hg^{2+}	[52]

stoichiometry was shifted from 1:1 to 1:2 (metal:ligand) with increasing ionophore concentration. Veauthier et al. [44] used a calix[4]pyrrole Schiff base as binucleating ligand for Cu^+ and Cu^{2+}. In Cu^+ complexes, the metal centers were found to have a distorted tetrahedral geometry, while with Cu^{2+} the metal centers assumed distorted square planar geometry.

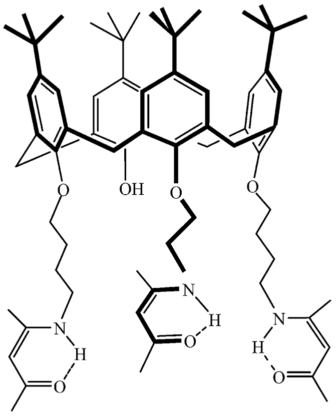
Torgov et al. [45] studied Pd^{2+} and Ag^+ complexation by tetraalkyl(tolyl)thiomethylcalix[4]arenes from main fission products. The stoichiometry and structural features of the complexes were studied by extraction, IR and mass spectroscopy methods, and quantum mechanical calculations. Chinese and Japanese chemists synthesized 1,3-alternate thiacalix[4]arene bearing two rhodamine B lactams to capture Cr^{3+} and Fe^{3+} in a fluorescent sensor. The association constants and stoichiometric ratios of the complexes were determined, and they showed that the presence of Fe^{3+} or Cr^{3+} induced the sensor to form a stable 1:1 complex [46]. The complexation and binding behaviors of 1,3-alternate thiacalix[4]arene with Ag^+ were examined by ^1H NMR titration experiments in Japan [26]. Indian chemists synthesized the *meso*-tetra(methyl) *meso*-tetra(4-hydroxy phenyl) calix[4]pyrrole, *meso*-tetra (methyl) *meso*-tetra(3,5-dihydroxy phenyl) calix[4]pyrrole and their azo dyes and studied their efficiency towards Cu^{2+} using UV–Vis spectrophotometry. The experimental results showed a distinct color change from yellow to red upon complexation [47].

Turkish scientists [48] synthesized four azocalix[4]arenes and investigated their complexes with Cu^{2+}, Ni^{2+} and Co^{2+} by means of UV–Vis, IR, and ^1H-NMR spectroscopic techniques. They reported that all the complexes have a metal:ligand ratio of 2:1 and the azocalix[4]arenes complexes with Cu^{2+}, Ni^{2+} are square-planar, while the Co^{2+} complexes are octahedral with water molecules as axial ligands. The thermal stability of metal:azocalix[4]arene complexes with Ag^+, Hg^+ and Hg^{2+} were also reported. Deligöz [22] reviewed azocalixarenes complexation for transition metal cations and reported a wide variety of their applications by the functionalization of the side arms.

Russian and Ukrainian chemists [49] synthesized the monomeric and the polymeric 1:2 complexes of a tetraphosphineoxide calix[4]arene with Co^{2+} and Ni^{2+} nitrates. Base upon their results, in the monomeric complexes each metal cation was coordinated by two bidentate NO_3-ligands and two proximal P=O groups at the calixarene skeleton.

Tanaka et al. [50] studied the complexation of thiacalix[4]arene with Ag^+. Bouhroum et al. [51] reported the synthesis and crystal structure of *p-tert*-butyl-*thia*calix[4]-arene and *p-tert*-butylcalix[4]arene derivatives. They established their cation-binding properties by liquid–liquid extraction of metal picrates from water into dichloromethane. The stability constants were determination in acetonitrile using UV-absorption spectrophotometry. They found the stoichiometry of complexes to be 1:1 and the location of the metal cations was shown by ^1H NMR to be nearby the sulfur atoms.

Japanese chemists [33] investigated the complexation of π-coordinate calix[4]arene derivatives toward Ag^+. Competitive complexation of three calix[4]arene derivatives demonstrated a significant effect of olefinic substituents and their location on Ag^+ complexation. They determined the stability constants for Ag^+:calix[4]arene derivative complexes in methanol using a reference ligand (18-crown-6). Sliwa and Deska [52] reviewed the calixarene complexes with soft metal ions including copper, silver, gold, zinc, cadmium, and mercury cations. They introduced the calixarenes bearing β-ketoimine groups (**06**) enable to complex with transition metal cations (Cu^{2+}, Ag^+ and Hg^{2+}) in a cone conformation.



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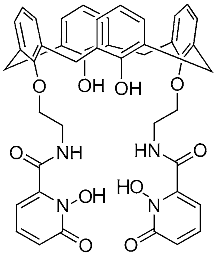
f-Block (lanthanide and actinide) cations

The complexation selectivity of calixarenes with *f*-block cations has often been explained in terms of the size-fit concept that the calixarene forms a more stable complex with the cation which is more suitable in size for the calixarene cavity. Table 4 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and *f*-block cations.

Mariani et al. [10] selected calixarene-based picolinamide ligands and determined the distribution coefficients for actinides and lanthanides. Leydier et al. [53] synthesized hydroxypyridinone (**07** and **08**) and sulfocatecholamide (**09**) calixarene ligands and determined their binding abilities for uranyl cation. They exhibited significant affinity towards uranyl ion at acidic and basic pHs, respectively.



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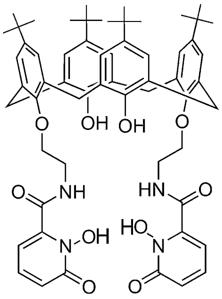

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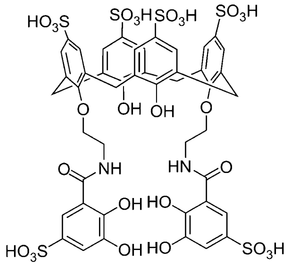

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Table 4 List of calixarenes used in complexation studies with *f*-block cations

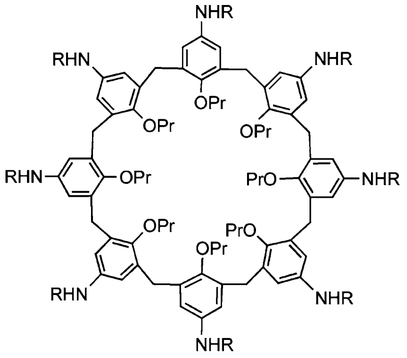
Type of calixarene	Analytes were used	References
Calixarene-based picolinamide	Actinides and lanthanides	[10]
Hydroxypyridinone and sulfocatecholamide calixarene	Uranyl	[53]
–	Gd^{3+}	[37]
Phosphorylated calixarenes	Europium, americium, thorium and uranyl cations	[54]
Thiacalix[4]arene complex	Tb^{3+}	[50]

Mewis and Archibald [37] reviewed some biomedical applications of macrocyclic ligand complexes like functionalised a calixarene to give four Gd^{3+}-DOTA (1,4,7,10-tetraazacyclododecane-1,4,7-triacetic acid) units attached on the upper rim. Karavan et al. [54] used phosphorylated calixarenes for recognition of europium, americium, thorium and uranyl ions and studding their complexes in single media (methanol and acetonitrile) followed by UV-spectrophotometric and isoperibolic calorimetric titrations. Japanese chemists [50] studied the structure of thiacalix[4]arene complex with Tb^{3+} and discussed how the donor atoms (sulfur and oxygen) showed high selectivity toward Tb^{3+}.

Molecular compounds

This sub-section focuses on the applications of calixarenes in complexation studies of molecular compounds. Table 5 presented the content of this subsection including the complexation studies conducted on calixarene derivatives and molecular spices.

Heparin recognition of calix[8]arene polycations (**10–13**) was compared with two other heparin antagonists: protamine and polylysine. Experiments confirmed that calixarene derivatives have a very high specificity and affinity than other antagonists towards heparin neutralization as in aqueous solution as in blood [55].



R = L- Lys
R = $CO(CH_2)_6NH_2$
R = L- Lys
R = $CO(CH_2)_6NH_2$

10-13

Baldini et al. [2] reviewed the fundamental aspects of multivalency and the properties of calixarene-based multivalent ligands in lectin binding and inhibition, protein surface recognition, DNA condensation and cell transfection, crystal engineering, self-assembly, and nanofabrication. Haino et al. [56] revealed that syn isomer of a double calix[5]arene selectively captured higher fullerenes from fullerene mixtures and by elevation of the temperature more than 100 °C, its conformational was changed to the anti isomer and liberated the captured fullerenes. Drug toxicity in humans and animals is a major concern; Hence, Brazilian chemists [57] investigated the complexation properties of detoxificant agents. They investigated the

Table 5 List of calixarenes used in complexation studies with molecular spices

Type of calixarene	Analytes were used	References
Calix[8]arene polycations	Heparin	[55]
–	Lectin, proteins, DNA and cells	[2]
Double calix[5]arene	Fullerenes	[56]
p-Sulfonic acid calix[6]arene	Pyrrolizidine	[57]
Sulfonatocalixarene	Topotecan	[58]
p-Sulfonatocalix[6]arene	Phenothiazine dyes	[59]
p-Sulfonatocalix[4,6,8]arenes	NADPH oxidase	[60]
p-Sulfonatocalix[*n*]arenes	Heparin	[61]
Calix[4]arene phosphonic acids	Methyl esters of amino acids	[62]
p-Ooctanoylcalix[4]arene	Tetrahydrofuran	[63]
Calixarenes, thiacalix[4]arene-tetrasulfonate and calix[6]arene-hexasulfonate	Fullerenes	[64]
p-Sulfonatocalix[8]arene	Phenothiazine dyes	[65]
1,2,3-alternate Calix[6]arene	Piperidine and triethylamines	[66]
Octaethyl-*p*-*tert*-butylcalix[8]arene	Methylene blue	[67]
Tetrabromocalix[4]arenes	Nitrile	[68]
p-Sulphonic acid calix[6]arene	Anesthetic tetracaine	[69]
p-Sulfonatocalix[*n*]arenes	Bovine serum albumin (BSA)	[70]
bis-1,3-Urea calix[4]arenes	α-amino acids	[71]
4-Sulphonato-calix[*n*]arenas	Niclosamide	[72]
p-Sulfonated calix[4, 6]arenes	Carbamazepine	[73]
Calix[4]resorcinarene	2-Naphthol and 1,5-naphthalenediamine	[74]
Calix[4]arene bis-hydroxymethylphosphous acid	Glycine, L-leucine, L-alanine, L-valine, and L-isoleucine	[75]

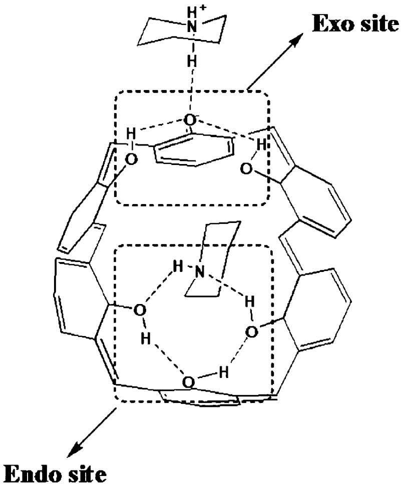
inclusion complexation of a toxic alkaloid (pyrrolizidine) and *p*-sulfonic acid calix[6]arene by NMR techniques.

Wang et al. [58] prepared inclusion complexes of topotecan with sulfonatocalixarene and investigated the stoichiometry, complex stability constants, and inclusion mode by means of 2D NMR and UV–Vis spectroscopy. They elucidated that the dimethylaminomethyl group of topotecan and the quinoline ring were encapsulated in sulfonatocalixarene and the complex was more soluble than free topotecan. Inazumi et al. [59] studied the inclusion complexation of *p*-sulfonatocalix[6]arene with three kinds of phenothiazine dyes spectrophotometrically in a mixture of ionic liquid and ethanol and determined their association constants under external static pressure up to 767 bar. The results of study revealed that with increasing external pressure, the inclusion equilibrium was shifted to the dissociation side in the alcohol–water mixtures; while, it was shifted to the association side in the ionic liquid mixture.

French researchers [60] used three water soluble calix[*n*]arene derivatives including *p*-sulfonatocalix[4,6,8]arenes to investigate the effects of them on the activation of NADPH oxidase in neutrophils. They showed that all three molecules do not induce NADPH oxidase activation, and hence do not stimulate neutrophils and are not cytotoxic. Silva et al. [61] investigated the anti-thrombotic activity of water soluble *p*-sulfonato-calix[*n*]arenes and six *O*-mono-substituted derivatives (like heparin) and proposed a mechanism for the anticoagulant effect of those calixarenes. Dziemidowicz et al. [62] synthesized calix[4]arene phosphonic acids with various substituents at the lower rim and studied their complexing properties towards methyl esters of six amino acids using ^{1}H NMR spectroscopy. They observed mixed 2:1 and 1:2 (host–guest) complexes with all amino acids methyl esters.

Shahgaldian et al. [63] reported double inclusion of the guest molecules (tetrahydrofuran) in *p*-octanoylcalix[4]arene complex. One tetrahydrofuran molecules held in a four-fingered molecular hand formed by the aliphatic chains and the other deep in the aromatic cavity. Kunsagi-Mate et al. [64] used photoluminescence and quantum chemical methods to study the fullerenes encapsulation with water-soluble calixarenes, thiacalix[4]arene-tetrasulfonate and calix[6]arene-hexasulfonate. They reported that functionalization of calixarenes and fullerenes induced significant changes in the molecular encapsulation processes.

Japanese chemists examined the effects of solvent polarity and pressure on the inclusion complexation of *p*-sulfonatocalix[8]arene with phenothiazine dyes. They resulted that depending on the bulkiness of the guest dyes, solvent polarity and external pressures increase the inclusion equilibrium constants. They also established the structures of the inclusion complexes using ^{1}H NMR measurements [65]. Korean researchers [66] investigated the hydrogen bonding networks by studying the binding nature of the 1,2,3-alternate calix[6]arene with piperidine (**14**) and triethylamines. The reported that calix[6]arene derivative strongly binds with triethylamines and piperidines at endo and exo binding sites. They discussed the proton transfer within the hydrogen bonding and the hydrogen bonding types, low barrier hydrogen bonding, normal hydrogen bonding, and short strong hydrogen bonding.



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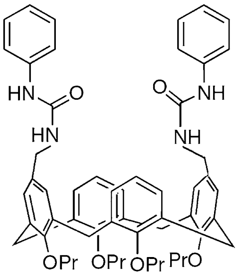
Inazumi and Sueishi [67] determined the equilibrium constants for the inclusion complexation of octaethyl-*p*-*tert*-butylcalix[8]arene octaacetate with methylene blue and they characterized the structure of the inclusion complex by 2D ROESY-NMR measurements. They found that calix[8]arene derivative forms a 1:1 inclusion complex with methylene blue in the upper main cavity. Australian chemists [68] synthesized tetrabromocalix[4]arene derivatives as inclusion hosts for nitrile guests and used X-ray to investigate the guests position inside and outside the calix[4]arene bowls. Calixarenes also have been used as pharmaceutical drug carriers, to improve the bioavailability of medicines. In Brazil, the complexation of the local anesthetic tetracaine with *p*-sulphonic acid calix[6]arene was investigated using ^{1}H NMR experiments [69].

Binding stoichiometries and association constants for parent *p*-sulfonatocalix[*n*]arene derivatives with bovine serum albumin (BSA) were determined using electrospray ionization mass spectrometry. Silva et al. [70] concluded that the strength of the interactions between the BSA and macrocycle is inversely proportional to the size of calix[*n*]arene ring: $(4 > 6 \gg 8)$.

Bew et al. in United Kingdom [71] reported the ability of five bis-1,3-urea calix[4]arene derivatives (**15–19**) to complex fourteen *N*-protected α-amino acids including *N*-Boc glycine, *N*-acetyl-(*S*)-phenylalanine, *N*-Cbz-proline, *N*-Fmoc-(*S*)-valine, *N*-Fmoc-glycine, *N*-Fmoc-(*S*)-proline, *N*-Fmoc-(*S*)-phenylalanine, *N*-Fmoc-(*S*)-tryptophan, *N*-Fmoc-(*S*)-arginine, *N*-Fmoc-(*S*)-histidine, *N*-Fmoc-(*S*)-histidine-Trt, *N*-Fmoc-(*S*)-phenylglycine, *N*-Fmoc-(*S*)-*tert*-butoxityrosine, *N*-Fmoc-(*S*)-3,5-diiodotyrosine.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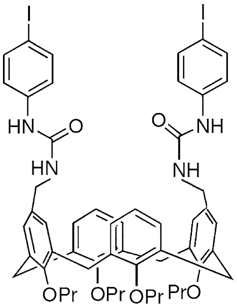
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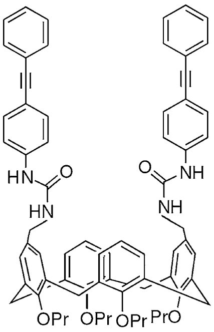
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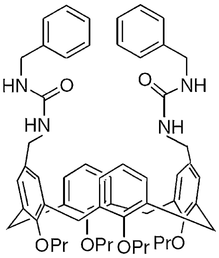
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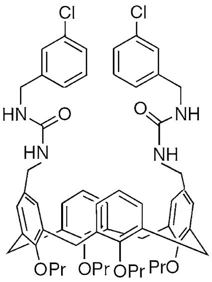
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American chemists [72] investigated the complexation between the 4-sulphonato-calix[*n*]arenas (water-soluble calixarenes) and niclosamide (a poorly water-soluble anthelmintic drug) by phase solubility studies. Carbamazepine is a poorly water soluble anticonvulsant drug. Indian chemists [73] studied the effect of *p*-sulfonated calix[4]-arene and *p*-sulfonated calix[6]arene on aqueous solubility of carbamazepine by means of HPLC, DSC, PXRD, FTIR, UV–Vis, and FT-Raman spectroscopy. Their results were in good conformity to signify the formation of 1:1 calix[6]arene:drug and 2:1 calix[4]arene:drug complexes. Drug dissolution rate of inclusion complex was more than physical mixture and more than drug alone. In Russia, Kharlamov et al. [74] investigated the association properties of water soluble calix[4]resorcinarene with 2-naphthol and 1,5-naphthalenediamine by NMR methods. They resulted that the pH dependency of those complexes makes them prime candidates for pH-responsive molecular machines applications.

Polish and Ukrainian chemists [75] studied the host–guest complexes (1:1) of calix[4]arene bis-hydroxymethylphosphous acid with glycine, L-leucine, L-alanine, L-valine, and L-isoleucine residues in methanol solution with the aid of the titration experiments followed by ^{1}H NMR and UV spectroscopic methods. The stability constants for macrocycle and aliphatic L-amino acids were determined and the results indicated that the host–guest complexation was under control of the direct electrostatic interaction between amino acid residue NH_3^+ group and negatively charged calixarene phosphoryl group. They correlated the stability of the inclusion complexes with the size of the aliphatic amino acid's side-chain.

Organic cations

In this sub-section the applications of calixarenes in complexation studies of organic cations is presented. Table 6 summarizes the recent studies conducted on the calixarene complexes with organic cations.

German chemists [76] prepared calix[4]arenes bearing one cycloheptatrienyl and calix[4]arenes with one tropylium substituent and studied the complexation of them with

Table 6 The list of calixarene derivatives were used in complexation studies of organic cations

Type of calixarene	Analytes were used	References
Calix[4]arenes bearing cycloheptatrienyl and tropylium substituent	Quinolinium, ammonium and tropylium ions	[76]
p-Sulfonatocalixarenes	Pyridinium, dipyridiniums and phenanthrolinium	[34]
Calixcrowns, calixbiscrowns	Amines and alkyl ammoniums	[20]
Calix[4–8]crowns, calix[4–8]biscrowns	Tertiary amines	[19]
Calix[*4,6*]arenesulfonates and thiacalix[4]arene tetrasulfonate	Benzyltrimethylammonium	[77]
Calix[*4,6*]arenesulfonates and thiacalix[4]arene tetrasulfonate	Pyridinium	[78]

organic cations such as quinolinium, ammonium and tropylium ions. Guo et al. [34] studied the complex structures, binding abilities and molecular selectivity of *p*-sulfonatocalixarenes and calculated the complex stability constants via calorimetric and spectroscopic methods. According to the results of their studies, in the cases of pyridinium guests, *p*-sulfonatocalixarenes also form stoichiometric 1:1 complexes with dipyridiniums and phenanthrolinium. The host–guest binding modes were determined by the 2D NMR and they show that pyridinium guests are included into the cavity of *p*-sulfonatocalixarenes with the different patterns. Figure 3 presents a graphical illustration for their interactions and steric conformations.

Korean and French researchers [20] reviewed the complexing properties of calixcrowns, calixbiscrowns and resorcinarenecrowns and reported their ionophoric properties towards amines and (alkyl) ammoniums. Salorinne and Nissinen [19] investigated the ionophoric properties of calix[4–8]crowns, calix[4–8]biscrowns and resorcinarenecrowns towards tertiary amines. They attributed the selectivity to the size of the crown ether moieties and the conformation of the parent calixarene. The complex stability constants, the binding mode, and thermodynamics were determined for 1:1 inclusion complexation of calix[*4,6*]arenesulfonates and thiacalix[4]arene tetrasulfonate with benzyltrimethylammonium [77] and pyridinium guest ions [78]. The binding affinities from the viewpoint of π–π interactions, electrostatic interactions and size/shape relationship between host and guest were discussed.

Anions

This sub-section focuses on the applications of calixarenes in complexation studies of anionic spices. Table 7 shows recent complexation studies on anions recognition using calixarene derivatives.

