DESIGN AND SYNTHESIS OF CALIXARENE BASED MOLECULAR SCAFFOLDS FOR IONIC RECOGNITION

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APRIL, 2014

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by

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Submitted

In fulfilment of the requirements of the degree of

Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

APRIL 2014

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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ACKNOWLEDGEMENTS

First and foremost, I would like to thank my supervisor Prof. H.M. Chawla for not only allowing me to accomplish research under his guidance, but also for encouraging me to think independently and develop a scientific attitude with his utter patience and enthusiasm.

I would also like to thank all the past and present heads of the departments of Chemistry at IIT Delhi for providing me necessary facilities required for the completion of this research work.

I would like to express my sincere thanks to CSIR for providing financial help in the form of Junior Research Fellowship (JRF) as well as Senior Research Fellowship (SRF) so as to carry out research work successfully.

I would like to extend my profound gratitude to all my teachers who planted the seed of curiosity into me and nourished it with the water and fertilizer of their experiences. Although it is not possible to write the names of all of them, it is true that their contribution has left irremovable signature on my heart.

I would like to pay my special thanks to my seniors Dr. Rahul, Dr. S.N. Sahu, Dr. Shubha, Dr. Jyotsna and Dr. Parminder for bestowing enough confidence on me regarding various issues at research level and also lending a patient ear to all my endless queries.

I am also thankful to all my labmates Tanu, Preeti, Priyanka, Sanjay, Ravi, Manoj, Nitin, Dr. Shahid, Lakhbeer and Kuljeet for maintaining a co-operative and healthy environment in the lab. I am extremely grateful to Ms. Seema Arora, Personal Secretary of Prof. H.M. Chawla for her constant support and help.

I would also like to thank Mr. Keshav and Mr. Alok for recording the NMR data reported in this thesis. The staff of the Instrumentation Laboratory of Chemistry Department also deserves special mention.

Though it is difficult to mention the name of all colleagues and friends who contributed directly or indirectly in this achievement, I would like to thank some of my friends Benu, Megha, Rohini, Divya, Surabhi and Vidisha for constant source of encouragement during all these years and gave me untiring help during my difficult moments.

I am deeply indebted to my family for their love and support. My gratitude goes to my husband Dr. Vimlesh Mishra for his support and encouragement whenever I am confronted with hard time. Finally, I would like to acknowledge the most important personalities of my life, my parents. I put my deepest sense of regards and gratefulness to my father Mr. G.N. Shukla and mother Ms. Archana Shukla for their true blessings.

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}H, ^{13}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 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}C NMR, IR and mass spectroscopy. The fluorescein appended calix[4]arene derivatives exhibit selective binding with 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 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-naptho-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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