

## Advances in Contemporary Research

### Analytical applications of thiacalixarenes: A Review

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Analytical applications of various thiacalixarenes with their derivatives have been discussed. The metal binding affinities of such thiacalixarenes have been summarized.

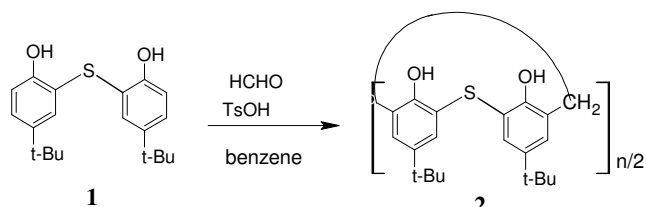
#### Introduction

The increase in industrial activity in recent years has resulted in contamination of ground and surface water by toxic metal ions<sup>1</sup>. In developing countries, water pollution generated by industrial effluents has been a serious issue<sup>2</sup>. For ecologically sustainable growth, monitoring of metal ions such as Cr<sup>6+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> in natural water as well as in bio-fluid samples is required. Toxic heavy metals such as cadmium, mercury, copper and lead are hazardous to human health<sup>3</sup> as well as to the environment because of their accumulative and persistent character. The importance of detection of heavy metals<sup>4-7</sup> and controlling the level of such pollutants have generated increasing interest in the development of novel sensors, such as calixarene-based ionophores, ion selective electrodes or chemically modified field effect transistors.

Calixarenes functionalized at lower and upper rims have generated increasing interest both in fundamental and applied chemistry. These macrocycles have been used for catalysis, molecular recognition or ion separation, and sensors<sup>8-11</sup>. Recently, thiacalix[4]arenes have been reported as a novel member of the well-known calixarene family. The presence of four sulfur atoms results in many novel features as compared with classical calixarenes, such as different complexation ability with sulfur contribution, easy chemical modification (oxidation) of bridges and different size and different conformational behavior of this novel macrocycle. Hence, thiacalix[4]arene exhibits a broad range of interesting functions which makes this compound a good candidate for many applications in supramolecular chemistry<sup>12-23</sup>.

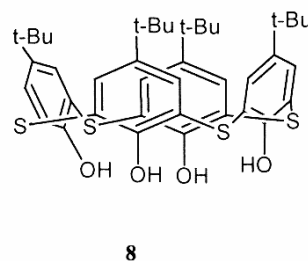
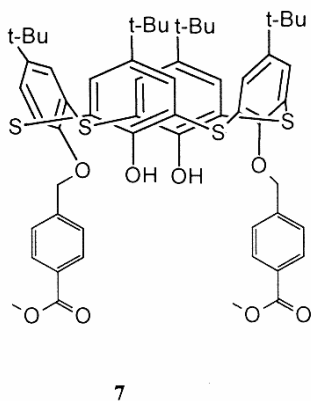
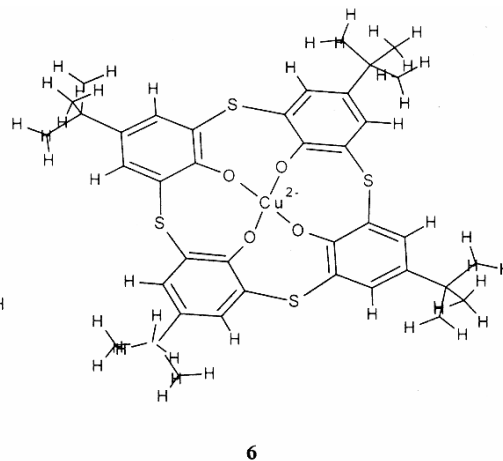
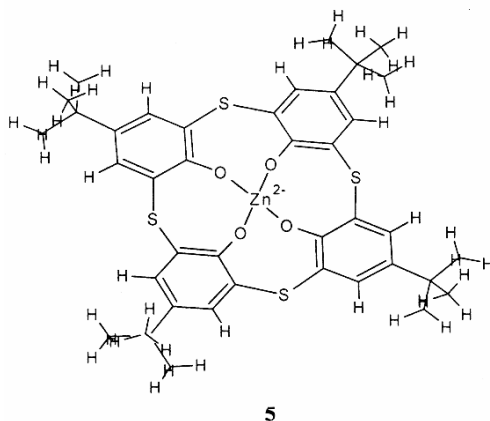
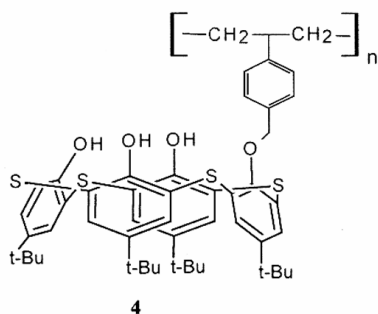
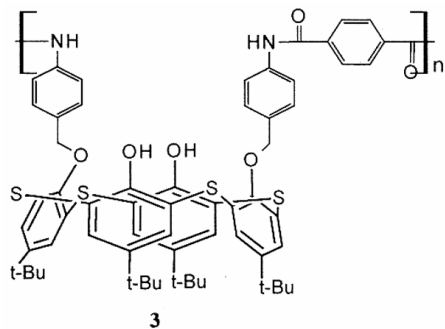
#### Solvent extraction studies