Lang and his team in Czech Republic, investigated the stoichiometry of complexation of calix[4]arenes bearing two *p*-nitrophenyl-ureido functions at the upper rim. Substitution pattern and anion concentration factors were studied on distal and proximal isomers and showed that while the distally substituted receptor forms 1:1 complexes with anions, the corresponding proximal derivative prefers the 2:1 stoichiometry under identical conditions [79]. Nabeshima et al. [28] introduced a multi-responsive calix[4]arene macrocycle that can recognize $CF_3SO_3^-$ and BF_4^-. Its recognize ability to those anions was increased in a stepwise manner using Na^+ and Ag^+ as effectors. The enhancement of the K_a reached factors of 1500 and 2000 for NO_3^- and $CF_3SO_3^-$, respectively, in the presence of both Na^+ with Ag^+, compared to the free.

As discussed, phenolic units bridged by methylene spacers in meta-position are called calixarenes, although in recent years macrocycles with related subunits such as resorcin or pyrrole and other spacers such as sulfur are also

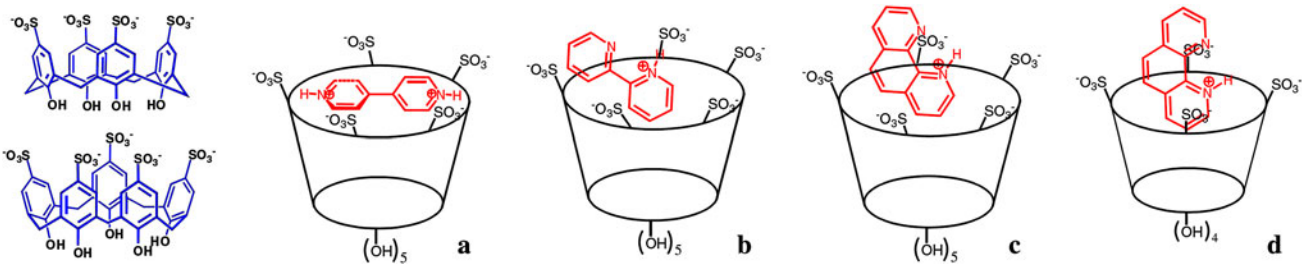


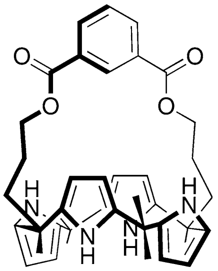
Fig. 3 Illustration of different patterns to include pyridinium guests into the cavity of *p*-sulfonatocalix[4,5]arenes

Table 7 List of calixarenes and anions used in extraction researches

Type of calixarene	Analytes were used	References
Calix[4]arenes bearing *p*-nitrophenyl-ureido functions	Various anions	[79]
Multi-responsive calix[4]arene	$CF_3SO_3^-$ and BF_4^-	[28]
Calix[4]imidazolium[2]pyridine cation	F^-	[80]
Calix[4]pyrrole	Carbonate	[30]
Calixpyrrole	Several chloride salts	[81]
Hexahomotrioxacalix[3]arene triamide	Cl^- and Br^-	[82]
Phenyl, pyrrole, and furan strapped calix[4]pyrroles	F^-, Cl^-, Br^- and carboxylate	[83]
Amido *p-tert*-butyl calix[4]arene	Various anions	[84]
Multi-calixarenes	Picrate	[85]

considered to belong to the same class. Calixpyridines and calixpyrroles belong to calixarenes and there are some analytical applications of them. In Korea [80] a calix[4]imidazolium[2]pyridine cation was synthesized and formed a complex with F^- anion in a 1:1 stoichiometry, which can be used as a macrocyclic ionophore for F^-. Custelcean et al. [30] illustrated the anion-recognition behavior of the calix[4]pyrrole for carbonate anion and Sessler et al. [81] studied the interaction of calixpyrrole with several chloride salts.

Yamato et al. [82] synthesized the cone-conformation of lower rim functionalized hexahomotrioxacalix[3]arene triamide and studied the anion complexation of triamide by ^{1}H NMR titration experiments. They reported that macrocycle:triamide binds halides through the intermolecular hydrogen bonding among the NH hydrogens in a 1:1 fashion in $CDCl_3$. They calculated the association constants from changes in chemical shifts of the amide protons to be $K_{a,Cl^-} = 223\ M^{-1}$ and $K_{a,Br^-} = 71.7\ M^{-1}$. Therefore, it revealed that macrocycle:triamide shows a preference for Cl^- complexation than Br^- complexation. Gross et al. [83] compared the binding properties of a series of phenyl (**20**), pyrrole (**21**), and furan (**22**) strapped calix[4]pyrroles towards fluoride, chloride, bromide and carboxylate anions. They sowed that the pyrrole-strapped system of macrocycle displayed the highest affinity to anions.



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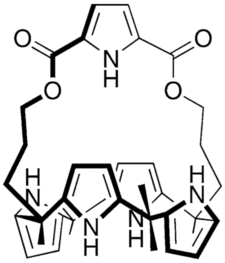

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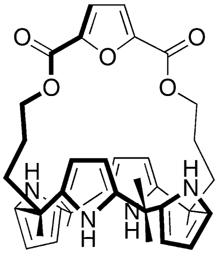

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Spherical halides, planar trigonal nitrate and tetrahedral hydrogen sulphate were subjected in some researches as their tetrabutylammonium salts. Hamdi et al. [84] studied the binding properties of 1,2,3,4-amido derivatives of *p-tert*-butyl calix[4]arene towards various anions by ^{1}H NMR. They determined the stability constants, varying from 0.76 ± 0.10 to 2.13 ± 0.04 for the mononuclear complexes. Othman et al. [85] prepared hyperbranched molecules based on multi-calixarenes and attached them to synthesized cores. Their complexation studies of prepared ligand with $Zn(Pic)_2$ showed that the ligand preferred to bind the picrate anions.

Calixarenes applications in separation techniques

The analytical application of calixarenes in separation techniques was reviewed in four subsections including solvent extraction, liquid chromatography, transport phenomena and electrophoresis.

Applications in solvent extraction

Calixarenes extract neutral and ionic species; hence, many studies have focused on this area. This section followed by the abstracted tables, which listed the research works on calixarenes ability to extract guest spices.

s-Block (alkali and alkaline earth) cations

The solvation of alkali metal ions in the source phase, in the receiving phase and at the liquid–liquid interface demonstrates the active role of solvent on the structural features of the extracted complexes and on the effect of counterions. Solvent also markedly contributes to the thermodynamics of cation complexation in homogeneous liquids and of transfer from one liquid phase to the other. Table 8 presents the content of this subsection including the solvent extraction studies using calixarene derivatives and *s*-block cations.

India chemists [86], extracted radio ^{137}Cs using nitrobenzene solutions of calixcrowns from nitric acid solution of nuclear waste. They used calix[4]arene-bis(crown-6), calix[4]arene-bis(benzocrown-6) and calix[4]arene-bis(napthocrown-6) for that propose. Tu et al. [87] synthesized di-ionizable calix[4]arene-1,2-crown-4 ethers that exhibited high Ba^{2+} selectivity ($Ba^{2+} \gg Sr^{2+} > Ca^{2+} > Mg^{2+}$) in alkaline earth metal solutions into chloroform. Recently, Chinese chemists [88] synthesized 1,3-[(2,4-diethylheptylethoxy)oxy]-2,4-crown-6-calix[4]arene and immobilized it into the pores of the SiO_2–P particles. It showed strong adsorption ability and excellent selectivity for Cs^+ over all the tested metals including Mo^{6+}, Pd^{2+}, La^{3+}, Y^{3+}, Ru^{3+}, Rh^{3+}, Cs^+, and Zr^{4+}.

Li et al. [89] synthesized triazole-modified calix[4]diethylester and dimethylester and examined their selectivity towards alkali metal cations via two-phase extraction experiments. The cavity formed by two ester group is preferable for the complexing alkaline metal ions such as the Cs^+. Meanwhile, both modified calix[4]arenes displayed different selectivity towards alkali metal ions as illustrated in Fig. 4.

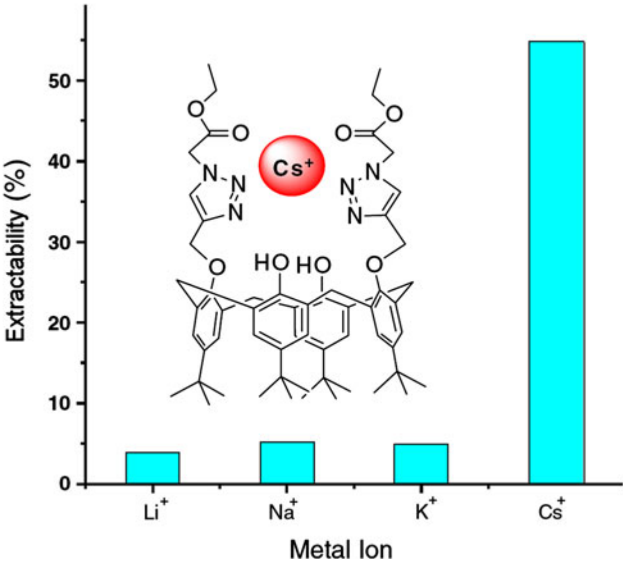


Fig. 4 Illustration of extractability of alkali metal ions by triazole-modified calix[4]diethylester

Table 8 List of calixarenes used to extract *s*-block cations via solvent extraction procedures

Type of calixarene	Analytes were used	References
Calixcrowns	Radio ^{137}Cs	[86]
Calixcrowns	Ba^{2+}	[87]
Calixcrowns	Cs^+	[88]
Triazole-modified calix[4]diethylester and dimethylester	Li^+, Na^+, K^+ and Cs^+	[89]
p-tert-Octylcalix[4,6]arenes tetracarboxylic acid	Alkali metal cations	[90]
Calixbiscrowns	Cs^+	[91]
p-tert-Butylcalix[4]arene-1,3-thiacrown-5	Alkali and alkaline earth metal cations	[92]
Calix[4]arene with two distal methoxycarboxy and butoxy groups	Alkali and alkaline earth metal cations	[93]
Hexahomotrioxacalix[3]arene triamide	Alkali metal cations	[82]
1,3-alternate Thiacalix[4]arene bearing carboxylic and aminopyridyl groups	Na^+, K^+ and Cs^+	[94]
1,2-Calix[4]crown-7, 1,3-calix[4]crown-7, 1,2-calix[4]crown-9 and 1,3-calix[4]crown-9	Sr^{2+}	[95]
p-tert-Butylcalix[4]arene-1,3-thiacrown-5 ether	Ba^{2+}	[96]
n-Homo calixnaphthalenes	K^+	[97]

Ohto et al. [90] investigated the solvent extraction of alkali metal ions with *p-tert*-octylcalix[4]arene tetracarboxylic acid and *p-tert*-octylcalix[6]arene hexacarboxylic acid. The first one selectively extracted sodium ion among alkali ions at extremely low pH, while the other one exhibited only poor extraction ability for all alkali metals examined. They observed that two sodium ions were simultaneously extracted by a single molecule of calix[4]arene derivative and they found that the second sodium extraction was facilitated by the uptake of the first sodium. The authors proposed the self-coextraction mechanism of sodium ions. Vicens [91] described the development of calixbiscrowns for cesium removal in nuclear waste and related extraction methods.

American chemists [92] prepared *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 di(carboxylic acid) and evaluated its influence on competitive solvent extractions of alkali and alkaline earth metal cations. Park et al. [93] synthesized four calix[4]arene stereoisomers with two distal methoxycarboxy groups and two distal butoxy groups. They studied the influence of calix[4]arene conformation on metal ion complexation via extractions of alkali and alkaline earth cations from aqueous solutions into 1,2-dichloroethane. In Japan, Yamato et al. [82] synthesized the cone-conformation of lower rim functionalized hexahomotrioxacalix[3]arene triamide and discussed its extractability for alkali metal ions from water into dichloromethane.

The effect of proton-ionizable group (carboxylic moiety) on the solvent extraction of some alkali metal (Na^+, K^+ and Cs^+) with 1,3-alternate thiacalix[4]arene bearing one carboxylic moiety and three aminopyridyl groups was investigated in China [94]. Chinese researchers [95] synthesized cone conformers of 1,2-calix[4]crown-7, 1,3-calix[4]crown-7, 1,2-calix[4]crown-9 and 1,3-calix[4]crown-9. Synthetic calixarenes showed mediocre affinity for alkali and alkaline earth metal picrates in two-phase extraction experiments. They reported the selective extraction of Sr^{2+} by 1,2-calix[4]crown-9 among other alkaline earth metal cations. Researchers in United Stats synthesized the cone conformation of *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 ether and evaluated its complexing properties by solvent extractions of Ba^{2+} from aqueous solutions into chloroform and found that the macrocycle was efficient extractant with Ba^{2+} selectivity in competitive solvent extraction of alkaline earth metal cations [96]. The chemists in Canada and Jordan [97] synthesized two new large-ring *n*-homocalixnaphthalenes that demonstrated high extraction capability for K^+.

p-Block cations

In Texas, Tu et al. [87] used calix[4]arene-crowns to extract Pb^{2+} in single species extraction.

Ulewicz et al. [98] investigated Pb^{2+} transportation through a calix[4]crown-6 derivatives/membrane and studied the influence of attached group of calix[4]-crown-6 on the selectivity of Pb^{2+} transport. Tu et al. [96] examined the extraction ability of cone conformation of *p-tert*-butylcalix[4]arene-1,3-thiacrown-5 ether towards Pb^{2+} and showed its high extraction ability in single species solvent extractions.

d-Block (transition and heavy) cations

Most processes to separate transition metal ions from aqueous solutions depend on ion exchange processes, in which the desired metal cation replaces a different metal cation or protons from an anionic group in a complexing agent. Such complexing agents are deployed on solid supports in processes using ion exchange resins, or in a water immiscible liquid in solvent extraction. Although toxic metal ions may be sequestered in this way, true purification of the aqueous stream is not achieved because: (a) in the case of proton exchange the pH of the stream may be significantly lowered; (b) the number of ions present in solution is, at best, unchanged and is often increased; and (c) the anion remains in the solution. The harmful effects of anionic species such as phosphate and sulfate have led to control of environmental discharge levels for these species. These considerations, combined with novel separation technologies to process leach solutions in primary metal recovery, had led the researchers to investigate a new class of extractant. These extractants simultaneously sequesters both a transition metal cation and its attendant anion such as calixarenes. There are few examples of ligands which simultaneously bind cations and anions. Table 9 shows recent extraction studies that carried out on *d*-block cations using calixarene derivatives.

Gong et al. [99] examined the extraction behavior of 1,3-dipropyn-2-yl-oxycalix[4]arene towards Hg^{2+}. With equal mole ratio of Hg^{2+} and calixarene, the extractive percent reached to 99.1%. Ersoz [5] reviewed mercury transport in liquid membranes by calixarene derivative carriers and demonstrated various investigations up to 2007 regarding selective transport of Hg^{2+} in using calixarene derivatives as carrier. Qureshi et al. [8] applied Pederson method for the extraction of Cu^{2+}, Co^{2+} and Ni^{2+} *p*-by morpholinomethylcalix[4]arene using their picrates in two-phase extraction experiments.

Deligoz and Erdem [100] used nine ligands including two diazo-coupling calix[*n*]arenes, four phenol derivatives and three ester derivatives to investigate ionophore solvent extraction of Ag^+, Hg^+, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+} and revealed that the best extraction efficiency was obtained with *p*-(4-phenylazophenylazo) calix[4]arene and 2-(5-bromo-2-pyridylazo)-5-diethylamino phenol. O'Dwyer and Cunnane [43] used *O*,*O*″-bis[2-(methylthio)-ethyl]-*tert*-butylcalix[4]arene ionophore to

Table 9 List of calixarenes and *d*-block cations used in extraction researches

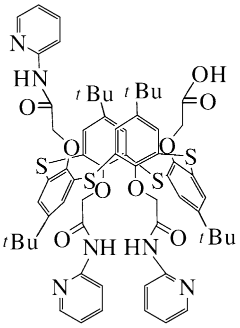
Type of calixarene	Analytes were used	References
1,3-Dipropyn-2-yl-oxycalix[4]arene	Hg^{2+}	[99]
–	Hg^{2+}	[5]
p-Morpholinomethylcalix[4]arene	Cu^{2+}, Co^{2+} and Ni^{2+}	[8]
Diazo-coupling calix[*n*]arenes	Ag^{+}, Hg^{+}, Hg^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and Cr^{3+}	[100]
O,*O*″-bis[2-(Methylthio)-ethyl]-*tert*-butylcalix[4]arene	Ag^{+}	[43]
Calix[6]crown	Cr^{3+}, Mo^{6+} and W^{6+}	[101]
Tetraalkyl(tolyl)thiomethylcalix[4]arenes	Pd^{2+} and Ag^{+}	[45]
Tolylthiamethy calix[4,6]arenes	Au^{3+}	[102]
–	Hg^{2+}	[103]
Calix[4]crown-6	Cd^{2+} and Zn^{2+}	[98]
Di-ionizable calix[4]crowns	Hg^{2+}	[87]
Calix[4]pyrrole hydroxamic acid	Vanadium	[104]
Calix[4,6]arenes bearing phosphine oxide groups	Ru^{3+} and Zn^{2+}	[105]
Hexahomotrioxacalix[3]arene triamide	Transition metal cations	[82]
1,3-alternate Thiacalix[4]arene possessing aminopyridyl and carboxylic groups	Cu^{2+}, Zn^{2+}, and Ag^{+}	[94]
Azocalix[4]arenes	Ag^{+}, Hg^{+} and Hg^{2+}	[48]
Azocalixarenes	Fe^{3+}	[22]
Calix[4,6]arenes bearing phosphine oxide	Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}	[106]
Thiacalixarenes	Cu^{2+} and Cd^{2+}	[107]
Distal-bis[(2-pyridylmethyl)oxy]thiacalix[4]arenes	Ag^{+}	[108]
p-*tert*-Butyl-*thia*calix[4]arene and *p*-*tert*-butylcalix[4]arene derivatives	Ag^{+}	[51]
p-Azophenylazocalix[4]arene	Te^{4+}, Pd^{2+}, and Fe^{3+}	[109]
Tetrahydroxy-tetraphenylazocalix[4]arene	Copper, cobalt, rhodium and iridium cations	[110]
p-*tert*-Butylcalix[4]thiacrown-5	Hg^{2+}	[96]
Calix[4,6,8]arene derivatives bearing pyridino groups	Tc^{7+}	[111]

facilitate Ag^{+} transferring at the water|1,2-dichloroethane interface. Agrawal and Sharma [101] used 37,38,39,40,41,42-hexahydroxy7,25,31-calix[6]crown hydroxamic acid to investigate extraction mechanism, kinetic of transport, speciation, liquid–liquid extraction, sequential separation and trace determination of Cr^{3+}, Mo^{6+} and W^{6+}. The maximum transport was observed at 35, 45 and 30 min for last cations, respectively.

Torgov et al. [45] used tetraalkyl(tolyl)thiomethylcalix[4]arenes to extract Pd^{2+} and Ag^{+} from main fission products. Torgov et al. [102] also studied Au^{3+} extraction from hydrochloric media by calix[4,6]arenes upper-rim functionalized with alkyl- or tolylthiamethyl groups. The most effective extractants were calixarenes with CH_2–S–CH_3 and CH_2–S–nC_4H_9 groups. Alpoguz et al. [103] made a flat-sheet-supported liquid membrane by calix[4]arene derivatives as carriers and Celgrad as solid support and investigated the transport behavior of Hg^{2+} into membrane from aqueous solution. Ulewicz et al. [98] investigated transport of Zn^{2+} and Cd^{2+} ions through a polymer inclusion membrane using calix[4]crown-6 derivatives and studied the influence of the group attached type to the calix[4]-crown-6 on the selectivity and efficiency of cations transport across polymer.

Tu et al. [87] synthesized di-ionizable calix[4]arene-1,2-crown-4 ethers, which exhibited high extraction ability for Hg^{2+} in single species extraction. The extraction of vanadium with the host calix[4]pyrrole hydroxamic acids were studied using examination of ICP-AES and UV–Vis spectroscopy by Jain et al. [104]. Russian and Ukrainian researchers synthesized the calix[4,6]arenes grafted with different phosphine oxide groups and used them to extract Ru/Zn complexes. They investigated The Ru/Zn synergism and the calixarene macrocyclic effect in the extraction process and concluded that calixarene conformation, its size and electronic nature of substituents at phosphorus atom influence the extraction [105].

Japanese chemists discussed the extractability of transition metal ions from water into dichloromethane by hexahomotrioxacalix[3]arene triamide [82]. Chinese researchers synthesized a 1,3-alternate thiacalix[4]arene possessing three aminopyridyl and one carboxylic group (**23**) and they studied it in the solvent extraction of some transition metal including Cu^{2+}, Zn^{2+}, and Ag^{+} from aqueous solutions into chloroform [94]. They found that the introduction of carboxylic acid moiety (proton-ionizable group) into the macrocycle could further improve its Ag^{+} extractability with high selectivity.



