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Review

Coordination chemistry of calix[4]arene derivatives with lower rim functionalisation and their applications

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ABSTRACT

This article presents a systematic review of the coordination chemistry of calix[4]arenes, which have been functionalised at the lower rim and are in the cone conformation. Particular attention is given to the use of the resulting metal complexes in terms of fluorescence, catalysis, electrochemical sensing, extraction and biological applications. It will cover the period January 2000 to May 2007. However, a large body of work involving the direct attachment of metals to the phenolic oxygen atoms of the lower rim of the calix[4]arene will not be covered by this review, for the reason that the calix[4]arene has not been functionalised in the strictest sense.

1. Introduction

Calixarenes are a fascinating class of macrocyclic molecules which have been used extensively in supramolecular chemistry. The parent calix[n]arenes ($n = 4, 6, 8$) are prepared by the facile condensation reaction of formaldehyde with phenol or its derivatives. Their development as a force within supramolecular chemistry has resulted from their synthetic availability and their relative ease of modification, coupled with the presence of various cavities which are capable of binding cationic, anionic or neutral species, which becomes apparent from the number of review articles and books available [1–11]. Recently, thiacalix[4]arenes have become easily accessible and because of the presence of four sulphur atoms instead of the methylene bridge, they represent promising building blocks or molecular scaffolds for the development of more elaborate supramolecular systems. Several recent reviews are available on thiacalix[4]arenes [7,12–14] and so this type of calix[4]arene will not be reviewed in this article. This review will only consider the calix[4]arene family of compounds and especially those compounds which are initially derivatised at the lower or narrow rim, and then contain some metal ion complexed by that functionality. In some instances, functionalisation of the calix[4]arene has occurred at both the upper and lower rim, but only those cases

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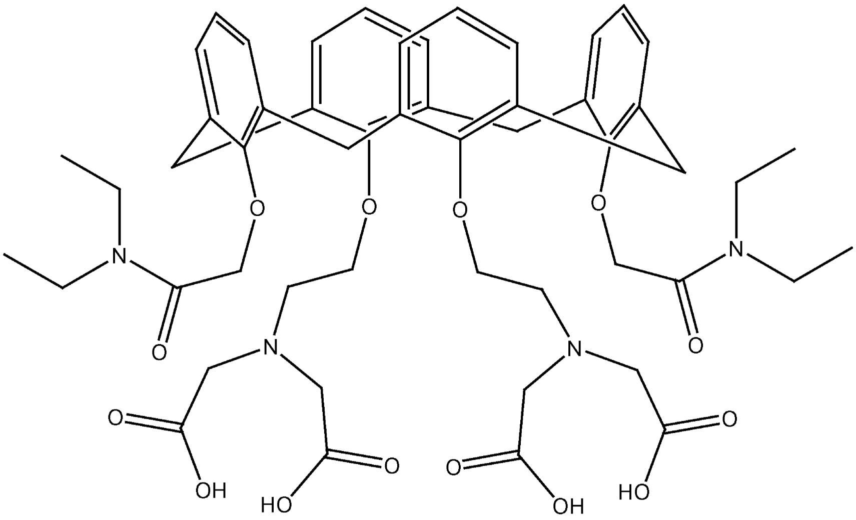

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Fig. 1. Structure of diamide tetraacid calix[4]arene **1**.

involving metal complexation at the lower rim will be discussed herein. Rather than deal with each metal on an individual basis, it seemed more appropriate to consider the applications of these metal complexes and review the area using that criterion instead.

2. Biological applications

Biological applications of calix[4]arene derivatives are not common and are limited to uses of such derivatives in bioassays, imaging or a small number of *in vivo* studies.

The supramolecular approach to synthetic molecules with biological applications, including recognition and self-organisational properties, often comprises of rigid scaffolds with amino acids or peptides as the organisational elements. Botta, Casnati and coworkers used this approach to convert a calix[4]arene into its diamide tetraacid derivative (**1**) to subsequently make the Gd(III) metal complex [15] (Fig. 1). The metal centre was complexed using only two of the coordinating arms of the functionalised calix[4]arene with the remaining coordination sites being occupied by water molecules. This Gd(III)-**1** complex was stable in the pH range of 4–9 and had a stability constant of 1 × 10^{13} M^{-1} in water at pH 6.8, which ensured the integrity of the complex in the presence of proteins. The binding interaction with human serum albumin (HSA) was investigated and the resulting high binding affinity of Gd(III)-**1** to HSA was believed to result from the cooperative effect of the hydrophobic interaction resulting from the aromatic macrocycle and the coordination of donor groups of the protein.

Rao and co-workers synthesised and characterised Sn(IV) complexes of calix[4]arene-diacid derivatives and evaluated their protective value against blood and tissue oxidative stress in lead exposed male albino Wistar rats [16]. Their results showed that two Sn(IV) complexes were able to reverse the effect of lead significantly in blood and kidney and to some extent in liver. They attributed this effect to the ability of Sn(IV) complexes to prevent absorption of lead to the target tissues.

Lippard and co-workers constructed a replica of a portion of the potassium channel from *Streptomyces lividans* using the tetraacid derivative of calix[4]arene as the template for their studies [17]. Four valine–glycine–tyrosine sequences were attached to the calix[4]arene, one amino acid at a time, in an effort to create a structural mimic of the region where cations are located in the potassium channel. They found that the first metal binds to the oxygen-rich

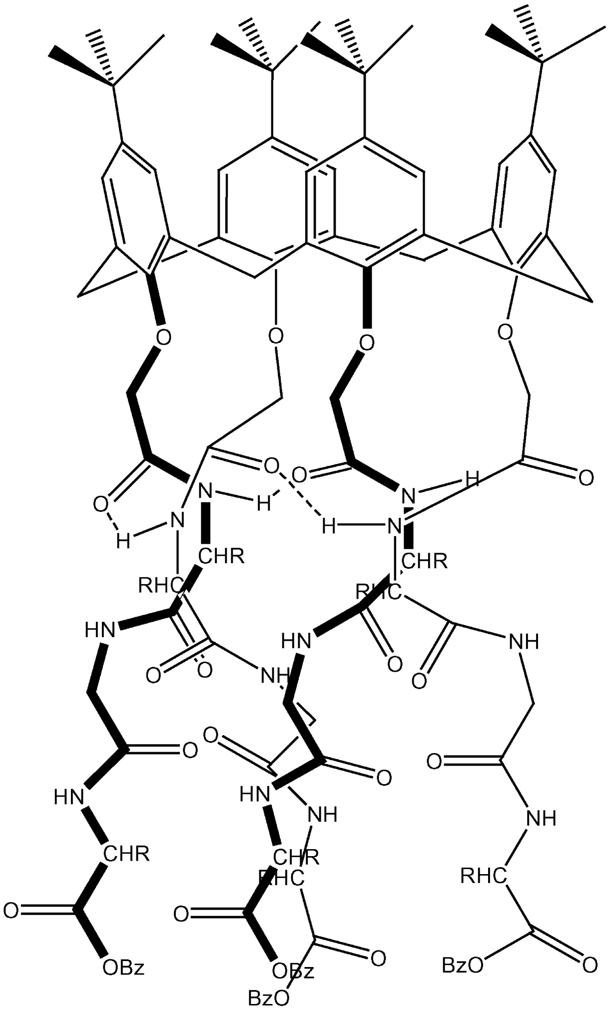

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Fig. 2. Structure of tri-peptide derivatised calix[4]arene **2**.

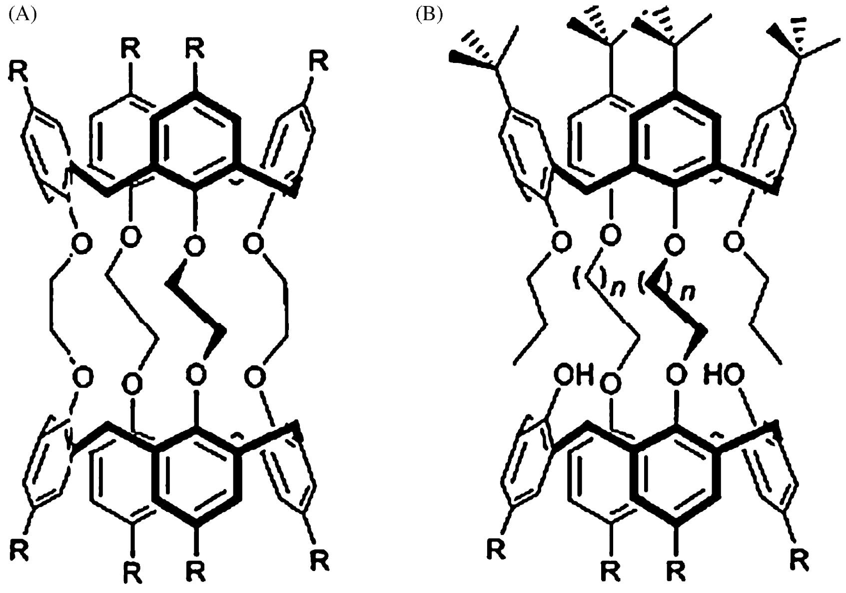

Fig. 3. Structure of calix[4]tubes investigated as structural mimics for the potassium channel in *S. lividans*.

envitronment formed by the four –OCH$_2$O– units, similar to the binding site of the natural channel. They also found that in the model compounds that they used, such as **2**, metal ion binding required that the cyclic network of interchain N–H. . .O=C hydrogen bonds involving the valine amide had to be broken (Fig. 2).

Beer and co-workers also looked at the use of calix[4]arene derivatives as structural mimics for the *S. lividans* potassium channel [18–21]. They have looked at the use of calix[4]tubes (**3A**), based on a bis(calix[4]arene) scaffold connected by four alkylene chains, and calix[4]semitubes (**3B**), which are bis(calix[4]arene) scaffolds connected by two alkylene chains, which are less rigid than the calix[4]tubes (Fig. 3). They established the mechanism for the insertion of metal ions into calix[4]tubes, which occurs in three stages. Initially, the calix[4]tube is uncomplexed. Then, in the second stage, the metal enters the top of the calix[4]arene and forms an intermediate by interacting with the aromatic rings. Finally, the metal proceeds into the centre of the calix[4]tube and forms bonds to the eight oxygen atoms present. They also discovered that the mechanism for the incorporation of metals into the calix[4]semitube occurs through a horizontal or “side-on” route, rather than *via* the vertical pathway through the annulus of the calix[4]arene. They believe that this alternative mechanism accounts for the faster kinetics of complexation exhibited by the calix[4]semitubes.

Yang et al. have also looked at some bis(calix[4]arene) derivatives, particularly with regard to the complexation of either metal cations or amino acids [22–23]. They have reported the synthesis of a bis(calix[4]arene) composed of a calix[4]arene unit and a thiacalix[4]arene unit (**4**) (Fig. 4). They found that **4** showed good extraction abilities towards both hard and soft cations, which could be attributed to the fact that the subunits could bind hard and soft cations, respectively. The compound also showed good extraction selectivity for silver over mercury and also caesium or potassium over sodium. The calix[4]arene derivative also showed good extracting ability towards α-amino acids, with some selectivity shown between different amino acids. No comment was included on the effect on amino acid extraction by addition of various metal cations. They have also looked at the complexation properties of tris(calix[4]arene) units and these derivatives exhibited higher extraction for hard metal cations.

Brechbiel and co-workers synthesised a tetramercapto-calix[4]arene and its astatine complex for an *in vivo* study of the possible use of the complex as an α-radioimmunotherapy agent [24]. A biodistribution study of the complex was performed in female nude mice. The activity of the ^{211}At isotope was measured in the blood and various organs of the mice at four time points post-injection. The study suggested that the ^{211}At-**5** complex was unstable *in vivo*, since the pattern of distribution of ^{211}At after injection of ^{211}At-**5** complex closely matched that of free ^{211}At ion (Fig. 5).

Europium(III) and terbium(III) complexes of macrocyclic ligands are of interest because of their potential use as labels in bioaffinity assays, most of which are based on time-resolved measurements of the metal luminescence upon ligand excitation followed by a ligand to metal energy transfer. Many of the widely used organic fluorophores have fluorescence lifetimes in the pico- to nanosecond range, whereas Eu(III) and Tb(III) complexes have considerably longer fluorescent lifetimes. Thus, such compounds are excellent markers for biological assays, in which a clear differentiation between the signal and background is needed for increased sensitivity. Ungaro’s and Sabbatini’s group have developed 2,2’-bipyridine lariat calixcrown macrocycles (**6**–**9**) which form highly luminescent Eu(III) and Tb(III) complexes [25] (Fig. 6). The group synthesised new calixcrown ligands by introducing either one or two bipyridyine moieties as pendant arms on the macrocycle and whose complexes with Eu(III) and Tb(III) ions showed excellent photophysical properties.

In a later paper, this group reported the isolation of novel calix[4]arene polycarboxylic-2,2’-bipyridine mixed ligand complexes of Eu(III), Gd(III) and Tb(III) [26]. Their complexes were designed based on the knowledge that polyamino–polycarboxylic acid ligands form strong complexes with hard metal cations, including the lanthanides, but additional chromophoric units were needed to improve the photophysical properties of the targeted receptor. Fig. 7 shows the compounds **10** and **11** isolated by the group. The complexes with Eu(III), Gd(III) and Tb(III) were isolated and were soluble in protic solvents such as methanol.

He and co-workers have more recently published a calix[4]arene-based chromogenic chemosensor for the detection of α-phenylglycine anion [27]. Phenylglycine is a chiral synthetic amino acid used in the manufacture of β-lactam antibiotics such as semisynthetic cephalosporin and penicillin. Therefore, efficient and rapid monitoring of the relative concentration of each enan-

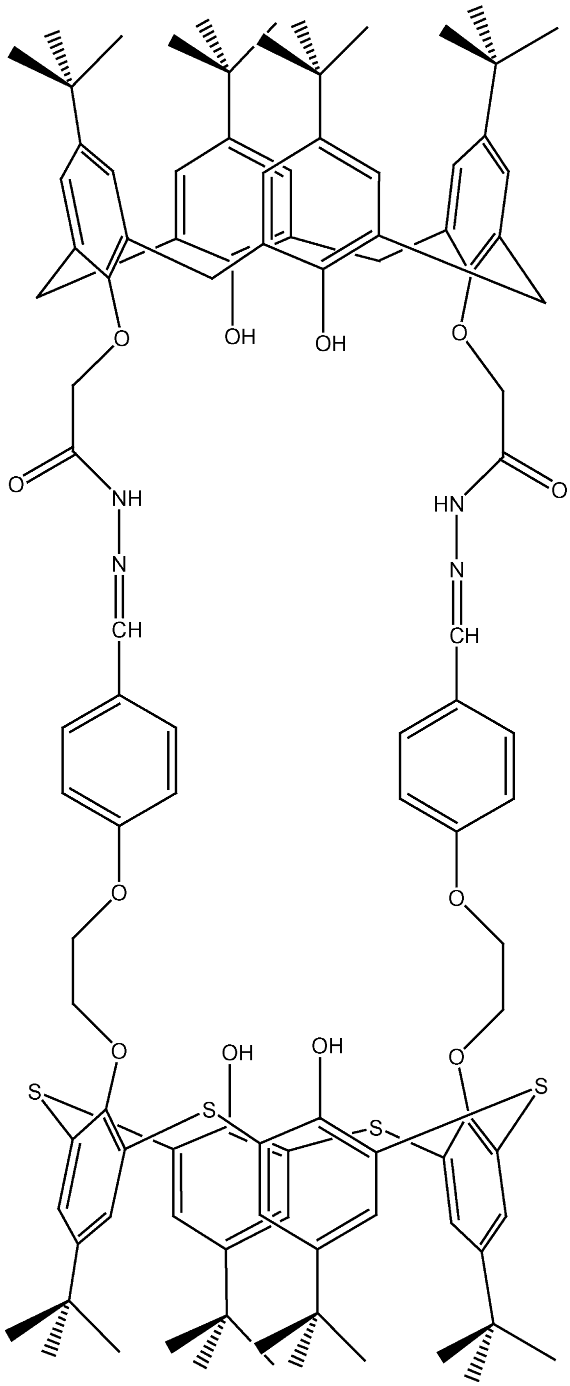

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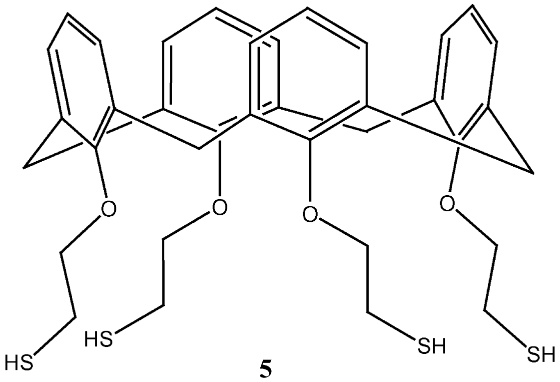
Fig. 4. Structure of bis(calix[4]arene) derivative **4**.

tiomer is desirable. The receptors designed by He and co-workers are in shown in Fig. 8. UV/vis absorption and ^{1}H NMR spectroscopy were used to study the enantioselective recognition ability of the receptors towards the enantiomers of *t*-butylammonium L- and D-α-phenylglycine. The two receptors **12** and **13** displayed different chiral recognition abilities towards the enantiomers and formed 1:1 complexes with the guests. They found that receptor **12** has a better enantioselective recognition ability and this was attributed to steric effects, a relatively good preorganized structure and the better hydrogen-bonding ability of **12**. In addition, the obvious colour change on complexation of **12** and the α-phenylglycine anion indicate that **12** may have potential as a chiral chromogenic sensor for the enantiomers of the α-phenylglycine anion.



5

Fig. 5. Structure of tetrmercapto calix[4]arene **5**.

Coleman and co-workers reported the study by ESI/MS of the determination of the selectivity for ternary complexation between 25,27-diphosphoryloxy-calix[4]arene **14** and a series of metal cations and amino acids [28] (Fig. 9). In particular, they found that that the amino acids complex exterior to the cavity of the calixarenes. They studied a number of metal ion–aminoacid–calix[4]arene complexes but found that zinc forms strong tertiary complexes with cysteine, serine and histidine. Competition experiments involving mixtures of amino-acids and **14** in the presence of zinc showed remarkable selectivity for the complex **14**–Zn(II)-histidine.

3. Catalysis

Calix[4]arene derivatives have been used in catalytic reactions over the last two decades because they tend to be highly stable towards hydrolysis, a factor which makes them highly useful as catalysts [4]. Several groups have investigated the use of calixarenes derivatised with various phosphorus-containing functional groups in transition metal-catalysed olefin hydroformylation [29–41]. The main interest in these particular metallocavitands is that a metal can be loosely tethered at an entrance to a receptor cavity, thereby favouring interactions between properly oriented, coordinated substrates and the inner part of the hollow molecule. A recent review by Matt and co-workers covers this topic in greater detail, as it describes the use of cavitands such as calixarenes, substituted at either the upper rim or the lower rim, and cyclodextrins [34].

Matt and co-workers have studied olefin hydroformylation using both rhodium and nickel catalysts containing calix[4]arene derivatives containing phosphorus(III) centres [29–34]. For their calix[4]arene derivatives, the phosphorus atoms are either directly connected to the phenolic oxygen atoms (phosphinites (OPR_2) or phosphites ($OP(OR_2)_2$)), or separated from the oxygen atoms by alkyl spacers (phosphines ($O(CH_2)_nPR_2$)). Examples of calix[4]arene-phosphinite derivatives are shown in Fig. 10 [29]. In these cases, the coordinating atoms are separated by 12 bonds, which will act as chelators when two adjacent binding sites are used. Cationic species bearing poorly coordinating solvent molecules provide chelate complexes similar to the palladium complex shown in Fig. 10. In these complexes, the metal centres sit below the cavity. However, in the case of calix[4]arene-phosphites, as shown in **17**, Fig. 11, where the phosphorus atoms bear small substituents (OEt) and the two side groups have been replaced by a single polyether chain that connects two opposing phenol units, reaction with $AgBF_4$ afforded complex **17** quantitatively. In this

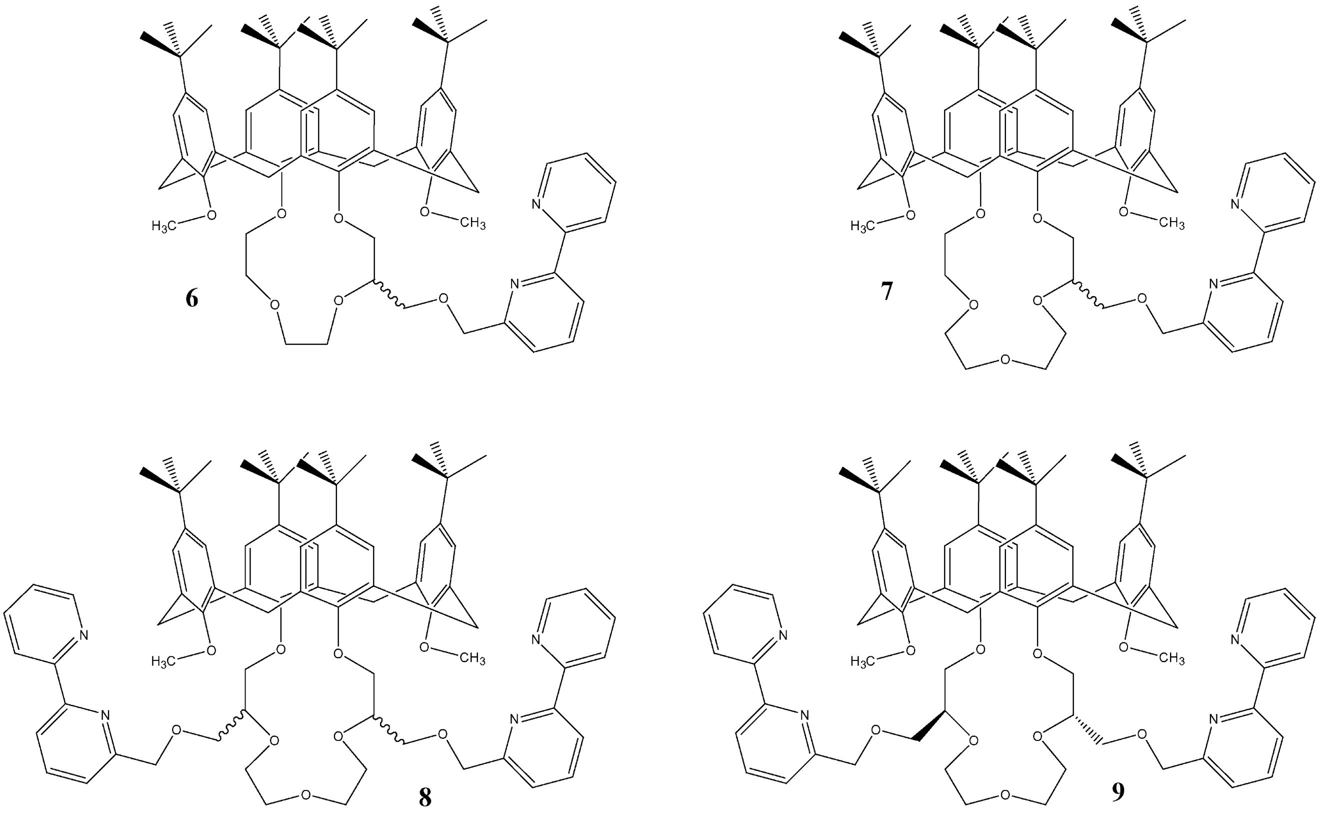
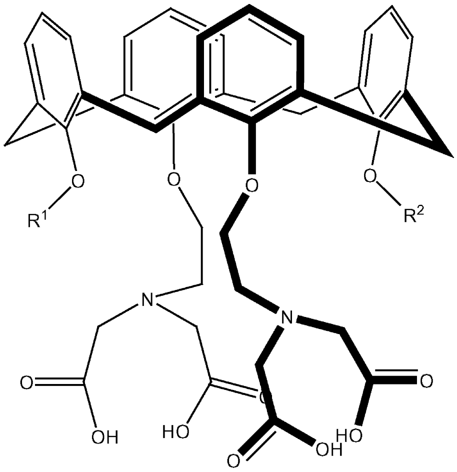


Fig. 6. Structures of 2,2'-bipyridine lariat calixcrowns **6**–**9** studied by Ungaro and Sabbitini.

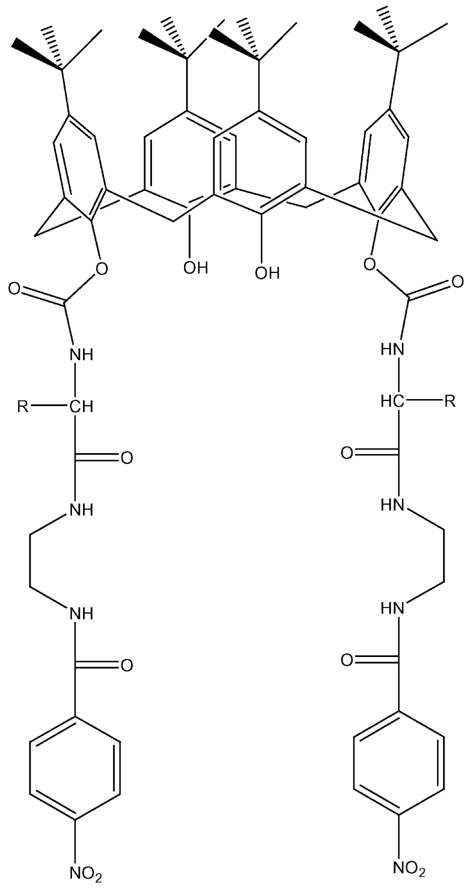
case, the calix[4]arene acts as a platform with the pocket for the metal ion to reside in being generated by the encircling substituents [29,32]. They assessed several calix[4]arene derivatives, containing either phosphites or phosphinites, mixed with [Rh(acac)(CO)$_2$] for the hydroformylation of both alkenes and styrene [29–31,33–35]. They concluded that, where small phosphorus-containing functional groups were present, as in Fig. 10, the hydroformylation of olefins or styrene resulted in the high regioselectivity in favour of branched aldehydes, a feature which is not unusual for rhodium phosphine complexes, as shown by Mortreux and co-workers [42]. However, calix[4]arenes, such as **18** and **19** in Fig. 12, provided examples of hemispherical chelators which were able to drive olefin hydrofromylation reaction towards the formation of linear products. The authors attribute this to a “pocket” effect which results from the degree of steric protection by the *O*-alkyl substituents about the metal as well as the large P–Rh–P bite angle which surpasses 90°. They have also looked at the palladium complexes of some of these ligands (**15**–**19**) and have assessed them as catalysts in allylic alkylation catalysis [29,30,33,35]. Under the reaction conditions used, they found that full conversion of the substrate occurred after 4 h, generally. Their findings show that the palladium centre remains accessible to the substrate despite its location inside a pocket. When they used the palladium complexes of **18** and **19** as the catalyst for the reaction of 3-phenylallyl acetate with dimethyl malonate, they found that the linear product, dimethyl 2-cinnamylmalonate, was formed with over 98% selectivity [35]. This unusual selectivity was explained by the presence of the “pocket” about the metal centre.



R^1=R^2=6-CH$_2$-2,2'-bipy **10**
R^1=R^2=5-CH$_2$-2,2'-bipy **11**

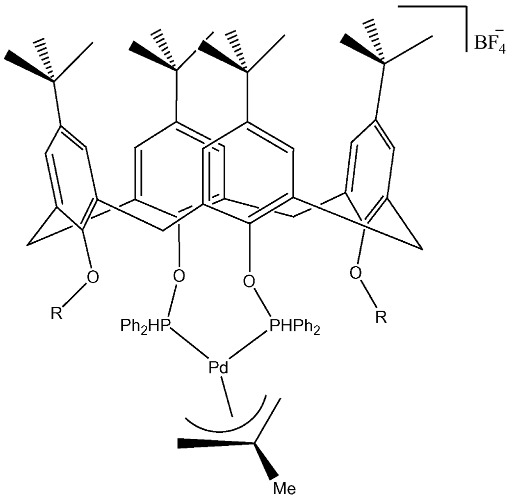
Fig. 7. Structure of calix[4]arene polycarboxylic-2,2'-bipyridine mixed ligand macrocycles **10** and **11**.

They also investigated the use of nickel(II) complexes of **20** as catalysts for the oligomerisation of ethylene [32] (Fig. 13). X-ray crystal studies carried out on the complexes [NiX$_2$·**20**] show that the diphosphane ligand can accommodate either tetrahedral or distorted tetrahedral coordination geometries, but not a square-planar geometry. As a result of possessing this flexible geometry, they assessed the NiCl$_2$·**20** complex as a catalyst for ethylene oligomerisation using methylaluminoxane (MAO) as an activator. They found that the reaction produced C$_4$ to C$_{12}$ oligomers, when the reaction was stopped after 1 h, with no catalyst deactivation. They suggested that the bulky calix[4]arene core is remote from the nickel centre, a fact observed in the X-ray studies, resulting in an uncrowded metal environment which facilitates the reductive elimination steps.



12 R = CH_3
13 R = $PhCH_2$

Fig. 8. Structure of the chromogenic calix[4]arene sensors **12** and **13**.



15 R = CH_2CH_2OMe
16 R = $CH_2C(O)OMent$

Fig. 10. Structures of cali[4]arene derived hydroformylation catalysts **15** and **16**.

The group of Schmutzler, Börner and co-workers have also looked at the rhodium(I) catalysed hydroformylation of olefins, using calix[4]arene derivatives containing phosphorus diamides (**21**–**25**) [38–40] (Fig. 14). Rhodium complexes of all phosphorus ligands were tested in the hydroformylation of 1-octene. They observed that all the complexes could be successfully employed in the reaction with the yield and regioselectivity of the hydroformylation being dependent on the structure of the ligand and the reaction conditions. Catalysts based on the calix[4]arenes containing the phosphorus diamide groups exhibited superior activity in comparison to the corresponding phosphites (**22** and **24**). They also studied the formation of catalysts containing either a monosubstituted dirhodium complex (**26**) or a bis-rhodium complex, but no hydroformylation results on these materials were reported [39] (Fig. 15). The hydroformylation reaction of 1-octene by rhodium(I) catalysts containing calix[4]arenes with phosphite functional groups was also undertaken [40]. The formation of aldehydes as products in all cases was observed, with no alcohol formation or olefin hydrogenation occurring. The yield and selectivity was dependent on both the type of ligand used and also on the Rh:ligand ratio, resulting in the speculation that a tighter pocket favours the formation of Rh(*n*-alkyl) intermediates over that of Rh(*i*-alkyl) ones. This conclusion, although requiring more investigation, is also favoured by Matt and co-workers [34].

Kleij et al. have looked at the synthesis of functionalised metallacalix[4]arenes that possess organometallic groups covalently attached to a calix[4]arene support [41]. They initially functionalised the lower rim with 4-iodobenzyl groups that were easily converted into organometallic groups that possess a direct and stable palladium–carbon bond, as that shown in **27**, with the potential for tunable metal centres *via* electronic and/or steric modifications (Fig. 16). This is undoubtedly advantageous in cases where the ligand modifications could lead to improved catalytic properties of these materials.

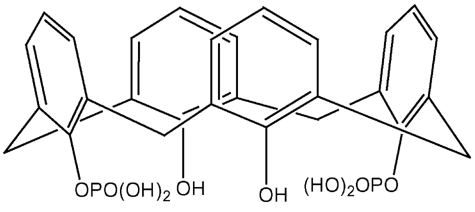


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Fig. 9. Structure of diphosphoryloxyl-calix[4]arene **14**.

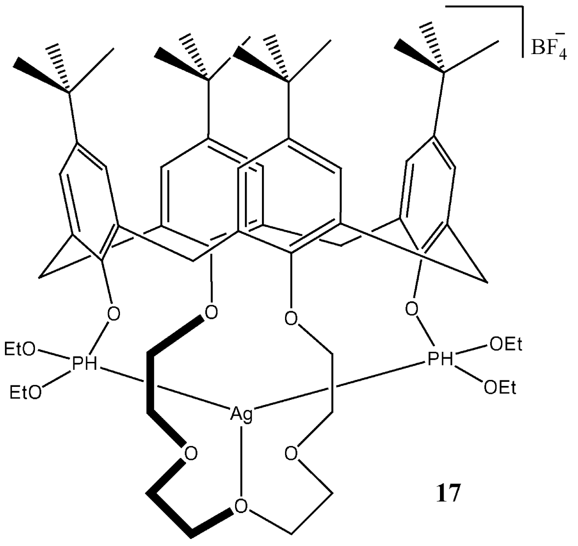

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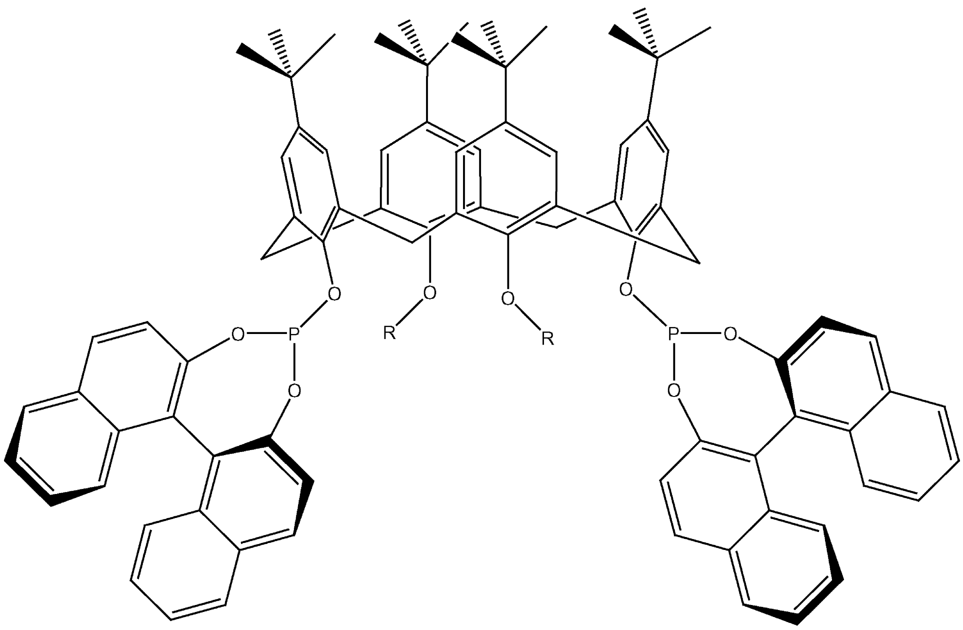
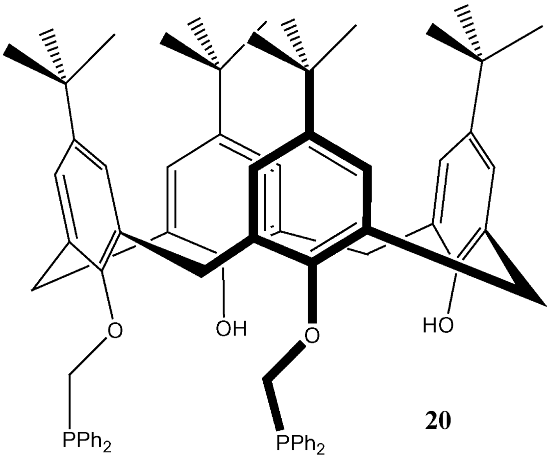
Fig. 11. Structure of **17**.



18 R=$CH_2CH_2CH_3$
19 R=CH_2Ph

Fig. 12. Structure of calix[4]arene macrocycles **18** and **19** containing phosphite-derived substituents.

Milstein and co-workers have attached bipyridine groups to the lower rim of a calix[4]arene and used this ligand (**28**) to then make rhodium(I), palladium(II) and nickel(II) complexes [43] (Fig. 17). X-ray crystallographic studies of the metal complexes revealed the presence of a monometallic nickel complex and of a dimetallic rhodium and a dimetallic palladium complex. The catalytic studies of the binuclear metal complexes have not been reported. Karakhanov and co-workers have looked at supramolecular catalysts based on metal complexes of calix[4]arenes and these were found to be very efficient as mass-transfer promoters for biphasic Wacker oxidation of olefins in water [44]. The oxidation of unsaturated compounds to methyl ketone with dioxygen in water/olefin mixtures was achieved using palladium complexes of modified calix[4]arenes. The activity of complexes of palladium with water-soluble calix[4]arenes modified with benzylnitrile groups (**29**–**31**) differed depending on the number of carbon atoms in the substrate (Fig. 18). For **29** and **31**, the maximum yield was at 1-hexene oxidation, whereas the activity for **30** was in 1-heptene oxidation. In styrene oxidation, the palladium complexes of **30** and **31** are significantly more active that catalytic systems based on **29**, with ketone yields increased from 5% in the case of **29** to 60% and 45% for those involving **30** and **31**, respectively.



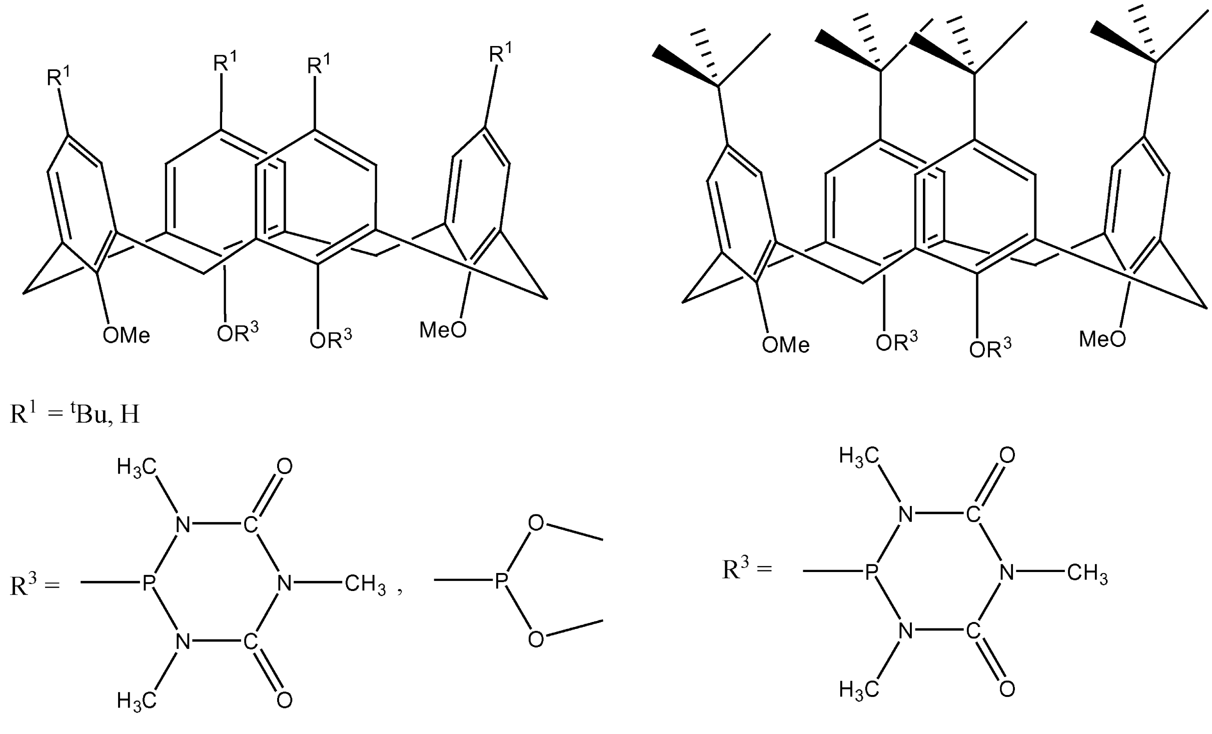
20

Fig. 13. Structure of phosphine disubstituted calix[4]arene **20**.

4. Complexation

Since Gutsche first published the one-pot synthesis of calixarene-based macrocycles [1], the investigation of the complexation properties of these compounds has been of intense interest. The interest is driven by the selective nature of complexation of the target guests of calixarenes which has given rise to their application in a number of areas as discussed in this review. Specifically this section deals with those studies which have been undertaken on the nature of the complexation process.

One of the important processes in the management of nuclear wastes is the intra- and inter-group separation of lanthanides and actinides. To fulfil this need, several separation strategies have been studied and developed but it is solvent extraction which is the most frequently investigated and since the early 1990s such studies has been well funded. Numerous papers on the efficiency of calixarene derivatives as extracting agents in such processes are available. Liu et al. have published a number of complexation thermodynamic studies on calixarenes with light lanthanoids nitrates. In 2001, they synthesised a novel *p*-*tert*-butylcalix[4]arene Schiff base **34**, shown in Fig. 19, and the complexation thermodynamics of **34** with light lanthanide(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu and Gd) was determined using titration calorimetry [45] and compared to results published previously for **32** and **33** [46,47]. They showed that bis(cyanomethyl)calix[4]arene **32** gave a very flat K_S profile and lower cation-binding abilities than **33** (for La(III) and Ce(III)) and **34** (for all lanthanoids examined). This poor cation



21-24

25

Fig. 14. Series of phosphorous diamide calix[4]arenes, **21–25**.

selectivity and binding ability may be attributed to the distortion of calixarene structure arising from the repulsive interaction between the dipoles of 1,3-bis(cyanomethyl) groups. These workers deduced that the lower-rim disubstitution plays a crucial role in determining the spatial arrangement and orientation of the calix[4]arene's donor atoms, leading to the alteration of the cation binding ability and selectivity for lanthanides. From this study they also observed that possessing multiple donor atoms in the relatively flexible side-arms, calix[4]arene Schiff base **34** gave much higher K_S values over the whole range of lanthanides employed than the correspond-

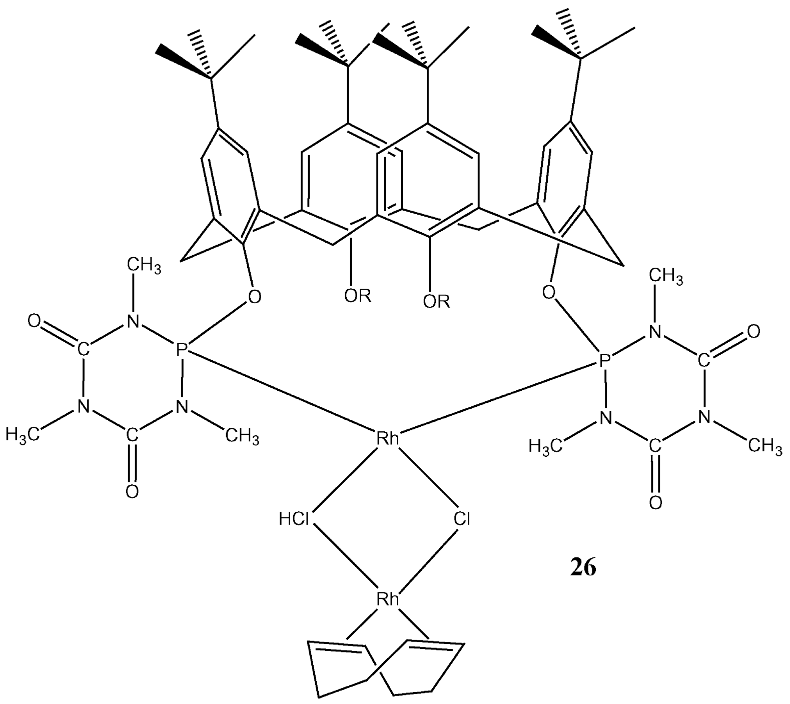


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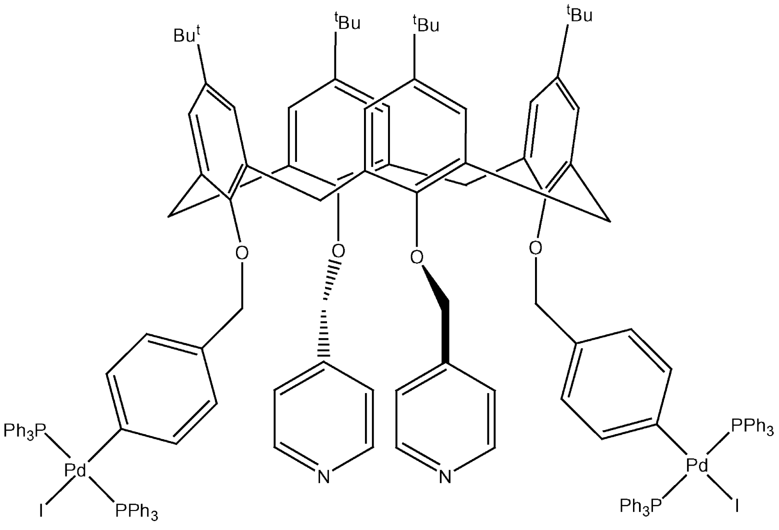
Fig. 15. Structure of rhodium complex of phosphorous diamide calix[4]arene **26**.

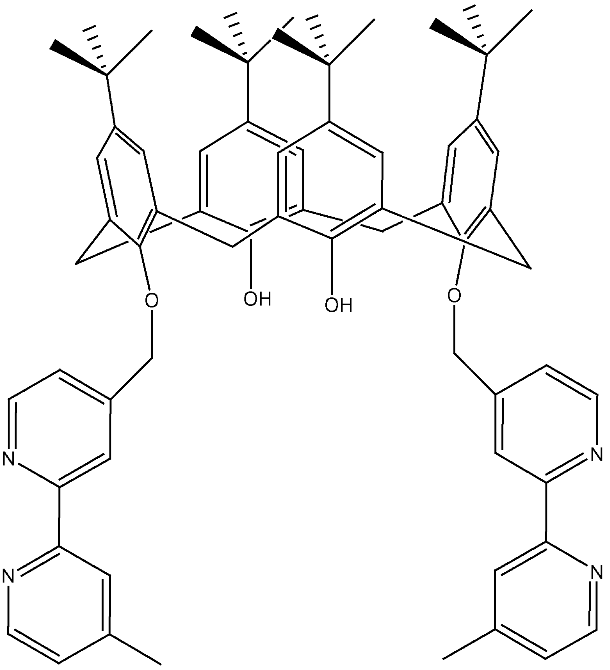


27

Fig. 16. Structure of metallacalix[4]arene **27**.

ing values obtained with **32** or **33** (except for La). In addition the strongest binding of Eu(III) ion by **34** is attained not by the largest enthalpic gain but by the smallest entropic loss.

In a study by Liu et al. in 2004, microcalorimetric titrations in acidic aqueous solution were used to determine stability constants and thermodynamic parameters for the complexation of the calixarenes **35**–**37**, shown in Fig. 20, with a series of lanthanoid(III) nitrate cations [48]. This study was related to their earlier studies [47] but the addition of the sulphate group on the upper-rim allowed the behaviour of water-soluble calixarenes to be investigated. These workers found that the introduction of four carboxyls to the lower rim of *p*-sulfonatocalix[4]arene could alter not only the binding ability, but also the relative cation selectivity for lanthanoids. The profile of K_S values for **36** displayed a broad peak for Nd(III) and Sm(III) ions. One reasonable explanation for these results is that the trivalent Nd(III) and Sm(III) ions are best accommodated in the preorganized 3D cavity composed of four carboxyl groups. They also found that the complexation of calix[4]arenes (**35**–**37**) with lanthanoid(III) ions is driven predominantly by the favourable entropic change, typically showing large positive entropy changes ($T\Delta S = 26–34\,\mathrm{kJ\,mol^{-1}}$) and somewhat smaller positive enthalpy changes($\Delta H = 4–12\,\mathrm{kJ\,mol^{-1}}$). They assigned this observation to the fact that both dissociated trivalent lanthanide(III) ions and free calixarene derivatives are heavily solvated by ion-dipole and hydrogen-bonding interactions, respectively. Therefore, the cation binding of water-soluble calixarene derivatives with lanthanide(III) ions in acidic aqueous solution requires the extensive desolvation of interaction between host and guest cation, affording the highly positive entropy change upon complexation, as observed in the case of complexation with crown ethers in methanol [49,50].