Based on the results of Gutsche *et al.*<sup>24,25</sup>, Koni *et al.* have carried out acid catalyst condensation of *para*-substituted phenols with sulfur to give acyclic oligomers (see Scheme 1) since the numbers of bridging sulfides have a distinct effect on the extractability of sulfur-bridged oligomers of phenol<sup>26</sup>. Thiacalixarenes have three intrinsic properties, viz. larger cavity, oxidizability of bridging sulfur and coordination to transition metal ions<sup>27</sup>. Their ability to bind metal ions has been investigated by solvent extraction method in several studies<sup>28, 29</sup>. Study of its binding ability toward first transition metal ions (Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>) and Mg<sup>2+</sup> ion by solvent extraction has been carried out by the dimer method<sup>30</sup>. This thiacalixarene shows a high selectivity towards Cu<sup>2+</sup> at pH 5.5 by coordination of the O<sup>-</sup>, S<sup>-</sup>, O<sup>-</sup> donor sets. Also, polymeric thiacalix[4]arene derived from terephthaloyldichloride (Merrifield) resin is better at removing alkali (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and Cs<sup>+</sup>) and heavy metal (Cu<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>) cations than the precursor thiacalix[4]arenes. Two new polymeric thiacalix[4]arenes formed by the reaction of 5,11,17,23-tetra-*t*-butyl-25, 27-bis[(4-aminobenzyloxy)-26,28-dihydroxy]thiacalix[4]arene with terephthaloyl dichloride (**3**) and that of 5,11,17,23-tetra-*t*-butyl-25,26,27,28-tetra-hydroxy-thiacalix[4]arene with chlo-



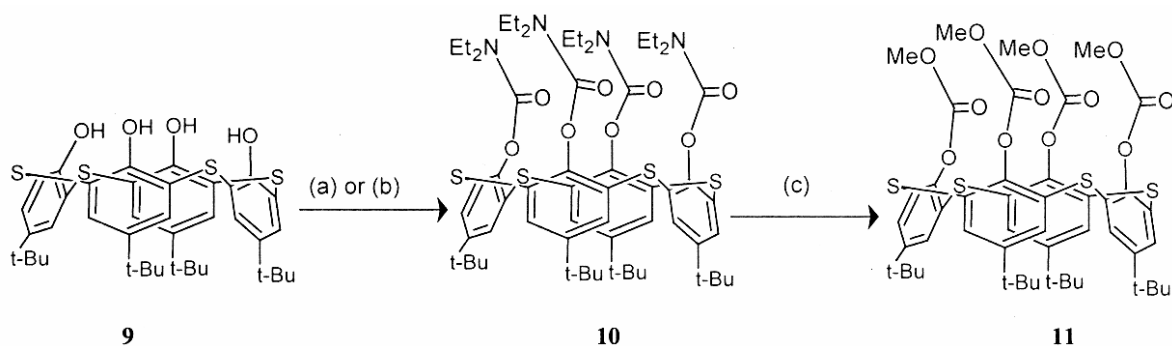
Scheme 1

romethylated polystyrene (Merrifield resin) (**4**) have been synthesised and complexation studies carried out by using liquid-liquid and solid-liquid extraction procedures<sup>31</sup>. Both the soluble polymer and the cross-



linked polymer derived from Merrifield resin are more efficient for separation and removing transition metals from solution than the precursor thiacalix[4]arene<sup>31</sup>.

The complexation of *p*-*tert*-butylthiacalix[4]arene and its zinc complex have been investigated using quantum chemical calculations<sup>32</sup>. Conformational structures and energies of thiacalix[4]arene and *p*-*tert*-butylthiacalix[4]arene have been determined and compared with those of sulfonylcalix[4]arene and *p*-*tert*-butylsulfonylcalix[4]arene molecules<sup>32</sup>. Stabilities of the *p*-*tert*-butyl thiacalix[4]arene conformers are in the order: cone > partial cone > 1,3-alternate > 1,2-alternate. The stability order of *p*-*tert*-butyl thiacalix[4]arene conformers is the same as that of calix[4]arene and thiacalix[4]arene conformers but different from those of sulfonylcalix[4]arene and *p*-*tert*-butylsulfonylcalix[4]arene which have the 1,2-alternate conformer as the most stable species. Comparative studies of the complexation features of thiacalix[4]arene towards the transition metal ions like Zn<sup>2+</sup> and Cu<sup>2+</sup> have also been analyzed in detail. Two and five discrete binding modes have been studied<sup>33</sup> and the position of the deprotonated phenols seems to influence the structural pattern of binding



(a)  $\text{ClCH}_2\text{CONEt}_2/\text{K}_2\text{CO}_3/\text{NaI}/\text{acetonitrile}/\text{reflux } 15 \text{ h}$ ; (b)  $\text{ClCH}_2\text{CONEt}_2/\text{Cs}_2\text{CO}_3/\text{NaI}/\text{acetonitrile}/\text{reflux } 15 \text{ h}$ ;  
 (c)  $\text{CH}_3\text{OH}/\text{HCl}/\text{reflux } 48 \text{ h}$

