SYNOPSIS

The contents of this thesis entitled **"An Endeavor in Receptor Design for Solid State Recognition of Anions/Hydrated Anions"** have been divided into seven chapters based on the results of experimental work carried out during the research period.

Chapter 1: Introduction

This chapter provides a brief introduction on '*supramolecular host-guest chemistry*' of ionic species with special reference to recognition of anions or hydrated anions. Supramolecular chemistry offer many possible avenues like recognition, catalysis and transport. Anions are ubiquitous in nature. Hence, molecular recognition of anionic species has attracted great interest during the last decades because of the imperative role in various biological and environmental processes. Extensive research effort has been expended toward understanding how host structure influences anion binding with the goal of discovering more effective and more selective anion receptors. A very large number of artificial systems for recognition and sensing of anions have been designed and synthesized by properly exploiting supramolecular concepts. One successful approach for preparing anion hosts has been to synthesize molecules that offer an array of H-bonding sites to the guest. Because H-bonds exhibit directionality, it should be possible to achieve a structure-based recognition for anions of particular shape and size. The binding of anion guests within preorganized macrocyclic systems is relatively more predicated easy to understand supramolecular association but the binding processes of acyclic receptors is unpredictable and very tough to control due to freedom of many conformation. Hence it is great challenge to study receptor-anion assembly of flexible acyclic receptor. Sometimes specially design acyclic receptor forms capsular assemblies which have shown a number of interesting properties e.g. encapsulation of anion/anion–water clusters, capturing aerial CO_2 as carbonate, selective salt extraction and anion transportation. On the other hand, Understanding the hydration of anions at the molecular level is thus important as the surface speciation and reactivity of aerosols, which play a key role in atmospheric and oceanic chemical cycles. The characterization of an isolated solvated ion serves to add to information about the solvation properties. As the properties of hydrated ions are quite

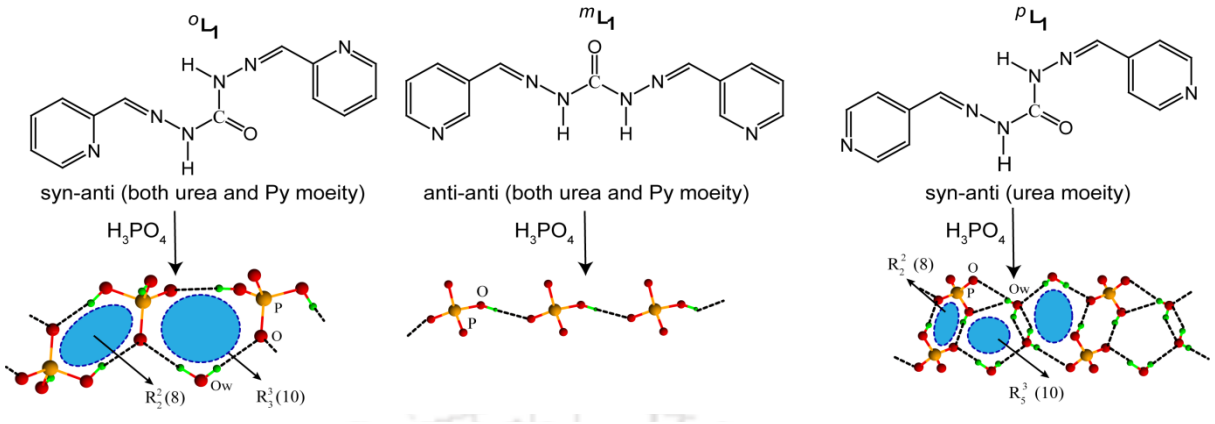
different from those of isolated ions (in the gas phase) or ions in nonpolar media and are governed by the nature of the surrounding hydration network.

Chapter 2: Experimental Methods and Characterization

Chapter **2** describes detailed report of the various reagents used in the synthesis of the receptors, their synthetic procedures, crystallization details, binding study and specifications of analytical instruments employed in the characterization of synthesized receptors and their various complexes.

