Urea Functionalized Acyclic Receptors: Anion Coordinated Hydrogen Bonded Supramolecular Self-assembly

A Dissertation

Submitted in partial fulfillment for the degree of

Doctor of Philosophy

Biswajit Nayak

(Roll No. 156122040)

Thesis Supervisor: Prof. Gopal Das

Department of Chemistry

Indian Institute of Technology Guwahati

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Dedicated To

My Parents...

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

STATEMENT

I do hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology Guwahati, India, under the guidance of Dr. Gopal Das, Professor, Department of Chemistry, Indian Institute of Technology Guwahati, India. In keeping with the general practice of reporting scientific observations, due acknowledgements have been made wherever this work is based on the findings of other investigators.

Biswajit Nayak

3rd September, 2020 **Biswajit Nayak**

IIT Guwahati

INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI

Department of Chemistry

CERTIFICATE

This is to certify that **Mr. Biswajit Nayak** (Roll No. 156122040) has been working under my supervision since July, 2015 as a regular registered Ph.D. student. His thesis entitled **"Urea Functionalized Acyclic Receptors: Anion Coordinated Hydrogen Bonded Supramolecular Self-assembly"** is an authentic record of the results obtained from the research work carried out under my supervision in the Department of Chemistry, Indian Institute of Technology Guwahati, Assam, India. I am forwarding his thesis to submit for the award of degree of Doctor of Philosophy, from this institute. I hereby certify that he has fulfilled all the requirements, according to the rules of this institute regarding the investigations embodied in his thesis and this work has not been submitted elsewhere for a degree.

Dr. Gopal Das
(Thesis Supervisor)
Professor
Department of Chemistry
IIT Guwahati
Assam - 781039, India

Acknowledgement

The ride en route for the completion of my thesis with the outcome of the year of experience, idea generated in the form of knowledge, was full of ups and downs, clear the way to fruitful success. Standing at the final stage of a unforgettable journey, when I look back over the five years of my research journey I have been supported and assisted by a large number of people, in regards to whom I want to convey my word of deepest appreciations for their kindness, grace, attention, encouragement, and support.

At the very outset, I would like to express my deepest gratitude towards my parents for having constant faith in me. Their eternal blessing and continuous support has shown me the right path and guided me this far, and this will take me far forward in future to achieve success. Thank you for instilling me with a strong passion for learning and for doing everything possible to put me on the path to greatness. I want to express my earnest gratitude towards my PhD supervisor Prof. Gopal Das, for his kind support, insightful advice and encouragement. I sincerely thank him for his constant guidance and freedom to work which assisted me in completing the work assembled in the thesis. I would also like to be grateful to my doctoral committee members, Prof. Sandip Paul, Dr. Lal Mohan Kundu and Dr. Akshai Kumar A. S for their advice and suggestions. I would also like to thank Head of the Department, Scientific officer Dr. Babulal Das and other technical and non-technical staff members of the Department of Chemistry, IIT Guwahati for providing me with the necessary facilities whenever required. I sincerely appreciate the staffs of the central instrument facility, for their help and guidance in handling several analytical instruments, required during my research work.

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now has become my brother from another mother and an integral part of my family. I cannot express in words for his constant support and guidance.

I also owe my obligations to my other seniors, batch mates and juniors of PhD fraternity of the chemistry department for their help and support.

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One of the things worth mentioning is about my badminton at IIT Guwahati, my PhD life is incomplete without this as we used to spend daily 3 hours in the court playing our sweats out forgetting everything. I would like to thank my badminton buddies Swapnali Madam, Kishor Bhaya, Dhanesh, Jagadish, Uttam Bhai, Subrat Bhai, Panda Sir, Saikia Sir, Charu Sir for being the part of my journey.

No words would express my feelings for my teachers from my school, college and university to whom I owe a debt for their teachings and benevolence.

Still, many names are missing whose contribution and help is worth mentioning.

Biswajit

The insides of this thesis entitled **"Urea Functionalized Acyclic Receptors: Anion Coordinated Hydrogen Bonded Supramolecular Self-assembly"** have been divided into five chapters established on the results of experimental work performed during the research period.

Chapter 1: Introduction

This chapter provides a brief introduction on 'supramolecular host-guest chemistry' regarding the recognition of anions/hydrated anions within the preorganized cavity or self-assemblies of artificial acyclic receptors, isomeric with respect to either terminal substituents or preliminary materials. The recognition of anions of diverse dimensionalities by acyclic artificial hydrogen bonding scaffolds has happened as one of the prominent and dynamic arenas of research within the domain of supramolecular chemistry since anionic species with negative charges are ubiquitous and their significance in biological, environmental, chemical, medical as well as industrial processes is an immense interest of research which cannot be undervalued. Over the last two decades, numerous acyclic hosts having multi-arm hydrogen-bonding functionalities, mostly tripodal type of receptors have been synthesized for anionic guests because they have better capabilities to form molecular capsules with topological complementarities, as compared to those with any rigid or less hydrogen bonding-functionalized acyclic flexible dipodal receptor systems. Therefore we lay emphasis on the field of recent developments of flexible dipodal receptor systems basically for encapsulation or entrapment of anion/hydrated anions in solid and solution state.

As opposed to the metal ions which are spherical, anionic species have a wide range of shapes (such as spherical, planar, tetrahedral, octahedral etc.) and sizes. Therefore, the recognition of anions within the self-assemblies of flexible dipodal scaffolds is considered to be one of the challenging tasks to the supramolecular researchers. Furthermore, encouraged by the recognition tools exploited by Nature, anion coordination chemistry has materialized into a prominent and active field of research within the realm of ''supramolecular chemistry'' with new synthetic receptors capable of recognizing anions with environmental and biomedical relevance. Acyclic receptors with amide, pyrrole/indole and urea/thiourea groups have widely been employed for anion binding and encryption, from the beginning of anion receptor chemistry. Researchers are deeply involved in recognition of anionic guest species within the macrocyclic or acyclic host molecules, because of its various dynamic roles in biological systems, alongside having adverse effects on the environment. Subsequently, inspired by the natural processes of effective and selective anion binding of proteins by precise noncovalent interactions, such as SBP (sulfate binding protein) from S. Typhimurium and in PBP (phosphate-binding protein) from E. coli. etc., many acyclic artificial anions binding podands have extensively been employed in the past

two decades. The anion binding propensity of receptors varies with the appended peripheral functions (electron-withdrawing and donating functionalization) since both the position and the nature of functional groups influences the hydrogen bonding capability of a particular receptor. The binding of anionic guests within the preorganized tripodal receptor systems are widely studied till last decade but the binding processes of acyclic rigid dipodal receptors containing positional or electronic aryl substituents with less preorganized cavities or less number of binding sites remain more elusive in literature. The structural features of the crystal void such as, shape, size, position or electronic properties are controlled by the super-structure which is formed, when two or more geometrically and functionally opposite receptor subunits are self-assemble. These kinds of anion induced self-assemblies formed by hydrogen bond donation of receptors have exposed a number of motivating properties, e.g., anion recognition in water, encapsulation of anion-water clusters within dimeric/trimeric/tetrameric host assemblies, entrapment of cyclic fluoride-water tetramer, bare and hydrated asymmetric sulfate, sulfate-water-sulfate adduct, within linear dipodal receptors, fixation of aerial carbon dioxide (CO_2) as carbonate-water cluster even in dipodal receptor system, selective salt extraction from water, trans-membrane anion transportation etc.

Chapter 2: Experimental methods and characterization

In this chapter, a thorough comprehensive report of the various reagents used in the synthesis of the receptors, their synthetic pathways, crystallization details, binding study and specifications of analytical instruments employed in the characterization of designed and synthesized free receptors and their various anion complexes with anions/hydrated-anions and anionic associations are represented thoroughly.

Chapter 3: Naphthyl Substituted Electron-Rich Bis-Urea Neutral Receptors: Halides and Oxyanions Binding via Cooperative vs. Non-Cooperative Modes

(*ChemistrySelect,* 2018**, 3,** 3548)

The chapter describes the design and syntheses of two electron-rich naphthyl ring containing bisurea receptor derived from *ortho* (**L_1**) and *meta* (**L_2**)-phenylenediamine moiety for investigating their anion coordination behaviour. Receptor **L_1** self-assembled in the presence of organic terephthalate anion into a dimeric pseudo-capsular host-guest assembly sealed by tetrabutylammonium counter cation. However, *meta* based receptor **L_2** self-assembled in 2:4 host-guest fashions with H-bonded dihydrogen phosphate tetrameric anionic guest in the presence of an excess n-TBA (H_2PO_4). Further, receptor **L_1** has been found to self-assemble into unimolecular cooperative 1:1 complex in presence of spherical chloride anion and planar acetate

anion. Moreover, receptor **L_2** forms similar kind of non-capsular host guest assembly in the presence of spherical halides like Cl^-, Br^-, and F^-. To validate the result obtained in the solid-state studies, ^{1}H-NMR titration experiments have also been performed using n-TBA salts of anions to inspect the solution state anion binding behaviour of isomeric receptors **L_1** and **L_2**.

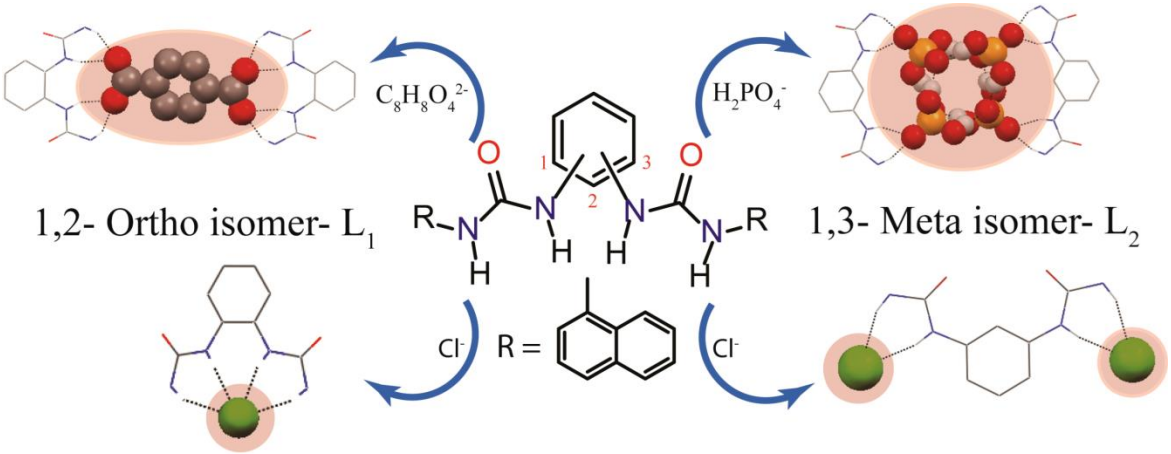

Fig 1. A comprehensive representation of molecular receptor structures and key finding of research work included in the **Chapter 3.**

Chapter 4: Effect Of Terminal Substituent on Flexible Bis-Urea Receptors: A Comprehensive Analysis of Host-Guest Binding

(***Cryst. Growth Des.***, 2019, **19**, 2298)

In this Chapter, three linear flexible bis-urea receptors (**L_3-L_5**) with different terminal substituents have been synthesized for a comprehensive analysis of host-guest binding propensity in their neutral form. It has been established that, with the existence of electron-withdrawing or π-acidic phenyl substituents, they act as a possible system that can proficiently coordinate with anions of diverse dimensions constantly initiated by the size of the countercations. The 3,5-bis(trifluoromethyl)phenyl-derived isomer (**L_3**) can readily form cooperative neutral self-assemblies irrespective of the size the monovalent halides (viz. chloride, bromide, and iodide anions) and non-cooperative neutral self- assemblies with planar divalent carbonate anion. The meta isomer **L_4** captures spherical halides, i.e. chloride and bromide, in an isostructural way, forming a 1:2 host-guest assembly, whereas the isomeric *para* receptor **L_5** shows cooperative binding with chloride anions, having coordination number 3. However, due to the greater flexibility and lesser hydrophobicity of receptor **L_4** and **L_5** in comparison to receptor **L_3**, successful crystallization of any oxyanion complexes through the *meta* and *para* isomers was not successful.

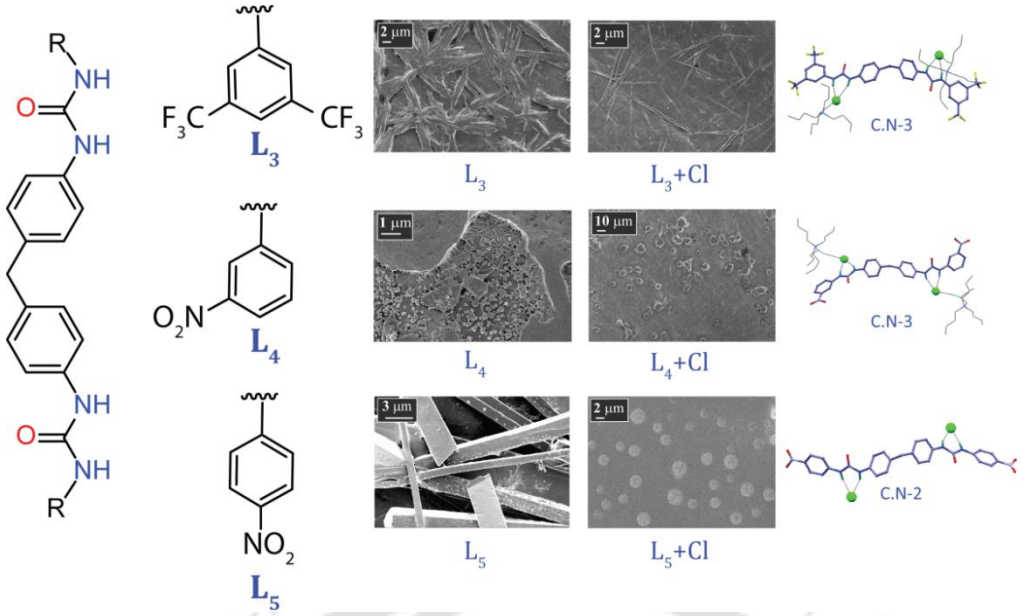

Fig 2. A comprehensive representation of molecular receptor structures and key finding of research work included in the **Chapter 4**.

Chapter 5: Aromatic Meta-Substitution Based Positional Isomeric Receptors for Encapsulation of Hexafluorosilicate Anions

(***Cryst EngComm***, 2019, **21**, 7172)

The highlight of this chapter is that, with the cyano group as a terminal substituent, three positional isomeric bis-urea receptors (**L6-L8**) have been synthesized for extensive analysis of host–anion binding propensity in their neutral form.

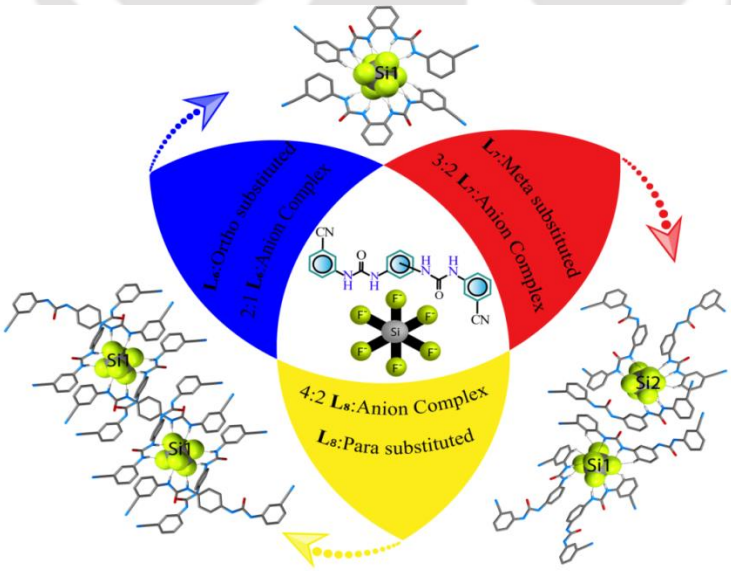

Fig 3. A comprehensive representation of the research work included in the **Chapter 5**.

The existence of electron-withdrawing or π-acidic phenyl substituents in the receptors **L_6-L_8** supports efficient binding of the octahedral hexafluorosilicate anion within their dimeric cavity. **L_6** and its cyano-substituted *para* isomer receptor **L_8** have been found to entrap water-free naked SiF_6^{2-}, while the *meta* receptor has been found to trap hydrated SiF_6^{2-} within its cavity. In the presence of excess fluorides, **L_6** self-assembles to form dodeca-coordinated hexafluorosilicate complex and **L_8** self-assembles to form octa-coordinated hexafluorosilicate complex in the solid-state via cooperative and non-cooperative H-bonding interactions of urea moieties respectively. However, the *meta* receptor **L_7** self assembles to build a 3:2 host-guest assembly, where the two SiF_6^{2-} units show different coordination environments. FESEM imaging studies corroborated the result obtained in the solid-state.

Conclusion and Future Perspective

In summary, this thesis delivers some significant conclusions in the field of 'anion coordination supramolecular chemistry' where some of linear flexible artificial acyclic receptors coordinate with anions/hydrated anions driven by the size of anion or structural design of host in solid-state or positional or electronic effect of terminal aryl substituents. The solution state anion binding studies, FESEM imaging studies and Hirshfeld surface analyses of host-guest complexes heavily validated the solid-state results of the anion-receptor complex. Overall, the current outcomes from the experimental studies provide the anionic guest induced polymeric aggregated assembly formation *via* neutral host-guest associations. Interesting features have uncovered by the individual receptor in the presence of a specific anion/hydrated anions. Receptor **L_1** has been shown to encapsulate organic terephthalate anion into a dimeric pseudo-capsular host-guest assembly sealed by a tetrabutylammonium counter cation, while its isomeric receptor **L_2** self-assembled in 2:4 host-guest fashions with H-bonded dihydrogen phosphate tetrameric anionic guest in the presence of an excess n-TBA (H_2PO_4). The cooperative neutral self-assemblies with the monovalent halides, non-cooperative neutral self-assemblies with planar divalent carbonate anion, 1:2 host-guest assemblies with chloride and bromide, and cooperative binding with chloride have been found to be captured within the neutral self-assemblies of receptors **L_3-L_5**. Receptor **L_6** and its cyano-substituted *para* isomer receptor **L_8** have been found to entrap water-free naked SiF_6^{2-}, while the *meta* receptor **L_7** has been found to trap hydrated SiF_6^{2-} within its cavity.

Hence, in the thesis, some of the various fundamental and inconsistent concepts of supramolecular chemistry and adaptability of the acyclic receptors as efficient building block through systematic development have been successfully established. Several specialized applications such as drug delivery, transmembrane anion transport, salt solubilization,

extraction, catalysis, stabilizing the anionic reactive intermediates inside the molecular assembly *etc*. can be achieved by the recognition of anions or hydrated-anions within the molecular assembly or molecular cavity which can expand significantly and bring immense advances in the field of supramolecular chemistry. However, the basic work in tuning the binding of anions/hydrated-anions inside the molecular assembly is highly appreciated for these applications to reach their prospective. From a fundamental lookout, the results included in this thesis are very convenient, but there is other challenging sides in supramolecular chemistry that need to be advanced, mainly from an applicative approach. Based upon the extraordinary anion/hydrated-anion binding molecular assembly, research in these areas with importance on biomedical, environmental, and technological applications, seem to be upcoming.

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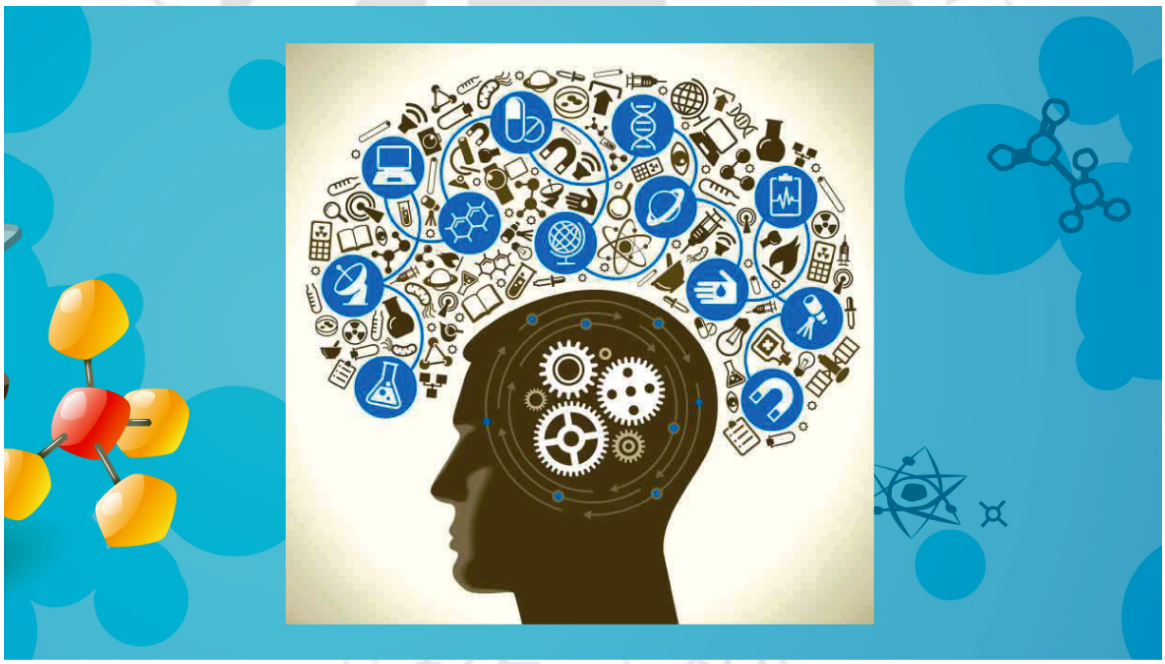
Chapter 1

Introduction



1.1 Supramolecular Chemistry: An Introduction to Host-Guest chemistry

In 1987, Jean-Marie Lehn, one of the leading proponents, who won the Nobel Prize for his work in the area of supramolecular chemistry, has defined as the 'chemistry of molecular assemblies and of the intermolecular interactions'. The chemistry between host and guests are widely known as supramolecular chemistry commonly this can be uttered as 'chemistry beyond the molecule' and other descriptions include phrases like the chemistry of the 'non-molecular chemistry' and non-covalent bond'. While classical chemistry stresses on the coordinative bond and covalent bond formation, supramolecular chemistry scrutinizes the weaker and reversible noncovalent interactions between molecules such as hydrogen bonding, halogen bonding, ion-ion and ion-dipole interactions, cation–π and anion–π interactions, π–π interactions, Van der Waals forces, and hydrophobic effects.[1] In contrast to the strong covalent bond(s) within a single molecule, incorporating these type of non-covalent interactions into complex systems provides the novel pathway to explore the essence of the field of supramolecular chemistry. Mainly supramolecular chemistry concentrations on the chemical systems together with a distinct number of assembled molecular architecture or components and also refer to the chemistry beyond that of molecules. Molecular recognition, molecular self-assembly, recognition of anions, mechanically-interlocked molecular architectures, dendrimers, and molecular electronic devices are various significant concepts that have been explained by supramolecular host-guest chemistry.[1] Considering the new opportunities and challenges in the field of supramolecular chemistry, it is one of the fastest and ever growing research areas of chemical endeavour and continuing to attract an increasing number of researchers into the area for logical discovery and use, real world relevant contribution.