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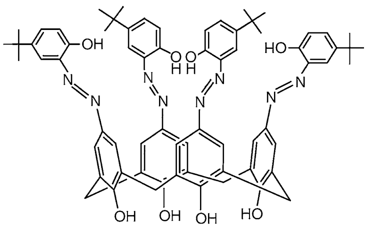
The Ak's research team in Turkey [48] synthesized azocalix[4]arenes and studied the solvent extraction of Ag^{+}, Hg^{+} and Hg^{2+} from the aqueous phase to the organic phase. Deligöz [22] reported the use of azocalixarenes (**24**–**27**) in liquid–liquid extraction of various transition metal cations from the aqueous phase to the organic phase. In a part of his review paper, the complexation of four azocalixarenes with transition metal cations was discussed and the results is presented in Fig. 5. He also claimed that azocalixarenes were used for selective extraction of Fe^{3+} cations from the aqueous phase to the organic phase.



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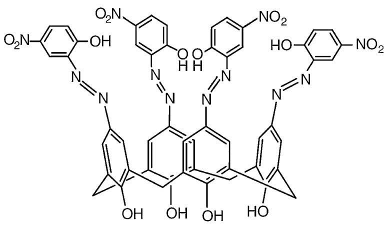

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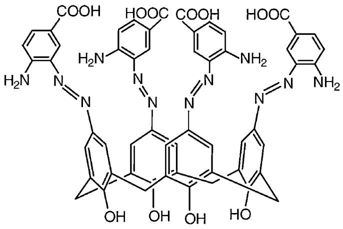

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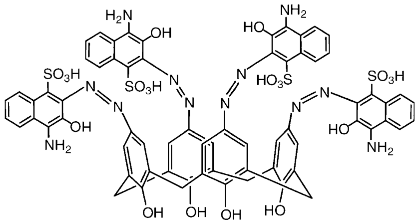

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Russian and Ukrainian researchers [106] used calix[4,6]arenes bearing four or six phosphine oxide donor groups at the upper or at the lower rim to study the extraction of non-ferrous and two valence metal nitrates. The extraction constants for the both types of upper and lower rim were determined to be $Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. For the upper (wide) rim phosphorylated calix[4]arenes, M_2L and ML_2 complexes were more stable, while the lower (narrow) rim phosphorylated calix[4]arenes, provided better stability of ML complexes. Thiacalixarenes are a class of calixarenes in which the bridging methylene groups are replaced with sulfur. Figure 6 illustrated that they are able to capture guest metal ions by coordinating with the bridging sulfur and adjacent phenol oxygen as well as *p*-substituent, aromatic ring, and hydrophobic cavity. Iki [107] reviewed a 200-fold pre-concentration of Cu^{2+} and Cd^{2+}.

Yamato et al. [108] synthesized *distal*-bis[(2-pyridylmethyl)oxy]thiacalix[4]arenes and described its conformational studies. The used calix[4]arenes showed strong Ag^{+} affinity in two-phase solvent extraction, which led to 97%

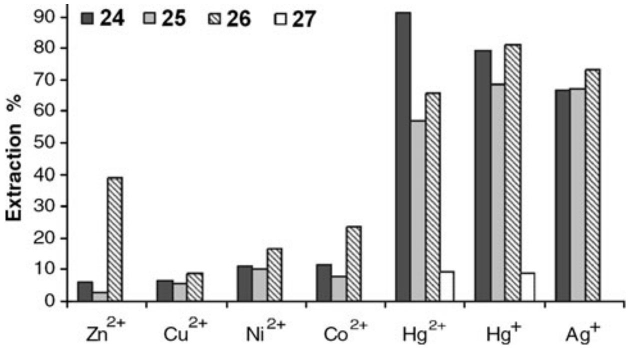


Fig. 5 The extraction efficiency of azocalixarenes towards transition metal cations

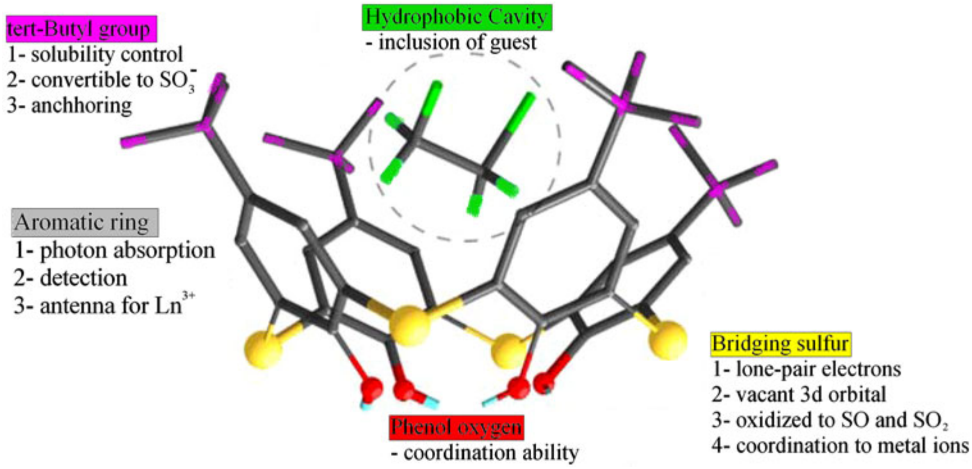


Fig. 6 Illustration of interaction sites in thiacalixarenes

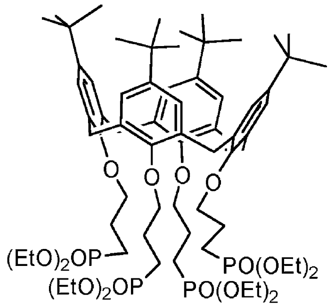
extraction, while no significant extraction was observed for K^+. Bouhroum et al. [51] synthesized *p-tert*-butyl-*thia*calix[4]arene and *p-tert*-butylcalix[4]arene derivatives and used them in liquid–liquid extraction of metal picrates from water into dichloromethane. They reported 99% extraction for Ag^+. Indian chemists [109] used *p*-[4-(3,5-dimethylisoxazolyl)azophenylazo]calix[4]arene to extract tellurium, palladium, and iron cations and determined them by spectrophotometric methods. The interference of various ions was studied and optimum conditions were developed for the extraction procedure of Te^{4+}, Pd^{2+}, and Fe^{3+}.

Hungarian and Indian researchers [110] extracted copper, cobalt, rhodium and iridium cations from nitric acid by 25,26,27,28-tetrahydroxy-5,11,17,23-tetra-[4-(*N*-hydroxyl-3-phenylprop-2-enimidamido)phenylazo] calix[4]arene and determined the trace amounts of cations spectrophotometrically. The extraction of Hg^{2+} in single species solvent extractions by a *p-tert*-butylcalix[4]thiacrown-5 derivative was presented by Tu et al. [96]. Ludwig and Dzung [111] used calix[4,6,8]arene derivatives bearing pyridino groups at the lower rim for solvent extraction of Tc^{7+}.

f-Block (lanthanide and actinide) cations

The research and development activities for the partitioning and transmutation of long-lived actinide radionuclides are actively in progress in advanced nuclear countries. Long-lived actinide radionuclides contained in the spent nuclear fuel can be recovered by the separation processes using high temperature molten-salts and recycled to the reactor for transmutation. The resulting waste, will show a remarkable reduction in the radiological toxicities and can be disposed of under milder conditions. At present, various concepts for the transmutation of long-lived actinide radionuclides are being studied in several countries. One of the concepts for the transmutation is the solvent extraction. This sub-section also reviewed the ability of calixarene derivatives for solvent extraction of actinide radionuclides. Table 10 presents the content of this subsection including the recent studies conducted on extraction of *f*-block cations using calixarene derivatives.

Mariani et al. [10] selected calixarene-based picolinamide ligands for liquid–liquid extraction of ^{241}Am and ^{152}Eu in high radioactive nitric solutions before and after γ-irradiation. Determination of the separation factors between elements of the two families was carried out by using γ-spectrometry and ICP-mass spectrometry. Matulkova and Rohovec [112] in Czech Republic, synthesized the calix[4]arenes (**28** and **29**) with four phosphonic acid groups on the lower rim and characterized their extraction behavior on certain lanthanide ions (La^{3+}, Eu^{3+} and Yb^{3+}). The extraction efficiencies of the prepared macrocycles were declined with decreasing radius of the lanthanide ions.



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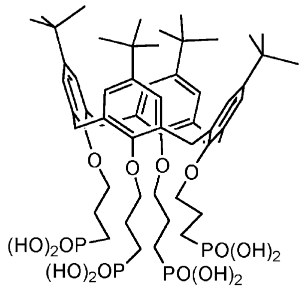

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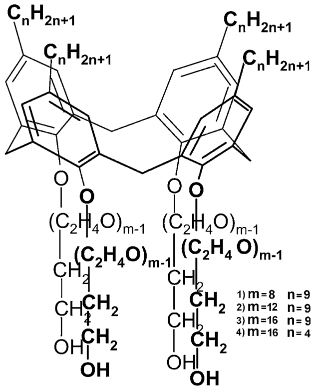
Table 10 List of researches on the extraction of lanthanides and actinides using calixarenes

Type of calixarene	Analytes were used	References
Calixarene-based picolinamide	Actinides and lanthanides	[10]
Propylene phosphonic acid calix[4]arene	La^{3+}, Eu^{3+} and Yb^{3+}	[112]
Cyclophanic calix[4]arene surfactants	La^{3+}, Gd^{3+} and Lu^{3+}	[113]
Calix[4]arene-*o*-vanillinsemicarbazone	U^{6+} and Th^{4+}	[114]
p-Octasulfonato-calix[8]arene	Permeable for NaCl, $MgCl_2$, $ZnCl_2$ and strongly rejected $LaCl_3$, $CeCl_3$, $PrCl_3$, $SmCl_3$	[115]
Phosphorylated calix[4]arene	Th^{4+} and Eu^{3+}	[116]
Calix[6]arene derivative	Am^{3+} and Eu^{3+}	[117]
Calixarenes bearing phosphine oxide	Europium, americium, thorium and uranyl cations	[50]

Conventional surfactants associate through closed model resulting in the formation of rather small micelle-like in cloud point extractions. Mustafina et al. [113] used non-ionic cyclophanic surfactants based on calix[4]arene platforms (**30–33**) with Triton X100 to enhance the aggregation of La^{3+}, Gd^{3+} and Lu^{3+} in cloud point extractions.



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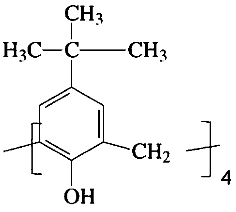
Jain et al. [114] developed a chelating polymeric sorbent using calix[4]arene-*o*-vanillinsemicarbazone for simultaneous preconcentration of U^{6+} and Th^{4+} from aqueous solutions with preconcentration factors of 143 and 153, respectively. Toutianoush et al. [115] built a layer-by-layer assembly of *p*-octasulfonato-calix[8]arene and polyvinylamine on porous polymer support. The membranes were permeable for NaCl, less permeable for divalent metal chlorides ($MgCl_2$ and $ZnCl_2$), and strongly rejected rare earth metal chlorides ($LaCl_3$, $CeCl_3$, $PrCl_3$ and $SmCl_3$). Yaftian et al. [116] studied the extraction of thorium(IV) and europium(III) by a phosphorylated calix[4]-arene in dichloromethane and investigated the effects of ligand concentration, types of diluent and concentration of the salting-out agents.

Sansone et al. [117] synthesized five calix[6]arene derivatives and studied the liquid–liquid extraction for Eu^{3+} and Am^{3+} from aqueous nitric acid to *o*-nitrophenylhexyl ether. Karavan et al. [54] evaluated the liquid–liquid extraction of europium, americium, thorium and uranyl ions from nitric acid solutions into two diluents dichloromethane and *m*-nitrobenzotrifluoride. They used three series of phosphorylated calixarene derivatives bearing phosphine oxide or phosphonate groups either at the wide or the narrow rims as extractants.

Molecular compounds

This sub-section focuses on the applications of calixarenes in solvent extractions for determination of molecular compounds. Table 11 presented the content of this sub-section including the extraction studies conducted on calixarene derivatives and molecular spices.

Liu and co-workers [118, 119] used poly-dimethylsiloxane (PDMS) membranes filled with calixarene and calixarene derivatives (**34** and **35**) for evaporative removal of benzene from dilute aqueous solution end they revealed that due to the higher hydrophobicity of calixarene derivative over calixarene, calixarene derivative-filled PDMS membranes exhibited higher separation factor than calixarene-filled PDMS membranes. In addition, both calixarene and calixarene derivative-filled PDMS membranes showed better permselectivity than control PDMS membranes.



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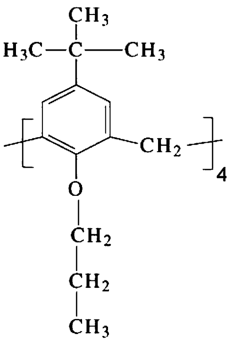

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Table 11 List of calixarenes used in extraction studies with molecular spices

Type of calixarene	Analytes were used	References
–	Benzene	[118]
–	Benzene	[119]
Calix[6]arene and calix[8]arene carboxylic acid derivatives	Amino acids	[120]
Calix[6]arene carboxylic acid derivative	Adenine and cytosine	[121]
Sol–gel calix[4]arenes	Organochlorine pesticides	[122]
p-Sulfonato-calix[*n*]arenes	Neutral and charged aromatic compounds	[123]
Functionalized calix[*n*]arenes	Amines, amino acids and peptides	[124]
Sol–gel diglycidyloxy-calix[4]arene	Propranolol enantiomers	[125]
Calix[6]arene carboxylic acid derivatives	Cytochrome C and lysozyme	[126]
Chiral calix[4]arene diamide derivatives	α-amino acid methylesters	[127]
p-*tert*-Butylcalix[4]arene bearing phenylethylamine	Chiral α-amines and α-amino acid methylesters	[128]
Calixarenes bearing acid or amido moieties	Native amino acid and amino acid esters	[129]
Calix[6,8]arenes bearing carboxylic acid	Catecholamines	[130]
p-*tert*-Butylcalix[6,8]arene	L-Tryptophan methylester and L-tyrosine methylester	[131]
1,3-bis-Arylformyl-hydrazone substituted thiacalix[4]arene and 1,3-bis-acyl hydrazone-bridged calix[4]arene derivatives	α-amino acids	[132]

Researchers studied the calixarene carboxylic acid derivatives as powerful extractants for biologically important amino compounds. Based upon their work, the larger macrocycles calix[6]arene and calix[8]arene carboxylic acid derivatives were more effective for adsorption of amino acid derivatives on the impregnated resin than the calix[4]arene derivative [120]. Shimojo and Goto [121] used a calix[6]-arene carboxylic acid derivative incorporating *tert*-octyl groups at the upper rim. In isooctane neither calix[6]arene nor D2EHPA were very effective at nucleobase extraction but addition of D2EHPA along with calix[6]arene drastically enhanced the efficiency of adenine and cytosine extraction and one nucleobases forms a stable complex with one calix[6]arene and two D2EHPA molecules.

Dong et al. [122] used a sol–gel calix[4]arene/hydroxy-terminated silicone oil coated fiber for headspace solid-phase microextraction of 12 organochlorine pesticides and their metabolites in radish sample followed by gas chromatography determination. Tieke et al. [123] in Germany, made a layer-by-layer assembled membrane containing polyelectrolytes, *p*-sulfonato-calix[*n*]arenes and Prussian Blue-type complex salts. Then they studied them as molecular sieves and ion sieves for size-selective separation of neutral and charged aromatic compounds. The ability of functionalized calix[*n*]arenes to form complexes, to act as extractants in liquid–liquid extraction for ammonium ion, amines, amino acids, and peptides has been the topics of recent papers. Mutihac et al. [124] investigated the effect of the factors that influence the separation of above biological amine compounds by liquid–liquid extraction using the calix[*n*]arenes.

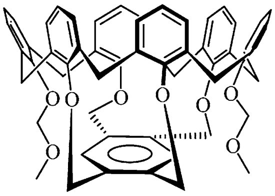
Zhou et al. [125] made a new type of diglycidyloxy-calix[4]arene coated fiber by sol–gel method. Using combination of headspace solid-phase microextraction and capillary zone electrophoresis, the simultaneous determination of propranolol enantiomers in human urine was achieved. Oshima et al. [126] described quantitative extraction and recovery of two proteins (with similar molecular weights), cytochrome C and lysozyme, using calix[6]arene carboxylic acid derivatives. Turkish researchers, Kocabas et al. [127], reported the extraction properties of chiral calix[4]arene diamide derivatives towards some selected α-amino acid methylesters. In Turkey, a chiral *p*-*tert*-butylcalix[4]arene bearing phenylethylamine was synthesized and its liquid phase extraction properties towards some chiral α-amines and α-amino acid methylesters was reported [128].

Hamdi et al. [129] synthesized cone calixarenes bearing acid or amido moieties and used them in the extraction of native amino acid and amino acid esters. Japanese chemists investigated the extraction behaviors of catecholamines using calix[6,8]arene carboxylic acid derivatives. They reported that the calix[6]arene derivative selectively extracted dopamine with 1:1 complexation over other catecholamines, while calix[8]arene derivative extracted both dopamine and adrenaline due to the large cavity for induced-fit recognition. They stripped the dopamine extracted with the calixarene by contacting the organic solution with a fresh acidic solution [130].

Romanian chemists, Mutihac and Mutihac, studied the extractability of some amino acid methylesters (L-tryptophan methylester and L-tyrosine methylester) using *p-tert*-butylcalix[6,8]arene as extractant from the aqueous phase into chloroformic phase in the presence of a counter ion (tropaeolin 00) at pH ≈5.0. They concluded that the inclusion properties of the calixarenes are correlated with their structural properties and also they suggest further possibilities for optimal separation of amino acids [131]. Chinese researchers [132] synthesized 1,3-bis-arylformyl-hydrazone substituted thiacalix[4]arene derivatives and 1,3-bis-acyl hydrazone-bridged calix[4]arene derivatives to study their extraction ability towards α-amino acids. They showed similar binding properties with high extraction percentage but low extracting selectivities. hydrazone-bridged biscalixarene with calix[4]arene and thiacalix[4]arene subunits exhibited not only high extracting abilities but also good extracting selectivities towards α-amino acids.

Organic cations

Selective extraction of organic ammonium attracts an important research interest due to the application of biological systems. Calixarenes present attractive possibilities in the host–guest chemistry, and their architecture is such that they also possess hydrophobic cavities generated by the aromatic walls of phenol residues, which are potentially useful for the inclusion of alkyl ammonium ions. Korean chemists [133] synthesized a quadruply bridged calix[6]arene derivative (**36**) and extracted alkylammonium cations with picrate anion into chloroform by two phase solvent extraction. They deduced the percentage extraction from the absorbance at 355 nm in the aqueous layer. The extraction efficiency for ammonium picrate, ethylammonium picrate, *n*-propyl ammonium picrate, and *n*-butylammonium picrate, was 2.4, 3.7, 2.7, and 2.8% respectively.



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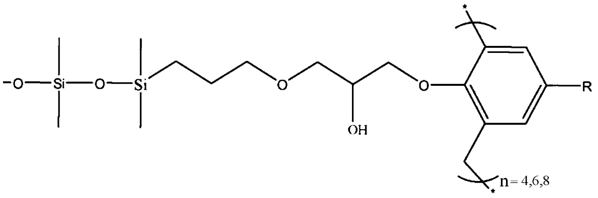
Anions

Wintergerst et al. [134] used *meso*-octamethylcalix[4]pyrrole as an ion-pair receptor for cesium chloride and cesium bromide. Their experiments were conducted in nitrobenzene solution via liquid–liquid extraction. Memon et al. [135] synthesized two polymer appended thioalkylcalix[4]arenes, which had high extraction ability toward $Na_2Cr_2O_7$ as compared to their monomeric precursors. They studied liquid–liquid extraction and solid–liquid batch wise sorption procedures on them and concluded that the calix[4]arene based polymeric resins have higher extraction ability than their monomeric precursors. Memon et al. [136] synthesized three amino/nitrile calix[4]arenes immobilized onto polymeric backbone and investigated its dichromate extraction.

Chromatographic applications

Calixarenes, following cyclodextrines and crown ethers, are the third generation of macrocycles used in HPLC as stationary phases [137]. Table 12 summarizes some researches carried out using calixarenes in liquid chromatography.

Sliwka-Kaszynska et al. [138] used six aspects including surface coverage, hydrophobic selectivity, aromatic selectivity, shape selectivity, hydrogen bonding capacity and ion-exchange capacity to study 12 calix[4]arene stationary phases (**37**), which were synthesized before by them.



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Chromatographic performance of six calixarene bonded silica gel stationary phases was investigated by using PAHs, aromatic positional isomers and *E*- and *Z*-ethyl 3-(4-acetylphenyl) acrylate isomers as probes [11]. Ding et al. discussed separation mechanism based on the different interactions between calixarenes and analytes, chromatographic behaviors of those analytes on the calixarene, and the effect of polar groups in the aromatic isomers on separation selectivity. In order to characterize the chromatographic behavior of calixarene-bonded stationary phases and to test the applicability of established models predicting retention factors, Schneider and Jira [139] analyzed 31 solutes of highly various molecular structures at different composition mobile phase from 0 to 98% (v/v) methanol. They showed the influence of methanol content for non-polar, polar and ionic solutes and differences of their behavior on the differing column types.

