

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

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**DEPARTMENT OF CHEMISTRY  
INDIAN INSTITUTE OF TECHNOLOGY DELHI  
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CALIXARENE BASED MOLECULAR  
RECEPTORS FOR IONIC RECOGNITION**

**by**

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**DEPARTMENT OF CHEMISTRY**

*Submitted*

*in fulfillment of the requirements of the degree of*

**Doctor of Philosophy**

**to the**



**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

**JULY 2015**

***DEDICATED***  
***TO MY***  
***DAUGHTERS***

## CERTIFICATE

This is to certify that the thesis entitled “**Design and Synthesis of Calixarene based Molecular receptors for Ionic Recognition**” being submitted by **Ms. Tanu Gupta** 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. Tanu Gupta** has worked under my guidance and supervision and has fulfilled the requirements for the submission of the 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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## ABSTRACT

The thesis titled “**DESIGN AND SYNTHESIS OF CALIXARENE BASED MOLECULAR RECEPTORS 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. Additionally, an attempt has been made to present an overview of literature published on heterocyclic calixarene based molecular receptors for their prominent applications in the field of ionic and molecular recognition.

**Chapter 2** of the thesis primarily describes the design and synthesis of four new heterocyclic calix[4]arenes bearing heterocyclic ring structures such as isatin hydrazone and quinoline in their molecular scaffold. Various characterization techniques employed to identify structures of designed compounds have been duly explained in the chapter.

**Chapter 3** describes the experiments carried out to evaluate ion recognition potential of synthesized heterocyclic calix[4]arene derivatives. The synthesized receptors were examined for their interaction with various metal ions and anions in the form of their perchlorate and

tetrabutylammonium salts respectively. Evaluation studies were conducted by employing spectroscopic techniques such as UV-vis, fluorescence,  $^{13}\text{C}$  NMR, IR and mass spectroscopy.

**Chapter 4** of the thesis discusses the design and synthesis of a novel upper rim upper rim linked bis-calix[4]arene receptor. The receptor has been doubly bridged at the upper rim by means of carbohydrazide linkers. Synthesis of an appropriate acyclic, non-bridged reference compound has also been described in the chapter. Structural characterization of both the compounds has been discussed in detail.

**Chapter 5** of the thesis describes the ion recognition capability of the designed bis-calixarene receptor. A study on its interaction with perchlorate salts of various metal ions through spectroscopic analysis reveals that it is a highly selective molecular receptor towards ferric ion in preference to other transition metal ions through a 1:1 binding stoichiometry.

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## NOTES

1. All melting points reported in this thesis are uncorrected and have been recorded on an electric melting point apparatus (Toshniwal, India).
2. UV-visible spectra have been recorded on Perkin Elmer's (Lambda 35) spectrophotometer.
3. FT-IR spectra have been recorded on KBr discs on a [5-DX] Nicolet FT-IR spectrophotometer.
4. Fluorescence spectra have been recorded on FL 3-11, Fluorolog-3 modular spectrofluorometer with single Czerny-Turner grating excitation and emission monochromators having 450 W Xe arc lamp as the excitation source and PMT as the detector.
5.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra have been recorded on a 300 MHz Bruker 300 DPX 300 instrument at room temperature in deuterated solvents ( $\text{CDCl}_3$ ,  $\text{D}_2\text{O}$ ,  $\text{CD}_3\text{OD}$ ,  $\text{CD}_3\text{SOCD}_3$ ) using tetramethylsilane (TMS) as an internal standard with the values of chemical shifts reported on  $\delta$  scale. The abbreviations s, brs, d, dd, t, q and m indicate singlet, broad singlet, doublet, double doublet, triplet, quartet and multiplet respectively.
6. FAB-mass spectra of the synthesized compounds have been recorded on a JEOL SX 102/DA- 6000 Mass Spectrometer at Central Drug Research Institute, Lucknow using m-Nitrobenzylalcohol as the matrix and Argon/Xenon (6kV, 100mA) as the FAB gas.
7. The high resolution mass spectra of the synthesized compounds have been recorded on a micrOTOF-Q II 10262 mass spectrophotometer in positive mode by ESI technique.
8. Elemental analysis has been carried on a Perkin Elemer's 240C-CHN Analyzer.

9. The completion of the reactions have been monitored by *Thin Layer Chromatography* performed on silica gel (Silica gel-G; Merck) coated glass plates using iodine for visualizing the spots.
10. Purification of the synthesized compounds has been carried out by column chromatography over silica gel (60-120 mesh; Merck).
11. For the sake of convenience, the names of calixarene derivatives used in this thesis have been shortened.
12. Abbreviations used in this thesis are:
- DMF- N,N'-Dimethylformamide;
- CDCl<sub>3</sub>- Deuterated Chloroform
- D<sub>2</sub>O- Deuterated water;
- DMSO-*d*<sub>6</sub>- Deuterated dimethyl sulfoxide;
- TBA- Tetra butyl ammonium.
- THF- Tetrahydrofuran