CHAPTER 1

Introduction
Resume

Progress made in chemistry of calix[4]resorcinarene by almost all the research groups in terms of their synthesis, conformational behavior, functionalization, cavitands and capsules, monolayers, formation of complexes, host-guest systems and their applications has been comprehensively reviewed.
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1. Introduction to resorcinarene

Calixarenes are a class of cyclo-oligomers formed by condensation between phenol and aldehyde and are classified as third generation supramolecules. First and second generation are Cyclodextrins (1) and crown-ethers (2), respectively.

The term "calixarene" is derived from Greek word, calix meaning vase or cone shaped and arene stands for the phenolic moieties present in the macrocyclic array.\(^{[3,4]}\)

As host molecules, calixarene and calix[4]resorcinarene have recently received considerable attention. The calixarenes are macrocyclic compounds comprising four or more phenolic moieties joined in cyclic array at the meta-positions by methylene bridges. The calixarene family can be divided into two major categories (i) the phenol-derived cyclooligomers e.g. p-tertbutylicalix[n]arene (3) and (ii) the resorcinol-derived cyclooligomers e.g. calix[4]resorcinarenes (4) as shown in following figure.
Two different zones can be distinguished in calixarenes, viz., the region of phenolic hydroxy groups and the para-position of the phenols, which are called the 'lower rim' and the 'upper rim' of the calixarene, respectively (Figure 1).

The calix[4]resorcinarenes are resorcinol-derived calixarenes such as C-methylcalix[4]resorcinarene (4). The bracketed number is inserted between the calix-and-resorcinarene. The substituent, which is introduced by the starting aldehyde at the methylene carbon, is indicated by a prefix "C-substituent". Calix[4]resorcinarene has an important advantage over calix[n]arenes that they are readily obtainable with various substituents at the sites of the bridging
methylene groups and various functionalization on the hydroxy group as well as upper rim.

2. Historical developments of resorcinarene

Resorcinarenes have a long history, stretching back to 1872 when Adolph von Baeyer reported reactions between phenol and aldehydes. Several years later Michael reported that the product was formed by combination of an equal number of benzaldehyde and resorcinol molecules and loss of an equal number of water molecules. However, it took several decades to determine the structure of the product. In 1940, Niederl and Vogel, from molecular weight determinations, showed that the ratio between aldehydes and resorcinol in the product is 4:4. They proposed a cyclic tetramer structure (4), which was finally proved in 1968 by Erdtman and coworkers by a single crystal X-ray analysis.

The official IUPAC-name for resorcinarene (4) is 2,8,14,20-tetraalkylpentacyclo[19.3.1.1^3.7.19.13.1^15.19]octacosa-1-(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene-4,6,10,12,16,18,22,24-octol.

Gutsche and Bohmer classified them as calixarenes by calling them calix[4]resorcinarenes or resorcinol-derived calix[4]arenes, Some other different names like Hogberg compounds or simply octols do also appear in literature. In the absence of any suitable trivial name in the literature, Schneider and Schneider in 1994 suggested its name as resorcinarene. The resorcinarenes are resorcinol-derived calixarenes e.g. C-methylcalix[4]resorcinarene (4) if R is CH₃. The bracketed number is inserted between the calix and resorcinarene, which is usually 4 and in very few reports 6, signifying whether it is tetramer or hexamer. The substituent, which is introduced by the starting aldehyde at the methylene carbon, is indicated by a prefix "C-substituent". Recently, the name, calix[4]resorcinarenes has also been used as "resorcin[4]arenes".

The work on resorcinarenes and its derivatives had seen many advances in last two decades and has been reflected in various general reviews which covers their applications, design, structure, synthesis, characterization,
functionalization\textsuperscript{[24,25]}, complexation properties and their use as host-guest systems\textsuperscript{[26-34]}, cavitands and capsules\textsuperscript{[35-39]}. Reviews on coordinative properties of resorcinarene towards transition metals\textsuperscript{[40,41]}, resorcinarene-encapsulated nanoparticles\textsuperscript{[42]}, resorcinarene-based multinuclear metal complexes\textsuperscript{[43]} and self assembled monolayers of calix[4]resorcinarenes\textsuperscript{[44]} are also available in literature.

3. Synthesis

Calix[4]resorcinarenes can be easily obtained by acid catalysed condensation of resorcinol with various aliphatic or aromatic aldehyde, by heating the constituents to reflux in a mixture of ethanol and concentrated HCl for several hours, usually cyclotetramer crystallizes out from reaction mixture, in a reasonable to high yields via simple one step reaction without using template, although for different aldehyde, different optimal reaction conditions exist\textsuperscript{[11,13,45]}. We do not get tetrameric product when resorcinol is having electron withdrawing substituent such as NO\textsubscript{2} or Br at the 2-position\textsuperscript{[13]}. In certain cases, formaldehyde and 2-methyl resorcinol or Pyrrogallol yields isolable amounts of tetrameric product\textsuperscript{[46]}. The question, which groups substituted on the resorcinol and aldehydes moieties tolerate the fourfold oligomeric cyclization reactions has been well addressed by Donald J. Cram et al.\textsuperscript{[13]} and Schneider et al.\textsuperscript{[47]}. However, there are many new synthetic routes, for various types of resorcinarenes, which have emerged over number of years and in this section we are reporting only those routes which are somewhat different from conventional mineral acid catalyzed cyclooligomerisation. Different derivatives of calix[4]resorcinarene obtained by conventional method are reported in (Table 1).

Trifluoromethanesulfonate salts, the so-called triflates, such as ytterbium (III) triflate\textsuperscript{[48]} and bismuth(III) triflate\textsuperscript{[49]}, have been described as efficient catalysts for the synthesis of calix[4]resorcinarenes. Recently, lanthanide(III) tosylates and lanthanide(III) nitrobenzenesulfonates\textsuperscript{[50,51]} have also been used as efficient, inexpensive, recyclable, and environmentally friendly catalysts for the synthesis of calix[4]resorcinarenes (5a,b) and their catalytic efficiency was found to be comparable to that of the triflate salts.
Microwave assisted synthesis\textsuperscript{[52]} of calix[4]resorcinarenes using resorcinol and aldehydes, catalysed by 12-tungstophosphoric acid type Keggin (H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40}13H\textsubscript{2}O) or concentrated HCl, gives excellent yield (>90\%) with short reaction times (<3–5 min) and does not require harsh conditions.

Pyrogallol[4]arenes (7\textsubscript{a–f})\textsuperscript{[53]} have also been synthesised in excellent yields by cyclocondensation of pyrogallol (6) with aromatic aldehydes under microwave irradiation.

New type of octahydroxypyridine[4]arenes (8\textsubscript{a–f}) derived from condensation of 2,6 dihydroxy pyridine with a number of aliphatic and two aromatic aldehydes in acidic media have been obtained\textsuperscript{[54]}. The reactivity of 2, 3-dihydroxypyridine is lower than that of resorcinol or 2-hydroxyresorcinol, so harsher conditions must be applied, but the cyclization reactions are, in principle, comparable.
Acid catalyzed condensation of 2,6-dihydroxypyridine hydrochloride with diethyl 2,2-diethoxyethylphosphonate on prolonged heating gives water-soluble pyridinocalixarene (9) with four fragments of phosphonic acid (a product of full hydrolysis of the corresponding ester) on the lower rim of the molecule was obtained\[55^6\].