Liu et al. [140] prepared four bonded silica stationary phases including β-cyclodextrin, *p-tert*-butyl-calix[8]arene, chloropropyl, and ODS and applied them to separate

Table 12 The list of calixarenes used in liquid chromatography, recently

Concept of study	Type of calixarene	Analytes were used	References
Study of 12 CSP	Calix[4]arene	–	[138]
Chromatographic performance of CSP	–	PAHs	[11]
Chromatographic behavior of CSP	–	–	[139]
Retention mechanisms of CSP	Calix[8]arene	Steroids	[140]
Partition of Cs^+ and Sr^{2+}	Calix[4]arene-R14	Cs^+–Sr^{2+}	[141]
Partition of Cs^+ and Sr^{2+}	Calix[4]arene-R14	Cs^+–Sr^{2+}	[142]
Retention of caffeine on CSP	Naphthyl-calix[4]arene and *tert*-butyl-calix[4]arene	Caffeine	[143]
Steric and polar interactions in CSP	Six CSP	–	[144]
Application and interactions of CSP	–	–	[137]
Characterization of CSP and calixarene mobile phases	Calixarene, calixresorcinarene and calixpyrrole	Organic and inorganic solutes	[145]
Mobile phase in analytes retention	CSP (CALTREX® AIII)	Tricyclic neuroleptics	[146]
Determination of retention profiles in CSP	–	Oxadiazoles	[147]
CSP conditions on the separation	Calix[8]arene	Tricyclic neuroleptic	[148]
Calix[4]arenes in mobile phases	Calix[4]arenes	Benzene or uracil derivatives	[149]
Determination of a tablet formulation	–	Paracetamol, caffeine and acetylsalicylic acid	[150]
Determination of a tablet formulation	–	Celecoxib	[151]
Fluorine–fluorine interactions in CSP	Fluorinated calix[4]arene	Fluorine compounds	[152]
Commercially vs. CSP	Calix[4]arenes	–	[138]
Sorbent chromatography	*p-tert*-Butylcalix[6]arene hexacarboxylate	Cr^{6+}	[153]
Pre-column derivatization reagent	Thiacalixarenes	Ni^{2+}, Fe^{3+}, Al^{3+}, and Ti^{4+}	[107]
Extraction chromatography for metal ions existing in photographic waste	2-Pyridylcalix[4]arene	Ag^+	[154]

CSP calixarene stationary phases

steroids via chromatography. They showed that the retention mechanisms of the four stationary phases for steroids were obviously different, and excellent separation was achieved on β-cyclodextrin bonded silica stationary phase. The retention process on β-cyclodextrin exhibited inclusion complexation, hydrogen-bonding and weak hydrophobic interaction, while for *p-tert*-butyl-calix[8]arene bonded silica stationary phase, π–π and hydrogen-bonding besides hydrophobic interaction played an important role. Zhang et al. [141, 142] synthesized two kinds of macroporous silica-based polymeric materials, Calix[4]arene-R14/SiO_2–P and TODGA/SiO_2–P, and used them to partition effectively Cs^+ and Sr^{2+} from a highly active liquid waste by extraction chromatography. In packed column of Calix[4]arene-R14, all of the simulated elements were separated effectively into two groups: Sr-group (Na, K, Sr, Fe, Ba, Ru, Pd, Zr, Mo) and Cs-group (Cs, Rb). The harmful element Cs^+ flowed into the second group along with Rb^+ because of their close sorption and elution properties towards Calix[4]arene-R14/SiO_2–P, while Sr^{2+} showed no sorption and flowed into Sr-containing group. In packed column of TODGA, the Sr-group was separated into four groups: non-sorption group (Ba, Ru, Na, K, Fe, Mo); Sr; Pd; Zr. Packed column of TODGA showed the excellent separation efficiency from others.

Kimiko et al. [143] compared naphthyl-calix[4]arene and *tert*-butyl-calix[4]arene bonded silica on retention of caffeine and showed that naphthyl-calix[4]arene bonded silica retained strongly caffeine in similar to calix[4]arene bonded silica. Schneider et al. [144] characterized six different calixarene-bonded phases at pH 3 and 7. They found that ionic and polar interactions dependent on pH value, while steric interactions are less dependent and hydrophobic interactions remain unchanged. They confirmed distinct differences of the supported interactions between calixarene-bonded and common alkyl-bonded silicates. Meyer and Jira [137] reviewed and summarized the application possibilities and interactions of calixarenes as stationary phase in HPLC. Sliwka-Kaszynska [145] in a short review focused on recent advances in synthesis and characterization of calixarene, calixresorcinarene and calixpyrrole stationary phases, chemically bonded or dynamically adsorbed onto silica gel or used as mobile phase additives, and its application to separation of organic and inorganic solutes by high performance liquid chromatography.

Hashem and Jira [146] investigated the retention behavior of nine tricyclic neuroleptics on three different RP-HPLC columns. Based upon their experiments, two recently developed columns, calixarene-bonded (CALTREX® AIII) and monolithic (Chromolith® Performance RP-18e), were compared with a conventional RP-C18 HPLC column (LiChrospher®). The results elucidated how the mobile phase conditions affect the analytes retention on the columns. Under their laboratory conditions, a calixarene-bonded phase was the best for that separation, a monolithic phase gave comparable results and the conventional RP column was the least effective. Grzegorz et al. [147] determined the retention profiles in series of oxadiazoles in narrow-bore HPLC systems, which can be useful in encapsulation optimization of 1,3,4-oxadiazolurea-type drugs with calixarenes. Hashem and Jira [148] studied the effects of different chromatographic conditions on the separation of nine tricyclic neuroleptics and the effect of structural differences of analytes by a new HPLC-stationary phase with calixarenes. They showed that chemical structure and pK_a of neuroleptics influenced their separation on the calix[8]arene stationary phase.

Addition of calix[4]arenes to two mobile phases improves chromatographic separation of benzene or uracil derivatives on separon supports [149]. Kalchenko et al. also discussed the structure of the calixarenes and their complexes with benzene or uracil derivatives in context of the chromatographic separation. Simultaneous determination of paracetamol, caffeine and acetylsalicylic acid in a tablet formulation by was done by Hashem [150] using calixarene stationary phases with detection limits of 0.488, 0.977 and 7.813 ng μL^{-1}, respectively. He and his colleagues also used another method for extraction and quantification of celecoxib in tablets with detection limit of 0.122 μg mL^{-1} [151].

In Poland, a new fluorinated calix[4]arene-bonded silica gel stationary phase ($CalixBzF_{10}$) was synthesized, structurally characterized, and used as a selector in liquid chromatography for fluorine-containing compounds and non-fluorinated analytes. Barc and Sliwka-Kaszynska [152] showed that retention time of basic analytes depends on the mobile phase pH and fluorine–fluorine interactions are involved in the separation process of fluorine-containing analytes. There are some comparisons between commercially available stationary phases and calix[4]arene stationary phases. Such comparisons between 12 calix[4]arene stationary phases and some phenyl, fluorophenyl and fluoroalkyl columns were reported by that author [138]. Figure 7 shows the chemical structures of investigated silica based 1,3-alternate disubstituted calix[4]arene stationary phases.

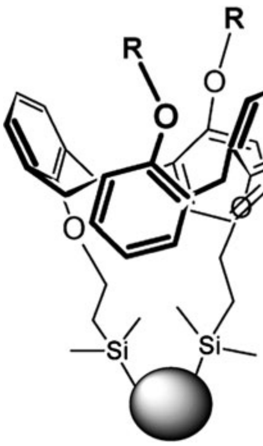


Fig. 7 Chemical structures of 12 silica based calix[4]arene stationary phases including Calixper (R = *n*-propyl), CalixHex (R = *n*-hexyl), CalixDdc (R = n-C_{12}) and etc.

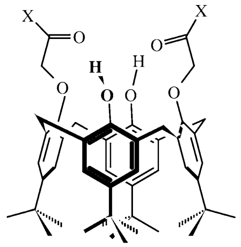
Tabakci in Turkey [153] used *p-tert*-butylcalix[6]arene hexacarboxylate containing both amide and acid moieties and immobilized it on the aminopropyl silica gel surface. The prepared sorbent was highly effective for Cr^{6+} at pH 1.5. They also studied the effect of pH, contact time, sorbent dosage, initial Cr^{6+} concentration and temperature on Cr^{6+} sorption and the sorption isotherms. Iki [107] reviewed thiacalixarenes as a pre-column derivatization reagent for the highly selective and sensitive determination of Ni^{2+}, Fe^{3+}, Al^{3+}, and Ti^{4+} at sub-ppb levels with reversed-phase HPLC. Japanese chemists [154] synthesized three different resins by methylene crosslinking of 2-pyridylcalix[4]arene and investigated their adsorption behavior towards the metal ions existing in photographic waste. The resins showed absolute efficiency for adsorption of Ag^+ with no affinity for other coexisting ions. The range of maximum loading capacity of Ag^+ on the resins was found to be 0.69–1.29 mol kg^{-1}. Column chromatographic separation of Ag^+ in presence of excess of Na^+ was carried out and selective adsorption of Ag^+ was achieved.

Applications in transport phenomena

Solvent extraction, which is carried out by various organic liquid extractants, with or without diluents or modifiers, has been used for the recovery of metal cations and anions. Synthetic resins, which contain functional groups similar to those used in solvent extraction, are also widely used in hydrometallurgy for separation of metallic ions and in wastewater purification. The use of resins bearing active functional groups is a form of extraction that involves a solid substrate. Such a substrate may be active in the ion extraction process. The ability of calixarenes to form complexes as carriers in transport through liquid membranes has been the central topics of many researches. In this sun-section, some recent studies are reviewed. Table 13 shows the topic of researches on the transport applications of calixarene derivatives.

A lead-ion selective membrane was made by Bochenska et al. [155] using *p-tert*-butylcalix[4]arene-thioamides as ionophores. Mutihac et al. [131] in Romania, investigated the transport through liquid membrane of L-tryptophan methylester and L-tyrosine methylester using *p-tert*-butylcalix[6,8]arene as carrier. The transport depended on the pH, the structure of calixarenes, the structure of amino acids, and the nature of anion used as ion pair for cation-receptor complexes. The properties of solvent involved in liquid membrane played an important role in selecting membrane systems and also in membrane stability. Mutihac et al. [124, 156] studied the ability of functionalized calix[*n*]arenes as carriers in transport through liquid membranes of different biological amine compounds including ammonium ion, amines, amino acids, and peptides. They presented the effect of the factors that influence the separation of above compounds by transport through liquid membranes using the calix[*n*]arenes.

Bochenska et al. [51] synthesized the *cone* and *partial cone* conformers of *p-tert*-butylcalix[4]arene-crown-6 derivatives and examined their ability to complex alkali, alkaline earth and soft cations as ionophores in ion-selective membrane electrodes. They used UV absorption spectrophotometry to compare complexing properties of two synthesized compounds in the PVC membrane with liquid–liquid extraction of alkali metal picrate in acetonitrile solution. Kim et al. [157] used a series of calix[4]arenes (**38–42**) substituted by acid and amido functions, glycolic chains, and hydroxyl groups as carriers in liquid membranes. Transport of aromatic amino acid methylesters (**43–45**) through liquid membrane (from the aqueous source phase to the aqueous receiving phase) assisted by the pH gradient. They discussed the influence of calixarene and amino acid structures upon transport through liquid membranes.

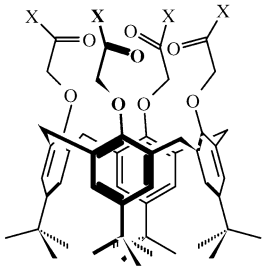


X = OH

X = $NHCH(CH_2OH)_2$

X = $NHC(CH_2OH)_3$

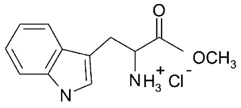
38-40



X = OH

X = $NH(CH_2)_2O(CH_2)_2OH$

41 and **42**



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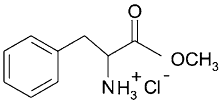

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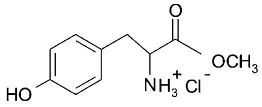

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Table 13 The list of transport applications of calixarene derivatives

Type of calixarene	Analytes were used	References
p-tert-Butylcalix[4]arene-thioamides	Pb^{2+}	[155]
p-tert-Butylcalix[6,8]arene	L-Tryptophan methylester and L-tyrosine methylester	[131]
Functionalized calix[*n*]arenes	Ammonium ion, amines, amino acids, and peptides	[124]
Functionalized calix[*n*]arenes	Biological compounds	[156]
p-tert-Butylcalix[4]arene-crown-6	Alkali, alkaline earth and soft cations	[51]
Calix[4]arenes substituted by acid, amido, glycolic, and hydroxyl groups	Aromatic amino acid methylesters	[157]

Calixarenes applications in electroanalytic methods

Potentiometric, voltammetric and other techniques are reviewed in this section, followed by the abstracted tables, which listed the researches conducted on calixarenes complexes.

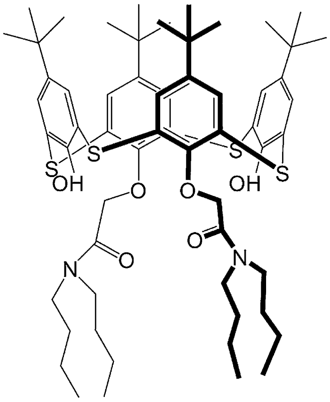
Potentiometric applications

El Nashar et al. [158] reviewed pharmaceutical and biological applications of calixarenes using potentiometric sensors from 2001 up to 2009.

s-Block (alkali and alkaline earth) cations

In this sub-section, the potentiometric methods are reviewed for the determination of *s*-block cations. Table 14 presented the topic of researches were done on the potentiometric behavior of *s*-block cations using calixarene derivatives.

Zine et al. [159] described potassium-ion selective microelectrodes with calix[4]crown-5 ionophore and linear response range of 6×10^{-6} to 1×10^{-1} M and detection limit of 1.8×10^{-6} M. Gupta et al. [160] evaluated an ionophore for the analysis of Sr^{2+} by a carboxy methoxy calix[6]arene derivative. The sensor was used as an indicator electrode in the potentiometric titration of sodium carbonate with Sr^{2+}. Korean researchers [161] prepared a thiacalix[4]arene diamide derivative (**46**) and investigated its electrochemical property and complexation behavior toward various metal ions by voltammetry. The electrode exhibited selectivity toward Sr^{2+} cation over alkali, alkaline earth and transition metal ions while conventional calix[4]arene diamides showed selective binding property with Ca^{2+}. They reported that this is due to the bigger size of thiacalix[4]arene than those of calix[4]arene.



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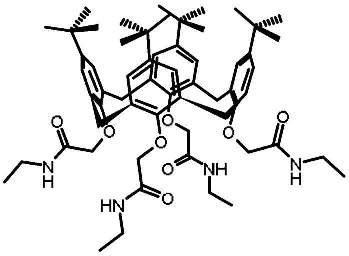
Polish and French chemists [51] prepared the *cone* and *partial cone* conformers of *p*-*tert*-butylcalix[4]crown-6 derivatives to examined their complexation ability towards alkali and alkaline earth metal cations as ionophores in ion-selective PVC membrane electrodes. A 5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26.2S-bis (diphenylphosphinoylmethoxy)calix[4]arene has been used in Iran [17] as an ionophore in a PVC coated graphite membrane Ca^{2+}-selective electrode. The membrane comprised 6% calix[4]arene, 61% ortho-nitrophenyloctyl ether as solvent mediator, 30% PVC, and 3% sodium tetraphenylborate as anion excluder. The electrode exhibited a near-Nernstian response over a concentration range of Ca^{2+} 1×10^{-5} to 1×10^{-3} M and the detection limit was 3.6×10^{-6} M. The working pH range of the electrode was 4–7.

p-Block cations

This sub-section focuses on the applications of calixarenes in potentiometric determination of *p*-block cations. Table 15 illustrated the researches were carried out on the potentiometric behavior of *p*-block cations using calixarene derivatives.

Bochenska et al. [155] applied five tetrasubstituted *p*-*tert*-butylcalix[4]arene-thioamides as ionophores in lead-ion-selective membrane. The tertiary calix[4]thioamides showed remarkable selectivity to lead ions while the secondary calix[4]thioamides formed less stable electrode membranes. Chen et al. [162] tested seven double-armed calix[4]arene amide derivatives to make lead ion-selective electrodes. Jain et al. [163] used 5,11-dibromo-25,27-dipropoxycalix[4]arene ionophore in PVC based membrane sensors selective to Pb^{2+}. Sensor exhibited a nernstian response in the concentration range 2.5×10^{-6} to 5.0×10^{-2} M. In Poland, Bochenska and Lesinska [164] evaluated three lipophilic *tert*-butylcalix[4]arene amides (**47**–**49**) as lead ionophore. One of them had the best selectivity coefficients towards Pb^{2+} in the presence of copper and cadmium ($\log K_{Pb,M} < -3$) and cobalt, nickel, and alkaline earth metal ions ($\log K_{Pb,M} < -4$).



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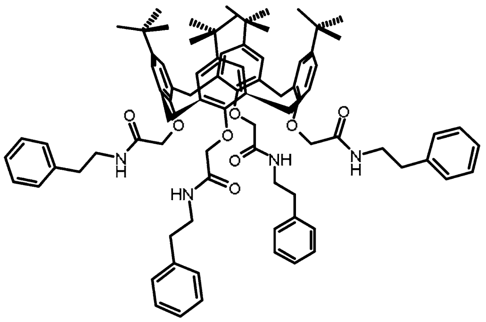

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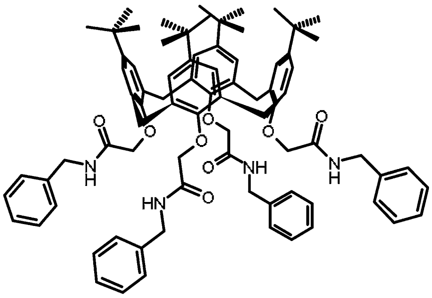

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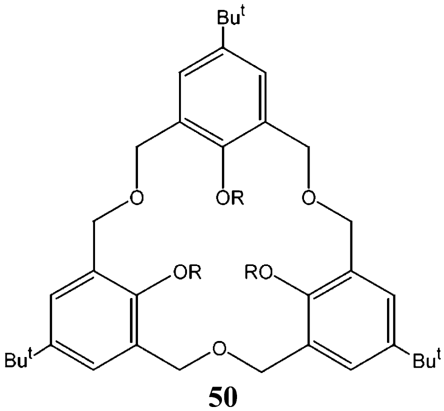
Yaftian et al. [165] made a coated wire-type lead ion-selective electrode based on a 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(diphenylphosphinoylmethoxy)calix[4]arene over a concentration range of 1×10^{-5} to 1×10^{-2} M, detection limit of 1.4×10^{-6} M and response time of 17 s. they also investigated the selectivity of the electrode performance towards lead ions over Th^{4+}, La^{3+}, Sm^{3+}, Dy^{3+}, Y^{3+}, Ca^{2+}, Sr^{2+}, Cd^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, NH_4^+ Ag^+, Li^+, Na^+ and K^+ ions. Yaftian et al. [12] prepared a lead-selective membrane electrode based upon a phosphorylated hexahomotrioxacalix[3]arene (**50**) and tested it in a aqueous solution of Pb^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cd^{2+} over a concentration range of 1×10^{-8} to 1×10^{-4} M, detection limit of 0.4×10^{-8} M and response time of 7 s. The selectivity of electrode was examined relative to Ag^+, NH^{4+}, Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, La^{3+}, Sm^{3+}, Dy^{3+}, Er^{3+}, Y^{3+} and Th^{4+}. The characteristics of the sensor were compared with those of a tetraphosphorylated calix[4]arene based Pb^{2+}-ISE, reported before by this author.



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Bochenska et al. [51] studied the complexation ability of *p-tert*-butylcalix[4]crown-6 ionophores towards soft cations in ion-selective PVC membrane electrodes.

Table 14 The list of calixarenes, *s*-block cations used in potentiometric techniques

Type of calixarene	Analytes were used	References
Calix[4]crown-5	K^+	[159]
Carboxy methoxy calix[6]arenes	Sr^{2+}	[160]
Thiacalix[4]arene diamide derivative	Sr^{2+}	[161]
p-tert-Butylcalix[4]crown-6	Alkali and alkaline earth metal cations	[51]
Tetra-*tert*-butyl-bis(diethylcarbamoylmethoxy)-bis(diphenylphosphinoylmethoxy)calix[4]arene	Ca^{2+}	[17]

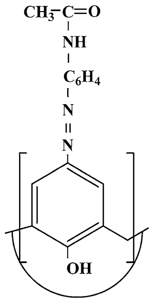
Table 15 The list of calixarenes, *p*-block cations used in potentiometric techniques

Type of calixarene	Analytes were used	References
Tetrasubstituted *p-tert*-butylcalix[4]arene-thioamides	Pb^{2+}	[155]
Double-armed calix[4]arene amide derivatives	Pb^{2+}	[162]
5,11-Dibromo-25,27-dipropoxycalix[4]arene	Pb^{2+}	[163]
tert-Butylcalix[4]arene amides	Pb^{2+}	[164]
5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetrakis-(diphenylphosphinoylmethoxy)calix[4]arene	Pb^{2+}	[165]
Phosphorylated hexahomotrioxacalix[3]arene	Pb^{2+}	[12]
p-tert-Butylcalix[4]crown-6	Soft cations	[51]

d-Block (transition and heavy) cations

The determination of transition metals in environmental, physiological fluids, industrial and other samples is of considerable interest in analytical chemistry. Moreover, in recent years several studies have linked the concentrations of specific transition metals to various diseases. Traditionally, atomic absorption spectrophotometric techniques have been used by most analytical chemists to determine transition metals but these techniques have their limitations. Flame atomic absorption spectroscopy has limited sensitivity for some transition metals, and graphite atomic absorption spectroscopy is susceptible to solute vaporization interferences such as depression of element signal. For instance, the protein content of the physiological fluid samples can cause absorption abnormalities and high sodium chloride content can hamper sensitivity, linearity, and cause burner clogging. Table 16 summarizes recent studies based on potentiometric studies on *d*-block cations using calixarene derivatives.