Chapter 3: Linear Pyridine-Urea Receptor and Its Interaction with Hydrated Anions: Effect of positional isomer

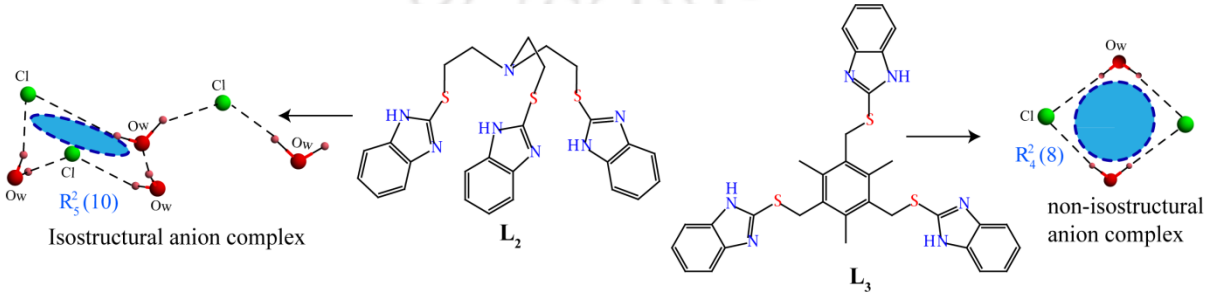
In this chapter, the preparation of three isomeric pyridine-urea based receptors (^{o}**L$_1$**, ^{m}**L$_1$** and ^{p}**L$_1$**) and their anion complexation study in presence of inorganic acid has been described. The receptor is enriched with urea as H-bonding site and pyridine as a protonation site. Three isomers behave distinctively on treatment with acids. Upon acidification with H_3PO_4 results three different assembles of anion or anion-water cluster. Formation of stable discrete water hexamer and hybrid iodide-water cluster $[I_4\text{-}(H_2O)_6]^{4-}$ containing a tetrameric core of either water or iodide water respectively, infinite sulfate-water chain containing chair like sulfate-water hexamer $[(SO_4)_2\text{-}(H_2O)_4]_\infty^{4-}$, infinite chain of dihydrogen phosphate–water trimer $[(H_2PO_4)_2\text{–}H_2O]_\infty^{2-}$ and a simple perchlorate-water chain has been observed by *ortho* isomer. Whereas *meta* isomer gave simple 1-D infinite $[HPO_4]_\infty^{2-}$ chain. The *para* isomer stabilizes infinite chain of 1-D tetrameric cluster $[(SiF_6^{2-})_2\text{-}(H_2O)_2]_\infty^{4-}$, nitrate-water cluster $[(NO_3)_2\text{-}(H_2O)_6]_\infty^{2-}$ containing two fused rings, assembly of phosphate-water with minimum repeating unit $[(HPO_4^{2-})_2\text{–}(H_2O)_3]^{4-}$ and perchlorate-water cluster. Depending upon position of N-atom in the pyridine moiety, it offers various types of anion-water combination. Notably various conformation of the receptor and projection of urea hydrogen is observed while binding of anions occured. In all cases the anions are stabilized by N–H···O (urea NH and PyH^+), O···H_2O (lattice water), C–H···O and anion···π^+ interactions. Moreover other supramolecular interactions like anion···anion/anion–π^+ and π^+···π/ π^+···π^+ also play an important role in complexation and packing of molecules in the solid state.



Scheme 1. A comprehensive representation of the research work presented in chapter 3.

Chapter 4: Aliphatic and Aromatic Capped Tripodal Receptors for Hydrated Anion Recognition: Effect of Ligand Flexibility