New calix[4]resorcinarenes (10, 11)\[56^6\] and (12)\[57^6\] have been synthesized by the condensation of resorcinol with the corresponding aldehyde (acetal) and
with photoswitchable chromogenic azo group and an ionophoric part (i.e., residue of benzo-15-crown-5) on the lower rim, respectively.

\[ R = H, \quad R' = CH_2N^+H_2Me.CF_3SO_3^- \]

\[ R = Me, \quad R' = CH_2N^+H_2Me.CF_3SO_3^- \]
New synthetic conditions for the fully selective formation of the rctt chair stereoisomers of octa-O-alkyl resorcin[4]arenas (13-17) in acetic acid–H₂SO₄ or acetic acid–HCl mixtures have been described and it is proposed\textsuperscript{[58]} that this isomer is the thermodynamic product under Bronsted-acid-catalysis, an unprecedented observation in resorcinarene chemistry.

13 R₁ = H, R₂ = Me, R₃ = 4-C₆H₄OH
14 R₁ = H, R₂ = Me, R₃ = 4-C₆H₄OC₆H₄
15 R₁ = H, R₂ = Me, R₃ = CH₃
16 R₁ = H, R₂ = Me, R₃ = CH₂CH₂CH₂OH
17 R₁ = H, R₂ = Me, R₃ = CH₂CH(CH₃)₂

Another example involves the cyclocondensation of 1,3-dialkoxybenzenes (18a,b) with 1,3,5,-trioxane, catalyzed by Sc(OTf)₃ to produce resorcin[4]arene (19a,b) octaalkyl ethers as the major products. In addition, 'confused' resorcin [4]arene (20a,b) octaalkyl ether bearing one alkoxy group at the intra annular position were also obtained as the minor products\textsuperscript{[59]}.
Ladder polymer (CRA-polymer)\textsuperscript{[60]} have been synthesized using a one-pot method by the condensation reaction of resorcinol and 1, 4-butanedial [(CH\textsubscript{2})\textsubscript{2}(CHO)\textsubscript{2}] in the presence of concentrated HCl in ethanol at 80°C for 48 hours afforded a soluble polymer (CRA-polymer) in quantitative yield.

4. Mechanism and stereochemistry

The mechanism of the acid-catalyzed condensation reaction for the formation of calix[4]resorcinarenes had been thoroughly studied\textsuperscript{[47]} (Scheme 1). Under acidic conditions, first, the aldehyde gets protonated to serve as the initial electrophile which adds to resorcinol. The alcoholic hydroxyl of the subsequent adduct was protonated again generating a mole of water. Removal of water affords a carbocation intermediate, which undergoes second electrophilic addition to another resorcinol to form a dimer. Sequential coupling of the dimer with resorcinol units results in trimer, tetramer, or higher oligomers containing more than four monomers. Since the condensation reaction was reversible under acidic conditions, most of the higher oligomers disappear towards the end of the reaction although they were present during the intermediate reaction time. The linear tetramers cyclize rapidly to form calix[4]resorcinarenes once they were formed in the reaction mixture. The cyclization was too fast for tetramers to be isolated. The cyclization was favored, due to their lack of conformational strain, by the formation of hydrogen bonds between proximal phenolic hydroxyl groups of adjacent resorcinol units in the folded structures\textsuperscript{[21]}.
Scheme 1

Calix[4]resorcinarene
A kinetic and molecular modeling study\textsuperscript{[47]} of the acid-catalyzed reaction of acetaldehyde and resorcinol concludes that:

a) Ring closure to the calix[4]resorcinarenes is at least as fast as chain propagation.

b) The macrocyclic products are the thermodynamic sinks of the reaction.

c) Linear oligomers having more than four-aryl unit's dipolymerize fast in comparison with ring opening, thus promoting the formation of cyclic tetramer, pentamer and hexamer.

Although i.e. reaction with RCHO appears to yield only calix[4]resorcinarenes, but the cyclocondensation of 2-alkylresocinarenols with 1,3,5-trioxane in ethanol-conc. HCl (4:1 v/v) yields mixtures containing both calix[4]resorcinarenes and calix[6]resorcinarenes and the later was isomerised to the former on prolonged heating in the reaction media\textsuperscript{[61]}.

Calix[4]resorcinarenes are non-planar molecule because it exist in different isomeric form\textsuperscript{[13,62,63]}. The stereochemistry is generally defined as a combination of the following three stereochemical criteria:

(I) The first criterion is the conformation of macrocyclic ring. As the macrocycle ring has five highly symmetrical conformations: crown (C_4v), boat (C_{2v}), chair (C_{2h}), diamond (C_s), and saddle (D_{2d}), calix[4]resorcinarenes can have five corresponding stereoisomers (Figure 2).
(II) The second criterion is the relative configuration of the substitutes at the ethylene bridges, giving the all-cis (ccc), cis-cis-trans (cct), cis-trans-trans (ctt) and trans-cis-trans (tct) resorcinarene stereoisomers. (Figure 3).

(III) The last criterion was the individual configuration of methylene bridge substituents, which may be either axial or equatorial in conformations of the
macrocycle with C symmetry. Combination of these three criteria results in a great number of possible stereoisomer. However, only four have been reported experimentally so far. The boat conformation is usually reported as a crown conformation partially due to the presence of two boat isomers, which interconvert rapidly to give a time-averaged crown conformation. The interconversion between boat, chair, and diamond isomers, however, does not occur since it requires the breaking of at least two covalent bonds. They are diastereomeric isomers. All of them can be produced in a reaction. Under homogeneous acidic conditions, the product ratio is mainly determined by the thermodynamic stability of the different isomer because the condensation reaction is reversible under such conditions. The relative solubility of the different isomers in the reaction solvent plays a key role in determining the product ratio if the reaction is performed under heterogeneous conditions. The ratio of different diastereoisomers depends greatly on the reaction conditions used although there are many factors that may affect the presence or absence of a specific isomer.