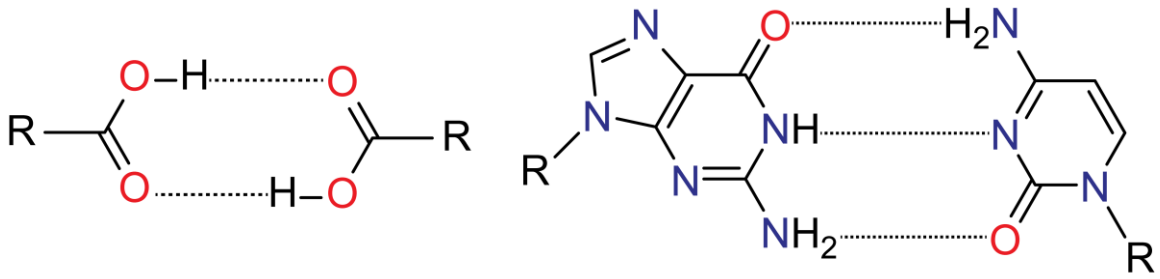
In supramolecular host-guest chemistry, originally in the complexations, development between a 'host' and a 'guest' in supramolecular chemistry, the host is normally referred to a large number of molecule or aggregate just as an enzyme or artificial acyclic and cyclic compounds holding a sizeable central cavity and the guest may be a simple neutral molecule, an ionic species (cation/anion), or a more sophisticated molecule such as a hormone, neurotransmitter possessing divergent binding sites or pheromone.[1] Successively, the region where the host or guest molecule shared a non-covalent interaction is known as a binding site. From the thermodynamic point of angle, by the action of chelate effect or macrocyclic effect, the solidity of a supramolecular host-guest complex can be improved. In comparison of cyclic hosts just as corands (e.g. crown ethers) with acyclic host, the macrocyclic effect makes cyclic hosts up to a factor of 10^4 times more stable than closely related acyclic hosts with the similar type of binding sites. On account of, the guest binding inside the preorganized cavity of macrocyclic systems is

relatively straight forward to recognize but the processes of binding of acyclic receptors keep on more elusive. Moreover, in order to bind, a host molecule must have contained appropriate binding sites having the correct electronic character (hydrogen bond donor/acceptor ability, polarity, hardness or softness etc.) to complement the guest. Upon guest binding, if a host molecule does not go through a substantial alteration conformational change, then the host is said to be preorganized and this type of host preorganization is becoming a key concept which represents a major enhancement in the overall free energy of guest complexation.[2]

1.2 Hydrogen bond

A hydrogen bond may be regarded as a certain kind of dipole-dipole interaction, where there is a link between two molecules resulting from an electrostatic attraction between a proton in one molecule and an electronegative atom in the other or in particular in which a hydrogen atom attached to an electronegative atom (or electron-withdrawing group) is attracted to a neighbouring dipole on a contiguous molecule or functional group. In supramolecular chemistry, the hydrogen bonding has been described as the 'master key interaction'[1] because of its relatively strong (4-120 kJ mol^{-1}) and highly directional nature and hydrogen bonds are usually denoted as D–H···A and typically comprise a hydrogen atom attached to an electronegative atom such as O or N as the donor (D) and a similarly electronegative atom, time and again bearing a lone pair, as the acceptor (A). Typical examples comprise the formation of carboxylic acid dimer and base pairing in DNA by hydrogen bonding (Scheme 1.1). There are also significant H-bonding interactions including hydrogen atoms attached to carbon, rather than electronegative atoms such as O and N (electronegativities: C: 2.55, H: 2.20, N: 3.04, O: 3.44). Consequently, the force involves in directing the crystallization processes and self-assembly of organic molecules is possibly the most important discriminating cohesive force called hydrogen bonding.[3] The molecular Self-assembly is the process, where molecules adopt a defined arrangement by virtue of rotations about single bonds (intramolecular torsions) and intermolecular hydrogen bonding (Scheme 1.2, types of non-covalent interactions). Additionally, the molecular self-assembly is self-repairing, highly precise and self-controlling since equilibrium-directed processes are implicated.[4] Hydrogen bonds occur in a range of lengths, strengths as well as geometries. And most importantly the solid-state structure can be determined sufficiently by a single, strong hydrogen bond per molecule and exercise an impact in the solution as well as in the gas phases. The objective of the thesis is to explore the molecular self-assembly of some simple acyclic rigid or flexible dipodal receptors in the course of investigating their coordination behaviour with anions/hydrated anions depending upon the

guest dimensions or electronic or positional isomeric effect of terminal aryl receptor substituents.



Scheme 1.1 A hydrogen bonded carboxylic acid dimer and base pairing in DNA (Guanine-Cytosine) by hydrogen bonding interactions.

1.3 Anion receptor chemistry

Unlike the transition-metal coordination chemistry, anion receptor chemistry has attracted ever growing attention in supramolecular chemistry, due to the crucial roles that anions play in medicine, biology, and environmental science as well as their possible applications in a wide range of areas such as catalysis, sensors, transmembrane, transport functional materials, and so on.[5] The binding of anions with the synthetic receptor (host) falls into the realm of 'supramolecular chemistry'.[6] The binding attractions between anions and their hosts are mostly attributed to hydrogen-bonding and/or electrostatic interactions, with the former being the more significant in promoting selective binding through topological complementarity. Anions also take part in regulating osmotic pressure, maintaining cell volume, activating signal transduction pathways, and in the production of the electrical signal. Anions are universal in nature and roughly 70% of all enzymatic sites contain anions, playing vital structural roles in many proteins, which are critical for manipulation and storage of genetic information (DNA and RNA are polyanions). It is important to note that, being the primary determinant of many diseases, the disruption of anion flux across the cell membranes is increasingly recognized. In fact, at least 14 mitochondrial anion transport system have been pointed out so far, which is known to be mediated anion transport through cell phospholipid bilayers. These comprise (among others) systems responsible for the trafficking of ATP, ADP, citrate maleate, phosphate, oxaloacetate, sulfate, fumarate, and glutamate and halide anions. In recent times, several X-ray crystal structures have been solved that have allowed the direct visualization of enzyme-anionic substrate complexes that are stabilized *via* multiple hydrogen-bonding interactions (Figure 1.1).[7] Moyer and Bonnesen *et al.* has pointed out the significant understandings of the factors influencing anion recognition in the traditional analytical sense, where simple physical properties such as size, charge, hydrophilicity and basicity tend to govern the selective exchange of one anion over another.[8] They deduce that rightly selective anionic hosts must include some

elements of strategic design, together with appropriately positioned hydrogen bond coordination sites and also introduced the term bias for this type of phenomenon. The theory of double valence for anions is introduced by the multiple hydrogen bonding sites accompanied by the resulting topological considerations in anion receptors besides the transition-metal ions.

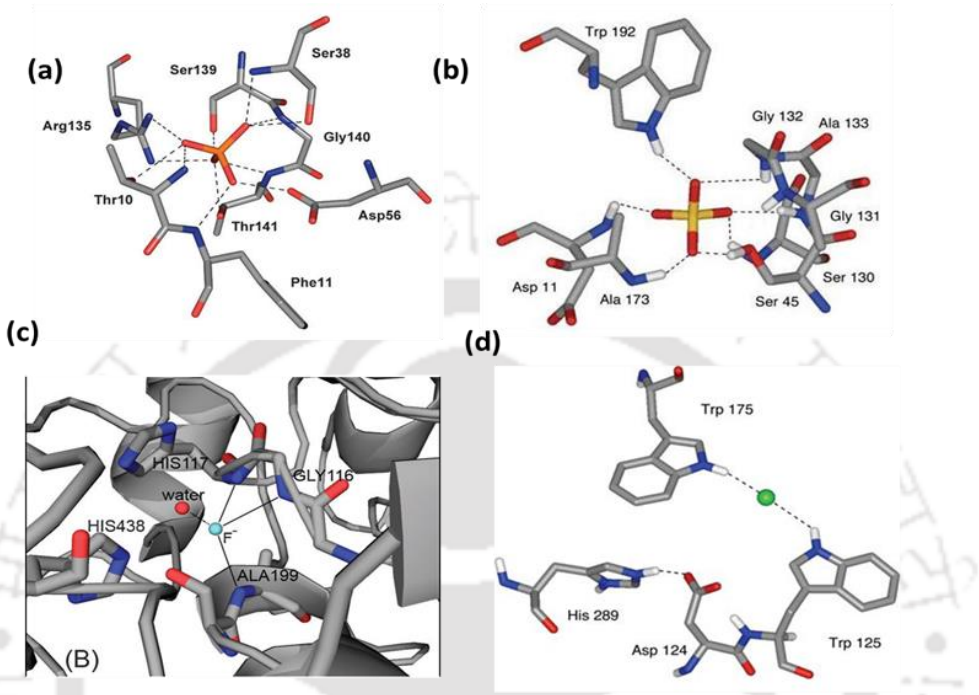
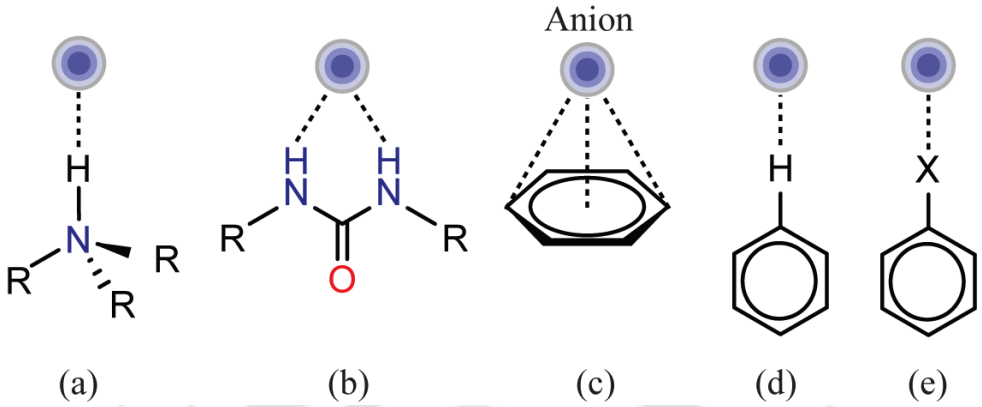


Fig. 1.1 Anion binding in biology depicting, (a) binding mode of phosphate anion in phosphate-binding protein, (b) binding mode of sulfate anion binding in sulfate-binding protein, where the sulfate is bound by seven hydrogen bonds from -NH and -OH bond donor group, (c) mono hydrated fluoride anion binding in human butyrylcholinesterase complex (PDB code = 2XMC) and (d) enzymatic active site of haloalkane dehalogenase the presence of a bound chloride anion.

It is important to note that, for an anionic guest, the negative charge on the anion is the primary valence and the hydrogen bonds to the anion is provided with the secondary valence.[9] In defining the theories of complementarity for a certain anion, Bowman-James and co-workers have categorized the anion binding based on the coordination numbers, which is very helpful and it also can assist to formulate the design strategies of optimal anion-binding host structures.[10] The best effectual way to bind anions to comprise in taking advantage of their negative charge and accordingly, ammonium and quaternary ammonium receptors have been the primary receptors of choice since they make sure an adequate electrostatic attraction reinforced by hydrogen bond contacts with the coordinated anions.[11] However, urea/thiourea, pyrrole, amide, and indole functions have been the subject of challenging research for their performance in constructing neutral anion receptors *via* favourable hydrogen bonding interactions.[12] At the same time, in particular, assuming that the -NH protons are acidic enough, when an electron-withdrawing substituent is hosted into the molecule, deprotonation might occur in the presence

of a highly basic anion, such as hydroxide, acetate and fluoride.[13] To increase the acidity of the -NH protons by introducing electron-withdrawing substituents, extensive structural modifications on the hydrogen bonding scaffold have been attempted such as $-NO_2$ and $-CF_3$ through the



Scheme 1.2 Anion binding by different types of noncovalent interactions, (a) electrostatic N−H···A$^-$ interaction by an ammonium cation, (b) complementary N−H···A$^-$ interaction by an urea function, (c) anion–π interaction, (d) C−H···A$^-$ weak interaction by an aryl function and (e) C−X···A$^-$ halogen bonding by a halocarbon (X = F$^-$, Cl$^-$, Br$^-$ and I$^-$).

mediation of a π-system. The coordination environment with size and shape complementary for a particular anion is accelerated by the construction of a preorganized binding cavity or cleft using rigid (polynorbornane or calixarene) or flexible structural skeleton. Recently, Custelcean group have studied the structural role of anions in crystal engineering as anions play diverse roles in the formation of crystals.[14] Experimental confirmations for electrostatic anion–π interactions existence in the solid and solution state, their theoretical calculations have also been complemented, besides conventional N–H···A hydrogen bonding.[15] Though, the examples of anion–π interactions in crystals stay extremely rare in experimental pathways because the C–H···A hydrogen bonds tend to prevail in competition with anion–π interactions.[16] The charge transfer involving the weak σ interaction from the anion to an arene system become another competitor, and that is geometrically characterized by the anion being located above the periphery instead of the centre of the arene. More recently, a new type of noncovalent interaction which is highly directional (∠D−X−A close to linear) in nature and acts like hydrogen bonds, has been established both experimentally and theoretically, exhibiting the noncovalent interaction involving an electrophilic halogen atom (halocarbon) and a high electron density centre (like anion).[17]

1.4 Urea functionalized acyclic receptors: a thorough literature review of solid-state studies

In solid-state, the development of advanced and novel synthetic receptors comprising flexible or rigid scaffolds for the effective recognition of anions is remaining a challenging task, though

nature demonstrates how proteins can efficiently and selectively bind anions *via* weak intermolecular forces with hydrogen bonds being vital in determining binding selectivity *by* topological complementarity. Anions generally have very high solvation energies that must be compensated by the host for effective anion recognition and complexations. Ever since the early days, for host-guest binding of anion coordination chemistry, having -NH functions the macrocyclic and acyclic tripodal scaffolds derived from tris(2-aminoethyl)amine have used extensively.[18] Flexible dipodal anion receptors with rigid aromatic isomeric diamine spacers having less number of –NH functionalities are comparatively less in the research literature and have been the exceptional case of interest in recent days as a consequence of their lesser chance to form cooperative anion complexes along with less preorganized cavity to encapsulate or entrapping an anion compared to tripodal receptors. Moreover, the binding ability of acyclic receptors depends on the attached terminal aryl functionality unit, because the hydrogen bonding capability towards the anions of different size and dimensions are consistently and systematically transform by the one or more functional groups attached to terminal aryl unit. As a result of potential ability to encapsulate the larger anions (nitrate, phosphate and sulfate) in solid-state, from the last two decades numerous flexible acyclic receptors comprising either electron-donating or electron-withdrawing terminal aryl substituent have been vastly reported. Owing to the ability to turn as hydrogen-bond donors,[19] urea based neutral receptors is the most used scaffold for the effective recognition of anions. After the seminal papers by Wilcox[20] and Hamilton[20] on urea-anion interactions, a variety of anion receptors have been reported containing one or more urea fragments.[21]

Wu and co-workers have reported a sequence of oligourea receptors containing receptor **1** and **2**. Depending upon the number of urea groups existing in these receptors, they bind to the chloride anions *via* H-bonding either in a mononuclear assembly or a dinuclear foldamer.[22] Single crystal X-ray crystallography study of receptor **1** reveals that a single chloride anion is found to wrap around by receptor **1**, forming mononuclear crescents. The two peripheral urea groups bind to chloride anion *via* four hydrogen bonds, whereas the middle one of the urea group made an intermolecular H-bond, which attaches neighbouring complexes into an endless ribbon. Receptor **2,** which have longer chain analogues formed a dinuclear foldamer complex with Cl^-, where two chlorides anions are entrapped within a helix (Fig. 1.2c). From two alternating urea groups, each chloride anion is bound *via* four H-bonds. The $Cl^{\cdots}Cl$ distance is found to be 3.613(9) Å, which demonstrated that in the formation of this complex; a huge amount of electrostatic repulsion has been overcome.

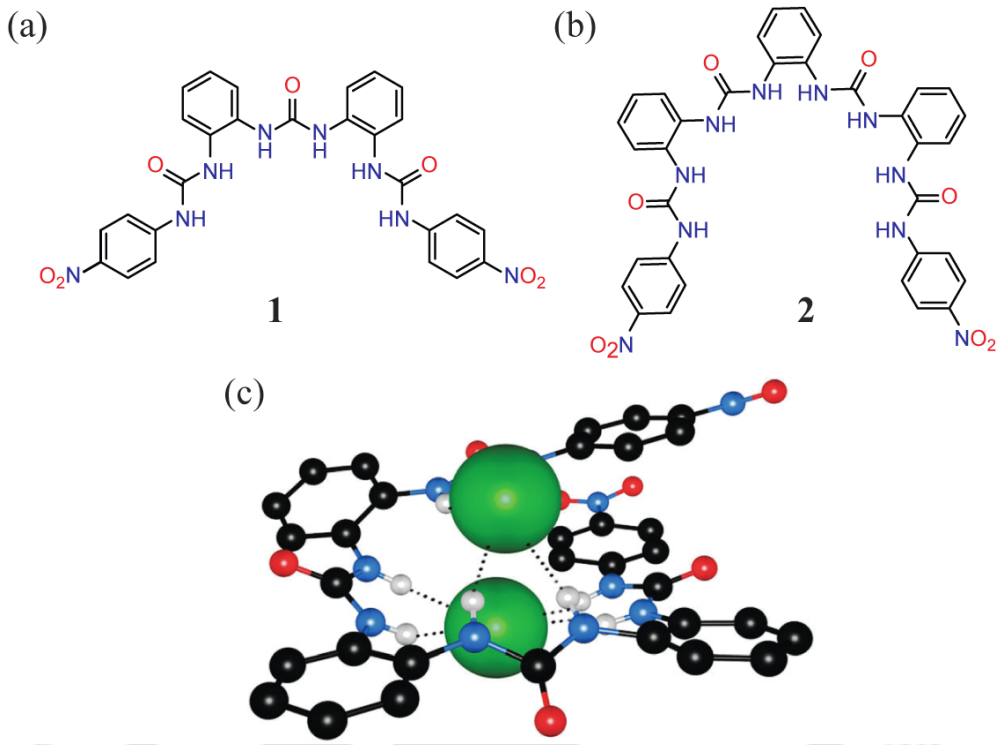


Fig. 1.2 (a) Molecular structure of receptor (a) **1** and (b) **2** comprising of *o*-phenylenediamine spacer (c) single crystal X-ray structure of the complex of receptor **1** with TBACl.

Incorporating repeating bis-urea units, Wu *et al*. have also reported tetra-urea receptors **3**[23], continuing their effort on receptors containing various urea groups. In the solid-state, on the coordination of phosphate anions with the receptor **3**, it was found that it forms a captivating dinuclear triple helix like structure, where three of the ligands are enfolded around two PO_4^{3-} centres (Fig. 1.3b). In the complex, from three distinct receptors, six urea groups are bound to each phosphate anion through twelve H-bonds. In solution state, the interaction of receptor **3** with PO_4^{3-} anions were also studied through (^{1}H) proton NMR titration in DMSO-d6, where it was found that in solution, the foremost species was also a 3:2 host-guest aggregate.

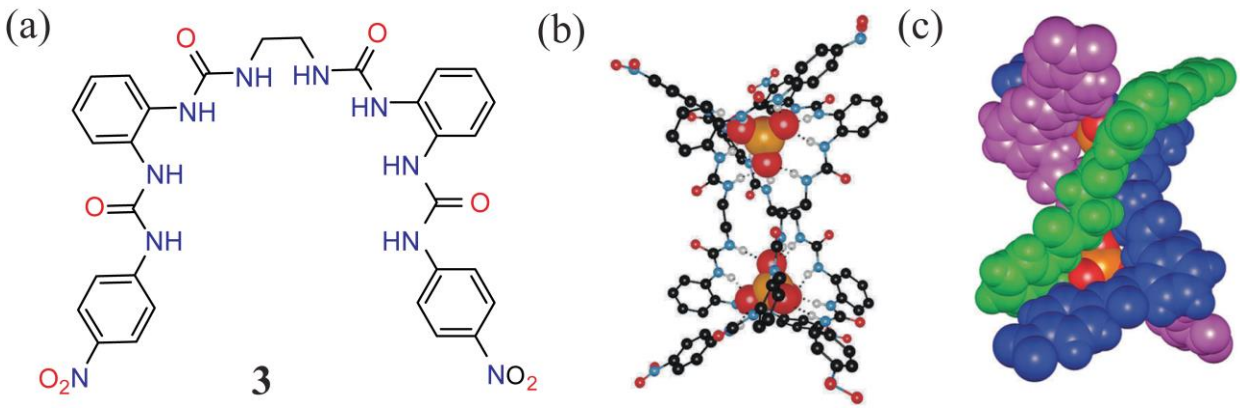


Fig. 1.3 (a) Molecular structure of receptor **3** (b) single crystal X-ray structure of triple helix complex formed by receptor **3** and PO_4^{3-} shown in ball-and stick , and (c) spacefill model of PO_4^{3-} bound receptor **3**.

