

**Synthesis and Characterization of Calixarene based Molecular
Receptors for Chemical Separation and Detection.**

by

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Submitted

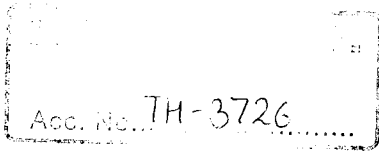
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to the



Indian Institute of Technology, Delhi

December 2008



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CERTIFICATE

This is to certify that the thesis entitled “**Synthesis and Characterization of Calixarene based Molecular Receptors for Chemical Separation and Detection**” being submitted by **Mr. Parminder Singh** 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. Parminder Singh** 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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ABSTRACT

The thesis title, “**Synthesis and Characterization of Calixarene based Molecular Receptors for Chemical Separation and Detection**” deals with some aspects of chemistry of calixarenes that can serve as useful building blocks for designing molecular receptors for ionic and molecular recognition. The calix[n]arene derivatives have been synthesized by using methods available in the literature or modifications thereof. They have been characterized by UV, IR, NMR and X-ray diffraction analysis. The synthesized derivatives were also examined for ionic recognition through flame photometry. **Chapter I** of this thesis presents an overview of the general aspects of molecular recognition by taking examples from the recent literature with special emphasis on calixarenes based molecular receptors for recognition of alkali, alkaline earth and transition metal ions, lanthanides and actinides.

Though parent calixarenes evince poor response to ion transport and extraction protocols, functionalized calixarenes possess useful recognition attributes. **Chapter II** of the thesis embodies the research work carried out on the synthesis of new macrocyclic calix[4]arene-crown ethers, incorporating varying spacer units in the parent and substituted calix[4]arenes. Optimized procedures for obtaining cone conformation of calix[4]arene-crown ethers as well as their characterization by IR, NMR and FAB mass analysis have been reported.

Chapter III describes the attempted and successful routes employed in the laboratory for the synthesis of new macrocyclic azocalix[4]arenes incorporating arylazo- and heteroarylazo- units. Details of the procedures adopted for the synthesis and

characterization of new arylazocalix[4]arenes by IR, NMR and FAB mass analysis is the subject matter of Chapter III.

Chapter IV illustrates our efforts on the synthesis of double calix[4]arenes through base catalyzed condensation routes. Structural elucidation of these double calix[4]arenes reveal that the synthesized derivatives were determined to exist in the *cone*- conformations.

Most of the studies carried out so far on alkali metal ion recognition have been through shifts produced in the NMR or UV absorption maxima when ionic species interacts with the macrocyclic hosts. The methods though successful in giving primary recognition characteristics in solution, it does not reveal distinction between different alkali metals as the response is usually measured by the picrate concentration in the organic phase. **Chapter V** describes our attempts to determine the interaction of sodium and potassium with the synthesized calix[4]arene-crown-*n* derivatives. It has been observed that calix[4]arene-crown-*n* ethers selectively recognize sodium and potassium. The synthesized calix[4]arene-crown-*n* compounds were examined for their interactions with sodium and potassium through flame photometry.

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