5. Functionalization

Calix[4]resorcinarenes, being very versatile molecular platform, can be functionalized at two, four, six, eight, twelve, sixteen or more sites depending upon the reagent, aldehyde, resorcinol and conditions used to carry out the reaction. We can have functional group of our choice at all or either of three available positions (R₁, R₂, R₃) and can control their numbers too to get various calix[4]resorcinarenes derivatives. One can expect these derivatives to exhibit somewhat different or extra properties than those exhibited by the monofunctionalised molecules. In this section we have reviewed various possible functionalisation of calix[4]resorcinarenes (Figure 4) at R₁ and/or R₂ and/or R₃, which has been divided into two i.e. gross and selective. As there are many reports on routine gross functionalisation, they have been summarized in (Table 1) and in the form of dendrimers where as selective functionalisation has been extended to crown derivatives of calix[4]resorcinarenes.
### 5.1. Full

**Table 1. Functionalization of calix[4]resorcinarenes**

<table>
<thead>
<tr>
<th>R₁ in figure IV</th>
<th>R₂ in figure IV</th>
<th>R₃ in figure IV</th>
<th>Ref.</th>
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</thead>
<tbody>
<tr>
<td>C₆H₄Br</td>
<td>H</td>
<td>COCH₂Et</td>
<td>8b</td>
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<tr>
<td>Et</td>
<td>O(CO)Me</td>
<td>(CO)Me</td>
<td>64</td>
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<tr>
<td>C₁₁H₂₃</td>
<td>COOH</td>
<td>Me</td>
<td>65</td>
</tr>
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<td>CH₃</td>
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<td>SO₂C₆H₄Me(Tos)</td>
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<td>C₆H₄Br</td>
<td>H</td>
<td>(CO)Me</td>
<td>67</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>O(CO)Me</td>
<td>(CO)Me</td>
<td>68</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>OSO₂C₆H₄Me</td>
<td>SO₂C₆H₄Me</td>
<td>68</td>
</tr>
<tr>
<td>CH₂ipr</td>
<td>H</td>
<td>CH₂(C=CH)</td>
<td>69</td>
</tr>
<tr>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>70</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>H</td>
<td>CH₂COOH</td>
<td>71</td>
</tr>
<tr>
<td>C₁₁H₂₃</td>
<td>H</td>
<td>CH₂COOH</td>
<td>72</td>
</tr>
<tr>
<td>C₅H₁₁, C₆H₁₃</td>
<td>CH₂NR(COCH₃)</td>
<td>H</td>
<td>73</td>
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<tr>
<td>CH₃</td>
<td>H</td>
<td>CH₂C=CH,</td>
<td>74</td>
</tr>
<tr>
<td>(CH₂)₂Ph</td>
<td>H</td>
<td>CH₂C=CCH₃, CH₂</td>
<td>75</td>
</tr>
</tbody>
</table>

Figure 4
<p>| p-CH₃C₆H₄ | H, Me | C=CH₃{Co₂(CO)₆} | 76 |
| C₉H₁₉ | H | COMe | 77 |
| Ph,C₆H₄OH, Ferrocene (Fc) | H | CH₂COOEt, CH₂CONHNH₂, CH₂CONHN=CH-Fc | 78 |
| Ph, Fc(Ferrocene) | H | | 78 |
| CH₃ | | | 79 |
| Et | CH₂N(CH₂)₅ | H | 80 |
| CH₃, C₂H₅, C₅H₁₁ | CH₂N⁺H₂R(R = C₄H₉, C₆H₁₁) | H | 81 |
| Ph | | | 82 |
| C₅H₁₁ | | | 83 |
| CH₃ | CH₂NMe₂, CH₂Net₂ | H | 84 |
| Ph | | | 85 |
| Me | CH₂NHCH₂CH₂NMe₂ | H | 86 |
| Me, C₉H₁₉, C₆H₄O(CH₂)₁₁CH₃ | CH₂SO₃Na | H | 87 |
| CH₂CH(CH₃)₂ | CH₂OCH₃, CH₂OC₂H₅, CH₂OC₃H₇, CH₂OC₄H₉, CH₂OC₅H₁₁, CH₂OC₆H₁₃ | H | 88 |
| Me | CH₂SR (R= 2-Naphthyl, C₆H₅, 4-ClC₆H₄, 4-MeC₆H₄, tert Bu) | H | 89 |
| Me | NO₂ | H | 90 |
| Me | -N₂C₆H₄SO₃Na | H | 91 |
| Me | H | CH₂COOEt, CH₂CONHNCHR₁CH₂OH(R₁ = C₃H₅,CH₃, R₂ = H, Ph), OCH₂CONHNCHR₂RC₃H₃ (R = Ph, C₆H₁₁) | 92 |
| CH₂CH₂Ph | H | PPh₂ | 93 |</p>
<table>
<thead>
<tr>
<th>Compound</th>
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<tbody>
<tr>
<td>Ph</td>
<td>H</td>
<td>(\text{CH}_2\text{CON(C}_2\text{H}_5)_2), (\text{CH}_2\text{CON(}\text{CH}_2\text{CH}_2\text{CH}_3)_2), (\text{CH}_2\text{CON(}\text{CH}_3\text{)Ph,}) (\text{CH}_2\text{CONNH(CH}_3\text{)Ph})</td>
<td>94</td>
</tr>
<tr>
<td>Fc (Ferrocene)</td>
<td>H</td>
<td>(\text{CH}_2\text{CON(C}_2\text{H}_5)_2), (\text{CH}_2\text{CONH CH}_3), (\text{CH}_2\text{CONH(CH}_2\text{)_3}) CH\text{}_3)</td>
<td>94</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>(\text{COCH}_2\text{CH}_2\text{Br,}) (\text{CH}_2\text{COOC}_2\text{H}_5), (\text{CH}_2\text{CH}_2\text{OH,}) (\text{CH}_2\text{CH}_2\text{OCOCH(}\text{CH}_3\text{)Br,}) (\text{CH}_2\text{CH}_2\text{OCOC(}\text{CH}_3\text{)_2Br})</td>
<td>95</td>
</tr>
<tr>
<td>C\text{}_2\text{H}_6</td>
<td>H</td>
<td>(\text{COCH(CH}_3\text{)Br,}) (\text{COC(CH}_3\text{)_2Br})</td>
<td>96</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>(\text{C}_6\text{H}_3(\text{CN})_2)</td>
<td>97</td>
</tr>
<tr>
<td>(\text{C}<em>11\text{H}</em>{23})</td>
<td>-N\text{}_2\text{C}_6\text{H}_4\text{NO}_2</td>
<td>H</td>
<td>98</td>
</tr>
<tr>
<td>(\text{CH}_2\text{CH}_2\text{SO}_3\text{Na})</td>
<td>H</td>
<td>(\text{CH}<em>2\text{CH}</em>{(\text{CH}_3)_2}) (\text{CH}<em>2\text{CH}</em>{(\text{CH}_2\text{CF}_2)_9})</td>
<td>99</td>
</tr>
<tr>
<td>CH\text{}_2\text{CH(}\text{CH}_3\text{)}_2</td>
<td>H</td>
<td>(\text{CH}_2\text{-O-}\text{(CH}_2\text{)_n}) (n = 1,2,3,4)</td>
<td>100</td>
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<tr>
<td>CH\text{}<em>2\text{CH}</em>{(\text{CH}_2\text{CF}_2)_9}\text{CH}_2\text{Br,}) (\text{CH}_2\text{CH}_2\text{N}_3,) (\text{CH}_2\text{CH}_2\text{NH}_2,) (\text{CH}_2\text{CH}_2\text{NHCH}_2\text{Ph,}) (\text{CH}_2\text{CH}_2\text{NHCH}_2\text{C}_6\text{H}_4\text{N})</td>
<td>H</td>
<td>Me</td>
<td>101</td>
</tr>
<tr>
<td>CH\text{}_2\text{CH(CH}_2\text{CF}_2\text{)_9}\text{CH}_2\text{N}_3</td>
<td>H</td>
<td></td>
<td>102</td>
</tr>
</tbody>
</table>
5.2. Dendrimers

Dendrimers are well-defined, highly branched, three-dimensional compounds with a large number of reactive end groups. Recently, they have received considerable attention as new synthetic materials\textsuperscript{[103]} and their use as new functional materials in nanotechnology, with both biochemical and medical applications in view\textsuperscript{[104,105]}.