Gale and co-workers explore the receptor architecture by providing one *ortho*-phenylenediamine based receptor **4** and another two bis-urea clefts were synthesized by the reaction of 3,3'-diaminobenzidine with phenyl isocyanate. In the solid-state, two receptors (**4**) capture a single terephthalate anion (Fig 1.4c), where each carboxylate group of the terephthalate anion was bound to all four of the urea -NH hydrogen bond donor groups in the bis-urea cleft. The receptor **4** adopts a cleft conformation with the two urea groups twisted out of plane such that the pendant aryl groups are oriented in the same direction. The tetra-urea functionalized biphenyl receptor **5** (Fig. 1.4a) was found to form a neutral cooperative complex with acetate, benzoate (Fig. 1.4d) and terephthalate, where each carboxylate group was entrapped in the bis-urea hydrogen bond donor cleft of the neutral receptor molecules in solid-state.[24]

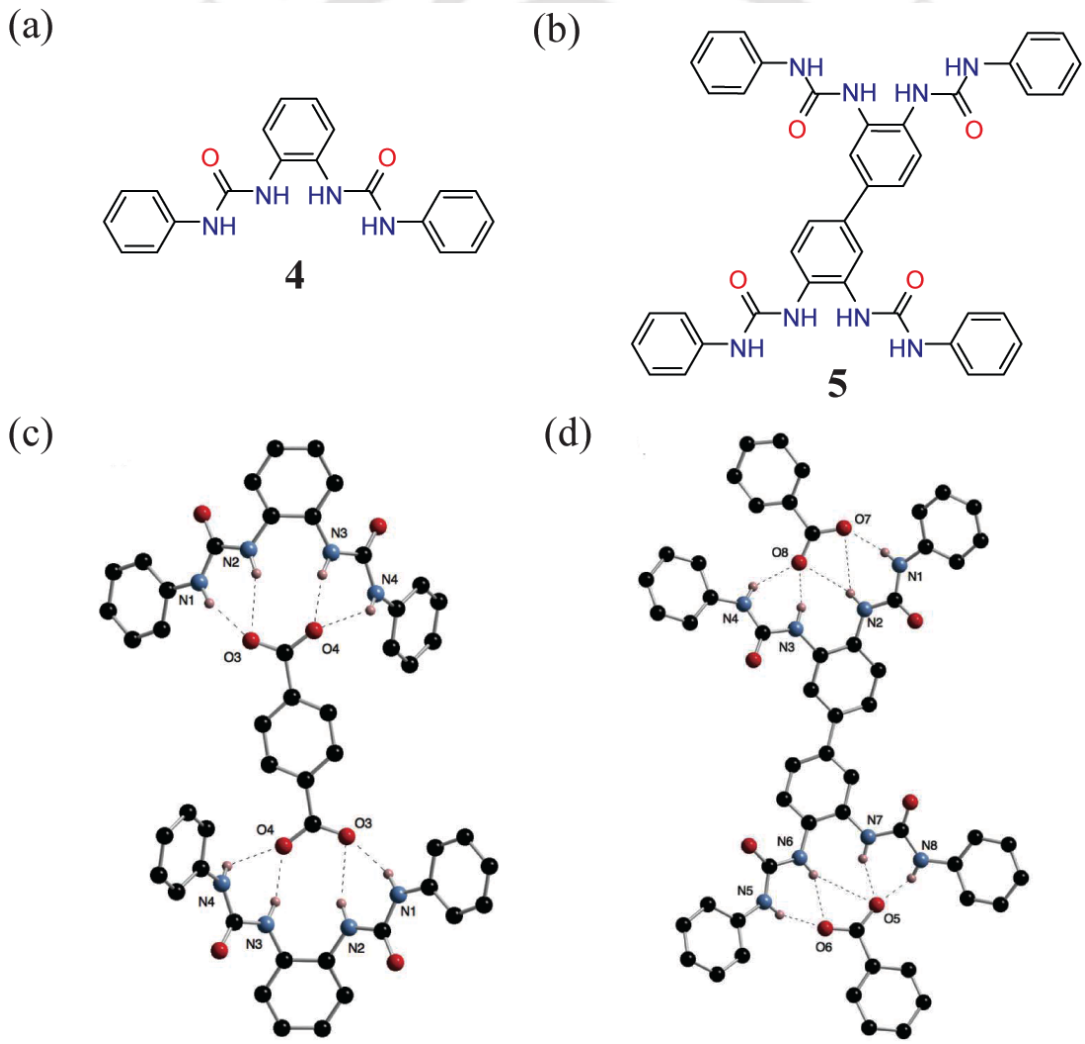


Fig. 1.4 (a) Molecular structure of receptor (a) **4** and (b) receptor **5**, (c) X-ray structure (partial) of the anion-receptor complex **4** (terephthalate) and (d) X-ray structure (partial) of the anion-receptor complex **5** (benzoate)**.**

The saturated coordination number for tetrahedral anions (e.g. sulfate) is 12 have demonstrated by the calculations by Hay *et al*. and this can be satisfied by **6** urea groups situated along the six

ends of the tetrahedral shaped anion.[25] Wu's group have reported saturated sulfate coordination with urea based receptors constructed on the $CuSO_4$ complex of a naphthyl-decorated 3-pyridylurea **6**, where a sulfate anion was located inside a two C3-tris-urea clefts round the six-coordinate copper centre. In this complex, each cavity was additionally interdigitated with another one from a neighbouring complex, therefore binding the sulfate in the cavity (Fig. 1.5b). In hydrogen bonding, all the six urea arms inside the capsule participate along with the entrapped sulfate ion (Fig. 1.5c).[26]

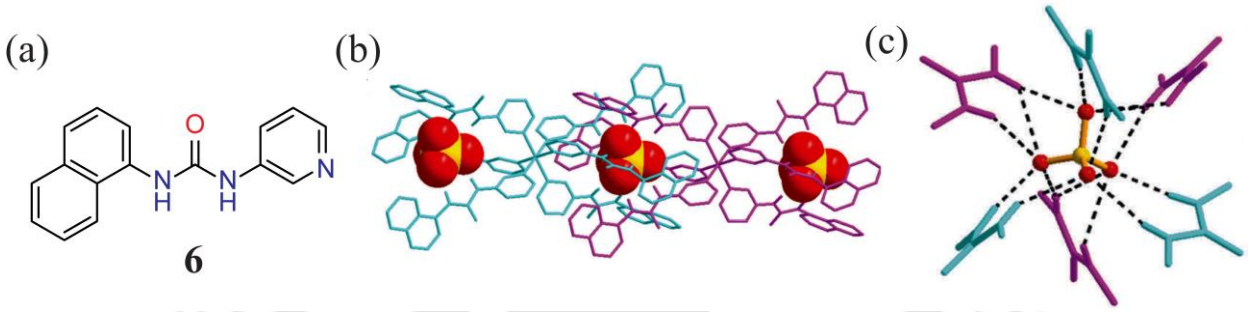
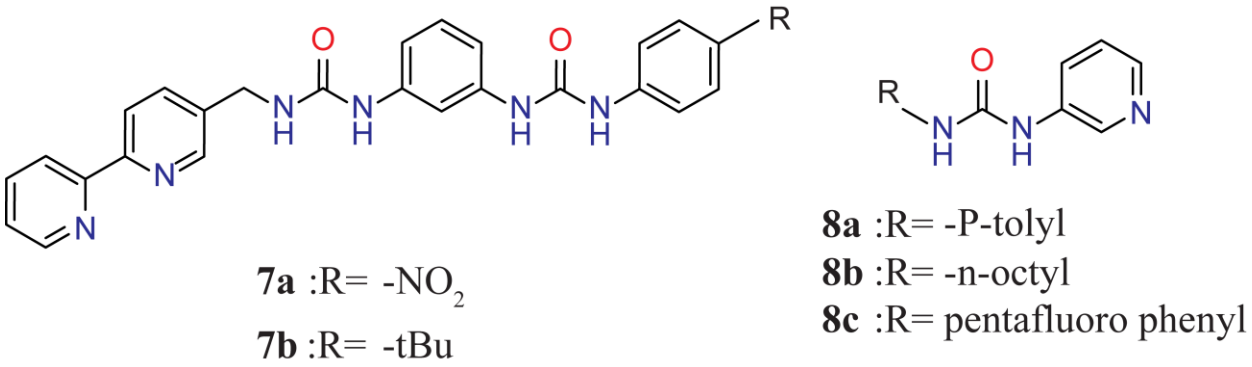


Fig. 1.5 (a) Molecular structure of receptor **6**, (b) sulfate encapsulation by many hydrogen bonds from six urea groups in the $[SO_4(urea)_6]^{2-}$ capsule (c) crystal structure showing fragment of the $CuSO_4$ complex of **6**, showing the C3-tris-urea cavity encapsulating a sulfate anion.

Recently Custelcean and coworkers have established ditopic 2, 20-bipyridine-bis (urea) receptors **7a** and **7b** (Fig 1.6a). Through self-assembly process, the receptors **7a** and 7**b** forms ion-pair triple helicates and mesocates with $NiSO_4$ or $FeSO_4$ respectively. The metal ion in these ion-pair complexes (Ni^{2+}/ Fe^{2+}) is stabilized *via* octahedral coordination of three bipyridine units, and with the help of 12 N−H···O hydrogen bonds, the sulfate anion is encapsulated by three bis-urea functions.[27]



Scheme 1.3 (a) Various bipyride (**7a-7b**) and pyridine (**8a-8c**) based acyclic ion-pair receptors having anion binding urea functions.

In the presence of silver nitrate, sulfate and triflate salts, Steed et.al have reported the solid and solution state binding properties of pridylureas **8a** and **8b** (Scheme 1.3).[28] They found that a 1:1 receptor-salt complex was formed, when the counter anion was nitrate, where the triflate and

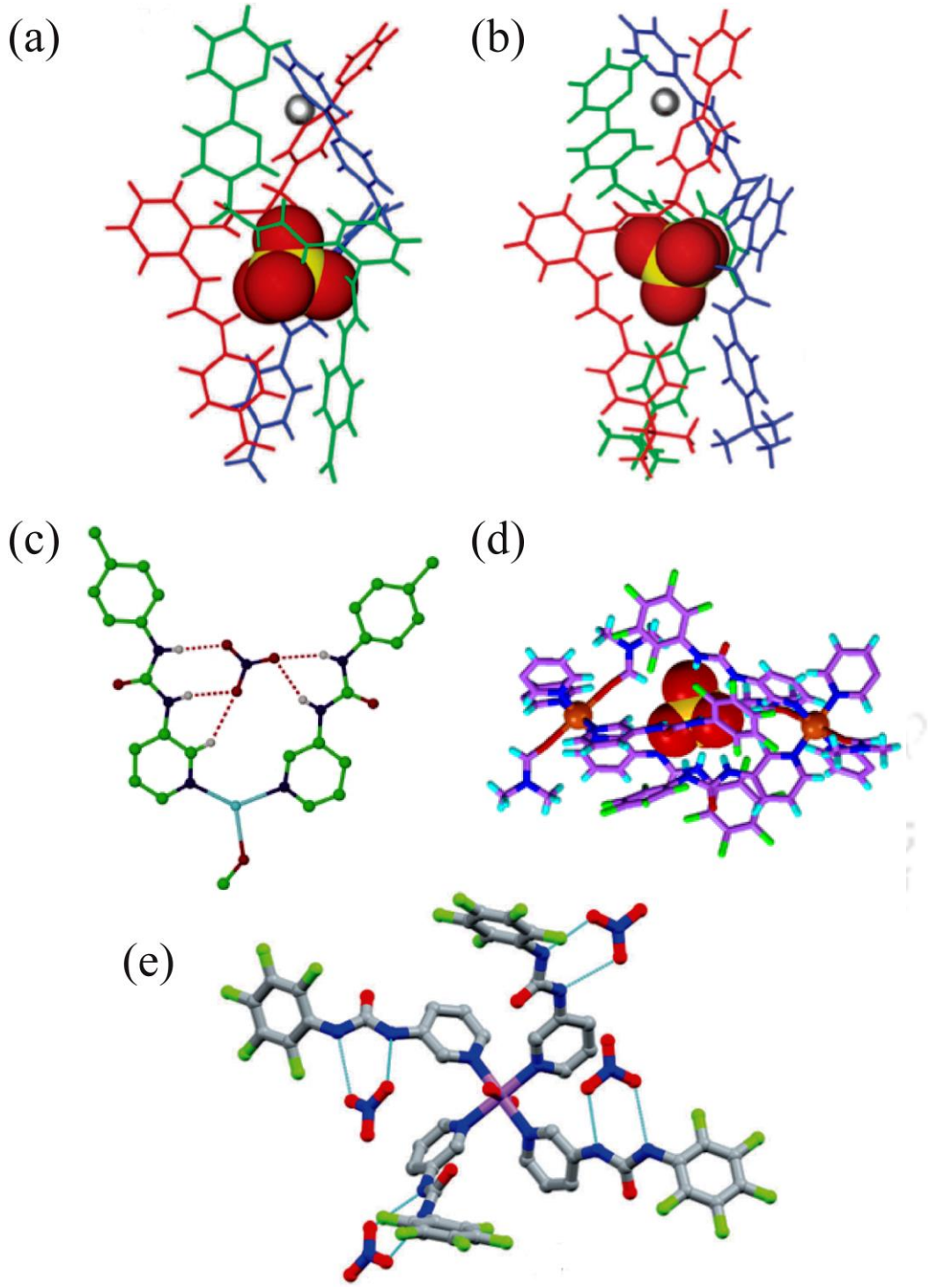


Fig. 1.6 X-ray structures showing: (partial) of the ion pair-receptor complexes depicting (a) self-assembly of receptor **7a** with $NiSO_4$ and (b) self-assembly of receptor **7b** with $NiSO_4$, (c) formation of the discrete $[Ag(\mathbf{8a})_2]NO_3$ MeOH complex , (d) second sphere recognition of SO_4^{2-} in $CuSO_4$ complex of **8c**, and (e) $CuNO_3$ complex of **8c.**

sulfate salts work for the stabilization of the extended structures in the solid-state with pyridal ligands (Fig. 1.6c). On the basis of ^1H NMR spectroscopic studies, the researchers concluded that in solution the simple silver nitrate complex was formed. These same researchers subsequently put forward other examples of this paradigm.[29] Based on the parallel concepts, in

the presence of Cu^{2+}, for the effective binding of sulfate anion counter ion Ghosh *et al*. have independently prepared the mono-urea receptor **8c** respectively. Four **8c** receptors is coordinated to the Cu^{2+}, thus forming $CuSO_4$ complex of **8c** and in a distorted octahedral arrangement two DMF molecules facing trans to each other and thus forming two oppositely located inversion-related C2-symmetric clefts. Along the C2-axis two molecules of the Cu^{2+} complex are aligned to create a cavity that encapsulates a SO_4^{2-} ion in its centre (Fig. 1.6d). In hydrogen bonding formation, all the four urea arms of the receptor interact with the encapsulated SO_4^{2-} within the capsule.[30] Fabbrizzi *et al*. have reported a chiral cyclohexylene-linked bis-urea **9** (Fig. 1.7a).[31] The receptor binds to the $H_2PO_4^-$ anion strongly in the 1:2 host-guest binding mode in a DMSO solution. The X-ray analysis of the crystal structure shows that to bind to two $H_2PO_4^-$ anion, from each receptor **9** the two urea groups are aligned which are then dimerized over 2 solid hydrogen bonds (Fig. 1.7c).[31]

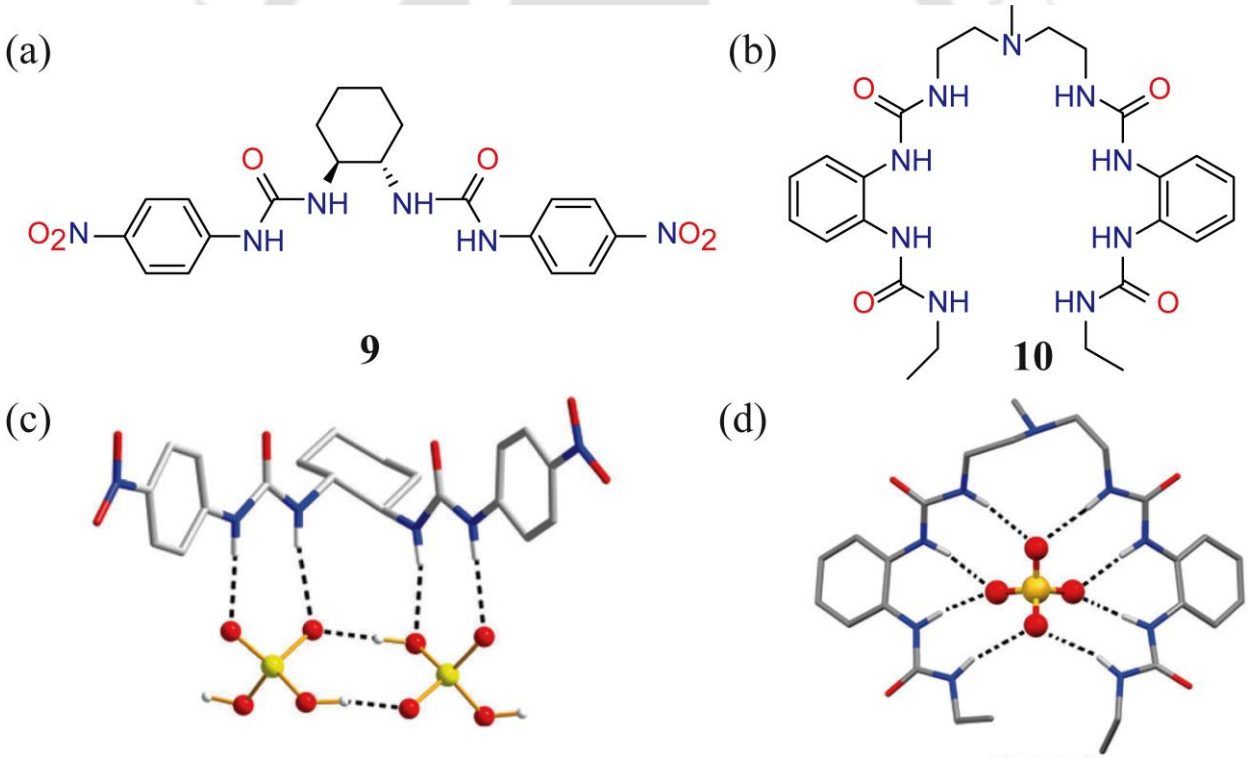


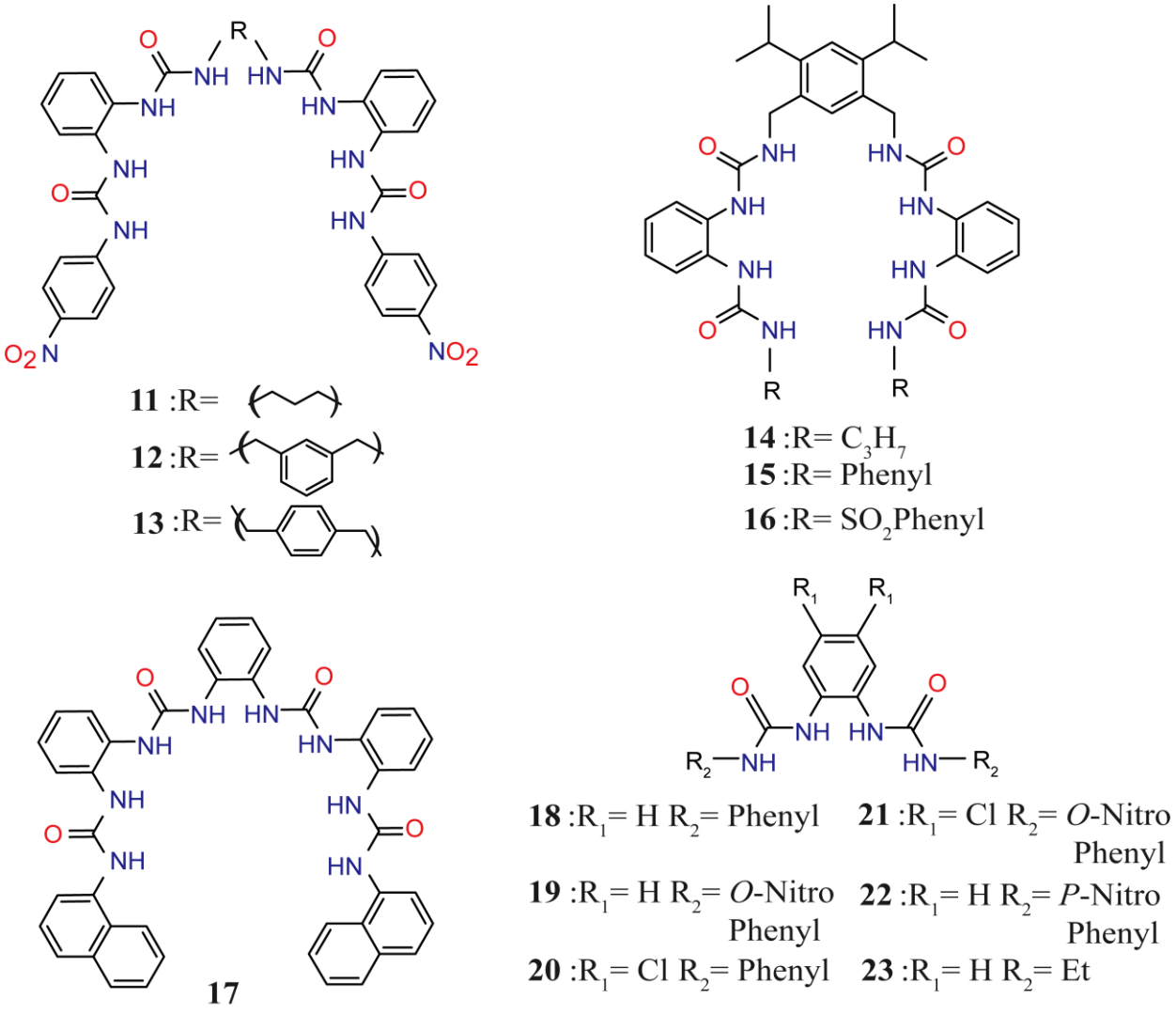
Fig. 1.7 (a) Molecular structure of receptor (a) **9** and (b) receptor **10**, (c) crystal structure of **9**.$(H_2PO_4^-)_2$, (d) the crystal structure of **10**.SO_4^{2-}.

Bowman-James et.al have described the sulfate selective tetrakis-urea receptor **10** (Fig. 1.7b), where the receptor integrates mutually rigid (*ortho*-phenylene) linkers and flexible (methylene-diethylene ammonium).[32] In the sulfate complex **10**.SO_4^{2-}, hydrogen bonding all four urea groups of the receptor **10** were involved with the sulfate through 8 H-bonds (Fig. 1.7d). In

water-DMSO solution, the selective and ‘‘water-tolerant’’ sulfate binding of the receptor **10** was also observed, and by ^{1}H-NMR titration the binding constants were determined.

In 2000, Reinhoudt *et al.*[33]and Wu *et al.* [34] in recent past have also reported anion receptors using the preorganized hydrogen-bond donor platform of *ortho*-phenylenediamine connector and some oligourea-based (tris-urea, tetrakis-urea) connector. In the building of the tris-urea receptors, *ortho*-phenylene spacer was used by Wu’s group **18** and tetrakis-urea receptors **11**-**13** (Scheme 1.4) which verified very high affinities towards phosphate and sulfate anions through formation of unimolecular or dimeric receptor capsule or assemblies of mesocate, helicate, and mono-bridged host-guest motifs in solid state.[34] By modification the rigidity and length of the linkers, these *o*-phenylene linked tris-urea or tetrakis-urea receptors have been establish to trap oxyanions, specifically the phosphate or tetrahedral sulfate in solid state *via* formation of neutral helicate, mono-bridged, mesocateor capsular assemblies. Reinhoudt and co-workers reported three acyclic receptors **14**-**16** (Scheme 1.4), where two *ortho*-phenylene bis-urea moieties donating four hydrogen bond, which exhibited the enhance complex formation with $H_2PO_4^-$ over Cl^- in quantitative proton (^{1}H)-NMR (DMSO-d6) studies[33], even though there was no solid-state proof. In the field of supramolecular chemistry, the studies of rigid *ortho*-phenylenediamine based bis-urea receptors for biologically relevant anions; mainly oxyanions has become a very active research area and have established to be excellent oxyanions receptors both in solution and in the solid-state. Wu and coworkers have verified recognition of anions by a class oligourea-based receptors, where a special emphasis have been given to oligoureas having *ortho*-phenylene-spacer in the course of application of anion coordination and the self-assembly of vital supramolecular structural design including helicates, tetrahedral cages and so on.[34] Gale *et. al.*, Bowman-James *et. al.* and Wu *et. al.* have reported rigid *ortho*-phenylene connected similar kinds of bis-urea receptors **18**-**23**, which belong to the class of corresponding tetradentate receptors for the anion. Gale and coworkers studied the anion binding properties of **18**-**22** (Scheme 1.3), which revealed selective binding for Y-shaped carboxylate anions over other anions studied (HSO_4^-, $H_2PO_4^-$, Cl^-, Br^-).[35] The simple urea receptor **18**, displayed excellent selectivity for carboxylates in solution, and the crystal structure interpretation in the solid-state of the benzoate complex displaying four H-bonds between the anion and receptor through cooperative binding.[35] However, the binding affinity of carboxylate anions have been controlled by variable functional groups in receptors **18**-**22**, in solid as well as in solution state.[35] Conversely, in a DMSO solution the $H_2PO_4^-$ anion was similarly bound significantly, the binding of acetate anion is much stronger as decided. In recent years, the *ortho*-phenylene-connected bis-urea receptors **22**, **23** were also used in the binding of divalent SO_4^{2-}, CO_3^{2-} anions

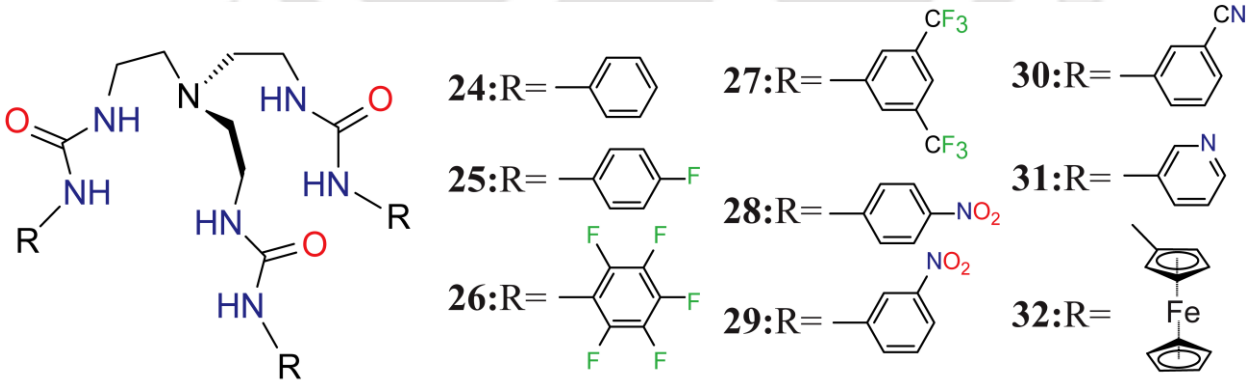
as well as trivalent PO_4^{3-} anion. With the evidence of X-ray structures, Bowman-James *et al.* have reported the receptor **23** as a sulfate selective receptor in water-mixed DMSO-d6 systems, where around a single SO_4^{2-} ion; two of the receptors **23** form a bis-chelate in 2:1 host-guest fashion.[32]



Scheme 1.4 (a) Representative molecular structures of tris-and tetrakis-urea anion-receptors **11-17** containing flexible or rigid spacers and using most convergent aromatic diamine (*o*-phenylenediamine) as linkers, and representative structures of *o*-phenylenediamine based dipodal receptors **18-23.**

Successively, the anion coordination behaviours of **22-23** also studied by Wu and coworkers towards higher coordinating oxyanions (CO_3^{2-}, SO_4^{2-}, and PO_4^{3-}),[36] where the bis-urea receptors **22-23** with trivalent PO_4^{3-} readily formed the tris chelates $[PO_4(\mathbf{L})_3]^{3-}$ in the solid-state, even though the solution binding studies by ^{1}H-NMR and UV-Vis spectroscopy showing diverse binding properties of the receptors toward phosphate such as receptor **22** holds the 3:1 host-guest binding ratio, receptor **23** forms 1:1 complex. Hence, as confirmed by the crystal structures of $(\mathbf{23})_2.SO_4^{2-}$, $(\mathbf{23})_2.CO_3^{2-}$ and $(\mathbf{23})_3.PO_4^{3-}$, the bis-urea receptors given an analogous

conformation as observed in the benzoate complex of **18**. Note that, as the hydrogen-bond accepting potentiality is stronger as the anion charge rises, hence the higher charged anions exposed an affinity to attract more than one receptor to saturate their coordination number. So, in the cases of divalent carbonate and planar sulfate, two bis-urea receptors were involved giving the coordination number of eight, while in case of trivalent phosphate, the three bis-urea receptors were involved giving coordination number of twelve. As with the anionic guests, urea functionalities can create two-directional hydrogen bonds, a variability of tren-based acyclic receptors containing urea moiety (Scheme 1.5) have been established and applied for anion recognition in solid and solution state past several years. With ^{1}H-NMR experiments, anion binding properties of tripodal urea receptors **24** was studied.[37] In this receptor, upon binding of a dihydrogen phosphate anion, a 1:1 complex stoichiometry was suggested *via* six H-bonds inside the tripodal cavity. The single crystal X-ray structures of the carbonate complex of **24** exposed that the two receptor molecules oriented in face-to-face are fashion encapsulate a carbonate anion in the centre *via* twelve strong hydrogen bonding interaction.[38] Gale et. al with their prolongation of previous work have recently designed a series of fluorinated tripodal anion receptors **25-27** comprising urea groups (Scheme 1.5) and studied their anion coordination behaviour and properties of transportation.[39] Captivatingly, Ghosh and co-workers have shown efficient aerial carbon dioxide fixation as carbonate in presence of TBAOH using a tripodal urea receptor **26**, by crystallizing the carbonate encapsulated molecular capsule, trailed by regeneration of free receptor from the capsule.[40]



Scheme 1.5 Representative molecular structures of flexible aliphatic Tris(2-aminoethyl)amine (tren) based tris-urea anion-receptors.