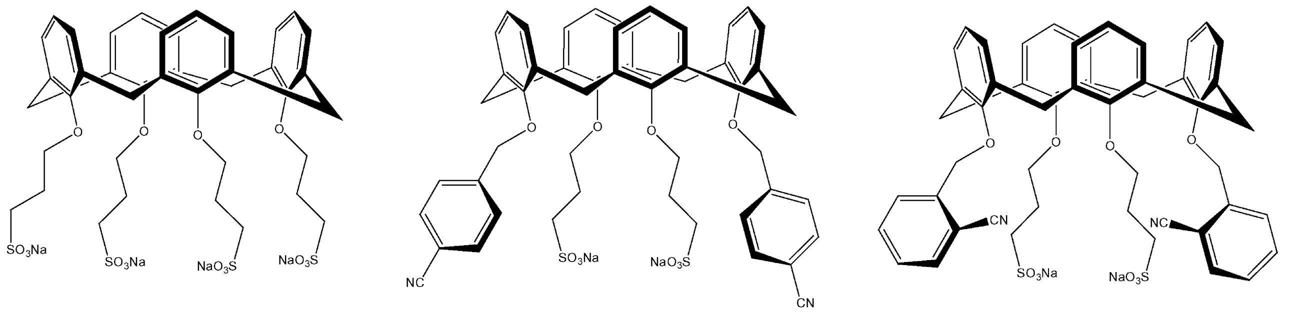


28

Fig. 17. Structure of bis(pyridyl) substituted calix[4]arene **28**.

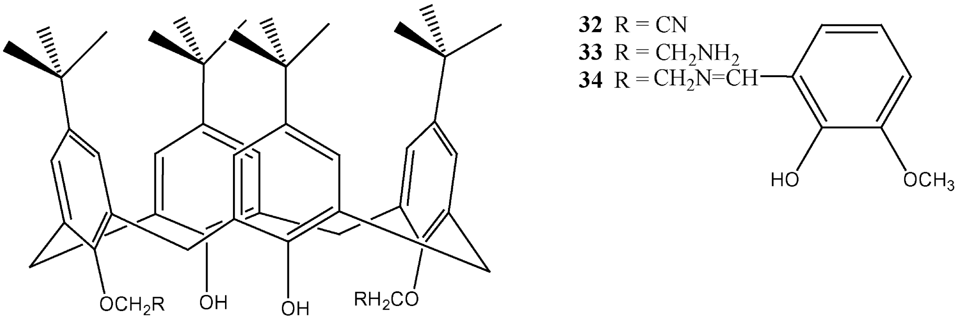
Yaftain et al. investigated the use of a phosphorylated calix[4]arene derivatives (**38** in Fig. 21) in the extraction of thorium(IV) and europium(III) ions [51]. They found that the solvent extraction of thorium(IV) and europium(III) ions by **38** in dichloromethane proceeded *via* a solvation mechanism and by the formation of a cation complex with a metal:**38** ratio equal to 1 and that the ligand extracts efficiently these ions from nitric acid medium.

Vicens and co-workers have investigated calixarenes containing simultaneously hard and soft ion binding sites, namely the ionophoric tetra(2-pyridylmethyl)amide calix[4]arene **39** and the related tetra(benzyl)amide **40** [52] (Fig. 22). Stability constant determinations in acetonitrile and extraction studies showed that **39** formed much more stable complexes with Cu(II) and Co(II) ions than with alkali or alkaline earth cations. In a later study, this group investigated the complexing properties of four dimalonate and one diester calix[4]arene derivatives toward alkali and alkaline earth cations in acetonitrile [53]. This study was carried out in order to observe the influence of the type and the number of carbonyl sites



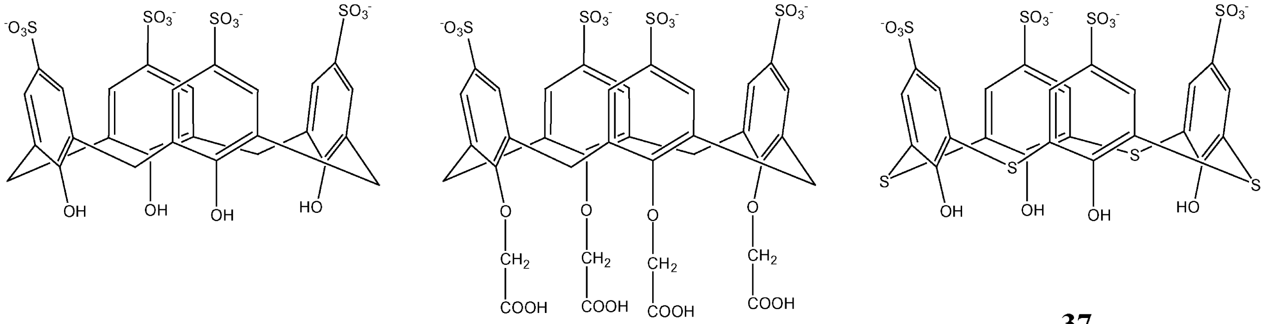
29 **30** **31**

Fig. 18. Structures of ligands, **29–31**, used to complex Pd(II).



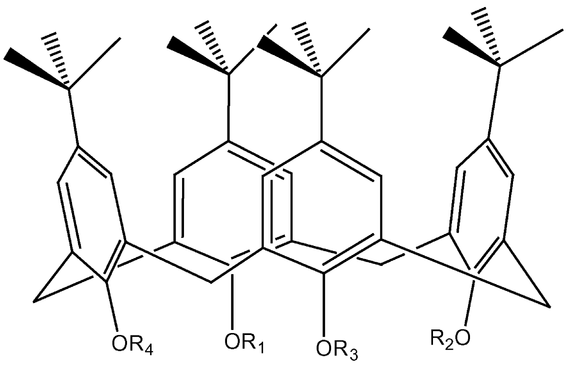
32 R = CN
33 R = CH_2NH_2
34 R = $CH_2N{=}CH$–

Fig. 19. Series of Schiff base-derived calix[4]arenes **32–34**.



35 **36** **37**

Fig. 20. Series of water soluble calix[4]arenes **35–37**.

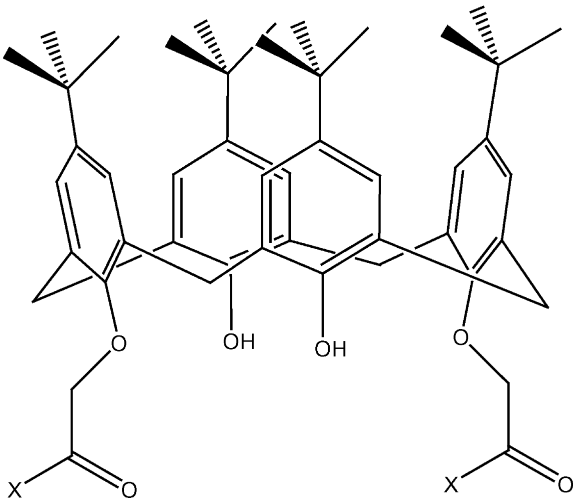


38 $R_1 = R_2 = R_3 = R_4 = CH_2P(O)Ph_2$

Fig. 21. Structure of phosphorylated calix[4]arene **38**.

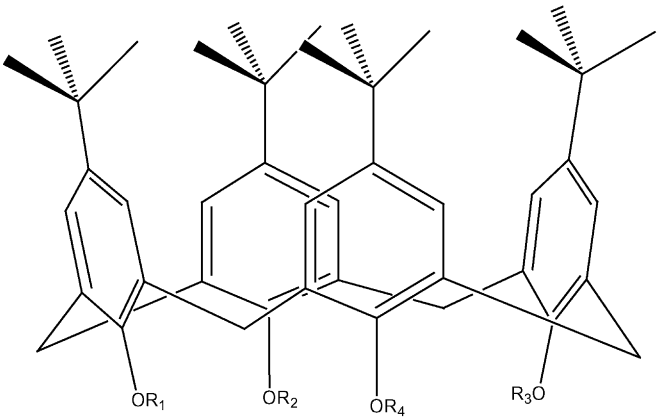
on the strength of metal cation complexes. The ligands studied are shown in Fig. 23. They observed a number of trends from these studies, namely:

(i) that there was an increase in the cavity dimension with increasing number of ester groups going from diethyl ester to dimalonate and through to diethyl ester-dimalonate derivatives;
(ii) that the more bulky the substituent on the malonate, the more the ligand displayed an opened cavity suitable for the complexation of the largest cations;
(iii) that the results obtained from alkaline complexation showed that the substitution of an ethyl ester group by an ethyl ester malonate increased selectivity somewhat but does not greatly affect the stability of complexes;
(iv) that significant complexation selectivities were observed for the dimalonate ligands **42** for Na(I) and Ba(II), and for ligand **43** for Rb(I) in the alkaline series;



39 X = $NHCH_2Py$
40 X = $NHCH_2C_6H_5$

Fig. 22. Structure of diamide calix[4]arenes **39** and **40**.



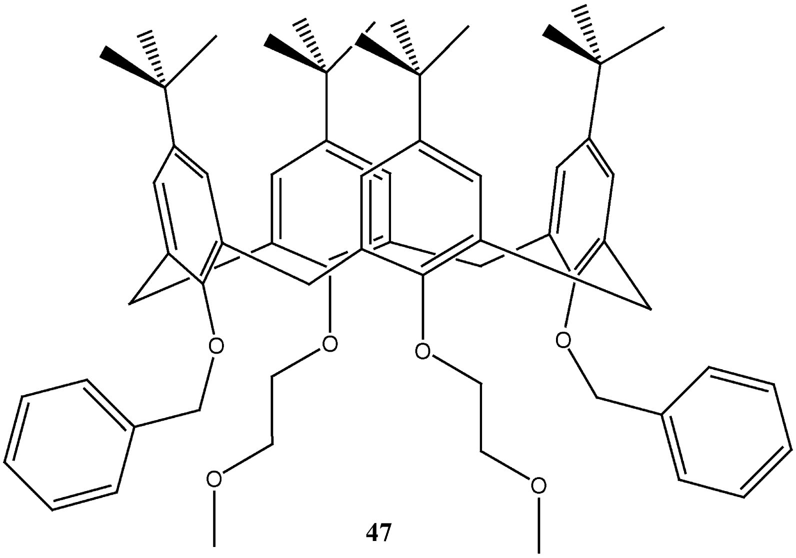
41 $R_1 = R_3 = H$ $R_2 = R_4 = CH_2CO_2Et$
42 $R_1 = R_3 = H$ $R_2 = R_4 = CH(CO_2Et)_2$
43 $R_1 = R_3 = H$ $R_2 = R_4 = C(CH_3)(CO_2Et)_2$
44 $R_1 = R_3 = CH_2CO_2Et$ $R_2 = R_4 = CH(CO_2Et)_2$
45 $R_1 = R_3 = CH_2CO_2Et$ $R_2 = R_4 = C(CH_3)(CO_2Et)_2$
46 $R_1 = R_3 = CH_2CO_2Et$ $R_2 = R_4 = CH_2CO_2Et$

Fig. 23. Alkali and alkaline earth cation selective calix[4]arenes **41–46**.

(v) it was noted that in the solvent system studied here, namely acetonitrile, ester derivatives were able to form biligand species particularly with Na(I) and Ca(II) ions.

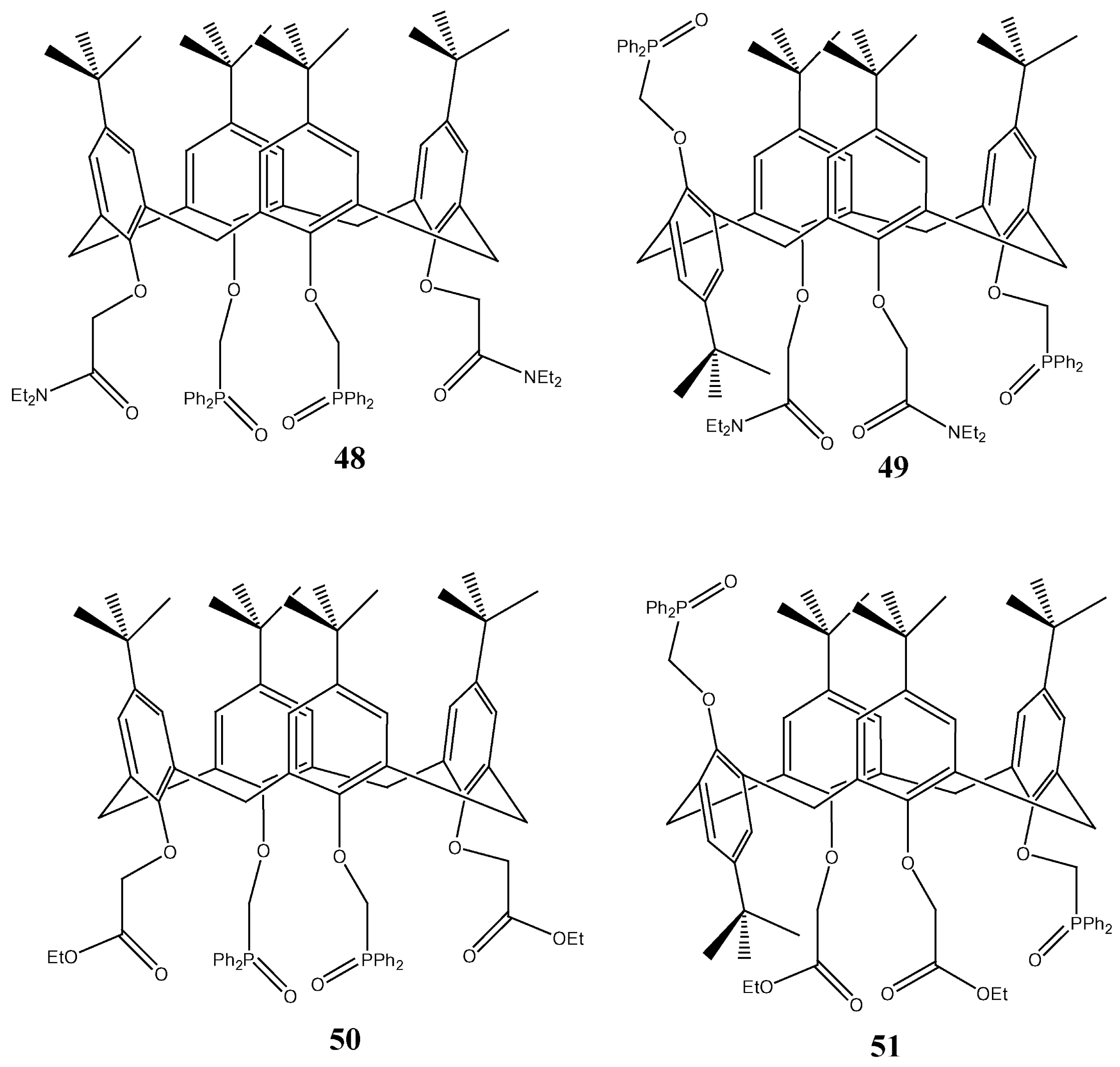
In a later related study, this same group determined the crystal structure of the acetonitrile inclusate of the complex formed between sodium trifluoromethanesulfonate (triflate, $CF_3SO_3^-$) and the narrow-rim functionalised calix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,27-di(phenylmethoxy)-26,28-di-(2-methoxy-ethoxy)calix[4]arene (**47**) [54] (Fig. 24). The structure showed that the diether pendent arms do not chelate the sodium cation, although coordination of all four phenolic oxygen atoms does draw the calixarene into a nearly symmetrical cone form.

Yaftian, Matt and co-workers had also investigated the binding properties of *cone*-5,11,17,23-tetra-*tert*-butyl-25,27-bis(diethylcarbamoylmethoxy)-26,28-bis(diphenylphos-phinoylmethoxy)calix-[4] arene (**48**) towards alkali metals and compared them with those of the corresponding *partial-cone* conformer (**49**) [55]. Both hybrid ligands form stable 1:1 complexes with alkali picrates in tetrahydrofuran. An investigation of the transport properties of the two calix[4]arenes showed that the extraction efficiency of **48** decreases on-going from Li/Na to Cs, while that for **49** presents a peak selectivity for Na (with the following order Na > K > Rb > Li > Cs). They later extended this study to the structures **50** and **51** shown in Fig. 25 [56]. The amide-containing calixarenes were found to be more efficient for alkali metal complexation than those bearing ester substituents. While sodium ions are selectively complexed by the two mixed amide-(phosphine oxide) calixarenes, the two ester-containing isomers **50** and **51** turned out to be selective towards potassium and rubidium ions, respectively. With all four ligands, the lowest stability constants were found for the lithium and caesium ions.



47

Fig. 24. Structure of **47**.



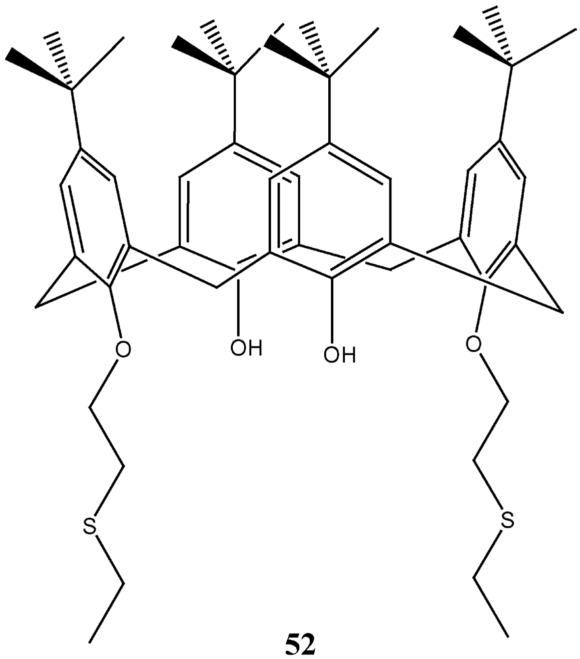
48 **49** **50** **51**

Fig. 25. Series of bis(diphenylphosphinylmethoxy)calix[4]arenes **48–51** investigated by Matt *et al.* [55].

De Namor has long been interested in the quantitative assessment of the selective behaviour of a range of calix[4]arene ion complexes. Her work in this area, prior to 2000, has been extensively reviewed [57]. She has published a number of detailed studies, since 2000, on a range of calix[4]arene derivatives including complexation studies of calix[4]arene ketone derivatives with sodium ions [58,59], complexation of calix[4]arene ester, ketone and acetamide derivatives with lanthanides [60], complexation of calix[4]arene pyridine derivatives with lead and mercury cations [61], complexation of calix[4]arene amines and amides with lanthanides [62], complexation of a partially substituted calix[4]arene aminophosphate derivative with a range of cations [63], complexation of calix[4]arene ester and ketone derivatives with lead and cadmium ions [64], complexation of calix[4]arene with mixed pendant arms (di-functionalised with ethylethanoate and ethylthioethoxy groups) with a range of cations [65,66]. Many of these studies offered a comprehensive investigation into the role of solvation of host and guest species in a given medium, and indeed medium effects feature as one of the main areas of focus of investigation in all of these studies.

For example, one paper in 2005 looked at the effect of solvent control on the ability of a partially substituted lower rim calix(4)arene derivative 5,11,17,23,-tetra-*tert*-butyl[25,27-bis(hydroxy)-26,28-bis(ethylthioethoxy)]-calix(4)arene, **52**, to complex soft metal cations (Hg(II) and Ag(I)) in a wide variety of solvents [67] (Fig. 26). Solvent–ligand interactions were assessed from ^{1}H NMR measurements involving **52** and various solvents in $CDCl_3$ and the formation of a 1:1 **52**-CH_3CN adduct was reported. In this study, the effect of solvent on cation complexation was clearly shown using a number of spectroscopic and electrochemical techniques. It was found, for example, that in acetonitrile, **52** was more selective for Hg(II) relative to Ag(I) by a factor of 2.2×10^3. But, surprisingly, in methanol the selectivity is reversed to an extent that the affinity of **52** for Ag(I) is 1.4×10^3 higher than that for Hg(II). However, **52** was unable to recognise these cations selectively in *N*,*N*-dimethylformamide while little complexation of cations by **52** was seen in propylene carbonate. Thermodynamic studies revealed that, in acetonitrile, the thermodynamics of cation complexation by the hydrophilic cavity of a calix(4)arene containing mixed pendant groups is built up from thermodynamic data for the same process involving derivatives with common functionalities at the narrow rim. This was a unique example of the additive contribution of pendant arms in the field of thermodynamics of calixarene chemistry.

De Namor et al. have synthesised two calix[4]arene derivatives containing mixed pendent arms [68]. They carried out the



52

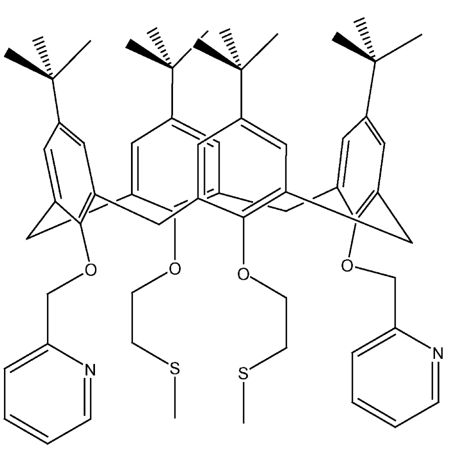
Fig. 26. Structure of bis(ethylthioethoxy) substituted calix[4]arene **52**.

transfer thermodynamic experiments of these ligands to various alkali metal ions out and showed that the calix[4]arenes undergo selective solvation in nonaqueous solvents. They also found that **53** interacts with Li(I) and Na(I) but not with other alkali metal ions, while **54** did not interact with any alkali metal ions (Fig. 27). They also determined that 1:1 metal:calix[4]arene complexes were formed. They had earlier looked at the interaction of silver perchlorate with a series of calix[4]arene derivatives containing pendant arms having a number of different functional groups [69]. Here they found that the solvent system played a role in the stoichiometry of the complex formed in the extraction process with a 1:1 complex (ligand:metal cation) being formed in the water-nitrobenzene process while a 1:2 complex (ligand:metal cation) being formed in the water-dichloromethane process.

In nearly all of the studies carried out by de Namor et al., the effect of medium on the binding of metal ions at the lower rim was considered. All of these studies are important as calix[4]arenes are more likely to enter specific interactions with the solvent than any other macrocycle due to the ability of a hydrophobic cavity to host neutral species (Fig. 28). In particular, the involvement of acetonitrile in the hydrophobic cavity of the ligand exerts an "*allosteric effect*" by which the hydrophilic cavity in the adduct is more receptive to host cations than that for the free ligand. This same effect has been noted by a number of other workers who have investigated calix[4]arenes in the cone conformation. Pochini and co-workers have investigated in apolar media the effect of the acidity of CH groups within the guests on the binding ability of the aromatic cavity of rigid cone conformers of *p-tert*-butylcalix[4]arene when those guests contain acid CH_3 and CH_2 groups [70]. They found that in $CDCl_3$ and/or CCl_4, CH_3Y and CH_2XY guests show different binding modes with the acidity of the CH_2XY guests strongly affects the binding efficiency whereas the guest acidity does not seem to be the sole parameter in determining the stability of the complexes with CH_3Y guests. With methylene containing guests, the polarisability of the X and Y groups strongly affect the binding process.

Creaven et al. noted a similar phenomenon in their studies on a number of sodium salt complexes of the tetraethyl ester *p-tert*-butylcalix[4]arene (**57**) which were isolated both with and without upper-rim encapsulated acetonitrile or methanol [71] (Fig. 29). Upon dissolution in $CDCl_3$, **57** remained largely complexed to the sodium cation but ca. 90% of the upper-rim bound solvent was released, reflecting the relative values of the binding constants for complexation of the two guest species. Selective decomplexation of lower-rim bound sodium cations could be successfully achieved using low-pressure light sources, triggering the immediate expulsion of the upper-rim bound solvent. These studies have also helped to understand the relationship between a guest binding at the lower rim of a calixarene and the "*allosteric effect*" that this confers on upper-rim binding of neutral species. The difference in binding constant for the two guests confers essentially a "one-way allosterism" and removal of the lower-rim bound guest, in this case by photodecomplexation, resulted in the immediate expulsion of the upper-rim guest.

Arnaud-Neu et al. have studied the binding properties of calix[4]arene diamide dicarboxylic acids in methanol solution [72]. The compounds **58**–**61**, shown in Fig. 30, were synthesised and their complexation behaviour towards alkali and alkaline earth cations investigated. The compounds displayed a remarkable selectivity for alkaline earth over alkali metal ions. In particular, the high



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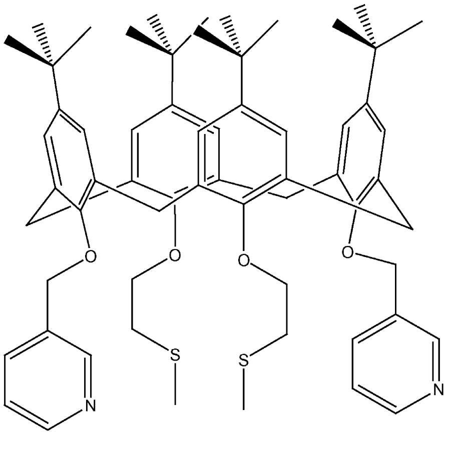
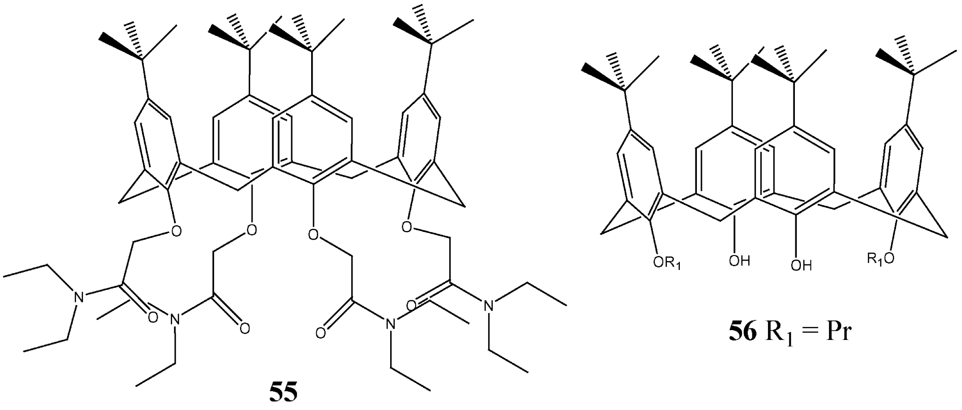


54

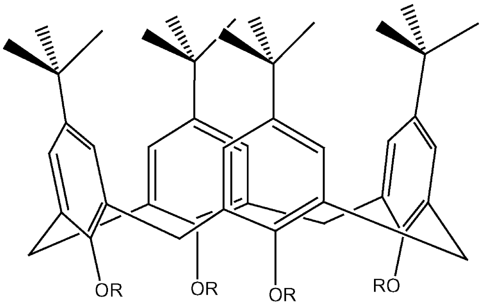
Fig. 27. Structure of calix[4]arenes **53** and **54** containing mixed pendant arms.



55

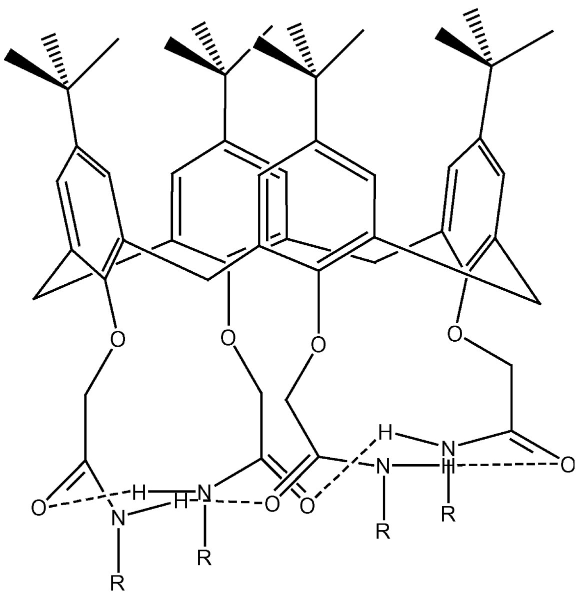
56 R_1 = Pr

Fig. 28. Structures of **55** and **56**.



57 R = $CH_2COOCH_2CH_3$

Fig. 29. Structure of tetraethylester *p-tert*-butylcalix[4]arene **57**.

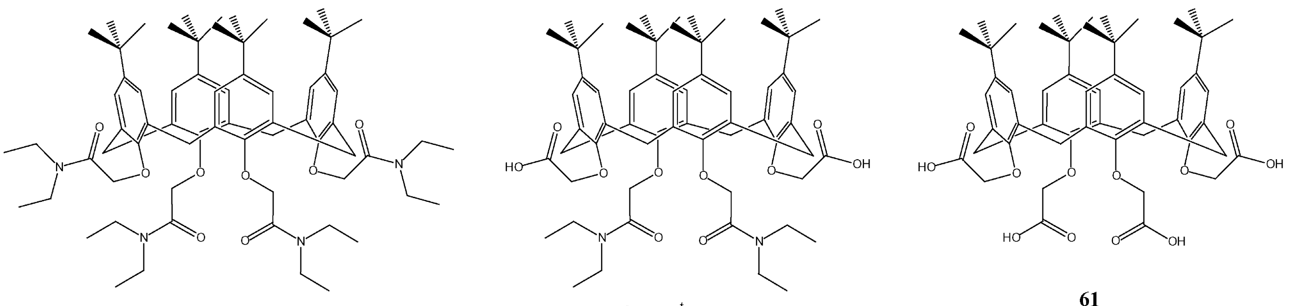


62 R =$CHPhCOOCH_3$

Fig. 31. Structure of amino acid-derived calix[4[]arene **62**.

Sr(II)/Na(I) selectivity would indicate the suitability of these ligands for the treatment of nuclear waste in weakly acidic or basic conditions.

Tomišić et al. have also studied hydrogen bonding and solvent effects on the complexation behaviour of derivatised calix[4]arenes with alkali metal cations [73]. Calixarenes with carbonyl-containing substituents, which include calixarene ketones, esters or amides, are effective receptors for alkali and alkaline earth cations and have been studied by numerous groups. In addition derivatives having substituents with both a hydrogen-bond acceptor (carbonyl group) and a hydrogen-bond donor (e.g. –NH– group in secondary amides). A small number of calix[4]arene derivatives bearing amino acid or peptide substituents have been recently suggested [17] to serve as synthetic models for the potassium channel in the cell membrane. They prepared the ligand **62** shown in Fig. 31 and carried out a quantitative comparison of the abilities of **62** for binding different alkali metal cations using spectrophotometric, conductometric and potentiometric methods. The solvent effect on the binding properties of **62** were also of interest and therefore two solvents with different affinities for hydrogen bonding, i.e. methanol and acetonitrile, were examined. The calix[4]arene amino acid derivative was found to have a lower affinity for alkali

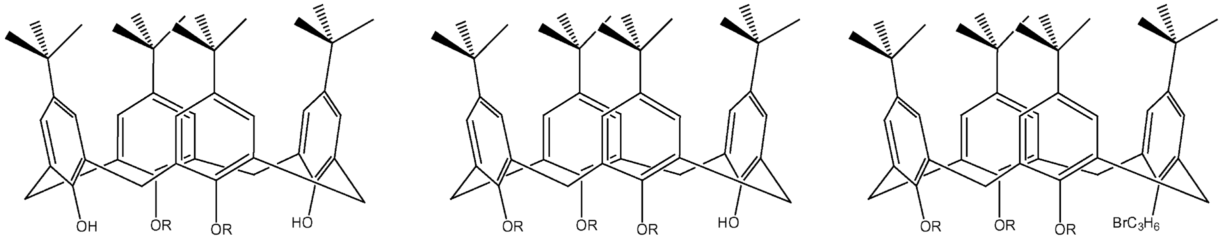


58

59 R = ${}^tBu$
60 R = H

61

Fig. 30. Series of calix[4]arene diamide dicarboxylic acids, **58**–**61**.



63 **64** **65**

R = C_3H_7

Fig. 32. Series of calix[4]arenes, **63–65**, chosen to study cation–π interactions.

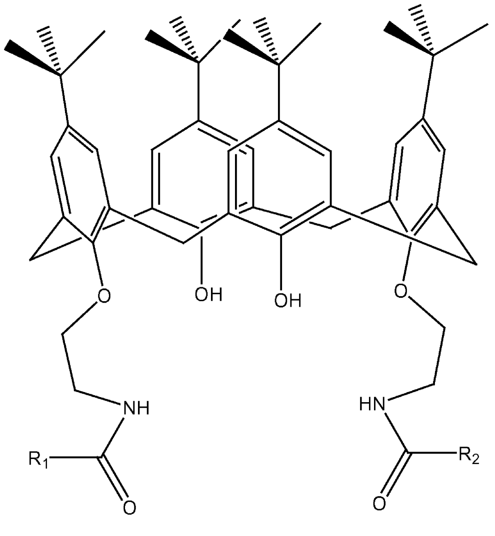
metal cations compared to tertiary amide derivatives in both solvents investigated. However, in acetonitrile, **62** was shown to bind Na(I) and Li(I) cations quite strongly, whereas its affinity for K(I) ions was moderate. The ligand showed little or no affinity for the other alkali metal cations. In the case of Li(I) ions, the difference between its solvation in MeCN and MeOH is reflected in the large difference in the complexation equilibria in the two solvents. As the extent of Na(I) and K(I) solvation does not greatly differ in the two solvents, the lower stability of their complexes with **62** in MeOH is predominantly a consequence of hydrogen-bonding interactions of methanol molecules with the cation binding sites of the ligand, i.e. carbonyl oxygens.

Monajemi and co-workers in 2006 evaluated the alkali metal ion binding selectivities of a series of calix[4]arenes in chloroform solution [74]. This group was particularly interested in studying cation–π interactions. The ligands they studied (**63**–**65**) are shown in Fig. 32. The ligands formed exclusively 1:1 (metal ion to ligand ratio) complexes with alkali cations and it was found that the chloroform solvent stabilized *endo* complexes. In fact, from their results they predicted that in weakly polar solvents *endo* complexation is preferred, whilst in more polar solvents, like acetonitrile, *exo* complexation is preferred.

Electrospray mass spectrometry (ESMS) was also use to study Pd(II) complexes of lower-rim amino acid substituted calix[4]arenes by Zhu and co-workers [75]. The coordination reaction between *trans*-$[Pd(Py)_2Cl_2]$ and calixarene derivatives was investigated. The *trans*-$[Pd(Py)_2Cl_2]$ only reacts with **66** to form a mononuclear complex, while $PdCl_2$ reacts with all the ligands to give the mononuclear complexes Pd(**66**)Cl_2, Pd(**67**)Cl_2, Pd(**69**)Cl_2, Pd(**71**)Cl_2 and the binuclear complex Pd_2(**66**)Cl_4, depending on the ligand, molar ratio, reaction temperature and time (Fig. 33). However, the synthesis of these molecules showed an interesting result. The BOC groups in **67** and **68** can be cleaved sequentially during their reaction with an excess of $PdCl_2$. These findings may be useful for the modification of two identical amino groups in the same molecule with different functional groups and for the direct synthesis of some Pd(II) complexes of amino acid substituted calixarenes from the corresponding N-BOC-protected derivatives without pretreatment.

Kimura and co-workers also looked at π-coordinate calix[4]arene derivatives towards soft metal ions such as Ag(I) and Tl(I) ions using electrospray ionisation mass spectrometry [76]. They found that in the Ag(I) complexes of **73** and **74** the metal ion interacts mainly with the aromatic skeleton (Fig. 34). The ^1H NMR data was not indicative of any significant interaction between the Ag(I) and olefinic moiety of the octenyl groups of **74**, probably because the olefinic moieties are too far from the aromatic skeleton to bind the metal ion cooperatively with the latter π-coordinate moiety. In addition, the NMR spectra of the Tl(I) complexes showed that the metal ion interacts only with the aromatic skeleton in any of the complexes of the calix[4]arene derivatives.

Žinić and co-workers looked at the attachment of one, two or four amino acid groups to the lower rim of a calix[4]arene and their subsequent complexation reactions with alkali metals [77]. The X-ray crystal structure of the $NaClO_4$ complex of the calix[4]arene compound functionalised with four *N*-acetyl-phenylglycine methyl



66 $R_1 = R_2 = \text{L-H}_2\text{N-}\underset{\displaystyle |\atop \text{CH}_2\text{CH}_2\text{-S-CH}_3}{\text{C}}\text{*H-}$

67 $R_1 = R_2 = \text{L-BOC-NH-}\underset{\displaystyle |\atop \text{CH}_2\text{CH}_2\text{-S-CH}_3}{\text{C}}\text{*H-}$

68 $R_1 = R_2 = \text{BOC-NH-CH}_2\text{-}$

69 $R_1 = \text{L-BOC-NH-}\underset{\displaystyle |\atop \text{CH}_2\text{CH}_2\text{-S-CH}_3}{\text{C}}\text{*H-}$

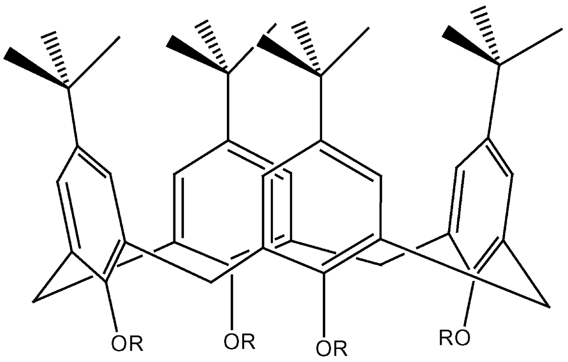
$R_2 = \text{L-NH}_2\text{-}\underset{\displaystyle |\atop \text{CH}_2\text{CH}_2\text{-S-CH}_3}{\text{C}}\text{*H-}$

70 $R_1 = \text{BOC-NH-CH}_2\text{-}$

$R_2 = \text{NH}_2\text{-CH}_2\text{-}$

71 $R_1 = R_2 = \text{NH}_2\text{-CH}_2\text{-}$

Fig. 33. Series of diamino-acid derived calix[4]arenes **66**–**71**.



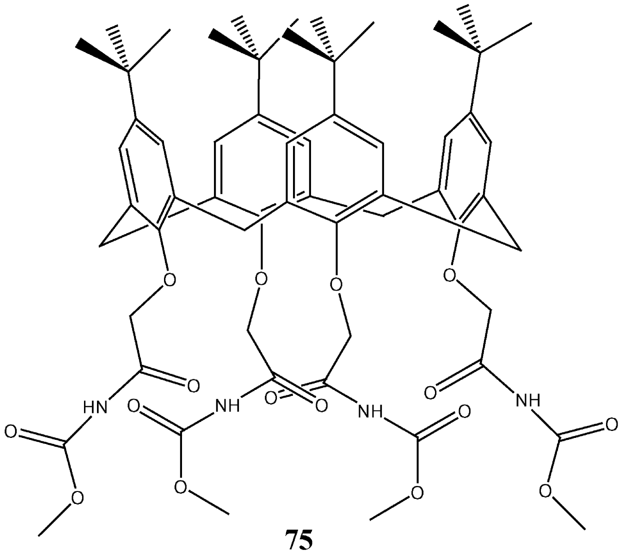
72 -$CH_2CH{=}CH_2$
73 -$(CH_2)_2CH_3$
74 -$(CH_2)_6CH{=}CH_2$

Fig. 34. Structures of calix[4]arenes **72**–**74**.

ester units (**75**) was obtained and showed that the sodium was bound in a regular square antiprism coordination between eight oxygen atoms, four phenolic oxygen and four amide oxygen atoms (Fig. 35). The solution analyses using ^{1}H NMR spectroscopy agreed with these findings.

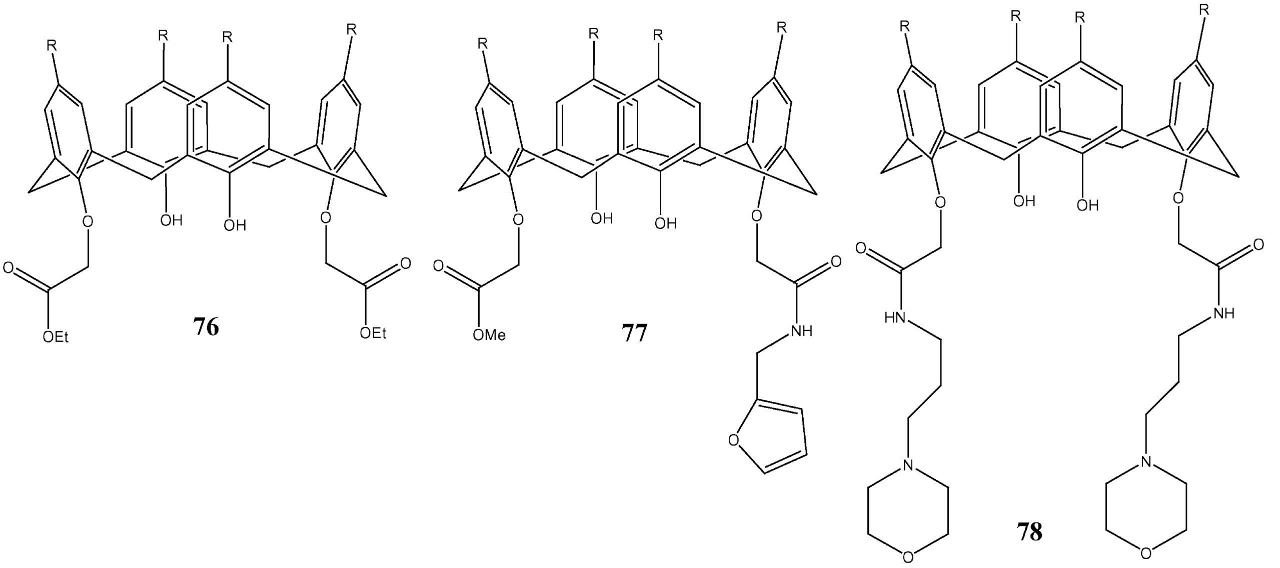
Yilmaz and co-workers have recently reported a study of the complexation of a series of mono and diamide derivatives of calix[4]arenes, which were prepared by previously reported methods, with alkali and alkaline earth cations [78] (Fig. 36). Whilst picrate extraction experiments were used to study the complexation behaviour of the ionophores, the effect of reaction time and steric hindrance of the primary amides on the synthesis of the ionophores was also reported.

Calix[4]arenes with a similar architecture were also studied by Molard and Parrot-Lopez [79]. The binding sites in the molecule studied by this group were based on terpyridyl moieties, as shown in Fig. 37. Such moieties allow multiple complexation sites with a predefined but somewhat flexible geometry so as to allow complexation to proceed accompanied by energy relaxation and hence eliminate too highly sterically constrained stereochemistries. The studies of Ni(II) and Cu(II) complexation by UV/vis spectroscopy show the existence of M_2L-type complexes and allow the determination of stability constants of both, respectively: $\log K_{21} = 13.4$ and 12.8. With $CoCl_2$, there existed an equilibrium between a M_2L and a M_4L type complex where chlorine intervenes in the coordination.



75

Fig. 35. Structure of **75**.



76

77

78

Fig. 36. Structure of mono and diamide calix[4]arenes **77** and **78**.

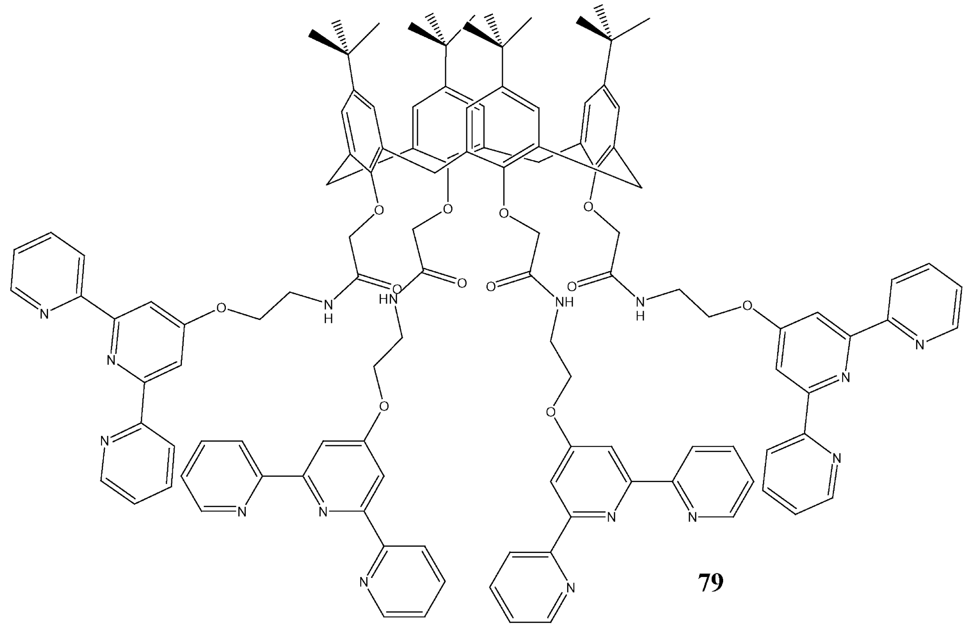
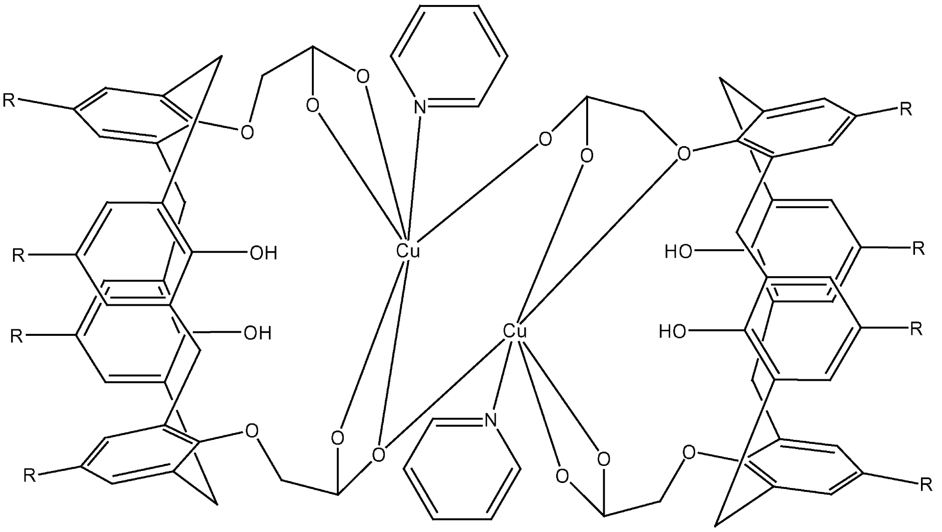
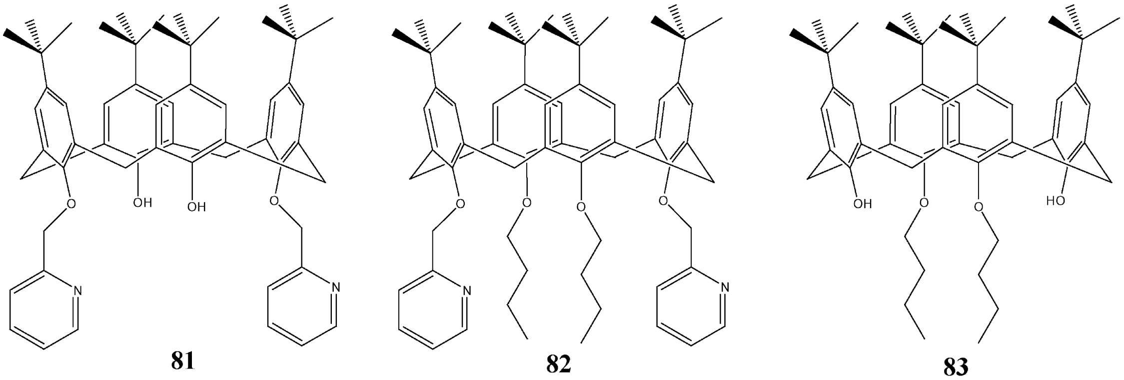


Fig. 37. Structure of terpy substituted calix[4]arene **79**.