Belhamel et al. [166] made a PVC membrane with 5,11,17,23,29,35-hexakis-*tert*-octyl-37,38,39,40,41,42-hexakis(*n*-phenylthiocarbamoylmethoxy)calix[6]arene ionophore to make a nickel ion-selective PVC membrane electrode with linear response range of 5×10^{-6} to 1×10^{-2} M. Mahajan et al. [167] prepared a Hg^{2+} sensors by incorporating three different calix[4]arene derivatives ionophores a showed linear concentration ranges and detection limits of order $\sim 10^{-6}$ M with response time of 20 s. Tyagi et al. [168] used a PVC based membrane containing *p-tert*-butyl-calix[4]arenethioether to measure Hg^{2+}. The sensors were found to work in partially non-aqueous media up to 40% (v/v) acetone, methanol or ethanol with linear concentration range of 7.2×10^{-8} to 1.0×10^{-1} M and response time of 14 s. Kumar and Shim [169] prepared a Cr^{3+}-selective electrode using *p*-(4-acetanilidazo)calix[4] arene (**51**) ionophore. The linear concentration range of 9.8×10^{-7} to 1.0×10^{-1} M and response time of 14 s were reported. The electrode selectivity over most of the common cations including Li^{+}, K^{+}, Na^{+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Sr^{2+}, Ba^{2+}, Cs^{+}, Pb^{2+}, Zn^{2+}, Mg^{2+}, Cd^{2+}, Al^{3+}, Fe^{3+} and La^{3+} was examined successfully.



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Gupta et al. [170] used a bridge modified 4-*tert*-butylthiacalix[4]arene (**52**) to prepare a cobalt selective sensor with detection limits of 0.3 ppm, linear working range of 5.3×10^{-6} to 1.0×10^{-1} M and response time of 10 s. The sensor possesses excellent selectivity for Co^{2+} over a large number of cations such as Na^{+}, K^{+}, Ag^{+}, Ca^{2+}, Mg^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Li^{+}, Ba^{2+}, Zn^{2+}, Sr^{2+}, Cr^{3+} and Ni^{2+}.

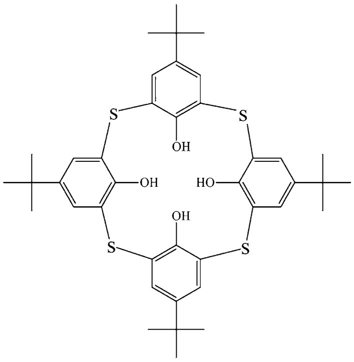

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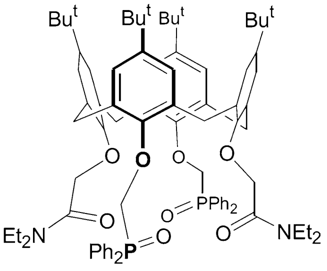
Table 16 List of calixarenes and *d*-block cations used in potentiometric techniques

Type of calixarene	Analytes were used	References
5,11,17,23,29,35-Hexakis-*tert*-octyl-37,38,39,40,41, 42-hexakis(*N*-phenylthiocarbamoylmethoxy)calix[6]arene	Ni^{2+}	[166]
Calix[4]arene derivatives	Hg^{2+}	[167]
p-tert-Butyl-calix[4]arenethioether	Hg^{2+}	[168]
p-(4-Acetanilidazo)calix[4]arene	Cr^{3+}	[169]
4-*tert*-Butylthiacalix[4]arene	Co^{2+}	[170]
Thiacalix[4]arene derivative	Ag^{+}	[171]
Thiacalix[4]arene derivatives	Ag^{+}	[172]
p-Sulfonic calix[*n*]arene ($n = 4, 6, 8$)	Ag^{+}	[173]
5,11,17,23-tetra-*tert*-Butyl-25,27-dihydroxy-calix[4] arene-thiacrown-4	Ag^{+}	[174]
Amide-phosphoryl *p-tert*-butylcalix[4]arene	Ag^{+}	[175]
Benzothiazolylacetamidoalkoxy calix[4]arenes derivatives	Ag^{+}	[13]
Benzothiazolyl calix[4]arenes derivatives	Ag^{+}	[176]

Csokai et al. [171] in Hungary, synthesized thiacalix[4]arene ionophores comprised of cyclic or linear *O*,*S*,*N* ligating and π-coordinate groups on the lower rim and used H NMR to study their ability to Ag^+ binding. They found that calix[4](*O*,*S*,*N*)crowns were stronger binders than π-coordinators and thiacalixarene ionophores were superior to calixarenes. Evtugyn et al. [172] in Russian federation, developed a Ag^+-ion selective electrode with thiacalix[4]arene ionophore. Linear response range from 1.0×10^{-2} to 5.0×10^{-7} M and response time of 12 s were reported. They fully eliminated the interfering effect of Hg^{2+} and Fe^{3+} ions, by controlling the pH and using NaF as a masking agent, respectively. Mousavi et al. [173] also prepared a potentiometric Ag^+ sensors with three ionophores including *p*-sulfonic calix[4]arene, *p*-sulfonic calix[6]arene and *p*-sulfonic calix[8]arene.

Demirel et al. [174] used 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4 to prepare a silver-selective PVC membrane potentiometric sensor with nernstian response concentration range of 1.0×10^{-2} to 1.0×10^{-6} M. The electrode showed high selectivity towards Ag^+ ions over Pb^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Sr^{2+}, Mg^{2+}, Ca^{2+}, Li^+, K^+, Na^+, NH_4^+ ions but not over Hg^{2+}. Parsa et al. [175] constructed a coated-wire type silver ion selective electrode using a modified *p*-*tert*-butylcalix[4]arene by amide-phosphoryl groups (**53**) with linear nernstian response over the range 1×10^{-6} to 1×10^{-2} M and detection limit of 6.3×10^{-7} M. The selectivity of the sensor was examined relative to NH_4^+, Li^+, Na^+, K^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Fe^{3+}, La^{3+}, Sm^{3+} and Th^{4+}.



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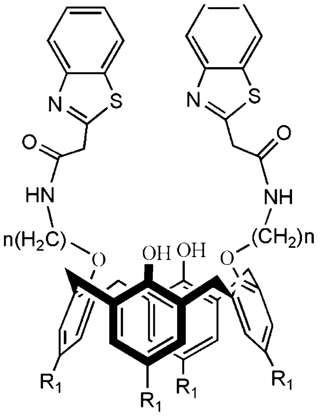
Morakot et al. [13] in Thailand synthesized and used four calix[4]arenes derivatives (**54**) with benzothiazolylacetamidoalkoxy pendant groups to prepare silver ion selective electrode. For calixarene 1, $n = 4$ and $R_1 =$ *tert*-Bu; calixarene 2, $n = 4$ and $R_1 = H$; calixarene 3, $n = 2$ and $R_1 =$ *tert*-Bu; and calixarene 4, $n = 2$ and $R_1 = H$. All of the ionophores showed response times less than 12 s. Table 17 shows their linear response range and limit of detection. Ngeontae et al. [176] also synthesized calix[4]arenes derivatives with benzothiazolyl pendant groups to prepare macro and micro Ag^+-selective membrane electrodes with detection limits of 5.0×10^{-7} M and linear working range of 1.0×10^{-6} to 1.0×10^{-2} M.



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f-Block (lanthanide and actinide) cations

Journal of the Chinese chemical society published Hassanzadeh et al. [177] paper including a thorium-ion selective sensor based on calix[4]arene bearing phosphoryl groups (**55**). Linear concentration range of 1×10^{-5} to 1×10^{-3} M and detection limit of 7.9×10^{-6} M thorium were reported.

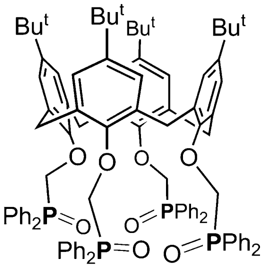

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Table 17 The linear response range and the limit of detection for Ag^+-ion selective electrode based on four benzothiazolyl-acetamidoalkoxy-calix[4]arenes [176]

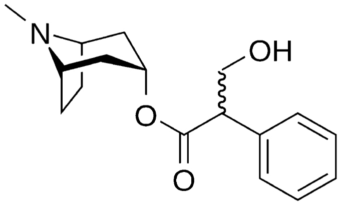
Parameters	Calixarene 1	Calixarene 2	Calixarene 3	Calixarene 4
Linear range (M)	5.0×10^{-6} to 1.0×10^{-2}	3.2×10^{-7} to 1.0×10^{-2}	8.0×10^{-6} to 1.0×10^{-2}	1.3×10^{-7} to 6.3×10^{-3}
Detection limit (M)	5.01×10^{-6}	3.16×10^{-7}	7.94×10^{-6}	1.26×10^{-7}

Molecular compounds

In this sub-section, the potentiometric methods are reviewed for the determination of molecular spices using calixarenes. Table 18 listed the potentiometric applications of calixarene derivatives to recognize the molecular spices.

Jin et al. [178] modified a glassy electrode via covering with a calix[4]arene and determined hydrogen peroxide and glucose with detection limit of 4.0×10^{-5} and 2.0×10^{-5} M, respectively. Iranian chemists [179] designed a PVC membrane potentiometric sensors with tetrabenzyl ether calix[4]arene ionophore to measure 2-furaldehyde in the linear concentration range of 5.0×10^{-5} to 1.0×10^{-1} M. Vaze and Srivastava [180] determined pyridoxine hydrochloride in pharmaceutical preparations based upon the use of calix[8]arene as a neutral carrier in a potentiometric sensor between pH 3.0 and 7.2. It showed a short response time of 20 s in concentration range of 1×10^{-1} to 6.2×10^{-6} M and detection limit of 1.6×10^{-6} M. They found that the mediator *o*-nitrophenyl octyl ether significantly increased the lifetime of the sensor. Kretz et al. [181] compared resist systems of a MOSFET sensor including hydrogen-silesquioxane, 4-methyl-acetoxy-calix[6]arene and chloro-methyl-tetrakis-methoxy-calix[4]arene in measuring the fluorine gas mixture.

Atropine (**56**) drug is administered via injection, eye drops, or in oral form to relax muscles by inhibiting nerve responses. Used to dilate the pupils and as an antispasmodic. Zareh and Malinowska [182] prepared a atropine selective membrane electrode using three calixarene derivatives: 37,40-bis-[(diethoxy-thiophosphoryl)oxy]-5,11,17,23,29,35-hexakis(1,1-dimethyl-ethyl)-calix[6]arene-8,39,41,42-tetrol; 37,38,39,40,41-pentakis-(diethoxythiophosphoryl)-oxy]-5,11,17,23,29,35-hexakis (1,1-dimethylethyl)-calix[6]-arene-42-ol; and 37-[(diethoxythiophosphoryl)oxy]-5,11,17,23,29,35-hexakis-(1,1dimethylethyl)-calix[6]arene-38,39,40,41,42-pentol. Their practical linear ranges were 1.9×10^{-6} to 7.9×10^{-3} M, 7.9×10^{-6} to 7.9×10^{-3} M, and 6.3×10^{-6} to 7.9×10^{-3} M, respectively. The recovery percent and the relative standard deviation values were determined to be 97.5–99.1% and 0.39–0.72% for five determinations, respectively. The electrode was applied successfully for analyzing atropine sulfate in eye drops and injection solution.



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Organic cations

Polish and Belgian researchers [183] discussed the mechanism of potentiometric signals generation by liquid membrane electrodes incorporating undecylcalix[4]resorcinarene derivatives upon stimulation by uncharged aniline derivatives. They proved that in the conditions where all aniline derivatives exist as uncharged molecules, cationic potentiometric signals were observed for all undecylcalix[4]resorcinarene liquid membrane electrodes. They claimed that the main parameters crucial for this phenomenon were the acidity–basicity of the hosts and guests and the lipophilicity of the guests played a secondary role. Japanese chemists [184] prepared a highly selective methylammonium-selective membrane electrode by *p*-1,1,3,3-tetramethylbutylcalix[6]arene-hexaacetic acid hexaethyl ester and showed the highest response to methylammonium among various organic ammonium ions and inorganic cations.

Anions

In this sub-section the fast detection of anion spices by means of potentiometric techniques has been summarized. Table 19 listed the potentiometric applications of calixarene derivatives to recognize the anion guest spices.

Schazmann and Diamond [185] synthesized two urea-calix[4]arenes ionophore, which the first, revealed a strong response to all anions following the Hofmeister selectivity order and the second one showed a high selectivity of nitrate over chloride (a common interferant of nitrate in fresh and marine water samples). Babu et al. [186]

Table 18 The list of calixarene derivatives were used in potentiometric applications to recognize the molecular guest spices

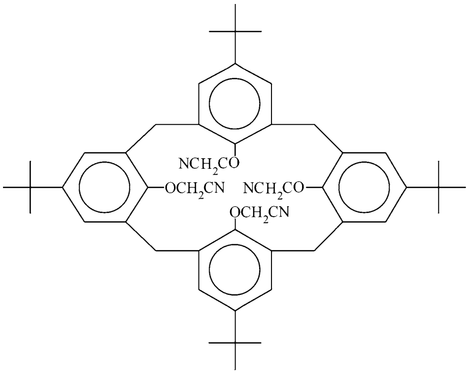
Type of calixarene	Analytes were used	References
Calix[4]arene derivative	Hydrogen peroxide and glucose	[178]
Calix[4]arene derivative	2-Furaldehyde	[179]
Calix[8]arene derivative	Pyridoxine hydrochloride	[180]
4-Methyl-acetoxy-calix[6]arene and chloro-methyl-tetrakis-methoxy-calix[4]arene	Fluorine	[181]
bis-[(Diethoxy-thiophosphoryl)oxy]-hexakis (1,1-dimethyl-ethyl)-calix[6]arene-ol derivatives	Atropine	[182]

Table 19 The list of calixarene derivatives were used in potentiometric applications to recognize the anion guest spices

Type of calixarene	Analytes	References
Urea-calix[4]arenes	NO_3^-	[185]
Ureido calix[4]arene derivative	Cl^-	[186]
tetra-*tert*-Butyl-tetracyanometoxy-calix[4]arene	SCN^-	[187]
Urea and thiourea-functionalised calix[4]arene	HPO_4^{2-}	[188]
hexa-*tert*-Butyl-hexakis(carbamoylmethoxy)calix[6]arene	HPO_4^{2-}	[189]
5,11,17,23-tetra-*tert*-Butyl-25,26,27,28-tetracyanometoxy-calix[4]arene	ClO_4^-	[190]
Urea-functionalized calix[4]arenes	CO_3^{2-}	[191]

synthesized a ureido moiety calix[4]arene derivative and examined its anion recognition abilities towards fluoride, chloride, bromide, iodide, nitrate and acetate by UV–Vis spectroscopy and H NMR. The ionophore showed a strong binding affinity for chloride ions and a chloride ion selective electrode was formed with the detection limit of 2.51×10^{-5} M. Erden et al. [187] in Turkey, prepared a thiocyanate ion-selective electrode from hydrogen ion-selective membrane containing 1% 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene as ionophore. The electrode exhibited a linear response over the range 1.0×10^{-1} to 3.0×10^{-5} M with response time of 10–15 s.

Kivlehan et al. [188] evaluated one urea-functionalised calix[4]arene and one thiourea-functionalised calix[4]arene for monohydrogen orthophosphate (HPO_4^{2-}) sensing with linear concentration range of 5.0×10^{-5} to 1.0×10^{-1} M. Gupta et al. [189] also used another ionophore to recognize monohydrogen orthophosphate anions with 5,11,17,23,29,35-hexa-*tert*-butyl-37,38,39,40,41,42-exakis(carbamoylmethoxy)calix[6]arene. The linear response range reported 1.77×10^{-5} to 1.0×10^{-1} M. Canel et al. [190] made a perchlorate ionophore using 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene (**57**). This ion-selective electrode exhibited a linear response over the range 1.0×10^{-1} to 1.0×10^{-5} M and response time of 10–15 s.



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Lee et al. [191] in Korea, prepared a PVC membrane electrode for CO_3^{2-} anions based on urea-functionalized calix[4]arenes ionophores. The linear response range of 5.0×10^{-4} to 1.0×10^{-1} M and detection limit of 1.2×10^{-4} M was obtained. The selectivity coefficients towards CO_3^{2-} in the presence of salicylate and iodide were reported.

Voltammetric applications

In this section, general methods are reviewed for determination and recognition of ion spices and molecular compounds by means of the voltammetric techniques.

s-Block (alkali and alkaline earth) cations

Alkali metals show the only oxidation state of +1 and they don't show any change in this oxidation number; hence, they don't have redox behavior in voltammetric methods.

p-Block cations

Torma et al. [192] made a calixarene-based chemically modified bismuth-film electrode on glassy carbon substrate for determination of lead ions via square wave anodic adsorptive stripping voltammetry with 0.02 μg/L detection limit and 0.05 to 0.6 μM dynamic range. Zheng et al. [193] provided a glassy carbon electrode coated with Langmuir–Blodgett film of allylcalix[4]arene for traces determination of lead. Limits of detection and linear response range were 1.7 and 22–5,600 μg/L respectively. Dong et al. [194] determined trace amounts of thallium using a glassy carbon electrode coated with Langmuir–Blodgett film of *p*-allylcalix[4]arene by anodic stripping voltammetry with linear voltammetric response of 5–250 μg/L and detection limit of 1.0 μg/L, respectively.

d-Block (transition and heavy) cations

This sub-section focuses on the applications of calixarenes in voltammetric determination of transition metal cations.

Table 20 presents the recent studies carried out on the voltammetric study of *d*-block cations using calixarene derivatives.

Iranian chemists [195] used differential pulse anodic stripping voltammetry to determine silver(I) at *p*-isopropylcalix[6]arene modified carbon paste electrode with dynamic range of 5.0×10^{-8} to 2×10^{-6} M and detection limit (3δ) of 4.8×10^{-8} M. A modified glassy carbon electrode with Langmuir–Blodgett film of a calix[4]arene derivative was prepared for silver recognizing by a stripping voltammetric method with 8×10^{-9} M detection limit at accumulation time of 180 s [196]. Zheng et al. [193] also used a similar way to recognize cadmium ions. Linear response range and detection limits were 20.7–5,200 and 2.2 µg/L, respectively. Dong et al. described a glassy carbon electrode coated with Langmuir–Blodgett film of *p*-allylcalix[4]arene for traces determination of cadmium [194] and mercury [197] by anodic stripping voltammetry. Linear voltammetric response of Cd^{2+} and Hg^{2+} were in the range of 10–300 and 0.07–40 µg/L, respectively. Their detection limits also were estimated to be 2.2 and 0.04 µg/L, respectively.

Chinese researchers [198] determined the trace amounts of Hg^{2+} by a coated glassy carbon electrode with the film of 4-*tert*-butyl-1-(ethoxycarbonylmethoxy)thiacalix[4]arene via anodic stripping voltammetry. The linear voltammetric response was in the range of 8.0×10^{-9} to 3.0×10^{-6} M with detection limit of 5.0×10^{-9} M. In Turkey, Canpolat et al. [199] measured trace amounts of copper with a calix[4]arene modified carbon paste electrode by differential pulse anodic stripping voltammetry with 1.1 µg/L detection limit in 10 min preconcentration time.

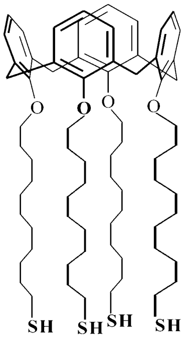
f-Block (lanthanide and actinide) cations

Researchers of Jerusalem [200], developed a modified electrode that was made by attachment of the 4-sulfonic-calix[6]arene to the cysteamine monolayer with high selectivity towards uranyl ions.

Molecular compounds

General methods are proposed for determination and recognition of molecular spices by means of the voltammetric reduction of a functional group in the molecule. Table 21 shows the recent studies carried out on the voltammetric study of molecular compounds using calixarene derivatives.

Iranian chemists [179] presented the adsorptive square wave voltammetry of 2-furaldehyde on a PVC-membrane electrode doped with tetrabenzyl ether calix[4]arene in order to elucidate the adduct formation between 2-furaldehyde and Girard's reagent T. They studied some interferences including Na^+, K^+, NH_4^+, formaldehyde, 5-hydroxymethyl 2-furaldehyde, excess of Girard's reagent T, organic solvents, isopropyl alcohol and *N*,*N*-dimethylformamide on the sensor's response. Recently, Slovakian chemists [201] synthesized 25,26,27,28-tetrakis(11-sulfanylundecyloxy)calix[4]arene (**58**) and used that in a mixtures with 1-dodecanethiols or hexadecanethiols to form a self assembled monolayers served as sensor for dopamine with detection limit of 50 pM discrimination ability between dopamine and epinephrine. They used cyclic voltammetry at presence of redox probe $[Fe(CN)_6]^{3-/4-}$ to evaluate the SAMs.