The X-ray structural elucidation of the complex grown from the six urea groups of the two receptors (**26**) molecules revealed that 16 hydrogen bonds are donated to encapsulate a CO_3^{2-} anion within the dimeric cage structure. As observed in the solid-state, the ^{1}H-NMR titration studies have also specified the best fit for a 1:2 stoichiometry of guest to host in the solution

state that supported the presence of capsular assembly. Utilizing an m-nitro substituted tripodal urea receptor **29**, a similar fixation of aerial CO_2 in presence of both TBAF and TBAOH has been exposed recently by Das et.al.[41] Ghosh and coworkers have also presented that the receptor **26** within its dimeric capsular assembly is capable of encapsulating sulfate anion, where 14 N−H···O hydrogen bonds from six urea functional groups stabilize the disordered sulfate anion.[42] Gale *et al.* and Das *et al.* independently have reported a similar mode of 2:1 host-sulfate binding within the cage of two receptors (**25** and **29**).[39,41] Another exciting illustration of 1:1 hydrated sulfate entrapment by the urea receptor **28** has been displayed by Ganguly, Das and coworker.[43] Structural investigation of the sulfate

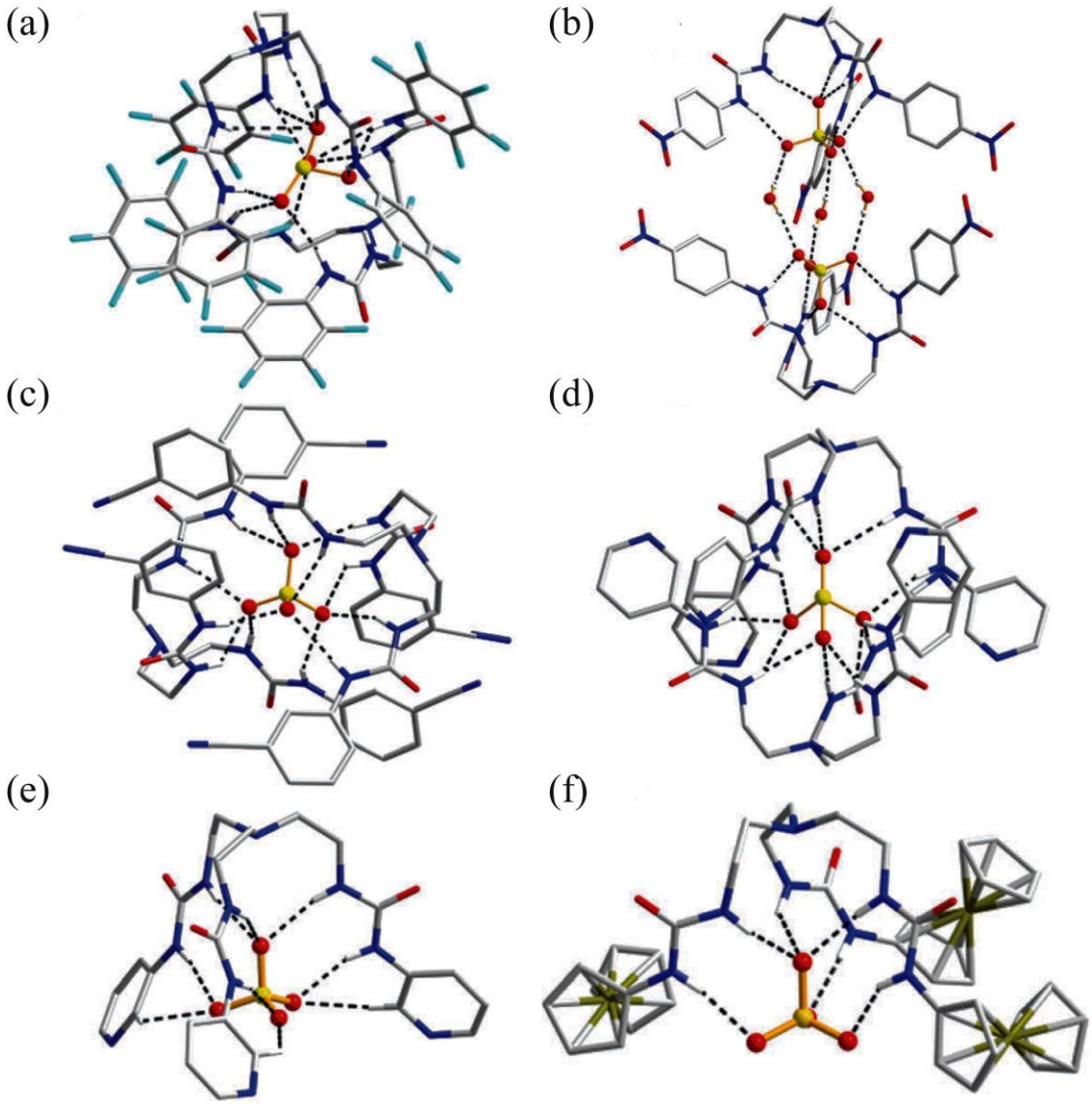
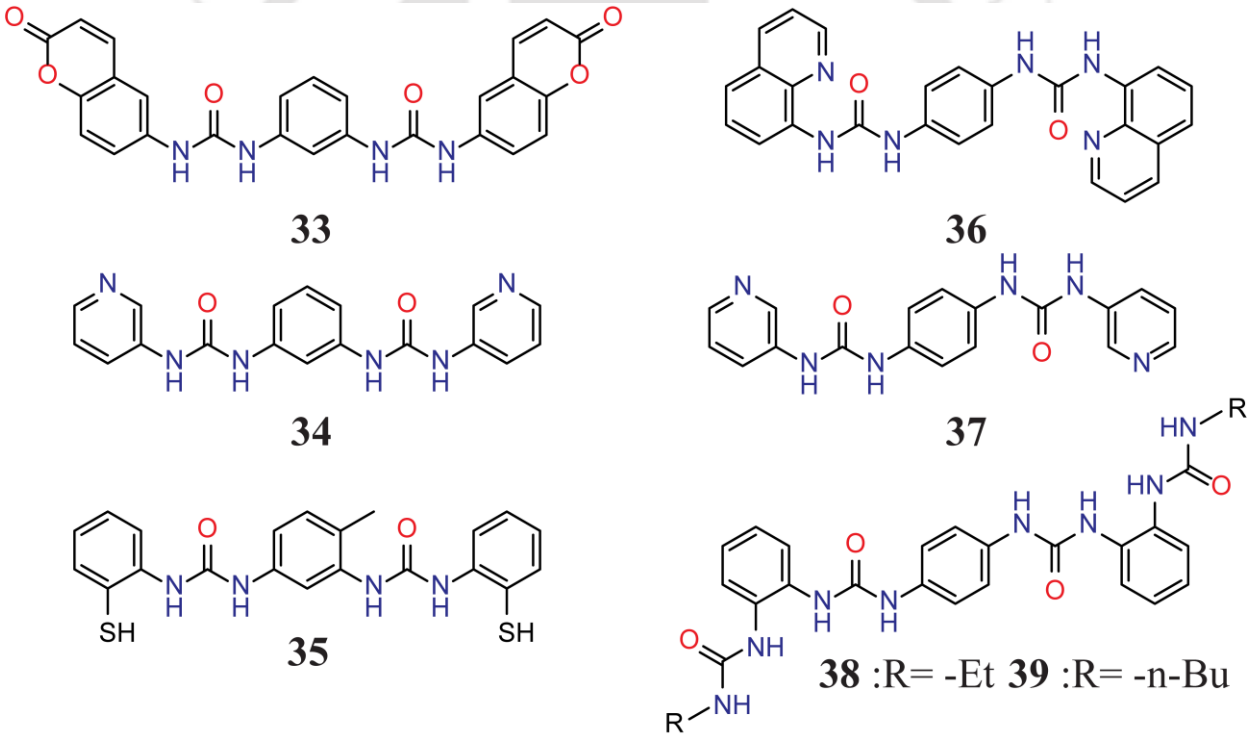


Fig. 1.8 Single X-ray Crystal structures showing binding environment of (a) $(\mathbf{26})_2.SO_4^{2-}$, (b) $(\mathbf{28})_2.SO_4^{2-}$, (c) $(\mathbf{30})_2.SO_4^{2-}$, (d) $(\mathbf{31})_2.SO_4^{2-}$, (e) $(\mathbf{31})_1.SO_4^{2-}$ and (f) $(\mathbf{32})_2.SO_4^{2-}$.

complex of **28** exposed that, all three urea functions are involved in N−H···O hydrogen bonding with a SO_4^{2-} that is further hydrogen bonded to isolated three water molecules. The concurrent interactions of three lattice water molecules with two encapsulated sulfate anions by O···H−O−H···O hydrogen bonds generate a rugby ball shaped sulphate-water-sulfate adduct held inside a pseudo dimeric assembly of receptor **28**. Structural study of the crystals of the dihydrogen phosphate complexes of **26** showed that inside the tripodal cavity a $H_2PO_4^-$ anion is bound by seven hydrogen bonding interactions. Furthermore, another $H_2PO_4^-$ is hydrogen bonded with the encapsulated $H_2PO_4^-$ to form a centrosymmetric dimer, with the arms between the two tripodal receptor entities.[39,44] Interestingly, it was found that after the addition of 2 equivalents TBAOH into the DMSO solution of complexes of **6c** results in 2:1 receptor-anion complex.[44] Through solution state ^{31}P-NMR studies, in solid-state the charge-dependent anion binding discrepancy of phosphates has been further confirmed by simple acid/base treatment. The tetrabutylammonium chloride complexes of receptors **26** and **27** crystallized as 1:1 complexes. In all the complexes, six N−H···Cl^- hydrogen bonds, one from each NH group binds to the chloride within the tripodal cavity.[39] Likewise; binding of fluoride within the tripodal cavity is also directed by six N−H···F^- H-bonds, as observed in the crystal structure of fluoride complex of **26**. The solution state anion binding of F^- with **26** was also evidently shown by the ^{19}F-NMR spectrum in DMSO-d6.[42] Interestingly when the receptor (**26**) is treated with $Bu_4N^+CN^-$, hydroxide entrapped pseudocapsular complex of **26** was formed.[44] In 2005 Custelcean and coworkers have firstly reported the single crystal X-ray structure of a sulfate complex **30** of tren-based trisurea.[45] Structural investigation of the complex reveals that the receptor **30** binds with Ag_2SO_4 *via* the cyano group CN to form a 1-dimensional coordination polymer, where the receptor capturing a sulfate ion with 12 hydrogen bonds, every two receptors formed a pocket (Fig. 1.8c) and it is the first example of sulfate coordination in a saturated mode. A 3-pyridyl-substituted analogue **31** was reported independently by Custelcean and Wu groups. From the X-ray crystal structure, it was found that the receptor **31** assembles a distinct 2:1 sulfate entrapping cage of MSO_4 (M = Zn, Cd, Mn, Co, Mg), in which 12 hydrogen bonds are donated by all the six urea groups to encapsulate sulfate ion (Fig. 1.8d).[46] The tripodal trisurea receptor **26** having pentafluorophenyl substitution was also reported by Ghosh *et al*., which formed an analogous 2:1 (host/guest) complex with a sulfate ion (as in the case of $(TBA)_2SO_4$) (Fig. 1.8b).[42]

In anion recognition chemistry, the design and synthesis of receptors derived from *meta*-phenylenediamine and the oligourea anion receptors based on most divergent binding site containing rigid *para*-phenylenediamine spacer have been a hardly explored for studies of

biologically or environmentally relevant anions become reflected as a less explored area. A *meta*-phenylenediamine based coumarin linked bis-urea receptor **33** (Scheme 1.6) is reported by K. Ghosh and co-workers, where the receptor in polar solvent DMSO fluorometrically distinguished isomeric aromatic dicarboxylates and also they exhibited that in organic solvent ditopic receptor are more sensitive towards dicarboxylates. In the course of receptor-anion interaction, the solution state UV-visible, fluorescence and ^{1}H-NMR analysis studies reveals that the receptor **33** is capable of differentiating isomeric aromatic dicarboxylates with moderate binding constant values.[47] In 2012, the Dastidar group reported a bis-pyridyl-bis-ureaa bis-pyridyl-bis-urea ion-pair receptor **34** having *meta*-phenylenediamine linker (Scheme 1.6), which exhibited selective SO_4^{2-} separation along with the formation of Cu^{II} coordination polymers capable of gelation.



Scheme 1.6 (a) Illustrative molecular structures of *m*-phenylenediamine based bis-urea anion-receptors **33**-**35** and representative molecular structures of urea anion-receptors **36**-**39** based on *p*-phenylenediamine spacer.

They demonstrated a series of four new coordination polymers is demonstrated by reacting receptor **34** and $CuSO_4$, $CuCl_2$, $CuBr_2$, and CuF_2 respectively from individual aqueous ethanolic DMF solution mixtures in (metal:ligand) 1:2 ratio and under these suitable conditions the systems produce metallogels.[48] In structure-property correlation, the single crystal structures of the coordination polymers were used and one of the coordinated Cu^{II} polymers of receptor **34**

has also been exploited for separating SO_4^{2-} anion for *in situ* crystallization from a complex mixture of different oxyanions. A *meta*-phenylenediamine and thiol based fluorescent bis-urea chemosensor **35** (Scheme 1.6) was synthesized and reported by Kuwar and co-workers and stress that the receptor exhibited excellent selectivity for Fe^{3+} ion with 'fluorescence off' mechanism in semi-aqueous phase despite the presence of anion binding bis-urea moieties, over other frequently coexistent interfering metal ions and the solution state binding studies were further supported by the detailed DFT calculations.[49] A *para*-phenylenediamine attached quinoline based bis-urea receptor **36** (Scheme 1.6) was designed and synthesized by Hossain *et al.* to inspect its binding capability with diverse anionic guests such as halides, nitrate, perchlorate, dihydrogen phosphate and hydrogen sulfate by UV-Vis titration experiments in DMSO. The outcomes from solution state binding studies confirmed that the linear bis-urea receptor showed high affinity and moderate selectivity towards hydrogen sulfate in 1:1 host-guest complexation mode over the other anions studied. The DFT studies suggested that an anion is bound within the dipodal receptor cleft *via* N–H···A and C–H···A interactions and subsequently the results from ^{1}H-NMR solution state studies also proposed that the binding aptitude is predominately governed by hydrogen bonding interactions and the basicity of anions.[50] Dastidar et al. reported the formation of a Borromean weave shaped coordination polymer sustained by urea-sulfate hydrogen bonding interactions when a pyridine substituted *para*-phenylenediamine based bis-urea receptor **37** (Scheme 1.6) is reacted with $ZnSO_4.7H_2O$. They have also proven that the coordination polymer could be exploited to separate sulfate anion selectively from a complex mixture of oxyanions (sulfate, nitrate, perchlorate and triflate) *via in situ* crystallization of the corresponding coordination polymers.[51] Two tetrakis urea receptors **38** and **39** have been reported by Custelcean and coworkers (Scheme 1.6). They demonstrated the co-crystallization of both ligands in their neutral form with *n*-$TBAH_2PO_4$ salts resulted in the isolation of discrete $(H_2PO_4^-)_4$ and $(H_2PO_4^-)_6$ anionic associations stabilized in the crystalline state by multiple urea hydrogen bonding interactions.[52]

1.5 Concluding remarks

Mainly, the acyclic receptors comprising rigid or flexible scaffolds with appropriately positioned binding sites can recognize hydrated-anions/anions or ion-pairs instantaneously both in solid and in solution phases, which also give assistance in the formation of the molecular self-assembly process. In anion receptor chemistry, acyclic receptors have exposed their high affinity towards anion assisted capsule and pseudo-capsule formation. The attached aryl terminals and the anion binding functions in the receptors were found to play a significant role headed for the formation of diverse microenvironment for selective anion binding and encapsulation. The commonly

higher coordination numbers of oxyanions similar to phosphates, sulfates, and carbonates assist in dimeric capsular assembly formation, whereas halides are apt to form unimolecular capsules. The rigid isomeric aromatic diamine based dipodal urea receptors have heavily depended upon the degree of merging of hydrogen-bond donor groups along with the electronic and positional isomeric effect of terminal aryl receptor substituents trailed by the dimension of guest assemblage, which has shown their effective potential towards the binding of anionic guests. Specifically, the urea moieties that have been utilized dominantly over the other functionalities can create two-directional hydrogen bonds with halides and oxyanions. Thus the design of sophisticated three-dimensional architectures with two or more urea functionalization is important to bind environmentally and biologically relevant anions through cooperative or non-cooperative interactions of H-bonding donor sites. To produce several tetrakis-urea anion receptors, convergent anion binding sites with more preorganized and cooperative architectures of rigid *ortho*-phenylene linker have been utilized. On the other hand, time and again in anion receptor chemistry, the tris(2-aminoethyl)amine constructed tripodal receptors commonly with π-acidic or electron-withdrawing terminals have exposed their high affinity towards anion assisted capsule and pseudo-capsule formation from the last two decades. In the case of ion-pair recognition, the bipyridine-bis(urea) and pyridylureas based receptors were found to form charge-separated ion-pair complex through the assembly process. The dipodal urea receptors containing rigid *ortho*-phenylenediamine spacer have been used more largely in the literature compared to its isomeric *meta*-phenylenediamine and *para*-phenylenediamine spacer. The site of the attached substituents in aryl terminals was found to play a substantial role in the direction of the formation of different microenvironment for anion encapsulation and hence the architecture of the resulting complex formation. Thus, the recognition of anions, hydrated-anions, anionic associations in the molecular receptor or capsules *via* self-assembly processes is definitely a fascinating and captivating research field which can develop significantly and bring vast improvements in specialized applications like (a) removal and extraction of toxic anions and salts from water, (b) exploiting the binding and selectivity of the molecular capsules to anionic species designed for the drug delivery, and (c) membrane transport, (d) solubilize insoluble anions/salts, (e) using the molecular capsules as molecular reactors by stabilizing the anionic reactive intermediates inside the nanocavity etc.

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Chapter 2

Experimental Methods & Characterization

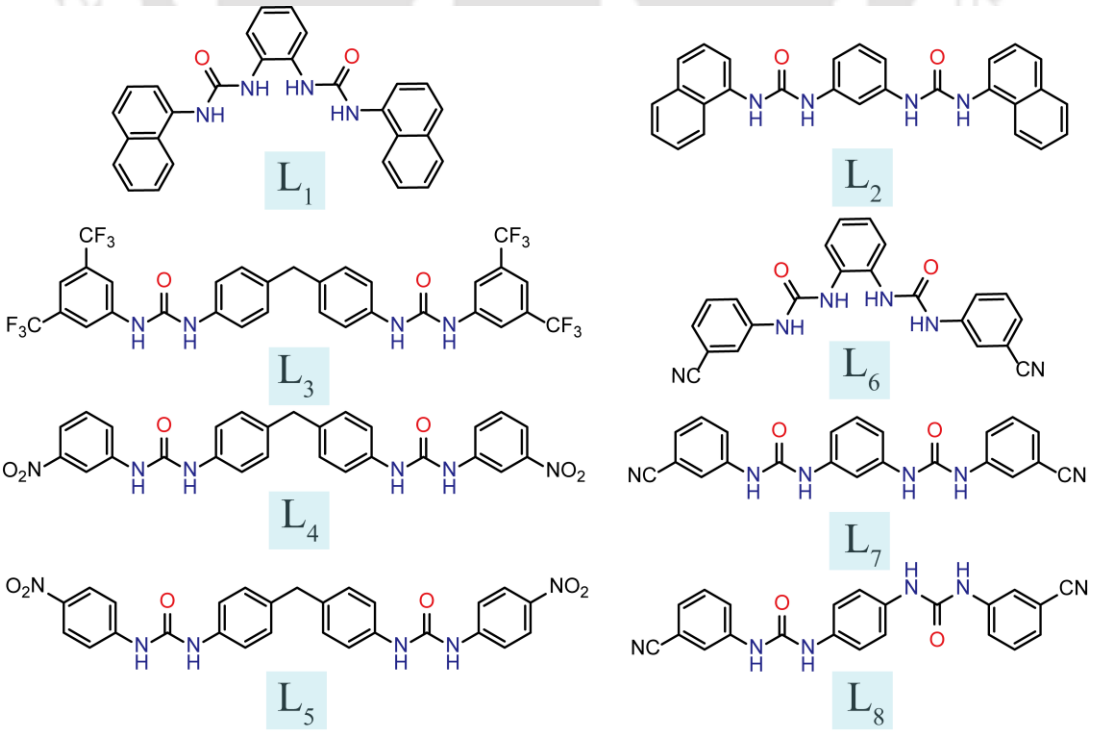
In this chapter, a thorough report of the several reagents used in the synthesis of acyclic dipodal receptors(**L_1-L_8**) (Scheme 2.1), their synthetic procedures, crystallization details and specifications of instruments/equipment employed in the characterization of synthesized receptors and their various complexes with anions/hydrated-anions are presented.