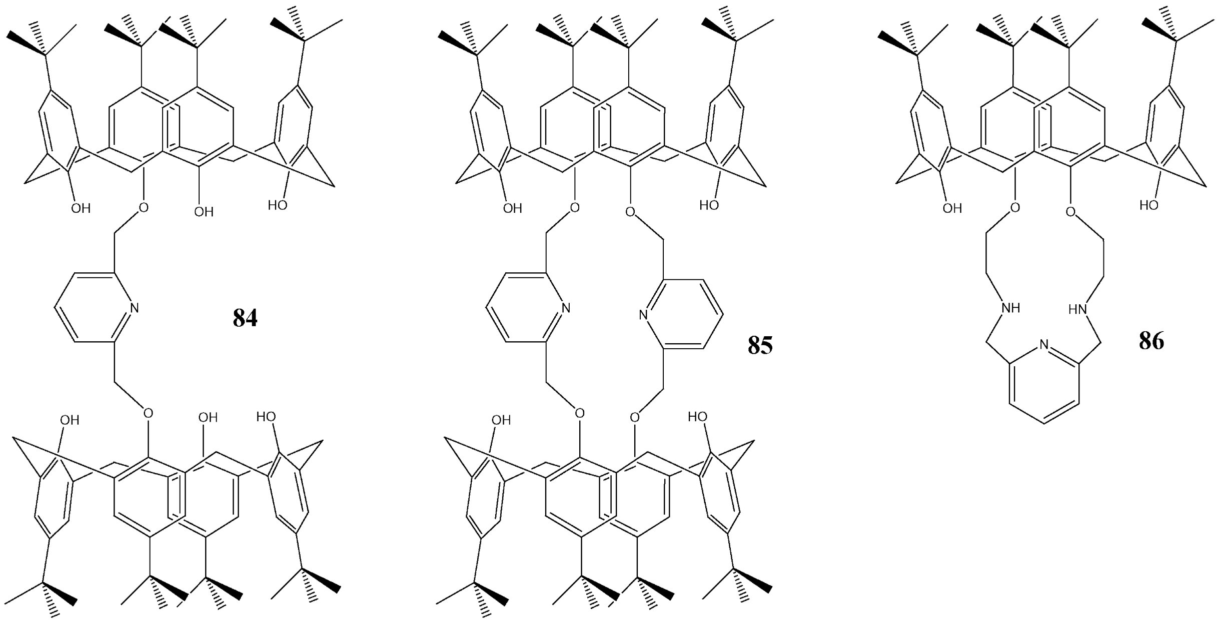
80

Fig. 38. Dinuclear calix[4]arene complex of Cu(II).



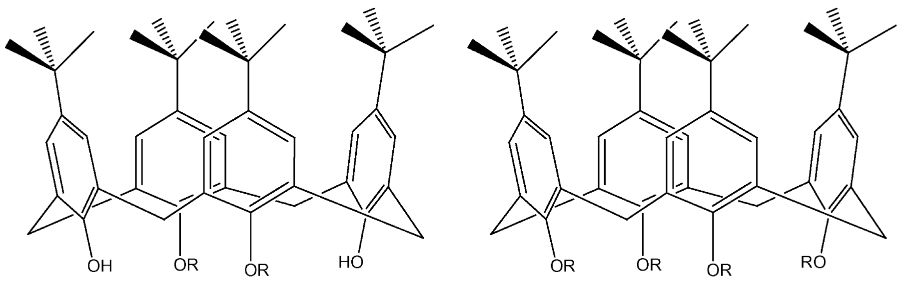
81 **82** **83**

Fig. 39. Structure of dipyridyl functionalised calix[4]arenes **81**–**82** and starting difunctionalised calix[4]arene **83**.



84 **85** **86**

Fig. 40. Structures of **84**–**86**.



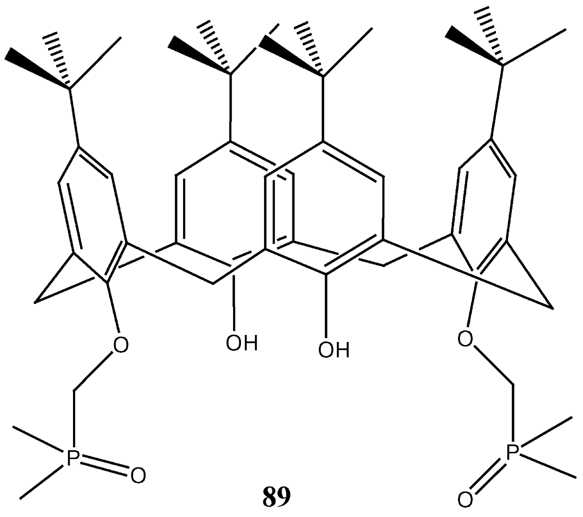
87 **88**

R = $CH_2C_6H_5$

Fig. 41. Alkali metal selective ether functionalised calix[4]arenes **87** and **88**.

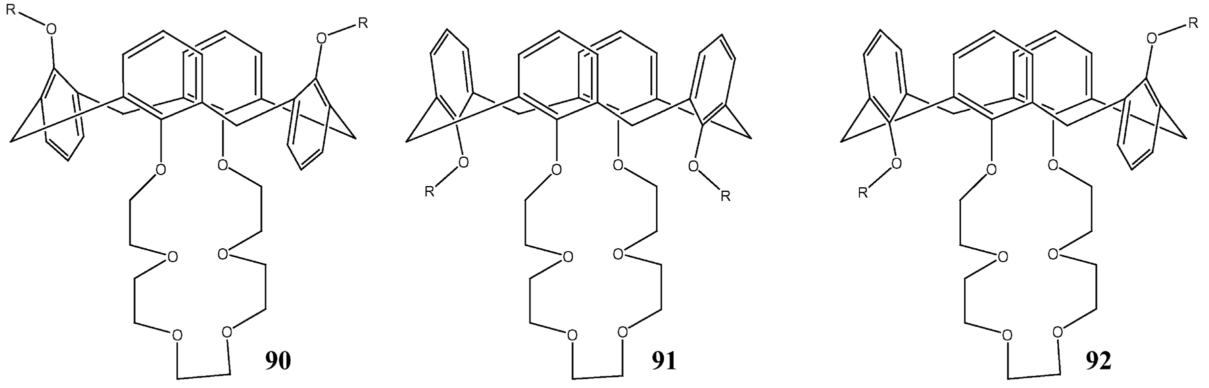
Rao and co-workers reported a series of dinuclear complexes of Mn(II), Fe(III), Co(II), Ni(II) Cu(II) and Zn(II) of the ligand shown in Fig. 38 [80]. These were the first example of dinuclear complexes of calix[4]arene. All of the complexes isolated had pyridine bound to the transition metal cation and were determined to be in an octahedral geometry and dinuclear as well as neutral behaviour. The ligand acts as dinegative in all the cases, and in case of Fe(III) complex it acts as trinegative, implying that the ligand uses one of the lower rim phenolic O^- in the binding. The mass spectra data strongly support the presence of dinuclear complexes. The FTIR spectra in all the cases are indicative of the presence of mono and bidentate as well as bridging nature of the carboxylate group.

A study by McGinley and co-workers reported on the chemical behaviour of metal ions, specifically copper(II) and copper(I) ions, complexed at the lower rim of functionalised calixarenes [81] (Fig. 39). They synthesised two copper(I) dipyridyl-calix[4]arene complexes, one of which had unprotected phenol groups present. Unusually in the presence of air, the copper(I) solutions of both ligands were slow to oxidise to give the corresponding copper(II) complexes. Following the oxidation cycle by both ^1H NMR and ESR spectroscopies indicated that in air, the metal oxidation is slow relative to that of the ligand. In addition ESR studies also suggested the presence of a phenoxy radical in one of the complexes. This



89

Fig. 42. Structure of phosphinoyl derived calix[4]arene **89**.



R =-$CH_2CH_2CHCH_3(CH_2)_3CH(CH_3)_2$, -$CH_2CH(CH_2CH_3)_2$, -$CH_2CH_2CH(CH_3)_2$

Fig. 43. Structures of calix-crowns **90–92**.

same group had earlier reported an unusual retention of the cone conformation in di-substituted calix[4]arenes [82].

Other pyridyl-containing calix[4]arene receptors (**84**, **85** and **86**) have been reported by Marchand et al. [83] (Fig. 40). The complexation properties of these receptors, which adopt the cone conformation, were estimated *via* picrate extraction experiments. The pyridyl containing calix[4]arene-crown-5, **86**, displayed better avidity and selectivity toward extraction of K(I) and Rb(I) picrates *vis-a-vis* the corresponding behaviour of **84** and **85**.

More recent studies on calixarene ether derivatives with alkali metal cations have focussed on di- and tetra-functionalised calixarenes and studied their complexation of alkali metals in methanol–chloroform mixtures (50:50 and 30:70 by volume) [84]. Gharib et al. found that whilst some selectivity was shown by **87** towards the cations, with **87** favouring Cs(I) and Li(I) cations over the other cations, the selectivity shown by **88** was considerably less (Fig. 41). This they attributed to the steric hindrance caused by the four benzyloxy groups located in the molecule.

Bünzli and co-workers have studied a series of phosphorous-containing calixarenes which have proven particularly useful for the extraction of transition metals [85]. Transition metal complexes of calixarenes have been used as models for mimicking biological processes. Bünzli and co-workers investigated the complexation of the phosphinoyl derived calix[4]arene, **89**, shown in Fig. 42, a compound they had previously studied as an extractant for lanthanide ions [86]. Both IR and ^{31}P NMR spectroscopic data show the coordination of phosphoryl groups through strong M(II)–O–P bonds. Magnetochemical measurements and optical spectra point to a tetrahedral arrangement of the ligands around Co(II) (high-spin d7), Ni(II) and Cu(II) ions. In view of the ligand conformation, tetrahedral coordination of the four phosphoryl groups can be ruled out, so that the coordination sphere of the metal ions probably contains either 1–2 water molecules and/or chloride or perchlorate ions. They also investigated the influence of the anion on the complexation of Cu(II) and Zn(II) and found that when the stability constants were determined for both with perchlorate and chloride salts only slight differences were obtained.

Guillon et al. published a paper on similar calix-crown structures, shown in Fig. 43, the structures differing only in the size of the crown ether moiety [87]. Their study focussed on the selective complexation of caesium ions and they found that the calix crowns in the 1,3-alternate conformation was the potent Cs(I) extractant. In addition, they found that a three carbon atom chain seems to be the minimal length required to restrict the flexibility of the calixarene skeleton and to modulate the lipophilicity of the ligands.

Whilst earlier a number of papers identified dual-binding calixarenes, ordinarily the calixarene bound allosterically solvent and cation or anion and cation. Nabeshima and co-workers synthesised and investigated the recognition behaviour of multi-point receptors with binding sites for different metal ions [88]. The calix[4]arenes synthesised are shown in Fig. 44. This group was interested in studying independent and cooperative responses to different kinds of stimuli in molecular devices. They had previously published a study of **93** whereby the host recognises Na(I) ions with the ester moieties, and Ag(I) ions with the bipyridine units to perform complete inhibition on Ag(I) binding with Na(I) ions [89]. They were now interested in investigating the chain length of the podant arms

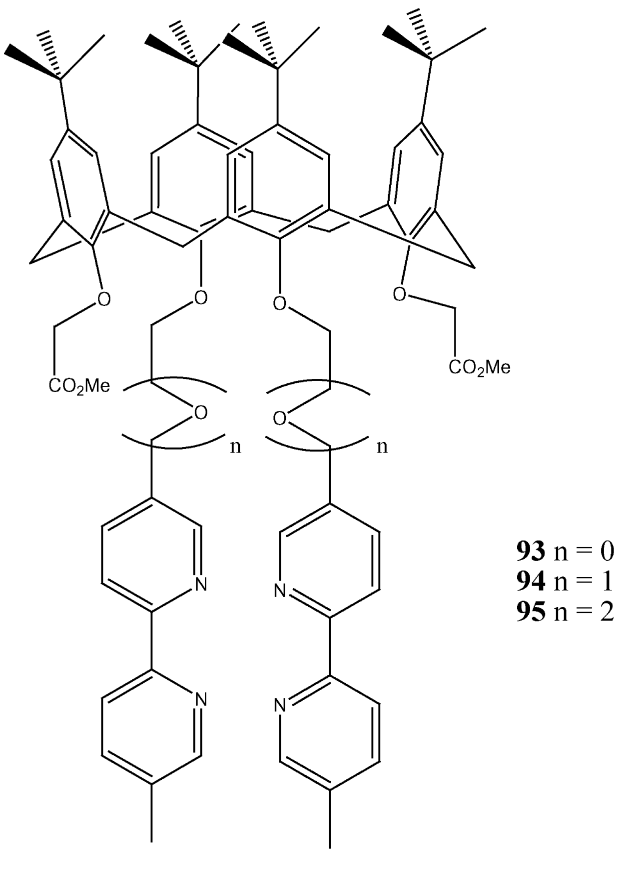


Fig. 44. Structure of multi-point calix[4]arene receptors **93–95**.

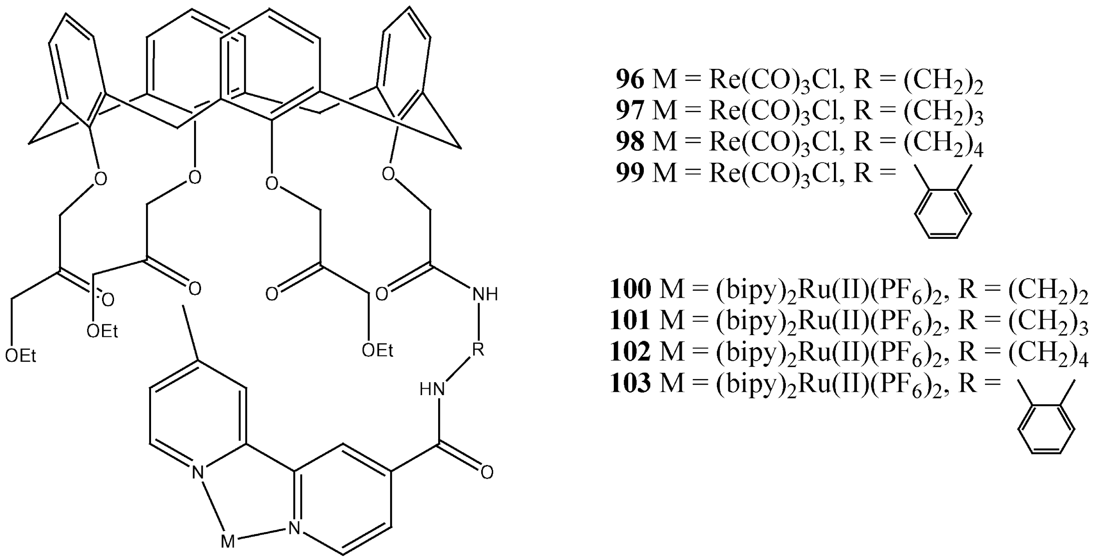


Fig. 45. Series of rhenium and ruthenium complexes of calix[4]arenes, **96**–**103**.

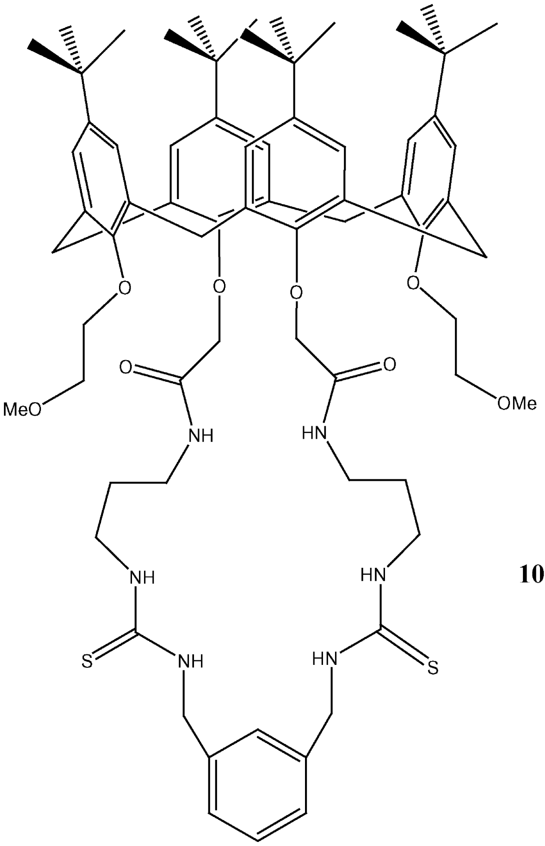
on this cooperative behaviour and thus synthesised the molecules shown above. They found that host **94**, with the shorter spacers, recognises Na(I) and Ag(I) ions cooperatively, and host **95**, with the longer spacers, captures them independently.

Anion recognition by calix[4]arenes is far less widely discussed than cation recognition. Nevertheless, there are a number of reports published in the last number of years. Beer and Hayes published a review in 2003 on transition metal and organometallic anion complexation agents and within this paper a number of calix[4]arene receptors are mentioned [8]. Whilst the majority of these are not covered by the scope of this review as most are pre-2000, one report by Beer and co-workers on the receptors shown in Fig. 45 is relevant to this review [90]. These molecules bind alkali metal (Li(I), Na(I))–halide(Br^-, I^-) ion pair species. ^{1}H NMR titrations indicated that the presence of a lower-rim bound cation greatly increased anion binding, with an increase of up to 60-fold observed with **99**. Halide binding enhancement is greater with the neutral rhenium(I) receptors **96**–**99** than for the charged ruthenium receptors **100**–**103**, which may be due to unfavourable electrostatic effects.

Another study by Kilburn and co-workers in 2003 investigated the anion-binding properties of a calix[4]arene-derived ditopic receptor **104** [91] (Fig. 46). They found that in the absence of Na(I) ions, the receptor binds acetate in preference to diphenylphosphate (as the tetrabutylammonium salts) which these workers attributed to the presence of electrostatic repulsion between the phenoxy groups of the latter and the ether oxygens in the receptor. However, in the presence of Na(I) ions, the selectivity is reversed. They attributed this to the preferential formation of a salt ion pair in free solution.

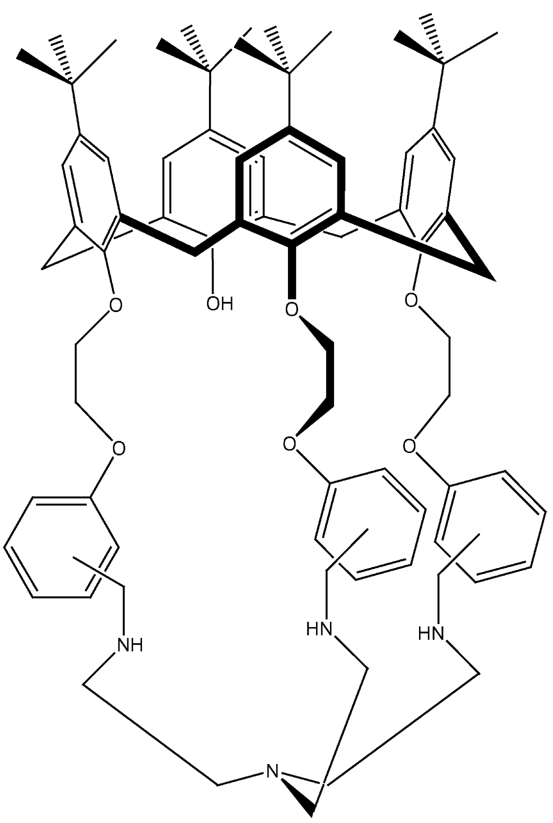
Tuntulani and co-workers have looked at tripodal aza crown ether calix[4]arenes containing both anion and cation binding sites [92,93]. They used derivatives containing either *ortho*- or *para*-substituted benzene rings on the lower rim. They found that both of these derivatives (**105**) were able to complex transition metal ions while the protonated versions (**106**) could be used to complex both cations and anions, with the simple alkali or ammonium cations bound between the oxygen atoms while the anions were contained by the four quaternary nitrogens (Fig. 47). Furthermore, they discovered that the binding ability of the receptor could be controlled by pH, that is, **105** can be converted to **106** by lowering the pH while **106** can become **105** on increasing the pH of the solution.

Casnati et al. have synthesised several di- and tetra-functionalised anion receptors by attaching 2,2,2-trifluoroethanol binding groups at the upper rim of a calix[4]arene, containing either crown ether or amide substituents at the lower rim [94]. They found that these calix[4]arene derivatives behave as ditopic receptors, since they bind cations and anions simultaneously and are capable of extracting ion pairs in organic media. Furthermore, when they used calix[4]arene **107**, a positive allosteric effect was

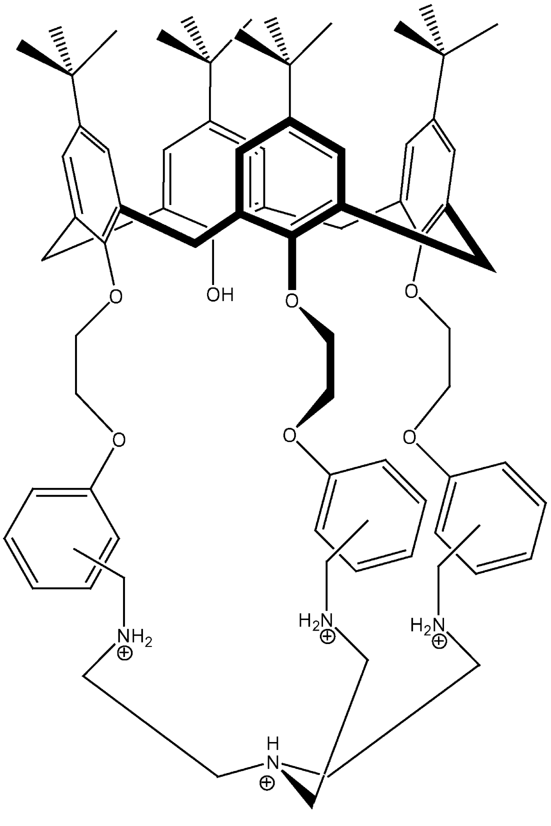


104

Fig. 46. Structure of **104**.



105

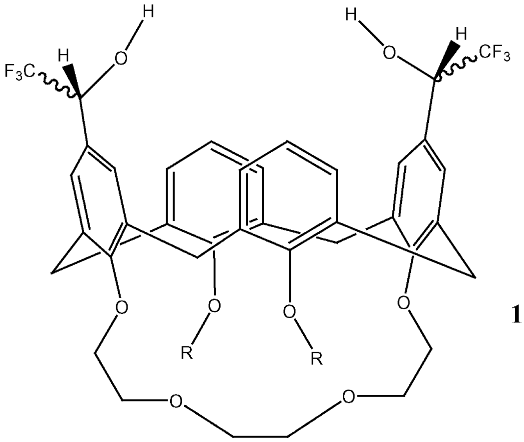


106

Fig. 47. Structure of tripodal azacrown calix[4]arenes **105** and **106**.

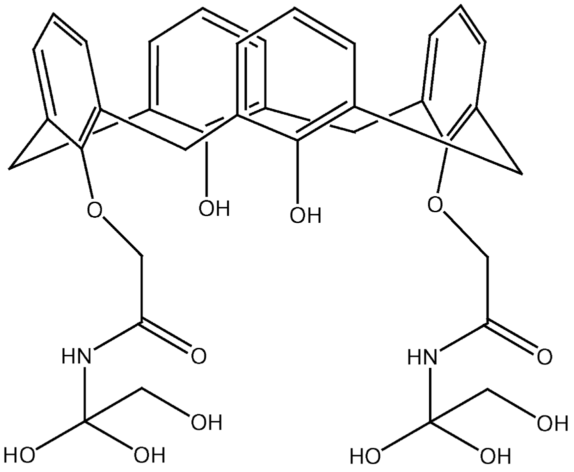
observed, that is, the coordination of sodium metal ion at the lower rim enhanced the binding of an acetate anion at the upper rim (Fig. 48).

De Namor et al. published a study in 2006 on cation/anion recognition by a partially substituted lower rim calix[4]arene hydroxyamide (**108**), shown in Fig. 49 [95]. They used ^{1}H NMR spectroscopy, conductometry, spectrophotometry and calorimetry in dipolar aprotic media to investigate the complexation ability of **108** with a series of cations and anions. These workers found that in studying the complexation of cations (alkaline earth, zinc and lead), a peak in selectivity was found when the standard Gibbs energies of complexation of **108** were plotted against corresponding data for cation hydration and was attributed to the key role played by the desolvation and binding processes in the overall complexation of this receptor and these cations in acetonitrile. In addition ^{1}H NMR studies suggested that this receptor is able to interact with cations through the carbonyl, the phenolic, and the hydroxyl oxygens of the pendant arms and with anions (fluoride, dihydrogen phosphate and pyrophosphate) through hydrogen bond formation involving the NH moieties in acetonitrile and *N*,*N*-dimethylformamide. Their conclusion was that **108** behaves as a ditopic ligand in dipolar aprotic media.



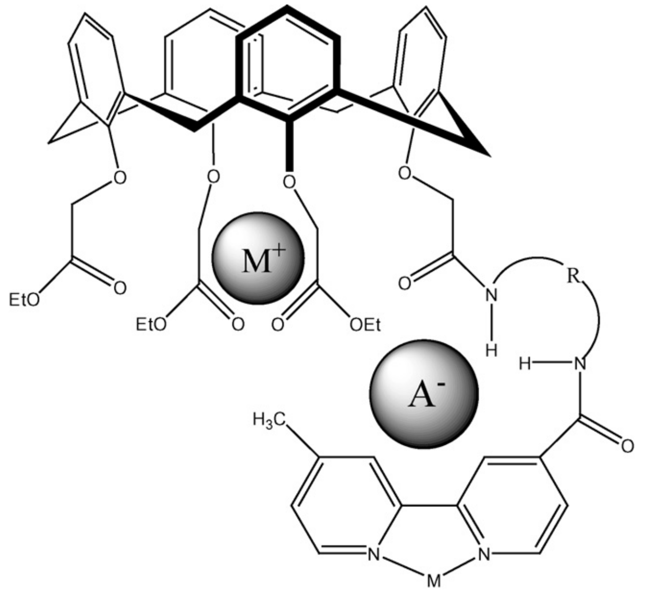
107

Fig. 48. Structure of **107**.



108

Fig. 49. Structure of **108**.



109 M - Re(CO)$_3$Cl, (bipy)$_2$Ru^{2+}(PF$_6^-$)$_2$

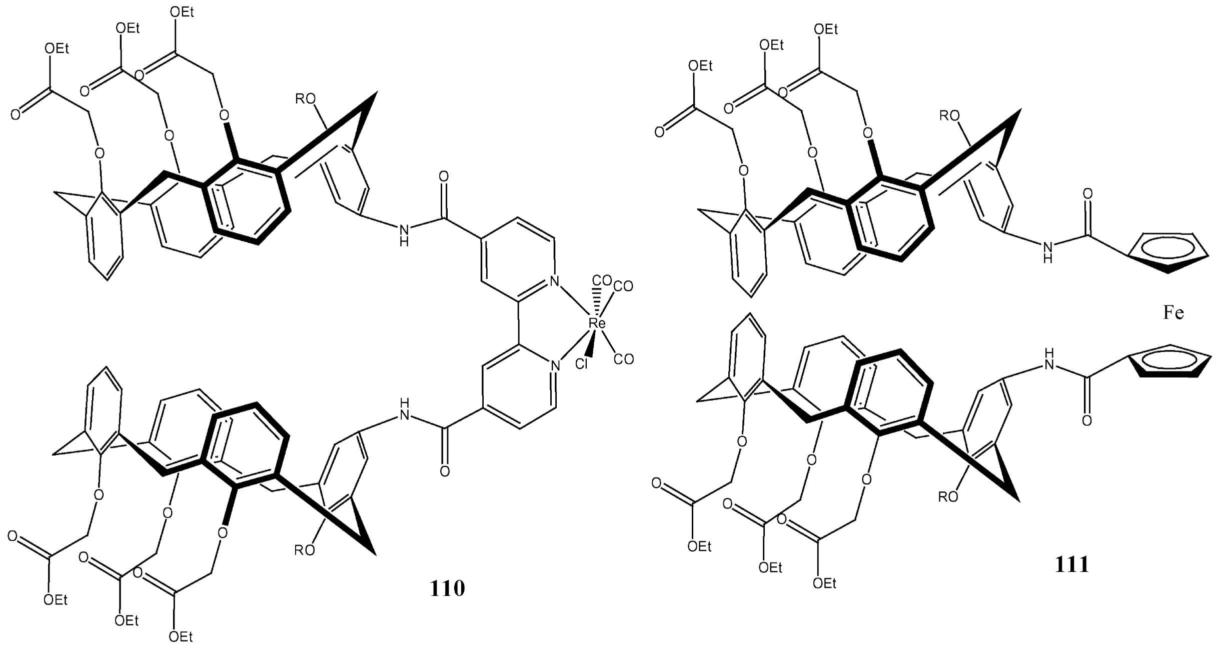
Fig. 50. Structure of heteroditopic rhenium(I) and ruthenium(II) bipyridyl calix[4]arene **109**.

Beer and co-workers have also looked at the use of calix[4]arene derivatives to complex ion pairs [90,96]. In one approach, a series of heteroditopic rhenium(I) and ruthenium(II) bipyridyl calix[4]arene receptors (**109**) were synthesised that simultaneously complex alkali metal cation–anion ion pairs at the lower rim (Fig. 50). They found that the lower rim ester co-bound alkali metal significantly enhanced the strength of bromide and iodide anion binding, with a sixty fold increase being displayed for [Li(**109**)]$^+$ where M = Re(CO)$_3$Cl. They also noted that the greatest enhancement of iodide binding for all the receptors they synthesised was with the co-bound sodium cation which correlates with the known selectivity preference of lower rim tetrasubstituted ethyl esters for the sodium metal cation [97]. They also observed that the degree of halide binding enhancement is considerably larger for the neutral rhenium(I) receptors than for the charged ruthenium(II) receptors which was attributed to unfavourable electrostatic effects.

A slightly different approach to the series of receptors **110** and **111** involved either the complexation of Re(CO)$_3$Cl with the bis-calix[4]arene-2,2’-bipyridyl linked derivative to give the receptors **110** or the condensation of 1,1’-bis(chlorocarbonyl)ferrocene with the mono-amine calix[4]arene synthon to give the receptors **111** [90] (Fig. 51). In both of these receptors, they found that simultaneous cation–anion ion pair binding was observed. In contrast to receptors of type **109**, both **110** and **111** type receptors cooperatively bind iodide anion at the upper rim *via* complexeation of two alkali metal cations at the two lower rims. However, the selectivity and strength of anion binding was shown to depend on the nature of the calix[4]arene bridging group with the ferrocene receptors (**111**) binding much more weakly than the rhenium(I) receptors (**110**).

A number of workers reported the synthesis and characterisation of cationic complexes of new calixarene derivatives. These included Bocheńska et al. who prepared a series of metal ions complexes of the piperidinyl-calix[4]arene derivatives and characterised the complexes by spectral data (IR, UV/vis, ^{1}H NMR, FAB MS), and elemental analysis [98]. They also reported the crystal structures of the ligand and its sodium complex. Deligöz reported the synthesis of the sodium and potassium complexes of two calix[4]arene derivatives, **112** and **113** (Fig. 52) and characterised them in a similar fashion [99].

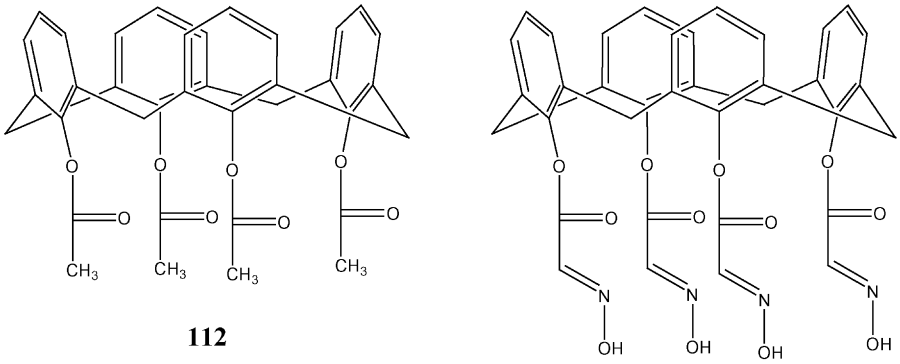
Wong et al. synthesised a series of oligophenylene substituted calix[4]arene-4 derivatives (**114**–**116**) bearing up to three phenylene units [100] (Fig. 53). The complexation reactions with silver(I) ions were substantiated by both ^{1}H NMR spectroscopic and high-resolution ESI- or MALDI-TOF mass spectrometry studies. The X-ray crystal structure of one silver complex containing an oligophenylene substituted calix[4]crown-4 derivative showed that the silver was bound at the lower rim within the crown ether while also binding to the phenolic oxygen atoms of the calix[4]arene itself.



110

111

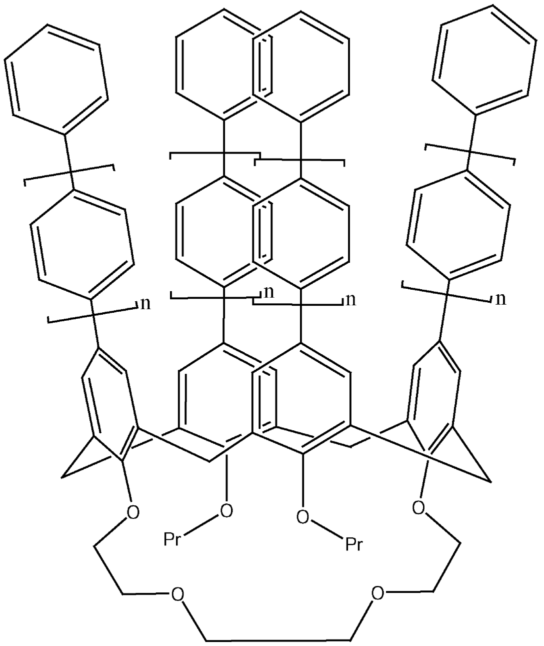
Fig. 51. Structures of **110** and **111**.



112

113

Fig. 52. Structures of **112** and **113**.



114 n = 0
115 n = 1
116 n = 2

Fig. 53. Series of oligophenylene substituted calix[4]crown-4-derivatives **114–116**.

Beer and co-workers have also reported the synthesis of a number of calix[4]arene-based dendrimers, containing up to seven calix[4]arene moieties, as well as an X-ray crystal structure of one dendrimer which contained three calix[4]arenes [101]. The dendrimer **117**, shown in Fig. 54, was used in preliminary lanthanide cation coordination investigations, using UV/vis experiments. These revealed that trimetallic complexes with La(III), Lu(III) and Gd(III) were formed in polar organic solvents, such as methanol, DMSO and acetonitrile.

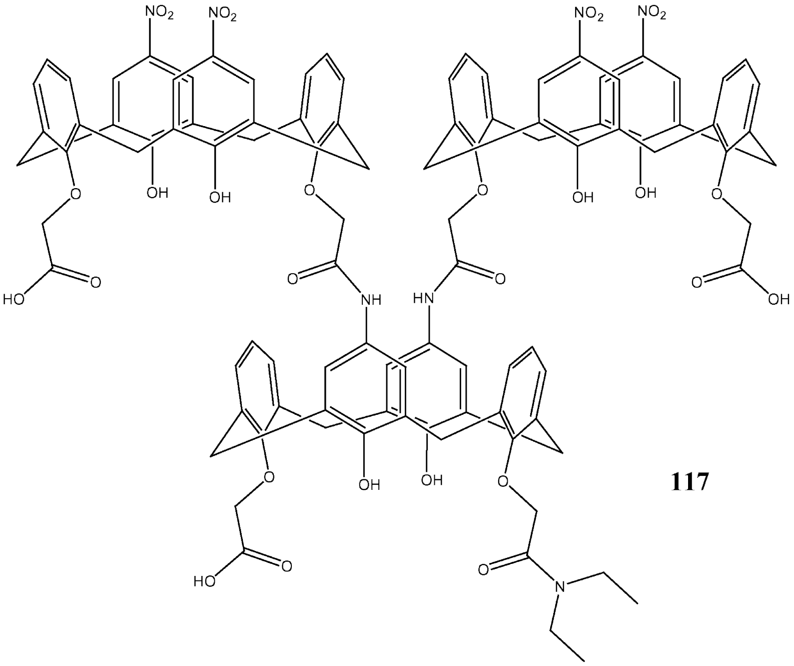
Grüner et al. synthesised calix[4]arene derivatives containing cobalt bis(dicarbollide) anions [102] (Fig. 55). A complete series of mono-, di-, tri- and tetrasubstituted derivatives bearing one to four cluster anions were obtained in the form of their alkali metal salts. The X-ray crystal structures of some of the derivatives revealed that the alkali metal was bound by the ethylene glycol chain and the calix[4]arene oxygen atoms.

5. Electrochemical sensing

Calixarenes have been widely used in the construction of ion-selective electrodes (ISEs) and their use in such devices has been reviewed in a number of papers [103–107]. A great deal of effort has been devoted in recent years to the design and synthesis of new calix[4]arenes to improve and enhance ion selectivities. Since the late 1980s a number of calixarene derivatives containing pendant ether, amide, ketonic and ester groups have been incorporated as neutral carriers into ISEs sensitive to alkali metal ions such as sodium ions [108–115], potassium ions [116,117] and cesium ions [118–120]. Up until 2000, rather fewer papers had dealt with ISEs based on calixarenes for heavy metal ions such as silver ions [121–123], lead ions [124] and thallium ions [125]. In 2000, He and co-workers published work based on selective electrodes for silver based on polymeric membranes containing calix[4]arene derivatives [126], which contained soft donor atoms such as nitrogen and sulphur atoms. They used the ionophores shown in Fig. 56 as other workers had previously found that nitrogen- or sulphur-containing tetrasubstitued calix[4]arenes were subject to interference from Na(I) ions [121,122]. The constructed electrodes, using the ionophores in Fig. 56, showed good selectivity and sensitivity towards Ag(I) ions in the presence of most ions tested but did show a response towards Hg(II) ions. He and co-workers also reported in the same year a related calix[4]arene structure, shown in Fig. 57, which showed good selectivity towards Ag(I) ions but again was subject to interference from Hg(II) ions [127].

In later work, Weng, Zhang and co-workers reported the synthesis of some pyridyl-functionalised calixarenes which had good selectivity towards Ag(I) [128]. Fig. 58 shows the reaction sequence towards isolating the calix[4]arenes studied. The Ag(I) selectivities of compounds **124**, **125** and **127** were determined by the potentiometric selectivity coefficients ($K^{\mathrm{pot}}_{\mathrm{Ag,M}}$) determined for polymer membranes containing these ionophores and which gave good selectivity for Ag(I) ($\log K^{\mathrm{pot}}_{\mathrm{I,M}} \le -3.4$) against most of the interfering cations examined (i.e. Na(I), K(I), NH_4(I), Mg(II), Ca(II), Ni(II), Cu(II), Zn(II) and Pb(II)), except for Hg(II). The interference from Hg(II) in the selective detection of Ag(I) was thought to be due to the existence of mercury in the form of Hg(OH)$^+$ at the pH used for the analyses. Hydrogen bonding between this species and the oxygens of the calix[4]arene close to the coordinating atoms of the pyridyl moieties was a possible reason given for the observed interference from Hg(II) ion.

In a later paper by this same group, they investigated the use of another soft donor atom, specifically selenium, in calix[4]arene ionophores **128–131** and compared their ion-selective behaviour to the compounds previously synthesised [129]. They prepared the series of ionophores shown in Fig. 59 and determined their selectivity towards Ag(I) ions and whilst selectivity for Ag(I) was good in all cases, Hg(II) ions again proved problematic. The performance of the selenium containing ionophores was superior in all cases to the sulphur-based analogues and to the traditional Ag_2S-based electrode. In a further development of this work they prepared novel



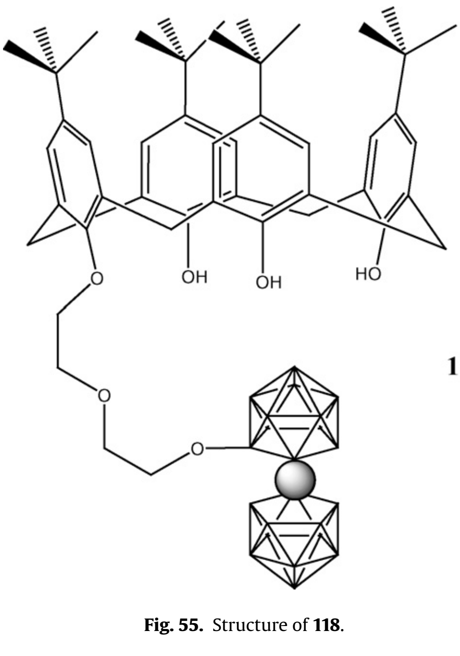
117

Fig. 54. Structure of calix[4]arene-based dendrimer **117**.

calix[4](diseleno)crown ethers **132** and **133**, from the same starting material as shown in Fig. 60 and prepared a Ag(I) selective ISE, which showed good performance characteristics but again suffered from interference from Hg(II) ion [130].

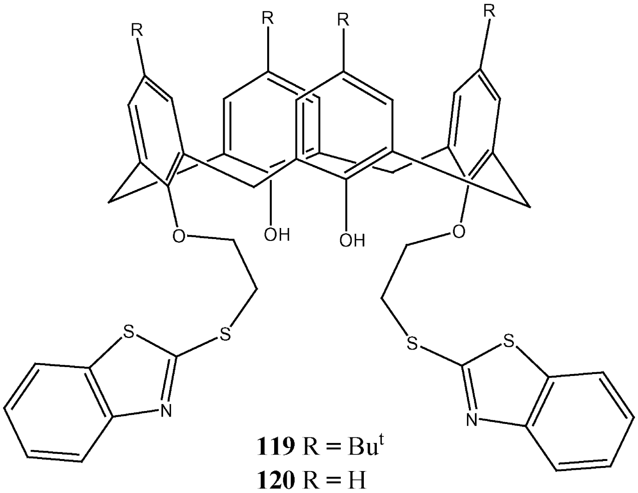
Kimura and co-workers developed a soft metal ISE based on π-coordinate calix[4]arene derivatives [131]. They prepared a series of derivatives containing ω-unsaturated alkenyl or saturated alkyl chains (Fig. 61) and from these prepared a number of PVC membranes containing the relevant ionophores. Complexation of the ionophores with Ag(I) and Tl(I) ions was monitored by ^{1}H NMR spectroscopy and these studies were used to determine the strength of interaction of the ionophores in solution with the respective cation and was correlated with their performance as ISEs. In the case of calixarene derivatives bearing an unsaturated alkenyl group (**134**–**137**), the longer the chains of the substituents are, the more significant the interference from Tl(I) ions was on the responses of the ISEs. However, for calixarene derivatives bearing a saturated alkyl group **138** and **139**, the substituent length does not affect the degree of Tl(I) interference. As reported above, the EMF responses for the conventional Ag(I)-selective electrode based on Ag_2S was subject to considerable interference from Hg(II) ions. The interference by Hg(II) ions was definitely improved in these electrodes based on the π-coordinate neutral carriers examined by this group.

Liu et al. synthesised a series of double-armed calix[4]arene derived amides and investigated their Pb(II) selective electrochemical behaviour [132]. The calix[4]arenes, shown in Fig. 62, were synthesised in good yields and ISEs, containing the above derivatives as neutral ionophores, were constructed in PVC membranes. All of the electrodes fabricated were selective for Pb(II) over a series of heavy metal, alkali metals and alkaline earth metal ions as well



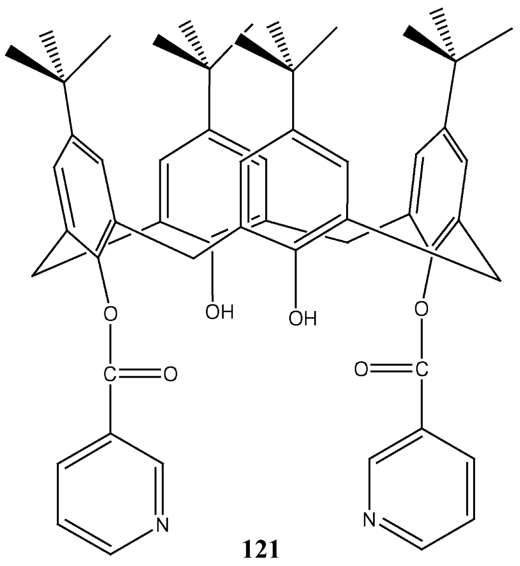
118

Fig. 55. Structure of **118**.



119 R = Bu^t
120 R = H

Fig. 56. Structures of calix[4] derivatives **119** and **120**.



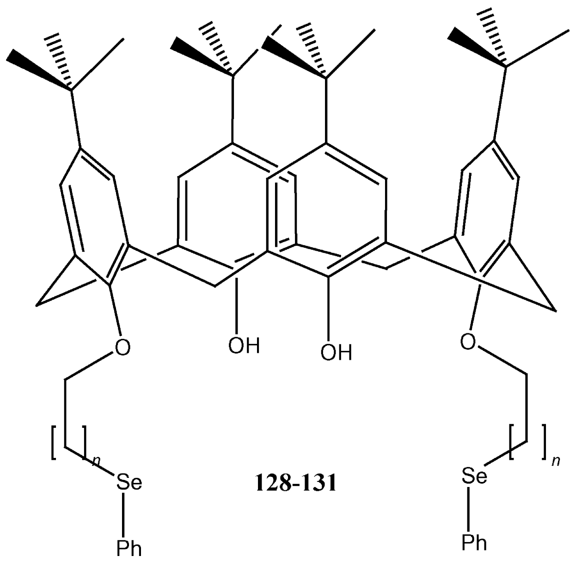
121

Fig. 57. Ag(I) selective calix[4]arene derivative **121**.

as ammonium ions. These workers concluded that the properties of Nernstian responses and the Pb(II) selectivity of the ISEs based on **142**–**148**, was because of the ability of these ionophores to discriminate various cations by the involvement of differently substituted side-arm functions at the lower rim of the calix[4]arenes.

This group has also published a series of papers on plasticised PVC membrane electrodes based on calix[4]arene derivatives with functional heterocyclic groups, such as Ag(I)-ISE [126,133–135], Hg(II)-ISE [136] and Pb(II)-ISE [137]. In 2004, He and co-workers, in a further development of this work, synthesised a new solid-state silver ISE based again on a tweezers-type calixarene derivative functionalised with 2-mercapto-4-methyl-6-hydroxyl-purimidine to give **149** shown in Fig. 63 [138]. They reported a new method for the preparation of an ISE which was composed of a PVC membrane containing the calixarene derivative as ionophore coated on a glassy carbon base electrode. Whilst the ISE had good response properties and performance, and could be applied for detecting silver ion of sub-micromolar level, the connection between PVC membrane and GCE was less compact, and so the overall stability of the ISE was limited over 20 days.

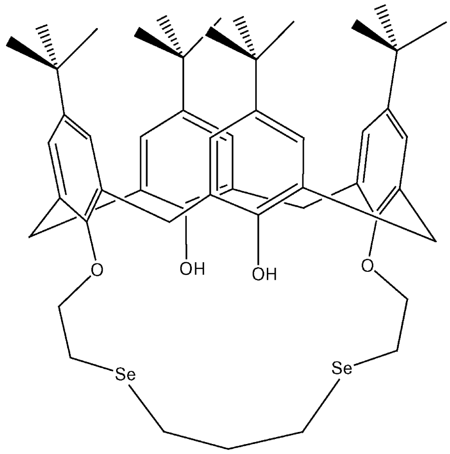
He, Chen and co-workers have more recently reported a series of lead selective PVC electrodes based on tweezers-like double-armed calix[4]arene amides **150**–**156** (Fig. 64) as ionophores, which exhibit excellent potential response and significantly higher selectivity for Pb(II) over alkali, alkaline earth and several transition metal ions [139]. They compared the properties of their ISEs to a number of previously reported lead selective electrodes, including some commercially available electrodes and found that the ISE based on **152** had the widest linear range of the electrodes tested and the electrode properties such as slope, response time,



128-131

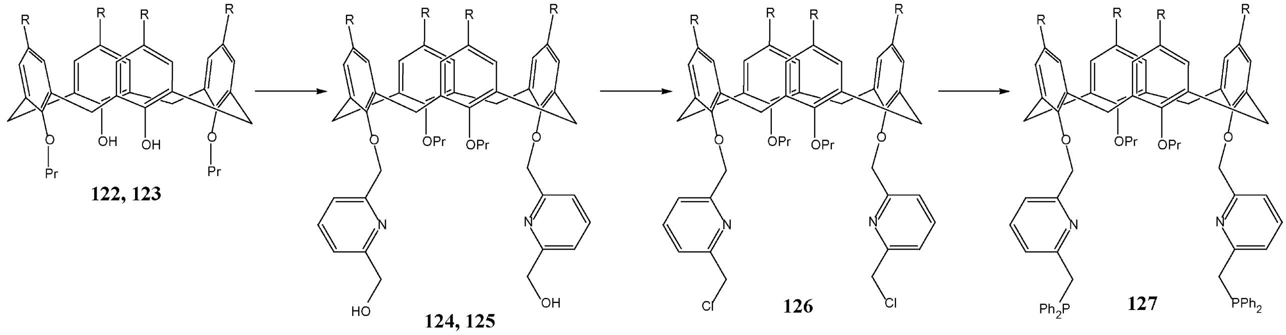
128 : n = 1; **129** : n = 2;
130 : n = 3; **131** : n = 5

Fig. 59. Series of calix[4]arene derivatives, **128**–**131**, investigated in Ag(I) selective ISE's.



