Chapter 1

Introduction
Chapter 1

Resume

A review of the literature describing the chemistry of supramolecules like calix[4]resorcinarene and their derivatives with corresponding references has been given. The different methods for their synthesis, functionalization, formation of nanoparticles, host-guest systems and their analytical applications have been comprehensively covered. The aim and scope of the present work have also been discussed.
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</table>
Chapter 1

1. Introduction to supramolecular chemistry

The concept of complex intermolecular interactions being described as ‘supramolecular’—literally ‘beyond or transcending, the molecule’—is now associated with Jean-Marie Lehn’s definition from the late 1970s: Just as there is a field of molecular chemistry based on the covalent bond, there is a field of supramolecular chemistry, the chemistry of molecular assemblies and of the intermolecular bond. The concept of supramolecular chemistry gained a wider scientific currency following the award of the 1987 Nobel prize in chemistry to Donald Cram, Jean-Marie Lehn and Charles Pedersen for their development and use of molecules with structure-specific interactions of high selectivity, Lehn refined his earlier definition of supramolecular chemistry in his Nobel lecture, calling it: the chemistry beyond the molecule bearing on the organized entities of higher complexity that result from the association of two or more chemical species held together by intermolecular forces [1].

Supramolecular chemistry is the study on non-covalent forces (close packing, hydrophobic effect, hydrogen bonding, dipole-dipole, cation-π, π–π, ion-dipole, van der Waals, ionic forces) and the structures created by these forces. It is inspired from biology and built on the shoulders of synthetic organic chemistry and inorganic coordination chemistry [2]. Supramolecular chemistry is a multidisciplinary field which impinges on various other disciplines, such as the traditional areas of organic and inorganic chemistry. A great deal of biological chemistry involves supramolecular concepts and in addition, a degree of technical knowledge is required in order to apply supramolecular systems to the real world, such as the development of nano technological devices [3].
Supramolecules, on time scale, can be classified as their generation where Cyclodextrins (1) and crown-ethers (2) are the first and second generation supramolecules, respectively Fig. 1.

Calixarenes are a class of cyclo-oligomers formed by condensation between phenol and aldehyde and are classified as third generation supramolecules. 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 [4, 5].

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-tert-butylcalix[n]arene (3) and (ii) the resorcinol-derived cyclooligomers e.g. calix[4]resorcinarenes (4) as shown in Fig. 2.

![Diagram of calixarene structures]

Fig. 2

Two different zones can be distinguished in calixarenes, viz., the region of phenolic hydroxy groups and the \textit{para}-position of the phenols, which are called the 'lower rim' and the 'upper rim' of the calixarene, respectively Fig. 3.

![Diagram of upper and lower rims]

Fig. 3
The calix[4]resorcinarenes are resorcinol-derived calixarenes such as C-methyl calix[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 substituent at the sites of the bridging methylene groups and various functionalization on the hydroxy group as well as upper rim [6, 7].


The first recorded synthesis of resorcinarenes was in 1872 by Adolf Von Baeyer, in his studies on the condensation of phenol-type dyes with aldehydes in acidic media [8]. Interest in the Bakelite™ process, through which the reaction of phenol with formaldehyde results in the formation of a brittle polymer, undoubtedly led to the first reproducible calixarene synthesis that appeared in the 1940's [9] and 1950's [10]. The correct structure of these compounds was proposed in 1940 by Niederland Vogel [11], and confirmed in 1968 by Ertzman et al. using single crystal X-ray diffraction [12, 13]. These compounds are known by a host of trivial names which includes calix[4]resorcinarenes, Höfqberg compounds [14], octols [15, 16] and recently resorcinarenes became the staple term used in the literature [17].

3. Mechanism and stereochemistry

In 1991 Weinelt and Schneider proposed a mechanism of the acid-catalyzed condensation reaction for the formation of calix[4]resorcinarenes which had been thoroughly studied [18] (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 favoured, 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 [7, 19, 20].
A kinetic and molecular modeling study [18] 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 depolymerise fast in comparison with ring opening, thus promoting the formation of cyclic tetramer, pentamer and hexamer.

Although i.e. reaction with R-CHO appears to yield only calix[4]resorcinarenes, but the cyclocondensation of 2-alkylresorcinols with 1, 3, 5-trioxane in ethanol-conc. HCl (4:1v/v) yield 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 [21].