Calix[4]resorcinarenes are suitable as core molecules because of easy synthesis and adequate space between functional groups. A number of synthetic approaches for synthesizing dendrimers have been described in literature. All methods involve stepwise processes such as several protection deprotection and continuous purification steps.

M. M Garcia et.al\textsuperscript{[106]} have done great amount of work in the area and have reported dendritic branches of poly(arylether) with peripheral n-propyl chains (21), dendritic branches of poly (arylether) with peripheral allyl chains \textsuperscript{[107]}, dendrimers with \pi-conjugated systems oligophenylenevinylene (OPV)\textsuperscript{[108]} and their supramolecular complexes with fullerene C\textsubscript{60} (22,23).
22 $R = \text{CH}_2\text{CH}_2\text{Ph}$

23 $R = \text{CH}_3\text{CH}_2\text{Ph}$
Dendrimers from resorcinarenes core with stilbene and 4-styrylstilbene\textsuperscript{[109]} and $\pi$-conjugated dendron branches with 16 (24\textit{a-c}) and 32 (25\textit{a-c}) stilbene groups\textsuperscript{[110]} have been synthesized. They have also shown the possibility of using these materials for the development of electrochromic devices such as smart windows.

Garcia et al.\textsuperscript{[111]} reported series of ferrocenyl ended dendrons with $n$-conjugated systems using resorcinarenes as core molecule and also studied cubic nonlinear optical resorcina\textsuperscript{[112]} of this first generation of resorcinarenes dendrimers. The dendrons were attached to eight functionalized resorcinarenes via Williamson reaction to obtain high molecular weight dendrimers. Compounds
(26a-c) have been prepared by a reaction of resorcinol with aldehydes. The dendrimers (29a-c) and (30a-c) were obtained from the dendrons (27-28) and resorcinarenes (26a-c) in acetone and K$_2$CO$_3$ at reflux for 3 days.

R = -(CH$_2$)$_2$C$_6$H$_5$ (26 a)
-(CH$_2$)$_4$-CH$_3$ (26 b)
-(CH$_2$)$_{10}$-CH$_3$ (26 c)
Simple and efficient synthesis of polyamidoamine-type dendrimers\textsuperscript{[113]} up to the third generation on the basis of calix[4]resorcinarenes with terminal salicylideneimine groups is reported. Compounds (31) and (32) were prepared via divergent method in seven steps with the corresponding tetraphenyl and tetra (hydroxyl phenyl) calix[4]resorcinarenes as the starting material.

\[ R = H, 31; R = OCH_2 CONH(CH_2)_3 N[CH_2 CH_2 CONH(CH_2)_3 N=CHC_6 H_4 (Ol+o)]_2; A = CH=NH(CH_2)_3 NHCOCH_2 CH_2, \text{ B = CH_3 CH_2 CONH(CH_2)_3 NH=CH} \]

5.3. Selective

Picolyl functionalized resorcinarenes (33a-c) serve as a multidentate ligand for the coordination of some transition metals such as palladium, zinc, nickel and copper\textsuperscript{[114]}.

\[ R = C_7 H_{15}, 33 \ a \text{ R = C}_7 H_{15}, 2 \text{ picoly}; \ b \text{ R = C}_2 H_7, 2 \text{ picoly}; \ c \text{ R = C}_7 H_{15}, 3 \text{ picoly} \]
Roger Hunter et al.\textsuperscript{[115]} have synthesized bridged resorcinarenes and have used them as templates for asymmetric catalysis. Resorcinarene tetrastilphonates (34a-f) and tetraphosphates (35a-c) of $C_2V$ symmetry are useful as molecular platforms for the design of cation receptors, containing different binding units in the molecules\textsuperscript{[116]}.

![Chemical Structures](image)

Alexander Shivanyuk et al. reported aminomethylation of resorcinarenes at the upper rim with bulky diisopropylamine and formaline leads to trisubstituted derivatives (36) where as analogous reaction with $C_{2v}$-symmetrical resorcinarenes tetraotylate gives the monoaminomethylated compound. The remaining unsubstituted resorcinol rings can be substituted to give novel resorcinarenes derivatives\textsuperscript{[117]}. They have also reported regioselective acylation of aminoresorcinarenes\textsuperscript{[118]}.
5.4. Resorcinarene crowns

As numbers of oxygen's in the crown ether moiety determine its selectivity toward cation binding i.e. crown-4 is selective to sodium; crown-5 is selective to potassium; and crown-6 is selective to cesium cations. Studies have been carried out to explore the cation -π interaction when crown ether moiety is attached to resorcinarene skeleton. The hydroxyl groups which are situated on the upper rim of resorcinarene enable the crown bridging on the “open” end of the cavity thereby making the resorcinarene (bowl shape) available to take part in the cation binding.

Tetramethoxy resorcinarene was used as the platform for the synthesis of resorcinarene bis-crowns\[119\], BC4 and BC5 (37,38). Later was found to accommodate two cations simultaneously inside the crown pockets formed by the crown ether bridges and the resorcinarene skeleton. BC5 was further improved by introducing tribenzo-bis-crown ethers\[120\], m- and p-TBBC6 (39) with the expectation that added aromatic functionality may improve its cation binding ability. The flexibility of resorcinarene bis-crown, in boat conformation, was also compared with resorcinarene core and tetramethoxy resorcinarene derivative\[121\]. Although m-TBBC6 and BC5 were found to be capable of binding (K\(^+\), Rb\(^+\) and Cs\(^+\)) but highest affinity was observed for Cs\(^+\) and no binding was observed with...
p-TBCC6, exemplifying the significance of the complementarity and preorganization for complexation in supramolecular chemistry.