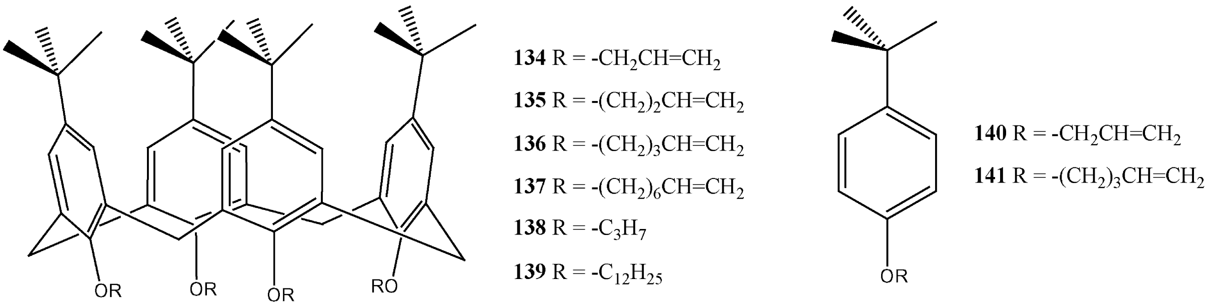
132 R = H
133 R = ^{t}Bu

Fig. 60. Structures of calix[4]crowns **132** and **133**.



122, 123 **124, 125** **126** **127**

Fig. 58. Reaction sequence towards isolating calix[4]arenes **122**–**127**.



134 R = $-CH_2CH{=}CH_2$
135 R = $-(CH_2)_2CH{=}CH_2$
136 R = $-(CH_2)_3CH{=}CH_2$
137 R = $-(CH_2)_6CH{=}CH_2$
138 R = $-C_3H_7$
139 R = $-C_{12}H_{25}$
140 R = $-CH_2CH{=}CH_2$
141 R = $-(CH_2)_3CH{=}CH_2$

Fig. 61. Series of calix[4]arenes **134**–**141** studied by Kimura et al. [131].

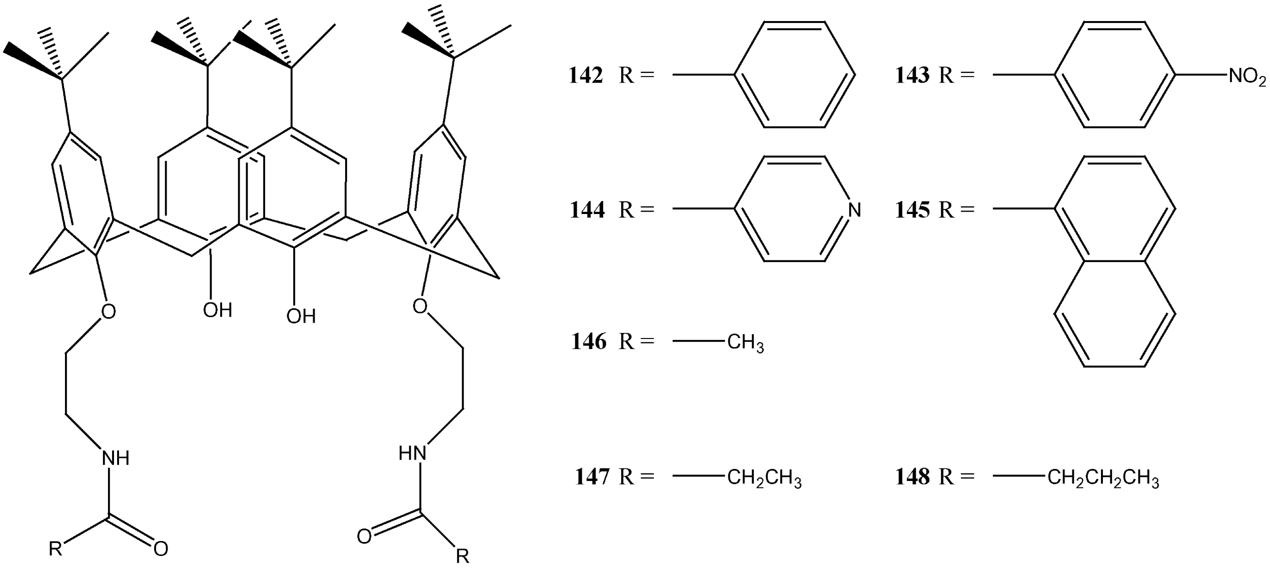
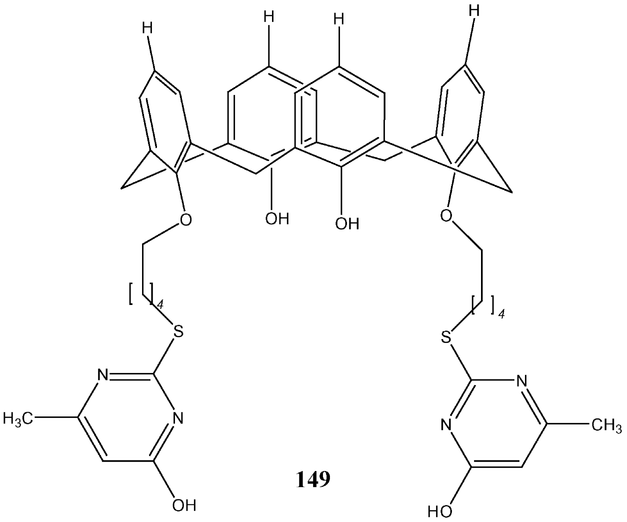


Fig. 62. Series of double-armed calix[4]arenes **142**–**148**.

detection limit, etc. compared favourably with those reported by others.

Matt and co-workers also investigated the use of a lead-selective electrode based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis-(diphenylphosphinoyl-methoxy)calix[4]arene (**157**) [140] (Fig. 65). The electrode prepared showed selectivity over some metal ions but was susceptible to interference from a number of ions including Th(IV) and Sm(III). They later published a paper on the use of this same compound as a thorium sensor [141].



149

Fig. 63. Structure of Ag(I) selective calix[4]arene **149**.

Mahajan et al. developed silver ion-selective poly(vinylchloride) (PVC) matrix membrane electrodes employing Schiff base *p-tert*-butyl calix[4]arene derivatives [142]. The calixarenes shown in Fig. 66 were used as neutral carriers in the development of ISEs whereby the N and O atoms act as donor atoms and co-ordinate effectively with silver ions. These sensors could measure silver ions in the concentration range between 1×10^{-5} and 1×10^{-1} M even in the presence of other metal ions such as Na(I), K(I), NH_4(I), Mg(II), Ba(II), Ca(II), Ni(II), Cu(II), Co(II), Pb(II), Hg(II), Cd(II) or Zn(II) at concentrations as high as 1×10^{-2} M.

Another PVC membrane electrode for silver ion was developed by Ganjali et al. which was based on a new cone shaped calix[4]arene as membrane carrier [143]. Whilst many of the Ag(I) ISE's developed contain donor sulphur atoms, this group argued that the interaction between sulphur atoms and Ag(I) ion is much stronger than that of ion-dipoles present between a metal ion and oxygen atoms. As a result metal–ion exchange equilibria are often slow in the membrane interface that in turn means that thia compound-based ion sensors have slow response times and relatively poor sensitivity. An Ag(I) ion, as a soft acid, can interact with a π-coordinate group and this interaction is quite selective and relatively weak. These workers developed a new calix[4]arene (Fig. 67) containing a π-coordinate group in the construction of a PVC membrane Ag(I) ion-selective electrode for sensitive and selective determination of silver ions in different samples. The idea

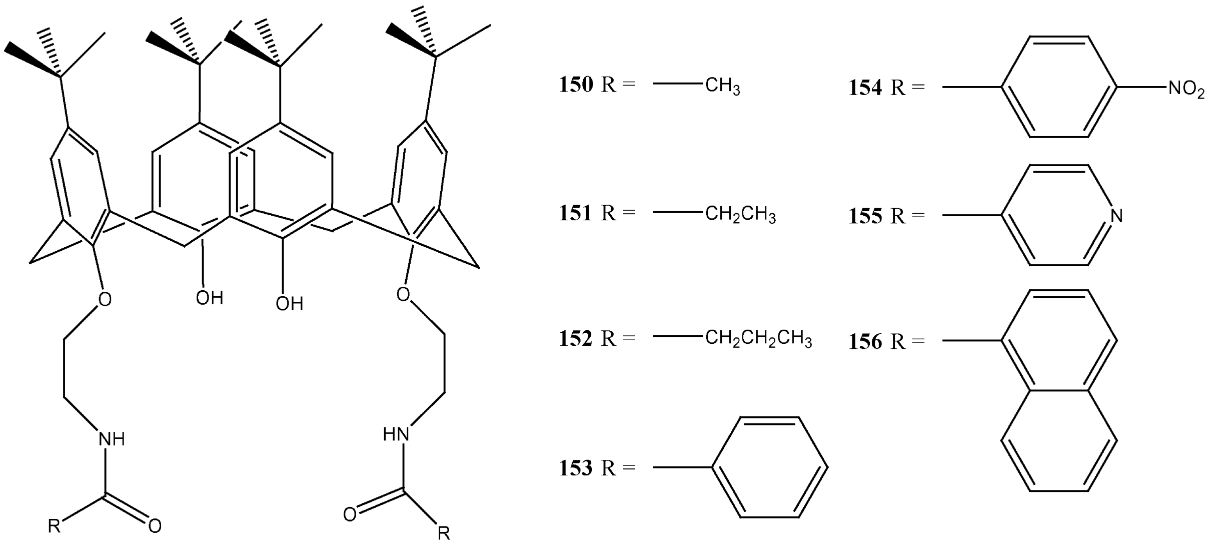
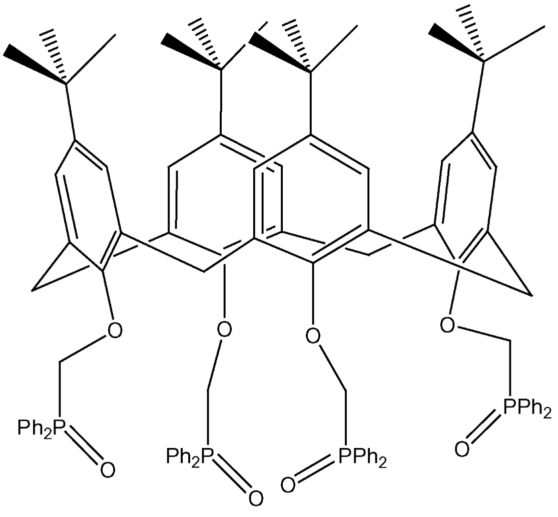


Fig. 64. Structures of calix[4]arenes **150–156**.

was similar to that used by Kimura and co-workers a year earlier [131] but the calix[4]arene derivative chosen was quite different. The analytical characteristics of the silver sensor were comparable to those developed by the groups of He and co-workers, showing a Nernstian response for Ag(I) over a wide concentration range (1×10^{-1}–8×10^{-6} M) and a limit of detection of 5×10^{-6} M [139].

Whilst many of the papers published over the last 7 years on the electrochemistry of calix[4]arenes have dealt with the development of electrochemical sensors, a numbers of papers have been concerned with the electrogeneration of redox active species. In particular, amongst the functionalised calixarenes, the calixquinones are of particular interest because of their potential use as redox systems. Earlier work by Morita et al. [144,145] and Gutsche and co-workers [146,147] had shown that chemical oxidation of calixarenes that contained unsubstituted phenol rings at the lower rim resulted in the formation of calix[4]arene-mono-, di-, tri- and tetra-quinones, the actual product depending on the number of free phenolic rings in the calixarene. Louati and co-workers in 2000 published a paper reporting the first electrochemical oxidation of calixarene diamide **162** leading to diquinone **163** in a final yield of 50% after column chromatography of bulk electrolysis products [148] (Fig. 68). The oxidation was shown to proceed by two distinct two-electron steps, each of them involving chemical transformations. Preliminary results indicated that **162** was suitable for the *in situ* electrochemical detection of alkali cations.



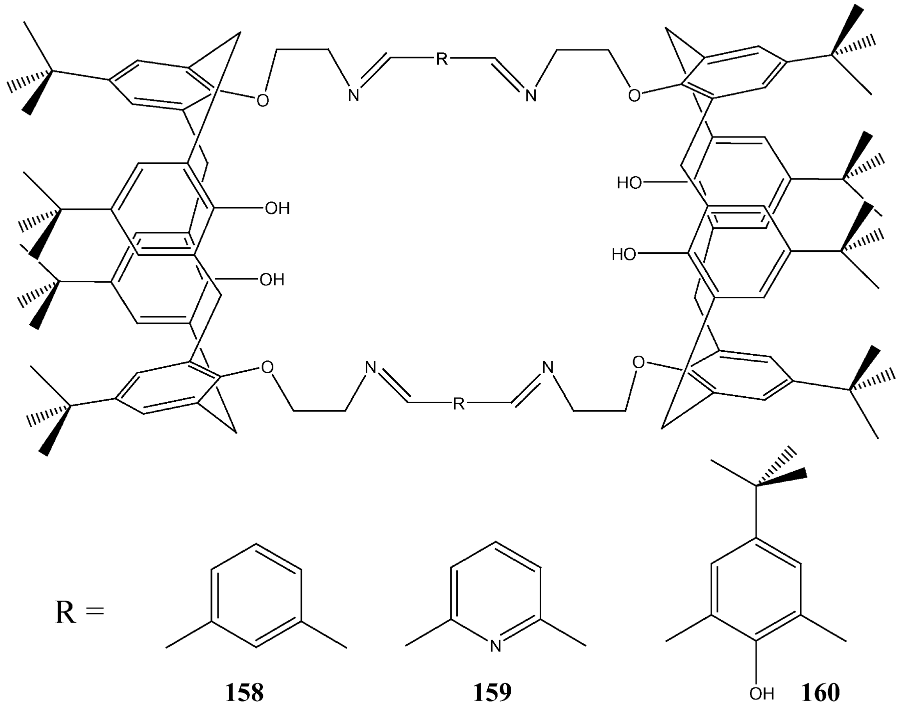
157

Fig. 65. Structure of **157**.

These same workers prepared a related ligand, a calix[4]arenediquinone, **165** shown in Fig. 69, which was formed by electrochemical oxidation of **164** [149]. They concluded that **165** was formed *via* nucleophillic attack of residual water on anodically generated diphenoxylium cations. This species too showed potential for electrochemical detection of Ag(I) ion.

Kim, Chang and co-workers reported a voltammetric-based redox-active monolayer of a novel calix[4]arene which recognised redox-inactive ionic species [150]. They reported that a calix[4]arene–disulphide–diquinone (**166**), which was not only redox-active but also highly selective for Ba(II) ions, spontaneously formed a stable and dense monolayer film on a gold surface (Fig. 70). The modified electrode did not suffer any significant interference by any alkali metal ions or Mg(II) ions. Only in large excess (100- and 500-fold concentrations) of Sr(II) and Ca(II) ions, respectively, was a voltammetric response as large as that due to the Ba(II) ion recorded. In addition, the modified electrode was found to be stable, durable, and reusable.

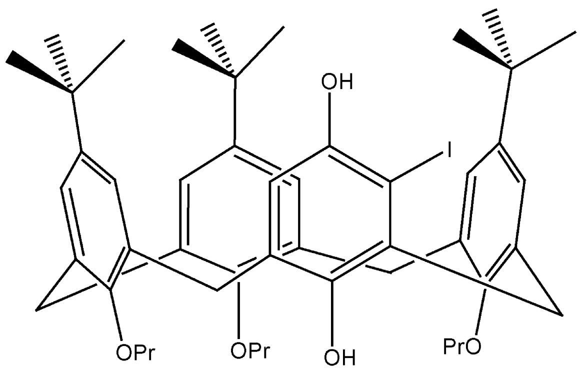
Jeon, Nam and co-workers investigated the use of a series of lipophilic triesters of calix[4]arene and their corresponding calix[4]quinones as PVC-based sodium ISEs [151]. They had previously reported the synthesis of these compounds [152]. In studying the electrochemical behaviour of the five calix[4]arenes shown in Fig. 71, they determined that the polymeric electrodes combined with the calix[4]arene triesters which have *para t*-butyl substituents had superior characteristics to those fabricated using the calix[4]arenes with no upper-rim substituents. In addition, a PVC polymeric electrode based on calix[4]arene triester **167** shows the best detection limit and selectivity coefficient in pH 7.2 buffer solutions, and a linear response in Na(I) concentrations of $1 \times 10^{-3.5}$–1×10^{-1} M compared with the other electrodes prepared in this work. The sodium selectivities were found to be dependent on the nature of the ionophore as well as the plasticizer used in the fabrication of the membrane electrodes.



158 **159** **160**

Fig. 66. Series of calix[4]arenes, **158**–**160**, used as carriers in Ag(I) selective ISE's.

In 2005, Tuntulani and co-workers discussed the use of calix[4]quinones, derived from double calix[4]arenes, in the determination of alkali metal ions [153]. They synthesised the compounds **172**–**174** shown in Fig. 72, and initially determined their complexation behaviour using ^{1}H NMR studies. They showed that receptors **172**–**174** form complexes with various alkali metal ions with receptor **172** selectively binding Na(I) ions while compound **173** prefers K(I) and Cs(I) ions. Interestingly, they showed by NMR spectroscopy that the dimethoxycalix[4]arene unit in **174** retains its cone conformation upon complexing K(I) ions and turns to mixed conformations upon binding Li(I) and Na(I) ions. Receptors **173** and **174** showed significant changes in cyclic and square wave voltammetry in the presence of alkali metal ions and that the shifts in voltammograms upon complexation were found to depend on the polarising abilities of metal ions. Most importantly, receptor **174** exhibited electrochemical switchable binding toward Na(I) and K(I) ions in which the reduced form of **174** forms more stable complexes with the metal ions.



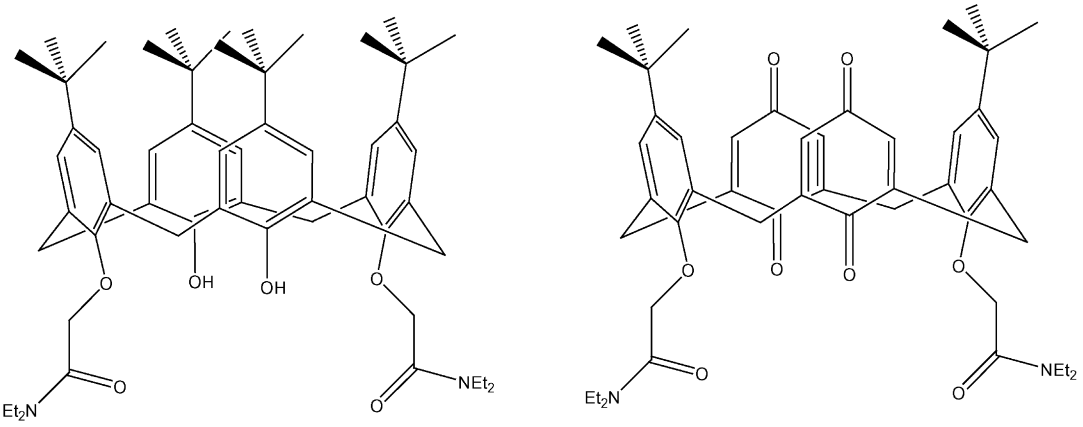
161

Fig. 67. Structure of **161**.

Determination of mercury(II) in aqueous media is of interest owing to the growing awareness of environmental pollution and toxicity. He and co-workers investigated the use of a novel calix[4]arene derivative containing a benzothiazole group which was coated on glassy carbon electrode (GCE) and used for the determination of aqueous Hg(II) ion [154]. They designed and synthesised a novel derivative that contained (benzothiazolyl)thioalkoxy and quinone units on the lower rim of the calix[4]arene (**175**), and investigated the hitherto unknown selective voltammetric behaviour (Fig. 73). They found that the CAL-GCE recognises selectively Hg(II) ion in aqueous solution by square wave voltammetry and by careful control of experimental conditions it was possible to limit the interference of other cations in solution.

Diamond and co-workers have also investigated the use of potentiometric techniques for the determination of soft metals using calix[4]arenes with nitrile functionality [155,156]. A series of known and novel calix[4]arenes derivatives were prepared as shown in Fig. 74. It was shown that **176**, **177** and **178** had strong selectivities towards silver(I) and mercury(II) over other cations. In an additional facet of this study, it was found that structural modification of the host ionophore had a more dramatic effect on selectivity patterns observed than changing other ISE membrane components like membrane plasticizer (affecting polarity). More importantly, given the reported interference of Hg(II) on other silver-selective ISEs, these workers also found that the positioning of electron-withdrawing groups and delocalising aromaticity proximal to the coordinating nitriles (**179** and **180**) led to a dramatic suppression of the Hg(II) response observed before and a corresponding Ag(I) selectivity.

Bocheńska et al. prepared a series of *p-tert*-butylcalix[4]arene-crown-6 derivatives and determined their ability to complex alkali, alkaline earth and some "softer" cations by using these compounds as ionophores in ISEs [157]. These workers determined the potentiometric selectivity coefficients and the complex stability constants in the membrane between these ionophores and the cations tested. They set out to find a correlation between the size of the substituents at the distal 2,4-positions of 1,3-



162 **163**

Fig. 68. Structures of **162** and **163**.

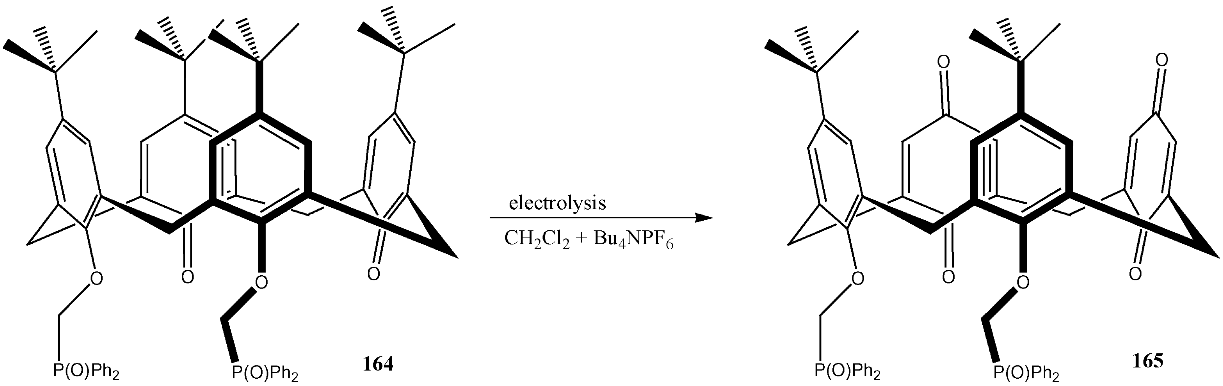


Fig. 69. Reactions conditions for the preparation of **165** form **164**.

substituted calix[4]crowns-6 (see Fig. 75) and the complexing ability of the compounds. What they found was that the *p-tert*-butylcalix[4]crowns-6 display selectivities depended on the nature of the 1,3-substituents and on the conformation, but that the length of alkyl substituents does not significantly influence the overall selectivity behaviour. The ionophores in the cone conformation are most selective for sodium ions whereas the partial cone conformations were selective for cesium ions.

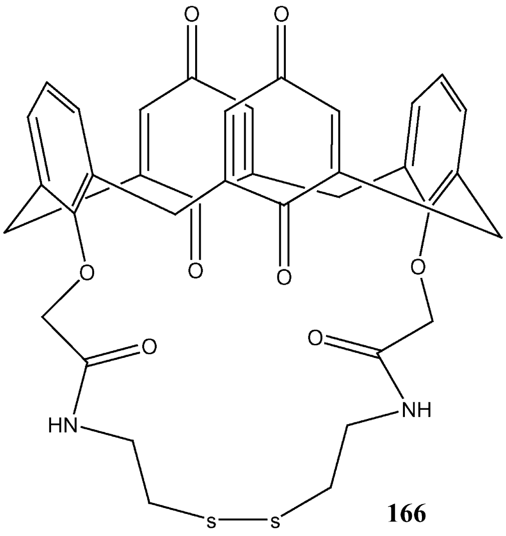
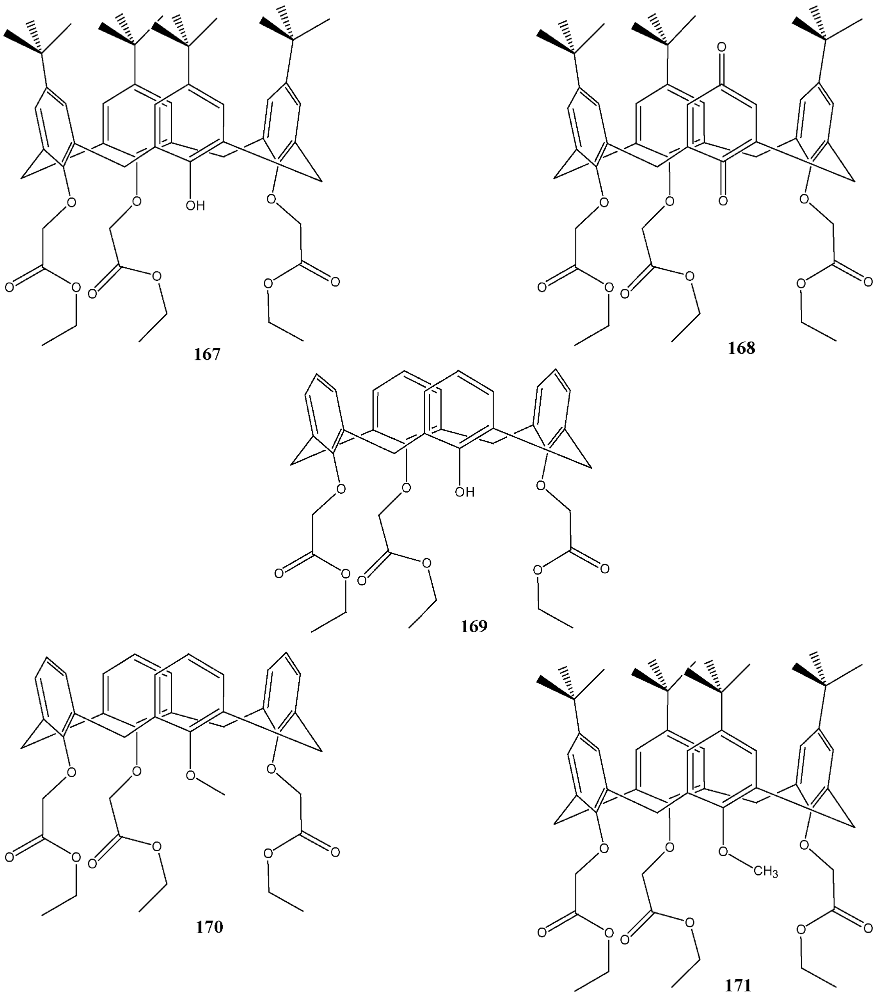


Fig. 70. Structure of **166**.

Bocheńska et al. investigated the use of calix[4]arene derivatives functionalised at the narrow rim by four arms with (dialkoxyphosphoryl)alkyl groups (**189** and **190**) [158] (Fig. 76). They behaved as a Ca(II)-selective ionophore in PVC-membrane electrodes (Ca-ISE) which had similar behaviour to an earlier ISE developed with a related derivative (**191**) [159]. ISEs were constructed using the novel compounds **189** and **190** as neutral ionophores and electrode membranes with three different plasticisers were made: bisbutylhexylsebacate (BEHS), *o*-nitrophenyloctylether (NPOE) and bis(butyl-pentyl)adipate BBPA. They studied the complexation behaviour of compounds **189** and **190** toward alkali metal ions, alkaline earth cations, Ni(II), Cu(II), Zn(II), Cd(II) and tetramethylammonium (TMAC) ions. As had been previously found for compound **191** [159], both compounds **189** and **190** are highly calcium selective, irrespective of the used plasticiser. However, the membranes plasticised with NPOE show the best properties. The group also prepared complexes of **189** and **190** with a number of cations and characterised these complexes by spectral data.

A molecular modelling study in 2000 used Monte Carlo conformational studies in conjunction with the Merck Molecular Force field, using *Spartan* SGI Version 5.0.1, to determine if molecular modelling could offer any insight into the reasons for the particular selectivity of a range of calix[4]arene ionophores [160] (Fig. 77). Diamond and co-workers concentrated their study on the ester and phosphine oxide derivatives of calix[4]arenes which had proven



167

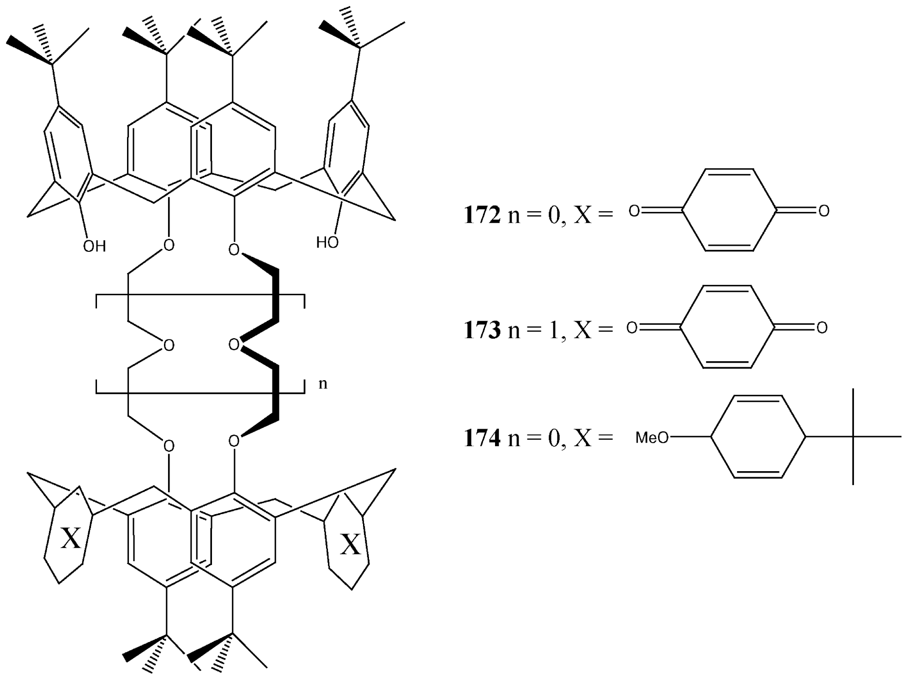
168

169

170

171

Fig. 71. Series of calix[4]arenes, **167–171** studied by Jeon et al. [151].

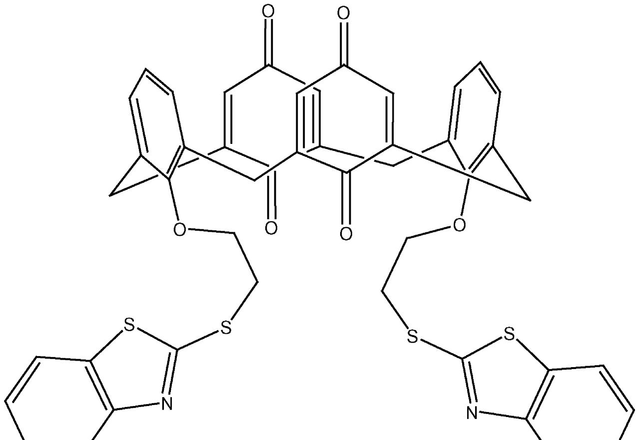


172 n = 0, X =

173 n = 1, X =

174 n = 0, X =

Fig. 72. Structures of double calix[4]arenes **172–174**.



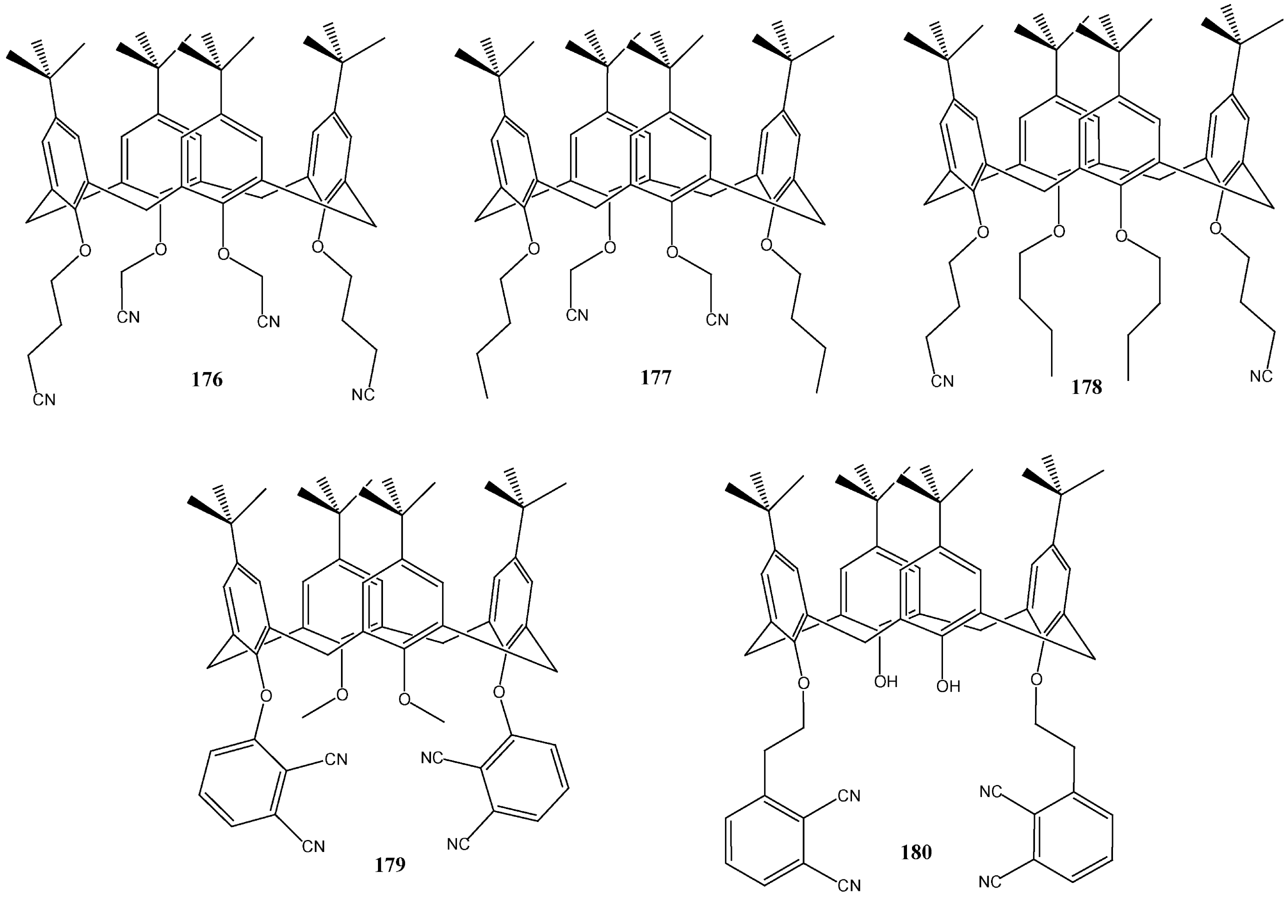
175

Fig. 73. Structure of **175**.

applications as ISEs. Their main conclusion was that the selectivity of the ethyldiphenylphosphine oxide derivatised calixarenes towards Ca(II) ions lies in a unique eightfold coordinate complex that involves close interaction of all four phenoxy and four phosphine oxide oxygen atoms with the Ca(II) ion. This is not possible with the analogous methyldiphenylphosphine oxide derivatised calixarenes as the closeness of the phenoxy oxygen atoms and the phosphine oxide oxygen atoms enables a number of ions to form stable eight coordinate complexes.

Pailleret and Arrigan investigated the electrochemical oxidation of tetraethyl ester *p-tert*-butyl calix[4]arene (**194**) in acetonitrile solution at a platinum electrode, an ionophore whose binding properties towards alkali metals are well known but which has no overt electrochemical signalling group [161] (Fig. 78). They found that the oxidation occurred in a number of processes, with the lowest process at a peak potential of 1.10 V. This was attributed to the one-electron oxidation of the aryl ether functionality present in the calixarene and so should provide a route to the electrochemical detection of calixarenes in nonaqueous mixtures. They found that unsurprisingly the oxidation behaviour was dependent on the presence of alkali metal cations in solution and that the shifts in the oxidation potentials observed were in good agreement with the order of selectivity for the alkali metal cations.

One unusual study published by Shao and co-workers in 2003 looked at the electrochemical recognition of alkali metal ions at the micro-water 1,2-dichloroethane interface using a calix[4]arene derivative [162]. The first example of using a supramolecule as a host (an ionophore) at the interface between two immiscible electrolyte solutions (ITIES) was described by Koryta in 1979 [163]. He used dibenzo-18-crown-6 (DB18C6) as an ionophore to facilitate the transfer of K(I) across the water/nitrobenzene interface. In that system the complexation between DB18C6 in the organic phase and K(I) ion in the aqueous phase makes the transfer Gibbs energy of the latter across the ITIES much lower and the transfer of K(I) across the water/nitrobenzene interface was facilitated. This facilitated ion transfer (FIT) phenomenon is the basis of electrochemical recognition at ITIES. Shao and co-workers investigated the calix[4]arene derivative tetraethyl ester *p-tert*-butyl calix[4]arene, (**195**) as a host



176 **177** **178** **179** **180**

Fig. 74. Nitrile functionalised calix[4]arenes, **176–180**, studied by Diamond et al. [155,156].

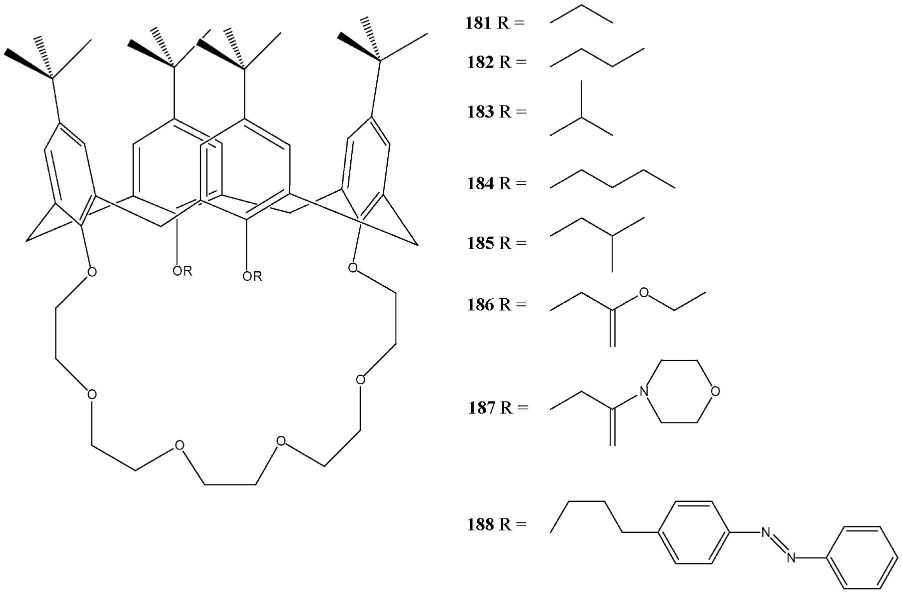


Fig. 75. Series of calix[4]aren-crown-6 derivatives, **181**–**188**.

to recognize alkali metal ions (Li(I), Na(I), K(I), Rb(I) and Cs(I)) at the interface between two immiscible electrolyte solutions [162] (Fig. 79). Their studies showed that the rate constants of these facilitated ion transfer processes, obtained using nanopipet voltammetry, together with the large association constants and the 'broad spectrum' recognition of metal ions suggest that this ionophore was worthy of further investigation.

Technology based on ISEs that target anions is considerably less developed than that based on cation recognition though a number of anions play fundamental roles in a variety of biological, medicinal and environmental processes. One report on a hydrogen ion-selective poly(vinyl chloride) membrane electrode based on calix[4]arene as a thiocyanate ISE has recently been reported [164] (Fig. 80). This ISE was developed when it was noted that

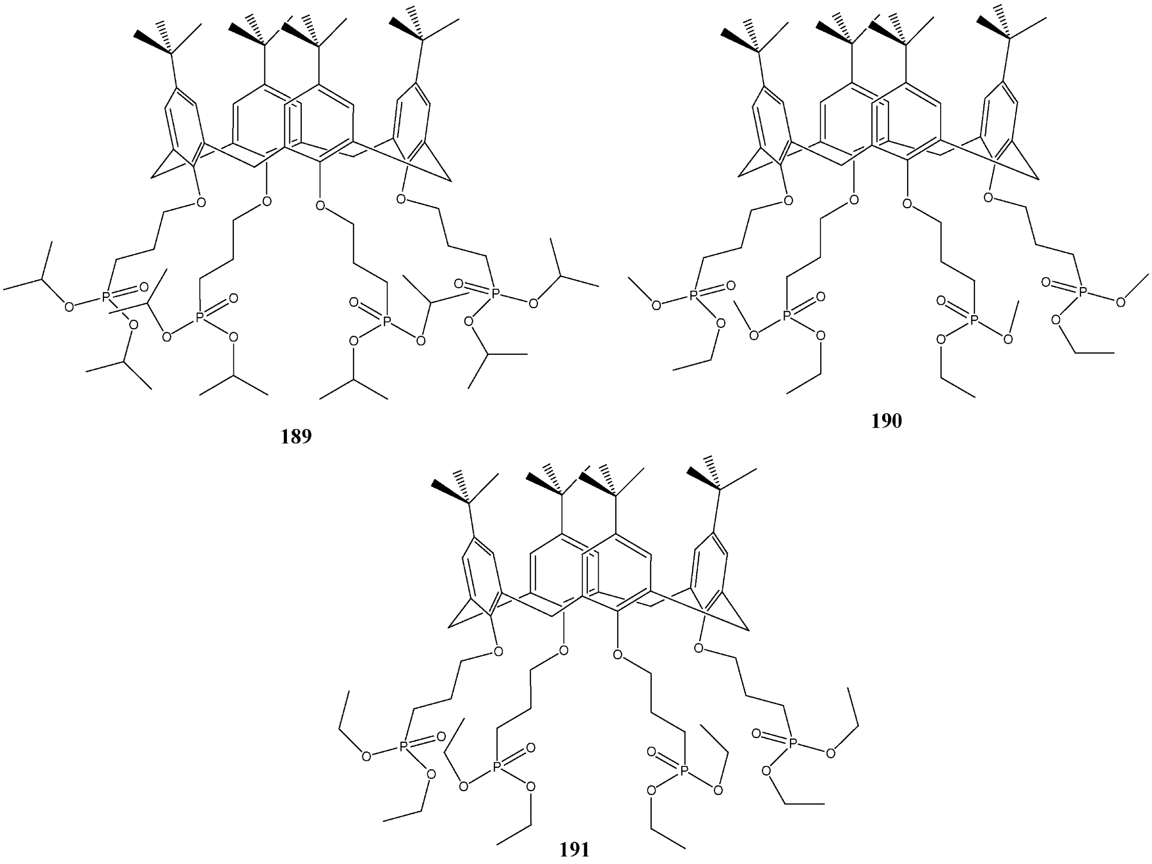


Fig. 76. Structures of (dialkylphosphoryl)alkyl functionalised calix[4]arenes **189**–**191**.

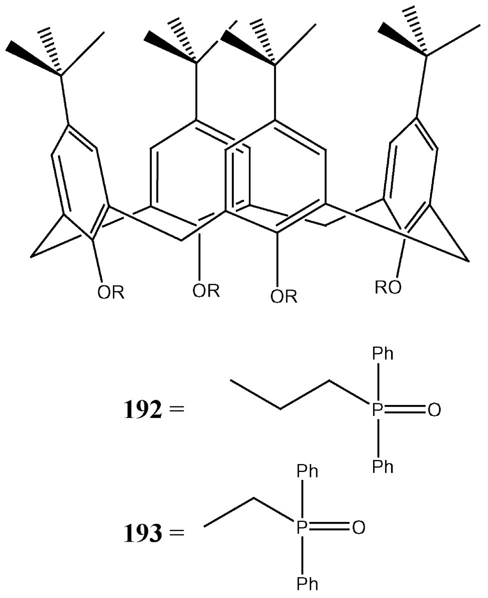
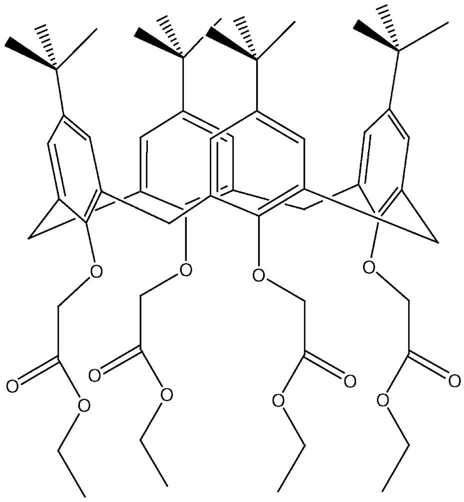


Fig. 77. Structures of **192** and **193**.

the response of an electrode, developed as a hydrogen ion ISE, was distorted in the presence of anions such as perchlorate and thiocyanate [165]. Overall, the performance characteristics of the electrode were good but the ISE did suffer from interference from iodide and perchlorate anions. It was noted however that this was also true for commercially available electrodes.

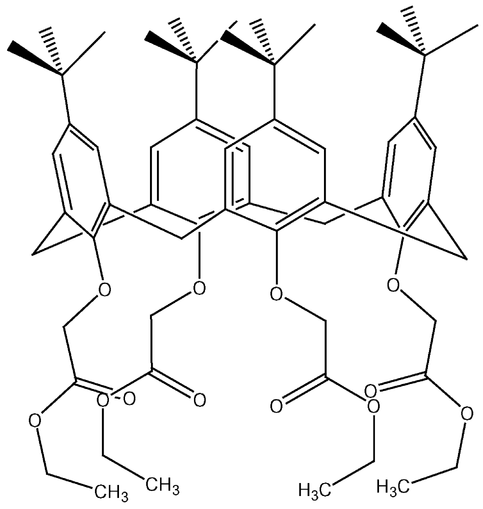
Beer and co-workers have reported the use of transition metal-directed self-assembly of calix[4]arene-based dithiocarbamate ligands, the bimetallic copper(II) complex (**198**) of which could electrochemically detect a number of anions [166]. The synthesis of the lower rim bound bimetallic complexes is shown in Fig. 81 but related complexes were formed at the upper-rim using similar methodology. ^{1}H NMR solution studies suggested all the lower rim complexes were dimeric in nature. Electrochemical anion sensing experiments with the copper bis(calix[4]arene) systems suggest ion pairing between the oxidised metal centre and anion.

Chen and co-workers have studied the use of calixarene derivatives containing sulphur in lateral chains in the field of surface plasmon resonance sensing [167]. A gold substrate modified with calixarenes (Fig. 82) as sensing films were shown to be able to selectively discriminate Ag(I) and Cu(II) from some other metal ions.



194

Fig. 78. Structure of **194**.

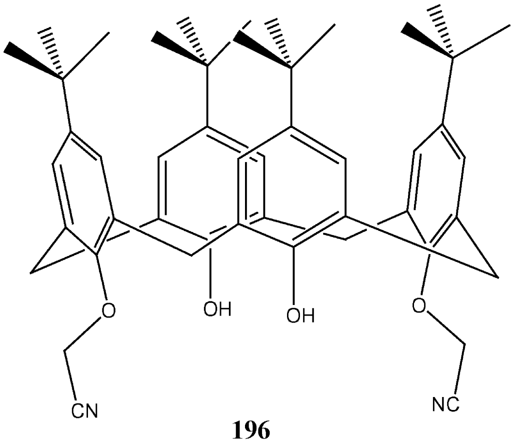


195

Fig. 79. Structure of **195**.