Scheme 2

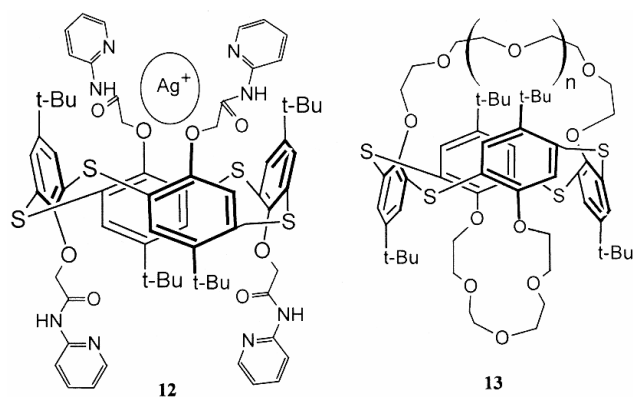
modes. The most stable mode of the different binding modes is predicted as a distorted square planar coordination, using two phenol and two phenolate groups in an opposite pattern. The results point to the stronger binding interaction of  $\text{Cu}^{2+}$  as compared to  $\text{Zn}^{2+}$  in all the binding modes, which is consistent with the available experimental data. The results show a higher complexation ability of  $\text{Cu}^{2+}$  (**6**) than of  $\text{Zn}^{2+}$  (**5**) for all of the binding modes<sup>33</sup>. Further, using AMI calculations, comparative study on complexation ability of 5, 11, 17, 23-tetra-*tert*-butyl- 25, 27-bis{[4-(methoxycarbonyl)phenyl]methoxy}-2, 8, 14, 20-tetra-thiacalix[4]arene **7** towards the transition metal ions  $\text{Zn}^{2+}$  and  $\text{Cu}^{2+}$  has also been carried out<sup>34</sup> to understand better the characteristic host-guest interactions in novel molecular receptors (**7**) and its parent compound (**8**). The structures of neutral and deprotonated species of the cone conformers of (**7**) and (**8**) have also been studied by the AMI method. The results show that the structure with two opposite deprotonated phenol groups is more stable than that with two adjacent deprotonated phenol groups.

### Separation of metal ions

Heteroditopic receptors were synthesized by introducing amide functions at the lower rim of the thiacalix[4]arene as efficient extractants for both cations and anions due to their high stability and hydrophobicity<sup>35</sup>. The presence of acetate functions in the opposite side and the sulphur atoms in the calix framework leads to high affinity towards  $\text{K}^+$  and  $\text{Ag}^+$  ions respectively. Replacement of diamide by tetraamido derivative of *p-tert* butylthiacalix[4]arene and its cone conformation has been demonstrated through transformation of (**10**) into the tetramethylester derivative (**11**) (see Scheme 2), which is known to have

a cone conformation. The ability of tetra(diethyl)-amide-*p-tert*-butylthiacalix[4]arene to bind with alkali and alkaline earth metal ions and some heavy and transition metal ions ( $\text{Ag}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ ) have been assessed through liquid-liquid extraction of the corresponding picrate salts from water into dichloromethane<sup>36</sup>. Results show that replacement of the bridging  $-\text{CH}_2$  units by sulphur atoms in thiacalixarenes led to a loss of selectivity within the alkali and the alkaline earth series. Also, the thiacalixarene became selective for  $\text{Pb}^{+2}$  ion among heavy and transition metal ions<sup>36</sup>.

$\text{Ag}^+$  ions have been determined by potentiometric sensors, based on glassy carbon electrode covered with polyaniline and neutral carrier, i.e., thiacalix[4]arene containing pyridine fragments in the substituents at lower rim (**12**). The presence of thiacalixarene in the surface layer improves the reversibility and selectivity of the signal towards transition metal ions<sup>37</sup>. The reaction of  $\text{Ag}^+$  with thiacalixarene was proved by extraction of the picrate complexes of transitory metals in the organic phase<sup>37</sup>. Cesium ion-selective electrodes have been fabricated



from thiacalix[4]mono (**14**) and bis(crown-6) ether (**13**) derivatives which show excellent potentiometric performances with  $\text{Cs}^+/\text{K}^+$  and  $\text{Cs}^+/\text{Na}^+$  selectivities comparable with those of the calixcrown-based sensors<sup>38</sup>. Among the thiacalix[4]bis(crown-6) ethers studied, the *tert*-butyl derivative has better selectivity for cesium than for the other alkali cations.