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Vaze and Srivastava [202] studied the adsorptive stripping voltammetric behavior of folic acid at plain carbon paste electrode and *p*-*tert*-butyl-calix[6]arene modified electrode with detection limit of 1.24×10^{-12} M. Zhang et al. [203] developed selective electrochemical method for

Table 20 List of calixarenes and their guest *d*-block cations used in the voltammetric techniques

Concept of study	Type of calixarene	Analyte	References
Differential pulse anodic stripping voltammetry	*p*-Isopropylcalix[6]arene	Silver	[195]
Stripping voltammetry	Langmuir–Blodgett film of a calix[4]arene derivative	Silver	[196]
Stripping voltammetry	Langmuir–Blodgett film of allylcalix[4]arene	Cadmium	[193]
Anodic stripping voltammetry	Langmuir–Blodgett film of *p*-allylcalix[4]arene	Cadmium	[194]
Anodic stripping voltammetry	Langmuir–Blodgett film of *p*-allylcalix[4]arene	Mercury	[197]
Anodic stripping voltammetry	4-*tert*-Butyl-1-(ethoxycarbonylmethoxy)thiacalix[4]arene	Mercury	[198]
Differential pulse anodic stripping voltammetry	Langmuir–Blodgett film of allylcalix[4]arene	Copper	[199]

Table 21 The list of molecular compounds and related calixarene derivatives were studied in voltammetric methods

Concept of study	Type of calixarene	Analytes were used	References
Adsorptive square wave voltammetry	Tetrabenzyl ether calix[4]arene	2-furaldehyde	[179]
Cyclic voltammetry	Calix[4]arene derivative	Dopamine	[201]
Adsorptive stripping voltammetry	*p*-*tert*-butyl-calix[6]arene	Folic acid	[202]
Voltammetric methods	Calix[4]arene crown-4 ether	Norepinephrine	[203]
Cyclic voltammetry	Calix[4]arene crown-4 ether	Dopamine	[204]
Cyclic and differential pulse voltammetry	*p*-tetra-Butyl calix[6]arene-L-Histidine	Epinephrine and serotonin	[205]
Voltammetric methods	Calixcrownchips	Antigens and antibodies	[206]
Voltammetric methods	c-methylcalix[4]resorcenarene and calix[8]arene	Nicotinamide	[207]

the determination of norepinephrine using a calix[4]arene crown-4 ether film modified glassy carbon electrode. Lai et al. [204] determined dopamine using a calix[4]arene crown-4 ether film modified glassy carbon electrode with dynamic range of 2.0×10^{-5} to 1.0×10^{-3} M and detection limit of 4×10^{-6} M. Journal of analytical chemistry published the investigations of Liu et al. [205] carried out by *p*-tetra-butyl calix[6]arene-L-histidine modified glassy carbon electrode for determination of epinephrine and serotonin by cyclic and differential pulse voltammetry in the presence of 1.0×10^{-3} M ascorbic acid.

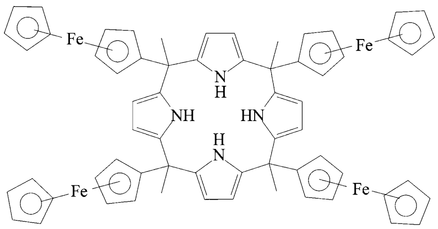
Development of immunosensors is increasingly finding applications in clinical diagnostics and biological researches. They consist of immobilization of antigens or antibodies on the surface of calixcrown and the direct electrochemistry of horseradish peroxidase. South Korean and Iranian chemists [206] used calixcrownchips and immobilized the alanine aminotransferase monoclonal antibody on thiol derivative of calixcrown (1,3-dimethoxy,2,4-dithiol-calix[4]crown-5-ether) fixed to a gold surface. They claimed that the calixcrownchip immunosensor microarray provided much better technical performance than a comparable enzyme sensor. Indian chemists [207] studied the electrochemical behavior of nicotinamide at modified carbon paste electrodes with macrocyclic compounds including c-methylcalix[4]resorcenarene and calix[8]arene. The increase in anodic peak current was used for finding linear working range, which was 0.1–500 μg mL^{-1} with a detection limit of 0.03 μg mL^{-1} by DPV. They also studied the interference from other vitamins like thiamine HCl (Vit. B_1), riboflavin (Vit. B_2), pyridoxine HCl (Vit. B_6), cynocobamine (Vit. B_{12}), *p*-aminobenzoic acid (PABA) and ascorbic acid (Vit. C). They claimed that the modified electrode could be used for the simultaneous determination of riboflavin, nicotinamide and pyridoxine HCl.

Organic cations

Chawla et al. [208] synthesized a series of calix[4]arene diquinones and investigated their interacts with ammonium ions. The interactions induced an unprecedented downfield shift in the NH proton resonance, which was attributed to polarization of the amidocrown ring of the calix[4]arene diquinone receptor. The observation has been confirmed by a significant anodic shift of the corresponding amidocrown-diquinone redox couple in cyclic and square wave voltammetric experiments.

Anions

Szymanska et al. [209] used a neutral redox-active receptor, based on ferrocene functionalized calix[4]pyrrole, as an active component in carbon paste ion-selective electrodes using Osteryoung square-wave voltammetry to detect aqueous anions (dihydrogen phosphate, fluoride, bromide and chloride). Irish researchers [210] characterized the interaction of a urea-functionalized calix[4]arene ionophore and phosphate using voltammetric ion transfer at the interface between two immiscible electrolyte solutions (ITIES). Voltammetry at the ITIES confirmed that the ionophore-facilitated transfer of monohydrogen phosphate occurred in preference to dihydrogen phosphate transfer. Rumanian chemists [211] investigated the electrochemical behavior of *meso*-tetraferrocenyl-tetramethylcalix[4]pyrrole (**59**) modified graphite electrodes via cyclic voltammetry. They used this technique to recognize F^-, Cl^-, Br^-, SO_4^{2-}, $H_2PO_4^-$, ClO_4^-, and NO_3^-.



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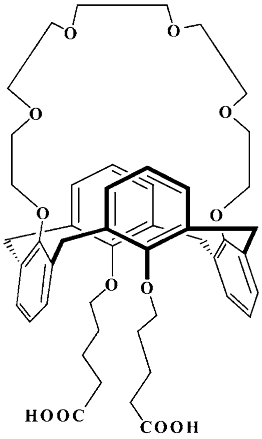
Other electroanalytical applications

Table 22 presents the recent studies carried out on the other electroanalytical techniques to recognize the *d*-block cations using calixarene derivatives.

Sosovska et al. [212] made conductometric chemosensors based on c-benzylresorcinolcalixarene for determination of amines and amino acids, which exhibited a better affinity than other macrocycles toward amine species. Zhang et al. [203] developed a calix[4]arene crown-4 ether film modified glassy carbon electrode for the determination of norepinephrine by electrochemical impedance spectroscopy. Two linear ranges were 5.5×10^{-7} to 9.7×10^{-6} M and 9.7×10^{-6} to 2.30×10^{-4} M and detection limit was 2.8×10^{-7} M. Filenko et al. [6] designed a conductivity gas sensor was functionalized with different calixarenes to measure volatile compounds like methanol, ethanol and propanol. Ijeri et al. [213] designed a sensor to determine amino acids that are neither electroactive nor with strong UV–Vis absorption has been explored. The sensor was based on capacitive sensing of amino acids using different calixarene derivatives (**60–63**) immobilized on silicon transducers.



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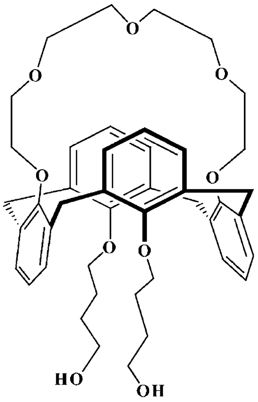

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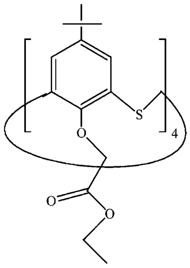

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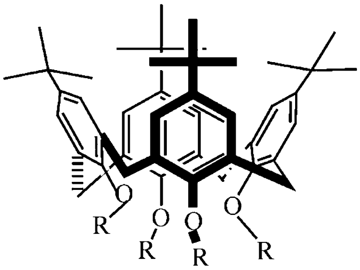


$R = CH_2COOCH_2CH_3$

63

The chemists of Athens [214] prepared an electrochemical flow injection analysis with resorcin[4]arene for measuring carbofuran in foods using a drop (50 μL) of sample. The response time and limit of detection were 80 s and 1.0 nM. Hassen et al. [215] studied the complexation of calix[4]arenes and two amino-acids (arginine and lysine) using faradic electrochemical impedance spectroscopy. They used three calix[4]arene coatings including a calixarene modified by the carboxylic acid groups, a benzyl modified calixarene, and a calixarene with sulphonated long chain. Limits of detection for first calix[4]arene coating were 1×10^{-3} and 6×10^{-3} M for arginine and lysine, respectively.

Calixarenes applications in spectroscopic techniques

Recent spectroscopic researches are reviewed in this section and followed by the abstracted tables, which listed those studies conducted on spectroscopic aspect of calixarene complexes.

Applications in luminescence

Among analytical methods, luminescence is an attractive detection method because of its intrinsic sensitivity, its response time and the possibility of imaging via fluorescence microscopy [216]. Valeur and

Table 22 List of calixarenes and their guest *d*-block cations used in the voltammetric techniques

Techniques were used	Type of calixarene	Analytes were used	References
Conductometric chemosensor	c-Benzylresorcinolcalixarene	Amines and amino acids	[212]
Electrochemical impedance spectroscopy	Calix[4]arene crown-4 ether film	Norepinephrine	[203]
Conductivity gas sensor	–	Methanol, ethanol and propanol	[6]
Capacitive sensing sensor	–	Amino acids	[213]
Electrochemical flow injection analysis	Resorcin[4]arene	Carbofuran	[214]
Faradic electrochemical impedance spectroscopy	Carboxylic-calixarene, benzyl-calixarene, and long chain sulphonated-calixarene	Arginine and lysine	[215]

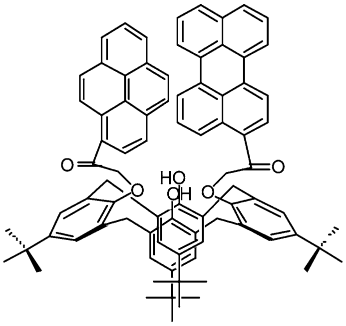
Leray [217] reported that calixarenes are building platforms in multichromophoric systems in which photoinduced phenomena are controlled by ions like electron, charge and proton transfers, excimer formation and resonance energy transfer. These calixarene-based multichromophoric systems are the base of molecular sensors.

The energy-transfer luminescence has been applied to displays, light-emitting diodes, lasers, bioanalyses, and optical amplifiers. The attractive features of energy-transfer luminescence are long emission lifetime, emissions at long wavelengths, sharp emission bands, and a large Stokes shift. To obtain strong emissions with a long lifetime, the ligand design is key factor. hence, a wide variety of ligands for luminescent complexes have been derived via the covalent joining of the ligating unit to an antenna group to absorb photons [107]. The review paper of Kim and Quang [218] deals with calixarenes used as fluorescent reagents for sensing cations and anions, by focusing on the mechanisms which control luminescence behavior.

s-Block (alkali and alkaline earth) cations

In this sub-section the applications of calixarenes in luminescent determination of alkali and alkaline earth cations are presented. Table 23 summarizes recent studies based on luminescence applications of calixarene derivatives to recognize alkali and alkaline earth cations.

Nishimura et al. [219] in Tokyo synthesized a calix[4]arene (**64**) having pyrene and perylene moieties as a Na^+ detectable fluorescent ionophore. By exciting the pyrene moiety at 342 nm, an energy transfer occurred from pyrene to perylene and caused a strong fluorescence emission of the perylene moiety at 535 nm. Na^+ at concentration range of 2.5×10^{-6} to 1.0×10^{-5} M remarkably quenched the fluorescence. By exciting the pyrene moiety at 342 nm, an excimer emission also occurred from calix[4]arene derivative. But in contrast, Na^+ at concentration range of 5.0×10^{-5} to 2.0×10^{-4} M decreased excimer emission.



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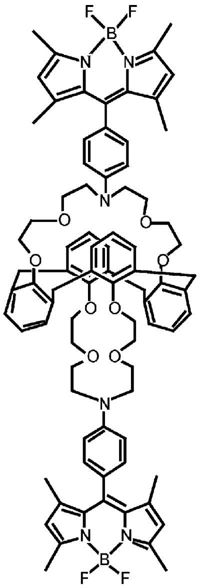
Miyaji et al. [220] synthesized a calix[4]pyrrole derivative and controlled its fluorescence emission properties by addition of Na^+ and anions. Fluorescence quenching by anions was observed only in the presence of Na^+. Chang et al. [221] synthesized their on–off chemosensor from a triazole-calix[4]crown derivative, which its emission was achievable by addition of K^+ or Ba^{2+} and its quenching by Hg^{2+}, Cu^{2+}, Pb^{2+} and Cr^{3+}. Malval et al. [222] synthesized a fluorophore containing a boron–dipyrromethene and a 1,3 alternate calix[4]bisazacrown-5 derivative (**65**). An efficient charge transfer reaction occurred in the excited state and led to a dual emission and a strong quenching. The sensor showed a high sensitivity and selectivity for potassium over sodium, cesium, calcium and barium cations in acetonitrile, ethanol, and ethanol–water mixtures.



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A calix[4]crown fluoroionophore bearing two-photon absorbing chromophores has been synthesized by Kim et al. [223] and it absorbed the light at 461 nm and weakly emit the fluorescence at 600 nm. Fluorescence intensity of Pb^{2+} with calix[4]crown·K^+ complex was increased rather than the fluorescence intensity of calix[4]crown·Pb^{2+} complex, because of the allosteric effect induced by the complexation of K^+ with a crown loop. Leray and Valeur [216] presented various calixarene-based sensors designed for recognition of Cs^+ ions in a review paper. Lee et al. [224] synthesized a calix[4]arene bearing one 2,3-naphthocrown-6 and two coumarin amide units at the lower rim as a fluorometric sensor for Cs^+. Intramolecular electron transfer from the naphthalene emission to the coumarin absorption afforded high fluorescence selectivity toward Cs^+.

In Seoul, Kim and Kim [225] synthesized a calix[4]arene diethyl ester derivative containing two proximal hydroxyl groups and two facing ethyl esters, which showed Ca^{2+} ion selectivity. A calix[4]arene-based fluorescence chemosensor with a strong excimer emission was prepared by Kim et al. [226] and exhibited a marked quenched excimer emission after Pb^{2+} complexation. Ca^{2+} broke the calix[4]arene·Pb^{2+} complex and the excimer emission band was revived, by which their on/off switch was proposed. American and Turkish researchers [227] linked the lower rims of di-ionized calix[4]arene to two dansyl (1-dimethylaminonaphthalene-5-sulfonyl) groups and investigated the influence of metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) on the spectroscopic properties of complexes using the spectrofluorimetric titration experiments in acetonitrile. On complexation by alkaline earth metal cations, both the absorption and emission spectra shifted to red and dansyl fluorescence was quenched. These effects were weaker with alkali metal cations.

p-Block cations

This sub-section focuses on the applications of calixarenes in luminescent determination of *p*-block cations. Table 24 shows luminescence applications of calixarene derivatives to recognize these cations.

Othman et al. [228] synthesized an Al^{3+}-calix[4]arene-based chemosensor which Al^{3+} ions significantly induced pyrenyl excimer emission at 475 nm. A two-photon fluoroionophore calix[4]crown was synthesized. Addition of an Al^{3+} or Pb^{2+} ion to a solution of the ligand causes a blue-shifted absorption and enhanced fluorescence [223]. Chang et al. [221] described a switchable fluorescent chemosensor which was composed of a triazole-modified calix[4]crown derivative. The fluorescence of macrocycle was strongly quenched by Pb^{2+} and the revival of emission from the strongly quenched complex was achievable by the addition of K^+, Ba^{2+} or Zn^{2+} cations. Kim et al. [226] prepared a strong excimer emission based on a calix[4]arene

Table 23 The list of calixarene derivatives were used in luminescence techniques to recognize the alkali and alkaline earth cations

Type of calixarene	Analytes were used	References
Calix[4]arene bearing pyrene and perylene moieties	Na^+	[219]
Calix[4]pyrrole	Na^+	[220]
Triazole-calix[4]crown	K^+ and Ba^{2+}	[221]
1,3-alternate Calix[4]bisazacrown-5	K^+	[222]
Calix[4]crown	K^+	[223]
–	Cs^+	[216]
Calix[4]arene bearing 2,3-naphthocrown-6 and coumarin amide	Cs^+	[224]
Calix[4]arene diethyl ester	Ca^{2+}	[225]
Calix[4]arene	Ca^{2+}	[226]
Calix[4]arene bearing dansyl (1-dimethylaminonaphthalene-5-sulfonyl) groups	Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}	[227]

Table 24 The list of calixarene derivatives were used in luminescence techniques to recognize *p*-block cations

Type of calixarene	Analytes	References
Calix[4]arene bearing pyrene moieties	Al^{3+}	[228]
Calix[4]crown	Al^{3+} or Pb^{2+}	[223]
Triazole-modified calix[4]crown	Pb^{2+}	[221]
–	Pb^{2+}	[226]
p-tert-Butyl-calix[4]arene	Pb^{2+}	[229]
–	Pb^{2+}	[216]
Calix[4]arene bearing two pyrene moieties	Pb^{2+} and In^{3+}	[230]
Calix[4]azacrown bearing two pyrene amide pendent groups	Pb^{2+}	[231]
Calix[4]arene bearing dansyl moiety	Pb^{2+}	[227]
Rhodamine homotrioxacalix[3]arene	Sb^{3+}	[232]

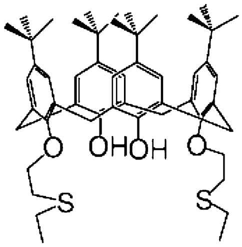
fluorescence chemosensor to recognize Pb^{2+} cation. When Pb^{2+} was bound to the two amide oxygen atoms linked to the fluorophores, the ligand exhibited a marked quenched excimer emission and by addition of Ca^{2+} into the complex the excimer emission band was revived, by which an interesting on–off switch fluorescence chemosensor was proposed. Liu et al. [229] synthesized a *p-tert*-butyl-calix[4]arene derivative in $CH_3CN–H_2O$. It exhibited highly selective fluorescent response to Pb^{2+} over alkali, alkali earth metal ions and some transition metal ions. Some calixarene sensors, which designed for lead recognition were reviewed by Leray and Valeur [216].

Two facing amide groups were linked to fluorescent pyrene units of a fluorogenic calix[4]arenes derivative to form a fluoroionophore. When orientations of the pyrene units were face-to-face π-stacked, the ligand showed a remarkably high selectivity for In^{3+}. While, the orientations of pyrene units were remote from each other, the ligand showed high selectivity for Pb^{2+} [230]. Kim et al. [231] synthesized a calix[4]azacrown bearing two pyrene amide pendent groups as a selective sensor for Pb^{2+} owing to the ratiometric changes of monomer and excimer emissions. Ocak et al. [227] investigated the influence of Pb^{2+} on the spectroscopic properties of calix[4]arene bearing dansyl moiety complex using the spectrofluorimetric titration experiments in acetonitrile. Pb^{2+} caused greater than 97% quenching of the dansyl fluorescence in the calix[4]arene derivative. Wu et al. [232] synthesized rhodamine homotrioxacalix[3]arene and studied the fluorescent enhancement of its complex with Sb^{3+} in the range of 500–600 nm using fluorescence spectroscopy.

d-Block (transition and heavy) cations

In this sub-section the applications of calixarenes in luminescent determination of transition metals are presented. Table 25 shows these applications in recognition of transition cations.

Li et al. [7] prepared a luminescent and stable quantum dots capped with sulfur calixarene (**66**) for selective determination of mercury ions in acetonitrile via its quenching effect. Even at a relatively higher concentration, the interference influence of other metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) were very weak. Only Pb^{2+} at a higher concentration produced a measurable quenching of luminescence.



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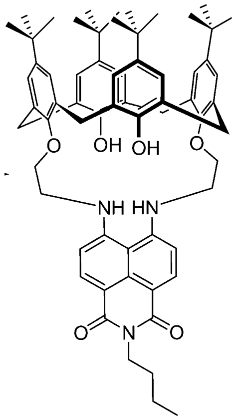
Othman et al. [228] synthesized a calix[4]arene-based chemosensor in CH_3CN solution which Hg^{2+} significantly induced fluorescence resonance energy transfer at 575 nm from pyrenyl excimer to rhodamine ring. Chen and Chen [233] used a dansyl amide-armed calix[4]azacrown to made a fluorescent chemosensor for Hg^{2+} with detection limit of 4.1×10^{-6} M. Leray and Valeur [216] in their microreview paper, present various calixarene-based sensors designed for the detection of mercury and cadmium. Talanov et al. [234] synthesized a one pendent *N*-dansyl-carboxamide calix[4]arene derivative and demonstrated selective optical recognition of Hg^{2+} by changing the fluorescence spectrum of sensor.