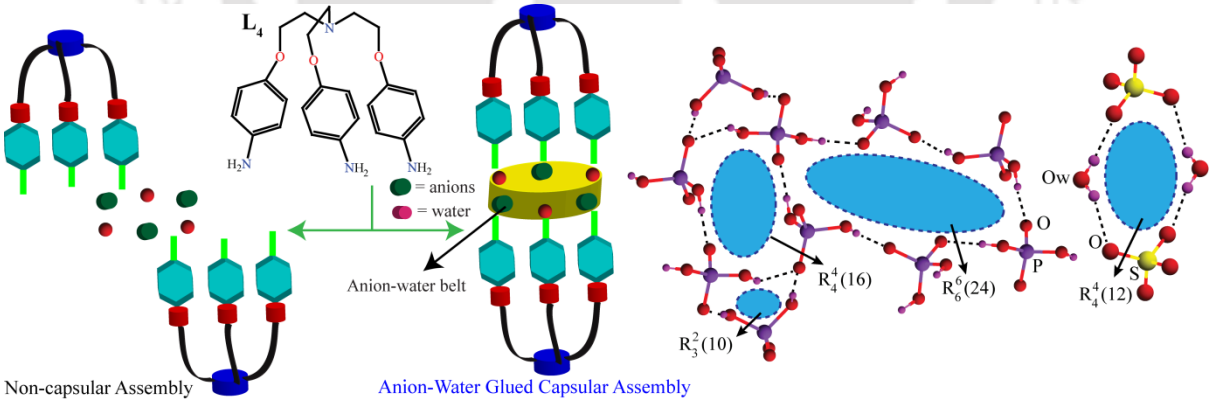
The key approach of this chapter is generating of multiple anions within a ligand framework and ligand structure directed anion-water assembly. Mercapto-benzimidazole substituted apical N-atom and benzene capped tripodal receptor **L2** and **L3** has been synthesized with three protonate site per molecule. The bowl shape and benzimidazole NH of the tripodal host offers suitable place and binding site favoring the formation of anion-water cluster. Two types platform remarkably affects the formation of anionic complex as well as anion-water aggregation. The N-atom based tripodal **L2** exclusively generate isostructural hybrid halide-water cluster ($[X_3(H_2O)_4]^{3-}$, X = Cl^-, Br^-) having cyclic pentameric puckered ring. The halide-water cluster is mainly stabilized by O–H···X^- and N–H···X^- H-bonds. Whereas benzene capped bowl shaped tripodal **L3** stabilizes infinite 1D water chain $[H_2O]_\infty$ and fluoride-water trimer $[F_2\text{-}(H_2O)_{0.5}]^{2-}$ or cyclic chloride water tetramer $[Cl_2\text{-}(H_2O)_2]^{2-}$ engulfed by the receptor and is governed by multiple non-covalent (hydrogen/halogen bond, CH···π and π···π) and electrostatic interactions. It is diprotonated (in spite of being three protonation sites) and form non-isostructural complex.



Scheme 2. A comprehensive representation of the research work presented in chapter 4.

Chapter 5: Hydrated Anion Glued Capsular and Non-capsular Assembly of a Tripodal Receptor

Chapter 5 describes the formation of capsular and non-capsular assembly of a newly synthesized polyammonium tripodal receptor **L_4**. The attachment of large number of H-bonding sites for the successful recognition of anions was introduced in this polyammonium based receptor.Highly effective anion receptors can be produced by combining electrostatics and hydrogen bonding; in fact our N_4 based receptor has multiple protonation sites able to contribute both. The receptor is highly efficient and form anion complex of widely spread like halide ions (F^-, Cl^-, Br^- and I^-) and oxyanions (NO_3^-, ClO_4^-, SO_4^- and $H_2PO_4^-$). Fluoride-water cluster and chloride ion belt mediated supramolecular assembly in bimolecular capsular fashion is established. On the other hand formation of non-capsular supramolecular association of the receptor is observed by chloride-water, bromide-water and iodide-water clusters. Moreover our observations underscore extended polymeric bromide-water cluster $[Br_5\text{-}(H_2O)_6]^{5-}$ having defined cyclohexane like chair conformation and discrete iodide-water cluster $[I_2\text{-}(H_2O)_4]^{2-}$ containing water tetramer in solid state. In case of oxyanion, infinite decameric dihydrogen phosphate cluster $[H_2PO_4^-]_{10}$ is reported. In addition, octahedrally arranged discrete anionic cluster $[Na(ClO_4)_6]^{5-}$, isolated discrete sulfate-hydrogen sulfate trimer $[SO_4\text{-}(HSO_4)_2]^{4-}$ and sulfate-water tetramer $[(SO_4)_2\text{-}(H_2O)_2]^{4-}$ is also described in solid state.