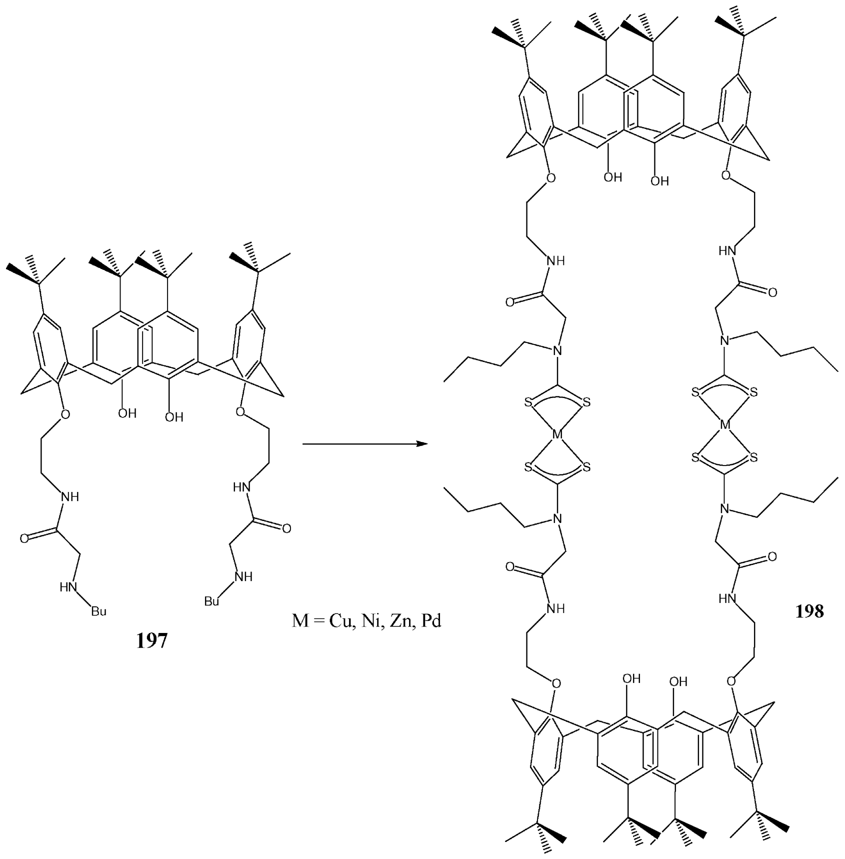
6. Energy transfer

Sciotto, Cohen, Purrello and co-workers have looked at the interactions of the tetra-cationic *meso*-tetrakis(*N*-methyl-4-pyridyl)porphyrin (H_2TMPyP) (**201**) with the octa-anionic form of 5,11,17,23-tetrasulfonato-25,26,27,28-tetrakis(hydroxycarbonylmethoxy)-calix[4]arene (C_4TsTc) (**202**) [168] (Fig. 83). Starting from a central 1:4 porphyrin/calixarene species, they showed, by structural and solution data, that it is possible to pile six porphyrins above and below the central porphyrin to form a 7:4 species. They were also able to complex both transition metal species to the porphyrin units as well as sodium metal ions to the lower rim of the calix[4]arene unit. They were able to activate an energy transfer process within this supramolecular species, when they used both Zn(II)-porphyrin and Au(III)-porphyrin units in the construction of the supramolecular species. They were able to assign a band at 450 nm in the absorption spectrum of a AuTMPyP/ZnTMPyP/AuTMPyP/(C_4TsTc)$_4$ species as arising from a Zn(II) → Au(III) energy transfer process.



196

Fig. 80. Structure of **196**.



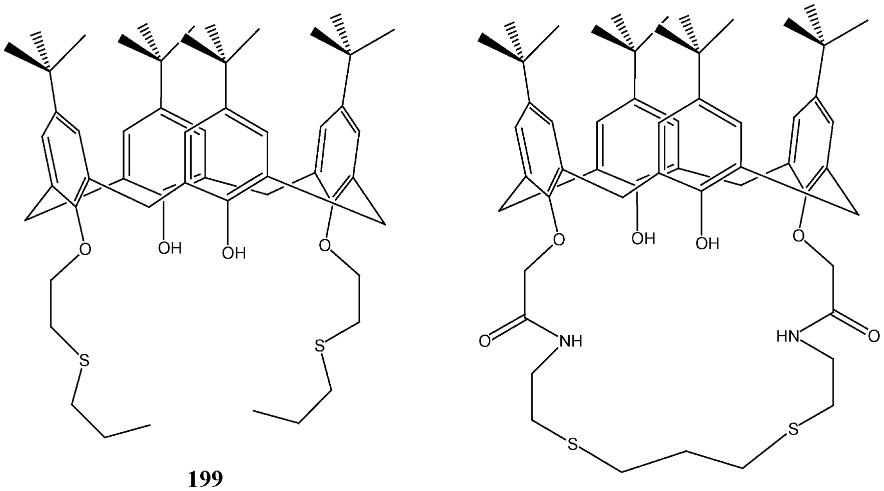
197

M = Cu, Ni, Zn, Pd

198

Fig. 81. Structure of bimetallic complex, **198**, from difunctionalised calix[4]arene **197**.

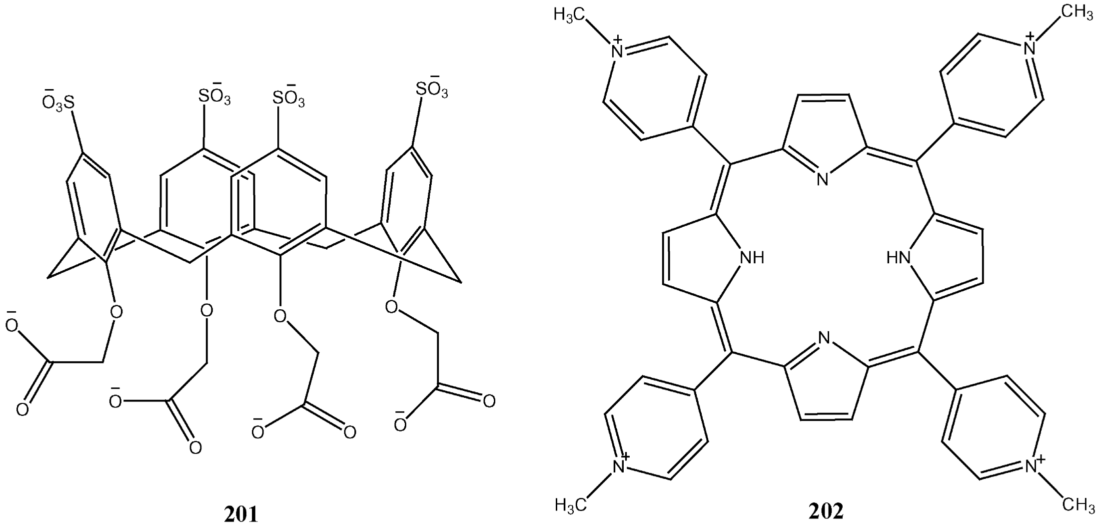
McGinley and co-workers have synthesised calix[4]arene derivatives which are capable of complexing different transition metal ions at both the upper and lower rims of the calix[4]arene [169]. They have synthesised mixed metal complexes with ruthenium(II) on the upper rim and several transition metal ions, including copper(II) and manganese(II) on the lower rim. Their initial studies, which are based on EPR spectroscopy, show that when the ruthenium(II)/manganese(II) complex is partially oxidised to ruthenium(III)/manganese(II) using ammonium cerium nitrate as oxidant, the oxidation occurred at the ruthenium centre only. Furthermore, when the EPR spectrum of the complex was rerun after 30 min, the sample showed an intensity decrease of ~30% in both the ruthenium(III) and manganese(II) signals, implying that either energy or electron transfer from the manganese(II) centre to the ruthenium(III) centre, with consequent oxidation of the manganese(II) to manganese(III) (Fig. 84). This suggested that the two metal centres are in communication with each other despite the fact that there is no direct pathway between them.



199

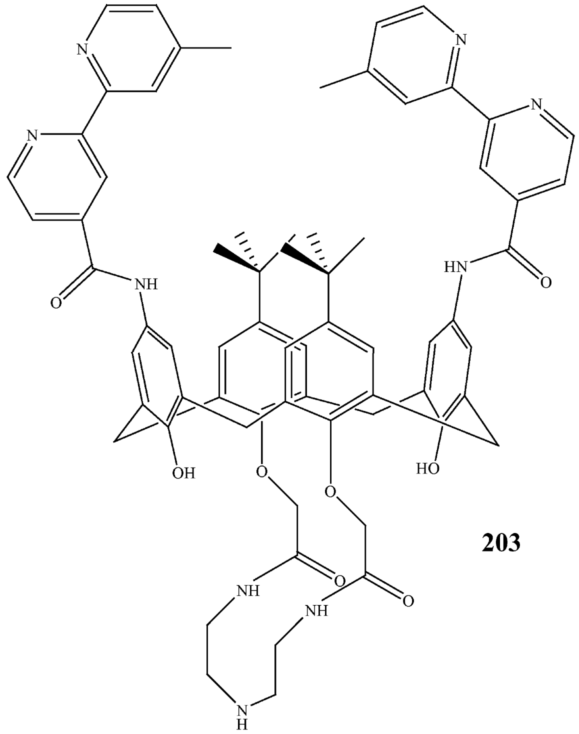
200

Fig. 82. Structures of **199** and **200**.



201 **202**

Fig. 83. Structures of **201** and **202**.



203

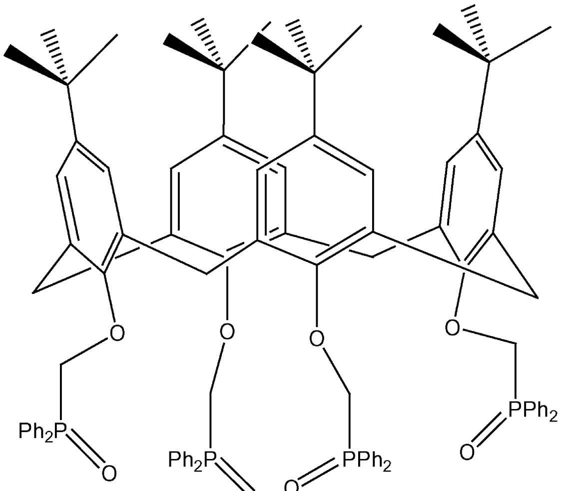
Fig. 84. Structure of **203**.

7. Extraction

Yaftian et al. studied the extraction of thorium(IV) and europium(III) ions, which were used as models for tetravalent and trivalent actinide ions, from aqueous nitrate media using calix[4]arene derivatives containing phosphine oxide units [170]. All the ligands exhibited good extracting properties towards the thorium(IV) ions, with the highest extraction percentage being observed for the tetraphosphorylated derivative (**204**), a ligand with eight potential oxygen binding sites, which is capable of forming a highly symmetrical cavity for encapsulation of the metal ion (Fig. 85).

The same group also studied the extraction of alkali metal picrates using a mixed amide-phosphoryl calix[4]arene derivative (shown in Fig. 86) [55]. They observed that stable complexes were formed which had a 1:1 cation/calix[4]arene ratio. They also observed that the extraction of the alkali metal cations decreased as one progressed down the group. This mirrored results that the group had obtained some years previously for extraction and transport experiments of alkali thiocyanates through a bulk liquid membrane [171].

Bartsch and co-workers synthesised a series of di-ionisible calix[4]arene derivatives containing N-(X)sulfonyl carboxamide functional groups [172–174]. The resulting proton-ionisible ligands exhibited high efficiency and selectivity in solvent extraction of metal cations. They also found that by varying the electronic properties of X, the acidity of the macrocyclic ligand could be tuned. Ionizable calix[4]arenes have been investigated by a number of groups. Another study by the same group on the effect of upper-rim substituents on the extraction behaviour of a series of di-ionizable calix[4]arene *N*-(X-sulfonyl)carboxamides (X = CF_3, Me, Ph and C_6H_4–4–NO_2) (**206**–**209**) and carboxylic acids (**210**) was published in 2002 [173] (Fig. 87). Competitive solvent extractions of



204

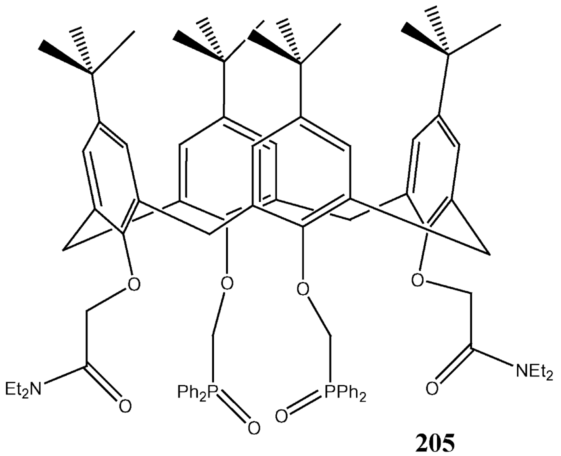
Fig. 85. Structure of **204**.

alkali and alkaline earth metal cations were carried out and it was determined that removal of the *para*-alkyl substituents resulted in significant changes in the efficiency and selectivity of metal ion separations by the carboxamide calix[4]arene extractants, while no such effect was observed for the corresponding carboxylic acids [173]. Removing one or both alkyl groups from the upper rim lead to a marked increase in the extraction of Li(I). In terms of alkaline earth metal ion extraction, the tetra-^{t}butyl derivative favoured the extraction of the Ba(II) ion, whereas the dealkylated derivatives showed different degrees of Ca(II)-selectivity. The tetra-^{t}butyl derivatives also exhibited high extraction ability for Pb(II) cations over most alkali, alkaline earth and transition metal ions [172].

Bartsch and co-workers also looked at mono-ionisible calix[4]arene derivatives containing N-(X)sulfonyl carboxamide functional groups and also in three different conformations [175,176] (Fig. 88). They observed that all the calix[4]arene derivatives in the cone conformation exhibited efficient alkali metal cation extraction with significant Li(I) selectivity over the other alkali metal cations. The major competing ion was Na(I). They also made the conformation rigid by choosing butyl groups on the remaining three positions of the lower rim or flexible by choosing a smaller methyl group instead. They found that ligand preorganisation in the appropriate conformation, by using the rigid butyl group, did not provide the expected improvement in metal ion recognition.

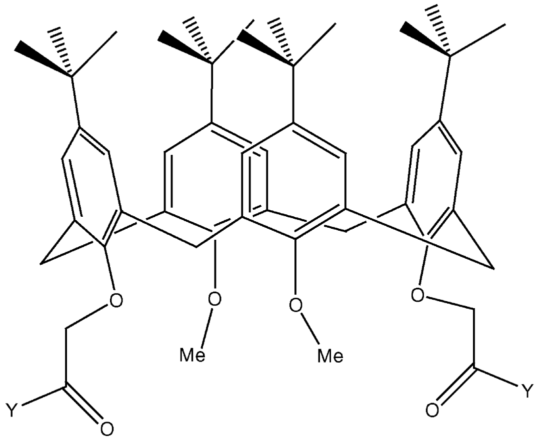
As an extension of this work, Bartsch and co-workers attached pendant proton-ionisible groups into calix[4]arene crown ethers, which are known to be efficient cation extractants [177–179] (Fig. 89). In this series of papers, the polyether chain was in the 1,3-bridging position of the distal phenol units and they looked at both the calix[4]arene-crown-5 and calix[4]arene-crown-6 derivatives. In the case of the calix[4]arene-crown-5 derivatives, they observed high extraction selectivity for Ba(II) over the other alkaline earth metal cations. When they increased the crown ether from crown-5 to crown-6, the selectivity towards Ba(II) was retained in the case of the tetra-^{t}butyl derivatives but was poorer when the alkyl groups were removed from the upper rim. This change in selectivity was attributed to the greater ligand flexibility available when the alkyl groups were removed.

In a further series of papers, Bartsch and co-workers attached pendant proton-ionisible groups into various calix[4]arene crown



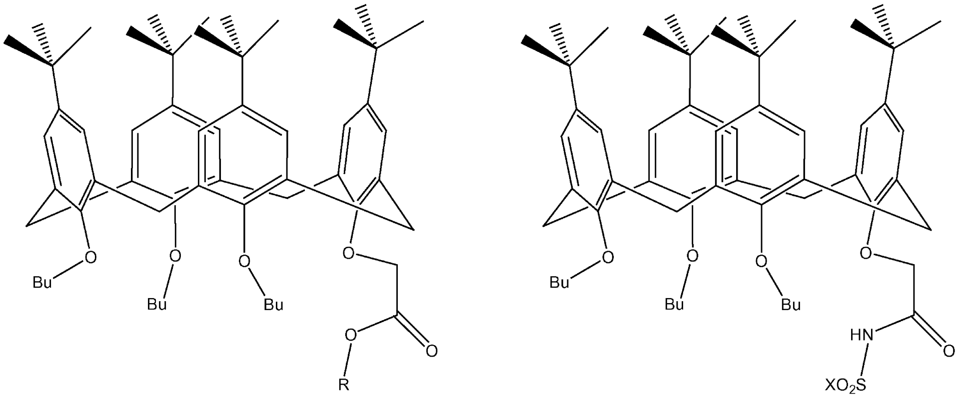
205

Fig. 86. Structure of **205**.



Y = $NHSO_2X$
206 X = CF_3
207 X = Me
208 X = Ph
209 X = C_6H_4-4-NO_2
210 Y = OH

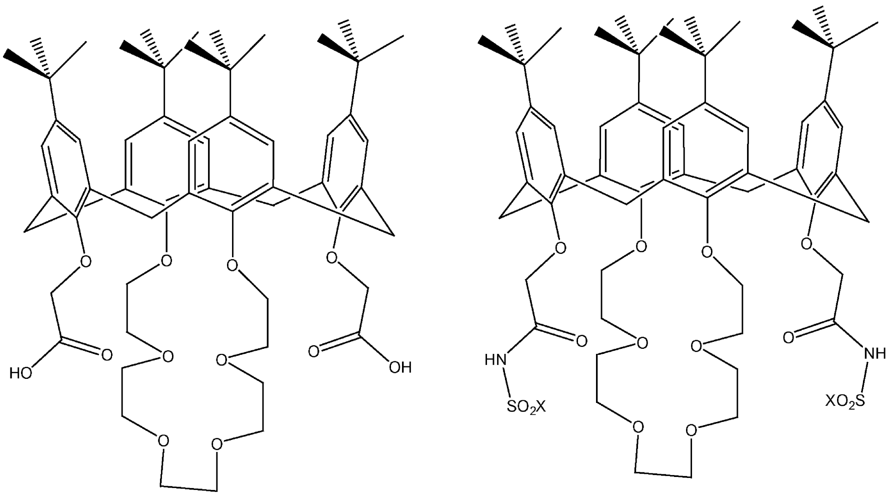
Fig. 87. Series of di-ionisable calix[4]arenes, **206–210**.



211 R = Et
212 R = H

213 X = Me
214 X = Ph
215 X = 4-$NO_2C_6H_4$

Fig. 88. Series of mono-ionisable calix[4]arenes, **211–215**.

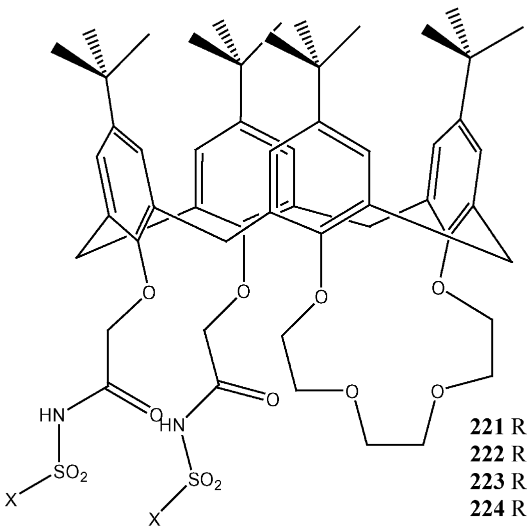


216

217 R = CH_3
218 R = C_6H_5
219 R = C_6H_4-4-NO_2
220 R = CF_3

Fig. 89. Series of calix[4]arene-crown-6 ligands, **216**–**220**.

ethers with the crown ether in the 1,2-proximal bridging position [180–183] (Fig. 90). In the case of the calix[4]arene-crown-4 derivatives, they observed that all the calix[4]arene derivatives, with four alkyl groups on the upper rim, were selective for Ba(II) in competative solvent extraction of alkaline earth metal cations from aqueous solution into chloroform. They believe that the large Ba(II) cation is accomodated by the calix[4]arene-crown-4 derivatives by the crown ether oxygens on one side and the two ionisable groups on the other side of the metal, since the small crown ether ring cannot accommodate the large metal ion. They also looked at the same series of di-ionisible calix[4]arene-1,2-crown-4 derivatives in which the four alkyl groups were replaced by hydrogen atoms and evaluated their extraction efficiency [183]. Again, all the derivatives were selective for Ba(II) cations over the other three alkaline earth metal ions. Further studies with crown-3, crown-5 and crown-6 derivatives [181,182] showed that these compounds were also efficient extractants with selectivity for Ba(II). The crown-3 derivatives were also tested with alkali metal ions and were found to be selective for Na(I) ion.

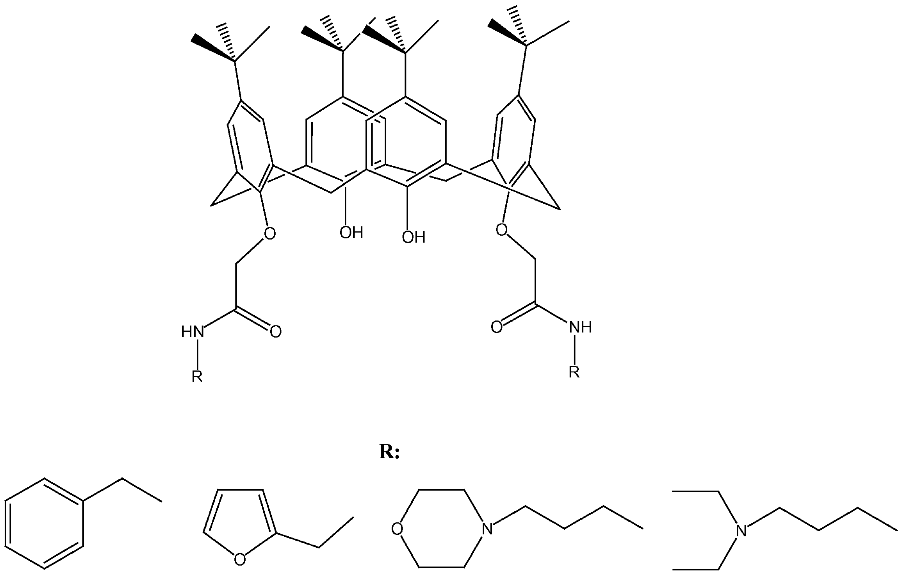


221 R = CH_3:
222 R = C_6H_5
223 R = C_6H_4-4-NO_2
224 R = CF_3

Fig. 90. Series of calix[4]arene-crown-4 derivatives, **221**–**224**.

Yilmaz and co-workers synthesised a series of four diamide derivatives from the reactions of primary amines with calix[4]arene diester derivatives, which existed in the cone conformation, shown in Fig. 91 [184]. They have previously found that amine base derivatives of calix[4]arenes are very effective towards chromate and dichromate anions [185,186]. They observed that the compounds **227** and **228** were better extractants of chromate and dichromate anions than **225** and **226**, and furthermore, that they were excellent at transferring the same anions from an aqueous phase to a dichloromethane phase. They have also reported the synthesis and extraction ability of calix[4]arene based “proton-switchable extractant” for metal ions and dichromate anions [187]. Calix[4]arene **229** was synthesised by the reaction of the acyl chloride derivative with isonicotinic acid hydrazide in the presence of pyridine (Fig. 92). This could then be converted to its methyl iodide salt by refluxing **229** with methyl iodide in acetonitrile or to its protonated form using acid. Calix[4]arene **229** did not extract alkali metal ions but showed excellent selectivty towards transition metals, while the protonated form is effective for transferring $HCr_2O_7^-/Cr_2O_7^{2-}$ anions from an aqueous to an organic layer. They have also synthesised a calix[4]arene-based macrocyclic molecule, see Fig. 93, which can efficiently bind both ions and chiral organic molecules [188]. In this paper, they report the synthesis and liquid–liquid extraction properties of the chiral calix[4](azoxa)crown-7 derivative towards metal cations. The chiral recognition properties are reported elsewhere [189]. The liquid–liquid extraction of metal picrates of the calix[4]crown-7 derivative showed it to be efficient and selective for Li(I) ions among the alkali metal ions and while it proved to be a good extractant for transition metal ions, it showed no selectivity towards these ions. They rationalised that the greater extraction ability towards Li(I) ions is probably due to the geometric constraints of the calix[4]arene cavity that substantially limit the deformation of the crown part and so force the small Li(I) ion into close contact with only three oxygen atoms.

In an earlier paper, Yilmaz and co-workers described the synthesis and liquid–liquid extraction properties of calix[4]crown-6 monomers **231** and **232** and the corresponding oligomer **233** [190]



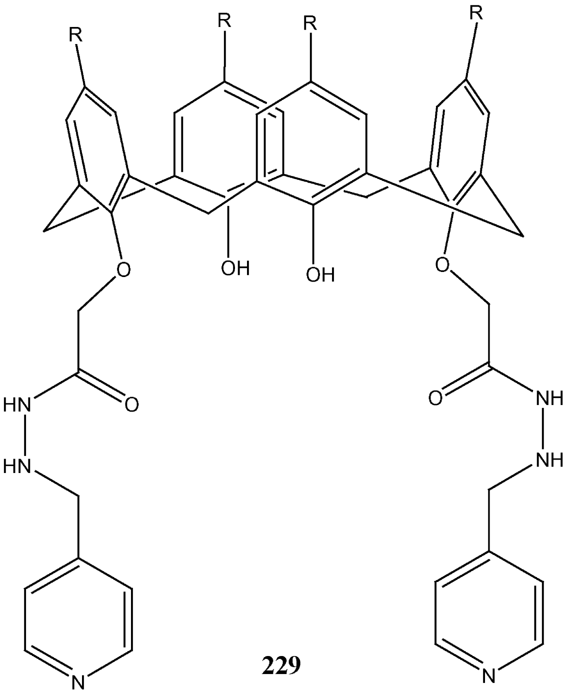
225 **226** **227** **228**

Fig. 91. Series of calix[4]arene diamides, **225**–**228**.

(Fig. 94). The cone conformation was maintained in all compounds. The monomer derivative **231** exhibited good extraction ability towards alkali metal cations, which the authors believe to be due to the influence of the nitrophenyl groups, helping the binding of ions in a sandwich-like manner opposite the crown moiety. There was a decrease in the extraction ability of the amino derivative also which the authors suggest is due to the amino hydrogen atoms forming intramolecular hydrogen bonds with the crown oxygen atoms. They have further investigated the extraction properties of similar calix[4]crown-6 monomers containing a thia-crown ether [191]. They observed that the thia-crown monomers **234** and **235** exhibited good extraction ability towards Cu(II), Hg(II) and Pb(II) but that on formation of the polymeric material **236** all selectivity was lost and the oligomer showed high affinity for all metal ions.

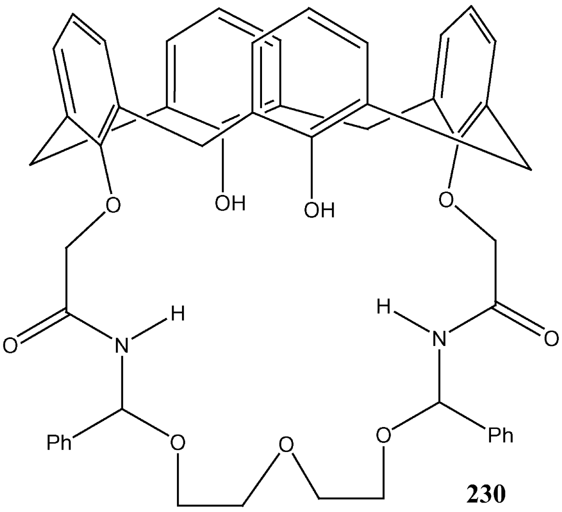
They have also reported the liquid–liquid extraction properties of the calix[4]arene nitrile derivatives, shown in Fig. 95 [192]. In this communication, they investigated the co-transport of metals (Hg(II), Pb(II) and Na(I)) from an aqueous solution through a bulk liquid membrane into an aqueous receiving solution using the calix[4]arene derivatives as the carriers. They observed that both carriers were efficient and selective for Hg(II) ions with respect to the other ions chosen, with the dinitrile derivative being better than the tetra-nitrile derivative.

They have also reported the synthesis of two oligomeric calix[4]arene crown derivatives *via* the condensation reaction with 1,5-dibromopentane [193] and the extraction ability of these polymeric materials was investigated. They observed that the selectivity of the oligomer **239** increased towards Na(I), but decreased towards Cu(II), Hg(II) and Pb(II) compared to the original monomer unit



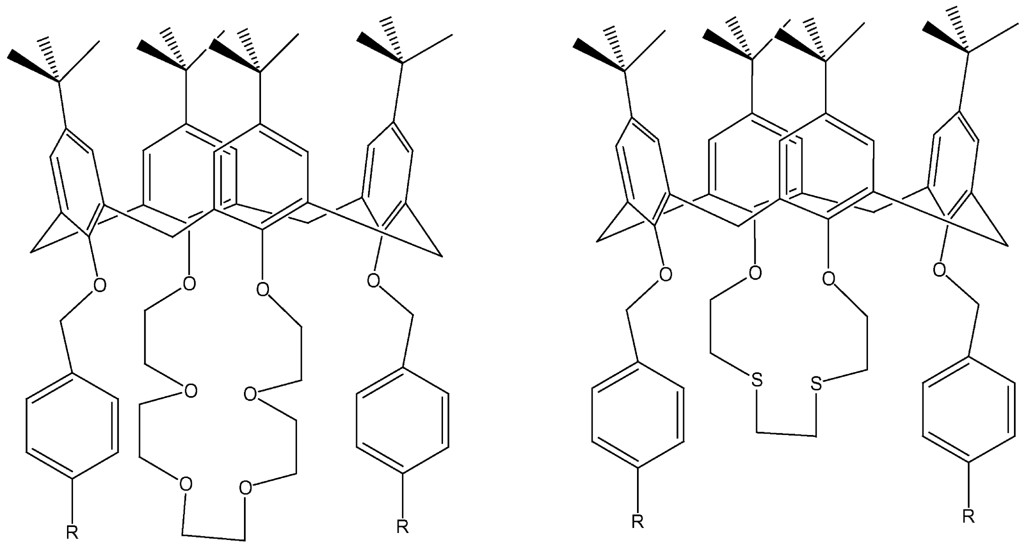
229

Fig. 92. Structure of **229**.



230

Fig. 93. Structure of **230**.



R = NO_2: **231**
NH_2: **232**
$NHCOC_6H_4CO$: **233**

R = NO2: **234**
NH2: **235**
NHCOC6H4CO: **236**

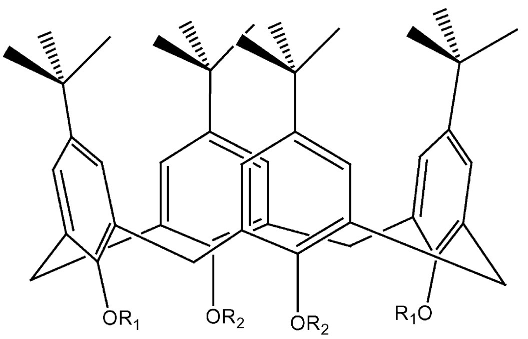
Fig. 94. Series of calix[4]arenes, **231–236**, studied by Yilmaz et al. [190].

(Fig. 96). They also observed that **240** was an efficient extractant for the transition metal cations compared to the monomer unit.

Sukwattanasinitt and co-workers synthesised a series of stilbene bridged calix[4]arene crown ether derivatives, on which they carried out a series of alkali ion extraction experiments [194] (Fig. 97). These compounds were all in the 1,3-alternate conformation and so will not be discussed in this review. However, in that paper, they also synthesised two calix[4]arene crown ether derivatives which they used for comparison purposes against the stilbene derivatives. They observed that the calix[4]arene crown-5 derivative showed a particularly greater K(I) selectivity than either the calix[4]arene crown-6 derivative or 18-crown-6 itself.

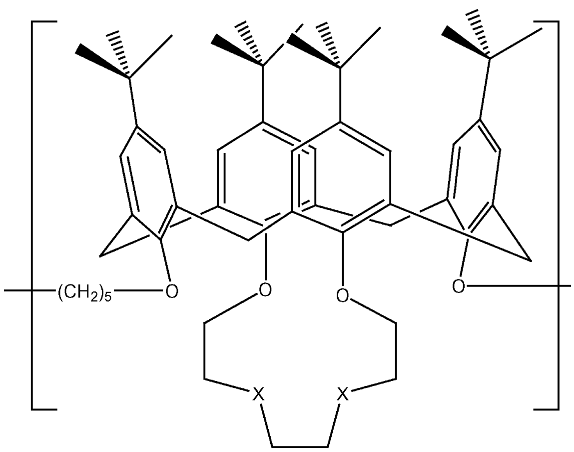
Chawla et al. synthesised a series of calix[4]arene(amido)mono-crown derivatives through aminolysis of calix[4]arene esters and intramolecular cyclisation of the intermediates [195] (Fig. 98). The compounds were also converted into azo-substituted derivatives, at the upper rim, in order to act as photoresponsive molecular receptors for transition metal ions. The only interactions they observed were with the alkali metal ions, which caused a red shift of approximately 130 nm in the UV/vis spectrum of the calix[4]arene(amido)mono-crown derivatives upon addition of the metal ion, and also with the Hg(II) ion, which caused a blue shift of approximately 38 nm.

Zhang and co-workers synthesised a series of calix[4]arene crown ether derivatives which contained selenium atoms as shown in Fig. 99 [196]. They confirmed the cone conformation of the derivative by NMR spectroscopy and X-ray crystallography. They used ^1H NMR titration to determine the extraction ability of the calix[4]arene(diseleno)crown ether and found that the greatest extraction percentage was observed with mercury ions, followed by silver ions, compared to other transion metal ion and alkali metal ions. They rationalised this in terms of the hard and soft acid and base theory in that the soft Hg(II) and Ag(I) ions were interacting with the soft selenium donor atoms whereas the harder metal ions had no interaction with the selenium atoms.



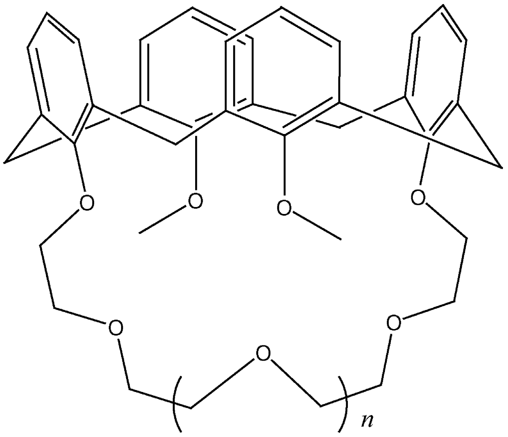
237 $R_1 = CH_2CN$, $R_2 = H$
238 $R_1 = R_2 = CH_2CN$

Fig. 95. Structures of **237** and **238**.



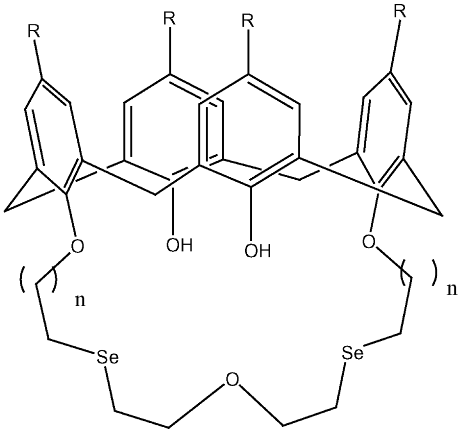
239 X = O
240 X = S

Fig. 96. Structures of **239** and **240**.



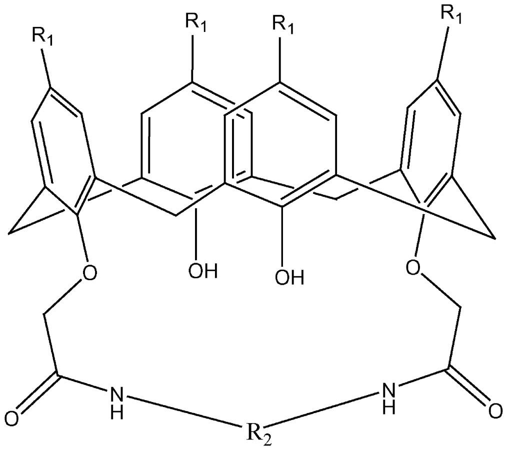
241 $n = 1$
242 $n = 2$

Fig. 97. Structures of **241** and **242**.



244 R = ^{t}Bu, n = 1
245 R = ^{t}Bu, n = 2
246 R = H, n = 2
247 R = ^{t}Bu, n = 3
248 R = H, n = 3

Fig. 99. Series of calix[4]arene crown ether ligands containing Se donor atoms, **244**–**248**.



243

Fig. 98. Structure of **243**.

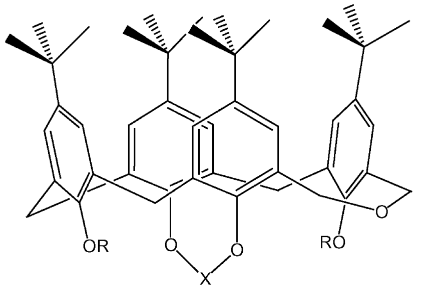
Marcos and Ascenso reported the synthesis of calix[4]arene-crown-6 derivatives having methoxypyridyl functional groups attached to the other two phenol rings of the calix[4]arene [197]. The binding properties of the calix[4]arene compound **250** towards alkali, alkaline earth, transition and heavy metal cations was assessed by both phase transfer and ^{1}H NMR titration experiments (Fig. 100). **250** is an efficient extractant for the alkali metal ions, but displays a strong affinity for the soft Hg(II) and Ag(I) ions. The authors assigned this difference in binding between the different metal ions to be due to the presence of the softer nitrogen donor atoms of the CH_2-pyridyl arms. They further deduced from their ^{1}H NMR experiments that **250** formed 1:1 complexes with K(I), Ca(II) and Ag(I) with the metal encapsulated in the cavity composed of the crown ether unit and the two pyridyl groups.

Xing et al. synthesised a range of calix[4]arene benzoate esters, shown in Fig. 101, and carried out alkali metal ion binding studies on them [198]. They observed that the methyl and ethyl benzoate ester derivatives exhibited high extraction ability for K(I) over other alkali metal cations. This was the first case of a calix[4]arene derivative in the cone conformation which showed selectivity for potassium cations over sodium cations.

Němcová et al. looked at the possibility of using calix[4]arenes for the spectrophotometric determination of lanthanides [199]. They chose the calix[4]arene derivative, shown in Fig. 102, as their choice of suitable reagent to interact with lanthanide ions. They also chose sulphophthalein dyes to convert the positively charged lanthanide-calix[4]arene complexes to products capable of extraction into an organic solvent. They found that their system could easily extract and detect the extraction of Gd(III)–**253**–bromophenol blue.

Asfari and co-workers reported the synthesis of a series of thiacrowncalix[4]arenes containing four sulphur atoms in the crown moiety and its complexation properties towards Cd(II), Hg(II) and Pb(II) ions were investigated by either ^{1}H NMR or solvent extraction experiments [200] (Fig. 103). The thiacrowncalix[4]arene compound exhibited better extracting power for both Cd(II) and Pb(II) than for Hg(II) ions, with a more pronounced extraction of lead compared to cadmium. However, the extracting ability of the compound was dramatically decreased in the presence of sodium nitrate which the authors explained by competitive sodium extraction.

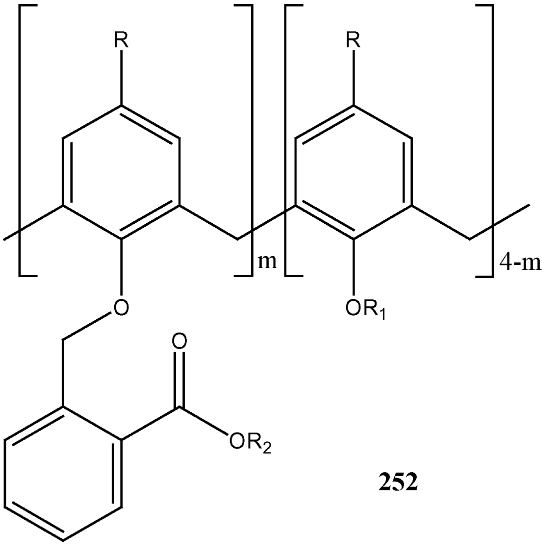
Arimura et al. investigated the ion-selectivity of the lipophilic calix[4]arene derivative containing several (ethoxy-



X = $(CH_2CH_2O)_4CH_2CH_2$

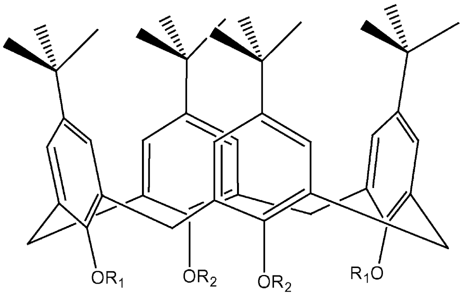
249 R = H
250 R = CH_2py
251 R = CH_3

Fig. 100. Series of calix[4]arene-crown -6 derivatives, **249**–**251**.



252

Fig. 101. Structure of **252**.



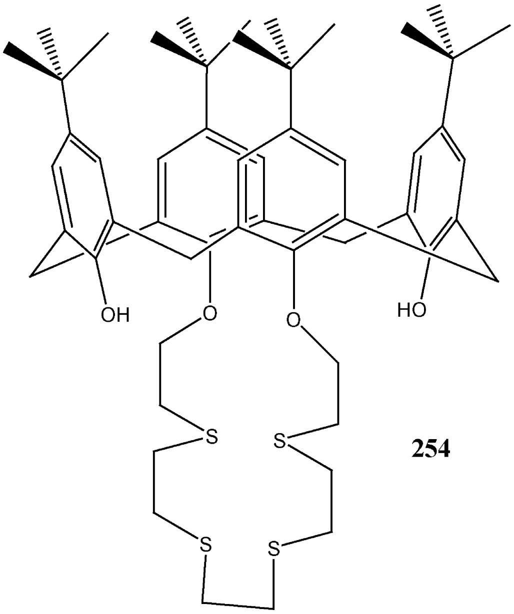
253

R_1 = -CH_2COOH
R_2 = -$CH_2COOC_2H_6$

Fig. 102. Structure of **253**.

carbonyl)methyoxy groups and found the selectivity was strongly dependent on the ionic size [201]. In order to study the binding ability of the calix[4]arene derivative, the solvent extraction of alkali metal picrates from water to tetrachloroethane was performed at 30 °C. The calix[4]arene derivative having two ester groups showed the highest extraction value for K(I) ion while those with four ester groups showed the highest extraction for Na(I) ion. They suggested that the rigid nature of the four ester groups is the origin of the Na(I) selectivity.

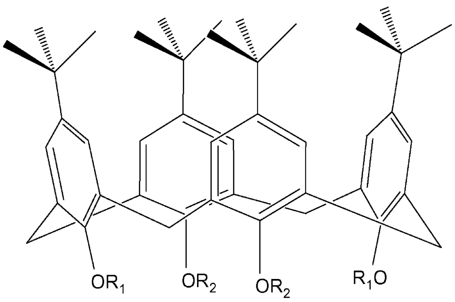
The complexation and extraction of alkali cation by [2+2'] calix[4]arene derivatives combining ethyl ester and methyl ketone, *tert*-butyl ester or diethylamide arms has been reported in the 1990's [202]. Abidi and co-workers synthesised a series of mixed [2+2'] calix[4]arene derivatives (shown in Fig. 104) and investigated the extraction and complexation properties of the synthesised calix[4]arenes towards alkali and alkaline earth metal cations by both UV and ^{1}H NMR spectroscopies [203]. They found that the stoichiometry of the formed complexes varied with the nature of the cation, giving either ML or ML_2 species. They also found that size effect was not the only contributing factor of the complex stability, but that the charge density of the cations and their solvation seemed to be other important factors, as well as the number and nature of the donor sites. The mixed [2+2'] methoxy-benzyl derivative showed selectivity for Na(I) cation with respect to all studied cations.



254

Fig. 103. Structure of **254**.

Dumazet-Bonnamour and co-workers have synthesised a series of β-ketoimine calix[4]arene derivatives having two, three or four such functional groups attached to the lower rim, with the aim of developing a class of selective transition metal ion receptors [204]. The complexation properties of two disubstituted and one trisubstituted calix[4]arene were studied with various transition metal ions using UV/vis titrations. Only in the cases of Hg(II), Ag(I) and Cu(II) ions were changes in the UV/vis spectra observed, indicating formation of, at least, one metal species. The stoichiometry of these metal complexes of derivative **263**, shown in Fig. 105, was determined by both Job plot and mole ratio methods, and shown to be 1:1 in all cases. They also demonstrated that at pH 8 derivative



255 $R_1 = R_2 = CH_3$
256 $R_1 = R_2 = CH_2CH_2OCH_3$
257 $R_1 = CH_2C_6H_5$, $R_2 = CH_3$
258 $R_1 = CH_2C_6H_5$, $R_2 = CH_2CO_2C_6H_5$
259 $R_1 = CH_2C_6H_5$, $R_2 = CH_2CH_2OCH_3$
260 $R_1 = CH_2CH_2OCH_3$, $R_2 = CH_3$
261 $R_1 = CH_2CH_2OCH_3$, $R_2 = CH_2CO_2C_2H_5$

Fig. 104. Series of [2+2'] calix[4]arene derivatives, **255–261**.

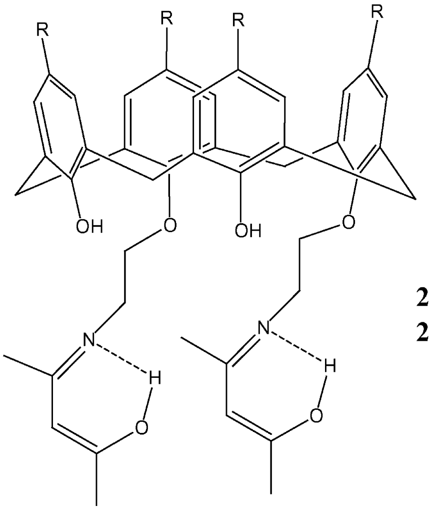


Fig. 105. Structures of **262** and **263**.

263 is an effective extractant for Pb(II), but is very ineffective for Cu(II), Ni(II) and Cd(II) ions.

Shimojo and Goto found that the tetrapyridyl calix[4]arene derivative, shown in Fig. 106, was soluble in a room-temperature ionic liquid, 1-alkyl-3-methylimidazolium hexafluorophosphate, where the alkyl group is either butyl, hexyl or octyl [205]. In competative extraction tests using several metal ions, only silver ions were transferred by the calix[4]arene from the aqueous phase to the ionic liquid. They further observed a difference between the extraction behaviour into an ionic liquid as opposed to extraction into chloroform. In the case of chloroform, silver extraction occurred at high nitric acid concentrations, whereas with the ionic liquid extraction, either at very low concentration or no nitric acid present, silver ions were efficiently transferred. Further studies showed that the calix[4]arene could be recycled with no loss of extraction ability.

Hundal and co-workers have synthesised a range of calix[4]arene derivatives with substitution at the lower rim incorporating imine units, as shown in Fig. 107 [206]. All the derivatives were found to be in the cone conformation, except in one case which existed in both the cone and 1,2-alternate conformations. Experiments testing ion transport across a liquid membrane were carried out on several alkali, alkaline earth and transition metal ions, and all calix[4]arene derivatives were found to be highly selective for the Ag(I) ion. The authors also report the surprising reductive ability of the ligands which they found, when, in the presence of copper(II) perchlorate in acetonitrile, colourless crystals of $[Cu(CH_3CN)_4]ClO_4$ were obtained.

