

**Studies on Synthesis and Applications of Functionalised
Calix[4]arenes**

by

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Submitted

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to the



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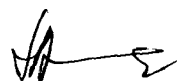


*DEDICATED
TO
MY PARENTS*

CERTIFICATE

This is to certify that the thesis titled “**Studies on Synthesis and Applications of Functionalised Calix[4]arenes**” being submitted by **Mr. Satya Narayan Sahu** 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. Satya Narayan Sahu** 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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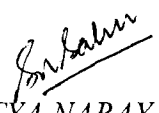
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ABSTRACT

The thesis titled, “**STUDIES ON SYNTHESIS AND APPLICATIONS OF FUNCTIONALIZED CALIX[4]ARENES**” presents the research work carried out on the synthesis and applications of some novel calix[4]arene derivatives. The synthesis of new derivatives has been achieved through innovation, modification and optimization of procedures available in the literature. The characterization and conformational analysis of new chemical entities have been accomplished by employing various spectroscopic techniques (*e.g.*, ^1H and ^{13}C NMR, FT-IR and UV-visible), single crystal X-ray and mass spectrometry. The molecular recognition capabilities of synthesized calix[4]arenes have been evaluated by using UV-visible, NMR, cyclic and squarewave voltammetric techniques and colorimetric analysis. The research work embodied in this thesis has been divided into five chapters.

CHAPTER I of the thesis presents an overview of literature published on the synthesis of electroactive supramolecular assemblies with special emphasis on molecular receptors based upon calixarene scaffolds and illustrates their prominent applications to ionic and molecular recognition.

CHAPTER II of the thesis describes the synthesis of some electroactive calix[4]arene monoquinones, diquinones, tetraquinone and a series of calix[4]arene(amidocrown)diquinones with variable ring sizes through reactions mediated by chlorine dioxide in the presence of aqueous phosphate buffer. Derivatization of calix[4]quinones has been successfully accomplished to yield new chromogenic azocalix[4]arenes and azocalix[4]quinones. The structural and conformational analysis of the synthesized compounds has been achieved by FT-IR, ^1H NMR, ^{13}C NMR spectroscopy, X-ray crystallography and mass spectrometry techniques.

CHAPTER III of the thesis describes the experiments carried out towards determination of primary recognition characteristics of synthesized novel calix[4]arene(amidocrown)diquinones and chromogenic azocalix[4]arene monoquinones for a variety of cationic and neutral guest species through the use of UV-visible, ^1H NMR spectroscopic and cyclic voltammetric techniques to examine the nature and the stoichiometry of interactions between the molecular receptors and the substrates.

CHAPTER IV of the thesis highlights the synthesis of a series of functionalized azocalix[4]arenes possessing various combinations of 4-nitrophenylazo and 2,4-dinitrophenylazo at their upper rim and phenylhydrazone, semicarbazone and thiosemicarbazone units at the lower rim of the calixarene scaffold. All the synthesized compounds have been characterized by UV-visible, FT-IR, ^1H NMR, ^{13}C NMR spectroscopic and mass spectrometric techniques. The synthesized molecular receptors have been evaluated for anionic recognition by UV-visible and colorimetric analysis for applications in real-time monitoring of biologically important anions.

CHAPTER V of the thesis describes the synthesis of novel heterocyclized calix[4]arenes possessing benzimidazole, diphenylimidazole, phenanthreneimidazole, acenaphtheneimidazole and benzothiazole moieties at lower rim of calixarenes through a series of condensation reactions by using sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) and ammonium acetate ($\text{CH}_3\text{COONH}_4$). Preliminary studies on the binding of anions by the synthesized receptors have been accomplished through UV-visible and ^1H NMR spectroscopic studies and colorimetric analysis to reveal that some of the synthesized compounds have a potential of developing into new sensor materials.

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