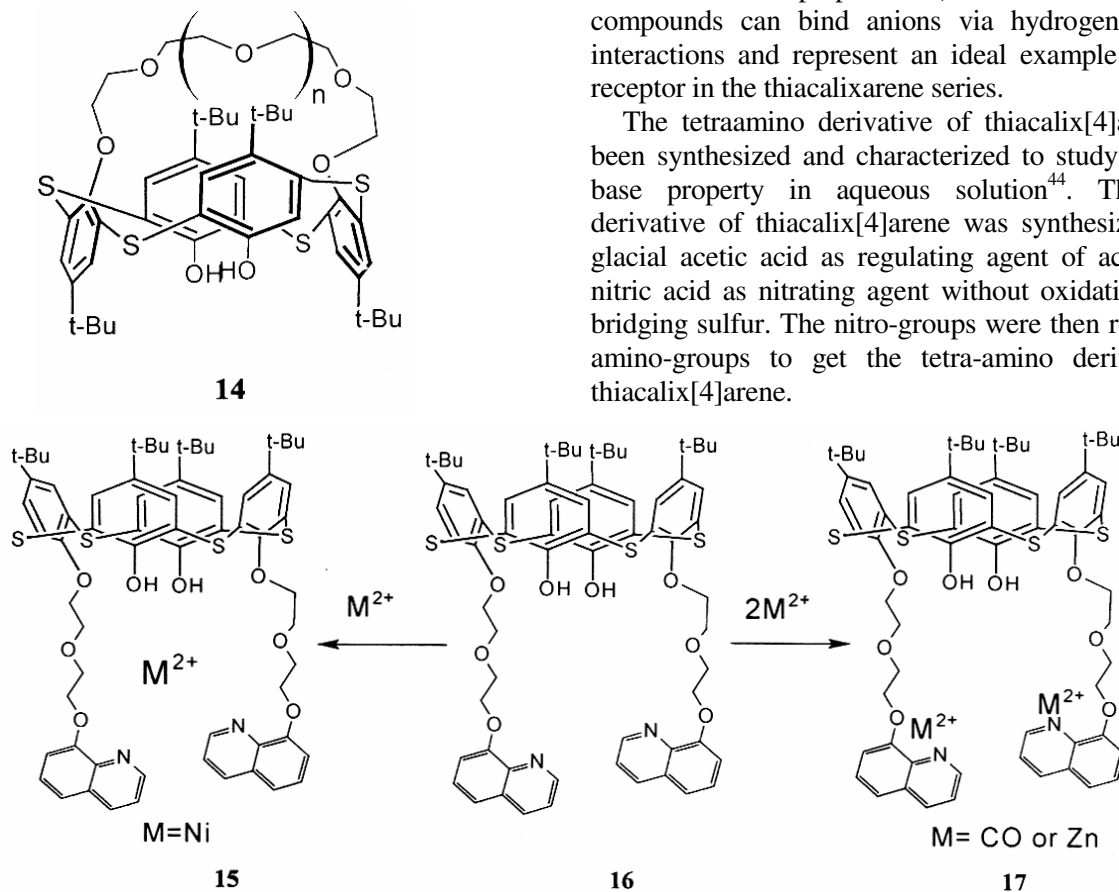
Thiacalix[4]crown trimers incorporating crown-5 and crown-6 have been prepared for separation of  $\text{Cs}^+$  and  $\text{Ag}^+$  ions<sup>39</sup>. Their conformations and complexation behavior characterized by X-ray diffraction and  $^1\text{H}$  NMR spectroscopy show that the  $\text{Cs}^+$  ion is encapsulated in the end-crown rings by the 1:2 complexation ratios while the  $\text{Ag}^+$  ion is entrapped in the central thiacalix unit in 1:1 ratio. Extractabilities of the thiacalix[4]crown trimers for  $\text{Ag}^+$  are higher than those of conventional calix[4]crown trimers.