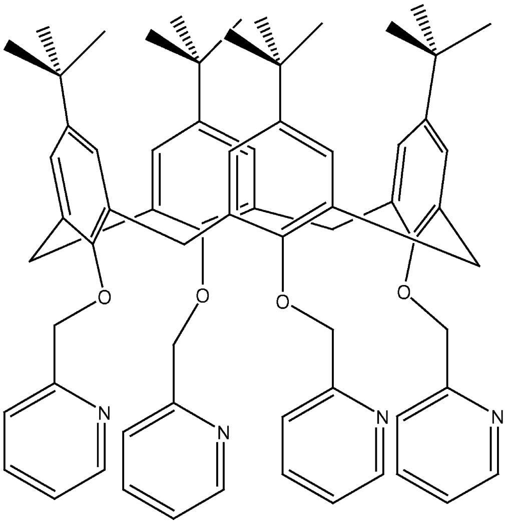


Fig. 106. Structure of **264**.

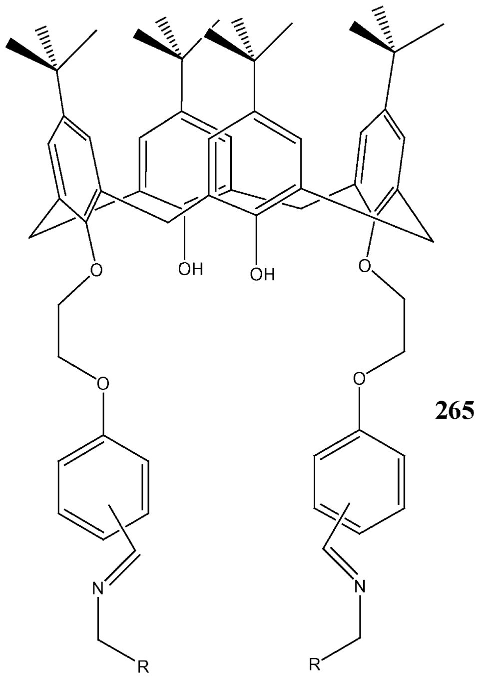


Fig. 107. Structure of **265**.

Calix[4]arenes having four carbamoylmethyl-phosphine oxide (CMPO) functional groups attached at the lower rim are know to be good extractants for lanthanides and actinides [207]. Böhmer and co-workers have increased the number of CMPO functions attached to the calix[4]arene skeleton, using procedures associated with dendrimer chemistry [208]. Two types of calix[4]arene derivative are shown in Fig. 108. The extraction properties of these two calix[4]arene derivatives were carried out using the conditions previously reported for other CMPO derivatives (conc. nitric acid as aqueous phase, *o*-nitrophenylhexylether as organic solvent). They observed that the extraction efficiency of their dendritic CMPO calix[4]arenes were considerable lower than those of previously reported calix[4]arene-CMPO derivatives [207]. The authors concluded that the simple accumulation of CMPO functions on a calix[4]arene was not an appropriate way to improve extraction properties.

Marchand et al. have reported the synthesis of calix[4]arene receptors containing an oxahexacyclic cage [209]. The complexation properties of the four new receptors were established *via* a series of alkali metal picrate extraction experiments. They found that only where long alkyl chains were attached as R^1 and R^2 (Fig. 109) did the calix[4]arene derivatives show selectivity as potassium ion extractants over other alkali metal ions. They also showed significant selectivity compared to the other calix[4]arene derivatives containing either methoxy or hydroxy groups as OR^1 and OR^2.

Beer et al. have synthesised a series of calix[4]arene derivatives having both acid and amide functionalities on the lower rim for use as extractants of lanthanide and uranyl ions from aqueous waste [210] (Fig. 110). The lanthanide ions and the uranyl ion all form dimeric 2:2 calix[4]arene:metal complexes which was confirmed by X-ray crystallographic and mass spectrometry studies.

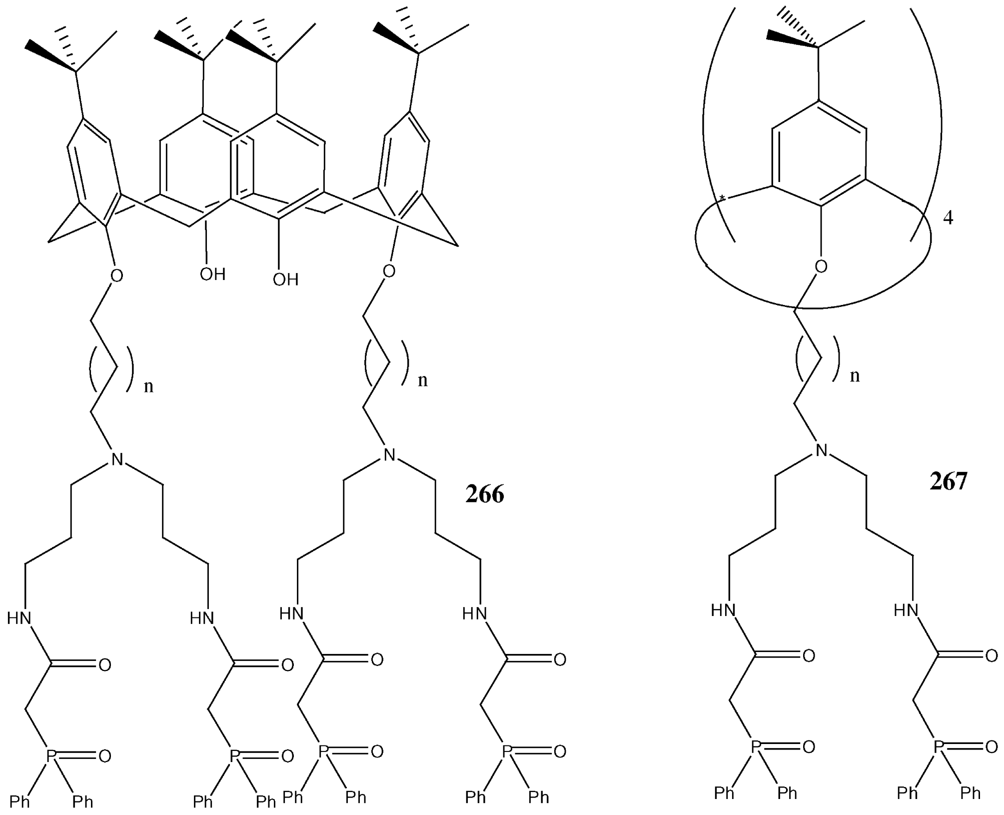
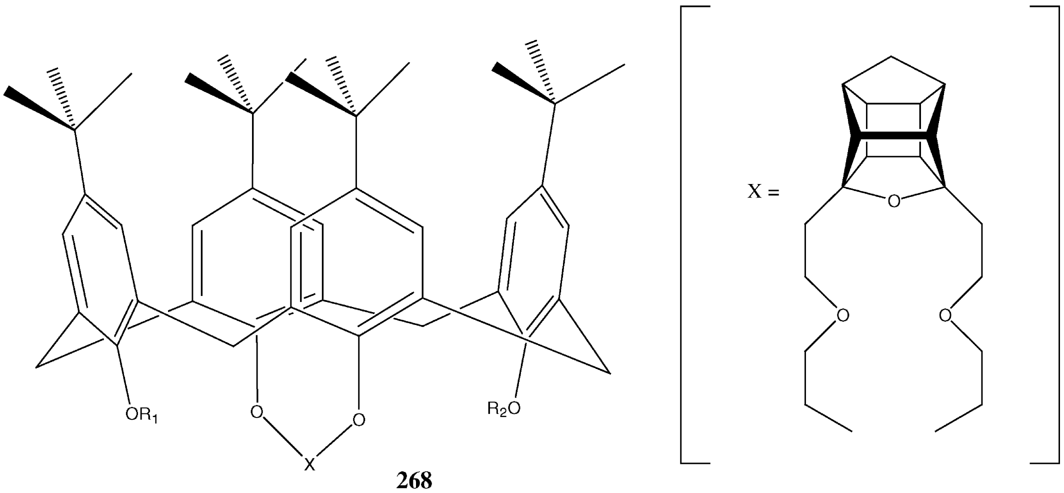


Fig. 108. Structure of dendrimeric calix[4]arenes **266** and **267**.

Two-phase solvent extraction experiments showed efficient, pH dependent uptake of both lanthanide and uranyl cations in the case of the *tert*-butyl substituents on the upper rim. Introduction of the di-nitro groups or complete removal of the *tert*-butyl substituents on the upper rim showed significant improvement in uranyl extraction.

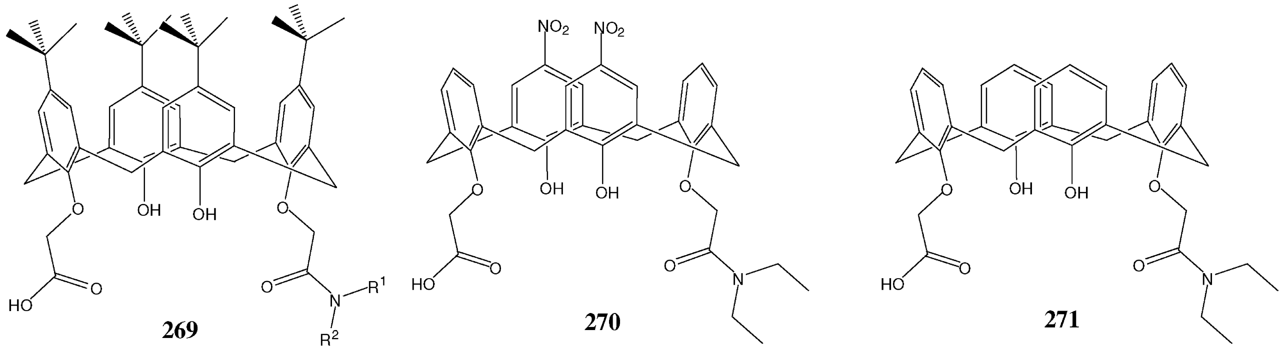
Lukeš and co-workers synthesised various bis(phosphonic) acid derivatives of calix[4]arene and tested them as extractants for lanthanide metal ions and thorium ion [211] (Fig. 111). The activity of all three ligands in the extraction of the above metal ions from 1 M nitric acid solution with their chloroform solutions was tested. They observed that the extraction efficiencies decreased with increasing alkyl chain length and that the calix[4]arene with the propyl chain derivative showed a huge selectivity for Yb(III) over La(III) by three orders of magnitude.

Regnouf-de-Vains and co-workers synthesised a calix[4]arene derivative containing two 2,2’-bipyridine and two benzyl groups in alternate positions at the lower rim [212] (Fig. 112). This compound was then subjected to complexation studies with various first row transition metal ions, giving in all cases complexes with tetrahedral geometry. Depending on the oxidation state of the metal ion and also on the coordinating ability of the counter-anion, the resulting complexes were either 1:1 or 1:2 metal:calix[4]arene stoichiometry.



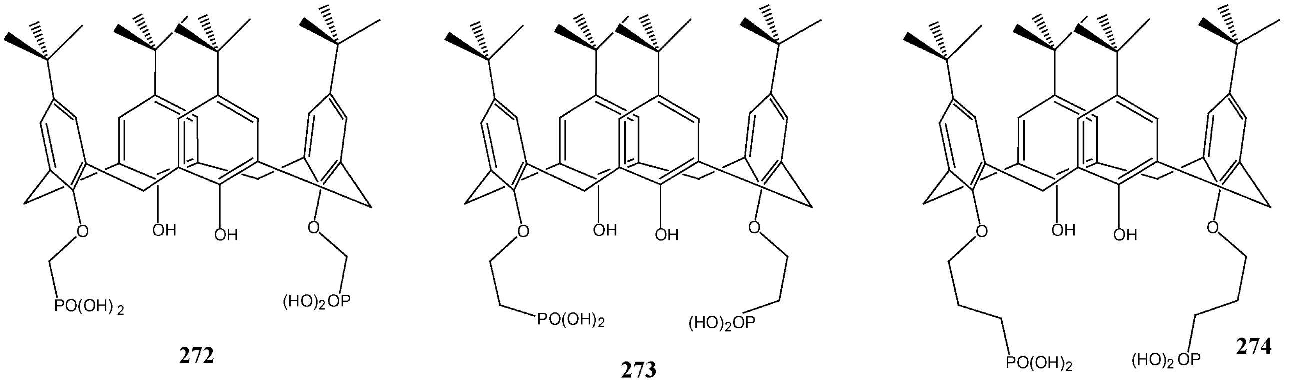
268

Fig. 109. Structure of **268**.



269 **270** **271**

Fig. 110. Series of monoacid monoamide functionalised calix[4]arenes, **269**–**271**.



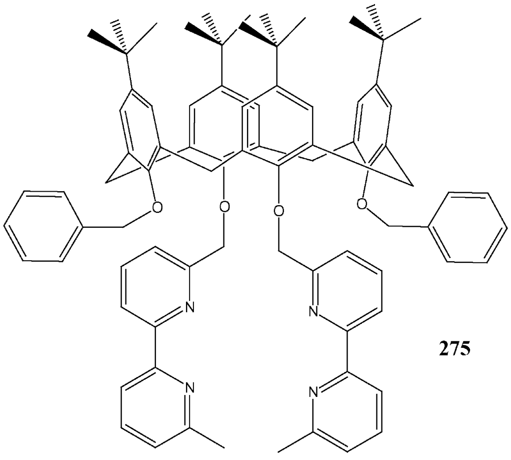
272 **273** **274**

Fig. 111. Series of bis(phosphonic acid) derivatives of calix[4]arenes, **272**–**274**.

Yaftian and Vahedpour have investigated the extraction of four lanthanide picrates from water into various chlorinated solvents using a calix[4]arene with four pendant arms containing phosphoryl groups as the extracting agent [213]. The solvents chosen were chloroform, dichloromethane and 1,2-dichloroethane and the authors found that the extraction efficiency increased with increased polarity of the solvent. The calix[4]arene derivative **276** (Fig. 113) extracted the four lanthanides ions (La(III), Pr(III), Nd(III) and Eu(III)) efficiently but without any selectivity being shown.

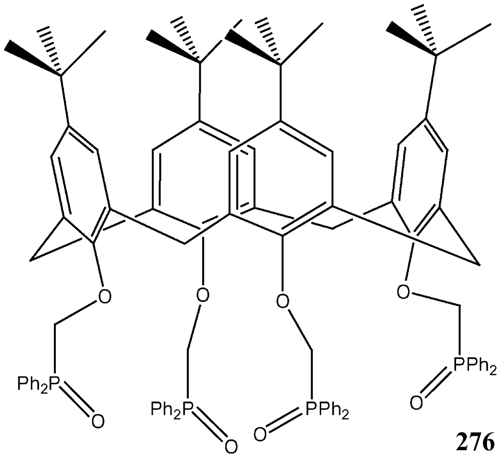
Zhu and co-workers examined the interaction of a calix[4]arene containing piperidine groups with sodium, lead and cadmium cations, using both ^{1}H NMR spectroscopy and electrospray mass spectrometry [214] (Fig. 114). In all cases, 1:1 metal:calix[4]arene complexes are formed with the metal encapsulated tightly in the cavity formed by the eight oxygen atoms, with the nitrogen of the piperidine playing no role in the complexation process.

Kalchenko and co-workers have synthesised a series of tetra-substituted calix[4]arenes containing phosphoryl groups on the lower rim, either all the same or mixtures of two different groups [215] (Fig. 115). They examined the alkali metal complexation reactions of the various calix[4]arene derivatives. They observed that all the complexes exhibited lithium ion selectivity, which was supported by the water–chloroform extraction of alkali metal picrates in the presence of the calix[4]arene derivatives. They were able to observe the extraction of the lithium ion using ^{1}H and ^{31}P NMR



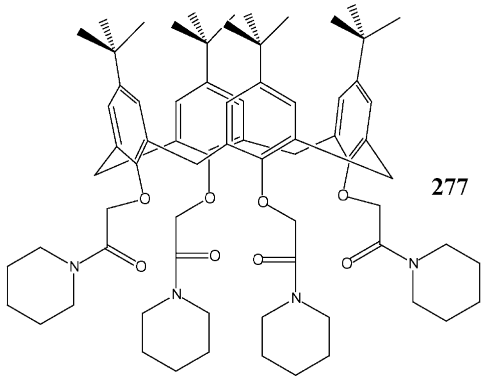
275

Fig. 112. Structure of **275**.



276

Fig. 113. Structure of **276**.



277

Fig. 114. Structure of **277**.

spectroscopies. In all cases, a 1:1 metal:calix[4]arene complex was observed.

Huang and co-workers have synthesised a series of calix[4]arene derivatives containing nitrogen or sulphur atoms at the lower rim [216]. The metal ion extraction abilities of these calix[4]arene derivatives were studied using liquid–liquid extraction experiments of aqueous metal picrates and dichloromethane solutions of the calix[4]arene ligands. The metal picrate salts included in the study were those of the alkali metals, alkaline earth metals and transition metals. All the calix[4]arene derivatives shown excellent selectivity for the silver ion over all other ions present. They further observed that among the ligands, the calix[4]arene derivatives which possess linear ligands rather than calix[4]crown derivatives showed better binding ability with the Ag(I) ion (Fig. 116).

Kang and Nam have synthesised a calix[4]arene derivative containing two urea moieties and two ester groups in the cone conformation [217]. The cation and anion binding properties of this calix[4]arene derivative were examined by ^{1}H NMR titration experiments in $CDCl_3$. The salts chosen contained alkali metal cations and a variety of halide anions. They observed that the alkali metal ions were bound at the ester groups while the anions were bound at the urea groups. They further discovered a significant increase in the strength of anion binding when the alkali metal cation was simultaneously bound. Furthermore, anion binding was enhanced more strongly in the presence of a sodium cation rather than a lithium cation, which the authors attributed to the stronger binding of the sodium metal to the ester groups (Fig. 117).

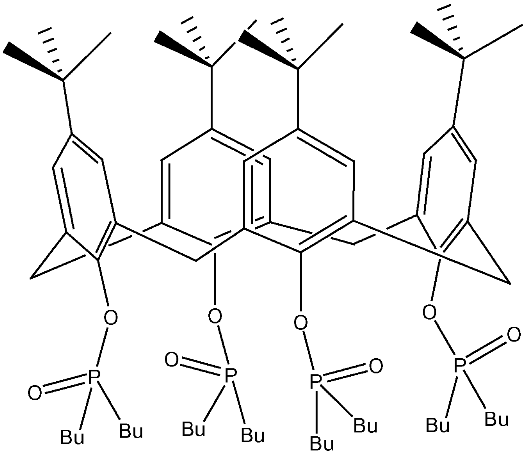
Chen and co-workers have synthesised a number of tripodal calix[*n*]arene derivative containing crown ether moieties [218]. They have developed a synthetic strategy that allows the convenient preparation of these compounds which were previously difficult to synthesise. Using this strategy, they have synthesised a calix[4]cryptand and a double calix[4]arene in which one subunit is a calix[4]crown derivative and the other is a calix[4]arene. The extraction ability of these derivatives of some picrate salts from water into chloroform was investigated. The salts chosen contained either alkali metal or ammonium cations. Both derivatives showed good extraction efficiency but no marked selectivity (Fig. 118).

A study by Abidi and co-workers in 2006 on two functionalised *p*-*tert*-butyl calix[4]arenes: tetra(*N*,*N*-dimethyl) aminoethylamide derivative **285** and related tetramethylammonium **286** and determined their complexation properties towards alkali and zinc metal cations [219] (Fig. 119). Their complexation properties were determined by UV/vis titration or ^{1}H NMR spectroscopy and revealed that 1:1 and 1:2 ligand:metal complexes were formed for both ligands. These workers found that the derivative *p*-*tert*-butylcalix[4]arene tetraamide **285** extracts efficiently alkali and alkaline earth cations from water to dichloromethane (average of up to 76%). ^{1}H NMR studies showed that in the case of mononuclear complexes, sodium cation was localised in the oxygenated cavity and zinc in the nitrogenated one.

8. Fluorescence/luminescence

Considerable effort has been devoted to the development of fluorescent chemosensors capable of selectively recognising specific chemical species with potential analytical applications in chemistry and biology [220–223]. Calixarene-based metalloreceptors are increasingly used in the development of both analytical fluorescent/luminescent sensors and highly fluorescent/luminescent lanthanide-containing probes [5,7].

For many years calixarenes have been used to monitor molecular recognition processes and photoluminescence spectroscopy as such systems offer a number of advantages in terms of sensitivity and flexibility. Calixarene-based photoluminescent sensors were first developed in the 1980s but more recent developments are discussed here. Casnati and co-workers studied the photophysical properties of a family of calix[4]arene-crowns and of their



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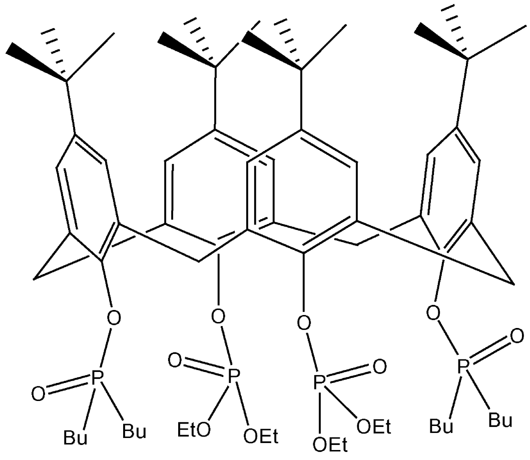
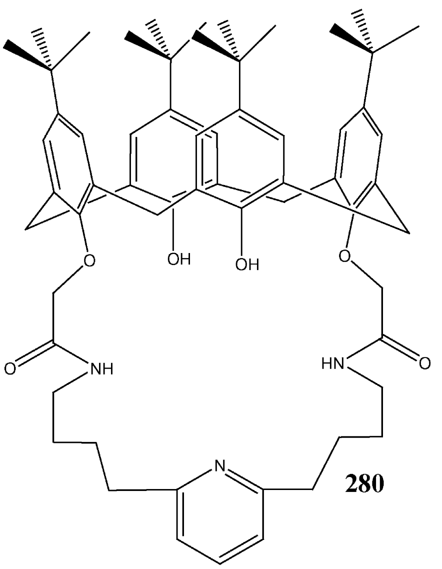


279

Fig. 115. Structures of **278** and **279**.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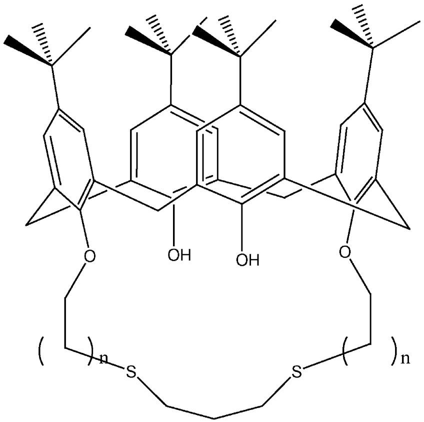

281

Fig. 116. Structures of **280** and **281**.

metal complexes and have reported that the cation–π interactions between the macrocycles and the alkali metals studied play a major role in tuning the luminescent properties of the host [224]. They found that the fluorescent quantum yields of calixarene complexes with alkali metals follows a precise trend for **287** and **288**, i.e. decreasing with increasing atomic numbers from potassium to caesium (Fig. 120). They exploited this interaction to determine the association constants between the calixarene derivatives and the metal ions studied.

Fluorescent chemosensors for cations typically consist of a cation recognition unit (an ionophore which in the examples studied here are calixarene-based) and a fluorogenic unit (fluorophore) linked by a spacer unit. Determination of calcium ions in biological systems has attracted much interest as the calcium ion is a vital link in excitation–contraction coupling; the regulation of intracellular calcium levels directly modulates cardiac and smooth muscle function. Xu and co-workers designed a highly selective calix[4]arene-based fluorescent probe for Ca(II) ions which showed considerably selectivity over ammonium, alkali and other alkaline earth cations [225]. The fluorescent enhancement of the calcium complex relative to the free ligand is reported as 260:1, considerably larger than all other calcium chromogenic receptors previously reported. The fluorescence enhancement upon complexation of the calcium ion is a result of the lone pair of the amide nitrogen ion, now bound to the calcium ion upon complex formation, no longer being available to quench the anthracene fluorescence due to intramolecular electron transfer. These same authors later published a similar study using the same fluorionphore for the detection of Cu(II) and Co(II) [226] (Fig. 121).

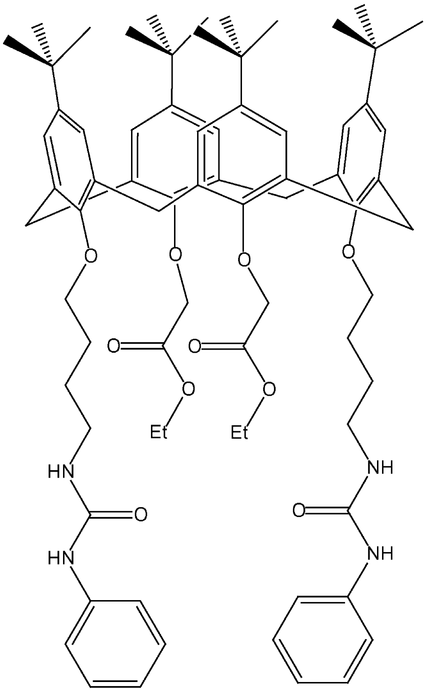
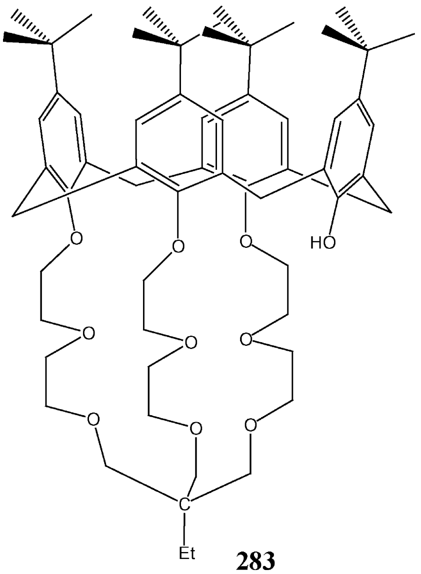

282

Fig. 117. Structure of **282**.

Chang and co-workers isolated a fluorogenic benzothiazolyl calix[4]arene-crown-5-based ionophore which selectively complexed calcium ions in aqueous media (dioxane-H_2O ratio of 80:20) [227]. The fluorescence behaviour of **294**, the synthesis of which is shown in Fig. 122, changed significantly upon addition of Ca(II) ions, and did not respond to additions of Li(I), Na(I), Mg(II) or K(I) ions. The change in fluorescent signal was attributed to the deprotonation of the phenol moiety assisted by the interaction with the calcium ion. Unfortunately, higher water content solvents (dioxane-H_2O ratio of 50:50) significantly affected the photoluminescence efficiency of the receptor and also resulted in a loss of selectivity towards the calcium ions. Chang later prepared the dinitro derivative of **292** and found the resulting ionophore to be selective for barium in the presence of other alkali and alkaline earth metals [228].

Kim et al. also developed a Ca(II)-selective chromoionophore which was based on the selective ionophoric properties of calix[4]arene diamides [229]. The calixarene substructure was functionalised with benzothiazolium ion moieties which exhibited a pronounced Ca(II) selectivity in aqueous methanol, even in the presence of competing Na(I), K(I) and Mg(II) ions of physiologically importance (Fig. 123). Given the free phenolic units in the ionophoric ligand, as expected, the ionophore also displayed pH sensitivity in its absorption behaviour, which could allow for the use of the ionophore as a new pH-probe in the region of pH 6.5.



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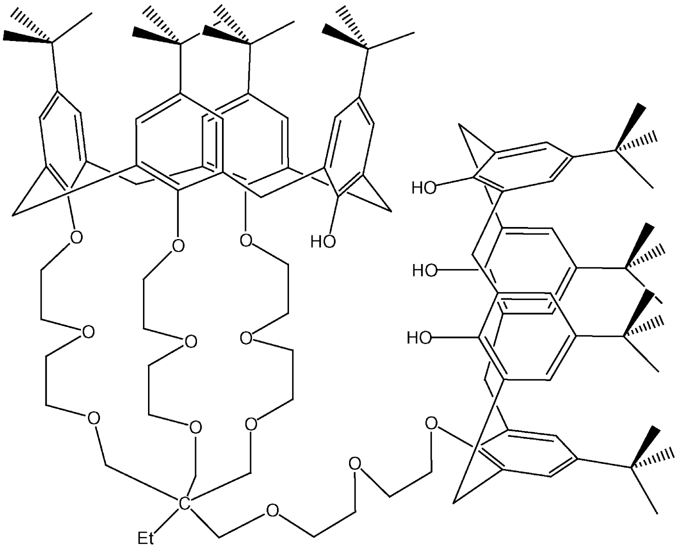
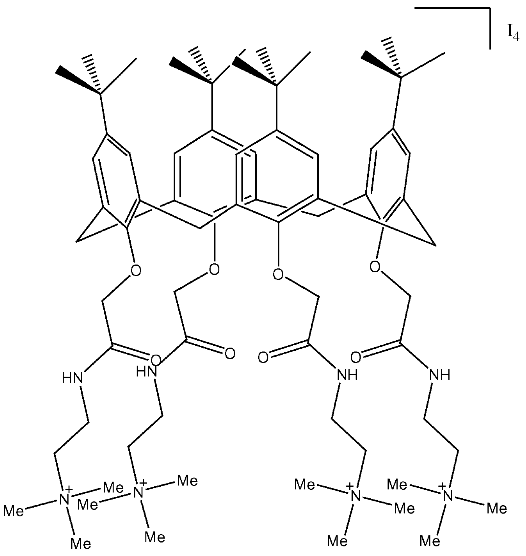


284

Fig. 118. Structures of **283** and **284**.



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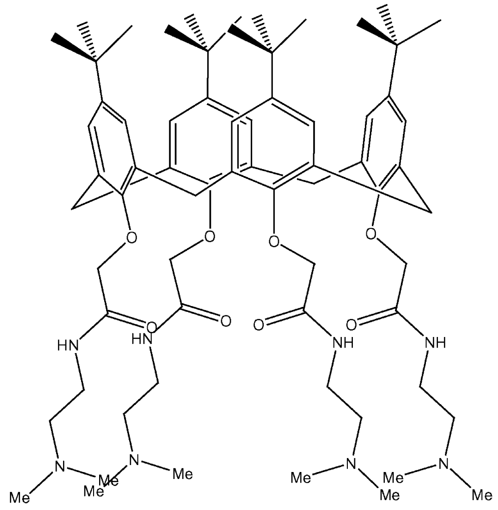
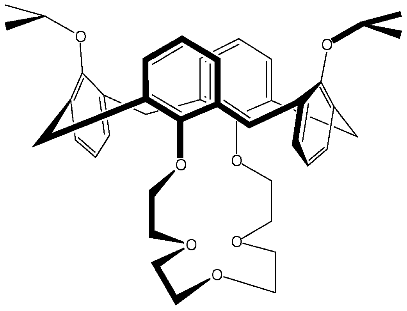


286

Fig. 119. Structures of **285** and **286**.



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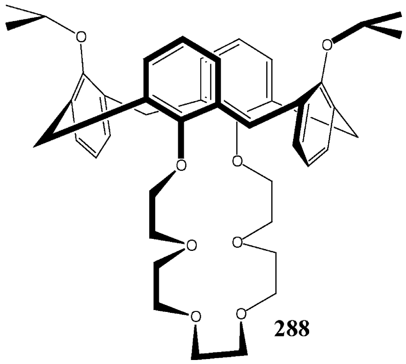

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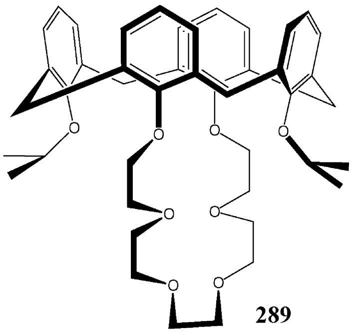


289

Fig. 120. Series of calix[4]arene-crown-6 derivatives, **287–289**.

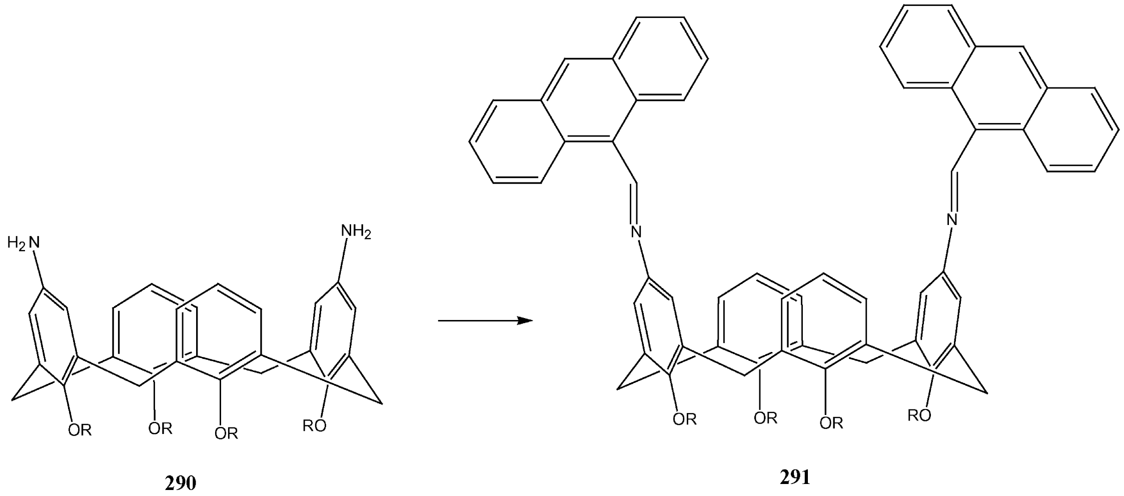


Fig. 121. Structure of **291**, used as fluorescent probe for Ca(II) and its precursor ligand, **290**.

Dumazet-Bonnamour and co-workers have also looked at chromogenic diamide-functionalised calix[4]arenes for the determination of a series of metal ions [230]. They reported the syntheses of a number of amide-substituted azocalixarenes: **297**, bearing one tertiary amide group at the lower rim of the phenylazocalixarene, **296** and **299** with two, and **298** with four (Fig. 124). Their conformations were studied by ^{1}H and ^{13}C NMR spectroscopy and X-ray diffraction analysis. They used atomic absorption spectrometry studies to determine the extraction properties of **298** and **299** towards Na(I), K(I), Mg(II), Ca(II), Mn(II), Ni(II), Cu(II), Pb(II) and Cd(II) ions and found that all three calix[4]arene derivatives favour the complexation of K(I) ion.

Kim et al. investigated the use of calix[4]monocrowns having diazophenol units with mono- and dialkylated compounds

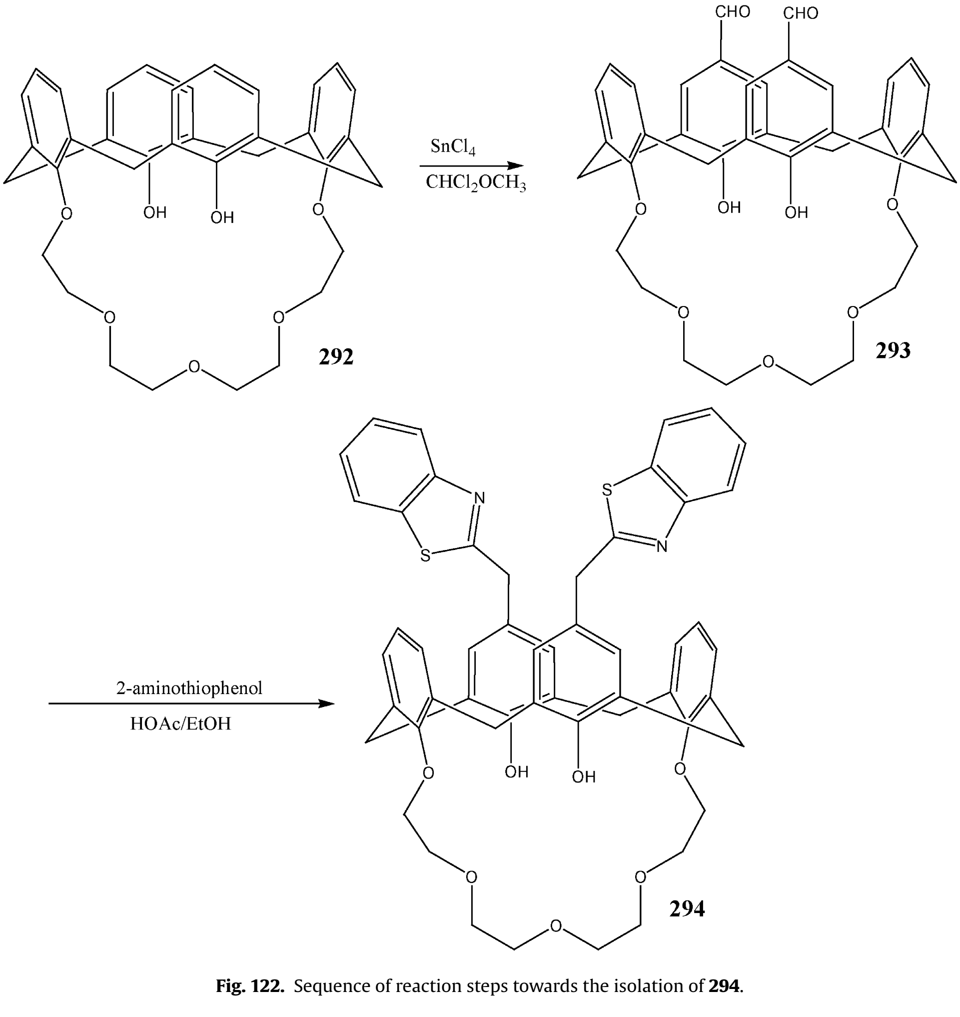
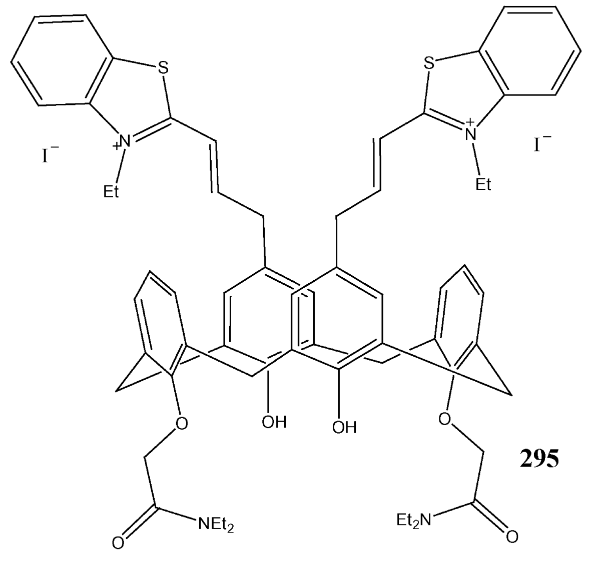


Fig. 122. Sequence of reaction steps towards the isolation of **294**.



295

Fig. 123. Structure of **295**.

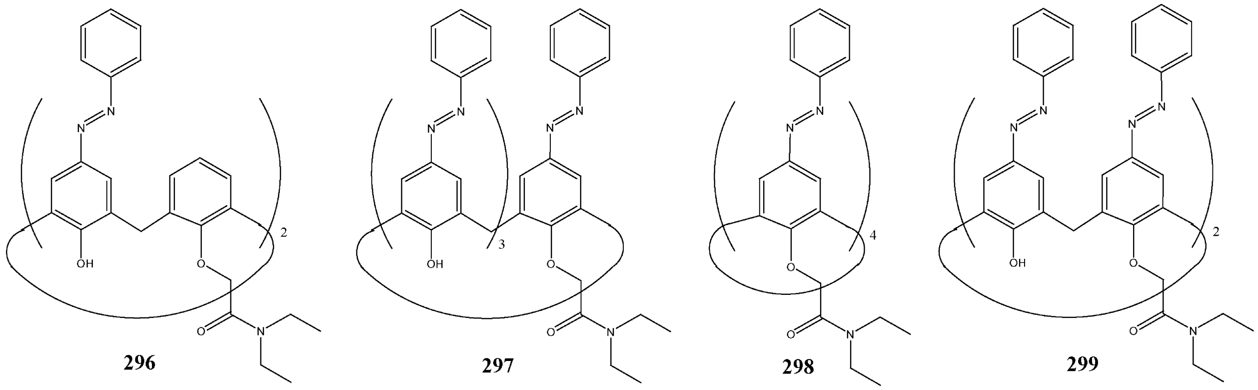
as potential chromogenic sensors [231]. They also wanted to investigate if there was any conformational dependence for the wavelength changes upon complex formation. They synthesised the series of compounds shown in Fig. 125 and measured the colour change upon metal ion complexation by UV/vis spectroscopy. Their main finding were that the diazo-calixcrown-6 (**303**) in the cone conformation showed a bathochromic shift upon Ca(II) ion complexation, while **301**, which is not a calix[4]crown, did not show any UV band shift. For monopropylated diazo-coupled calixcrown-6 (**306**), they found a marked UV band separation, a red and a blue shift. They assigned the former shift to the participation of the oxygen atom of the proximal phenyloxy group, and the latter to the oxygen atom of the distal propyloxy group. For the dialkylated azophenols (**305**, **307** and **308**), a hypochromic shift was noted driven by an electrostatic interaction between the oxygen atom of the alkyloxy group and the metal cation as well as the bathochromic band shift, which was explained by the π-metal complexation between the proximal azophenyl group and the metal ion.

In a later development of this work, the compounds, shown in Fig. 126, were isolated and their use as components in logic circuits investigated [232]. They synthesised a Pb(II) ion selective novel calixarene molecule containing pendant pyrene groups. The fluorescence intensity of **312** was shown to be selectively quenched upon addition of Pb(II) ion, which was explained by selective complexation with two amide oxygen atoms followed by a reverse photoelectron transfer; that is, electron transfer from a pyrene unit to an electron deficient carbonyl group occurs by metal ion complexation [233–235]. When $HClO_4$ was added as an acid and triethylamine as a base independently in the solution of **312**, the fluorescence intensity was markedly reduced in both cases. In the case of using the acid, the protonated oxygen atom behaves as a PET-acceptor to give a quenching fluorescence (reverse-PET). On the other hand, in the presence of triethylamine as a base, nitrogen anion was first formed by the base and acts as a PET-donor, that is, electron transfer from the nitrogen anion to the pyrene unit, giving a quenched fluorescence (normal PET). NOR logic gates could be operated by the combinational inputs of triethylamine and lead perchlorate. In addition, an XNOR gate was also operated when neither (triethylamine and HClO4) or both of two inputs are added.

Kim et al. have focussed more recently on a boron dipyrromethene (BODIPY) derivative of calix[4]arene, which showed a remarkable selectivity towards Ca(II) ion, see Fig. 127 [236]. BODIPY is a well-known constituent of fluorescence dyes with high quantum yields, large extinction coefficients and narrow emission bands. The spectral changes noted in the presence of Ca(II) ion were remarkable given that no other alkaline earth or alkali metal elicited any photophysical response.

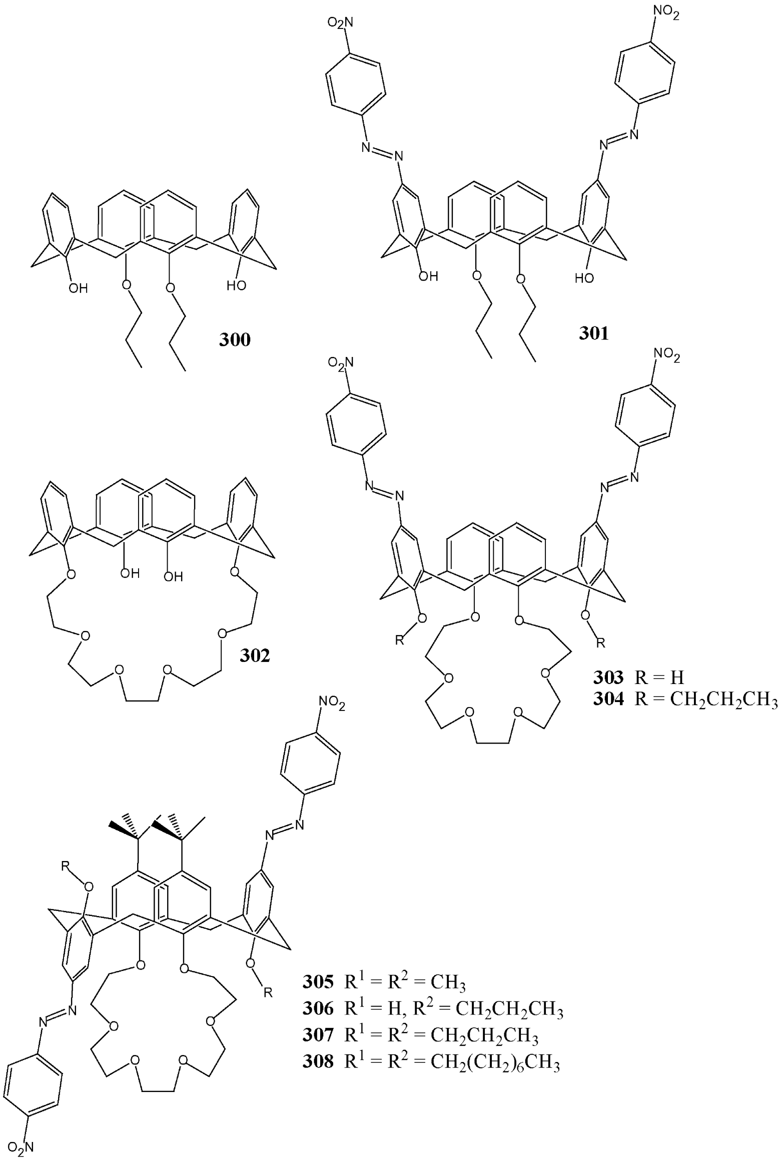
Sodium and potassium ion concentrations are also of interest as both are found in ion channels and ion pumps in living systems. Disorders in the metabolism of either ion, leading to disrupted homeostasis within the body, can severely affect the overall wellbring of the individual. A number of calixarene derivatives have found application as sensors for these ions including those reported by Tuntulani and co-workers [237] (Fig. 128). The quenching of the fluorescence intensity of **315** upon addition of Na(I) ions appeared to be linearly dependent on ion concentration and did not appear to be affected by the concentration of Li(I) or K(I) ions.

Tuntulani and co-workers had earlier reported photoswitchable receptors based on crown ether calix[4]arenes (**317** and **318**) in which the azo benzene unit was connected to the glycolic chains of the calix[4]crown [238] (Fig. 129). They studied their isomerization and inclusion properties. It was thought that the azobenzene crown ether calix[4]arenes was capable of forming complexes with both Na(I) and K(I) ions, and this group was interested in investigating the possibility of switching the complexation selectivity of the ionophores between the two cationic guests. The complexation studies showed that for **317**, the percentage of *cis* isomer increased in the presence of Na(I) ion while the amount of *trans* isomer increased in the presence of K(I) ion and the authors deducted that the *cis* form is suitable for binding Na(I) ions while the *trans* form is appropriate for K(I) ions. In case of compound **318**, it was found that *cis* to *trans* isomerization occurred to a reduced extent in the presence of K(I) ion.



296 **297** **298** **299**

Fig. 124. Series of chromogenic diamide functionalised calix[4]arenes, **296**–**299**.



