Name of the Scholar: Jyotsna rani kar

Name of Supervisor: Prof. Weqar Ahmed Siddiqui

Name of Co-Supervisor: Prof. H. M. Chawla

Department: Department of Applied Sciences & Humanities

Title of the Thesis: Design synthesis and applications of calixarenes

Abstract

The design and synthesis of new supramolecular hosts or receptors are in great demand in the area of supramolecular chemistry. In this thesis, we have chosen calixarene for the synthesis of different macromolecules as these are among the most well-known organic molecular host molecules which can be synthesized in large quantities from easily available starting materials and be easily modified for maximizing molecular recognition of target guest molecules. Calixarenes are macrocylic molecules possessing a cavity in their molecular architecture whose dimensions can be varied by varying '*n*' which represents the number of phenyl rings. Nowadays calixarene frameworks are used as basic platforms for the design of selective ionophores and much emphasis has been given to their applications as ion sensing supramolecular fluorescent systems with high selectivity (i.e., fluorescent chemosensors) for the detection of ions entrapped into its cavity through podant groups.

This thesis contains five chapters dealing with the synthesis and applications of calixarene based chemosensors.

The **first chapter** of this thesis gives a brief introduction to Supramolecular hosts or receptors, salient features of calixarene as supramolecule, synthesis, physical properties and complexation properties of calixarene based chemosensors and calixarene based fluoroionophores.

In **second chapter,** we have described the synthesis of coumarin and nitro-derivatized calixarene derivatives appended through varying length of alkyl chains. Their structures have been established through NMR, mass and IR spectroscopy. The X-ray crystal structure of one of the calix-coumarins has also been presented to show how the calixarene and coumarin units arrange themselves in the solid state. Photodimerization studies of two compounds were

studied on UVB irradiation to evaluate their potential application as photo recording materials.

In **third chapter,** we have reported the synthesis of calix[4]arene and coumarin based amido derivatives with varying binding sites. Some of the synthesized compounds were also tested for their sensing capacity towards transition metal ions with the help of NMR spectroscopy, UV-vis spectroscopy and fluorescence spectroscopy. One Calixarene derivative bearing two coumarin units connected by four amido binding sites was synthesized to act as fluorescent chemosensor which selectively detected Cu(II). This compound could be used as a potential chemosensor for further application.

In **chapter four,** we have described the synthesis of two types of calix[4]arene based receptors *i.e.* calix[4]arene based schiff's base and calix[4]arene based nucleobase. In the first part of this chapter, we have described the synthesis and characterization of a series of calix[4]arene based schiff's bases. Upper rim functionalization of calix[4]arene was done through formylation with HMTA/TFA to give bis formylated alkoxy calix[4]arenes which have been derivatized to give the schiff's bases. One of the synthesized calixarene based schiff's base was found to selectively recognize Cu^{2+} out of all the cations studied. The second part of this chapter has described synthesis of calix[4]arene based nucleobases. Our aim was to show how the attribution of the nucleobase (e.g. adenine in this case) towards metal ion complexation changes in a supramolecular assembly, as compared to its behaviour when it was alone. The cation binding behaviour along with the association constant of the host-guest complex of one of the adenine appended calixarene based nucleobasehas been determined through UV-vis spectroscopy. It was found to form 1:1 host-guest complex with $Zn(ClO_4)_2$ in methanol:acetonitrile (1:1,v/v) system and it showed high binding constant towards Zn^{2+}.

In **fifth chapter**, we have reported synthesis of calix[4]arene(amido)crown derivatives through aminolysis of the parent calix[4]arene and synthesis of a furanocoumarin, a dimeric coumarin and a dimeric furano coumarin. These compounds could be used as efficient fluorescence chemosensors.

The analysis of sensor properties in this thesis offers understanding at the fundamental level of the chemical and photophysical factors involved and illustrate the prospects for a number of analytical applications in environmental and biological areas.