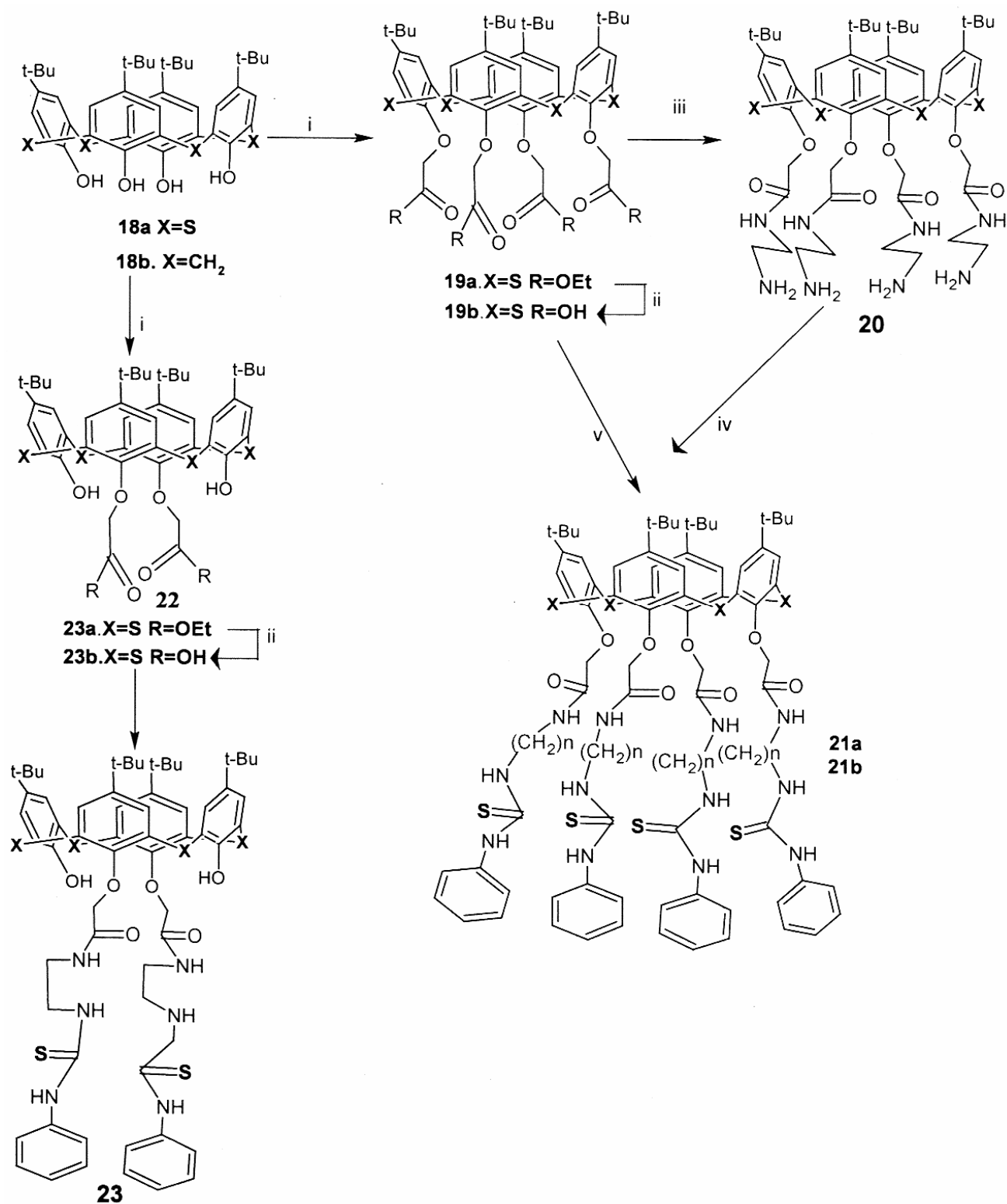
The effective separation of Am from radioactive waste by a chelating ion-exchange method has been carried out using an octylphenyl-N, N-diisobutylcarbomoyl phosphine oxide (CMPO) or thiacalix[4]arene compound impregnated silica ion-exchanger<sup>40</sup>. The separation of Cs and Sr can be achieved through a

CMPO impregnated silica ion-exchanger. Actinoids and lanthanoids can then be eluted from the CMPO-exchanger, and the resulting solution, recovered from the CMPO-exchanger, treated to separate the actinoids with a thiacalix[4]arene compound impregnated silica ion-exchanger in a weak-acid solution<sup>40</sup>. Separation of actinides from lanthanides involves very difficult procedures. New ion-exchangers, thiacalix[4]arene compounds impregnated with silica ion exchanger (CAPS) or CAPS- $\text{SO}_2$ , have been developed for separation of Am from lanthanides<sup>41</sup> and its efficiency is comparable with that of Cyanex301 impregnated silica ion-exchanger.

A lower rim substitution of diagonal quinolin-8-yloxy pendants via oxyethylene spacer (**16**) has been synthesized in one step and its coordination properties towards  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  ions studied by UV-vis, fluorescent spectra and  $^1\text{H}$  NMR titration<sup>42</sup>. The results show that (**16**) forms very stable complexes with the three metal ions, and the stoichiometries of **16**- $\text{Ni}^{2+}$ , **16**- $\text{Co}^{2+}$  and **16**- $\text{Zn}^{2+}$  are 1:1, 1:2 and 1:2, respectively. Moreover, anion receptors in the thiacalixarene series bearing four ureido or thioureido functions at the lower rim have been prepared<sup>43</sup> (see Scheme 3). These compounds can bind anions via hydrogen bonding interactions and represent an ideal example of anion receptor in the thiacalixarene series.

The tetraamino derivative of thiacalix[4]arene has been synthesized and characterized to study its acid-base property in aqueous solution<sup>44</sup>. The nitro-derivative of thiacalix[4]arene was synthesized using glacial acetic acid as regulating agent of acidity and nitric acid as nitrating agent without oxidation of the bridging sulfur. The nitro-groups were then reduced to amino-groups to get the tetra-amino derivative of thiacalix[4]arene.