As described earlier, Chang et al. [221] synthesized an on–off quenching chemosensor from a triazole-calix[4]-crown derivative. The fluorescence of macrocycle was strongly quenched by Hg^{2+}, Cu^{2+} and Cr^{3+}; however, the revival of emission was achievable by addition of K^+, Ba^{2+}, or Zn^{2+} ions. Xu et al. [235] synthesized a naphthalimide–calix[4]arene derivative (**67**) which was highly

Table 25 The list of calixarene derivatives were used in luminescence techniques to recognize the transition cations

Type of calixarene	Analytes were used	References
Quantum dots capped with sulfur calixarene	Hg^{2+}	[7]
–	Hg^{2+}	[228]
Dansyl amide-armed calix[4]azacrown	Hg^{2+}	[233]
–	Hg^{2+} and Cd^{2+}	[216]
One pendent *N*-dansylcarboxamide calix[4]arene	Hg^{2+}	[234]
Triazole-calix[4]crown	Hg^{2+}, Cu^{2+} and Cr^{3+}	[221]
Naphthalimide–calix[4]arene	Cu^{2+}	[235]
–	Cd^{2+} and Zn^{2+}	[236]
p-tert-Butyl-calix[4]arene	Zn^{2+}	[237]
1,3-alternate Thiacalix[4]arene bearing two Rhodamine B lactams	Cr^{3+} and Fe^{3+}	[46]
Calix[4]arene based podands possessing imine units and bearing anthracene moieties	Cu^{2+}	[238]
Calix[4]arene bearing dansyl groups	Ag^{+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+}	[227]
Rhodamine amide-armed homotrioxacalix[3]arene	Fe^{3+} and Ni^{2+}	[232]

selective fluorescent chemosensor for Cu^{2+}. Its showed a selective fluorescence quenching effect only with Cu^{2+} among the perchlorate salts of various metal ions (Ag^{+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cs^{+}, Cu^{2+}, Hg^{2+}, K^{+}, Li^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Rb^{+}, and Zn^{2+}).



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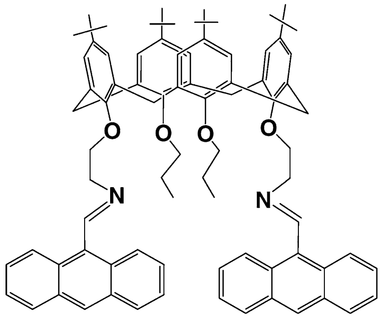
Park et al. [236] described synthesis and evaluation of a calix[4]arene derivative for detection of Cd^{2+} and Zn^{2+} by addition of various metal ions via fluorescent spectra changes. Dessingou et al. [237] described a *p-tert*-butyl-calix[4]arene derivative to be selective for Zn^{2+} ion over Ti^{4+}, VO^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mg^{2+}, Cd^{2+} and Hg^{2+}. The reaction of calix[4]arene derivative and Zn^{2+} was 1:1 stoichiometric; while H^{+} quenched the fluorescence of the complex and OH^{-} restored it. A sensitive ion-induced fluorescent sensor for Cr^{3+} and Fe^{3+} was prepared by Zheng et al. [46] using 1,3-alternate thiacalix[4]arene bearing two rhodamine *β* lactams. Indian chemists synthesized calix[4]arene based podands of *cone* (**68**) and of 1,3-alternate (**69**) conformations possessing imine units and bearing anthracene moieties and examined them for their cation recognition abilities by UV–Vis and fluorescence spectroscopy. The 1,3-alternate calix[4]arene derivative showed a selective fluorescence enhancement in presence of Cu^{2+} among the various cations tested (Li^{+}, Na^{+}, K^{+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Ag^{+} and Hg^{2+} ions). The color of tested solution changed from colorless to yellow in the presence of Cu^{2+} ions [238].



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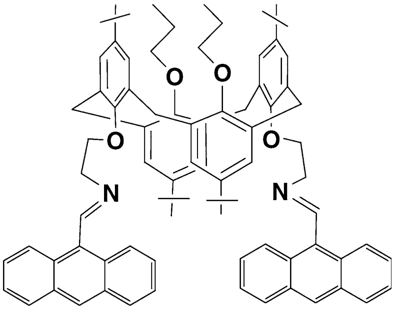

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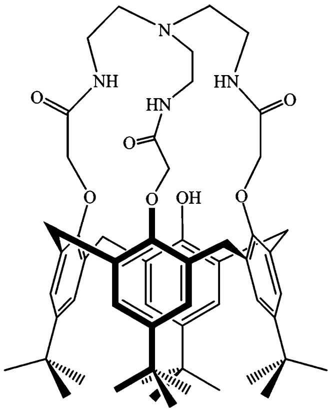
American and Turkish chemists studied the influence of some transition metal cations including Ag^+, Cd^{2+}, Co^{2+}, Fe^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+} and Fe^{3+} on the spectroscopic properties of calix[4]arene complexes bearing dansyl groups. They reported that transition metal cations interact strongly with the calix[4]arene. In particular, Fe^{3+} and Hg^{2+} caused greater than 97% quenching of the dansyl fluorescence [227]. Chinese and Japanese chemists synthesized a fluorescent sensor based on the rhodamine amide-armed homotrioxacalix[3]arene and investigated its sensing behavior toward metal ions by means of fluorescence spectroscopy. Upon the addition of Fe^{3+} and Ni^{2+}, they observed a significant fluorescent enhancement in the range of 500–600 nm [232].

f-Block (lanthanide and actinide) cations

Some of the trivalent lanthanide ions exhibit excellent luminescence characteristics when the native luminescence is enhanced by coordination with suitable calixarenes. These properties include large Stokes shifts (hundreds of nanometers), narrow bandwidths (typically a few nanometers), relatively long luminescent lifetimes (up to milliseconds), and, in certain cases, anti-Stokes luminescence. The enhancement of luminescence intensity by complexation of the trivalent luminescent lanthanide cations has been explained based on a ligand-to-metal energy transfer mechanism. Portuguese and French chemists [239] used two calix[4]azacrowns bearing amine and amide groups (**70** and **71**) and one calix[4]azacrowns bearing only amide groups (**72**) for the 1:2 and 1:1 complexation of Eu^{3+}, Tb^{3+}, Nd^{3+}, Er^{3+}, La^{3+} cations. The two macrocyclic ligands were observed to have opposite fluorescence behaviors, namely, fluorescence enhancement or quenching upon metal ion complexation and a long-lived lanthanide luminescence was sensitized by excitation in the π–π^* band of the aromatic moieties. Eu^{3+} luminescence was weak and much shorter lived than the Tb^{3+} emission.



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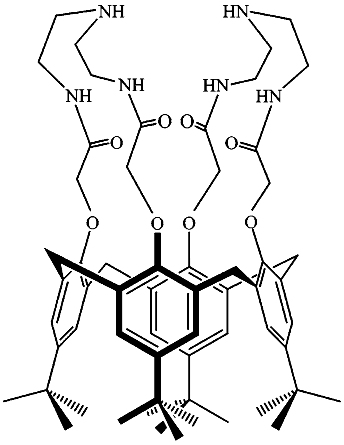

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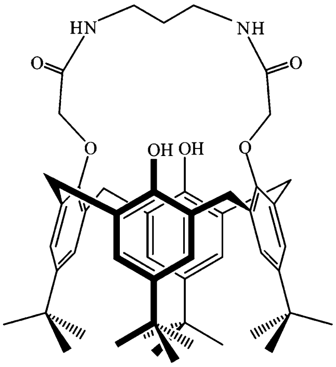

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Molecular compounds

This sub-section focuses on the applications of calixarenes in luminescent determination of molecular compounds. Table 26 presents the luminescence applications of calixarene derivatives to recognize molecular compounds.

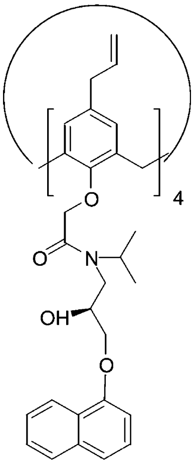
Li and Qu [240] used calix[4,7]arenes coated silica nanospheres, which were prepared via a sol–gel technique in aqueous media. It allowed highly sensitive determinations of PAHs by changing the calixarene coating via response enhancement of fluorescence intensity. They optimized the sensor conditions and they found that the relative fluorescence intensities of calix[4,7]arenes both increased linearly with increasing anthracene and pyrene concentration in the range 1.0×10^{-7} to 5.0×10^{-5} M and with detection limits of 2.45×10^{-8} and 2.94×10^{-8} M, respectively. Its fluorescence to other PAHs (acenaphthene, anthracene, 9,9-diflurofluorene, phenanthrene, fluoranthene, carbazole, biphenyl, fluorene, pyrene) were negligible. Nau et al. [241] investigated an enzymatic reaction including the hydrolysis of arginine to ornithine catalyzed by arginase. 1-Aminomethyl-2,3-diazabicyclo[2.2.2]oct-2-ene and *p*-sulfonatocalix[4]arene were used

Table 26 The list of calixarene derivatives were used in luminescence techniques to recognize the molecular compounds

Type of calixarene	Analytes were used	References
Calix[4,7]arenes	PAHs	[240]
p-Sulfonatocalix[4]arene	Arginine	[241]
–	Enantiomers of chiral amines	[242]
Sulfonatocalix[8]arene	Berberine	[243]
Calix[4]arenes and calix[4]resorcinarenes	Pyrene	[244]
Chiral calix[5]arene-Cu^{2+}	D-(+)-Gluconic acid δ-lactone	[245]
Thiacalixarenes	1-Ethylquinolinium	[107]

as the fluorescent dye and the macrocycle, respectively. *p*-sulfonatocalix[4]arene displayed binding constants of 6400 M^{-1} with arginine, 550 M^{-1} with ornithine, and 60,000 M^{-1} with the selected fluorescent dye. Depletion of the substrate allowed the fluorescent dye to enter the macrocycle and led to the desired fluorescence response.

Lynam and Diamond [242] developed a fluorescent molecular sensor, which could distinguish enantiomers of chiral amines. Fluorescence quenching studies were carried out using a calix[4]arene derivative (**73**) and excellent selectivity was observed for a long chain amino alcohol, phenylalaninol. They studied the solvent effect on the fluorescent properties of calix[4]arene and phenylalaninol in methanol, acetonitrile, and chloroform. They demonstrated that varying solvent polarity allows the wavelength of enantiomer selectivity to be tuned from 227 to 440 nm.



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Strong binding of berberine, a clinically important isoquinoline alkaloid, to 4-sulfonatocalix[8]arene leads to considerable fluorescence quantum yield increase at pH = 2. It utilized in the development of a fluorescent probe. Megyesi and Biczok [243] investigated the effects of the cavity size of sulfonatocalixarenes and pH on the stability and fluorescent properties of the complexes. Based upon their researches in Hungary, the stability of macrocycle complex diminished when sulfocalixarenes of smaller ring size served as host compounds but the pH affected the association strength to a much lesser extent. Pandey et al. [244] showed that calix[4]arenes and calix[4]resorcinarenes efficiently quench the pyrene fluorescence. They can be used in fluorescent probes to determine pyrene.

Fluorescent titration experiments of chiral calix[5]arene-Cu^{2+} complexes selectively recognized d-(+)-gluconic acid δ-lactone among various carbohydrates [245]. Iki [107] reviewed the application of thiacalixarenes and discussed the self-assembled formation of a luminescence receptor with Tb^{3+} ions. He used the receptor to detect 1-ethylquinolinium guest in 10^{-10} M.

Organic cations

thiacalix[4]arene-*p*-tetrasulfonate (CAS) and thiacalix[4]arene-*p*-tetrasulfonate (TCAS) formed luminescent complexes of $Tb^{III}\cdot(CAS)_2$ and $Tb^{III}\cdot TCAS$, respectively. They were utilized as a host for 1-ethylpyridinium, 1-ethylquinolinium, and nicotineamide adenine dinucleotide (NAD^+) guests, which quenched luminescence of $Tb^{III}\cdot(CAS)_2$ with a low detection limit of 5.94×10^{-8}, 6.71×10^{-10}, and 2.78×10^{-7} M, respectively ($S/N = 3$) [245].

Anions

In this sub-section, the luminescent methods are reviewed for the determination of anions using calixarenes. Table 27 listed these applications in recognition of the anion guest spices.

A two-faced naphthalimide–calix[4]arene was synthesized by Xu et al. [235] as a selective fluorescent quenching chemosensor for F^- over $H_2PO_4{}^-$, $HSO_4{}^-$, $CH_3CO_2{}^-$, I^-, Br^-, and Cl^- anions. They investigated the binding mode with F^- using H NMR and fluorescence changes. Lee et al. [224] also synthesized calix[4]arene-crown-6 as a fluorometric sensor for F^-. Chen et al. [246] analyzed dihydrogen phosphate anion in the presence of F^- using a sensitive fluorescence probe prepared by calix[4]-arene bearing naphthol-hydrazone groups. Lee et al. [247]

Table 27 The list of calixarene derivatives were used in luminescence applications to recognize the anion guest spices

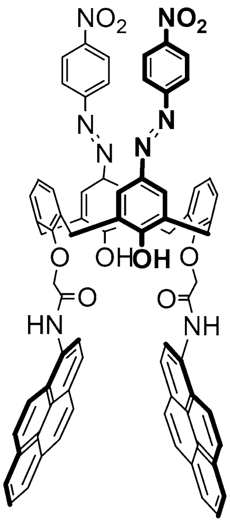
Type of calixarene	Analytes were used	References
Two-facednaphthalimide–calix[4]arene	F^-	[235]
Calix[4]arene-crown-6	F^-	[224]
Calix[4]arene bearing naphthol-hydrazone	F^-	[246]
–	F^-	[247]
1,3-alternate Tetrasubstituted calix[4]arene bearing pyrene moieties	Cl^-	[248]
Calix[4]pyrrole	Cl^-	[220]
Calix[4]arene bearing glycine and 1,8-diaminoanthracene moieties	AcO^-	[249]
Amidourea based calix[4]arene	Pyrophosphate and fluoride	[250]

synthesized a calix[4]arene-based fluoride sensor. Complexation caused selectively red-shift in UV–Vis absorption and in fluorescence emission due to H-bonding of fluoride to macrocycle.

Schazmann et al. [248] bridged urea functional groups with single methylene spacers to pyrene moieties; they synthesized a 1,3-alternate tetrasubstituted calix[4]arene derivative. The excimer emission of pyrene was quenched, with a simultaneous rise in the monomer emission solely by the chloride anion among other anions tested. The method had an LOD of 8×10^{-6} M with chloride in acetonitrile–chloroform solution. Miyaji et al. [220] synthesized a fluorophore based on calix[4]pyrrole and determined its association constants with various anions (like Cl^{-}) using both fluorescence titration. The fluorescence quenched by anions in the presence of Na^+. A bridged fluorescent calix[4]arene with glycine and 1,8-diaminoanthracene at the upper rim was prepared by Miao et al. [249]. This fluorescent ionophore recognized AcO^- over F^-, Cl^-, Br^-, $H_2PO_4^-$, NO_3^-, I^- and HSO_4^- anions. Quinlan et al. [250] synthesized amidourea based calix[4]arene as a bifunctional fluorescent calix[4]arene chemosensor for recognition of pyrophosphate and fluoride.

Colorimetric applications

Kang et al. [251] reported that the nitrophenylazo moieties on the upper rim of the calix[4]crown play a chromogenic role. They designed calix-luminophores (**74** and **75**) as fluoride chemosensor bearing both pyrene pendants with amide linkages and 4-nitrophenylazo group. The introduction of pyrene unit to calixarene platform was aimed to enhance the fluorescent property, while the incorporation with 4-nitrophenylazo group was expected to enhance the colorimetric property. These compounds were expected to recognize the F^- at the receptor sites.



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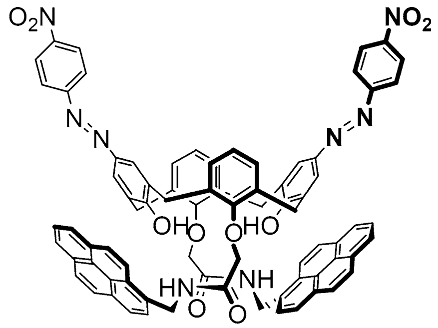

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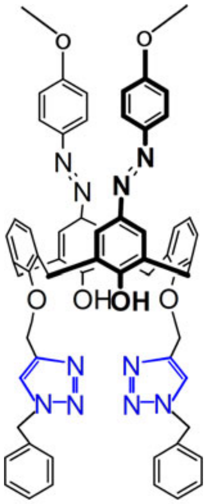
s-Block (alkali and alkaline earth) cations

In this sub-section, the colorimetric methods are reviewed for the determination of alkali and alkaline earth metal cations using calixarenes. Table 28 presents the colorimetric applications of calixarene derivatives to recognize the s-block cations.

Table 28 The list of calixarene derivatives were used in colorimetric detection of alkali and alkaline earth metal cations

Type of calixarene	Analytes were used	References
bis(Indolyl)calix[4]crown-6	Ca^{2+}	[252]
Triazole calix[4]arene and azocalix[4]arene	Ca^{2+}	[253]
–	Ca^{2+} and Ba^{2+}	[254]
Calix[4]crown-6 derivative	Cs^{+}	[224]
Diazophenylcalix[4]arenes bearing *ortho*-carboxyl groups	Alkaline earth metal cations	[255]

Lee et al. [252] synthesized bis(indolyl)calix[4]crown-6 and investigated the selective colorimetric changes of this calix-chromophore for alkaline earth cations. They observed that the binding ability of calix[4]crown for the Ca^{2+} binding enhances in the presence of F^{-}. Chang et al. [253], designed and synthesized triazole- and azo-coupled calix[4]arene (**76**) to recognize Ca^{2+} cations in a chromogenic sensor.



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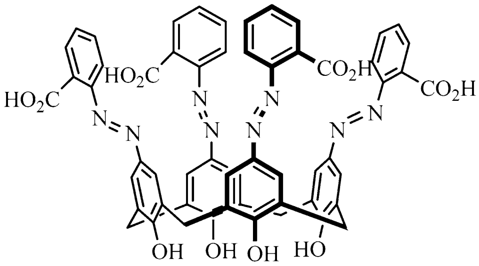
Chen and Chung [254] used two calix[4]arene derivatives as chromogenic sensors to sense Ca^{2+} and Ba^{2+} cations. A colorimetric on–off sensor for Cs^{+} recognition was also synthesized by Lee et al. [224] using a calix[4]crown-6 derivative. Kim et al. [255] synthesized two cone conformation of chromogenic diazophenylcalix[4]arenes. They revealed that the first compound (with the ortho-carboxyl groups) preferentially binds with alkaline earth and transition metal ions, whereas no significant changes in absorption spectra were observed in the presence of alkali metal ions. While the second compound (with the *ortho*-ester groups) showed selective complexation properties towards transition metal ions over alkali and alkaline earth metal ions.

p-Block cations

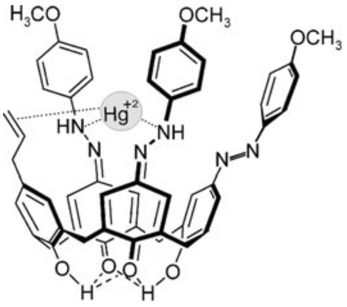
In Taiwan, Pb^{2+} chromogenic sensor were synthesized using azocalix[4]arene and triazolecalix[4]arene derivatives (**75**) [253]. Chinese chemists [254] reported the Pb^{2+} determination by means of calixarene chromogenic sensors. Vietnamese chemists [256] determined the trace amounts of lead ions in aqueous environmental samples using benzoic acid azophenylcalix[4]arene (**77**) via a colorimetric method at 440 nm. The calixarene derivative showed strong binding ability to Pb^{2+} with formation of a 1:1 complex. The dynamic range was determined to be 2.0×10^{-6} to 2.4×10^{-5} M and the detection limit was 1.4×10^{-6} M.



d-Block (transition and heavy) cations

One of the most easily perceptible aspects of coordination chemistry is the variety of colors that are observed for many transition metal complexes. These colors are a visual manifestation of quantum mechanics and are determined by the electronic structure of the compounds. Absorption spectra in the visible wavelength range provide quantitative measurements of color and have been used to determine the coordinated cation. Spectra also provide detailed information on electronic excited states of key importance for photochemistry and for a variety of optical materials properties. Table 29 shows the colorimetric applications of calixarene derivatives to determine the transition metal cations.

Ho et al. [257] prepared the upper-rim allyl- and *p*-methoxyphenylazocalix[4]arenes (**78**) and examined their efficiencies in chromogenic sensing of Hg^{2+} ion. Bingol et al. [258] determined a rapid test kit for early detection of Hg^{2+} in aqueous environment in the concentration range of 1×10^{-4} to 1×10^{-2} M. They used calix[4]arene derivative bearing benzothiazole azo groups at the upper rim as chromogenic chemosensor, and investigated its sensing properties with Pb^{2+}, Hg^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, Cr^{3+}, Ag^{+}. The chromogenic chemosensor showed high selectivity towards Hg^{2+} ion over the other heavy metal ions.



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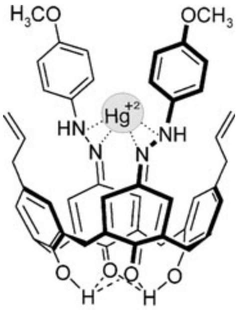

79

Kumar et al. [259] synthesized thiacalix[4]arene carrying azophenol appendage and studied their binding abilities towards Li^+, Na^+, K^+, Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^+, Pb^{2+} and Hg^{2+} ions. Their results revealed that the calixarene derivative showed selective chromogenic sensing for Cu^{2+}. Kim's research team [255] revealed that chromogenic diazophenylcalix[4]arenes bearing *ortho*-ester group captured the transition metal ions over alkali and alkaline earth metal ions. Lu et al. [260] synthesized a water-soluble chromium-selective chromogenic azocalix[4]arene. It possessed an absorbance maximum at 365 nm in buffered aqueous environment, but addition of Cr^{3+} induced a weak blue shift to 350 nm and a new absorption peak at 520 nm which increased along with the augment of the concentration of Cr^{3+}. They used the new method for determination of Cr^{3+} in the range of 9.35×10^{-4} to 4.45×10^{-3} M.