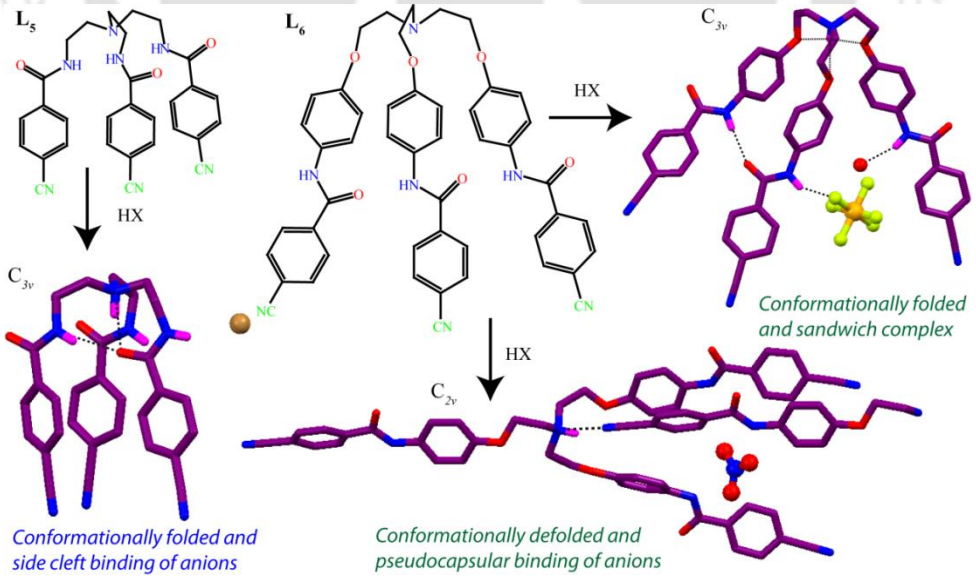


Scheme 3. A comprehensive representation of the research work presented in chapter 5.

Chapter 6: Anion Complexation with Cyanobenzoyl Substituted Tripodal Amide Receptors: A Comparative Study between First and Second Generation Receptor

Tripodal cyanobenzoyl appended triamide receptors with different length have been studied in this chapter. First generation tripodal receptor (**L_5**) and elongated second

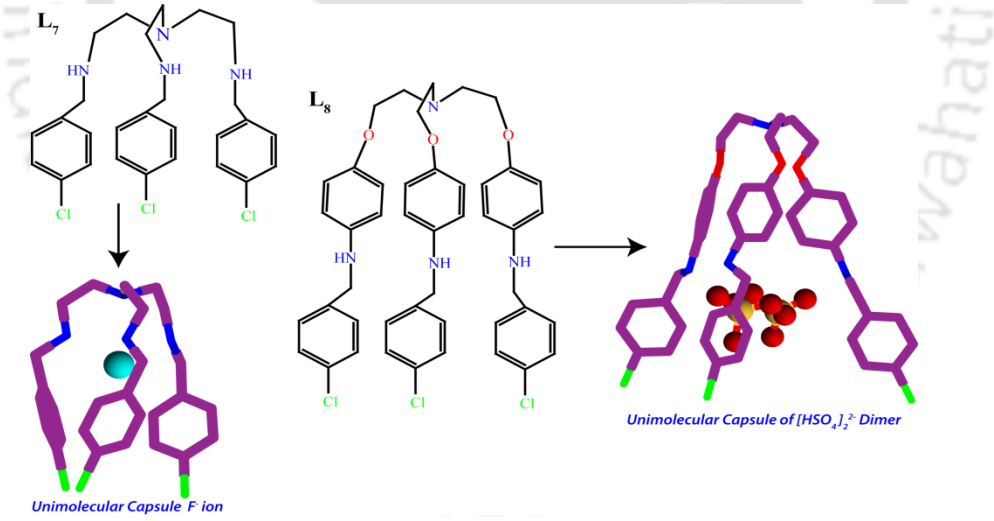
generation tripodal (**L6**) was synthesized. Two receptors were exploited for comparative study of anion binding was also carried out in solid and solution state. The dimensionality and nature of the anions play a crucial role in making various molecular interactions possible in complexation of various anions in both receptors. The self-alignment and orientation of the flexible second generation tripodal is greatly influenced by the size and shape of the anion. The X-ray structure shows **L5** is internally locked and could not welcome anions into its C_{3v} symmetric cavity, shows side cleft anions binding. Positioning of amide functionality to a distant position with respect to apical N-atom results a bigger cavity and subsequently intimidate the N–H···O=C intramolecular H-bond unlike in **L5**. The receptor form quasi-planar arrangement of the arms, with two arms close each other while third arm pointing to opposite direction giving pseudo capsular complex during H-bonding interaction. Finally comparison of the recognition of anionic guests of different shapes/geometry and solid state organization of the two kind of receptor of varying podal length is done successfully. Interestingly anion induced reorientation of the receptor **L6** was observed during recognition of octahedral SiF_6^{2-} anion. In the solid state –CN group provide further stabilization to the supramolecular complexes through C–H···π and anion···π interactions. Moreover the solution state interaction phenomena of two receptors in neutral form with the anions of various shape and size like spherical (F^-, Br^-, I^-), planner (NO_3^-), tetrahedral (ClO_4^-) and octahedral (SiF_6^{2-}) by detailed ^1H NMR studies along with their molecular binding was thoroughly analyzed.