Conformational aspects of calix[4]resorcinarenes

Due to the non-planarity of resorcinarenes, they can exist in many different isomeric forms [16, 22, 23]. The stereochemistry is generally defined as a combination of the following three stereochemical criteria:

1) The first criterion is the conformation of macrocyclic ring. As the macrocycle ring has five highly symmetrical conformations: crown (C₄v), boat (C₂v), chair (C₄h), diamond (C₃v), and saddle (D₁d), calix[4]resorcinarenes can have five corresponding stereoisomers Fig. 4.
2) The second criterion is the relative configuration of the substitutes at the methylene bridges, giving the all-cis (ccc), cis-cis-trans (cct), cis-trans-trans (ctt) and trans-cis-trans (tct) resorcinarene stereoisomers Fig. 5.
3) 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 [18]. 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 [24]. 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 [25, 26].
4. 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 [16, 27, 28], we do not get tetrameric product when resorcinol is having electron withdrawing substituent such as -NO\(_2\) or -Br at the 2-position [16]. In certain cases, formaldehyde and 2-methyl resorcinol or pyrogallol yield isolable amounts of tetrameric product [29]. 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. [16] and Schneider et al. [18].

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 cyclo oligomerisation. Different derivatives of calix[4]resorcinarene obtained by conventional method are reported in table 1.

The question regarding the substitution of the groups on resorcinol and aldehyde moieties tolerates the four-fold oligomeric cyclization reaction has been well established by Donald J. Cram et al. and Schneider et al. [30].

There are many routes for synthesis of different types of calix[4]resorcinarene, which have emerged over number of years. Here, only few different synthetic routes from conventional as well as microwave assisted methods by various mineral acid catalyzed cyclo oligomerisations are mentioned.
Chapter 1

Tri fluoromethane sulfonate salts, such as ytterbium(III) triflate [31] and bismuth(III) triflate [32], have been described as efficient catalysts for the synthesis of calix[4]resorcinarenes. Also, lanthanide(III) tosylates and lanthanide(III) nitrobenzenesulfonates [33-36] have been used as efficient, inexpensive, recyclable, and environment friendly catalysts for the synthesis of calix[4]resorcinarenes (5) and (6) and their catalytic efficiency was found to be comparable to that of the triflate salts.

Recently, a facile and simple procedure for the synthesis of calix[4]resorcinarene (7) derivatives was developed via a reaction of aryl aldehydes with resorcinol in the presence of catalytic amounts of tungstate sulfuric acid (TSA) under solvent-free condition [37].
Similarly, calix[4]resorcinarene derivative (8) has also been synthesized in the presence of catalytic amounts of Fe₃O₄ nanoparticles under solvent-free conditions [38].

Resorcinarene O-acetates (9) have been efficiently prepared in high yield by BF₃ OEt₂ catalyzed cyclocondensation of 1, 3-(dialkoxy carbonylmethoxy) benzenes with aromatic or aliphatic aldehydes in CH₂Cl₂ at room temperature [39].

Microwave assisted synthesis [40] of calix[4]resorcinarenes using resorcinol and aldehydes, catalysed by 12-tungstophosphoric acid type Keggin (H₃PW₁₂O₄₀.13H₂O) or concentrated hydrochloric acid gives excellent yield (>90%) within short reaction time (<3–5 min) and does not require harsh conditions.
Recently, synthesis of cyclic tetramers calix[4]resorcinarenes from Vanilin (4-hydroxy-3-methoxy benzaldehyde), Cinnamaldehyde (3-phenyl-2-propanal), Anisaldehyde (4-methoxybenzaldehyde) under microwave irradiation within very short reaction time have been reported [41].

Pyrogallol[4]arenes (11a-f) [42] have been synthesized in excellent yields by cyclocondensation of pyrogallol (10) with aromatic aldehydes under microwave irradiation.

New type of octahydroxy pyridine[4]arenes (13a-f) derived from condensation of 2,6-dihydroxy pyridine (12) with a number of aliphatic and two aromatic aldehydes in acidic media have been reported [43].
New calix[4]resorcinarene (14) [44] have been synthesized by the condensation of resorcinol with photoswitchable chromogenic azo group and an ionophoric part (i.e. residue of benzo-15-crown-5) on the lower rim.
Maslennikova et al. have recently synthesized new derivatives of hetero-functionalized resorcinarenes groups by modification of free reactive centers in the phospho resorcinarenes of different type [45].

