

**Synthesis and Applications of Calixarene based Molecular
Receptors for Molecular Recognition**

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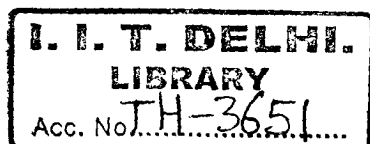
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Dedicated
To
My Father

CERTIFICATE

This is to certify that the thesis entitled **“Synthesis and Applications of Calixarene based Molecular Receptors for Molecular Recognition”** being submitted by **Mr. Rahul Shrivastava** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. Rahul Shrivastava** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.



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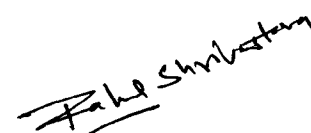
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Rahul Shrivastava

ABSTRACT

The thesis titled “**SYNTHESIS AND APPLICATIONS OF CALIXARENE BASED MOLECULAR RECEPTORS FOR MOLECULAR RECOGNITION**” presents the research work carried out on the synthesis, characterization and applications of novel calix[*n*]arenes derivatives. The structure and conformational geometry of synthesized new chemical entities have been determined by utilizing various spectroscopic techniques (¹H NMR, ¹³C NMR, IR, UV-visible and Mass spectrometry) while recognition of various anions by designed molecular receptors has been investigated by using UV-visible and NMR spectroscopy. The accomplished research work has been divided into five Chapters as detailed below:

Chapter I of the thesis presents a brief overview of the recent research work published on the conformational analysis of calixarenes derivatives and their use in the recognition of various ionic and neutral species. The emphasis of this chapter is to understand the salient features of calixarene chemistry relevant to the work presented in the thesis and the reference list is not meant to be exhaustive in nature.

Chapter II of the thesis describes our efforts to control the conformational flexibility of calix[6]arenes by synthesizing triply bridged symmetrical 5,11,17,23,29,35-hexa-*tert*-butyl-37,39,41-trimethoxy-38,40,42-(2,7,12-trialkoxy-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[*adg*]cyclononyl)calix[6]arene derivatives. A detailed NMR spectroscopic study has revealed that the synthesized multi cavity molecular receptors retain the calix[6]arene and 2,7,12-trialkoxy-3,8,13-trimethoxy-10,15-dihydro-5H-tribenzo[*adg*]cyclononene units in their cone conformation. While the alkyl spacers employed confer flexibility to receptors at room temperature, this flexibility gets reduced at low temperatures.

Chapter III of the thesis deals with the synthesis, characterization and anion recognition properties of new class of functionalized calix[4]arene hydrazone, semicarbazone or thiosemicarbazone derivatives. The synthesized receptors were examined for their interaction with various anions (F^- , Cl^- , Br^- , I^- , ClO_4^- , HSO_4^- , $H_2PO_4^-$, and PF_6^-) in the form of their tetrabutylammonium salts through the use of UV-visible, 1H NMR, DQF-COSY and ^{19}F NMR spectroscopic techniques. Some of the functionalized calix[4]arene hydrazone derivatives exhibit selective binding with fluoride ions via H-bond interactions in preference to Cl^- , Br^- , I^- , $H_2PO_4^-$, HSO_4^- , AcO^- , ClO_4^- and PF_6^- ions and elicit distinct colour change from yellow to dark purple through efficient deprotonation. On the other hand functionalized calix[4]arene semicarbazones or thiosemicarbazones exhibit enhanced selectivity towards HSO_4^- ion due to strong hydrogen bond interactions through a 1:1 binding-stoichiometry.

Chapter IV of the thesis presents the synthesis and characterization of novel ditopic calix[4]arene based receptors that possess the hydrazone and bipyridyl functions at their lower rim. These receptors recognize cobalt (II) and fluoride ions selectively and simultaneously with a distinct ‘naked eye’ colour change. This chapter also describes the synthesis of bipyridyl functionalized calix[6]arenes derivatives which exhibit selective recognition and high binding stability for iron (II). It is significant to note that the synthesized bis(bipyridyl) pendant calix[6]arene derivatives can differentiate different oxidation states of iron and copper to provide constitute the first example of speciation through molecular recognition by using synthesized calix[6]arene derivatives.

Chapter V of the thesis deals with the synthesis and characterization of novel calix[4]arene-based diacetylhydrazide receptors and dipyrromethane functionalized calix[4]arene derivatives. Single crystal X-ray analysis and detail NMR studies on one of the functionalized calix[4]arene diacetylhydrazide reveals that they have a unique

intramolecular hydrogen bonding motifs in their solid and solution state which help to keep these receptors in their cone conformation in chloroform. A study on their interaction with various anions through ^1H NMR spectrometric analysis shows that they are highly selective towards tetrahedral HSO_4^- ion in preference to Cl^- , Br^- , I^- , ClO_4^- and PF_6^- ions through a 1:1 binding stoichiometry.

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