2.1 Materials

All reagents and solvents were obtained from commercial sources and used as received without further purification. *ortho*-Phenylenediamine, *meta*-Phenylenediamine, *para*-Phenylenediamine, 4,4′-Diaminodiphenylmethane, 4-Nitrophenyl isocyanate, 3-Nitrophenyl isocyanate, 3,5-Bis(trifluoromethyl)phenyl isocyanate, 3-Cyanophenyl isocyanate, 1-naphthyl isocyanate were purchased from Sigma-Aldrich (U.S.A). All quaternary ammonium salts were purchased from Sigma-Aldrich (U.S.A). All sodium, potassium salts and deuterated solvent such as DMSO-d6, $CDCl_3$ were purchased from Merck chemicals (India) and used as received. Solvents for synthesis and crystallization experiments were purchased either from Merck, India, and dried using standard techniques, wherever mentioned in the synthetic procedures.

2.2 Experimental methods

^{1}H-NMR spectra were recorded on a Varian FT-600 MHz and FT-400 MHz instrument, chemical shifts were recorded in parts per million (ppm) on the scale using tetramethylsilane (TMS) or residual solvent peak as a reference.



Scheme 2.1 Representation of molecular structures of the receptors **L_1-L_8**.

^{13}C spectra were obtained at 150 MHz and FT-100 MHz at 298 K. The FT-IR spectra of the air-dried samples were recorded on a PerkinElmer FT-IR spectrometer with KBr disks in the range 4000-450 cm^{-1}. Thermal analysis (TGA) of dried samples was performed using an SDTA 851-E TGA thermal analyser (*Mettler Toledo*) with a heating rate of 5-10^oC/min in a N_2 atmosphere. The electrospray ionization mass spectrometry (ESI-MS) spectra of free receptors were recorded in methanol. FESEM imaging studies were performed by a drop (2 μL) cast method on glass plates covered with Al foil using a Gemini 300 FESEM instrument (Carl Zeiss). Association constants of anions with receptors were obtained by ^1H-NMR titrations of the receptor with tetrabutyl ammonium (TBA) anion salts in DMSO-d6 at 298 K. The initial concentration of the receptor solution was 10 mM. Aliquots of anions were added from the stock solutions up to 1:10 host-guest stoichiometry. The residual solvent peak in DMSO- d6 (2.50 ppm) was used as an internal reference, and each titration was performed with at least 10-15 measurements.

2.3 Single crystal X-ray crystallography

In each case, a crystal of suitable size was selected from the mother liquor and immersed in silicone oil, and it was mounted on the tip of a glass fiber and cemented using epoxy resin. The intensity data were collected using a Bruker SMART APEX-II CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube Mo-K_α radiation (λ = 0.71073 Å) at 298(3) K, with increasing ω (width of 0.3^o per frame) at a scan speed of 5 s/ frame. Subsequently, the X-ray crystallographic intensity data were also collected using a Supernova, single source at offset, Eos diffractometer using Mo-Kα radiation (λ = 0.71073 Å) equipped with a CCD area detector, and the corresponding data refinement and cell reduction were carried out by CrysAlisPro.[2.1] The SMART software was used for data acquisition. Data integration and reduction were undertaken with SAINT and XPREP software.[2.2] Multi-scan empirical absorption corrections were applied to the data using the program SADABS.[2.3] All the crystal structures were solved by direct methods using SHELXTL-2014[2.4] and were refined on F^2 by the full-matrix least-squares technique using the SHELXL-2014 program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms attached to all carbon atoms were geometrically fixed and the positional and temperature factors are refined isotropically. Hydrogen atoms attached with the amine/urea/thiourea nitrogen atoms were located from electron Fourier map and refined isotropically. Usually, temperature factors of hydrogen atoms attached to carbon atoms are refined by restraints -1.2 or -1.5 U_{iso} (C), although the isotropic free refinement is also acceptable. Graphics were generated using MERCURY 2.3[2.5] for Windows. PLATON/SQUEEZE[2.6] was used to refine the host framework in some host-guest complexes

excluding the disordered counter-cation or solvent molecules. All the crystallographic data have been deposited in the CCDC. Crystallographic parameters for data collection and crystallographic refinement details of the receptors and their anion complexes are summarized in the respective chapters.

2.4 Synthesis and characterization of receptors L_1-L_8

2.4.1 1-naphthyl based receptors L_1-L_2

The 1-naphthyl substituted bis-urea receptors have been synthesized in quantitative yield by the individual reaction of *o*-Phenylenediamine (0.324 g, 3.0 mmol) and *m*-Phenylenediamine(0.324 g, 3.0 mmol) with 1-naphthyl isocyanate (958 μL, 7.0 mmol) in dry acetonitrile medium separately. At room temperature, the individual reaction mixtures of amine and 1-naphthyl isocyanate were taken in two isolated 50 mL round bottomed flasks, stirred for overnight. Then, in each case, the off-white solid precipitate obtained, were filtered off and washed several times with acetonitrile, THF and then dried in a vacuum to yield receptors **L_1** and **L_2** from respective flasks. The precipitate thus collected of receptors **L_1-L_2** was dried in air and characterized by NMR, FT-IR, and ESI-MS. Yield: ~84% and ~85% based on respective **L_1** and **L_2**.

L_1: ^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 7.112-7.118 (d, 2H, ~3.6 Hz, Ar-H), 7.122-7.128 (d, 2H, ~3.6 Hz, Ar-H), 7.467-7.493 (t, 2H, ~7.8 Hz, Ar-H), 7.529-7.554 (t, 2H, ~7.2 Hz, Ar-H), 7.578-7.601 (t, 2H, ~7.2 Hz, Ar-H), 7.694-7.700 (d, 2H, ~3.6 Hz, Ar-H), 7.925-7.938(d, 2H, ~7.8 Hz, Ar-H), 8.047-8.059 (d, 2H, ~7.2 Hz, Ar-H), 8.203-8.218 (d, 2H, ~9.0 Hz, Ar- H),8.584(s, 2H, NH_a), 9.136 (s, 2H, NH_b). ^{13}C-NMR (150 MHz, DMSO-d6) δ (ppm): 116.50, 117.48, 118.12, 122.18, 123.55, 124.60, 126.29, 126.57, 129.09, 131.87, 134.40, 135.09, 141.56, and 154.34. IR spectra (KBr pellet): 3335 cm^{-1} (N-H), 3145 cm^{-1} (C-H), 1667 cm^{-1} (C=O), ESI-MS: m/z 447.2184 [**L_1**+H^+].

L_2: ^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 7.149-7.152(d, 2H, ~1.8 Hz, Ar-H), 7.162-7.166 (d, 2H, ~2.4 Hz, Ar-H), 7.224-7.251 (t, 2H, ~8.1 Hz, Ar-H), 7.472-7.498 (t, 2H, ~7.8 Hz, Ar-H), 7.540-7.565 (t, 2H, ~7.8 Hz,Ar-H), 7.596-7.621 (t, 2H, ~7.5 Hz, Ar-H), 7.632-7.646 (d, 2H, ~8.4 Hz, Ar-H), 7.846 (s, 1H, Ar-H), 7.932-7.945 (d, 2H, ~7.8 Hz, Ar-H), 8.065-8.078 (d, 2H, ~7.8 Hz, Ar-H), 8.135-8.149 (d, 2H, ~8.4 Hz, Ar-H), 8.756 (s, 2H, NH_a), 9.512 (s, 2H, NH_b). ^{13}C-NMR (150 MHz, DMSO-d6) δ (ppm): 108.20, 112.21, 117.67, 121.89, 123.60, 126.39, 126.58, 129.13, 129.98, 134.38, 134.99, 140.90, and 153.46. IR spectra (KBr pellet): 3339 cm^{-1} (N-H), 3132 cm^{-1} (C-H), 1672 cm^{-1} (C=O), ESI-MS: m/z 477.1824 [**L_2**+H^+].

2.4.2 4, 4′-diaminodiphenylmethane based bisurea receptors L_3-L_5

The 4,4′-diaminodiphenylmethane based flexible bis-urea receptors **L_3-L_5** were synthesized by the reaction of 4,4′-diaminodiphenylmethane(0.906 g, 6.0 mmol) as the starting material, with 3,5-Bis(trifluoromethyl)phenyl isocyanate (0.292 g, 2.0 mmol), 3-Nitrophenyl isocyanate (1.098 g, 6.0 mmol), and 4-Nitrophenyl isocyanate (1.098 g, 6.0 mmol), to produce **L_3**, **L_4**, and **L_5** respectively. At room temperature, the individual reaction mixtures of amine and all the three isocyanate were taken in two isolated 50 mL round bottomed flasks, stirred for overnight. Then, in each case, solid precipitate obtained, were filtered off and washed several times with acetonitrile, THF and then dried in a vacuum to yield receptors **L_3-L_5** from respective flasks. Yield: ~82%, ~85%, and ~79% of respective ligands **L_3-L_5**.

L_3: ^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 3.84 (s, 1H, CH_2), 7.14-7.16 (d, 4H, ~12 Hz, Ar-H), 7.38-7.40 (d, 4H, ~12 Hz, Ar-H), 7.62 (s, 2H, Ar-H), 8.12 (s, 4H, Ar-H), 8.90 (s, 2H, NH_a), 9.33 (s, 2H, NH_b). ^{13}C-NMR (DMSO-d6, 150 MHz) δ (ppm): 114.7, 118.5, 119.6, 123.0, 124.7, 129.6, 131.2, 136.2, 137.4, 142.5, and 152.9. IR spectra: broad band at 3314 cm^{-1} (N-H), 3116 cm^{-1} (C-H), 2926 cm^{-1} (C-H), 1556 cm^{-1} (C=C),1660 cm^{-1} (C=O). MS: calculated mass 708.1395, obtained ESI mass m/z 726.1779 (**L_3**+ NH_4^+).

L_4: ^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 3.84 (s, 1H, CH_2), 7.14-7.15 (d, 4H, ~6 Hz, Ar-H), 7.38-7.39 (d, 4H, ~6 Hz, Ar-H), 7.54-7.57 (t, 2H, ~6 Hz, Ar-H), 7.68-7.70 (d, 4H, ~12 Hz, Ar-H), 7.80-7.82 (d, 4H, ~12 Hz, Ar-H), 8.55 (s, 2H, Ar-H), 8.75 (s, 2H, NH_a), 9.16 (s, 2H, NH_b). ^{13}C-NMR (DMSO-d6, 150 MHz) δ (ppm): 112.4, 116.6, 119.2, 124.7, 129.6, 130.6, 136.2, 137.7, 141.7, 148.7, and 152.9. IR spectra: broad band at 3315 cm^{-1} (N-H), 3090 cm^{-1} (C-H), 2924 cm^{-1} (C-H), 1557 cm^{-1} (C=C), 1646 cm^{-1} (C=O), 1430 cm^{-1} (NO_2-asym), 1313 cm^{-1} (NO_2-sym), 1238 cm^{-1} (C-N). MS: calculated mass 526.1601, obtained ESI mass: m/z 527.1704 (**L_3** + H^+), m/z 544.1958 (**L_3** + NH_4^+).

L_5: ^{1}H-NMR (600 MHz) δ (ppm): 3.84 (s, 1H, CH_2), 7.15-7.16 (d, 4H, ~6 Hz, Ar-H), 7.38-7.39 (d, 4H, ~6 Hz, Ar-H), 7.67-7.68 (d, 4H, ~6 Hz, Ar-H), 8.17-8.19 (d, 4H, ~12 Hz, Ar-H), 8.84 (s, 2H, NH_a), 9.39 (s, 2H, NH_b). ^{13}C-NMR (DMSO-d6, 150 MHz) δ (ppm): 117.8, 119.3, 125.6, 129.4, 136.4, 137.5, 141.3, 146.9, and 152.4. IR spectra: broad band at 3341 cm^{-1} (N-H), 3088 cm^{-1} (C-H), 2923 cm^{-1} (C-H), 1596 cm^{-1} (C=C), 1650 cm^{-1} (C=O), 1411 cm^{-1} (NO_2-asym), 1332 cm^{-1} (NO_2-sym), 1237 cm^{-1} (C-N). MS: calculated mass 526.1601, obtained ESI mass m/z 527.1705 (**L_5**+ H^+).

2.4.3 *meta*-cyano substituted receptors L_6-L_8

The 3-cyanophenyl functionalized based bis-urea receptors **L_6-L_8** were synthesized by the following procedure. At room temperature, to 20 ml acetonitrile solution of *ortho*, *meta* and

para-phenylenediamine (0.324 g, 3.0 mmol), a 3-cyanophenyl isocyanate (0.864 g, 6.0 mmol) solution was added dropwise under vigorous stirring for 24 h. Precipitate of all the three reaction mixtures were filtered off separately after overnight stirring and then allowed to dry in a vacuum to yield **L_6**, **L_7**, and **L_8** respectively. Yield: ~80%, ~85%, and ~81% of respective ligands **L_6-L_8**.

L_6: ^{1}H-NMR (600 MHz, DMSOd6) δ 9.44 (s, 1H), 8.21 (s, 1H), 8.01 (t, ~1.8 Hz, 1H), 7.67 (ddd, J ~ 8.3, 2.1, 0.9 Hz, 1H), 7.58 (dd, ~ 6.0, 3.6 Hz, 1H),7.49 (t, ~ 8.0 Hz, 1H), 7.42 (d, ~7.6 Hz, 1H), 7.14 (dd, ~ 6.0, 3.5 Hz, 1H). ^{13}C-NMR (DMSO-d6, 150 MHz) δ (ppm): 153.58, 141.2, 130.66, 125.76, 124.95, 123.28, 121.21, 119.35, and 112.05. IR spectra: broad band at 3307 cm^{-1} (N-H), 3112 cm^{-1} (C-H), 2920 cm^{-1} (C-H), 1552 cm^{-1} (C=C), 1665 cm^{-1} (C=O). Calculated mass: 396.1335, obtained ESI mass: m/z 397.1438 (**L_6** + H^+).

L_7: ^{1}H-NMR (600 MHz, DMSO-d6) δ 8.95 (s, 2H), 8.89 (s, 2H), 7.98 (s, 2H), 7.76-7.60 (m, 3H), 7.49 (t, ~ 8.0 Hz, 2H), 7.42 (d, ~ 7.6 Hz, 2H), 7.23-7.14 (m, 1H), 7.09 (dd, ~ 8.0, 1.8 Hz, 2H). ^{13}C-NMR (150 MHz, DMSO) δ (ppm): 108.90, 112.06, 112.83, 119.34, 121.19, 123.34, 125.78, 130.66, 140.22, 141.307, and 152.78. IR spectra (KBr pellet): broad band at 3313 cm^{-1} (N-H), 3090 cm^{-1} (C-H), 2924 cm cm^{-1} (C-H), 1557 cm^{-1} (C=C), 1635 cm^{-1} (C=O), 1238 cm^{-1} (C-N). Calculated mass: 396.1335, obtained ESI mass: m/z 397.1441 (**L_7** + H^+).

L_8: ^{1}H-NMR (400 MHz, DMSOd6) δ 8.96 (s, 1H), 8.72 (s, 1H), 7.97 (s, 1H), 7.72-7.61 (m, 1H), 7.54-7.35 (m, 4H). ^{13}C-NMR (100 MHz, DMSO) δ (ppm): 152.95, 134.44, 130.64, 125.63, 123.28, 121.15, and 119.79. IR spectra: broad band at 3338 cm^{-1} (N-H), 3077 cm^{-1} (C-H), 2918 cm^{-1} (C-H), 1591 cm^{-1} (C=C), 1655 cm^{-1} (C=O), 1235 cm^{-1} (C-N). Calculated mass: 396.1335, obtained ESI mass: m/z 397.1431 (**L_8** + H^+).

2.5 Synthesis and characterization of anion complexes of the receptors L_1-L_8

2.5.1 Complexes of 1-naphthyl based receptors L_1-L_2

Upon slow evaporation of the 5 mL basic DMF or DMSO or mixed solution of individual receptors **L_1** (100mg, 0.225 mmol)/**L_2** (100 mg, 0.187 mmol) and excess tetrabutylammonium (10 eqv.) of respective anions, the neutral complexes of individual 1-naphthyl isocyanate based receptors **L_1** and **L_2** with anions or solvated anions were attained as suitable crystals for X-ray diffraction analysis. Most of the cases colorless crystals of the non-hydrated complexes were obtained at room temperature within one week to one month and they were collected by pressing between filter paper before characterization by different techniques.

Chloride complex [(n-TBA){(L_1)(Cl)}] (1a).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.914-0.939 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.267-1.328 (m, 8H, $TBACH_2$), 1.527-1.580 (m, 8H, $TBACH_2$), 3.136-3.164 (t, 8H, ~ 8.4 Hz, N+-$TBACH_2$), 7.084-7.090 (d, 2H, ~ 3.6 Hz, Ar-H), 7.094-7.100 (d, 2H, ~3.6 Hz, Ar- H), 7.458-7.484 (t, 2H, ~7.8 Hz, Ar-H), 7.522 7.545 (t, 2H, ~7.2 Hz, Ar-H), 7.558-7.581 (t, 2H, ~7.2 Hz, Ar-H), 7.620-7.634 (d, 2H, ~ 8.4 Hz, Ar-H), 7.448-7.754 (d, 2H, ~3.6 Hz, Ar-H), 7.758-7.764 (d , 2H, ~3.6 Hz, Ar-H), 7.915-7.928 (d, 2H, ~7.8 Hz, Ar-H), 8.038-8.051 (d, 2H, ~7.8 Hz, Ar-H), 8.337-8.351 (d, 2H, ~ 8.4 Hz, Ar-H), 8.890 (s, 2H, NH_a), 9.301 (s, 2H, NH_b). IR spectra (KBr pellet): 3388 cm^{-1} (N-H), 3152 cm^{-1} (C-H), 2868 cm^{-1} (C-H), 1671 cm^{-1} (C=O), 665 cm^{-1}(C-Cl). Yield 67% based on **L_1**.

Acetate complex [(n-TBA){L_1(CH_3COO)}] (1b).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.915-0.933 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.280-1.315 (m, 8H, $TBACH_2$), 1.512-514 (m, 8H, $TBACH_2$), 1.987 (s, 3H, Acetate-CH_3), 3.135-3.161 (t, 8H, ~ 8.4 Hz, N+-TBA-CH_2), 7.053-7.105 (m, 4H, Ar-H), 7.454-7.480 (t, 2H, ~7.8 Hz, Ar-H), 7.519- 7.543 (t, 2H, ~7.2 Hz, Ar-H), 7.757-7.582 (t, 2H, ~7.2 Hz , Ar-H), 7.607-7.620 (d, 2H, ~7.8 Hz, Ar-H), 7.754-7.807 (m , 4H, Ar-H), 7.913-7.926 (d, 2H, ~7.8 Hz, Ar-H), 8.074-8.086 (d, 2H, ~7.2 Hz, Ar-H), 8.300-8.314 (d, 2H, ~ 8.4 Hz, Ar-H), 9.268 (s, 2H, Ar-H), 9.469 (s, 2H, NH_a), 10.832 (s, 2H, NH_b). IR spectra (KBr pellet): 3392 cm^{-1} (N-H), 3149 cm^{-1} (C-H), 2872cm^{-1} (C-H), 1674 cm^{-1} (C=O).Yield 74% based on **L_1**.

Terephthalate complex [(n-TBA){(L_1)($C_8H_4O_4^{2-}$)}] (1c).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.908-0.933 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.261-1.322 (m, 8H, $TBACH_2$), 1.520-572 (m, 8H, $TBACH_2$), 3.124-3.154 (t, 8H, ~ 8.4 Hz, N^+-$TBACH_2$), 7.064-7.070 (d, 2H, ~ 3.6 Hz, Ar-H), 7.074- 7.080 (d, 2H, ~3.6 Hz, Ar-H), 7.281-7.306 (t, 2H, ~7.2 Hz, Ar-H), 7.373-7.398 (t, 2H, ~7.2 Hz, Ar-H), 7.438-7.464 (t, 2H, ~7.8 Hz, Ar-H), 7.569-7.583 (d, 2H, ~7.8 Hz, Ar-H), 7.855-7.870 (d, 2H, ~9.0 Hz, Ar-H), 8.005 (s, 4H, Ar-H, Terephthalate anion), 8.124-8.137 (d, 2H, ~7.8 Hz, Ar-H), 8.370-8.356 (d, 2H, ~ 8.4 Hz, Ar-H), 9.640 (s, 2H, NH_a), 10.190 (s, 2H, NH_b). IR spectra (KBr pellet): 3395 cm^{-1} (N-H), 3170 cm^{-1} (C-H), 2869 cm^{-1} (C-H), 1669 cm^{-1} (C=O).Yield 75% based on **L_1**.

Chloride complex [2(n-TBA){(L_2)$_2$(Cl)$_2$} H_2O] (2a).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.916-0.940 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.271-1.372 (m, 8H, $TBACH_2$), 1.531-583 (m, 8H, $TBACH_2$), 3.139-3.167 (t, 8H, ~ 8.4 Hz, N^+-$TBACH_2$), 7.211(s, 4H, Ar-H), 7.460-7.86 (t, 2H, ~7.8 Hz, Ar-H), 7.530-7.555 (t, 2H, ~7.8 Hz, Ar-H), 7.571-7.595 (t, 2H, ~7.2 Hz,Ar-H), 7.613-7.627 (d, 2H, ~8.4 Hz, Ar-H), 7.745 (s, 1H, Ar-H), 7.919-7.932 (d, 2H, ~7.8 Hz, Ar-H), 8.081-8.094 (d, 2H, ~7.8 Hz, Ar-H), 8.274-8.288 (d, 2H, ~8.4 Hz, Ar-H), 9.020 (s, 2H, NH_a), 9.563 (s, 2H, NH_b). IR spectra (KBr pellet): 3376 cm^{-1} (N-H), 3141 cm^{-1} (C-H), 2864 cm^{-1} (C-H), 1668 cm^{-1} (C=O), 661 cm^{-1} (C-Cl).Yield 70% based on **L_2**.

Bromide complex [2(n-TBA){$(L_2)_2(Br)_2$} H_2O] (2b).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.919-0.943 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.275-1.336 (m, 8H, $TBACH_2$), 1.536-1.558 (m, 8H, $TBACH_2$), 3.144-3.172 (t, 8H, ~ 7.8 Hz, N^+-$TBACH_2$), 7.161-7.173 (d, 2H, ~7.2 Hz, Ar-H), 7.213-7.240 (t, 2H, ~7.2 Hz, Ar-H), 7.467-7.494 (t, 2H, ~7.8 Hz, Ar-H), 7.539 7.563 (t, 2H, ~7.2 Hz, Ar-H), 7.588-7.613 (t, 2H, ~7.2 Hz, Ar-H), 7.7630-7.664 (d, 2H, ~8.4 Hz, Ar-H), 7.808(S, 1H, Ar-H), 7.930-7.943 (d, 2H, ~7.8 Hz, Ar-H), 8.055-8.067 (d, 2H, ~7.2 Hz, Ar-H), 8.163-8.177 (d, 2H, ~8.4 Hz, Ar-H), 8.782 (s, 2H, NH_a), 9.207 (s, 2H, NH_b). IR spectra (KBr pellet): 3378cm^{-1} (N-H), 3145cm^{-1} (C-H), 2864cm^{-1} (C-H), 1673cm^{-1} (C=O), 584cm^{-1} (C-Br).Yield 67% based on **L_2**.