New synthetic conditions for the fully selective formation of the \textit{rcct} chair stereoisomers of octa-O-alkyl resorcin[4]arenes (15a-e) in acetic acid-sulphuric acid or acetic acid-hydrochloric acid mixtures have been described [46] and which was found to be thermodynamic product under Bronsted acid catalysis, an unprecedented observation in supramolecular chemistry.
Another example involves the cyclo condensation of 1,3-dialkoxybenzene (16) with 1,3,5-trioxane, catalyzed by Sc(OTf)₃ to produce resorcin[4]arene (17a,b) octa alkyl ethers as the major products. In addition, 'confused' resorcin[4]arene (18a,b) octa alkyl ether bearing one alkoxy group at the intra-annular position were also obtained as the minor product [47].
Ladder polymer (CRA-polymer) [48] have been synthesized using a one-pot method by the condensation reaction of resorcinol and 1, 4-butanedial [CHO-(CH₂)₂-CHO] in the presence of concentrated hydrochloric acid in ethanol at 80°C for 48 hours afforded a soluble polymer (CRA-polymer) in quantitative yield. Diastereoselective synthesis of novel boron derivatives of resorcinarenes from L-amino acids and phenyl boronic acid have recently been reported [49].

The action of trifluoroacetic acid (TFA) on 2,4,6- trimethoxy benzyl alcohol (19) gave tetrameric compound as a maroon colour TFA complex in high yield (20), which upon treatment with acetone gave free colourless calix[4]phloroglucinarene (21), has also been reported [50].
The reaction of calix[4]resorcinarene with tosyl chloride in presence of triethylamine gave the tetratosyl derivative of resorcinarene (22) [51], which was converted into bis-l-proline-tetrasyl resorcinarene (23a) and bis-l-prolinol-tetrasyl resorcinarene (23b) by standard Mannich reaction using formaldehyde and correspondingly l-proline and l-prolinol [52].
Recently, the synthesis of tetrakis-thiomethyl-C-4-methoxyphenylcalix[4]resorcinarene (28) has been reported by using fennel oil as a starting material. Initially, p-anisaldehyde (25), the oxidized product of anethole (24) reacted with resorcinol by HCl-catalysed condensation reaction to give C-4-methoxy phenyl calix[4]resorcinarene (26), which upon chloro methylation with p-formaldehyde and HCl in presence of ZnCl\textsubscript{2} yielded tetrakischloromethyl-C-4-methoxy phenyl calix[4]resorcinarene (27). This finally reacted with thiourea followed by hydrolysis with sodium hydroxide solution to give tetrakis-thiomethyl-C-4-methoxy phenyl calix[4]resorcinarene (28) [53].

Calix[4]resorcinarene host-guest crystals having nano and micrometer sized dimensions have recently been synthesized with rapid nucleation of a crystalline phase [55]. Also resorcinarene-based deep cavitands alanine methyl resorcinarene acid (AMA), alanine undecyl resorcinarene acid (AUA) and glycine undecyl resorcinarene acid (GUA), which contain chiral aminoacids, have been synthesized [56]. Wenzel Thomas J. et al. report on a similar reagent that is prepared by a water-soluble, sulfonated calix[4]resorcinarene with L-pipecolinic acid substituent groups is an effective chiral NMR solvating agent for aromatic-containing substrates [57]. B. Karami et al. describe a new and green strategy based on the condensation of resorcinol with aryl aldehyde using Fe₃O₄ nanoparticle as a powerful, safe and recyclable catalyst under solvent-free conditions for the preparation of novel and known calix[4]resorcinarene derivatives [58]. Recently korshin et al. develop a new dynamic electro switchable supramolecular system consisting of tetra ferrocene-resorcinarene and viologen [59].