Combination of 1,2-crown[6]cavitands with resorcin[4]arenes resulted in potential receptor molecules\textsuperscript{[122]} with large hydrophobic surfaces. A new cavitand (41) bearing two rigid crown ether groups has been synthesized from tetrahydroxycavitand (40). The binding properties of this cavitand towards alkali metal ions as well as ammonium ion were also examined\textsuperscript{[123]}.
New macrocyclic carriers based on the aza-18-crown-6, aza-crown resorcinarene (ACR) (42) and aza-18-crown-6 bonded to an undecyl chain aza-crown undecyl (ACU) (43) have been used in dichloromethane as bulk liquid membranes (BLMs) to study the effect of cations on competitive transport among anions (ReO$_4^-$, NO$_3^-$, ClO$_4^-$). In most cases, ACR transports anions better than ACU. The carriers also showed selectivity for ReO$_4^-$ and ClO$_4^-$ over NO$_3^-$ with K$^+$ and Na$^+$ as the co-transported cations using neutral and basic aqueous phase solutions. Authors$^{[124]}$ have tried to establish if the individual cations in a mixture promote anion transport, then a mixture containing those cations will also transport anions. Also, if one of the cations in a mixture does not promote anion transfer, it may inhibit anion transport even though a promoting cation is present.
To further extend the existing crown ether calix[4]resorcinarene family, novel 'cloverleaf' crown ether calix[4]resorcinarenes (44a-b) and (45) have been synthesized\textsuperscript{125}, having one or two distal pairs of crown ethers annulated directly to the macrocycle via the peripheral resorcy1 oxygen atoms.

Cloverleaf resorcin[4]arene crown ether, $R = $ penty1
6. Cavitands and capsules

A widely exploited class of receptors for investigations into the forces involved in recognition are the resorcin[4]arene-based cavitands and capsules. We can define\textsuperscript{[126]} self-assembling capsules as receptors with enclosed cavities that are formed by the reversible noncovalent interaction of two or more, not necessarily identical subunits. The aggregate so formed should have a well-defined structure in solution and be capable of binding behavior that none of its individual components display alone. The efficient synthesis of cavitands and capsules which are large enough to entrap various guests is a great challenge.

Weak forces of interaction like dispersion force etc. along with CH-\pi interactions stabilize a new multicomponent assembly between cavitand host (46) and ditopic guests (47) and (48a-c)\textsuperscript{[127]}.

![Diagram of cavitands and capsules with chemical structures](image-url)
In contrast to metalation strategies that lead to either endo or exo functionalization. The functionalization of deep-cavity cavitands via electrophilic substitution has been investigated. Amino-pyridine substituted resorcinarene-based cavitand, dipyridyl-based cavitands and self-assembled coordination cage have also been synthesized. Self-assembled coordination cage (49), constitutes two tetrapyridyl-substituted resorcin[4]arene cavitands coupled through four square-planar palladium complexes. The coordination cage has the right size for the inclusion of large molecules such as fullerenes and forms 1:1 complexes with methano[60]fullerene derivatives bearing a dimethyl and a diethyl malonate addend, respectively.

Two novel tetrathiolated cavitands (tetrathiol cavitand and tetrabenzythiol cavitand) for the encapsulation of gold nanoparticles and their subsequent transformation into nondesorptive crosslinked shells have been reported. Synthesis and coordinative properties of the first tetraphosphine built upon a
resorcinarene cavitand (50) have been described\textsuperscript{[133]}. In the presence of Pd (OAc)\textsubscript{2} and a base, ligand (50) is active in Heck coupling reactions.

\[
R = C_5H_{11}
\]

Photocyclizable systems (51) and (52) of covalently linked dimers, containing two resorcin[4]arene moieties connected over two 9,10-functionalized anthracene units have been reported\textsuperscript{[134]}. 

\[
51 \quad n = 2, 1 \\
52 \quad n = 1, 2
\]
Paek and Park\textsuperscript{[135]} have reported versatile molecular capsules formed from resorcin[4]arene-based benzoylhydrazide cavitands. The synthesis of pyridyl-functionalized cavitand (53) that contains suitable hydrogen-bond acceptor moieties for the construction of asymmetric cavitand-based capsules is described \textsuperscript{[136]}.  

\begin{center}
\[
\begin{array}{c}
\text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \\
\text{O} \quad \text{O} \quad \text{O} \quad \text{O} \\
\text{R} \quad \text{R} \quad \text{R} \quad \text{R} \\
\text{R} \quad \text{R} \quad \text{R} \quad \text{R}
\end{array}
\end{center}

\[ R = (\text{CH}_3)_4\text{CH}_3 \]

Alexander Wei et al. have used surfactants derived from C-undecylcalix[4]resorcinarene, namely tetrabenzylthiol resorcinarene (TBTR) and a poly(dithiocarbamate) derived from tetra-N-methyl(aminomethyl) resorcinarene (TMAR-DTC), for encapsulating Gold nanorods (GNRs) and extracting them into organic solvents. The resorcinarene-encapsulated GNRs can be used as intermediates to form magnetic nanoshells and in the preparation of core–shell nanostructures\textsuperscript{[137]}. C-methyl pyrogallarene forms dimeric capsules with small quaternary and tertiary alkyl ammonium cations\textsuperscript{[138]}. C-alkyl-resorcin[4]arene form hexameric capsules and two molecules of the tetraethylammonium guests seem to be encapsulated within each hexameric capsule, regardless of the anion of these salts\textsuperscript{[139]}.  

J. L. Atwood and his various coworkers have rich contribution with respect to self assembled capsule derived from C-alkylpyrogallol[4]arene under various conditions.
Six-C-methylresorcin[4]arenes have been shown to self assemble with eight structural water molecules (through hydrogen bonding) as a hexameric nano-capsu[140]. The related C-alkylpyrrogalol[4]arens (PgC's) self-assemble without structural water molecules to form similar hydrogen-bonded nano-capsules[141]. Large multicomponent nanospheroid assemblies (55) have been prepared consisting of six C-pentlypyrogalol[4]arene (54) molecules and 12 Ga$^{3+}$ metal-ions which are held together by a combination of metal ion coordination and hydrogen bonding interactions[142].
They have also prepared C-chlorobutylpyrogallol[4]arene (56) and C-bromooctylpyrogallol[4]arene (57) by the acid catalysed condensation of the corresponding aldehyde and pyrogallol in ethanol and found that (56) to favour the formation of bi-layer arrays whilst (57) preferentially formed nano-capsules.

![Chemical Structure](image)

\[56 = R = (\text{CH}_2)_4 \cdot \text{Cl}\]
\[57 = R = (\text{CH}_2)_8 \cdot \text{Br}\]

The first metal coordinated pyrrogallol[4]arene encapsulating dimer has been synthesized and shows high nuclearity with respect to Zn\(^{11}\), arranged as a polar coordination belt. This high nuclearity zinc pyrogallol[4] arene dimer capsule is a successful follow-through on a model concept. This offers a spectrum of new and unusual opportunities for further investigations of metal chelation with molecular encapsulation\(^{1144}\). Structural study on two complexes formed (in water and acetonitrile) between cesium chloride and PgC’s with very different ‘lower rim’ character (PgC\(_4\)Cl, 56, and PgC\(_6\), 58) has been carried out. These studies afforded two related dimeric capsules, one head-to-head and one offset (56 CsCl and 58 CsCl respectively), that are facilitated by varied coordination of cesium to the ‘upper rim’ oxygen atoms and in one case to the aromatic ring of the host\(^{1145}\).
Julius Rebek, Jr. et al. have shown that fluorescence resonance energy transfer occurs from a fluorescent guest to a labeled resorcinarene and pyrogallolarenes capsule as host. They have also gleaned information regarding the degree of assembly and stability of the hexameric capsules under a variety of conditions\textsuperscript{1146,147}. Reversible encapsulation has changed the way scientists view molecular interactions. It is now becoming clearer that the behavior of molecules in dilute solution is really quite different from their behavior in capsules. The capsules self-assemble through a variety of forces, including hydrogen bonds, metal-ligand interactions and hydrophobic effects etc. Their lifetimes range from milliseconds to hours, long enough for NMR spectroscopy to reveal what is going on inside. Julius Rebek, Jr.\textsuperscript{148} has given a brief account of the physical properties and how the mechanical boundaries of the capsules dictate the behavior of molecules inside. He has probed the various regions of the capsule with guests of different shape. (26c, 59a,b), (60a,b) and (8d) self-assemble spontaneously into hexameric capsules in organic solvents have been demonstrated with the aid of diffusion NMR systems\textsuperscript{1149}. 