Fluoride complex [2(n-TBA){$(L_2)_2(F)_2$}] (2c).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.908-0.932 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.263-1.324 (m, 8H, $TBACH_2$), 1.521-1.573 (m, 8H, $TBACH_2$), 3.129-3.157 (t, 8H, ~ 8.4 Hz, N^+-$TBACH_2$), 7.124-7.151 (t, 2H, ~7.8 Hz, Ar-H), 7.259-7.272 (t, 2H, ~7.8 Hz, Ar-H), 7.350-7.375 (t, 2H, ~7.2 Hz, Ar-H), 7.405-7.445 (q, 2H, ~7.2 Hz, Ar-H), 7.497-7.510 (d, 2H, ~7.8 Hz, Ar-H), 7.598 (s, 1H, Ar-H), 7.825-7.839(d, 2H, ~8.4 Hz, Ar-H), 8.191-8.203 (d, 2H, ~7.2 Hz, Ar-H), 8.455-8.468 (d, 2H, ~7.8 Hz, Ar-H), 10.683 (s, 2H, NH_a), 11.176 (s, 2H, NH_b). IR spectra (KBr pellet): 3389 cm^{-1} (N-H), 3149 cm^{-1} (C-H), 2866 cm^{-1} (C-H), 1676 cm^{-1} (C=O), 583 cm^{-1} (C-F). Yield 70% based on **L_2**.

Phosphate complex [2(n-TBA){$(L_2)_2(H_2PO_4^-)_4$}H_2O] (2d).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.915-0.939 (t, 12H, ~7.2 Hz, $TBACH_3$), 1.267-1.328 (m, 8H, $TBACH_2$), 1.526-1.578 (m, 8H, $TBACH_2$), 3.315-3.34 (t, 8, ~ 8.4 Hz, N^+-$TBACH_2$), 7.178-7.190 (d, 2H, ~7.2 Hz, Ar-H), 7.207-7.232 (d, 2H, ~9.0 Hz, Ar- H), 7.465-7.492 (t, 2H, ~7.8 Hz, Ar-H), 7.536-7.560 (t, 2H, ~7.2 Hz, Ar-H), 7.584-7.610 (t, 2H, ~7.8 Hz, Ar-H), 7.625-7.638 (d, 2H, ~7.8 Hz, Ar-H), 7.796 (s, 1H, Ar-H), 7.926-7.940 (d, 2H, ~8.4 Hz, Ar-H), 8.057-8.070 (d, 2H, ~7.8 Hz, Ar-H), 8.165-8.179 (d, 2H, ~8.4 Hz, Ar-H), 8.893 (s, 2H, NH_a), 9.275 (s, 2H, NH_b). IR spectra (KBr pellet): 3388 cm^{-1} (N-H), 3147 cm^{-1} (C-H), 2862 cm^{-1} (C-H), 1669 cm^{-1} (C=O). Yield 70% based on **L_2**.

2.5.2 Complexes of 4, 4′-diaminodiphenylmethane based bisurea receptors L_3-L_5

The neutral host-guest complexes of different 4, 4′-diaminodiphenylmethane based receptors **L_3**-**L_5** with anions, hydrated-anions or solvated anions were attained as suitable crystals for X-ray diffraction investigation upon slow evaporation of the 5 mL basic DMF or DMSO or mixed solution of individual receptors **L_3** (100 mg, 0.225 mmol)/**L_4** (100 mg, 0.142 mmol)/**L_5** (100 mg, 0.142 mmol) and excess tetrabutylammonium/tetraethylammonium salts (10 eqv.) of respective anions. Most of the cases colorless crystals of the hydrated or non-hydrated complexes were obtained at room temperature within one week to one month and they were collected by pressing between filter paper before characterization by different techniques.

Spherical chloride complex [(n-TBA){(L_3)(Cl)}] (3a).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.92-0.95 (t, 12H, ~18 Hz, $TBACH_3$), 1.28-1.34 (m, 8H, $TBACH_2$), 1.54-1.59 (m, 8H, TBA CH_2), 3.15-3.18 (t, 8H, ~18 Hz, N^+-TBA CH_2), 3.84 (s, 1H, CH_2), 7.14-7.16 (d, 4H, ~12 Hz, Ar-H), 7.38-7.40 (d, 4H, ~12 Hz, Ar-H), 7.62 (s, 2H, Ar-H), 8.12 (s, 4H, Ar-H), 9.07 (s, 2H, NH_a), 9.63 (s, 2H, NH_b). IR spectra: 3187 cm^{-1} (N-H), 3187 cm^{-1} (C-H), 2963 cm^{-1} (C−H), 1671 cm^{-1} (C=O), 733 cm^{-1} (C-Cl). Yield: 67% based on **L_3**.

Bromide complex [(n-TBA){(L_3)(Br)}] (3b)

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.92-0.95 (t, 12H, ~18 Hz, $TBACH_3$), 1.28-1.34 (m, 8H, TBA CH_2), 1.54-1.59 (m, 8H, $TBACH_2$), 3.15-3.18 (t, 8H, ~18 Hz, N^+-$TBACH_2$), 3.84 (s, 1H, CH_2), 7.14-7.16 (d, 4H, ~12 Hz, Ar-H), 7.38-7.40 (d, 4H, ~12 Hz, Ar-H), 7.63 (s, 2H, Ar-H), 8.12 (s, 4H, Ar-H), 8.93 (s, 2H, NH_a), 9.38 (s, 2H, NH_b). IR spectra: 3233 cm^{-1} (N−H), 3183 cm^{-1} (C-H), 2965 cm^{-1} (C-H), 1708 cm^{-1} (C=O), 681 cm^{-1} (C=Br). Yield 65% based on **L_3**.

Larger iodide complex [(n-TBA){(L_3)(I)}] (3c).

^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 1.28-1.34 (m, 8H, $TBACH_2$), 1.54-1.59 (m, 8H, $TBACH_2$), 3.15-3.18 (t, 8H, ~18 Hz, N^+- $TBACH_2$), 3.84 (s, 1H, CH_2), 7.14-7.16 (d, 4H, ~12 Hz, Ar-H), 7.38-7.40 (d, 4H, ~12 Hz, Ar-H), 7.62 (s, 2H, Ar-H), 8.12 (s, 4H, Ar-H), 8.90 (s, 2H, NH_a), 9.33 (s, 2H, NH_b). IR spectra: 3264 cm^{-1} (N-H), 3152 cm^{-1} (C-H), 2968 cm^{-1} (C-H), 1709 cm^{-1} (C=O), 682 cm^{-1} (C-I). Yield 80% based on **L_3**.

Planar carbonate complex [(n-TBA){(L_3)(CO_3)}] (3d).

^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 1.09-1.11 (t, 12H, ~18 Hz, $TEACH_3$), 3.11-3.15 (q, 8H, N^+-$TBACH_2$), 3.84 (s, 1H, CH_2), 7.14-7.16 (d, 4H, ~12 Hz, Ar-H), 7.38-7.40 (d, 4H, ~12 Hz, Ar-H), 7.62 (s, 2H, Ar-H), 8.12 (s, 4H, Ar-H), 8.90 (s, 2H, NHa), 9.33 (s, 2H, NHb). ^{13}C NMR (DMSO-d6, 150 MHz) δ (ppm): 7.5, 52.1, 117.4, 118.5, 119.7, 122.1, 123.7, 124.8, 129.2, 131.2, 141.0, 141.9, 154.4, and 164.2. IR spectra: 3259 cm^{-1} (N-H), 3183 cm^{-1} (C-H), 2923 cm^{-1} (C-H), 1703 cm^{-1} (C=O).Yield 70% based on **L_3**.

Chloride complex [(n-TBA){(L_4)(Cl)}] (4a).

^{1}H-NMR (600 MHz, DMSO-d6) δ (ppm): 0.92-0.95 (t, 12H, ~18 Hz, $TBACH_3$), 1.28-1.34 (m, 8H, -$TBACH_2$), 1.54-1.59 (m, 8H, $TBACH_2$), 3.15-3.18 (t, 8H, ~18 Hz, N^+- $TBACH_2$), 3.84 (s, 1H, CH_2), 7.14-7.15 (d, 4H, ~6 Hz, Ar-H), 7.38-7.39 (d, 4H, ~6 Hz, Ar-H), 7.54-7.57 (t, 2H, ~6 Hz, Ar-H), 7.68-7.70 (d, 4H, ~12 Hz, Ar-H), 7.80−7.82 (d, 4H, ~12 Hz, Ar-H), 8.55 (s, 2H, Ar-H), 8.97 (s, 2H, NH_a), 9.44 (s, 2H, NH_b). IR spectra: 3212 cm^{-1} (N-H), 3172 cm^{-1} (C-H), 2963 cm^{-1} (C-H), 1703 cm^{-1} (C=O), 737 cm^{-1} (C-Cl). Yield 72% based on **L_4**.

Bromide complex [(n-TBA){(L_4)(Br)}] (4b).

^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 0.92-0.95 (t, 12H, ~18 Hz, $TBACH_3$), 1.28-1.34 (m, 8H, $TBACH_2$), 1.54-1.59 (m, 8H, $TBACH_2$), 3.15-3.18 (t, 8H, ~18 Hz, N^+- $TBACH_2$), 3.84 (s, 1H, CH_2), 7.14-7.15 (d, 4H, ~6 Hz, Ar-H), 7.38-7.39 (d, 4H, ~6 Hz, Ar-H), 7.54-7.57 (t, 2H, ~6 Hz, Ar-H), 7.68-7.70 (d, 4H, ~12 Hz, Ar-H), 7.80-7.82 (d, 4H, ~12 Hz, Ar-H), 8.55 (s, 2H, Ar-H), 8.82 (s, 2H, NH_a), 9.24 (s, 2H, NH_b). IR spectra: 3214 cm^{-1} (N-H), 3172 cm^{-1} (C-H), 2963 cm^{-1} (C-H), 1702 cm^{-1} (C=O), 737 cm^{-1} (C-Br). Yield 80% based on **L_4**.

Chloride complex [(n-TBA){(L_5)(Cl)}] (5a).

^{1}H-NMR (DMSO-d6, 600 MHz) δ (ppm): 0.92-0.95 (t, 12H, ~18 Hz, $TBACH_3$), 1.28-1.34 (m, 8H, $TBACH_2$), 1.54-1.59 (m, 8H, $TBACH_2$), 3.15-3.18 (t, 8H, ~18 Hz, N^+- $TBACH_2$), 3.84 (s, 1H, CH_2), 7.15-7.16 (d, 4H, ~6 Hz, Ar-H), 7.38-7.39 (d, 4H, ~6 Hz, Ar-H), 7.67-7.68 (d, 4H, ~6 Hz, Ar-H), 8.17-8.19 (d, 4H, ~12 Hz, Ar-H), 9.05 (s, 2H, NH_a), 9.64 (s, 2H, NH_b). IR spectra: 3213 cm^{-1} (N-H), 3172 cm^{-1} (C-H), 2963 cm^{-1} (C-H), 1702 cm^{-1} (C=O), 663 cm^{-1} (C-Cl). Yield 68% based on **L_5**.

2.5.3 Complexes of *meta*-cyano substituted receptors L_6-L_8

The neutral receptor-anion complexes of meta-cyano substituted receptors **L_6-L_8** with anions or hydrated-anions were attained as suitable crystals for X-ray diffraction analysis upon slow evaporation of the 5 mL basic DMF or DMSO or mixed solution of individual receptors *ortho*-**L_6** (100 mg, 0.25 mmol)/*meta*-**L_7** (100 mg, 0.25 mmol)/*para*-**L_8** (100 mg, 0.25 mmol) and excess tetrabutylammonium fluoride salts (10 eqv.). Most of the cases different shaped crystals of the hydrated or non-hydrated complexes were obtained at room temperature within one week to one month and they were collected by pressing between filter paper before characterization by different techniques. It is important to remark here that the silicon hexafluoride anion (SiF_6^{2-}) was not present in the reaction mixture before crystallization, and it is obtained by the reaction of the receptors and TBAF with glass-silica in DMF or DMSO or mixed solution, probably as a result of glass corrosion.

Octahedral hexafluorosilicate complex [(n-TBA){(L_6)(SiF_6)}] (6a).

^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm): 0.93 (t, ~7.3 Hz, $TBACH_3$) 1.30 (dd, ~14.6, 7.3 Hz, $TBACH_2$), 1.55 (d, ~ 7.6 Hz, $TBACH_2$), 3.27-3.03 (m, N^+-$TBACH_2$), 7.07 (dd, ~ 6.1, 3.6 Hz, Ar-H), 7.38 (d, ~7.6 Hz, Ar-H), 7.46 (t, ~ 8.0 Hz, Ar-H), 7.75 (dd, ~8.7, 5.2 Hz, Ar-H), 8.00 (s, Ar-H), 8.56 (s, NH_a),9.57 (s, NH_b). IR spectra: 3183 cm^{-1} (N-H), 3186 cm^{-1} (C-H), 2960 cm^{-1} (C-H), 1670 cm^{-1} (C=O), 583 cm^{-1} (C-F).Yield 66% based on **L_6**.

Hydrated hexafluorosilicate complex [(n-TBA){(L_7)(SiF_6)}] (7a)

^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm): 0.93 (t, ~ 7.3 Hz, $TBACH_3$) 1.29 (dt, ~14.5, 7.3 Hz, $TBACH_2$), 1.78-1.35 (m, $TBACH_2$), 3.24-3.06 (m, N^+-$TBACH_2$), 7.29-7.00 (m, Ar-H), 7.36 (d, ~7.7 Hz, Ar-H),7.44 (t, ~ 8.0 Hz, Ar-H), 7.63 (s, Ar-H), 7.77 (d, ~ 8.4 Hz, Ar-H), 8.01 (s, Ar-H), 9.15(s, NH_a), 9.54 (s, NH_b). IR spectra: 3229 cm^{-1} (N-H), 3187 cm^{-1} (C-H), 2961 cm^{-1} (C-H), 1702 cm^{-1} (C=O), 578 cm^{-1} (C-F).Yield 68% based on $\mathbf{L_7}$.

Naked hexafluorosilicate complex [(n-TBA){(L_8)(SiF_6)}] (8a)

^{1}H-NMR (400 MHz, DMSO-d6) δ (ppm): 0.93 (t, ~ 7.3 Hz, $TBACH_3$) 1.36-1.27 (dt, ~ 14.5, 7.3 Hz, $TBACH_2$), 1.60-1.52 (m, $TBACH_2$), 3.17-3.13 (m, N^+-$TBACH_2$), 7.54-7.35 (m, Ar-H), 7.71-7.62 (m, Ar-H), 7.97 (s, Ar-H), 8.74 (s, NH_a), 8.98 (s, NH_b). IR spectra: 3223 cm^{-1} (N-H), 3183 cm^{-1} (C-H), 2960 cm^{-1} (C-H), 1698 cm^{-1} (C=O), 571 cm^{-1} (C-F).Yield 76% based on $\mathbf{L_8}$.

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4. G. M. Sheldrick, *Crystal structure refinement with SHELXL*, *Acta Crystallogr., Sect. C: Struct. Chem*., 2015, **71**, 3.
5. Mercury 2.3 Supplied with Cambridge Structural Database, CCDC, Cambridge, U.K., 20011.
6. P. Van der Sluis and A. L. Spek, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 194.

Annexure 1

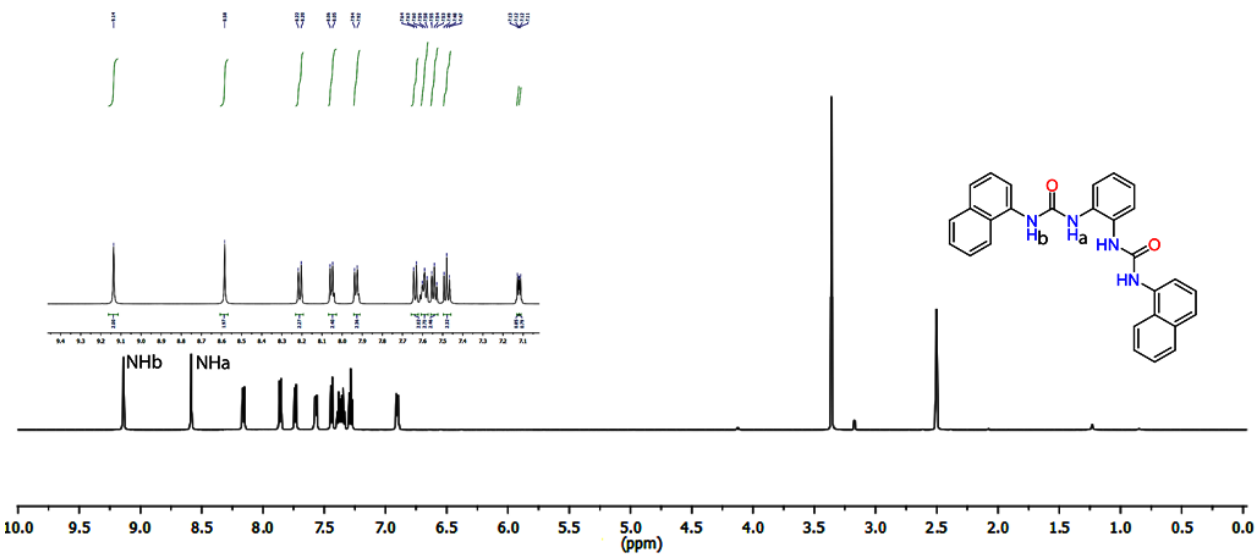


Fig. A2.1 ^{1}H-NMR spectrum of receptor $\mathbf{L_1}$ at 25ºC.

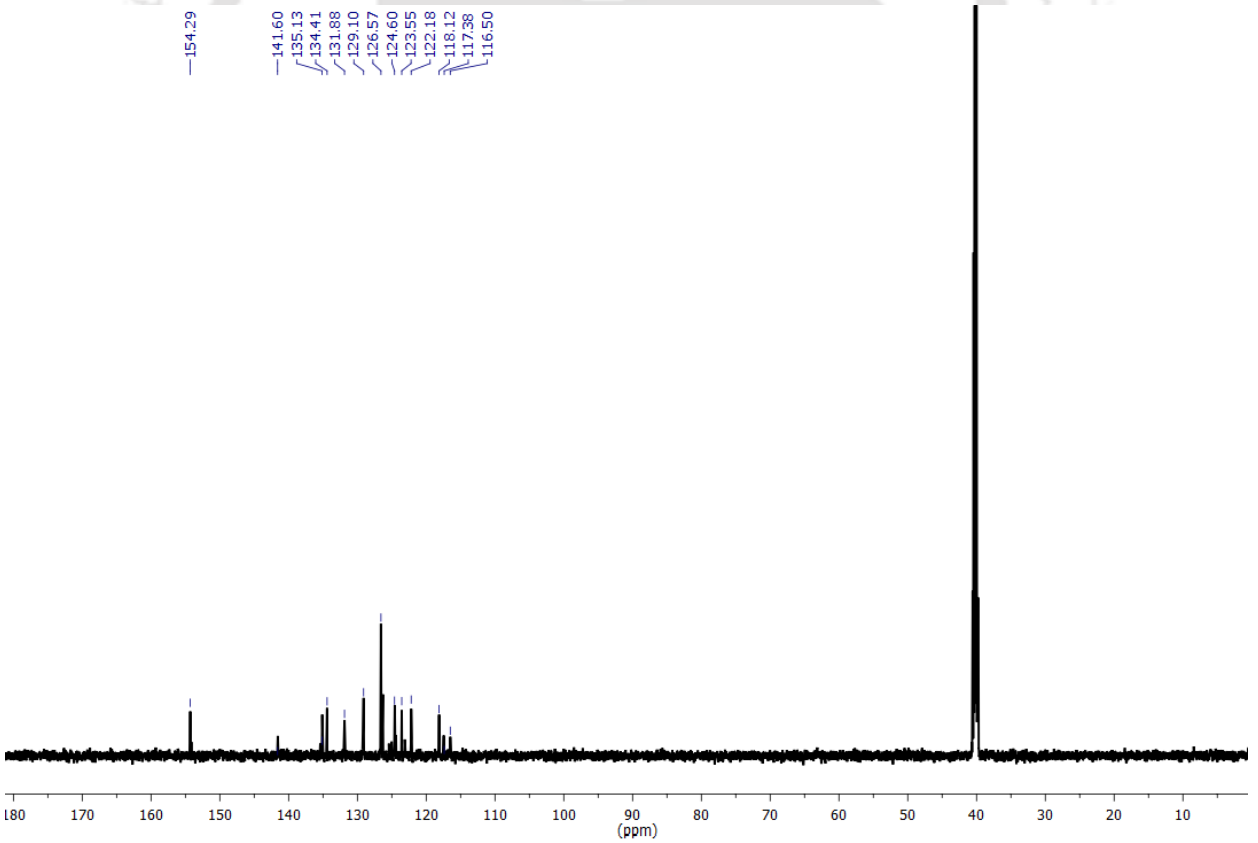


Fig. A2.2 ^{13}C-NMR spectrum of receptor $\mathbf{L_1}$ at 25ºC.

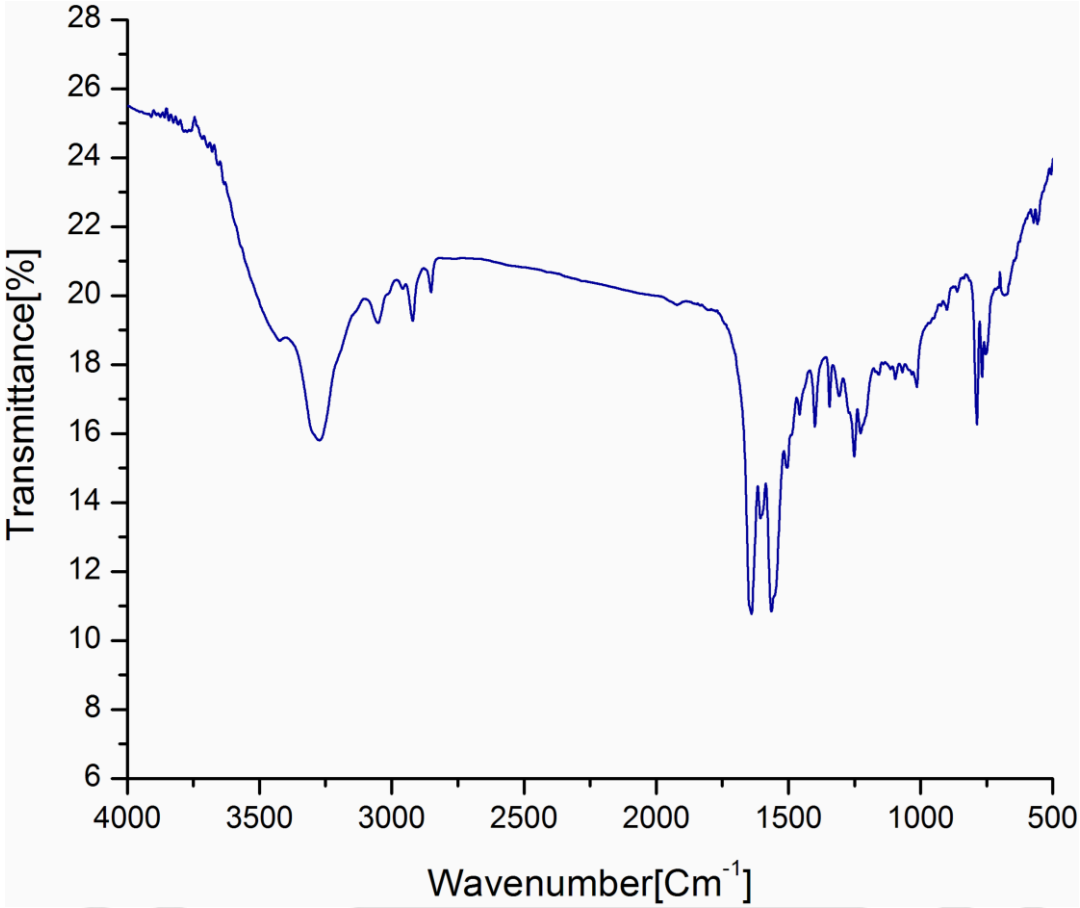


Fig. A2.3 FT-IR spectrum of receptor $\mathbf{L_1}$ recorded in KBr pellet at 25ºC.

