

**DESIGN AND SYNTHESIS OF CALIXARENE  
BASED MOLECULAR SCAFFOLDS FOR IONIC  
RECOGNITION**

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BASED MOLECULAR SCAFFOLDS FOR IONIC  
RECOGNITION**

*by*

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Submitted

*In fulfilment of the requirements of the degree of*

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to the



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**APRIL 2014**

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*DEDICATED  
TO  
MY PARENTS*

## **CERTIFICATE**

This is to certify that the thesis entitled “**Design and Synthesis of Calixarene based Molecular Scaffolds for Ionic Recognition**” being submitted by **Ms. Richa Shukla** 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 her. **Ms. Richa Shukla** 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 award of any degree or diploma.

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Richa Shukla

## ABSTRACT

The thesis titled “**DESIGN AND SYNTHESIS OF CALIXARENE BASED MOLECULAR SCAFFOLDS FOR IONIC RECOGNITION**” presents the research work carried out on the synthesis and applications of some novel calix[4]arene derivatives through modification, optimization and innovation of procedures available in the literature. New chemical entities have been identified by utilizing spectroscopic techniques (FT-IR, UV-visible,  $^1\text{H}$ ,  $^{13}\text{C}$  and high resolution mass spectral analysis) while their recognition characteristics have been examined by using UV-Visible, NMR, fluorescence and colorimetric methods of analysis. The accomplished research work has been divided into five chapters as given below:

**Chapter 1** of the thesis highlights some of the general aspects of molecular recognition. An attempt has been made to present an overview of literature published on calixarene based supramolecular assemblies for their prominent applications to ionic and molecular recognition.

**Chapter 2** of the thesis primarily focuses on the synthesis and characterization of new macrocyclic calix[4]arenes by incorporation of nitrogenous unit as binding site and anthraquinonoidal group as signaling unit in the calix[4]arene molecular architecture. The synthesized receptor recognizes zinc ions with high sensitivity and no interference from  $\text{Cd}^{2+}$  or other related metal ions examined. Quantitative UV-visible and fluorescence spectral measurements have been employed to unravel the nature and the stoichiometry of the target-molecular receptor interaction.

**Chapter 3** describes the experiments done to achieve the synthesis of fluorescein appended calix[4]arene derivatives. The synthesized receptors were examined for their interaction with various cations in the form of their perchlorate salts through the use of UV-visible, fluorescence,  $^{13}\text{C}$  NMR, IR and mass spectroscopy. The fluorescein appended calix[4]arene derivatives exhibit selective binding with  $\text{Cu}^{2+}$  in preference to related transition metal ions and elicit distinct color change through a 1:1 binding stoichiometry.

**Chapter 4** of the thesis embodies the synthesis of novel calix[4]arene based receptors that possess the quinoline function at their upper rim. The synthesized receptor exhibits selective recognition and high binding affinity for copper ions. The resulting  $\text{Cu}^{2+}$ .calixarene complex has been determined to further recognize cyanide ions as confirmed by mass and fluorescence spectroscopy.

**Chapter 5** of the thesis describes the synthesis of calix[4]-bis-2-naphtho-crown-[6] through a series of reactions and optimization of reaction parameters. Preliminary investigations on the recognition properties of synthesized molecular receptor reveal that it is useful for the extraction of cesium ions. This chapter also presents the synthesis of novel *tert*-butylcalix[4]arene. A study on its interaction with various cations through fluorescence spectroscopic analysis reveals that it is highly selective towards copper ions in preference to other transition metal ions through a 1:1 binding stoichiometry.

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