\[ R = \text{OH}, \quad R' = (\text{CH}_2)_4\text{Cl}, \quad \text{PgCl} \]

\[ R = \text{OH}, \quad R' = (\text{CH}_2)_8\text{CH}_3, \quad \text{PgC}_6 \]
7. Self assembled monolayers

Calix[4]resorcinarenes when incorporated within molecular assemblies of Langmuir-Blodgett (LB) films, monolayers and lipid bilayers allows selective molecular association. Organic molecules forming monolayers are amphiphilic and spontaneously spread at the air/water interface. The water phase provides an ideal smooth surface and a reservoir for a water soluble material. Self-assembled monolayers are formed as a result of effective van der Waals interactions among long-chain alkyl residues which contain a molecular cavity for targeted recognition of 'guest' molecules. For the translation of the intrinsic properties of molecules into material properties, it is essential to have control over the molecular interactions and orientation in the material. Different motivated researchers working in the area has accepted the challenge to manipulate molecular organization, structure and forces and thereby, control selectivity in binding. The work mentioned hereunder is either recent or important, if covered in earlier review on monolayers\textsuperscript{40}. 

\begin{align*}
\text{a} & \quad R = \text{isobutyl} \\
\text{b} & \quad R = \text{CH}_3 \\
\text{a} & \quad R = \text{isobutyl} \\
\text{b} & \quad R = \text{C}_{11}\text{H}_{23} \\
R & \quad = \text{C}_{11}\text{H}_{23}
\end{align*}
The calix[4]resorcinarene (61-63) form stable monolayers at the air-water interface. The interaction with Cu\(^{2+}\) ions (using CuCl\(_2\) containing sub phase) is weak in case of calix[4]resorcinarene (61) and strong in the case of (62) and (63) respectively\(^{150}\).

Amphiphilic water-insoluble tetrasulphonatommethylcalix[4]resorcinarene was synthesised and studied tensiometrically. Due to the presence of four sulphonatomethyl-groups at the upper rim, it is able to form stable noncollapsing films at the water–air interface. Compression isotherms were used to investigate the interactions of the macrocycle films with two polymers fed to the aqueous subphases: synthetic- polyethyleneimine (PEI) and natural – an oxidase enzyme caeruloplasmin (CP)\(^{151}\).

The interactions of dopamine to calix[4]resorcinarene (60b) which depends on the orientation of the calixarene molecules in the monolayer formed at the air-water interface were studied by analyzing their mechanical, thermodynamic, and electrical properties evaluated from measurements of pressure-area isotherms and Maxwell displacement currents (MDCs)\(^{152}\). The sensing behaviour of two calix[4]resorcinarenes (64,65) has been characterised in terms of modifications to their surface pressure–area isotherms, their UV–Vis
solution and LB film spectra, for a wide range of analytes and three amino acids lysine, alanine and glutamic acid. In particular, LB films of Calix (64) have proved to bind selectively to lysine, an important amino acid \cite{153}.

\[
\begin{align*}
64 & \quad R = C_6H_5 \quad X = \quad H_2C\cdots CH_3 \\
65 & \quad R = C_6H_5 \quad X = \quad H_2C\cdots CH_2\cdots OH
\end{align*}
\]

8. Complexation
8.1. With metal ion

Calix[4]resorcinarenes bearing eight hydroxamic-acid (66) groups (C4RAHA) have been used for liquid-liquid extraction, separations and Preconcentration of vanadium, uranium, thorium, Lanthanum and cerium\cite{154}.
Tetranonylcalix[4]resorcinol bearing acetylhydrazone (67) groups was found to be effective reagent for the liquid–liquid extraction of various metal ions (Li⁺, Na⁺, K⁺, Cs⁺, Ca²⁺, Pb²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Hg²⁺, La³⁺, Gd³⁺ and Lu³⁺)\textsuperscript{[155]}. New phosphorylated calix[4]resorcinarenes and cavitands were synthesized. Their extraction ability toward La³⁺, Gd³⁺, and Yb³⁺ ions were studied and found that cavitands are more efficient extracting agents than octasubstituted calix[4]resorcinarenes. The literature and spectral (\textsuperscript{31}P NMR) data suggest that the ligand in the extracted complex has most probably a “Kite” conformation\textsuperscript{[156]}. Pyrogallarenes have been shown as alkali metal receptors and in the resulting hydrogen bonded molecular cage, alkali metal cations are η⁶ coordinated to aromatic rings via strong cation–π interactions\textsuperscript{[157]}. Partially functionalized 5, 17-ethylthiomethylated calix[4]resorcarene, (68) interacts only with Ag⁺ in methanol and Hg²⁺ in propylene carbonate, acetonitrile, methanol and N,N-dimethylformamide. The results obtained with this receptor are compared
with fully functionalized resorcarene, (69) wherein Ag\(^+\) and Pb\(^{2+}\) forms complex in acetonitrile and Cu\(^{2+}\) and Ag\(^+\) in methanol\(^{[158]}\).

Selectivity and thermodynamic characteristics have been studied for exchange of protons in SO\(_3\)H groups of a sulfonated network polymer based on cis-tetraphenylcalix[4]resorcinarenes for Na\(^+\), Cu\(^{2+}\) and In\(^{3+}\) cations from aqueous solutions\(^{[159]}\). Puddephatt and Eisler\(^{[160]}\) describe the coordination chemistry of the versatile tetrakis(tetrathiophosphinate) resorcinarenes ligands (75-79) which differs significantly from the tetraphosphinite ligands (70-74) from which they are easily derived by oxidation with sulphur. The coordination chemistry of these new resorci-donor ligands \([(C_6H_2CH(CH_2CH_2-Ph)_{4})OC(O)R]_4[OP(=S)Ph_2]_4\) (L), have been investigated with Silver(I), Gold(I), and Palladium(II). Both silver (I) and gold (I) form cationic complexes of the type \([LM_2]^2^+\), in which the ligand acts as a bis (chelate). Gold (I) also forms the unusual complex \((AuCl)_2[Lau]^2^+\), which forms a supramolecular polymer through intermolecular aurophilic attractions. Palladium-II forms the complex \([LPd_2Cl_2\ (\mu-Cl)_2]\), in which the dipalladium(II) unit extends the natural bowl structure of the resorcinarenes. In addition to these results, it establishes the value of the resorcinarenes skeleton in forming polydentate ligands with very unusual and interesting coordination chemistry.
Acid-base and complexing properties of copper(II) and lanthanum(III) with aminoacetal derivative of calix[4]resorcinarenes (80) \([H_8L]\) were studied in 80 % isopropyl alcohol. The effect of surfactants of various characters on the protolytic processes and complexing has also been considered\[161\].
8.2. Host-Guest

Host–guest interaction of C-methylresorcin[4]arene (59b) and its derivative having four tert-butylsulfanyl methyl groups (81) at the extra-annular positions have been studied and it was found that bulky substituent create a deep cavity with a narrow entrance and improve the size and shape selectivity [162].