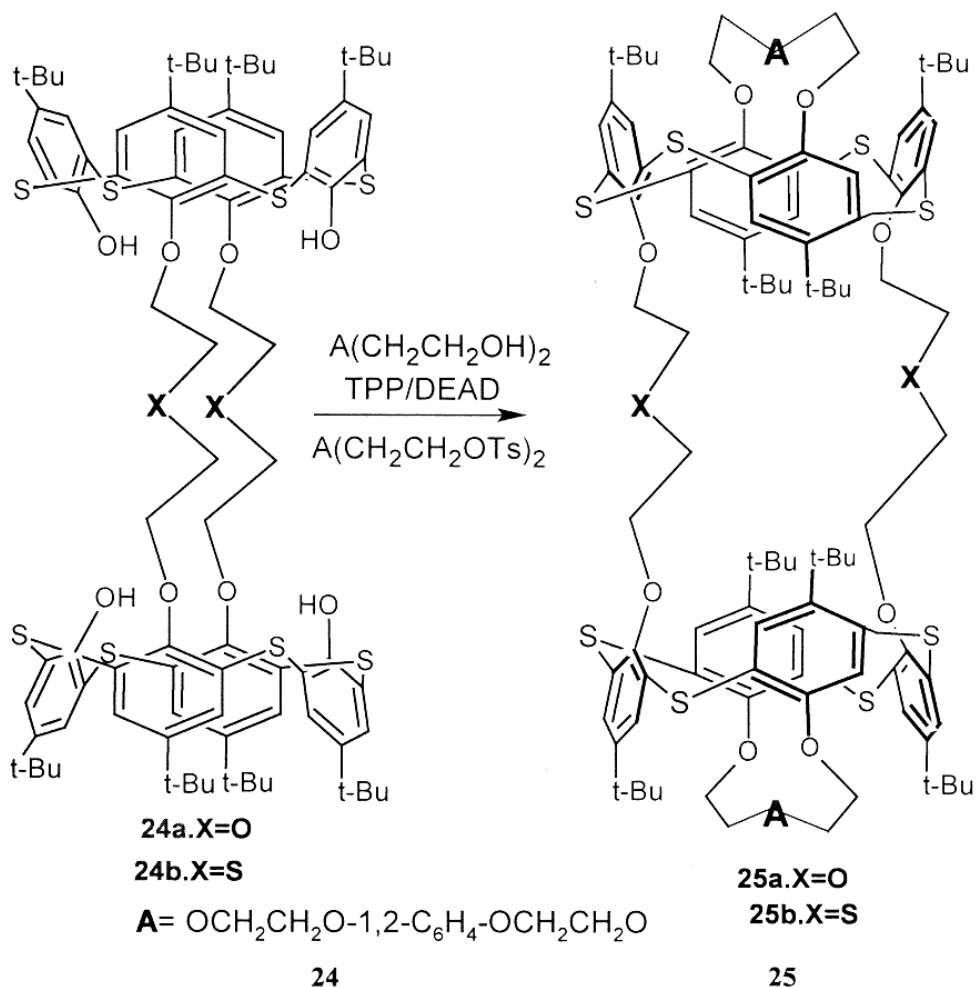
- (i) BrCH<sub>2</sub>COOEt/Na<sub>2</sub>CO<sub>3</sub>, acetone, reflux; (ii) NaOH, EtOH/water, reflux;  
 (iii) Ethylenediamine/THF, rt; (iv) phenyl isocyanate/*i*-PrOH, reflux;  
 (v) 23a– 23c/Et<sub>3</sub>N/THF, rt

Scheme 3

Thiacalixarene derivatives bearing amide groups effectively extract gold, palladium and platinum from chloride aqueous media via an ion-exchange mechanism<sup>45</sup>. With the thiacalixarene amide, the efficiency for gold separation was much higher than for the other two metal species and the recovery was almost complete. Moreover, thiacalixarene allows the selective extraction of Pd(II) via the formation of a  $\text{PdCl}_2\text{L}_2$  complex, where the metal is coordinated through S atoms. These ligands have also shown their effectiveness as carriers to transport gold and palladium from HCl solutions. Gold was selectively recovered from a mixture of Au, Pd and Pt in a supported liquid membrane system containing macrocycle thiacalix[4]arene, while palladium was transported through a plasticized polymeric membrane containing thiacalix[4]arene. Solid phase extraction systems prepared by adsorption of these ligands on activated polymeric cartridges have shown

good results<sup>45</sup>. Thiacalix[4]arene functionalized gold electrodes have also been used as sensors<sup>46</sup> since these materials present a strong affinity against sulphur derivatives and thiol groups which has an inert nature<sup>46</sup>.

With increasing lipophilism of substituents in the thiacalixarene fragments of the heterotube, increase in the binding efficiency of potassium and rubidium cations is observed. This is because the more hydrophobic and bulky groups offer better protection to the metal cation from the polar methanol molecules, which in turn favors the greater stability of the complex. The comparison of the "lipophilic layer thickness" (the distance from the first atom of the substituent and the plane through the carbons most remote from the first one) shows that this parameter is greater in 1-adamantyl groups than in *tert*-butyl groups<sup>47</sup>. Calix[4]tubes and semitubes comprising two conic calix[4]arene cores connected with alkaline



Scheme 4

linkers (see Scheme 4)<sup>48</sup> have also been utilized in the preparation of ionophores displaying exceptional selectivities for cesium,<sup>49</sup> rubidium<sup>50</sup> and potassium<sup>51-56</sup>.