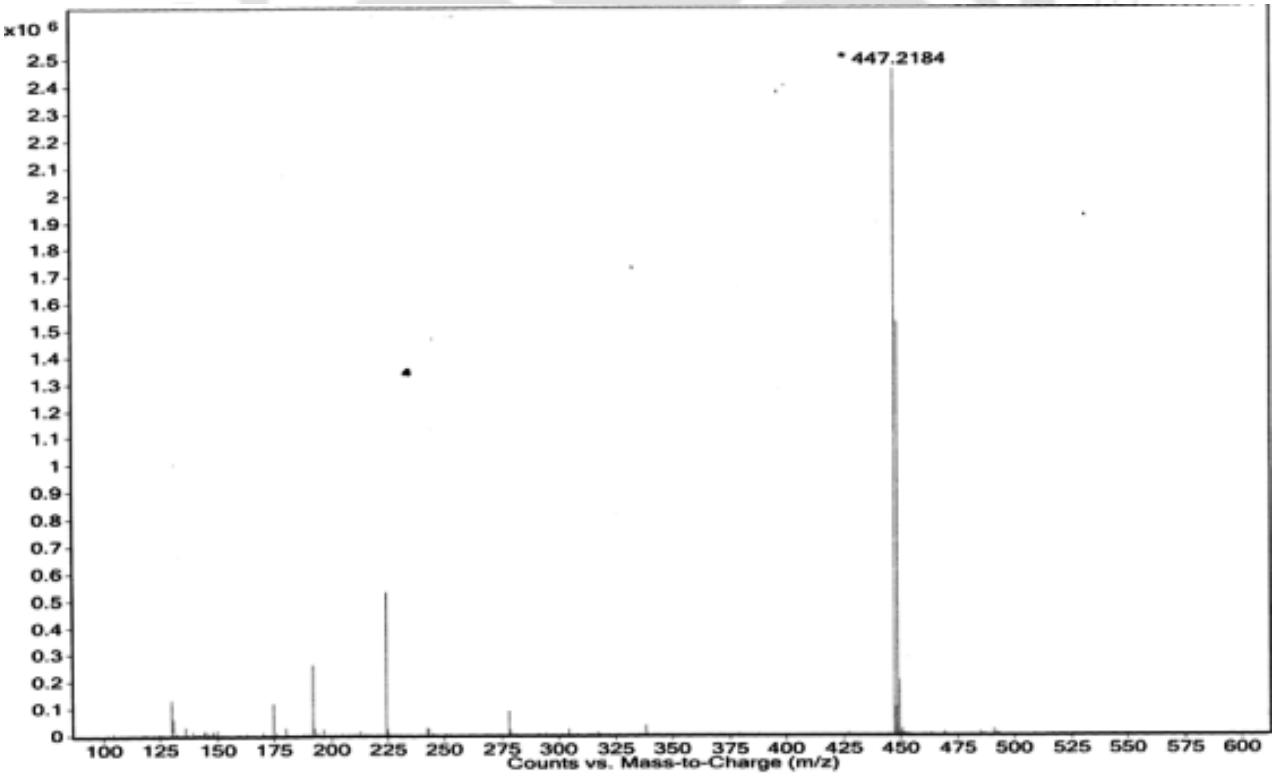


Fig. A2.4 ESI-Mass spectrum of receptor $\mathbf{L_1}$.

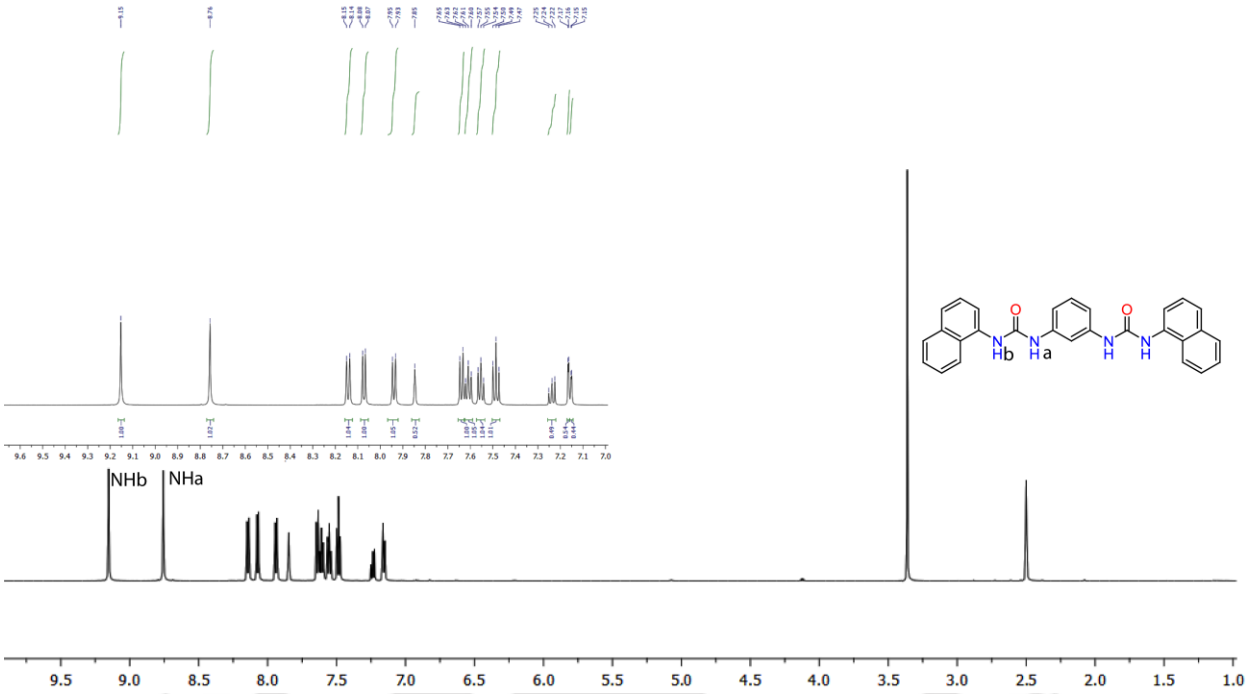


Fig. A2.5 ^{1}H-NMR spectrum of receptor $\mathbf{L_2}$ at 25ºC.

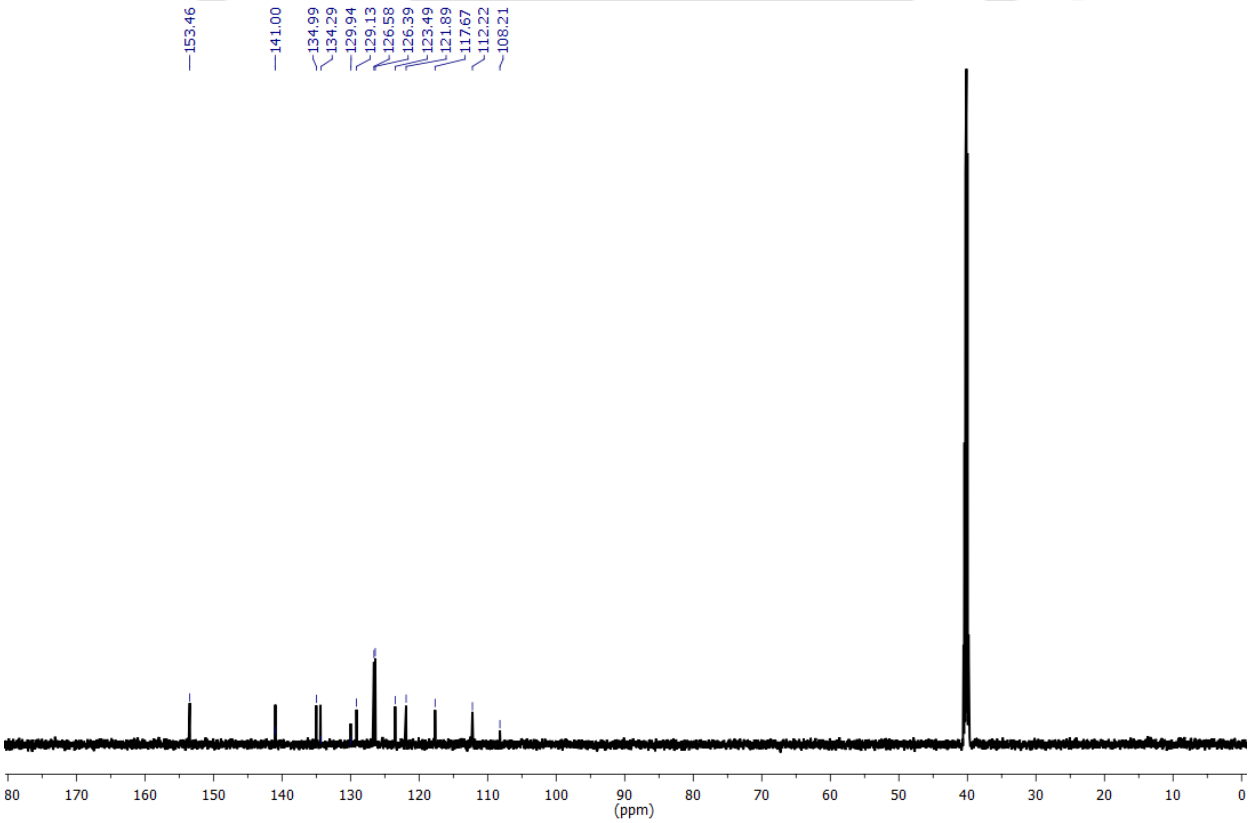


Fig. A2.6 ^{13}C-NMR spectrum of receptor $\mathbf{L_2}$ at 25ºC.

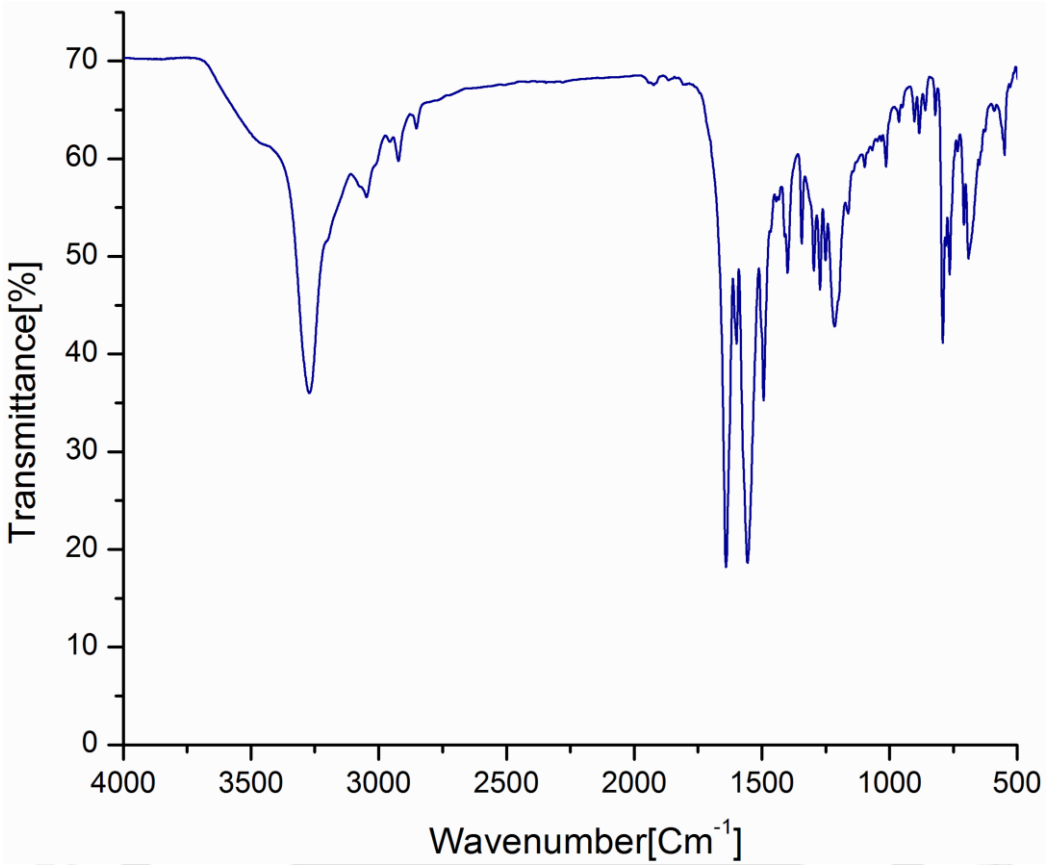


Fig. A2.7 FT-IR spectrum of receptor $\mathbf{L_2}$ recorded in KBr pellet at 25ºC.

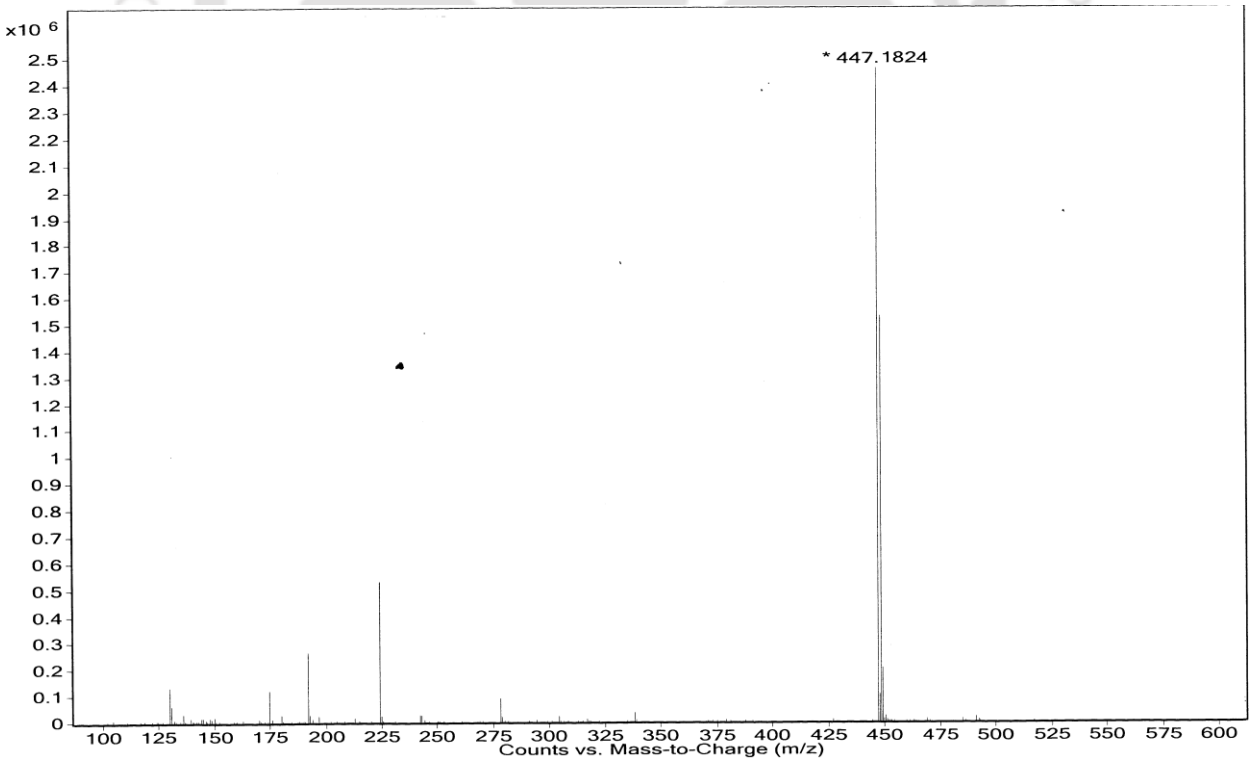


Fig. A2.8 ESI-Mass spectrum of receptor $\mathbf{L_2}$.

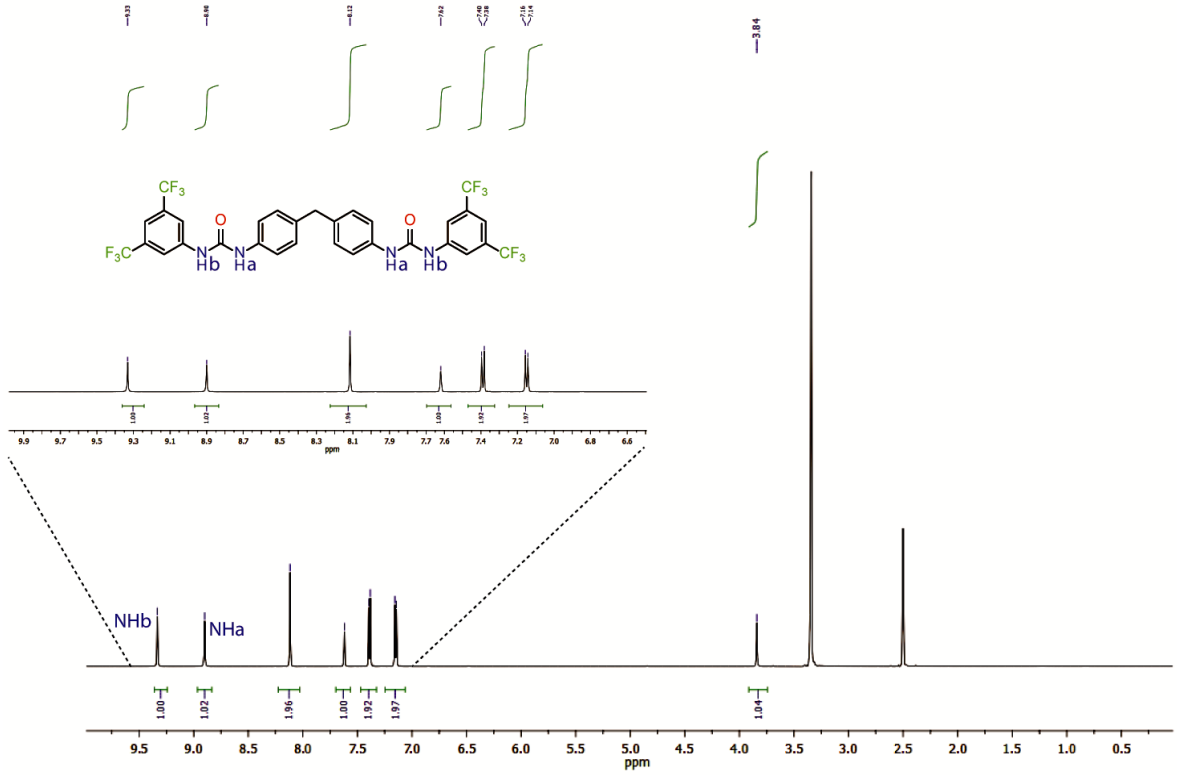


Fig. A2.9 ^{1}H-NMR spectrum of receptor $\mathbf{L_3}$ at 25ºC.

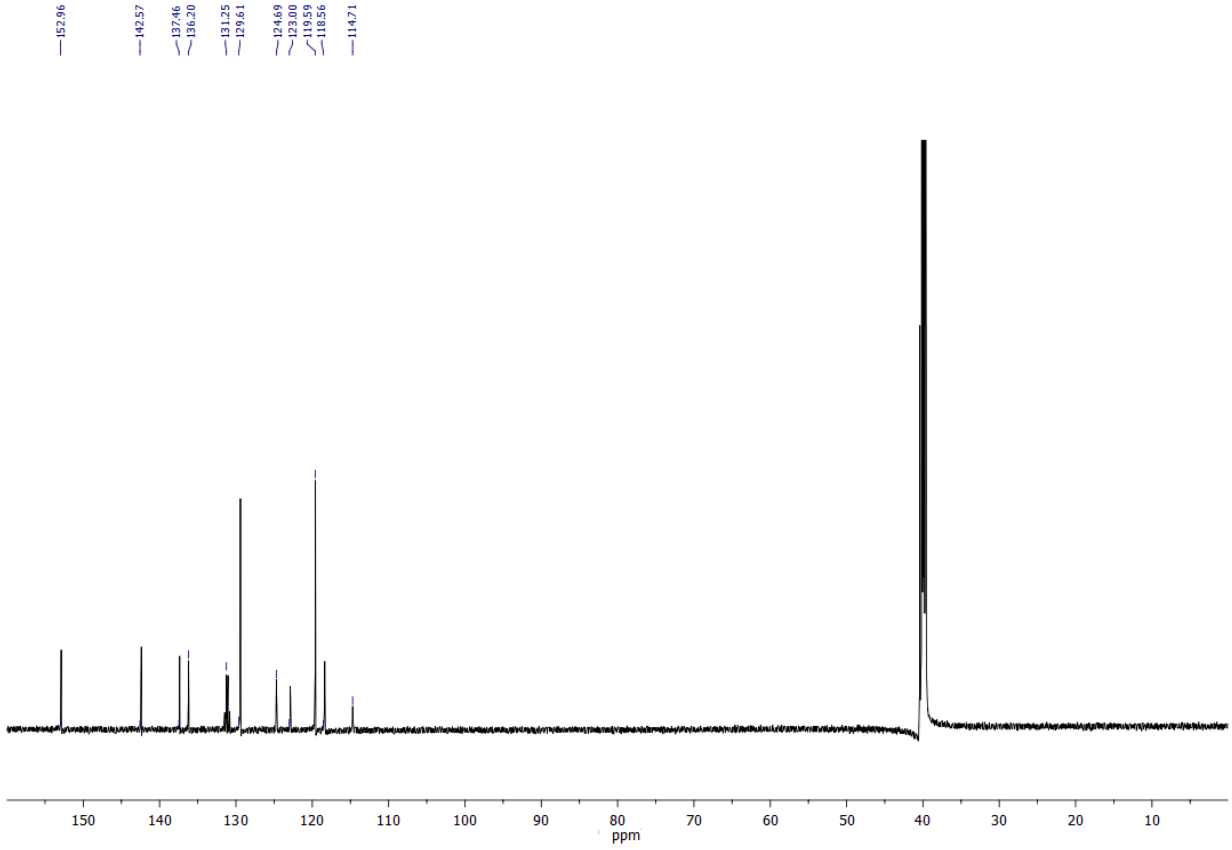


Fig. A2.10 ^{13}C-NMR spectrum of receptor $\mathbf{L_3}$ at 25ºC.

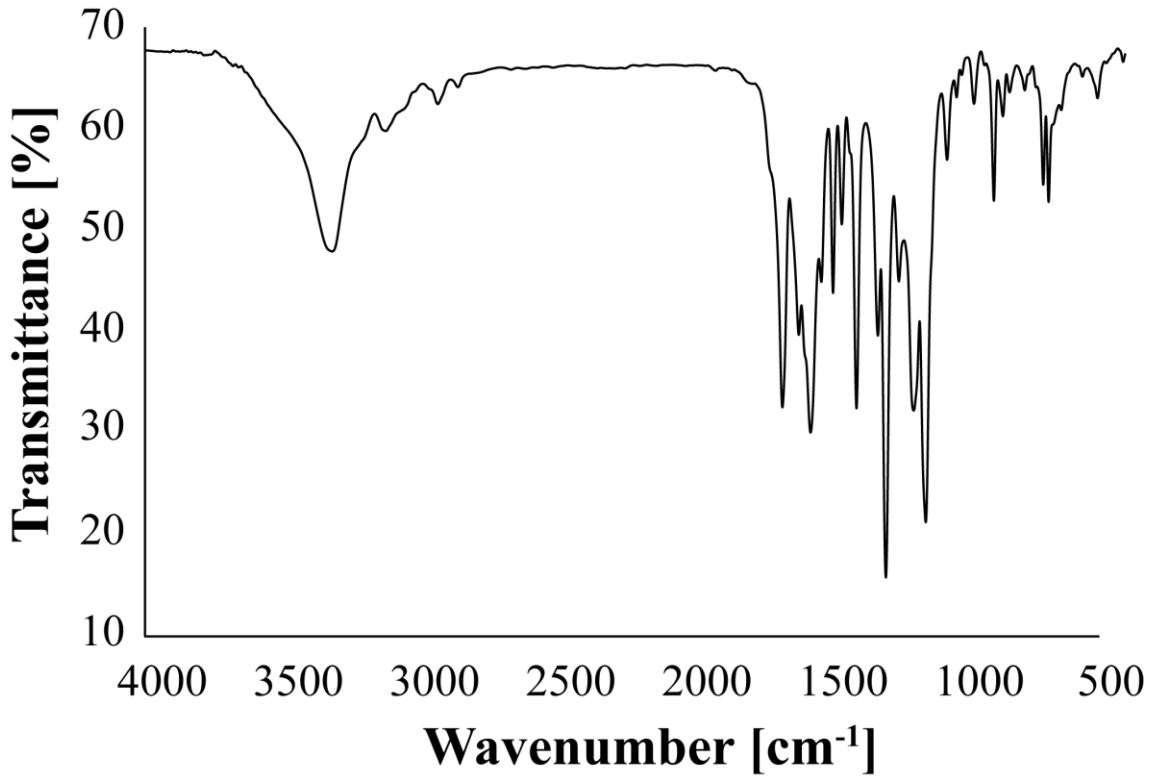


Fig. A2.11 FT-IR spectrum of receptor $\mathbf{L_3}$ recorded in KBr pellet at 25ºC.

