

STUDIES IN MOLECULAR ORGANIZATION FOR MOLECULAR RECOGNITION

by

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Department of Chemistry

Submitted

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to the



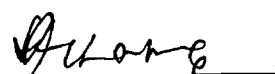
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CERTIFICATE

This is to certify that the thesis entitled "*Studies in Molecular Organization for Molecular Recognition*" being submitted by **Ms. Anuradha Santra** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Anuradha Santra 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 have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.


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Anuradha Santra
Anuradha Santra

ABSTRACT

The thesis titled, “**Studies in Molecular Organization for Molecular Recognition**” submitted by Ms. Anuradha Santra deals with some aspects of chemistry of calixarenes and their applications for ionic and molecular recognition.

Calix[n]arenes constitute an important class of compounds that can serve as useful building blocks for designing molecular receptors for ionic and molecular recognition. **Chapter I** of this thesis presents an overview of research work published on calix[n]arenes with emphasis on their rational synthesis and conformational characteristics. It also provides an account of recent research work published on calixarene 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 describes the synthesis of *p*-imidazolylicalixarenes from readily available raw materials via alkylation, formylation and reaction with aryl diketones in the presence of ammonium acetate and glacial acetic acid. Optimized procedures for obtaining cone conformation of *p*-imidazolylicalixarenes as well as their characterization by IR, UV, NMR and FAB mass analysis have been reported.

Chapter III contains experiments conducted to evaluate synthesized *p*-imidazolylicalix[n]arenes for recognition of alkali, alkaline earth and transition metal ions. It has been observed that some of the *p*-imidazolylicalixarenes can selectively interact with specific metal ions and are able to extract their metal picrates. Role of calixarene σ -frame work in the metal ion extraction has been delineated through UV, NMR and inductively coupled plasma atomic emission spectroscopy.

The synthesis of new chromogenic water soluble calix[n]arenes ($n=4,8$) has been reported in **Chapter IV**. The structure of the synthesized chromogenic calix[n]arenes were determined by chemical derivatization and spectroscopic methods. It has been observed that the octasodium salt of tetrakis(4'-carboxyphenylazo)tetrahydroxycalix[4]arene can selectively interact with copper ions. Details of experiments conducted and results obtained are discussed in this chapter.

Chapter V presents our results on the synthesis of rationally designed new upper rim-upper rim diazo double calix[4]arenes. Cone conformer of selectively alkylated bis(ethoxycarbonylmethoxy)calix[4]arene when coupled with bis(diazonium) salts of 4,4'-biphenyls yielded new chromogenic diazo double calix[4]arenes in a cone-cone conformation. Structural elucidation of these diazo double calix[4]arenes has been accomplished by IR, NMR and FAB-mass analysis while their aggregation behaviour or self assembling in DMSO has been preliminarily examined by UV spectroscopy.

Chapter VI explores the methods for determining fish freshness in the light of principles of molecular recognition. This chapter also presents the results obtained during experiments conducted towards development of new calix[n]arene based sensor materials for examining fish freshness and detection, discrimination and estimation of amines. It has been observed that the synthesized upper rim-upper rim diazo double calix[4]arene elicits a change in colour from yellow to purple when interacted with aliphatic amines. The nature of interaction of amines with diazo double calix[4]arene has been investigated spectroscopically as well as by application of Jobs continuous variation method and mole ratio plots.

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