Host–guest complex obtained by co-crystallisation of (59b) with 1,10-phenanthroline (82) and coumarin (83a,b) in presence of polar solvents has been studied by single crystal X-ray diffraction study[163].

Christoph A. Schalley et al.[164] have performed electrospray ionization Fourier-transform ion-cyclotron resonance mass spectrometric (ESI-FTICR-MS) experiments to assess the anion-binding behavior of hosts (26b,84-93) and anions (94-99). These experiments provide evidence for a cavitand–anion
interaction mediated by C-H···anion hydrogen bonds that involve the acetal protons pointing into the cavitand bowl.
The switchable baskets (100) and (101) have been constructed from a resorcin[4]arene bowl, to which two quinoxaline flaps are appended in anti-orientation. Two diazaphthalimide walls are connected to each other by a rigid hexa-2,4-diyne-1,6-diyl bridge in the case of (100) and by an octa-3,5-diyne-1,8-diyl unit in (101)(165).

The molecules completely surround suitable guests, such as cyclo- or oxacycloalkanes and bind them with high strength. The guest hosting properties of both molecules can be suspended by an external stimulus: portals delimiting the cavity are opened upon the addition of acid and instantly release the guest. The process is fully reversible: addition of base completely and immediately restores the guest-hosting properties of the switchable molecular baskets. New water-stabilized (104a,b) and (105) deep cavitand with three walls and an open
side have been synthesized and shown to be receptors for amines and ammonium cations bearing bulky aliphatic groups\[^{166}\].

8.3. Solid phase extraction

The impregnation of octacarboxymethyl-C-methylcalix[4]resorcinarene into a polymeric matrix, Amberlite XAD-4, exhibits a high chemical stability, reusability. It has been used for the separation of Th(IV) and U(VI) from other metal cations in synthetic solution\[^{167}\]. Amberlite XAD-16 resin impregnated with octacarboxymethyl-C-methylcalix[4]resorcinarene (OCMR) has been used for separation of La\(^{3+}\), Ce\(^{3+}\) and Y\(^{3+}\) from each other and also from UO\(_2\)^{2+} and Th\(^{4+}\).
by sequential elution system. The sorption capacity of (OCMR) was found to be higher compared to XAD-4 with same reagent because of the larger pore diameter of XAD-16 causing higher adsorption\[^{168}\]. Calix[4]resorcinarenes have been used as an alternative molecular imprinting by using host sites targeted for \(\alpha\)-tocopherol (natural antioxidant)\[^{169}\].

A polymer inclusion membrane (PIM) system with cellulose triacetate polymer as supporter and calix[4]resorcinarenes as carrier and new synthetic plasticizer 2-nitrophenyl octanoate (2-NPOT) has been developed by Baya Boutemeura et al. and applied them for the investigation of facilitated transport of Zn(II), Cd(II), and Pb(II) ions from aqueous nitrate source phase\[^{170}\]. Ion exchange resin (Amberlite IRA 900 Cl) (110) has been transformed into the sorbent of organic molecules from aqueous solutions using for the immobilization tetramethylsulfonate calixresorcin[4]arenes (106) and (107) with methyl and pentyl substituents on a lower rim. Binding properties of macrocycles (106) and (106) and their complexes with neutral organic molecules characterized by a considerably high potential of many-point hydrogen binding (parent substances of Xymedon (1,2-dihydro-4,6- dimethyl-N (\(\beta\)-oxyethyl)-2-oxopyrimidine, 108) and Dimephosphon (O,O-dimethyl-1,1-dimethyl- 3-oxobutylphosphonate, 109)\[^{171}\].
9. Applications

9.1. Liquid crystalline behaviour

Liquid crystals (LCs) are materials with potential for use as active media in optical applications. Their quick response to changes in electric fields enables them to be used to produce liquid crystal displays. Resorcinarenes that are fixed in the boat conformation have a three dimensional bowl-like shape, which gives them the ability to self-organise in ferroelectric (head-to-tail) or anti ferroelectric (head-to-head, tail-to-tail) columnar arrangements\textsuperscript{[172]}. Their liquid crystalline properties have been studied in detail\textsuperscript{[173,174]}. Particular interest in such columnar meso phases originates from their potential ferroelectricity when all the columns are oriented in the same direction.

Resorcinarenes become liquid crystalline when the following requirements are met\textsuperscript{[175]}:

(i) Small $R_1$ groups (see \textsuperscript{111}, \textsuperscript{112}, maximum $R_1=\text{CH}_3$) to allow an optimal core stacking.

(ii) The presence of at least twelve linear $R_2$ side chains, having 12 to 17 carbon atoms each, to cover the periphery of the core in a homogeneous manner.

(iii) Ester groups to connect the side chains to the periphery, without bulky substituents close to the macrocyclic core.

\begin{center}
\includegraphics[width=0.5\textwidth]{resorcinarene.png}
\end{center}

\begin{itemize}
    \item \textsuperscript{111} $R_1=\text{CH}_3$, $R_2=\text{COC}_3\text{H}_7$
    \item \textsuperscript{112} $R_1=\text{H}$, $R_2=\text{COC}_n\text{H}_{2n+1}$
\end{itemize}
Single crystal X-ray data of dodecabutyrate (111) reveal that the molecules are oriented in an anti ferroelectric arrangement, most probably as a result of the large dipole moment, which is calculated as 10.3D (based on X-ray data) for the monomer and almost zero for the anti ferroelectric pair\textsuperscript{172}. Dodecaesters of type (112), which have a conformationally mobile macrocyclic core, already exhibit liquid crystalline behaviour with 9-12 carbon atoms in the $R_2$ side chains\textsuperscript{176}. In this case, the presence of a fast ring-inversion process overcomes the constraint for anti ferroelectric coupling of the molecules within the columns. In this way, the mesogens should be able to align their dipoles freely under the influence of an electric field.

Koichiro Yonetake and co workers\textsuperscript{177,178} have reported C-methyloctakis(2-hydroxyethyl)calix[4]resorcinarenes (113) which was found to adopt a specific molecular structure due to the rigid bowl calix[4]resorcinarene core, i.e., a cone-like structure with mesogenic units aligned within the molecule, possessed a smectic A phase which transform to nematic. The supercooling of (113) for the phase transition was very small due to the molecular structure the nematic texture rapidly appears on cooling. Thus, (113) are expected to act as a high response LCs in its nematic phase.