Scheme 4. A comprehensive representation of the research work presented in chapter 6.

Chapter 7: Hybrid Anion-Water Cluster Mediated Self-Assembly of Tripodal Polyammonium Receptor: Effect of Length of the Receptor

This chapter showed two polyammonium functionalized tripodal receptor for encapsulation of anions. Once observing the effect of length in the amide based receptors, subsequently two amine based receptors of different length has been synthesized. The amine group increase presence of multiple anions and acts as H-bonding source. These two receptors trap anions within its C_{3v} symmetric cavity. The first generation tripodal **L**$_7$ owing to have smaller inner space, it encapsulate the small anions like fluoride [F⊂**L**$_7$], whereas second generation tripodal **L**$_8$ allows bigger oxyanion like sulfate. The specially designed C_{3v} symmetric tripodal of having enough cavity, on protonation with sulfuric acid, successfully encapsulates hydrogen sulfate dimer in a unimolecular capsular fashion [$(HSO_4)_2$⊂**L**$_8$]. Such a big dimer inside the cavity is favored by H-bonding (NH···O) and electrostatic interactions among HSO_4^- and NH_2^+ ions. Moreover, by virtue of multiple anions exterior HSO_4^- ions and crystallized water molecules assembled into unique hybrid $[(HSO_4)\text{-}(H_2O)]_4^{4-}$ cluster having different cyclic motifs. The $[(HSO_4)\text{-}(H_2O)]_4^{4-}$ cluster and Cl···Cl halogen bond act as a template in the formation of unimolecular capsule [$(HSO_4)_2$⊂**L**$_8$].



Scheme 5. A comprehensive representation of the research work presented chapter 7.

Conclusion

The concluding remarks on overall experimental works presented here may sound as the contribution to a vast wealth of anion recognition event. Solid state recognition of naked as well as hydrated anion by various synthetic receptors is relevant to biological systems which may open the opportunity of study of complex behavior of anions. Additionally it is

also instructive to know structural relationship of anion-water as solvated anion plays many roles in atmospheric chemistry and biology. All organic receptors contain at least one basic nitrogen atom which allows anion complexation with acid in protic solvent. Hence most of the anion complexes have inherent tendency to crystallize with at least one water molecule. This phenomenon renders the recognition of anion as a hydrated form with fascinating anion-water supramolecular architectures. Firstly pyridine-urea based three isomeric planar receptors $^{o}\mathbf{L_1}$, $^{m}\mathbf{L_1}$ and $^{p}\mathbf{L_1}$ which generate three different anion cluster $[(H_2PO_4)_2\text{-}H_2O]_\infty^{2-}$, $[HPO_4]_\infty^{2-}$ and $[(HPO_4)_2\text{-}(H_2O)_3]^{4-}$ respectively on treatment with H_3PO_4 acid. These receptors also stabilize other hydrated anions like $[(SO_4)_2\text{-}(H_2O)_4]_\infty^{4-}$, $[(SiF_6)_2\text{-}(H_2O)_2]_\infty^{4-}$ and $[(NO_3)_2\text{-}(H_2O)_6]_\infty^{2-}$ by N–H···O, O···H_2O, C–H···O and anion···π^+ interactions. The next receptors $\mathbf{L_2}$ and $\mathbf{L_3}$ were able to form capsular or noncapsular assembly in protonated state upon recognition of anion or hydrated anions. Thereafter synthetic modification of $\mathbf{L_4}$ lead to $\mathbf{L_5}$ and $\mathbf{L_6}$ having different length and cavity, effectively show side cleft and pseodu-capsular anion binding. Selective anion induced conformational change of $\mathbf{L_6}$ was observed in solid state. Secondly the ultimate outcome of ligand synthesis aiming of making big cavity for anions are done with $\mathbf{L_8}$ and $\mathbf{L_7}$ shows comparative study of effectiveness of cavity size. The $\mathbf{L_7}$ successfully encapsulate big anion like hydrogen sulfate dimer. Additionally the receptor stabilizes a big hydrogen sulfate-water cluster $[(HSO_4)\text{-}(H_2O)]_4^{4-}$. Small pocket of $\mathbf{L_8}$ is capable of encapsulating small anion like F^-.