300

301

302

303 R = H
304 R = $CH_2CH_2CH_3$

305 $R^1 = R^2 = CH_3$
306 $R^1 = H, R^2 = CH_2CH_2CH_3$
307 $R^1 = R^2 = CH_2CH_2CH_3$
308 $R^1 = R^2 = CH_2(CH_2)_6CH_3$

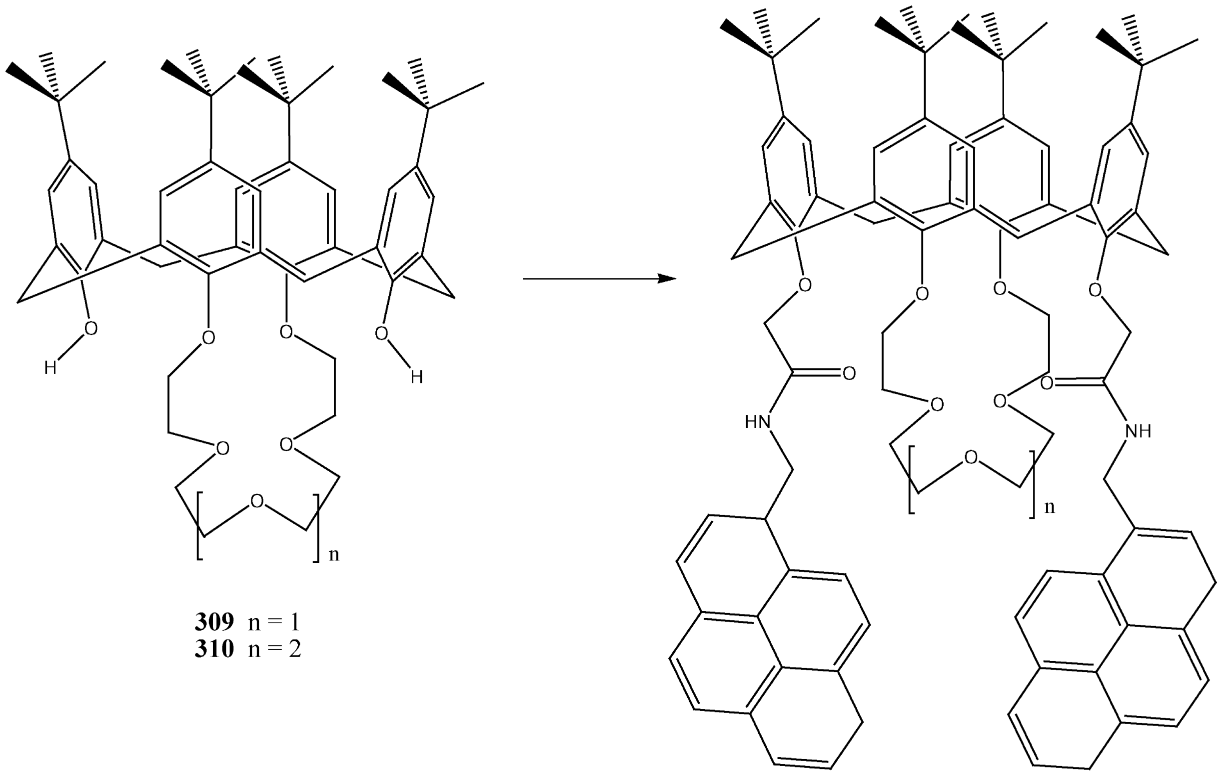
Fig. 125. Series of calix[4]arene-crown ethers, **300–308**.

Liu et al. reported the synthesis of bis(azophenol)-calix[4]arenes possessing multiple chromogenic donors (Fig. 130) and their cation binding ability for the alkali metal ions Na(I), K(I), Rb(I) and Cs(I) [239]. Host **319**, as shown in Fig. 130, was very selective for sodium ions, even in the presence of a large excess of other alkali metals. The chromophoric unit on **319** and **320** contains electron-withdrawing nitro groups, which would enhance the ionisation of hydroxy groups resulting in stronger electrostatic interaction with metal ions, giving the observed enhanced cation binding ability and selectivity for these two hosts.

Rockicki and co-workers have shown that bicyclocalix[4]arene derived crown ethers **322** and **323** are selective towards potassium and caesium ions [240] (Fig. 131). In the presence of these cations, the UV/vis spectra of **322** and **323** undergo significant changes as a result of the deprotonation of the *p*-nitrophenol unit and the changes were found to be linearly dependent on the concentration of the two cations.

Although earliest studies with calixarene-based ionophores concentrated on the complexation of alkali and alkaline earth metals, a number of more recent studies have focussed on complexation of transition metal complexes. Huang and co-workers developed a fluorescent sensor, derived from a calix[4]arene which possesses two 3-alkoxy-2-naphthoic acid moieties (**324**), whose fluorescence intensity was quenched in the presence of Cu(II) and Fe(III) ions but not in the presence of other cations [241] (Fig. 132). They also found that the quenching behaviour of the sensor was directly related to the pH of the solution, presumably as a result of the deprotonation of the carboxylate group. The electron-rich carboxylate group, particularly in the deprotonated form, can act as an electron donor and quench the aromatic fluorophore.

Rao and co-workers in a more recent paper investigated the photophysical behaviour of anthracene-anchored 1,3-di-derivatised calix[4]arenes towards divalent transition metal ions, namely Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) [242] (Fig. 133). Initial photophysical studies on the ligands themselves found that the conjugated imine moiety in **326** is responsible for the fluorescence quenching of the anthryl unit owing to the photo-induced electron transfer from the imine-N to the anthryl π-system. Binding of a metal ion in the central cavity prevents this electron transfer. As expected, fluorescent enhancement of **326** in the presence of



309 n = 1
310 n = 2

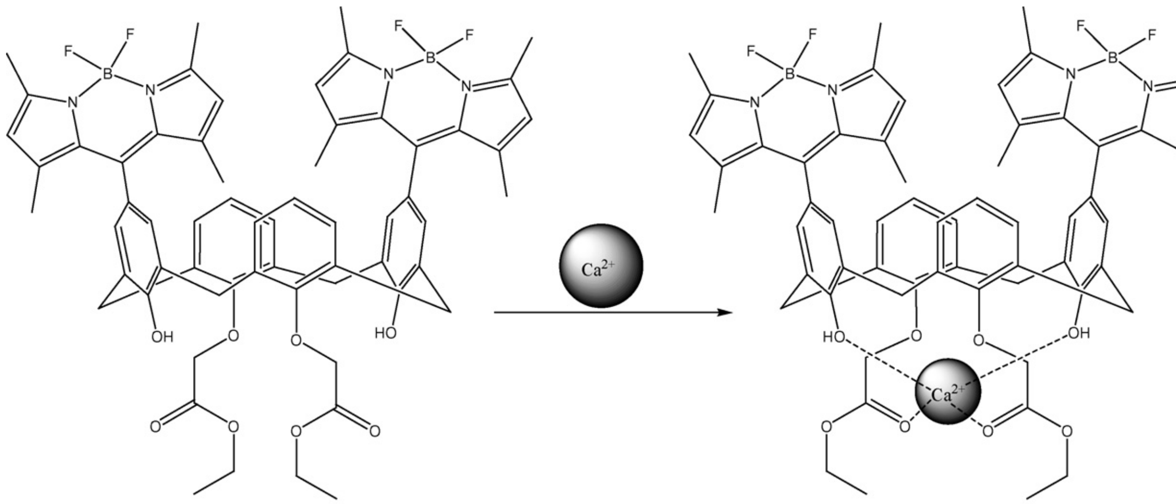
311 n = 1
312 n = 2

Fig. 126. Series of calix[4]arene crown ethers, **309**–**312**.

metal ions, specifically Fe(II) and Cu(II) ions, is much higher than that observed for **325** given the presence of the imine moiety on the former ligand.

In an extension of this work, Rao and co-workers investigated the ability of the lower rim di-amine derivative synthesised through *O*-alkylation to recognize Cd(II), Hg(II) and Pb(II) ions using emission spectroscopy [243]. They observed two types of interaction between the calix[4]arene ionophore and the metal ion, one in which the metal ion is bound at the lower rim, the other in which the metal ion interacts through the hydrophobic arene cavity and which interaction occurred depended on the nature of the metal ions present (Fig. 134). Specifically, Hg(II) ions only form complexes *via* the first type of interaction but the other two heavy metal ions can interact *via* both mechanisms.

Among fluorophores studied as chemosensors, pyrenes are one of the most useful fluorogenic units because they exhibit not only a well-defined monomer emission centered around 400 nm but also an efficient excimer emission around 480 nm. Jin et al. [244] and Shinkai and co-workers [245,246] had previously reported chemosensors in which the relative emission ratio of pyrene



313

314

Fig. 127. Structure of BODIPY substituted calix[4]arene, **313**, and its Ca(II) complex, **314**.

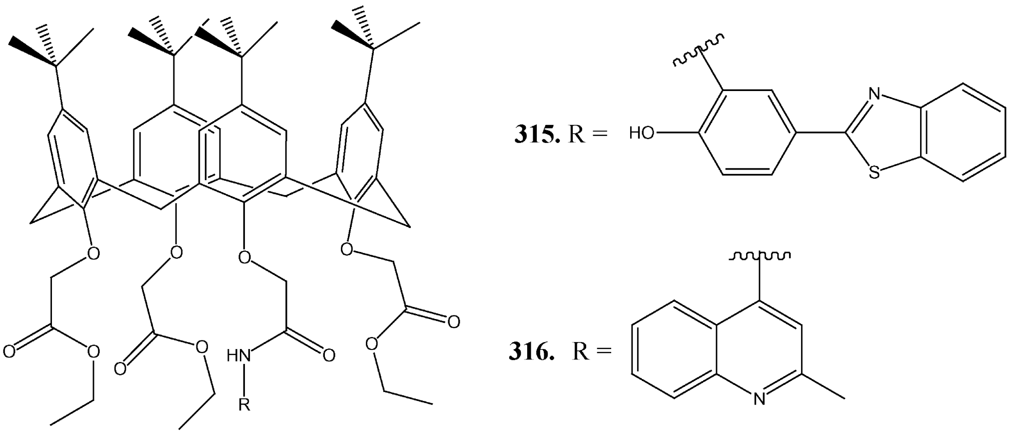
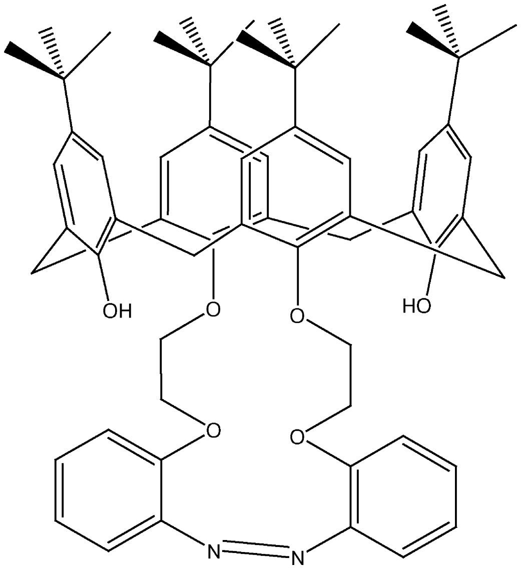


Fig. 128. Structures of **315** and **316**.

excimer to its monomer depended on the addition of metal ions. In a more recent paper, Kim et al. have reported a chromogenic calix[4]arene **328**–**330** with two facing amide groups linked to fluorescent pyrene units [247] (Fig. 135). Changes in the fluorescent spectrum of **328** in the presence of a number of metal ions indicated a high selectivity for In(III) ions over the other metal ions tested. Although compound **330** exhibited the same binding behaviour towards metal ions as **328**, as evidenced by NMR spectroscopy, it emits a considerably weaker fluorescence, which is attributed to quenching by electron transfer from the pyrene units to the nitro groups of the phenylazo moieties.

Tokita et al. have prepared a chromoionophore-derived calix[4]crown, **331**, possessing an effective signal-controllable function which responds to the presence of low concentrations of cations [248] (Fig. 136). They developed a chromoionophore which showed a colorimetric effect (“off–on” step) with calcium(II) ion but in the presence of a second ion (K(I)) which binds to **331** with a greater affinity than Ca(II) and in addition induces almost no colorimetric effect, the second ion would release the first ion efficiently to bring about an active “on–off” signal switch.

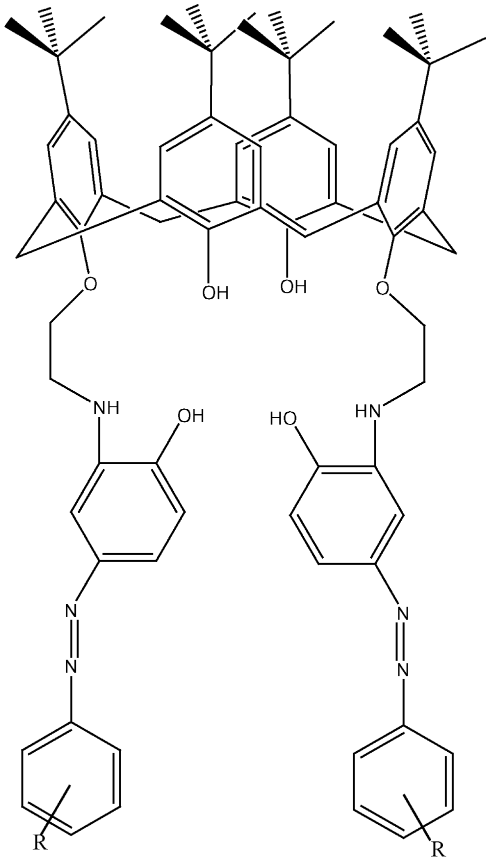


317 R = H
318 R = CH_3

Fig. 129. Structures of **317** and **318**.

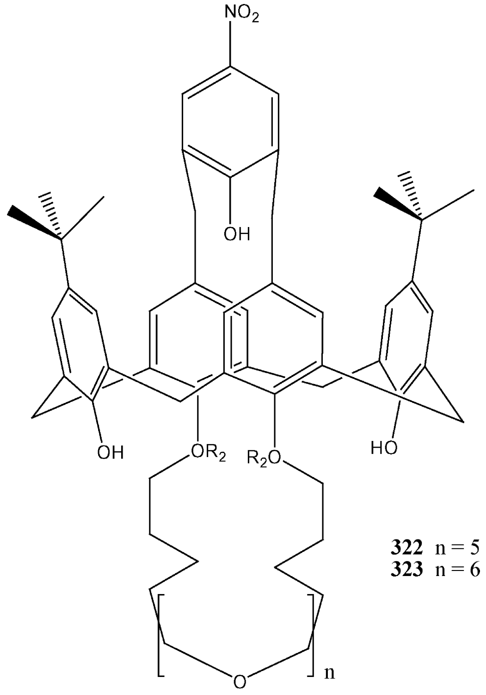
Bis(indoaniline)-derived calix[4]crown-5, **331**, was employed as the chromoionophore in these studies which showed promising results.

Modification of calixarenes with pyrene fluorophores has also been used by Kim and co-workers to develop a bifunctional fluorescent calix[4]arene chemosensor for both a cation and anion [249]. The fluorogenic calix[4]arene shown in Fig. 137 exhibited a characteristic excimer fluorescence in the absence of guest species but the emission is quenched in the presence of Pb(II) and Co(II) ions



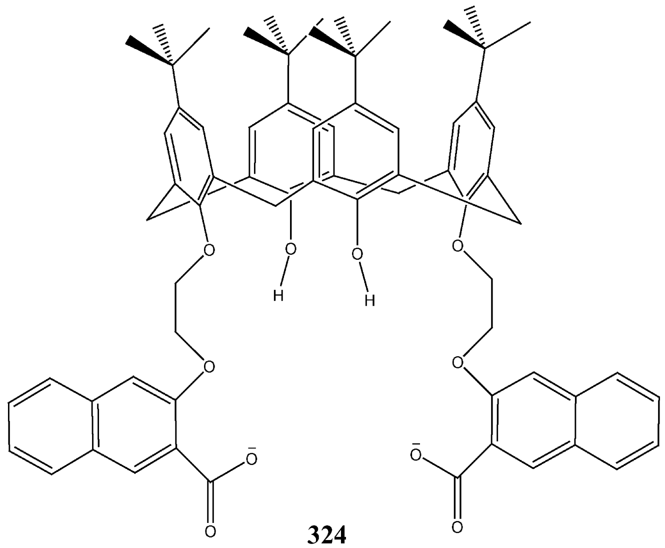
319 R = p-NO_2
320 R = o-NO_2
321 R = p-Cl

Fig. 130. Series of calix[4]arene derivatives, **319**–**321**, bearing multiple chromogenic sites.



322 n = 5
323 n = 6

Fig. 131. Structures of **322** and **323**.



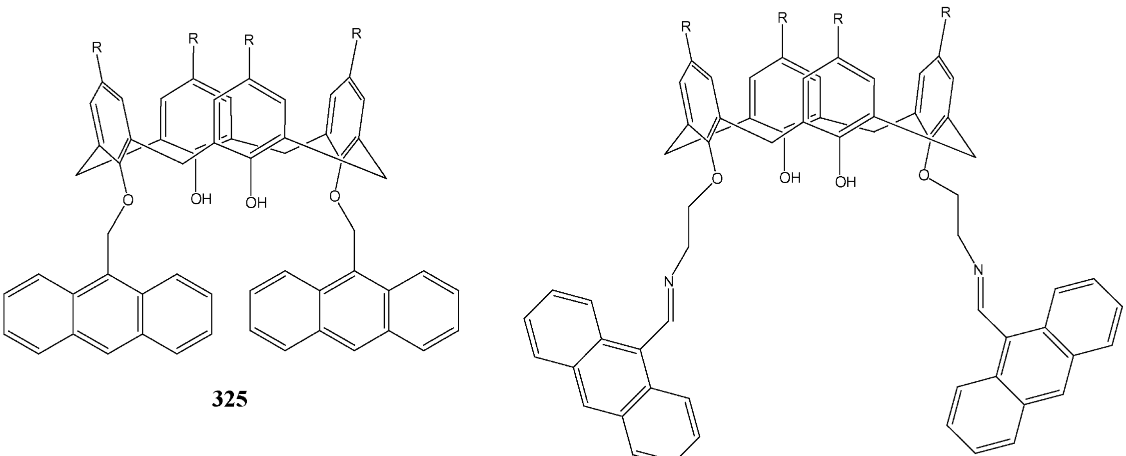
324

Fig. 132. Structure of **324**.

as a result of the combination of the heavy metal-effect, reverse photoelectron transfer (PET) and induced conformational changes. In addition, the presence of the F^- anion within the cavity also resulted in a decrease in the emission of the calix[4]arene-based chemosensor **332**, again based on a PET effect. The binding constants for metal species were on average 2–3 orders of magnitude greater for the cationic guest species. No competition studies were carried out to determine the selectivity of the reported ligand at this time.

In a related paper, these same workers isolated fluorogenic calix[4]arenes (**333** and **334**) bearing a pendent ethyleneamine on their triazacrown rings, with both being isolated in the cone conformation (Fig. 138) [250]. Compared with **336**, free **333** and **334** display relatively weak emission, which is though to be as a result of a PET process from the pendent amine group ($-CH_2CH_2NH_2$) to the fluorogenic pyrenes. Addition of various metal ions or anions to the solution of **333** or **334** reduces the PET because the pendent alkylamine takes part in the complexation, causing their fluorescence spectra to be changed. In the presence of a heavy metal Pb(II) cation, the monomer emission of the pyrene moiety of **333** and **334** is enhanced while the excimer emission is quenched, which is assigned to conformational changes of the facing carbonyl groups as well as to the participation of the ethyleneamine into the three-dimensional Pb(II) ion encapsulation. Upon addition of alkali metal ions, however, to both **333** and **334**, both monomer and excimer emissions are observed to increase, which is attributable to a chelation enhanced fluorescence and the retained conformations. Again for these calix[4]arenes, both **333** and **334** show a high selectivity for F^- anions over other anions tested. When the F^- anion is bound to **333** or **334** by hydrogen bonding between the amide NH of the triazacrown ring and F^-, both their monomer and excimer emissions are weakened due to PET from the bound F^- to the pyrene units.

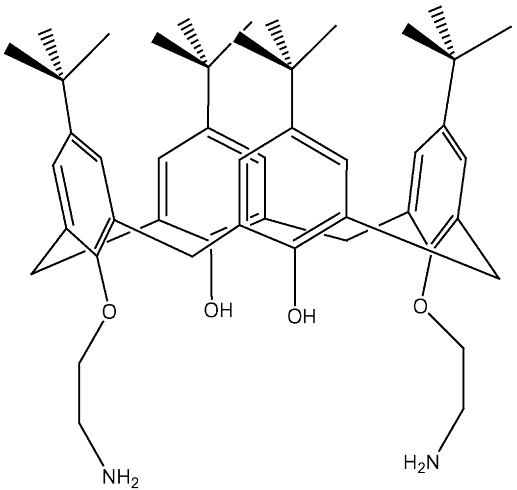
A paper by Ji et al. reported a similar calix[4]arene-based chemosensor with a pyrene fluorophore (**337**), whose excimer intensity was quenched in the presence of alkali and alkaline earth metals [251] (Fig. 139). They did report, however, that a PVC membrane was fabricated which responded to the presence of Sr(II) ions.



325

326

Fig. 133. Structures of **325** and **326**



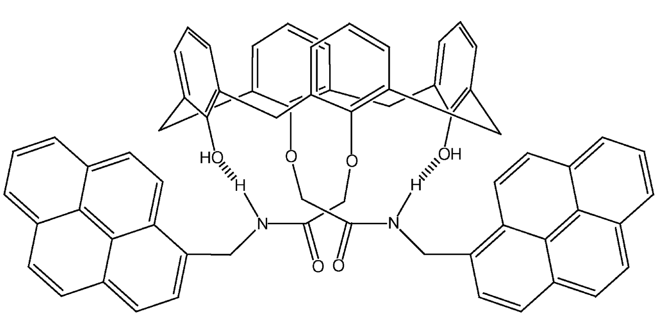
327

Fig. 134. Structure of **327**.

Copper(II) is not only a significant environmental pollutant but is an essential component of many enzymatic processes. Homeostasis of copper(II) levels within the body is essential for healthy living. Many of the Cu(II) sensors developed have been based on monoamide–diamine [252], diamide–diamine [253–255], triamine [256], tetraamine [257,258], hydroxamic acid [259] or *O*-acylhydroxylamine [260] based motifs as the ionophores, However, owing to protonation under acidic conditions, amino-based fluorescent sensors could show sensitive recognition for Cu(II) ions only within narrow pH regions, mostly under neutral conditions. A new calix[4]arene-based fluorescent compound with two thio-ether groups as ionophore and one 3-alkoxy-2-naphthoic acid moiety as fluorophore (**338**) was designed by Huang and co-workers [261] (Fig. 140). This new molecule exhibited highly selective binding of Cu(II) ions over alkali, alkaline earth and some transition metal ions, including Co(II), Ni(II), Zn(II), Mn(II), Cd(II), Pb(II), Hg(II), Ag(I) and Cu(I) in $CH_3OH–H_2O$ (2:1) within a wide pH region. These workers also noted that by controlling the pH of the solution, resulting in a protonation/deprotonation of the carboxylate group on the naphthyl ring, the fluorescence of the system could be turned on and off as the bound copper ion is bound/released respectively, acting as a molecular switch.

Huang and co-workers also went on to develop a new chemosensor *via* the alkylation of *p*-*tert*-butyl-calix[4]arene with three *N*,*N*-diethylacetamide groups and one methyl 3-ethoxy-naphthalene-2-carboxylate [262]. This chemosensor (**339**) exhibited a highly selective fluorescent response to Pb(II) over alkali, alkaline earth metal ions and some transition metal ions in $CH_3CN–H_2O$ (Fig. 141). Once again, this group showed the dependence of the analytical response on the pH of the analyte solution as OH^- competes with the host molecule for the Pb(II) cation.

In general, many fluorescent-based chemosensors for transition metal and heavy metal cations rely on quenching of a fluorescent signal to indicate complexation by a selective ionophore. More challenging has been the development of chemosensors whose fluorescent intensity is enhanced in the presence of such cations. Chang and co-workers reported in 2002 a fluorogenic ionophore based on the *p*-*tert*-butylcalix[4]arene-azacrown ethers



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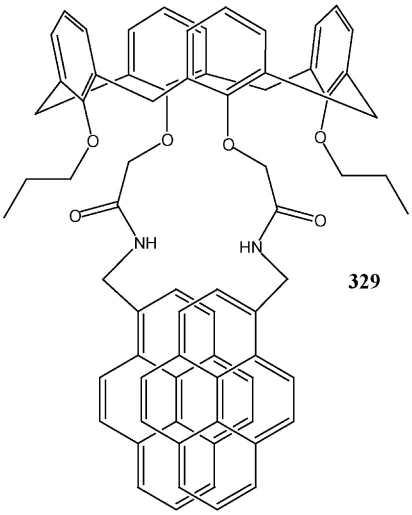

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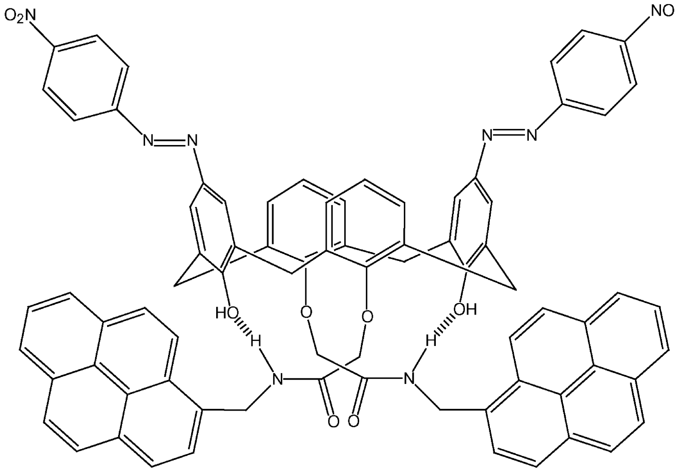

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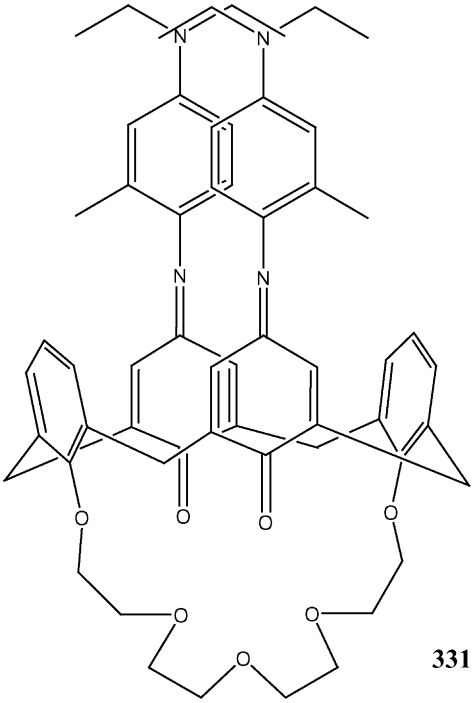
Fig. 135. Pyrene substituted calix[4]arenes, **328**–**330**.

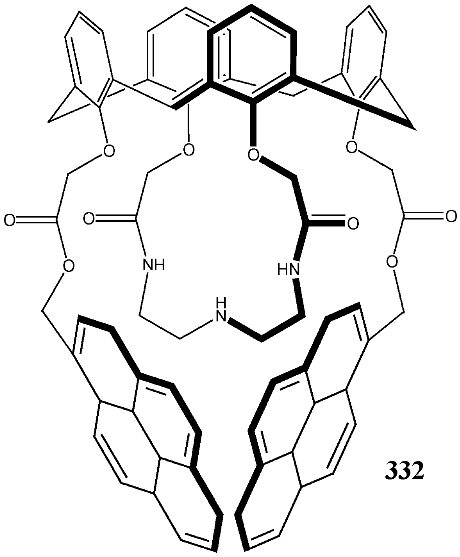


331

Fig. 136. Structure of **331**.

having anthrylmethyl moieties as the fluorophore [263]. Compound **341** exhibited pronounced selectivity with good sensitivity towards Hg(II) ions and which importantly used the signalling mode OFF–ON rather than ON–OFF, which is preferential in sensor development (Fig. 142).

In a later report by Banthia and Samanta, the synthesis of a calix[4]azacrown and a 4-aminophthalimide-appended calix[4]azacrown was detailed and they investigated the photophysical properties of these molecules in the presence of a series of transition metal ions [264]. The fluorescence intensity of the *N*-(4-aminophthalimidoethyl)calix[4]azacrown (**343**) (Fig. 143) increased in the presence of Fe(III), Ni(II), Cu(II) and Zn(II) ions, with the largest association constants determined for Fe(III) and Cu(II) ions ($K = 2.3 \times 10^5$ M^{-1} and 1.6×10^5 M^{-1}, respectively).



332

Fig. 137. Structure of **333**.

Harrowfield et al. synthesised a series of calix[4]arene derivatives (Fig. 144) in which the functional group contains a tridentate binding site suitable for the coordination of rare earth metal cations [265]. This group chose the mode of functionalisation exhibited by their ligands as it would differ significantly from that widely explored elsewhere, in the hope that novel relative orientations of rare earth metal and calixarene cavity moieties could be obtained. **344** was assigned cone conformation with **346** and **348** assigned partial cone and **345** was shown to be in both the cone and 1,2-alternate conformations. Whilst complexation of Eu(III) could be achieved, water was found to be a competing ligand and caused strong quenching of the lanthanide luminescence. Overall the ligands were shown to be poor binders of rare earth metal cations unless the ligands were in the anionic form.

Bünzli and co-workers prepared a *p-tert*-butylcalix[4]arene functionalised at its lower rim with ether-amide pendant arms which they showed could act as an inorganic–organic receptor [266]. They prepared a series of lanthanide complexes (Eu(III), Gd(III), Tb(III) and Lu(III)) and a crystal structure of the Lu(III) complex showed that the metal ion was 9-coordinate. The structure also identified an ether molecule inserted into the hydrophobic cavity defined by the aromatic rings of the upper-rim. NMR, IR, EPR and luminescent spectral studies on the other lanthanide complexes indicated that all the complexes had a similar structure. However, the photophysical properties of all the complexes were poor with quantum yields measured in acetonitrile relatively low.

Bagatin and Toma reported a calix[4]arene molecule which had been modified at the 1,3-positions with 8-hydroxyquinoline to generate a receptor which strongly bound Eu(III) and Tb(III) ions [267]. They first synthesised a *bis*-bromopropoxycalix[4]arene derivative by reacting *p-tert*-butylcalix[4]arene with $Br(CH_2)_3Br$ in the presence of K_2CO_3 and then reacting the 1,3-disubstituted derivative with 8-hydroxyquinoline in the presence of K_2CO_3 in acetonitrile to isolate the new receptor. However, the emission quantum yield was substantially lower than expected for the [Eu(III)·**351**] complex shown in Fig. 145, presumably because the lanthanide ion promotes intersystem crossing, thus lowering the quantum yield of the 8-oxyquinoline singlet state. On examining the phosphorescent spectra, it was noted that the emission from the [Eu(III)·**351**] complex matched the absorption band of the calixarene moiety at 280 nm, rather than the absorption of the 8-oxyquinoline group at 320 nm. The researchers concluded that the attachment of the 8-oxyquinoline moiety to the calixarene backbone facilitated the binding of the lanthanide ion though the lower-rim oxygen atoms as well as to the 8-oxyquinoline group and this interpretation of the binding of the lanthanide ions was supported by preliminary MM^+ molecular mechanics calculations. They later published a related study on the formation of a Zn(II) complex of this ionophore in the presence of a phenanthroline-based co-ligand [268].

Casnati et al. have also investigated the use of fluoroionophores for determination of lanthanide ion concentrations [269]. Ligands **352** and **353** are shown in Fig. 146 and their complexes with spherical cations including the lanthanides Yb(III), Nd(III) and Er(III) in acetonitrile were investigated. Surprisingly, complexation of **352** and **353** with alkali cations, Hg(II), Mg(II) and Zn(II) resulted in no changes in the absorption or emission spectra of the ligands which was unexpected given the significant shifts observed in the quinoline-functionalised crown ether complexes isolated by Prodi et al. [270–273]. However, these workers found that alkali and alkaline earth metal ion complexes exhibited a bathochromic shift and a quenching of the fluorescence band with respect to the free ligand, whereas the corresponding complexes of **353** present hypsochromic shifts of λ_{max} and an increase of fluorescence intensities for alkaline earth cation complexes. NMR spectroscopic data and semiempirical calculations on **352** show the presence of strong H-

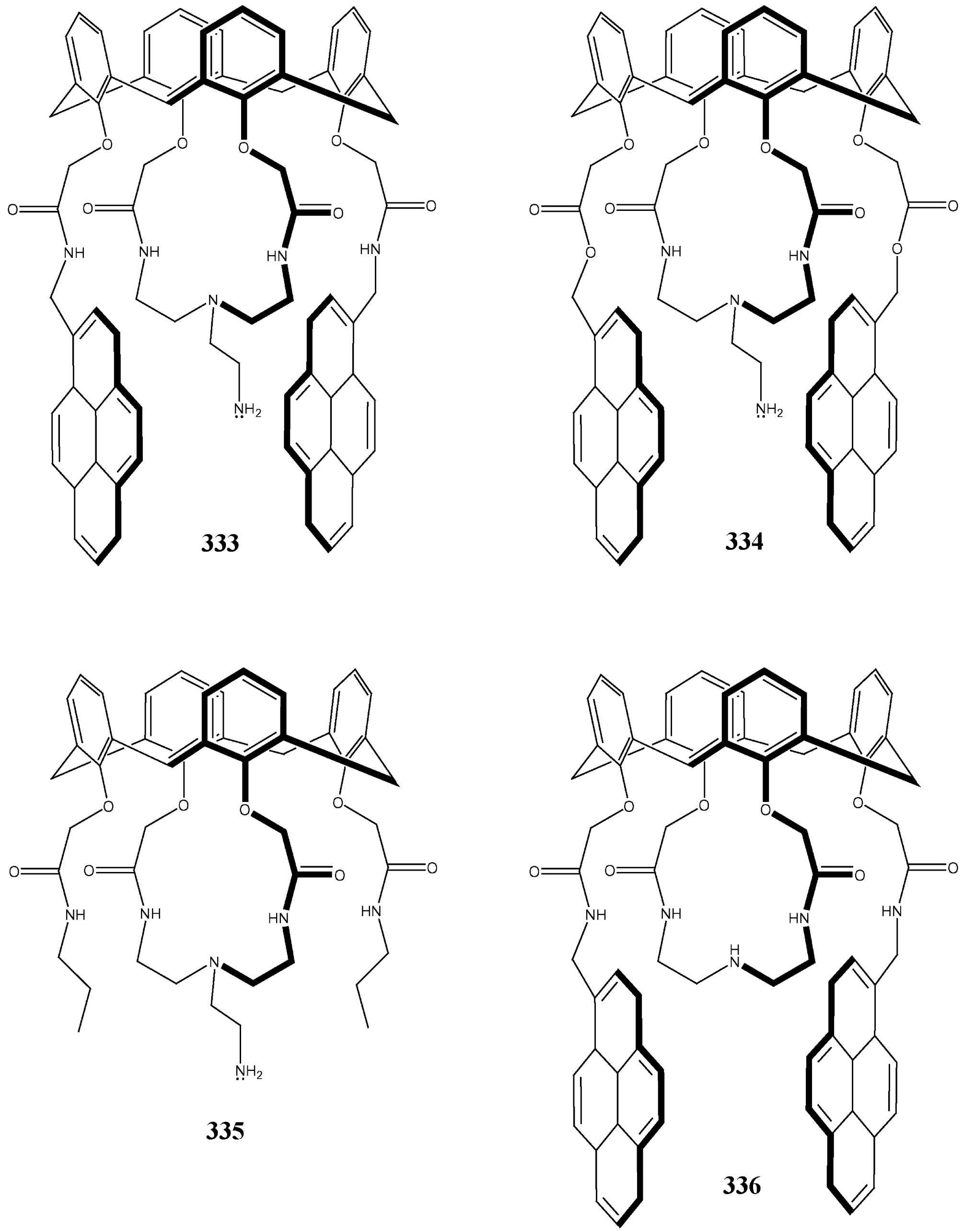
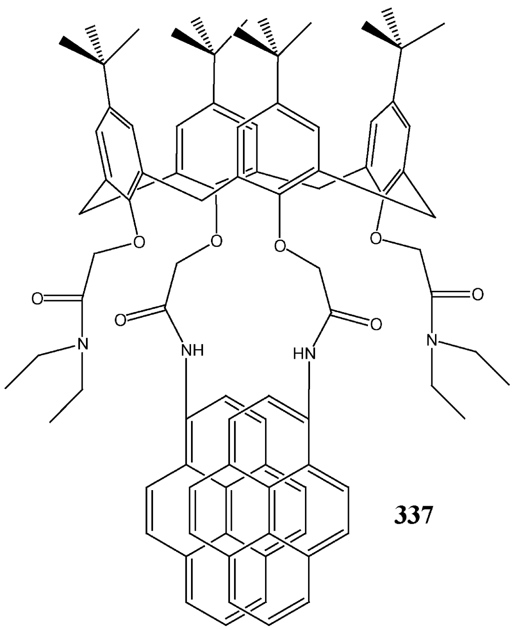


Fig. 138. Series of fluorogenic calix[4]arenes, **333**–**336**.

bonding between a proton on the quinoline moiety and one of the adjacent amide carbonyl groups which would indicate that this difference in the photophysical properties is due to a different mode of coordination of the quinoline nucleus to the metal ion. In the complexes of **352** both the quinoline N and O atoms are coordinated while in complexes of **353** the N atom is too far from the metal ion. Additional studies showed that ligands **352** and **353** do not form complexes with lanthanide ions in methanol but in acetonitrile complexation with Nd(III), Yb(III) and Er(III) ions resulted in a quenching of the fluorescent intensity of the ligands accompanied by an increase in the metal-centered luminescence, which indicates that an efficient energy transfer occurs.

Liu et al. have reported a number of double-armed calix[4]arene derivatives and their interactions with lanthanoid nitrates [45,47,274]. In all cases they found that the flexible donating side-arms allow for fine adjustments of the size and shape of the induced cavity which forms upon complexation with light lanthanoid nitrates. This group have more recently reported preliminary photophysical properties of two calix[4]arene isomers with benzaldehyde moieties when bound to Tb(III) ions [275]. UV/vis spectral shifts of the host compound **356**, upon addition of terbium(III) nitrate, were significant and the authors concluded compound **356** had potential as a chromogenic sensor (Fig. 147).

Gao and co-workers recently reported a novel photo-switchable molecular device based on metal–ionic recognition [276]. They used the photophysical properties of a spirobenzopyran moiety, as, under irradiation, the colourless neutral spiropyran forms are isomerised to their coloured, zwitter-ionic merocyanine form, resulting in a considerable enhancement in fluorescence intensity of the calix[4]arene derivative in the presence of europium(III) (Fig. 148). Such a system may well have application as a molecular logic switch. In two later reports, they studied the same system in

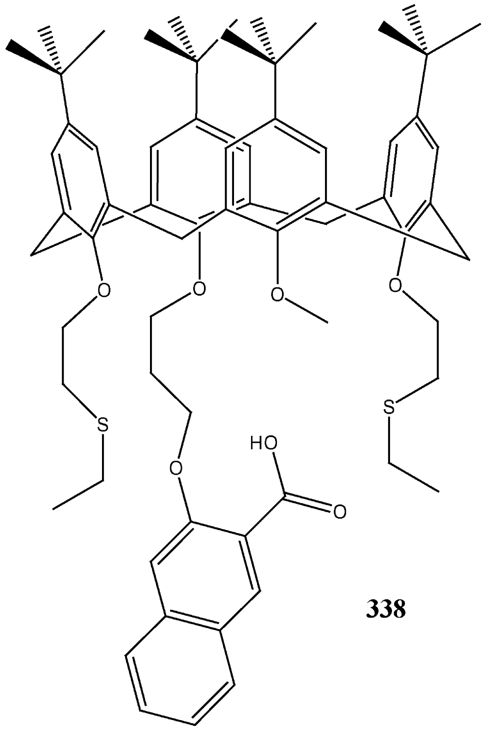


337

Fig. 139. Structure of **337**.

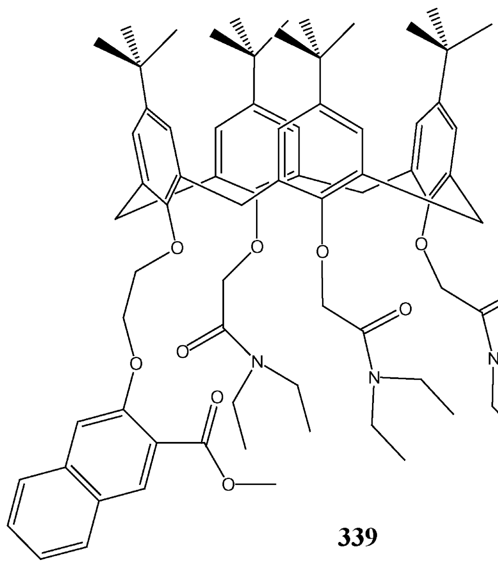
the presence of Mg(II), Ca(II) and also Eu(II) again [277] and in the presence of La(III) ions [278].

Interest in binding of rare earth metals has increased in general in recent years because their unique physical and chemical properties allow their use in a wide variety of electronic, optical and magnetic devices. Naturally the waste materials from related industries have been highlighted as valuable resources themselves and a number of groups have been working on recovery of rare earth metals from such sources. The use of calixarenes has been reported as useful extractants for metal ions [279–287], but the solubility of these complexes has limited their usefulness. Kubota et al. developed a novel calix[4]arene carboxyl derivative which showed remarkably high selectivity for the rare earth metals compared to commercially available extractants, PC-88A and Versatic 10 [288] (Fig. 149). Once again limited solubility in useful organic solvents proved problematic but was overcome through the use of a reversed micellar system, which was used to solubilize the calix[4]arene derivatives. The calixarenes which were not soluble in aliphatic solvents were dissolved by sonication of a reversed micellar solution which in turn was prepared by injecting an appropriate amount of water into an isooctane solution containing a known amount of anionic surfactant, sodium bis(2-ethylhexyl)sulfosuccinate (abbreviated as AOT). Extraction of three metals with the reversed micellar system was conducted by contacting the aqueous solution of metals with the isooctane solution containing either the anionic surfactant, AOT or AOT and **362** in separate stages. The derivatives showed good extraction profiles in the recovery of rare earth metals by using this reversed micellar system.



338

Fig. 140. Structure of **338**.

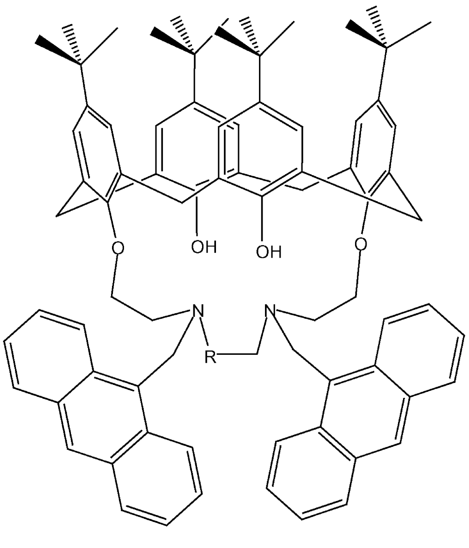


339

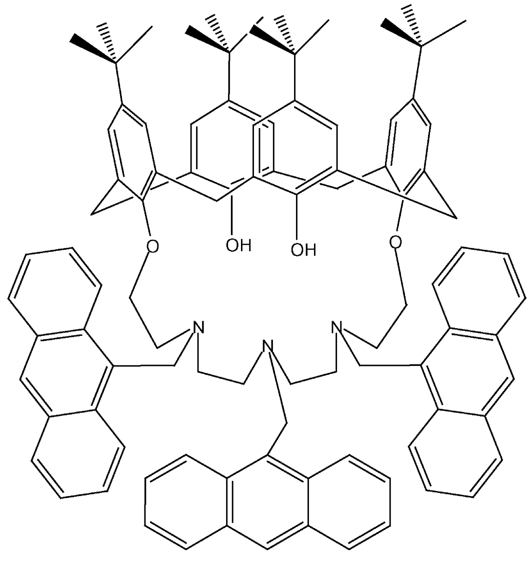
Fig. 141. Structure of **339**.

Whilst a number of calix[4]arene-based chemosensors have been developed for the detection of anions, those mentioned already were also selective for cations. Kim and co-workers have developed a calix[4]arene chemosensor which has been attached *via* amido linkage to two coumarin moieites [289]. Most anionic receptors are based on ligating units in a macrocycle having H-bonding interactions with the anions, such as those reported for calix[4]pyrroles [290]. This group developed a new anion PCT chemosensor which selectively responded to fluoride ions in the presence of other halides and other anionic species. This was ascribed to a PET effect from the fluoride ion to the coumarin. ^{1}H NMR studies showed that the interaction of amide hydrogen atoms with F^- ion promotes the delocalization of π-electrons from the anionic nitrogen atoms to the coumarin units eliciting a change of the π–π transition of the chromophore (Fig. 150).

Sensing harmful compounds is a critical topic for environmental monitoring. Leray, Lebeau and co-workers synthesised a calix[4]arene derivatised with two dansyl fluorophore units which was then grafted onto a mesoporous silica material *via* alkyl chains containing triethoxysilane groups with the intention of the optical sensing of mercury ions in water, as shown in Fig. 151 [291]. The characterisation of this organic–inorganic hybrid material showed that the arrangement of the host solid and the grafted fluoroionophore was not affected by the functionalisation process. They



340 R = CH_2
341 R = CH_2CH_2

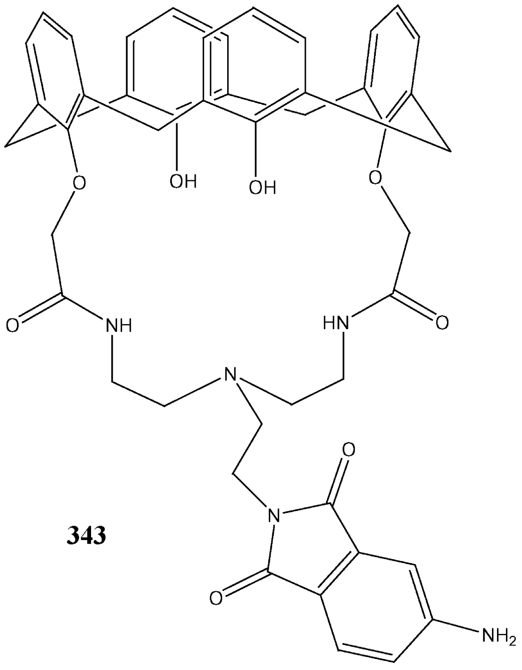


342

Fig. 142. Series of fluorogenic calix[4]arene derivatives, **340**–**342**.

then showed that this material was able to detect the Hg(II) ion in water in a matter of seconds and that the complexation of the Hg(II) ion caused a strong quenching of the fluorescence which was used to determine a detection level of 3.3×10^{-7} mol L^{-1}. Furthermore, they were able to show that the organic–inorganic hybrid showed a high selectivity towards the Hg(II) ion over interfering cations at low concentration.

An unusual report in 2002 by Diamond and co-workers described the synthesis of a propranolol amide derivative of *p*-allylcalix[4]arene (Fig. 152) which was capable of distinguishing chiral amines on the basis of their shape and chirality [292]. Specifically, it was found that **363** could discriminate between the enantiomers of phenylalaninol through the quenching of the fluorescence emission in methanol in contrast to an (*S*)-dinaphthylprolinol calix[4]arene derivative **364**, which could discriminate between the enantiomers of phenylglycinol, but not phenylalaninol. The formation of metal ion complexes of the *p*-allylcalix[4]arene propranolol amide derivative was shown to induce a more regular and rigid cone conformation in the calix[4]arene macrocycle, which in turn was shown to generate a significant enhancement in the observed enantiomeric discrimination.



343

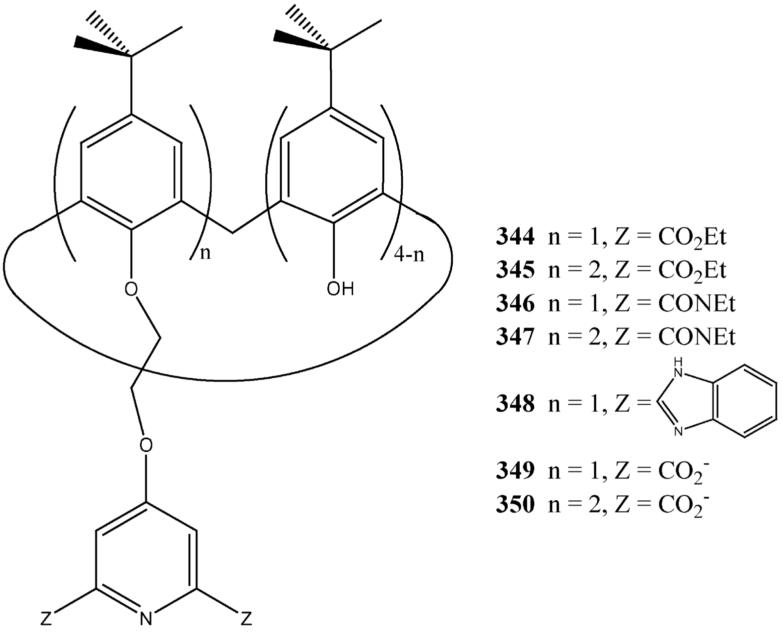
Fig. 143. Structure of **343**.

