The abstract of thesis entitled “STUDIES OF CALIX(n)ARENES BASED MATERIALS FOR CHEMICAL SENSORS” deals with calixarene based sensing of neutral molecules. Calixarene derivatives can form host–guest type complexes with neutral organic molecules; it is likely that they can be used for selective molecular recognition in chemical sensors measuring neutral species too. The thesis deals with complexation study by using pyrene derivative of calix[4]arene as a ligand for host guest inclusion complexation for cyclodextrin, p-sulfonatocalix[6]arene and p-sulfonatocalix[8]arene is used for sensing of ascorbic acid. Considerable attention has been given in synthesis of efficient artificial receptors for molecular recognition and sensing as they have wide functions in area of biological, medical, environmental, and chemical sciences. They are used in molecular recognition and also in food as dietary supplement, agricultural and chemical engineering. In the food industry, cyclodextrins are employed for the preparation of cholesterol free products; the bulky and hydrophobic cholesterol molecule is easily lodged inside cyclodextrin rings. Consumption of α-cyclodextrin can reduce blood sugar peaks following a high-starch meal. Weight loss supplements are marketed from α-cyclodextrin which claim to bind to fat and be an alternative to other anti-obesity medications. β-cyclodextrin complexes with certain carotenoid food colorants have been shown to intensify color, increase water solubility and improve light stability.

p-sulfonatocalix[n]arenes and their derivatives are group of water soluble and have capability to bind guest molecule in their cavity. Cavity of p-sulfonatocalixarene is π-electron rich, due to that it provides selective affinity for different guest. These are scaffolds for different functional group as well as for host-guest chemistry.

For the conventional development and growth of a multicellular organism, ascorbic acid (AA) is very much obligatory vitamin. Ascorbic acid used as antioxidant, additives in beverages, food cosmetic applications and in pharmaceutical formulations because it is absolutely oxidized.

The thesis is divided into five chapters. First chapter includes introduction, inclusion complexation study by fluorescence technique. Second chapter explain experimental procedure while third, fourth and fifth chapter deals with the results, discussion, conclusion. And future scope of the present work described at the end of thesis.
CHAPTER 1: INTRODUCTION

This chapter deals the brief introduction of scope of Calixarene, Cyclodextrin, p-sulfonatocalix(6) arene and ascorbic acid. Complexation study is useful for the detection of these target molecules and Ascorbic acid. The cyclodextrins (CDs) belongs to cyclic oligosaccharides family linked by α-1, 4-glucopyranose units. The family is made up of three major and well-known CDs: α-, β-, and γ-CD, containing six, seven and eight glucose subunits respectively. Host guest chemistry is most attracting field for complexation study. Calixarenes is known for its complexing ability for host since from last three decades. Calixarenes have suitable molecular architecture and properties for use of sensor material. There are many reports in literature on selective binding of various ions to functionalized calixarene.

CHAPTER 2: EXPERIMENTAL AND PROCEDURE

This chapter describes an experimental methods used for complexation studies. The synthesis of calixarenes like p-t-butyl calix(4)arene, calix(4)arene, p-t-butylcalix(6)arene, calix(6)arene,. The synthesis of p-sulfonatocalix(6)arene, p-t-butyl calix(4)arene, and its pyrene derivative is described, which are used for the complexation study. Chapter also describe the synthesis of Monosubstituted pyrene derivative of calix[4]arene, dissubstituted pyrene derivative of calix[4]arene. This chapter also describes the instrumental theory of UV-Visible spectrophotometry, Florometry and Time correlating single photon counting spectrophotometry, Scanning electron microscopy, HRMS principle etc.


This chapter describes the Fluorescent molecular probe having excimer emission property templated with γ -cyclodextrin (γ -CD) including calix[4]arene as ionophore and pyrene as fluorophore has been synthesised. With γ-CD, pyrene substituted calixarene (PCX4) shows strong excimer formation with very high intensity at 482 nm which is the characteristic peak and is used to study interaction between them. Binding study of these fluoroionophore PCX4 with γ-CD has been investigated in water and the recognition process is monitored by UV-Vis, steady-
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state and time-resolved fluorescence, FT-IR, SEM, HR-MS techniques. In present study, depending upon the concentration of \( \gamma \)-CD excimer formation is possible from both intramolecular (two pyrene moieties of the same PCX4 i.e. 1:1 (PCX4: \( \gamma \)-CD) complexation) and intermolecular (two pyrene moieties from two different PCX4s i.e. 2:1 (PCX4: \( \gamma \)-CD) complexation) stacking interactions. Since the monomer emission decreases at lower concentration of \( \gamma \)-CD, the weak excimer emission could be due to the dimerization of pyrene groups between two different PCX4s, which is an intermolecular process. Beyond 1.2 mM of \( \gamma \)-CD, the intramolecular excimer formation is predominant, resulting in a strong excimer emission. On the other hand, \( \gamma \)-CD induces downward pK\(_a\) shift in PCX4 which may find applications in drug delivery.


This chapter describes the Monosubstituted pyrene derivative of calix[4]arene is synthesized (MPCX4) and its self-assembly has been studied in basic medium. It shows ground state dimer due to aggregated self-assembly formation which has fluorescence emission at 450 nm. Hydrophobic interaction among the probes in water is due to presence of adjacent carbonyl group and short spacer of fluorophore, basic pH environment promotes self aggregated dimer formation. Photophysical properties of these fluoroionophore are investigated in water, by employing UV–Vis, steady state fluorescence and time resolved emission spectroscopic techniques. Effect of variable concentration of \( p \)-sulfonatocalix[6]arene shows quenching of dimer emission and leads to 1:2 and 1:1 inclusion complex formation and further confirmed by HR-MS study. The complex formed is further characterised by \(^1\)H-NMR, FT-IR and SEM techniques.
CHAPTER 5: PHOTOPHYSICAL STUDY OF SUPRAMOLECULAR INTERACTION BETWEEN P-SULFONATOCALIX [8] ARENE AND ASCORBIC ACID

Chapter 5 deals with the study of mode of inclusion complexation of p-sulfonatocalix[8]arene and ascorbic acid in aqueous solution has been investigated at different pH based on UV-Visible, fluorescence, FT-IR, $^1$H-NMR, HR-MS spectroscopic studies. Addition of ascorbic acid solution to p-sulfonatocalix[8]arene enhances the fluorescence intensity of sulfonatocalix[8]arene particularly at neutral pH with blue shift in absorption and in fluorescence spectra. As the number of their hydroxyl benzene sulfonate units in SCX8 hosts were capable of binding ascorbic acid molecule. Binding site and structures with stoichiometry are examined by $^1$H-NMR study. Binding constant (K) for the inclusion complex at different pH of acidic, neutral, basic calculated as $0.42 \times 10^2 \text{ M}^{-1}$, $0.84 \times 10^2 \text{ M}^{-1}$, $0.1038 \times 10^2 \text{ M}^{-1}$. Electrostatic interaction, hydrogen bonding, inclusion in hydrophobic environment plays important role in complexation.