Wu et al. [232] reported a significant colorimetric change upon the addition of Fe^{3+} and Ni^{2+} to rhodamine amide-armed homotrioxacalix[3]arene using UV–Vis spectroscopy. In Lyon, a new chromogenic calix[4]arene molecule was introduced to elaborate an optical fiber sensor able to detect heavy metal pollutants (copper, cobalt and cadmium) [261]. Kao team in Taiwan [16] used upper rim allyl- and arylazo-coupled calix[4]arenes (**79**) and showed substantial bathochromic shifts ($\Delta\lambda = 128$–162 nm) upon the addition of soft metal ions (such as Hg^{2+}, Cr^{3+} and Cu^{2+}).

f-Block (lanthanide and actinide) cations

Liu et al. [262] synthesized a calix[4]arene derivate carrying two spirobenzopyran moieties. The addition of lanthanide ions over other cations including Na^+, K^+, Mg^{2+}, Ca^{2+}, Fe^{3+}, Cu^{2+} and Zn^{2+} resulted in significant UV–Vis spectral shifts, 68–84 nm, in visible region. Chinese researchers in Beijing [15], synthesized the photochromic Schiff base derivative (**80**) through incorporation of two imine groups into the upper rims of calix[4]arene. Addition of Dy^{3+} or Er^{3+} ions to this calixarene framework results in the solution color change. They claimed this framework can electively recognize Dy^{3+} and Er^{3+} ion by naked eye over other lanthanide cations. Figure 8 presented the fluorescence emission spectra of **80** (1×10^{-5} M) in the presence of Er^{3+} and Dy^{3+} in CH_2Cl_2. The concentration of Er^{3+} and Dy^{3+} were 0.0, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1, 1.2, 1.4, 1.5, 1.6, 1.8, 2.0, 3.0, 4.0, 5.0×10^{-5} M at $\lambda_{ex} = 375$ nm.

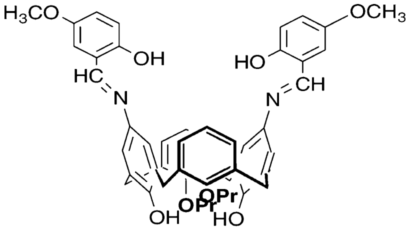

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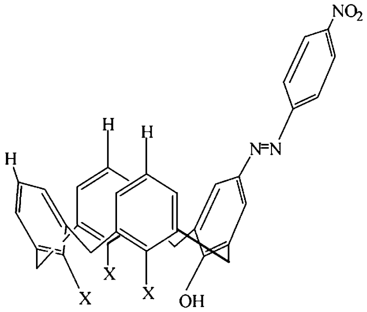
Table 29 The list of calixarene derivatives were used in colorimetric techniques to recognize the transition metal cations

Type of calixarene	Analytes were used	References
Allyl- and *p*-methoxyphenylazocalix[4]arenes	Hg^{2+}	[257]
Calix[4]arene bearing benzothiazole azo groups	Hg^{2+}	[258]
Thiacalix[4]arene carrying azophenol	Cu^{2+}	[259]
Diazophenylcalix[4]arenes bearing *ortho*-ester group	Transition metal cations	[255]
Azocalix[4]arene	Cr^{3+}	[260]
Rhodamine amide-armed homotrioxacalix[3]arene	Fe^{3+} and Ni^{2+}	[232]
–	Cu^{2+}, Co^{2+} and Cd^{2+}	[261]
Allyl- and arylazo-coupled calix[4]arenes	Hg^{2+}, Cr^{3+} and Cu^{2+}	[16]

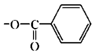
Molecular compounds

This sub-section focuses on the applications of calixarenes in colorimetric determination of molecular compounds. Table 30 presents the colorimetric applications of calixarene derivatives to recognize the molecular compounds.

Shirshov et al. [263] described recognition of several volatile alcohols (ethanol, isopropanol and penthanol) by digital registration of RGB components variation in interferential colored sensitive tetra-amyl-calix[4]resorchinolarene films. When Liu et al. [14] investigated spun films of nitrophenylazocalix[4]arenes (**81–84**) as gas-phase optical sensors under amine vapors, they observed a red shift of the visible absorption bands. The highest sensitivity was observed for *n*-hexylamine.

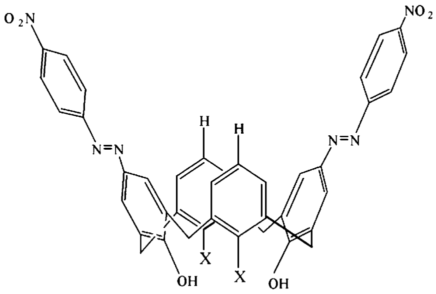


X = OH 5-(4’-Nitrophenyl)azo-25,26,27,28-tetrahydroxy-calix[4]arene (TQ-OH)

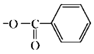


X = $-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5$ 5-(4’-Nitrophenyl)azo-25,26,27-tribenzoyloxy-28-hydroxycalix[4]arene (TQ-B)

81 and **82**



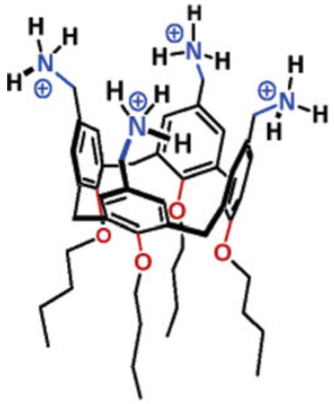
X = OH 5,17-Bis((4’-nitrophenyl)azo)-25,26,27,28-tetrahydroxycalix[4]arene (DQ-OH)



X = $-O-\underset{\underset{\displaystyle O}{\|}}{C}-C_6H_5$ 5,17-Bis((4’-nitrophenyl)azo)-25,27-dibenzoyloxy 26,28-dihydroxycalix[4]arene (DQ-B)

83 and **84**

Kolusheva et al. [264] embedded calixarene receptors (**85–87**) within vesicles comprising phospholipids and the chromatic polymer polydiacetylene for color detection of proteins. The colorimetric assay constitutes a generic platform for high-sensitivity detection of water soluble proteins.



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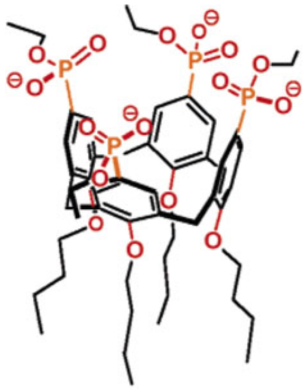

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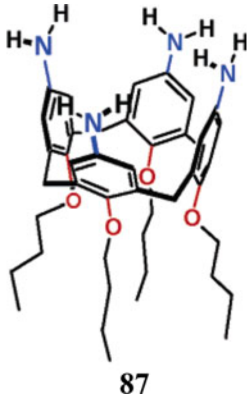


87

Xiong and Li [265] synthesized two silver nanoparticles modified with *p*-sulfonatocalix[*4*]arene and *p*-sulfonatocalix[8]arene for detection of optunal with 10^{-7} M limit of detection as a novel colorimetric probe for colorimetric detection of pesticides.

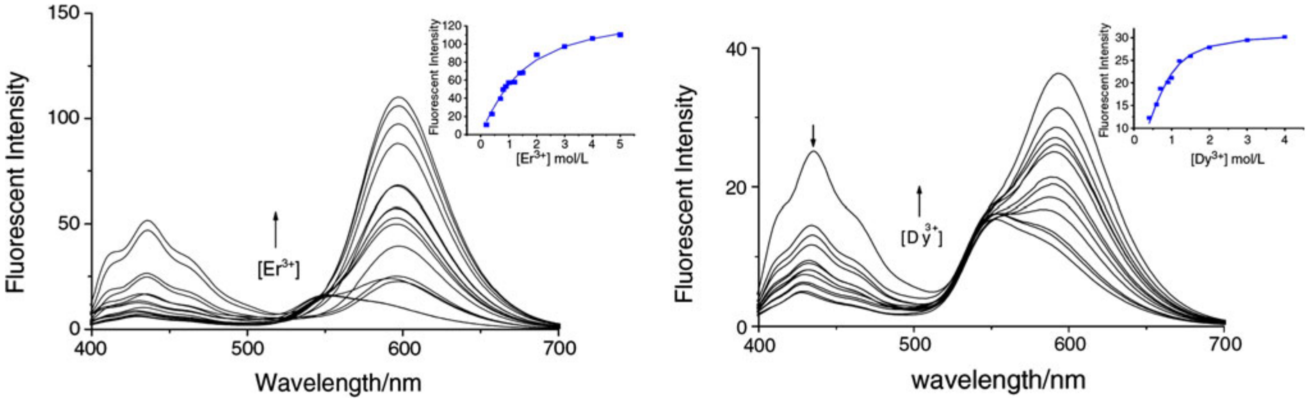


Fig. 8 The fluorescence emission spectra of **80** in the presence of Er^{3+} (*left*) and Dy^{3+} (*right*) in CH_2Cl_2

Table 30 The list of calixarene derivatives were used in colorimetric techniques to recognize the molecular compounds

Type of calixarene	Analytes were used	References
Tetra-amyl-calix[4]resorchinolarene	Ethanol, isopropanol and penthanol	[263]
Nitrophenylazo-calix[4]arenes	Amine vapors	[14]
Phospholipid calix[4]arenes	Water soluble proteins	[264]
p-Sulfonatocalix[*4*]arene and *p*-sulfonatocalix[8*n*]arene	Optunal and pesticides	[265]

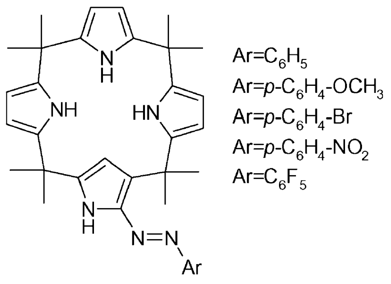
Organic cations

Tshikhudo et al. [266] used gold nanoparticles as optical marker to recognize pyridinium ions in aqueous systems by thiol-modified calixarene ligands. Chinese chemists [267] prepared *p*-sulfonatocalix[6]arene-modified gold nanoparticles as colorimetric probes to detect diaminobenzene isomers. Due to the intense surface plasmon absorption band centered at 520 nm, the color of calixarene-nanoparticle solution was red. While the color of complex solution was changed to a deep purple. Based upon their claim, diaminobenzene isomers bridged the nanoparticles via electrostatic and host–guest interactions, which induced the aggregation of the nanoparticles. Upon aggregation, the surface plasmon absorption band was broadened and shifted to red region so that the nanoparticle solution appeared a deep purple color. They examined the sensitivity of host macrocycle towards *o*-diaminobenzene, *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, *o*-chloroaniline, *p*-chloroaniline, *o*-toluidine, *m*-toluidine, *p*-toluidine and aniline, and concluded that the sensitivities were negligible.

Anions

The development of colorimetric sensors for anion recognition is currently a highly topical area of research. Anions are essential to life in many biological processes, in industry and in agriculture, which also puts them in the class of environmental pollutants. Therefore, much effort is currently being directed towards the development of synthetic anion receptors such as calixarene derivatives. Table 31 listed the colorimetric applications of calixarene derivatives to recognize the anion guest spices.

Calix[4]pyrroles are used as a complexation agent for anions recognition. Guests anions are bound to the macrocycles by hydrogen bonds to nitrogen atoms but the complex stability is not high enough for analytical use and for improving the binding ability, the basic calix[4]pyrrole skeleton was functionalized with various substitutions, in the *meso*-position of macrocycle or the b-positions of the pyrrole units. Gu et al. [268] studied the complexation of six α-arylazo-*N*-confused calix[4]pyrrole derivatives (**88–92**) with tetrabutylammonium salts of SCN^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, NO_3^- anions using UV–Vis spectroscopy in dichloromethane and acetonitrile solvents.



88-92

Table 31 The list of calixarene derivatives were used in colorimetric applications to recognize the anion guest spices

Type of calixarene	Analytes were used	References
α-Arylazo-*N*-confused calix[4]pyrrole derivatives	SCN^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, HSO_4^-, NO_3^-	[268]
Bis(indolyl)calix[4]crown-6	F^-	[252]
Amido-coumarin-calix[4]arene	F^-	[247]
Tetra-amidourea derived calix[4]arene	F^-	[269]
Calix[4]arene-crown-6 derivative	F^-	[224]
Amidourea based 1,3-disubstituted calix[4]arene	Acetate, fluoride, H-phosphate and etc.	[270]
Calix[4]pyrrole	Fluoride, chloride, di-hydrogen phosphate, bisulfate and nitrite	[271]
Octamethylcalix[4]pyrrole	Carboxylates	[272]
Amidourea based calix[4]arene derivative	Pyrophosphate and fluoride	[250]
Calix[4]pyrroles bearing dipyrrolylquinoxaline	Acetate, fluoride and dihydrogen phosphate	[273]
(*E*)-3-(*meso*-Octamethylcalix[4] pyrrol-2-yl)propenal	Acetate, fluoride and dihydrogen phosphate	[274]
Calix[4]pyrrole anion	Cl^-	[275]
–	α-Phenylglycine	[276]
Calix[4]pyrrole	Fluoride and acetate	[277]
N-confused calix[4]pyrroles	Anions	[278]
Octamethylcalix[4]pyrroles and *N*-confused calix[4]pyrroles	Anions	[279]

Lee et al. [247, 252] studied the selective colorimetric changes of bis(indolyl)calix[4]crown-6 and amido-coumarin-calix[4]arene sensors for recognition of fluoride anion. Lee et al. [269] used preorganized tetra-amidourea derived calix[4]arene sensor for fluoride ion detection. The complex excited at 343 nm and revealed excimer emissions at 448 nm. Recognition of F^- was achieved by a colorimetric on–off sensor. It was prepared using a calix[4]arene-crown-6 derivative that was synthesized by Lee et al. [224]. Irish researchers used amidourea based 1,3-disubstituted calix[4]arene with acetate, fluoride, hydrogen phosphate and hydrogen pyrophosphate anions in DMSO. Whilst this sensor gave rise to red shifts in its absorption spectra upon anion recognition, the sensing of fluoride and hydrogen pyrophosphate anions gave rise to large changes with concomitant color changes from yellow to purple, which were visible to the naked eye [270]. Linn et al. [271] investigated halides, dihydrogen phosphate, bisulfate and nitrite anions during interaction of Brooker's Merocyanine (BM) and calix[4]pyrrole (CP). BM interacted with CP changes the color of the solution due to the formation of CP–BM. Fluoride, chloride and dihydrogen phosphate anions displaced BM through the formation of a complex with CP, coloring the solution. Bisulfate protonated the BBM dye and made the solution almost colorless.

Nishiyabu and Anzenbacher [272] synthesized a chromogenic calix[4]pyrroles and made a octamethylcalix[4] pyrrole/polyurethane sensor films showed a strong response for aqueous carboxylates (antipyretics naproxen, ibuprofen and salicylate) without interfering of bicarbonate and carboxy termini of blood plasma proteins. A amidourea based calix[4]arene derivative was synthesized by Quinlan et al. [250] to prepare a bifunctional fluorescent calix[4]-arene chemosensor. At high concentrations of pyrophosphate and fluoride anions, significant colorimetric changes were also observed that were clearly visible to the naked eye for both of them. Yoo et al. [273] synthesized the calix[4]pyrroles bearing dipyrrolylquinoxaline as strapping elements and examined their selective colorimetric response when exposed to the acetate, fluoride and dihydrogen phosphate anions. Farinha et al. [274] in Portugal, used (*E*)-3-(*meso*-octamethylcalix[4]pyrrol-2-yl)propenal to recognize those anions.

Nishiyabu and Anzenbacher [275] prepared the calix[4]pyrrole anion sensors with high selectivity for chloride anion. Qing et al. [276] examined the chiral anion-binding ability of a calixarene derivative and they used it as a good chiral chromogenic chemosensor for the enantiomers of the α-phenylglycine anion. Farinha et al. [277] in Portugal, synthesized a calix[4]pyrrole derivative which displayed sharp changes in color in the presence of

Table 32 The list of calixarene derivatives were used in other spectroscopic techniques to recognize the guest spices

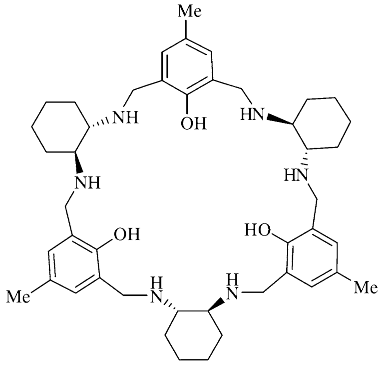
Type of calixarene	Analytes were used	References
Calix[8]arene	NO_2	[280]
Calix[4]crown	Antibodies	[281]
–	Secondary alcohol, cyanohydrins, and propargyl alcohols	[282]
Phosphorous-calixarenes	Aromatics, chlororganics, ketones and alcohols	[283]
–	Cations and molecular compounds	[284]

fluoride and acetate anions. American researchers [278] in a review paper reported that *N*-confused calix[4]pyrroles are a relatively recent arrival to the pyrrole macrocycles family, being for the first time identified in 1999. Yet, in a relatively short time these calix[4]pyrrole isomers attracted attention of the research groups interested in colorimetric anion sensing. They reviewed the *N*-confused calix[4]pyrroles and presented the results of colorimetric assays for anions and discussed their potential applications. Belgium and American chemists [279] investigated the properties of chromogenic octamethylcalix[4]pyrroles and their *N*-confused octamethylcalix[4]pyrrole isomers. The chromogenic octamethylcalix[4]pyrroles showed significantly stronger anion-induced color changes compared to the corresponding chromogenic octamethylcalix[4]pyrrole isomers.

Other spectroscopic applications

Table 32 presents other spectroscopic applications of calixarene derivatives to recognize the guest spices.

Richardson et al. [280] investigated the NO_2 gas-sensing properties of calix[8]arene/porphyrin LB films over the concentration range 0.13–4.60 ppm with a fast response time of 10–15 s. Attachment of proteins to a solid support is fundamental to development of advanced biosensors. Chen et al. [281] investigate the antibody surface coverage, the layer thickness, adsorption and orientation on a calix[4]crown utilizing surface plasmon resonance on a well-known protein artificial receptor molecule (ProLinker^{TM}). The immunoactivity of immobilized antibodies was compared using two different methods. In H NMR, chiral shift reagents achieve rapid determination of the enantiomeric excesses of chiral compounds. Lanthanide complexes, cyclodextrins, crown ethers, porphyrins and macrocycles are wide variety of chiral shift reagents. Tanaka and Fukuda [282] reported calixarene-like chiral macrocycle amine functions (**93**) as a highly sensitive chiral shift reagent for several kinds of secondary alcohol, cyanohydrins, and propargyl alcohols.



(*S,S,S,S,S,S*)-(+)

93

Koshets et al. [283] used calixarenes as sensitive coatings for quartz crystal microbalance (QCM)-based gas sensors. By changing the number of aryl fragments and the functional groups on calixarenes, sensitivity and selectivity of QCM have been studied for a wide range of volatile organic compounds (aromatics, chlororganics, ketones and alcohols). They found that sensors coated with phosphorous-containing calixarenes showed maximal sensitivity. Hungarian researchers [284] summarized different applications of optical spectroscopic methods in calixarene chemistry including vibrational spectroscopy, UV–Vis spectrometry, luminescence spectroscopy, ellipsometry and various optical microscopic methods in a review paper.

Calixarenes applications in chemometrics

Wang et al. [285] used chemometric methods to study the acid–base properties of mononitrocalix[4]arene by measurement of its UV absorbance at different pH. Iterative target transformation factor (ITTFA), principal component analysis (PCA) and evolving factor analysis (EFA) were used to resolve the acid–base fraction curves and to investigate the proton dissociation behavior of calix[4]arene derivative, respectively. By this work, pK_a values, fraction curves and pure absorbing spectra were determined. Sliwka-Kaszynska et al. [138] synthesized 12 calix[4]arene stationary phases and studied their surface coverage, hydrophobic selectivity, aromatic selectivity, shape selectivity, hydrogen bonding capacity and ion-exchange capacity. Then they used principal component analysis to compare 1,3-alternate calix[4]arene phases and commercially available phenyl, fluorophenyl and fluoroalkyl columns.

Cao et al. [286] investigated the frequency response for 22 organic vapors by piezoelectric thickness-shear-mode (TSM) acoustic wave sensors coated with four calixarene derivatives. By supramolecule recognition mechanism, 2,8,14,20-tetraethyl-4,6,10,12,16,18,22,24-octahydroxylcalix[4]arene was determined as the most efficient coating. They reported that this sensor can be used for on-line determination of 2-butanone vapor in air like gas chromatography. Ding et al. [287] used a chemical ant colony algorithm to solve the multivariate calibration issue of the multicomponent calixarene solution. They realized the pure spectra fitting and the simultaneous determination of the calix[4,6,8]arenas in the multicomponent supramolecular solution.

Conclusions

This paper has focused on the recent researches in the field of calixarenes as analytical tools. The examples described in this review illustrate the potential of them in the rapidly growing field of ion and molecular recognition. By searching in literatures, optimization of chelator design together with understanding of how to control the localization of ion complexes will be clarified. Applicability of calixarene derivatives in four main fields of separation, electroanalysis, spectroscopy and chemometrics was described with about 300 references. The reader is introduced with frontiers in analytical application of calixarenes in terms of complexation, solvent extraction, liquid chromatography, membrane transport, potentiometry, voltammetry, conductometry, electrochemical and spectroscopic sensors, luminescence, colorimetry and chemometrics techniques.

Acknowledgments This work was partially supported by National Iranian Oil Company and Islamic Azad University.

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