Calix[4]resorcinarene, a versatile molecular platform, can be functionalized at two, four, six, eight, twelve, sixteen and many more sites, depending upon the reagents used along with the applied reaction conditions. The various calix[4]resorcinarene derivatives can be obtained by functionalization on all or either of three available position (R₁, R₂ and R₃) of our choice. Here, we have mentioned various possible functionalization of calix[4]resorcinarene. Fig.6 at R₁ and/or R₂ and/or R₃, some of the examples are summarized in table 1.
Fig. 6
Table 1 Functionalization of calix[4]resorcinalenes

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</table>

6.1 Calix[4]resorcinarene modified metal nanoparticles

The synthesis of noble metal nanoparticles have attracted increasing interest nowadays because of their unique properties and promising applications [102-109]. The synthetic technique for fabricating nanoparticles involved the reduction of metal salts in presence of stabilizing or capping agent, which prevents them from aggregation and allows isolation of nanoparticles [110, 111]. Among all, calixarenes have gained much attention because of their potential application in both stabilizing as well as capping agent [112-115]. Calix[4]resorcinarene derived surfactants were highly effective at stabilizing metal nanoparticles of different sizes, creating opportunities to fabricate well-defined nanostructures with size-tunable materials properties. Wei et al. [114], made a comprehensive and systematic investigation of calix[4]resorcinarene grafted nanoparticles. The study of the dispersion and stability of calix[4]resorcinarene encapsulated gold nanoparticles through extracting gold particles from gold hydrosol into toluene or chloroform using calix[4]resorcinarene surfactant as an extractant have also been done. It was revealed that the calix[4]resorcinarene surfactants with sulphur functionalized head groups could make the mid nanometer sized gold particles stably dispersed in organic solvents [116]. The weakly ferromagnetic cobalt nanoparticles self-assemble into bracelet like rings with discrete particles count has also been reported [117]. The extraction of colloidal gold nanoparticles from aqueous solution and stabilizing their dispersion in organic solvents by two calix[4]resorcinarene derived tetrathiol cavitand tetraenes (34) and (35) has been done [118].
Chaoguo Yan et al. [119], have synthesized amphiphilic novel polyamino calix[4]resorcinarene surfactant (2, 8, 14, 20-tetranonyl-4, 6, 10, 12, 16, 18, 22, 24-octa(1-aminoethylcarbamoyl-) methoxy resorcinarene, TNMR) (36) which has a large hydrophilic head group with eight amino groups and four hydrophobic chains. They have shown that TNMR surfactant was not only a good ligand for gold nanoparticles, but also had a strong disaggregating effect on gold nano aggregates under microwave irradiation. Calix[4]resorcinarene functionalized metal nanoparticles including AuNPs, AgNPs, PtNPs, and PdNPs were also prepared in aqueous medium by using the microtubes as templates, hybrid materials were prepared via immobilizing nanoparticles onto the surface of microtubes [120].
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 (37) and (38) and cationic surfactants 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 (tetra-anionic) calix[4]resorcinarenes. Cast films of these materials were exposed to a variety of species and studied their adsorption into the films [121].
Atwood et al. have demonstrated the formation of C-n-hexyl pyrogalloI[4]arene based organic nanotubes in the solid state that show some potential to maintain their structure in the solution phase [122]. C-undodecyl calix[4]resorcinarenes capped anatase TiO₂ nanoparticles have been synthesized and could be isolated and redispersed in different non-aqueous solvent [123]. Self-assembled solid lipid nanoparticles (SLNs) based on a prolyl bearing calix[4]resorcinarene (L-RA-Pro) (39), their chemical modification with bovine serum albumin and their interactions with surface bound anti-albumin antibodies have been studied. This new approach for modifying calix[4]resorcinarene based SLNs may open new vistas for the use of these systems in drug targeting [124].
6.2 Calix[4]resorcinarene based fluorescent sensors

Two different hybrid cavitand calix[4]resorcinarenes (40) 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 [125], (40) is a good supramolecular fluorescent sensor system for choline and displays a pH-modulated binding affinity toward trimethyl alkyl ammonium ions [126].
Novel cyclophane-based resorcinarene tetramer, dodecamer, dansyl-appended cyclophane-based resorcinarene trimer and rotaxane-type resorcinarene tetramers receptors [127, 128] 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 behaviour of pyrene in the presence of different derivatives of calix[4]resorcinarene in basic media [129]. Calix[4]resorcinarene with appropriate appended groups have been found to be good candidates for recognition of cations and anions. Calix[4]resorcinarenes have received increased interest in synthesis of variety of chemosensors [130-132] bearing
different fluorescent groups. The dansyl substituted calix[4]resorcinarenes i.e. tetra
dansyl resorcinarene (41) [133] and octa dansyl resorcinarene (42) [68] have been
synthesized, and are found to be good fluorescent sensors for metal ions. Novel
cyclophane based resorcinarene tetramer, dodecamer, dansyl-appended cyclophane-
based resorcinarene trimer and rotaxane type resorcinarene tetramers receptors [127,
134, 135] have also been developed, which possessed unique properties as multivalent
hosts of hydrophobic molecular guest, as demonstrated by fluorescence spectroscopy.
Chawla et al. [132] have studied the fluorescence behaviour of pyrene in the presence
The detection of cations and anions are well established field in the realm of host–guest supramolecular chemistry and is an area of current interest. Fluorescence is a very sensitive technique which has been applied to single molecule detection [136-
Calix[4]resorcinarenes have been attracting current interest with a view to achieving the molecular design of molecular receptors for the recognition of guest molecules [140, 141]. Calix[4]resorcinarenes with appropriate appended groups have been found to be good candidates for recognition of cations and anions. Calix[4]resorcinarenes have received increased interest in synthesis of variety of chemosensors [130, 140, 141] bearing different fluorescent groups.