In addition to the compounds (24) and (25) in calix-crown chemistry, the reaction of *p*-*tert*-butylthiacalix[4]arene tetrahydrazide derivative in 1,3-alternate conformation with *o*-phthalaldehyde gives thiacalix[4]-1,3-2,4-aza-bis-crown in "1 + 2" condensation mode. Compared with the earlier synthetic methods for preparation of thiacalix[4]-bis-crowns, this synthetic route was simple with high yield. Liquid-liquid extraction showed the compound to be an excellent receptor for Zwitterionic amino acids and soft cations such as Ag<sup>+</sup> and Hg<sup>2+</sup> (ref. 57). The extraction percentage for methionine was 78%. These extraction results indicate that the thiacalix[4]bis-crowns are effective receptors not only for metal cations, but also for bioorganic molecules, such as amino acids.

### Mixed ligand complexes

Increase in the cavity size or increase in repeat units leads to better analytical applications in thiacalixarenes. Synthesis of novel hybrid calix[6]arenes by acid-catalyzed condensation between bis(hydroxymethyl) dimer and tetramer of *p*-*tert*-butylphenol bridged by sulfur have been reported, wherein part of the CH<sub>2</sub> group of calix[6]arene is replaced by sulfur<sup>58</sup>. In order to investigate the effect of bridging sulfur groups on the ability of calix[6]arenes as host molecules, physical properties and inclusion properties toward organic molecules were compared with those of calix[6]arene and *t*-butylcalix[6]arene. The replacement of CH<sub>2</sub> with sulfur has significant effect on conformational properties, strength of intramolecular hydrogen bonding, and inclusion property of calix[6]arene.

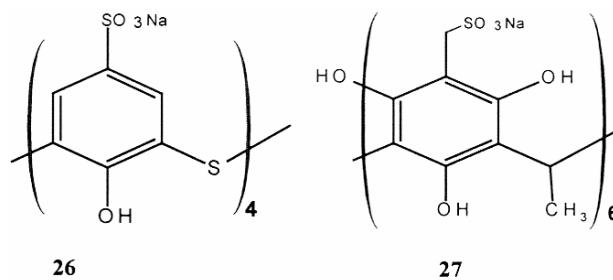
A series of new bis-calixarenes consisting of two *p*-*tert*-butylcalix[4]arene units linked through their lower rims with bridging moieties containing diimine units of different aromatic or heteroaromatic dialdehydes have been reported by Kumar *et al.*<sup>59</sup> Their complexation behavior was studied towards different metal ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, and Ag<sup>+</sup>) and it was found that these bis-calixarenes bind silver ion, but with poor selectivity, over the other metal ions.

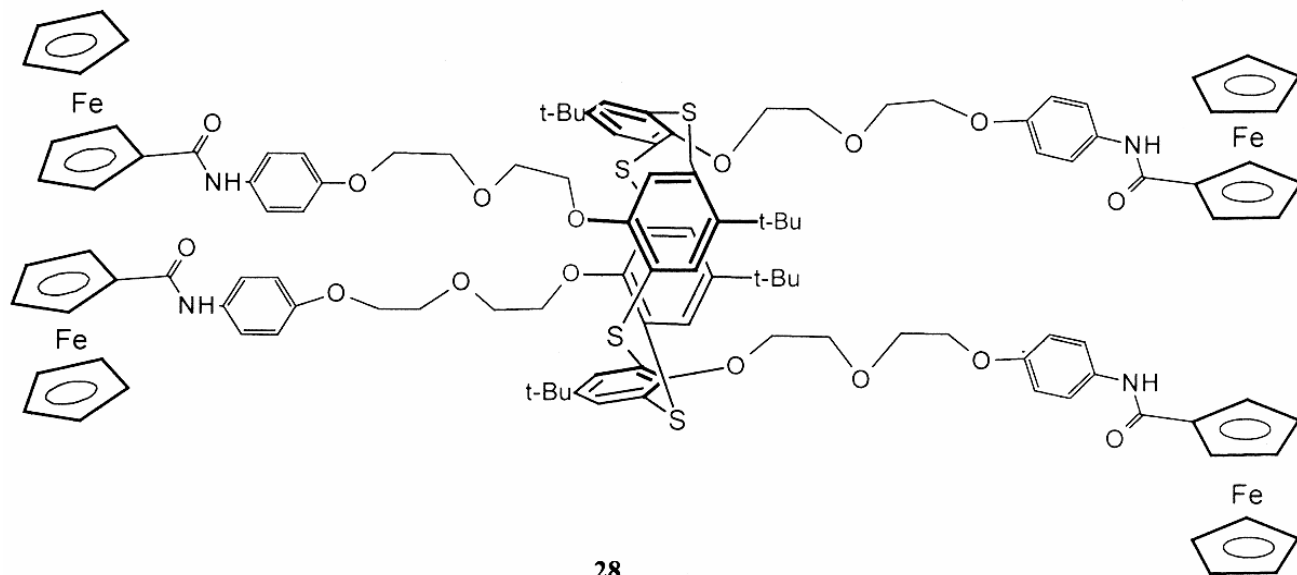
The strong antibacterial activity of silver ions has been the subject of much interest for the preparation of bio-active materials such as deodorizing clothes, agricultural sterilizing agent, etc. Therefore, studies

