STUDIES ON CALIX[n]ARENE BASED MOLECULAR RECEPTORS

by

N. VENKATESAN

Department of Chemistry

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Dedicated to
My
Parents

CERTIFICATE

This is to certify that the thesis entitled, ***Studies on calix[n]arene based molecular receptors*** being submitted by **Mr. N. Venkatesan** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the degree of Doctor of Philosophy in Chemistry is a record of bonafide research work carried out by him.

Mr. N. Venkatesan has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached a requisite standard.

The results embodied in this thesis have not been submitted, in part or in full, to any other University or Institute for the award of any Degree or Diploma.

(H. Mohindra Chawla)
Thesis Supervisor

Professor,
Department of Chemistry
Indian Institute of Technology,
New Delhi – 110 016, India.

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ABSTRACT

Calixarenes constitute an important class of macrocyclic compounds that can serve as useful building blocks for designing molecular receptors for ionic and molecular recognition. The thesis titled "***Studies on calix[n]arene based molecular receptors***" has been divided into six chapters.

Chapter I of this thesis presents an overview of research work published on calix[n]arenes during the last four years. Emphasis of this Chapter is on potential uses of calixarenes as molecular receptors for recognition of small organic molecules and their applications in the development of solid state sensors like chemically modified field effect transistors (CHEMFETS) and ion selective field effect transistors (ISFETS). The research work carried out on the synthesis of carbonyl group containing calixarenes (esters and amides) immobilized in the cone conformation have been discussed in **Chapter II**. Calixarene esters reported in this Chapter have been prepared by following the methods available in the literature while corresponding calix[n]arene amides were prepared by treatment of calixarene esters with 2-aminoethanol. Successful isolation of calix[8]arene diester with drastically reduced conformational mobility has also been presented in this chapter. Characterization of the synthesized calixarenes has been effected by analysis of their IR and NMR spectra. The solution structure of the calix[4]arene-distal diamides has been substantiated by analysis of the NMR and IR spectra and solvent dependent shifts of protons attached to different functions as well as NOE correlation patterns (NOESY) in different solvents.

Chapter III presents the results obtained on the synthesis and characterization of chromoionophoric calixarenes containing sulfur as one of the heteroatoms. **Chapter IV** presents the results obtained on the synthesis of a rationally designed new chromoionophore, containing -N=N- and –SR (thioether) as a "handle" on the top of the calixarene cavity and oxygen ligating functionalities at the lower rim. The synthesis is achieved by combining the chromogenicity and thiophilicity concepts reported earlier from our laboratory. The chromoionophore thus developed has been found to be useful for selective recognition of heavy and precious metal ions. A study on interaction of this chromoionophore with various metal ions (Co^{+2}, Cu^{+2}, Ni^{+2}, Pd^{+2}, Pt^{+2} and Hg^{+2}) through UV-VIS spectrometric analysis reveals that the synthesized chromoionophore is highly selective towards palladium and platinum. The potential use of the palladium chromoionophore complex for recognition of basic amino acids has also been explored and reported in Chapter IV.

In order to achieve various self-assembled supramolecular assemblies from functionalized calixarenes, several chromogenic calix[n]arenes containing long alkyl chains have been prepared in the laboratory. The synthesized molecules have been examined for their plausible self-assembling or aggregation in THF by dynamic laser light scattering technique. It has been observed that some of the synthesized derivatives do aggregate to form self-assembled supramolecules while others do not. Experiments conducted on dynamic laser light scattering studies from these derivatives and results obtained on these have been discussed in **Chapter V**.

Chapter VI incorporates the results obtained from the study of reactions of *p*-formylcalix[n]arenes with RMgX (R=Ph, C_2H_5) (Grignard reactions) and ethyl bromoacetate in the presence of zinc (Reformatsky reaction).This chapter also describes the condensation reactions of formylated calix[n]arenes with aromatic and aliphatic primary amines to yield Schiff bases. The products obtained have been characterized by IR, UV-visible and NMR analysis while initial studies on interaction of Schiff bases with some transition metal ions have also been reported in this chapter.

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