A mixture of octa-o-acetylated calix[4]resorcinarenes (CRAs) (43) with varying numbers of pyrene ethyl group was synthesized by acid-catalyzed condensation of resorcinol with 3-(pyren-1-yl) propanal, followed by acetylation. Fluorescence spectra of pyrene derivatives CRAs shows that they form two types of excimer and their excimer does not depend on the number of pyrenyl ethyl groups [142].

**Diagram**

Synthesis of fluorescent rotaxanes, which were composed of anionic cyclophane resorcinarene tetramers and disubstituted naphthalene fluorophore. These rotaxanes performed as a fluorescence sensing ability with remarkable histone binding
selectivity, which was a useful method for the detection of histone [142]. Novel cyclophane based resorcinarene tetramer, dodecamer, dansyl-appended cyclophane-based resorcinarene trimer and rotaxane type resorcinarene tetramers receptors [127, 134, 135] have also been developed, which possessed unique properties as multivalent hosts of hydrophobic molecular guest, as demonstrated by fluorescence spectroscopy.

Synthesis of region selective octa dansylated resorcinarene and tetra dansylated resorcinarene are described by reaction of calix[4]resorcinarene and dansyl chloride. Their binding study was also carried out by the fluorescence titrations and found good fluorescent sensors for various metal ions and acids [143].

6.3 Miscellaneous applications of calix[4]resorcinarenes

Calix[4]resorcinarenes and their functionalized derivatives have found various applications as macrocyclic receptors [144], dendrimers in biological systems [145-147], nano-capsules [148], nanoparticles [149-151], optical chemosensors [149], Supramolecular tectons [152-154], host molecules [155, 156], as components in liquid crystals [157, 158], photo resists [159-161], selective membranes [162, 163], surface reforming agents [164-166], as ion channel mimics [167], metal ion extraction agents [168-172], as a sensor [173, 174] as molecular switches [175] voltammetric sensor [176], capping-stabilizing agent [177], antibacterial Langmuir–Blodgett films [178], carbon fiber electrode [179].

Aim and scope

Calix[4]resorcinarenes are versatile supramolecular receptors and find application as optical sensors, electrochemical sensors, HPLC supports, anion transporting agents, chelating polymer and non-linear optical materials, nano-capsule, nano-particles, optical chemosensors, supramolecular tectons, host molecules
components in liquid crystals, photo resists, selective membranes surface reforming agents, anions and cation extraction agents.

Functionalized calix[4]resorcinarene with hydrazide groups hold the great potential to be used as a good reducing as well as stabilizing/capping agent for the formation of gold and silver nanoparticles. Highly stable aqueous fluorescent metal nanoparticles are known for their sensitivity and selectivity towards various metal ions and amino acids. Further, metal nanoparticles, specifically silver nanoparticles have gained significant interest over the years due to their very effective antimicrobial properties. Nanoparticles derived from calix[4]resorcinarene heralds many promises as sensor for bio-molecules, various organic and inorganic analytes etc.

**Aim of the work to be presented in the thesis:**


3. To explore the applications of metal nanoparticles for their selective and sensitive behaviour towards metal ions and amino acids in synthetic as well as real samples by spectrophotometry and spectrofluorimetry.

4. To investigate the antimicrobial activity of synthesized silver nanoparticles against various microbes.

5. To compare the behaviour of synthesised nanoparticles towards bio-molecules.
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Chapter 1


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Chapter 1


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