9.2. Fluorescence

Two different hybrid cavitand-resorcin[4]arenes (114a,b) are shown to be effective and selective for the molecular inclusion of positively charged organometallic sandwich complexes of appropriate size. The binding constants of the 1:1 complex formed with a series of neutral and positively charged
metallocenes have been calculated using different titration techniques\textsuperscript{179}, (114a) is a good supramolecular fluorescent sensor system for choline and displays a pH-modulated binding affinity toward trimethylalkylammonium ions\textsuperscript{180}.

\[
\begin{align*}
114a & \quad R_1 = \text{CH}_2\text{CH}_3; R_2 = \text{H} \\
114b & \quad R_2 = \text{CH}_2\text{CH}_3; R_2 = \text{COCH}_2\text{CH}_3
\end{align*}
\]

Novel cyclophane-based resorcinarene tetramer, dodecamer, dansyl-appended cyclophane-based resorcinarene trimer and rotaxane-type resorcinarene tetramers receptors\textsuperscript{181} have been developed which showed unique properties as multivalent hosts of histone as well as of hydrophobic molecular guests, as demonstrated by Surface plasmon resonance (SPR) measurements and fluorescence spectroscopy, respectively. Chawla et al. have studied the fluorescence behavior of pyrene in the presence of different derivatives of calix[4]resorcinarene in basic media\textsuperscript{182}.

### 9.3. Nano particles

Jerry L. Atwood et al. have demonstrated the formation of C-n-hexylpyrogallo[4]arene-based organic nanotubes in the solid state that show some potential to maintain their structure in the solution phase\textsuperscript{183}. C-undecylcalix[4]resorcinarenes-capped anatase TiO\textsubscript{2} nanoparticles have been synthesized and could be isolated and redispersed in different nonaqueous solvent\textsuperscript{184}. Self-assembled solid lipid nanoparticles (SLNs) based on a prolyl bearing resorcinarenes (L-RA-Pro) (115); their chemical modification with bovine
serum albumin and their interactions with surface bound anti-albumin antibodies have been studied. This new approach for modifying resorcinarenes based SLNs may open new vistas for the use of these systems in drug targeting\textsuperscript{1185}.

Two resorcinarenes-derived tetrathiocavitand tetraenes (116) and (117) can extract colloidal gold nanoparticles from aqueous solutions and stabilizing their dispersion in organic solvents\textsuperscript{1186}.

\[116 = R = (CH_2)_6 CH=CH_2, X = SH, 117 = R = (CH_2)_6 CH=CH_2, X = CH_3SH\]
Interaction with gold nanoparticles with self-assembly of thio-ether-footed resorcin[4]arenes was studied\textsuperscript{[187]}. Chaoguo Yan et al.\textsuperscript{[188]} have synthesized amphiphilic novel polyamino resorcinarenes surfactant (2, 8, 14, 20-tetranonyl - 4, 6, 10, 12, 16, 18, 22, 24 -octa (1-aminoethylcarbamoyl-) methoxyresorcinarene, TNMR) (118) which has a large hydrophilic head group with eight amino groups and four hydrophobic chains. They have shown that TNMR surfactant not only could be used as a good ligand for gold nanoparticles, but also had a strong deaggregating effect on gold nano aggregates under microwave irradiation.

Highly organized calix[4]resorcinarenes-based nanostructured materials have been synthesized by the ionic self-assembly route. A series of complexes formed from anionic calix[4]resorcinarenes (119) and (120) and cationic surfactants X have been studied for their structures and binding capacity for selected guests and have been shown to be composites consisting of four surfactant molecules to each (tetraanionic) calix[4]resorcinarenes. Cast films of these materials were exposed to a variety of species and studied their adsorption into the films\textsuperscript{[189]}. 

\begin{center}
\includegraphics[width=\textwidth]{molecular_structure.png}
\end{center}
9.4. Catalysis

Self assembled supramolecular systems based on amphiphilic sulfonatomethylated calix[4]resorcinarene\(^{190,191}\), aminomethylated calix[4]resorcinarenes\(^{192,193}\) and poly(ethylene) imines possess high catalytic activity in the hydrolysis of phosphorus acid esters. On the other hand bridged resorcinarenes have been used as templates for asymmetric catalysis\(^{194,195}\) and water-soluble calix[4]resorcinarenes sulfonic scid acts as a catalyst for dehydrative amination of alcohols in water\(^{196}\).

9.5. Miscellaneous applications

Besides the already mentioned uses and applications of calix[4] resorcinarene and their functionalized derivatives as cavitand, capsules, dendrimers, crown, monolayers, extraction of metal, non metal, neutral guest, host guest comlexation, liquid crystals, fluorophors and nanoparticles they have been found to be used as HPLC stationary phase\(^{197}\), Light-gated artificial ion channels\(^{198}\), Molecular glass resists\(^{199,200,201}\), imaging material for organic electronics\(^{202}\), chiral nmr solvating agents\(^{99}\), PVC supported liquid membrane electrodes\(^{203}\), multifunctional antiradical and antioxidant agents\(^{204}\), photoresist material \(^{205}\).
Chapter 1

Aim and Scope

Conventionally calix[4]resorcinarene macrocycles are synthesized by acid catalyzed condensation between resorcinol and virtually any aliphatic/aromatic aldehydes. The introduction of any chelating groups such as azo, azomethine or tetrasulfonato on the upper rim of calix[4]resorcinarene may further enhance/influence its complexing ability with various metal ions.

So the aim of the present work is:
To develop a rapid, convenient, efficient and environmental friendly method using microwave irradiation technique for synthesis of calix[4]resorcinarene based macrocyclic compounds.
To study the complexation behaviour of azocalix[4]resorcinarene dyes, synthesized by conventional method as well microwave irradiation technique, with various metal ions and develop the method for liquid-liquid extraction, preconcentration and transportation of metal ions.
To synthesize two new azocalix[4]resorcinarene Amberlite XAD-2 polymeric chelating resins, resin A and resin B by covalently linking diazotized Amberlite XAD-2 with C-methylcalix[4]resorcinarene and upper rim functionalized (2-hydroxyphenylazo)C-methyl calix[4]resorcinarene respectively and investigate them for the solid phase extraction, separation, preconcentration and trace determination of Cu, Zn, Cd, La, Ce, Th and U in synthetic as well as natural samples under optimum conditions.
To examine antimicrobial activity of azocalix[4]resorcinarene dyes against E. coli, S. aureus and A. niger, Rhizopus sp. To evaluate the dyeing performances of these dyes on fibers like cotton, wool and silk and study their fastness properties towards water, sunlight, washing and perspiration.
To synthesize water-soluble tetrasulfonatomethylcalix[4]resorcinarene by microwave irradiation and examine its interaction with cationic surfactants.
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Chapter 1