on extraction of silver ion with higher accuracy and on improving the recognition ability for soft metal ions, especially for silver ion, are of importance. Bhalla *et al.*<sup>60</sup> replaced the conventional calix[4]arene unit of bis-calixarenes with thiacalixarenes, which is an attractive host for soft metal ions. The performance of thiacalix[4]arene analogs of the bis-calixarenes (synthesized by using diamine as a molecular scaffold) as a host molecule for silver ions has been evaluated. To evaluate the binding ability of bithiacalixarenes toward different metal ions, two-phase solvent extraction of metal picrates (Na<sup>+</sup>, K<sup>+</sup>, Cs<sup>+</sup>, and Ag<sup>+</sup>) was carried out. The bithiacalixarenes, quantitatively and selectively, extract silver ions from the aqueous phase to the organic phase, while with the corresponding conventional bis-calixarenes the extraction was neither selective nor quantitative<sup>60</sup>.

### Water soluble thiacalixarenes

Thiacalixarenes have extensive utility in the field of analytical chemistry. Most of these compounds are insoluble in water. Some thiacalixarenes which are soluble in water having sulfonato groups like *p*-sulfonato thiacalixarene (26) and tetra-sulfonato-methylated calix[4]resorcinarene (27) been used as chelating agents in cloud point extraction of La(III), Gd(III) and Yb(III) ions with Triton X-100 as non-ionic surfactant<sup>61</sup>. The study indicates that both complexation ability and structure of calixarenes govern the extraction efficiency of lanthanides. The thiacalixarenes (26) and (27) form 1:1 lanthanide complex with similar stabilities in aqueous media but exhibit different extractability when used as chelating agents in cloud point extraction. Inclusion complexes of two sulfonated calixarene derivatives with C<sub>60</sub> fullerene have also been investigated by Kunsagi Mate *et al.*<sup>62</sup>. Both calixarene derivatives show higher photoluminescence intensity in the presence of C<sub>60</sub> fullerene. Significant emission of C<sub>60</sub> fullerene was not observed in the absence of calixarenes. The spectral changes were induced by a weak interaction between the calixarene hosts and the C<sub>60</sub> guest<sup>62</sup>.





Thiacalix[4]arene-tetrasulfonate salt has been obtained by the *ipso*-sulfonation of *p*-*tert*-butylthiacalix[4]arene<sup>63</sup>, while the calix[6]arene-hexasulfonate salt has been prepared by direct sulfonation of the parent calix[6]arene with concentrated H<sub>2</sub>SO<sub>4</sub><sup>64</sup>.

The hyperpolarized <sup>129</sup>Xe NMR spectroscopy has been successfully applied to investigate the inclusion complex formation between Xe and 4-sulfothiocalix[4]arene sodium salt (STCAS) in water using a new system which can supply hyperpolarized <sup>129</sup>Xe gas continuously to a sample tube directly<sup>65</sup>. This methodology of the hyperpolarized <sup>129</sup>Xe NMR spectroscopy system and analysis of experimental data have the advantage of increased efficiency, accuracy and simplicity. It is also a more precious and feasible analysis which can be applied to various solute-solvent interactions of Xe with different substrates in solution including proteins related to general anesthesia or those important in supramolecular chemistry.

The electrochemical study of thiacalix[4]-arenes(TCA), *p*-*tert*-butylthiacalix[4]arene(BuTCA) and their complexation behavior in the presence of various metal cations has been carried out<sup>66</sup>. TCA in pH 8 solution produced different responses to transition metal ions. The presence of even high concentration of alkali metal ions and alkaline earth metal ions led only to negligible changes with respect to TCA. Electrochemical properties of thiacalix[4]arenes with

electro-active phenol functional groups has been investigated through voltammetry and analytical applications using Cd<sup>2+</sup> ions<sup>66</sup>. Result shows that the anodic peak current of phenol in the presence of Cd<sup>2+</sup> ion increased as the concentration of the Cd<sup>2+</sup> ion increased.

Voltametric behavior of the novel ditopic ferrocene-based thiacalix[4]arene receptor (**28**) was investigated toward the cationic and anionic species to evaluate its potential electrochemical sensing capabilities<sup>67</sup>. This receptor was synthesised to develop new redox-active receptors capable of recognition and sensing of ionic or molecular guests which contains four identical polyether linked ferrocene amide moieties and exhibits a remarkable selectivity for electrochemical sensing of Eu(III) and dihydrogen phosphate ions, respectively. The present work substantially extends the applications of thiacalixarenes as molecular scaffolds.

## Conclusions

Thiacalixarenes have wide range of functions, conformational flexibility and chemical behavior which increases the importance of these compounds in supramolecular chemistry. Recent research work reviewed here shows many unmarked possibilities arising from modification in the classical calixarenes by sulfur atoms. This field is still developing and many captivating discoveries are still waiting for us in this promising and versatile field.



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