9. Membrane/solid support

The immobilisation of ion-selective ligands to form polymer-supported reagents is an expanding area of research. This section deals with the role of calix[4]arene derivatives in this area, either incorporated into polymeric materials, such as membranes, or as solid-support reagents.

Meng et al. have synthesised organosilicon calix[4]arene monomers and also their coploymer with tetraethoxysilane, and the adsorption ability of these polymer-resins towards both metal cation ions and human serum protein was explored [293,294]. They synthesised the two monomers (**365**, X = $(CH_2)_3$ and $(CH_2)_2NH(CH_2)_3$) using standard methods (Fig. 153). The polymers (**366**, X = $(CH_2)_3$ and $(CH_2)_2NH(CH_2)_3$) were obtained, in good yield, by the reaction of the monomer with two equivalents of tetraethoxy-silican in toluene with KOH as catalyst. The adsorption capacity of both polymers for Mg(II), Cu(II), Pb(II), Hg(II) and Au(III) ions was determined and it showed that the two polymer resins had poor adsorption ability towards alkaline earth metals but high adsorption ability towards transition metals. This was attributed to the presence of nitrogen donor atoms in the spacers of the calix[4]arene moieties.

Alexandratos and Natesan immobilised calix[4]arene and its diphosphorylated derivatives on cross-linked polystyrene and examined their ion-binding affinities [295]. The supported calixarene (R = H, **367**) complexed Cs(I) from a 10^{-4} M NaOH solution while the diphosphorylated derivatives complexed both Fe(III) and Pb(II) metal ions (Fig. 154). They summarised that the calix[4]arene acts as a platform on which the ligands could be immobilised in

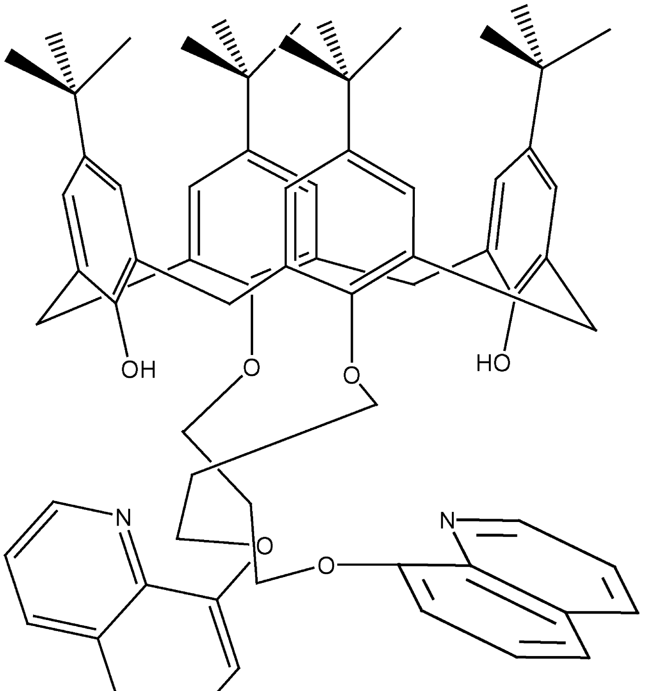


344 n = 1, Z = CO_2Et
345 n = 2, Z = CO_2Et
346 n = 1, Z = CONEt
347 n = 2, Z = CONEt
348 n = 1, Z =
349 n = 1, Z = CO_2^-
350 n = 2, Z = CO_2^-

Fig. 144. Series of functionalised calix[4]arenes, **344**–**350**, studied by Harrowfield et al.

close enough proximity to permit cooperative binding of the metal ions. They concluded that accessibility into the polymer network is unhindered, given the high Cs(I) and Fe(III)/Pb(II) affinities displayed by the various calix[4]arene derivatives.

Engrand and Regnouf-de-Vains have synthesised a bifunctional calix[4]arene for grafting to natural polymeric materials and for metal ion complexation [296] (Fig. 155). The tris-bipyridyl calix[4]arene was anchored to the polymer dextran-10,000 by means of a cyanuric linker. This material was able to complex and stabilise Cu(I) as both a solid and also in aqueous solution. The two limitations of the results obtained were the low yield of the grafting reaction, which was otherwise efficient, and the problem of the choice of solvent system for the grafting reaction itself, based on the solubility of the calix[4]arene derivative, the polymeric material dextran-10,000 and the Cu(I) salt used.



351

Fig. 145. Structure of **351**.

Ohto et al. have looked at the adsorption behaviour of transition metal ions on calix[4]arene tetracarboxylic acid derivatives impregnated into an Amberlite resin, which means that the calix[4]arene derivative is retained within the micropores of the polymer without any chemical bonds onto the polymer matrix [297]. They found that the Pb(II) ion was most efficiently adsorped onto the resin. They also carried out endurance tests of the impregnated resin as well as adsorption rates at different pH's to see if there was an industrial application for this product. They found that, while the resin may be useful in a selective and efficient removal of lead from polluted water, the major drawback would be its poor adsorption capacity.

Jain et al. have reported their work involving the development of calix[4]arene derivatives which are functionalised at the upper rim, *via* the reaction of an aldehyde with a semicarbazide to give a potential site for metal ion binding, and at the lower rim, by linking with commercially available Merrifield peptide resin, to give a polymeric chelating resin [298–301]. This work will not be discussed further, however, as the lanthanide metal ions are not attached at the lower rim.

Yilmaz and co-workers have developed several calix[4]arene-containing polysiloxane resin systems for the removal of heavy metal ions and dichromate anions [156,302–304]. A polymeric Schiff-base type calix[4]arene (**369**) containing two nitrile ligating sites at the lower rim was synthesised *via* a condensation reaction through the upper rim of the calix[4]arene moiety (Fig. 156). The objective was to investigate whether the complexing properties a dinitrile derivative of calix[4]arene could be improved by incorporating it into a polymeric backbone through the upper rim. The original dinitrile calix[4]arene derivative had been shown to be highly selective for Hg(II) ions in a two-phase extraction system [305,306]. Solvent extraction experiments were preformed to ascertain the effectiveness of **369** in transferring selected alkali and transition metal cations from an aqueous to the organic phase.

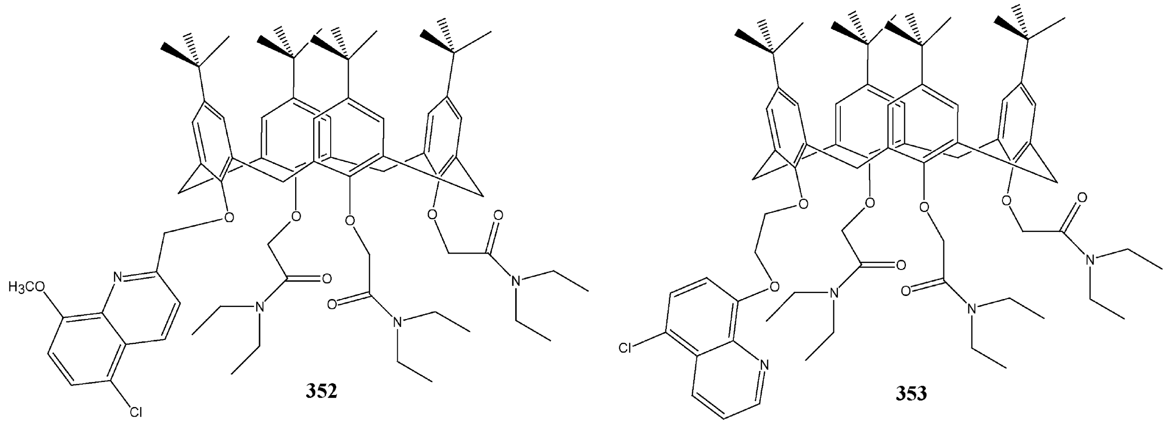


Fig. 146. Structures of **352** and **353**.

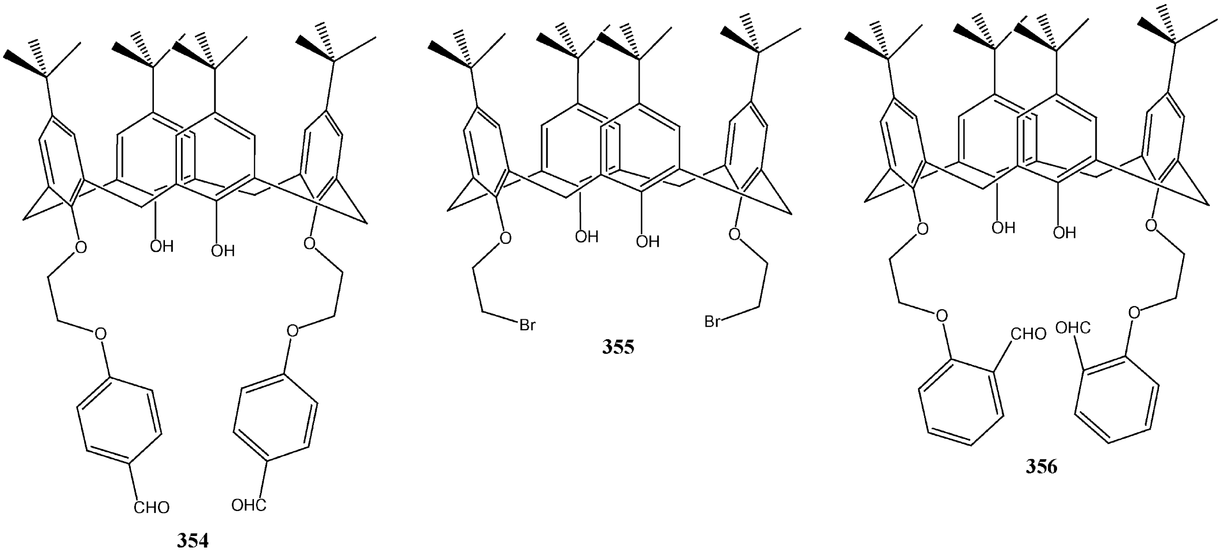


Fig. 147. Series of double-armed calix[4]arenes, **354**–**356**.

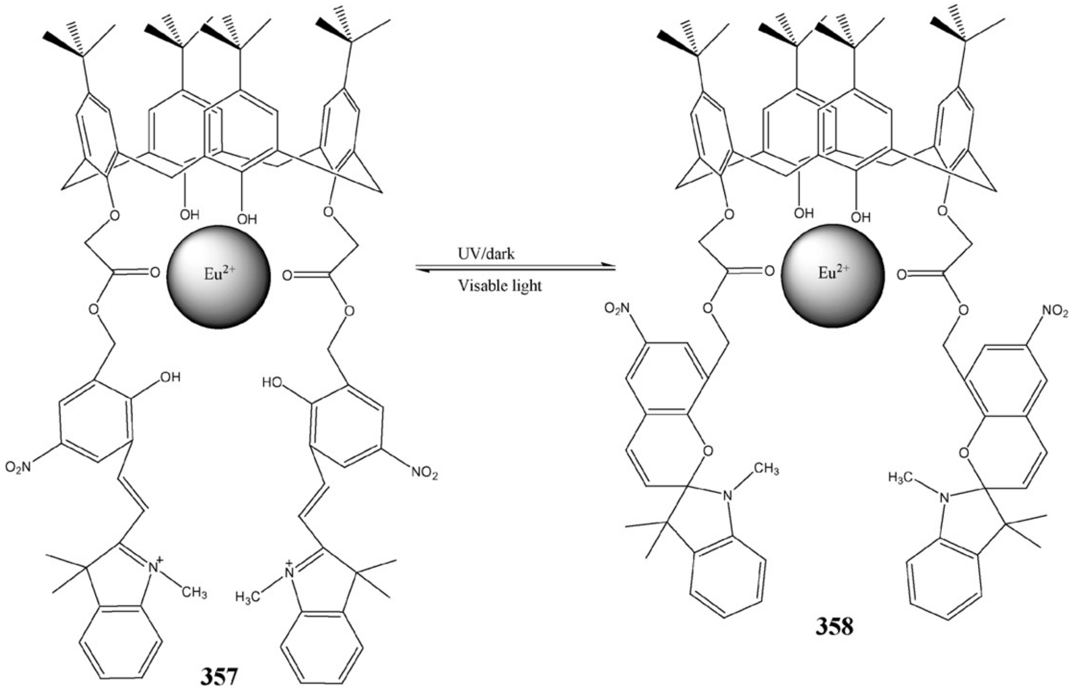
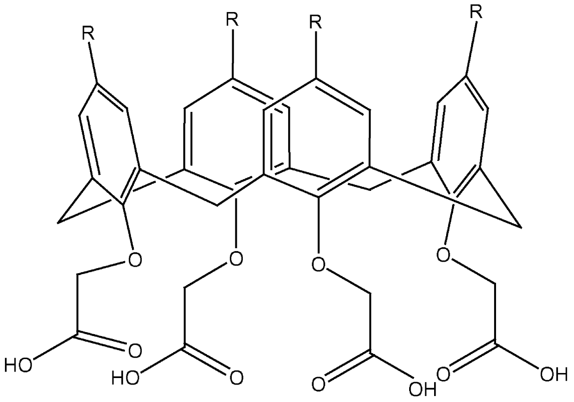


Fig. 148. Structures of photo-switchable molecular device based on calix[4]arene, **357** and **358**.

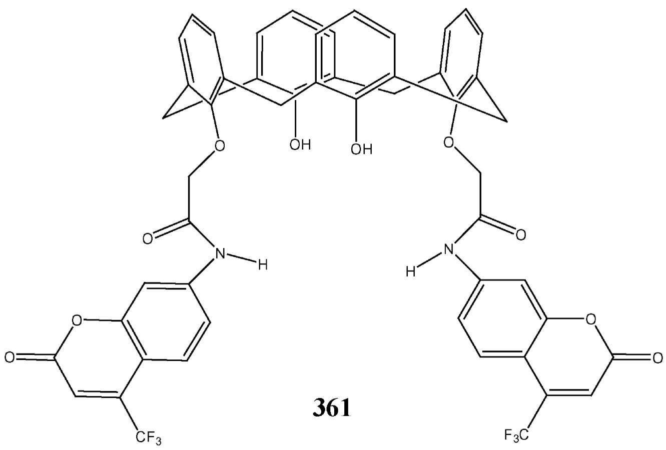


359 R = -CH(CH_3)$_3$
360 R = -C(CH_3)$_2$$CH_2$C($CH_3$)$_3$

Fig. 149. Structures of **359** and **360**.

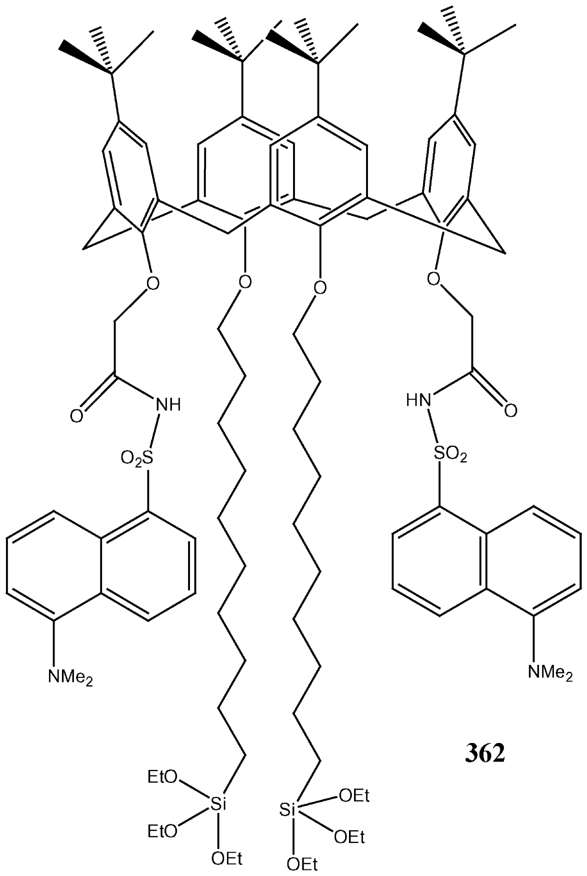
Sanchez-Cortes and co-workers have studied the adsorption of tetraethyl ester *p-tert*-butyl calix[4]arene (**370**) on both copper and silver films by reflection-absorption IR spectroscopy (RAIRS) and surface-enhanced IR (SEIR) in transmission and reflection-absorption configurations [307] (Fig. 157). The goal of this work was the accurate vibrational characterisation of **370**, paying particular attention to the structural markers of the ester groups which play an important role in the molecular adsorption on such metals. They deduced that a monodentate interaction of the C=O ester bond occurred leading to a change from trans to gauche in the structure of the carboethoxy chain. The adoption of a monodentate interaction is the result of an opening of the four carboethoxy groups of the lower rim in order to better accommodate them all on the surface.

They have also used dithiocarbamate calix[4]arenes (**371**) in the functionalisation of silver nanoparticles for pyrene detection by surface-enhanced Raman scattering (SERS) [308] (Fig. 158). They were able to detect the interaction of free pyrene with a surface-bound dithiocarbamate calix[4]arene and were further able to say that the most probable interaction mechanism for this host-guest system is based on a π–π stacking interaction where the pyrene adopts a perpendicular orientation with respect to the surface. Furthermore, this combination of SERS and the use of the dithiocarbamate calix[4]arene to functionalise the silver surface offers a promising tool in the detection of pollutants at trace con-



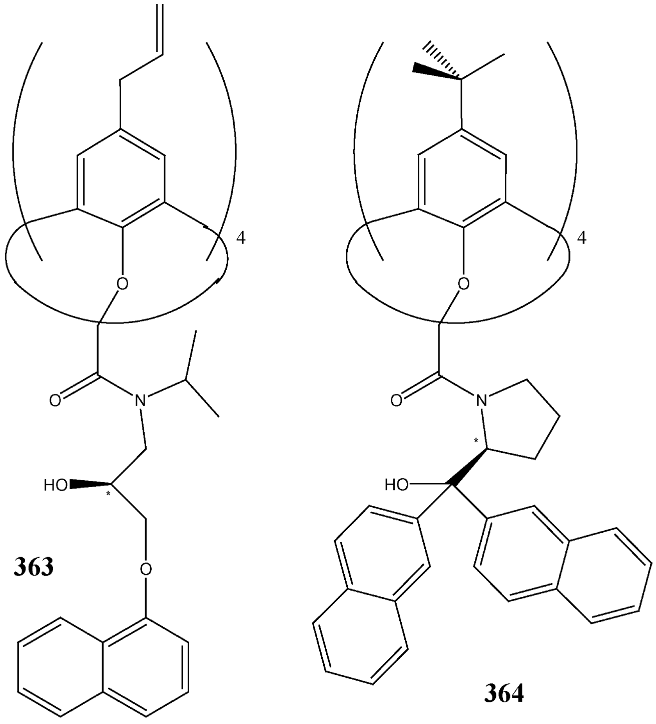
361

Fig. 150. Structure of **361**.



362

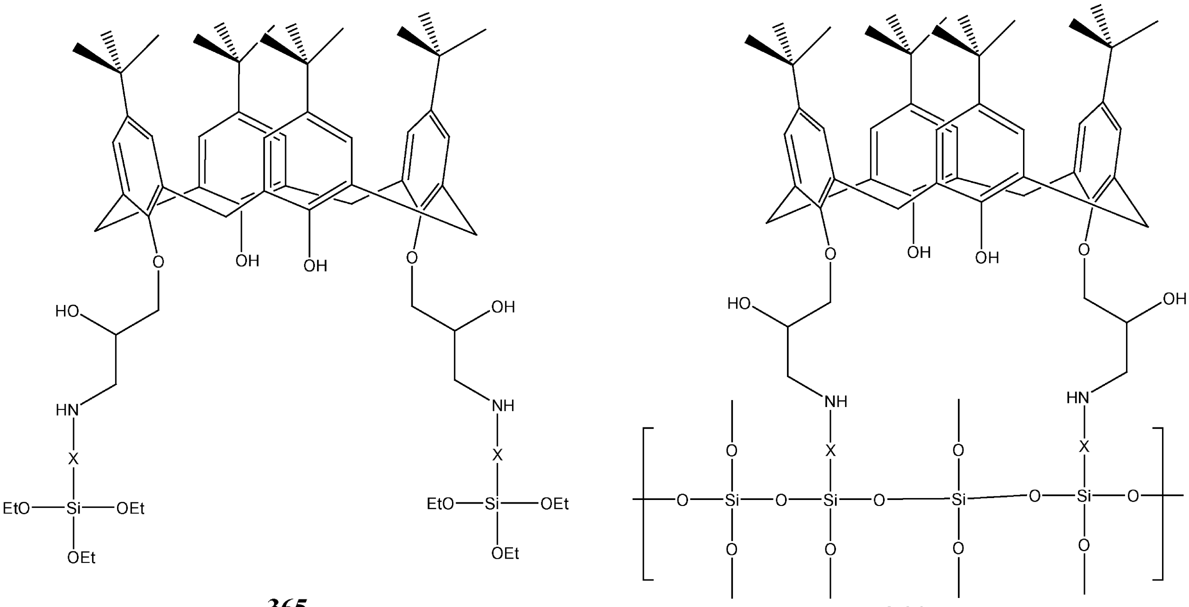
Fig. 151. Structure of **362**.



363

364

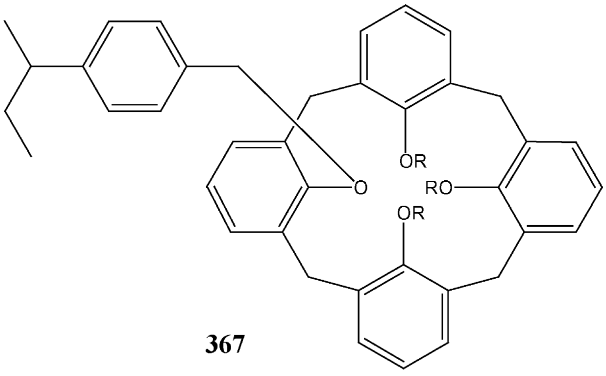
Fig. 152. Structures of **363** and **364**.



365

366

Fig. 153. Structures of **365** and **366**.

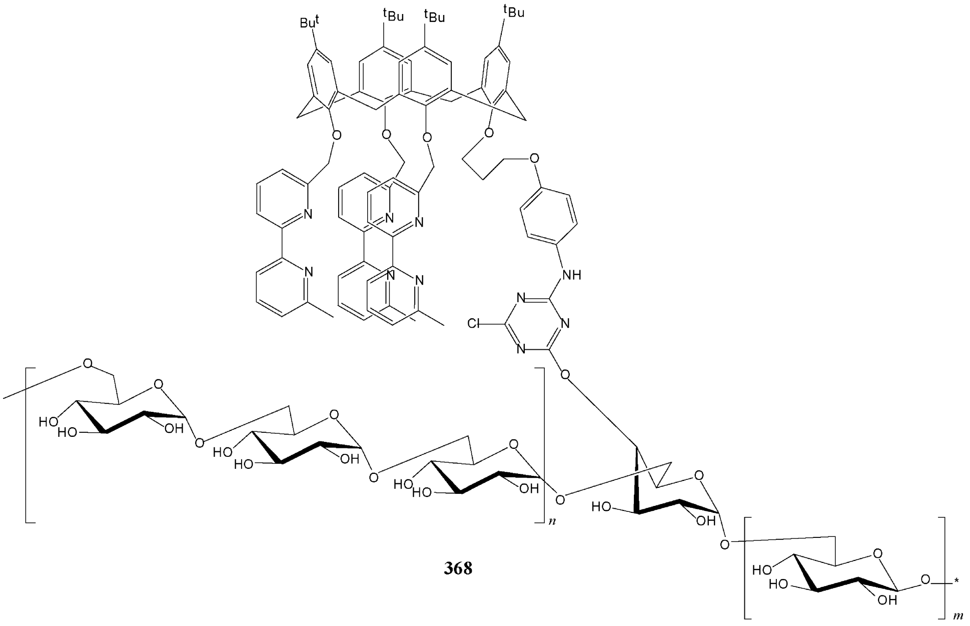


367

Fig. 154. Structure of **367**.

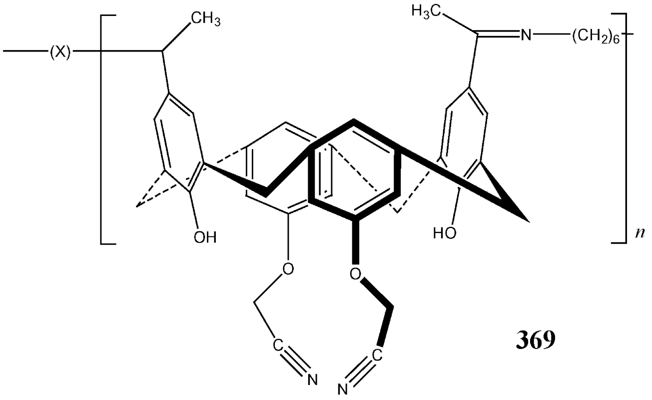
centrations. In a further paper, they reported that disubstituted calix[4]arenes can be successfully used in the detection of polycyclic aromatic hydrocarbons (PAHs) at trace concentration by means of SERS spectroscopy using silver metal colloidal suspensions or nanoparticle immobilised films [309]. The calixarene host is adsorbed onto the metal surface and captures the PAH close enough to the surface for the SERS detection to occur. They found that ester functionalisation on the lower rim gave increased adsorption onto the metal surface.

The calix[4]crown (**372**) was synthesised by Seyhan et al. and attached to a Merrifield chloromethylated resin, *via* a carboxylic acid linker attached to the free hydroxyl groups [310] (Fig. 159). The calixcrown anchored resin showed potential for the enrichment of trace metal ions from various matrices as well as good



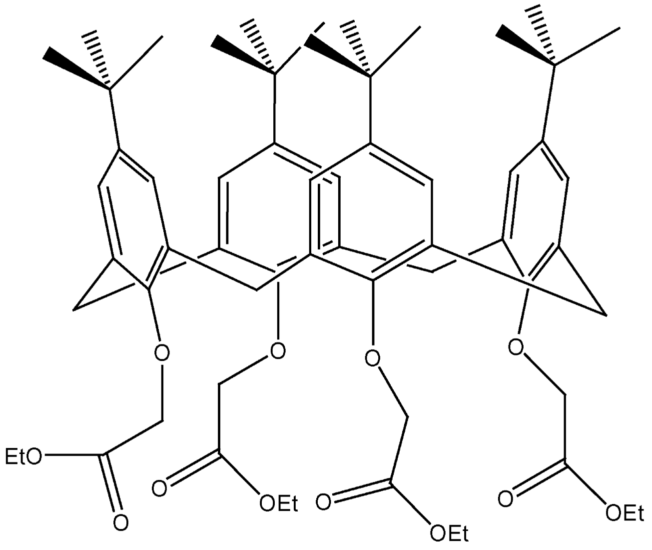
368

Fig. 155. Structure of **368**.



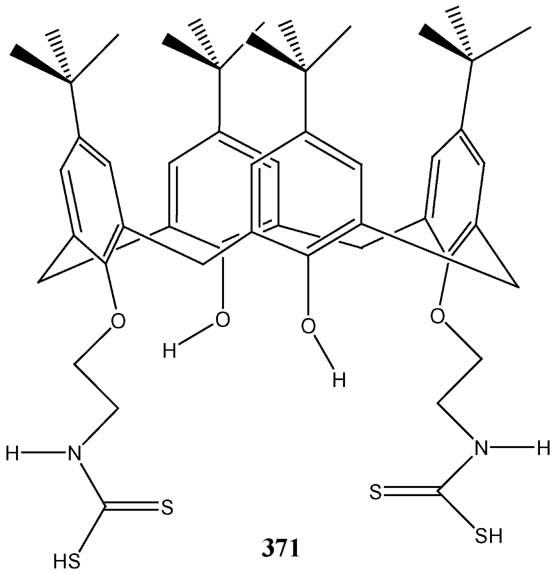
369

Fig. 156. Structure of **369**.



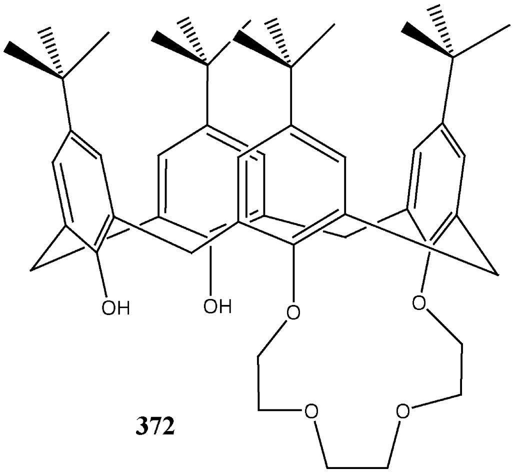
370

Fig. 157. Structure of **370**.



371

Fig. 158. Structure of **371**.



372

Fig. 159. Structure of **372**.

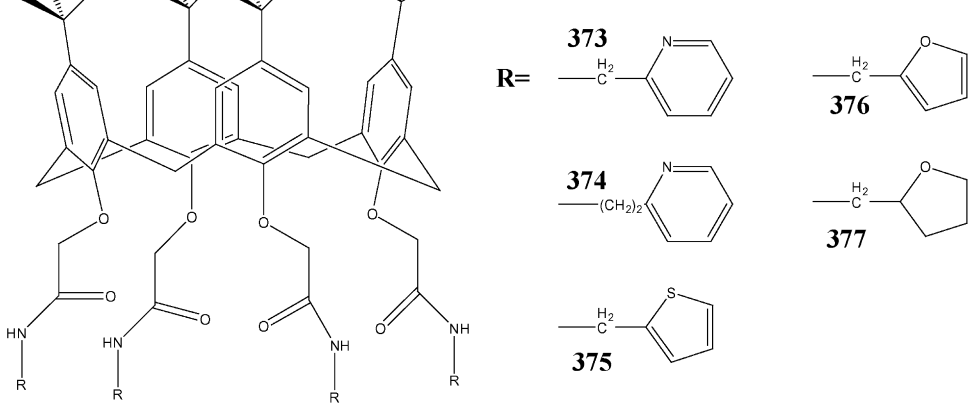
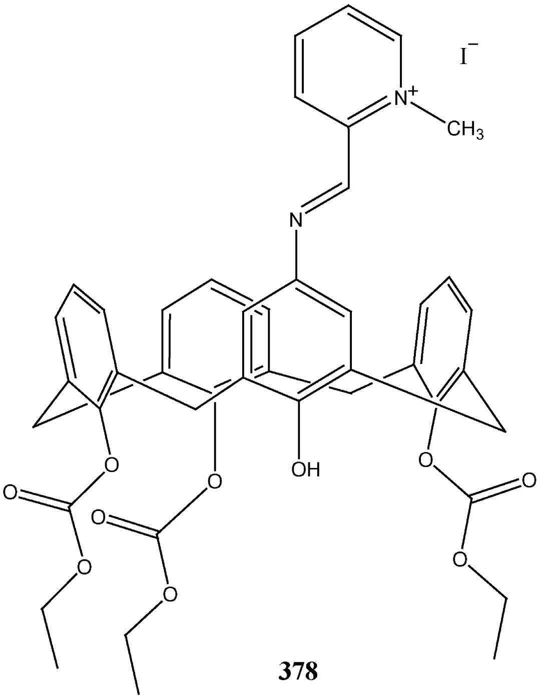


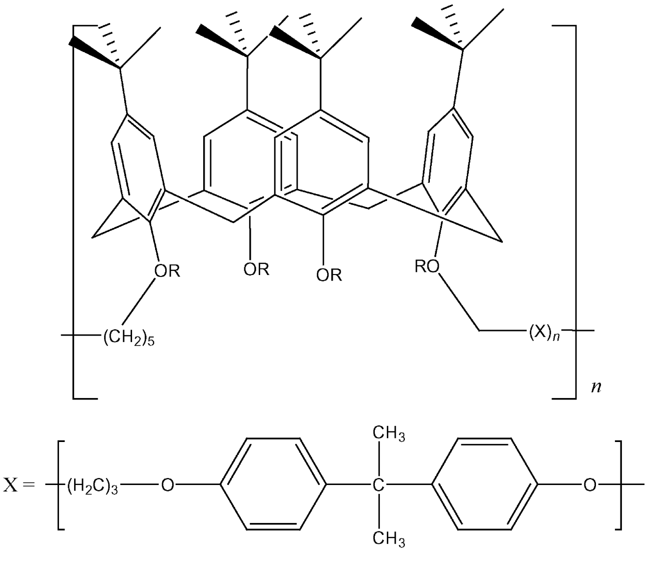
Fig. 160. Series of tetraamido functionalised calix[4]arenes, **373**–**377**.



378

Fig. 161. Structure of **378**.

selectivity among transion metal ions with some separations being made possible by pH control. They also found that the resin can be successfully regenerated for 12 operating cycles in the column. Furthermore, they found that the resin showed good preconcentration ability.



385

Fig. 163. Structure of **385**.

The work of Mohammed-Ziegler et al. focussed on monitoring the complex formation of several tetraamido-calix[4]arene derivatiives with alkali/alkali earth metal ions using both FT-IR, FT-Raman and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) [311]. The different derivatives are shown in Fig. 160. They observed that FT-Raman was not a suitable technique for the detection of differences between the different complexes formed, but that FT-IR could differentiate between the cations as a result of a difference in an amide vibrational mode.

Mohammed-Ziegler also published a complexation study using FT-IR spectroscopy on a calix[4]arene derivative containing ethoxycarbonylmethoxy groups in the coordination sphere and an iminopyridinium indicator group located on the upper-rim [312]. The study was carried out in acetonitrile solution and involved monitoring the changes in the carbonyl stretching frequency of the ethoxycarbonylmethoxy groups. The shift in this stretching

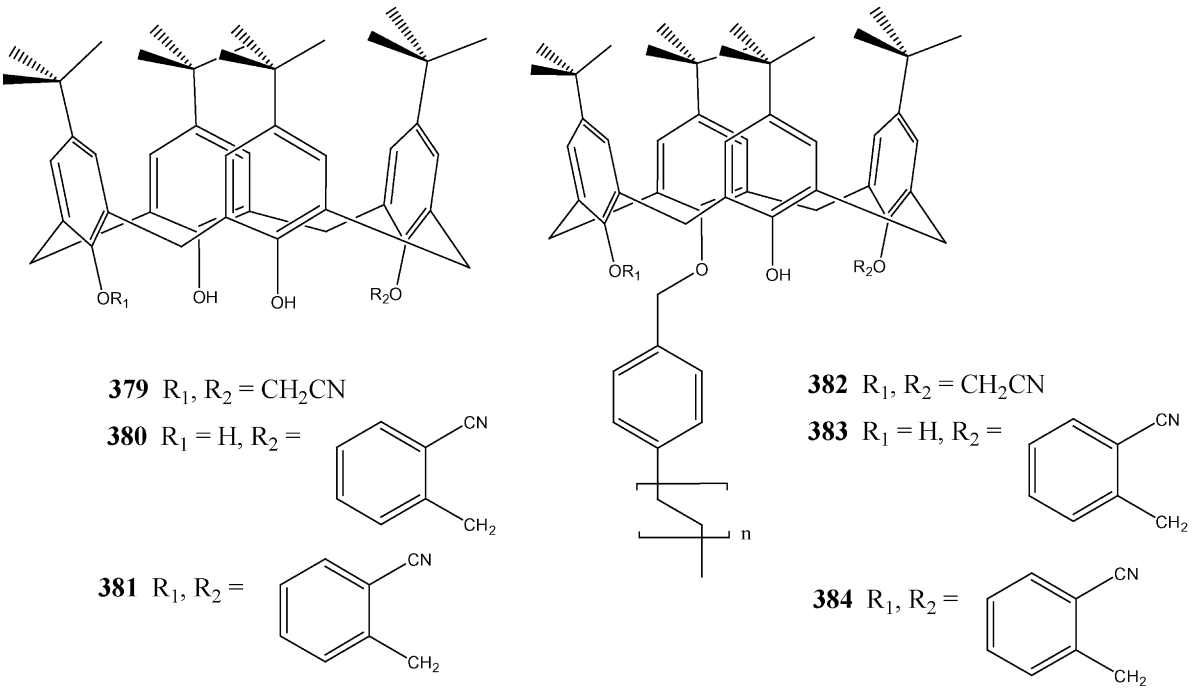
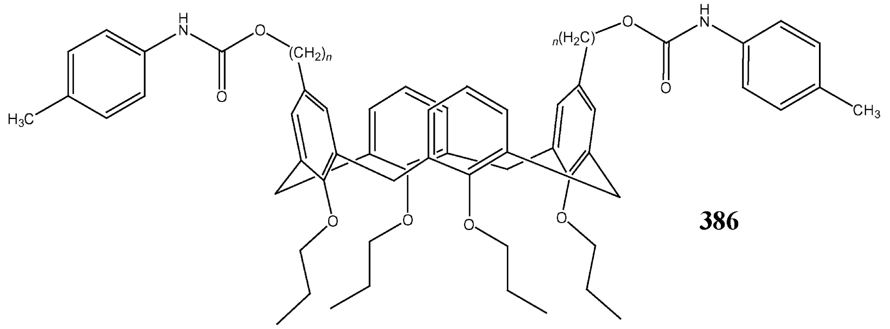
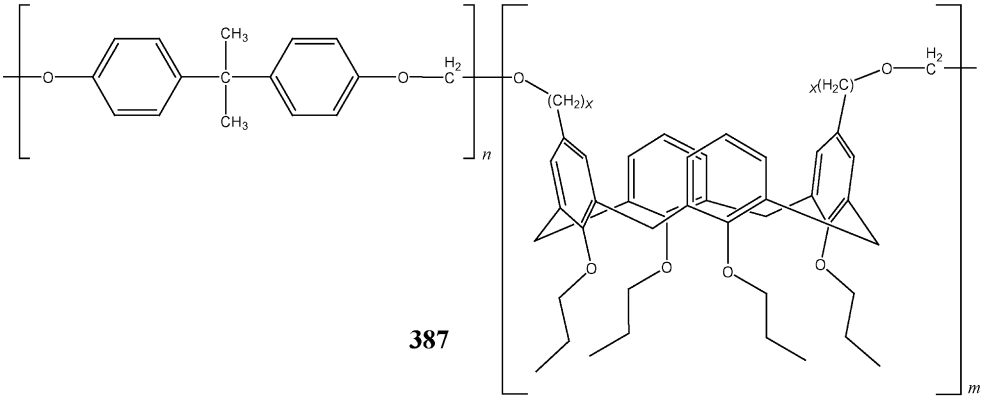


Fig. 162. Series of alkylnitrile and alkylbenzonitrile substituted calix[4]arenes, **379–384**.



386



387

Fig. 164. Structures of **386** and **387**.

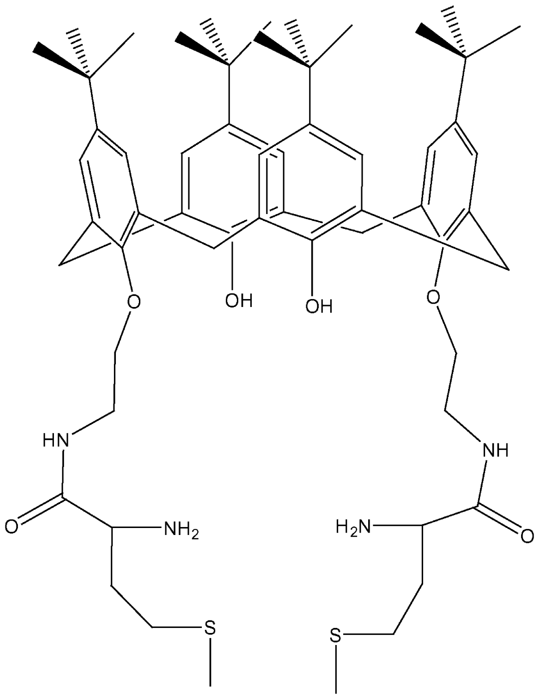
vibration band depended on complex formation as well as on the equilibrium constants of complex formation. In the case of sodium complex, a well-defined isobestic point was detected in the ν(C=O) region while altering the sodium concentration. Interestingly, the affinity of Tl(III) to form complexes with calixarene **378** was found to be comparable with those of lithium, sodium or calcium but the stoichiometry of the complex was found to be an M_2L type association with one molecule of triethylamine being necessary for the formation of each complex molecule (Fig. 161).

Yilmaz and co-workers also looked at extraction properties of alkylnitrile and alkylbenzonitrile substituted calix[4]arenes and also alkylnitrile and alkylbenzonitrile substituted calix[4]arene-based polymers [313]. The disubstituted nitrile derivatives **379**–**381**, shown in Fig. 162, were treated with Merrifield's resin in a nucleophilic substitution reaction to give the polymers **382**–**384**. The derivatives **379**–**381** were evaluated as potential extractants of alkali and transition metal ions from a two phase system. Extraction studies with **379** showed selectivity for Hg(II) while **380** and **381** are selective for both Hg(II) and Cd(II) cations. The polymers **382**–**384** are not selective and show more or less the same extraction behaviour towards all metal cations. In a further paper, Yilmaz and co-workers synthesised some copolymers containing pendant calix[4]arene units with nitrile functionalities at the lower rim with 1,5-dibromopentane and bisphenol-A (**385**) [314] (Fig. 163). They then carried out some phase transfer studies using liquid–liquid extractions. They concluded that the copolymers showed good phase transfer affinity towards alkali, alkaline earth and transition metal cations, although no selectivity was observed. They concluded that the high phase transfer efficiency shown by the copolymers could be ascribed to better preorganisation of the metal binding sites.

Marra, Scoponi and co-workers synthesised a number of calix[4]arene bis-urethanes and polyurethanes in both cone and 1,3-alternate conformations in order to study the intrinsic receptor properties of the macrocyclic system in the solid support [315]. An example of a calix[4]arene bis-urethane (**386**) and calix[4]arene polyurethane (**387**) is shown in Fig. 164. The extraction ability of the calix[4]arene polyurethanes towards metal cations was investigated, but not for all the compounds synthesised due to solubility problems, with the calix[4]arene bisurethanes being employed as model compounds. They observed that although metal binding did occur, the metal binding was a result of the urethane functionalities on the chain, rather than the calix[4]arene moiety which was ineffective. When the calix[4]arene polyurethanes incorporated crown ether units at the calix[4]arene, significant metal ion complexation was observed at the calix[4]arene moiety, particularly for the potassium, caesium and silver ions. They then concluded that the binding ability of calix[4]arene crown ether derivatives were not affected by incorporation into polyurethane supports.

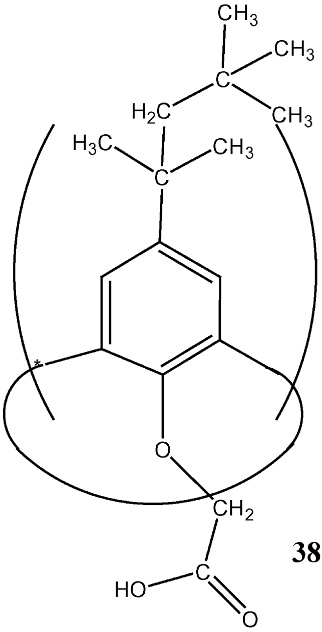
Zhu and co-workers demonstrated that methionine-derived calix[4]arenes and their Pd(II) complexes formed stable monolayers at the air–water interface [316]. The monolayers at the air–water interface were investigated by film balance measurements and Brewster angle microscopy. They observed that the molecules sit perpendicular to the water surface and that the $Pd_2(\mathbf{388})Cl_4$ complex formed a monolayer with remarkable mechanical strength, as demonstrated by a slow decrease in surface pressure during viscosity experiments (Fig. 165). This was attributed to the complexes ability to form polymeric materials through intermolecular chloride bridging. Neither the starting calix[4]arene derivative nor the $Pd(\mathbf{388})Cl_2$ complex can achieve the same mechanical strength.

Kubota et al. performed a kinetic study in the extraction of rare earth metals through a hollow-fibre membrane using the calix[4]arene carboxyl derivative **389** as the extractant [317] (Fig. 166). They found that the premeation rate through the membrane of metal ions was relatively slow. However, when a small amount of sodium ions was added, the permeation rate dramatically accelerated and they also observed that the selectivity between heavy rare earth metals (Er(III) and Ho(III)) and Y(III) also increased.



388

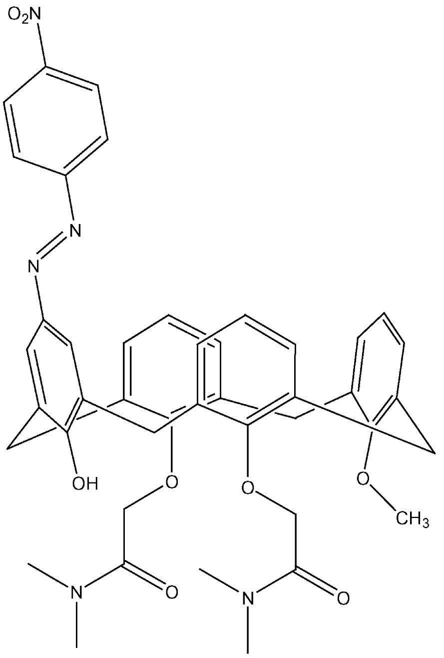
Fig. 165. Structure of **388**.



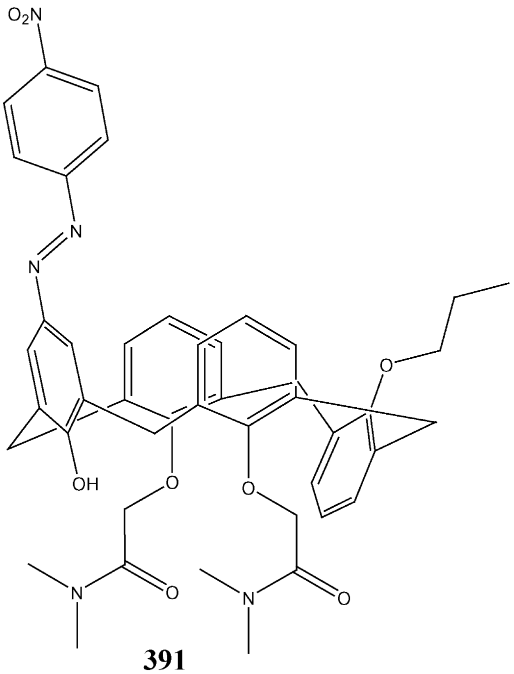
389

Fig. 166. Structure of **389**.

Reinhoudt and co-workers developed highly selective optical-sensing membranes, containing calix[4]arene-based chromoionophores which were Pb(II) selective [318]. They prepared plasticised poly(vinyl chloride) (PVC) optode membranes containing novel calix[4]arene chromoionophores **390** or **391** and one equivalent of a lipophilic anion respond to Pb(II) ions with high selectivity over alkali, alkaline earth and other heavy metal ions (Fig. 167). They found that complexation of Pb(II) ions within the membrane was accompanied by deprotonation of the chromoionophores, which causes a bathochromic shift of the absorption maximum λ_{max}. A number of other metal ions were tested, but only Cs(I) and Ag(I) produced a colour change and complexation of these monovalent cations induced a hypsochromic shifts of λ_{max} instead of the bathochromic shift caused by Pb(II) ions. The authors concluded that this was because the chromoionophores remain protonated upon complexation.



390



391

Fig. 167. Structures of **390** and **391**.

10. Conclusions

There is no doubt that since the report of the initial synthesis of calix[*n*]arenes by Gutsche [1] in the early 1980s that research into the design, synthesis and application of these macrocyclic ligands has grown exponentially. It is also clear from reviews of the literature that calix[4]arene-based macrocycles have considerable more applications that the larger ring systems. While to a certain extent this can be attributed to the easier synthetic route for calix[4]arenes this present review highlights the widespread applicability of this macrocycle. We have little doubt given the increasing numbers of patent applications for new technologies based on the use of calix[4]arene-derived compounds that interest in this area will continue to increase.

Acknowledgement

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