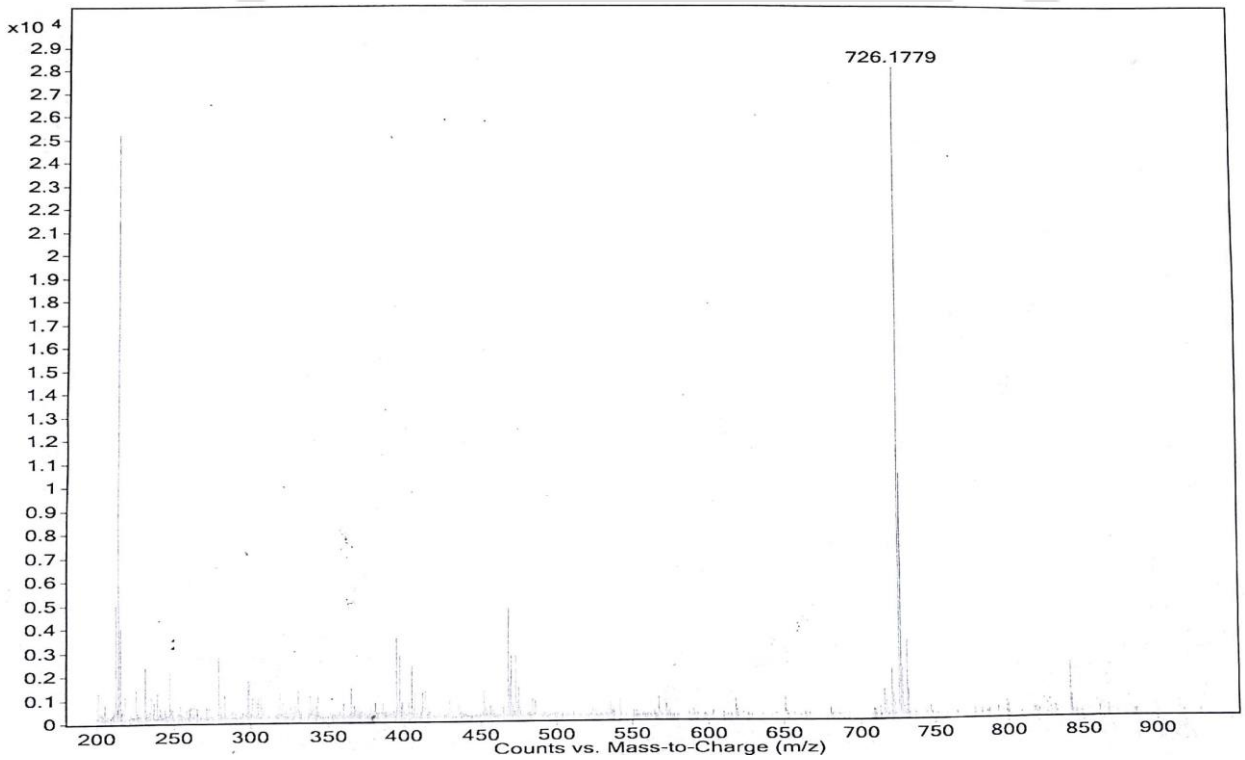


Fig. A2.12 ESI-Mass spectrum of receptor $\mathbf{L_3}$.

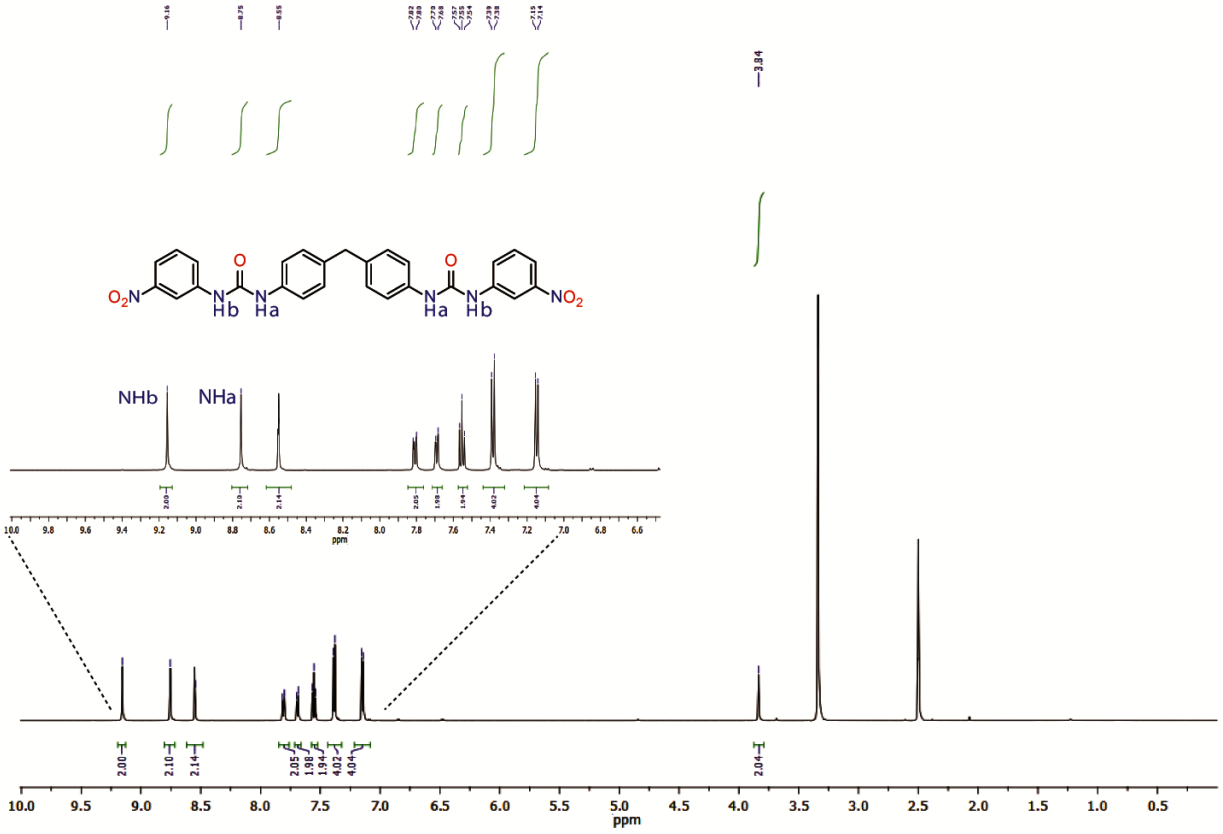


Fig. A2.13 ^{1}H-NMR spectrum of receptor $\mathbf{L_4}$ at 25ºC.

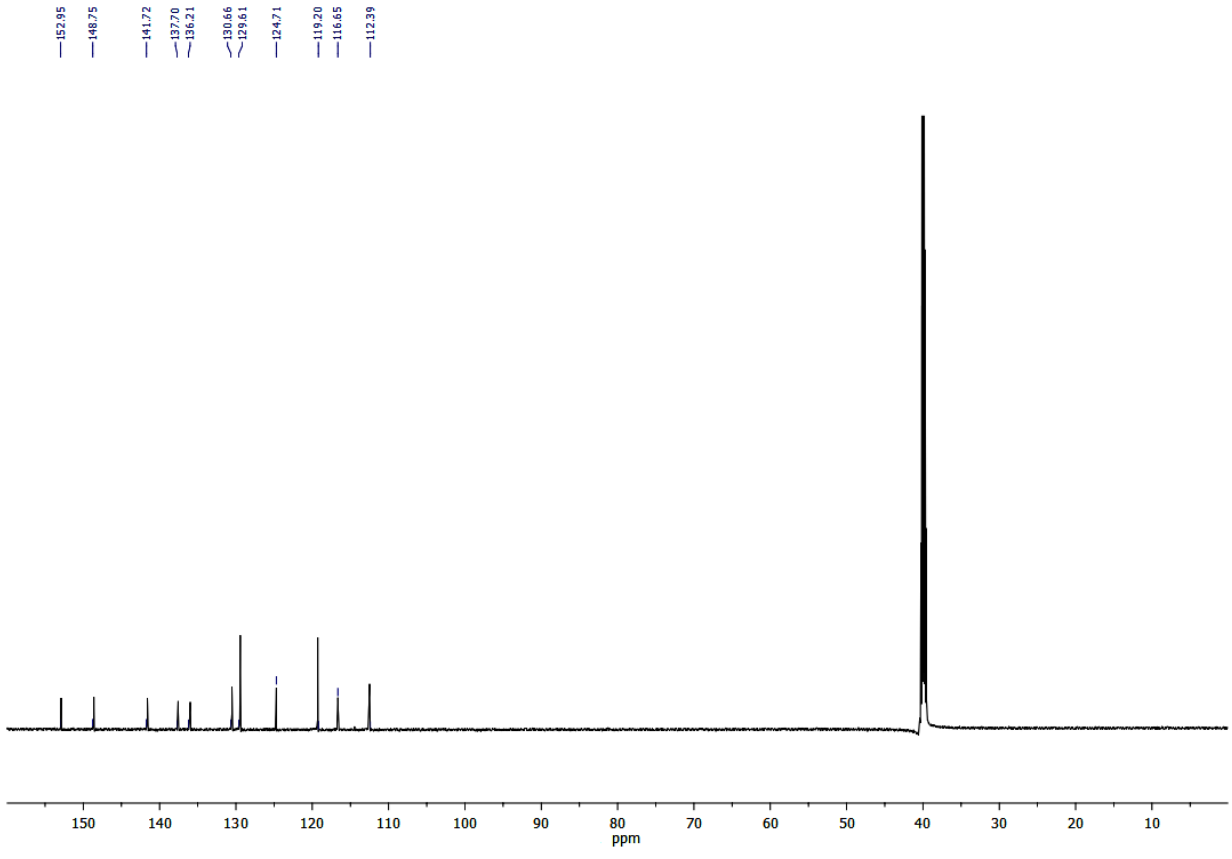


Fig. A2.14 ^{13}C-NMR spectrum of receptor $\mathbf{L_4}$ at 25ºC.

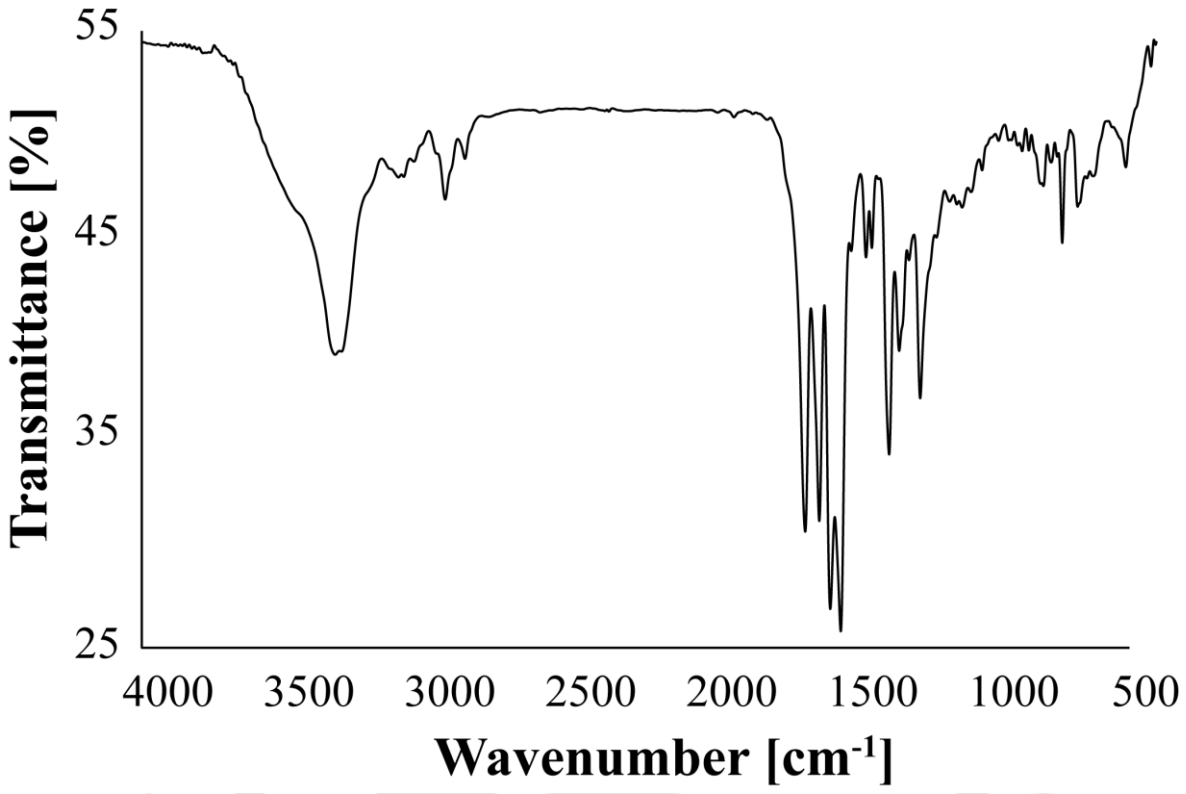


Fig. A2.15 FT-IR spectrum of receptor $\mathbf{L_4}$ recorded in KBr pellet at 25°C.

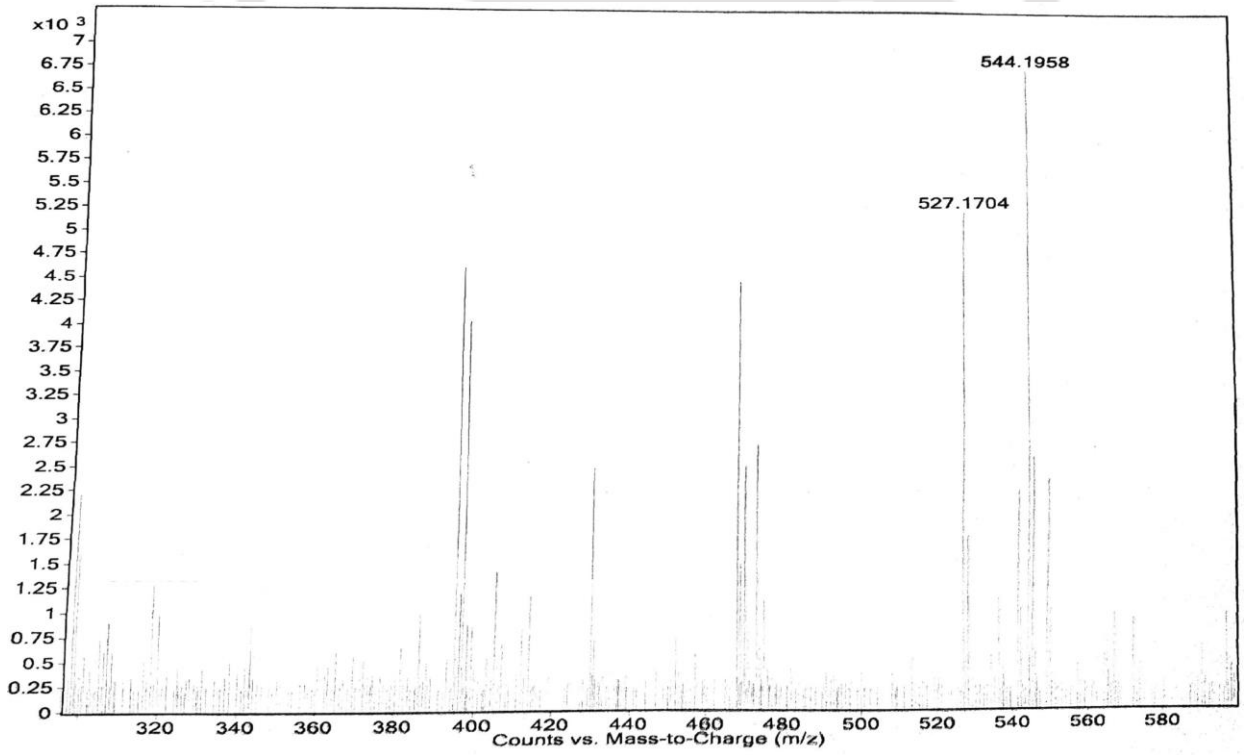


Fig. A2.16 ESI-Mass spectrum of receptor $\mathbf{L_4}$.

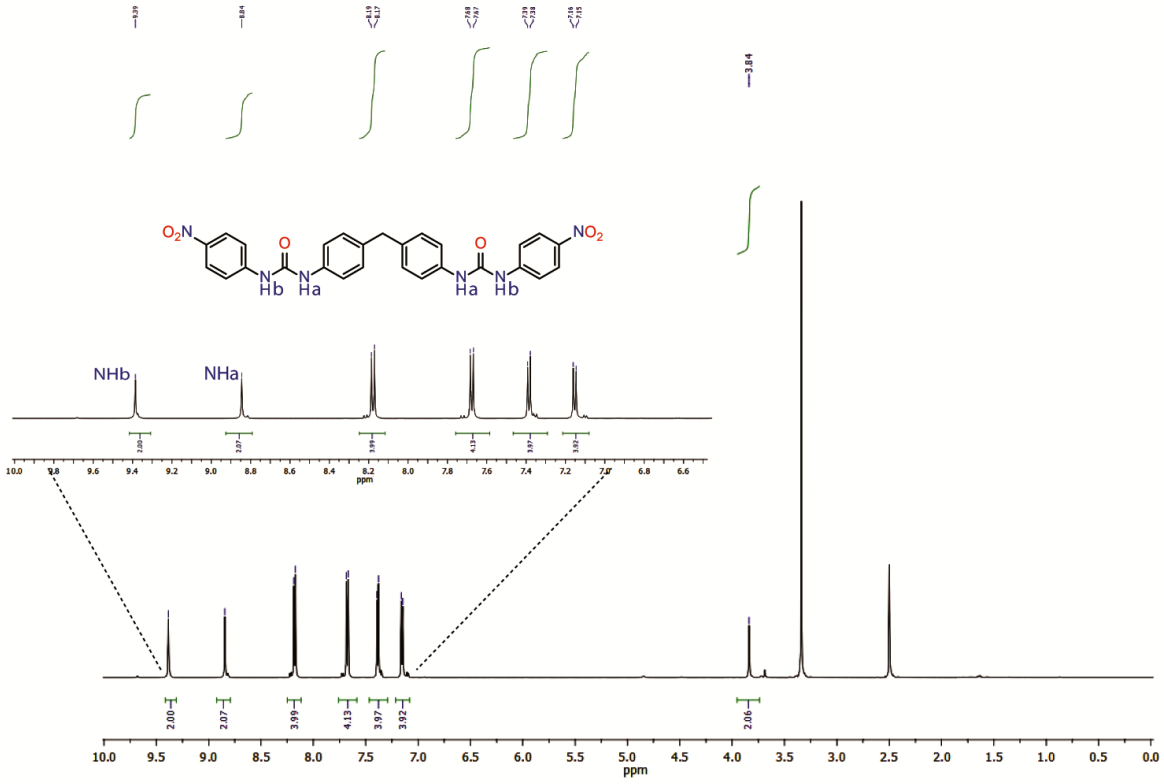


Fig. A2.17 ^{1}H-NMR spectrum of receptor $\mathbf{L_5}$ at 25°C.

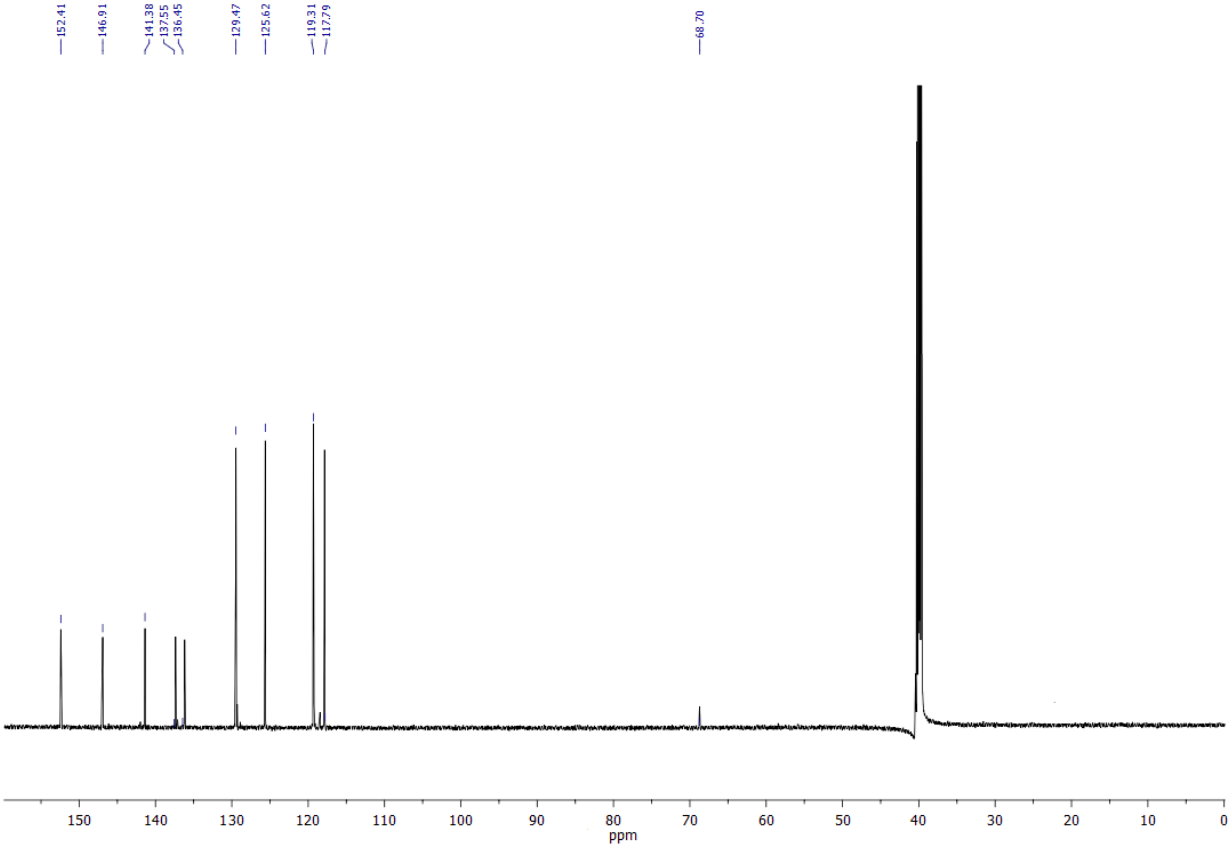


Fig. A2.18 ^{13}C-NMR spectrum of receptor $\mathbf{L_5}$ at 25°C.

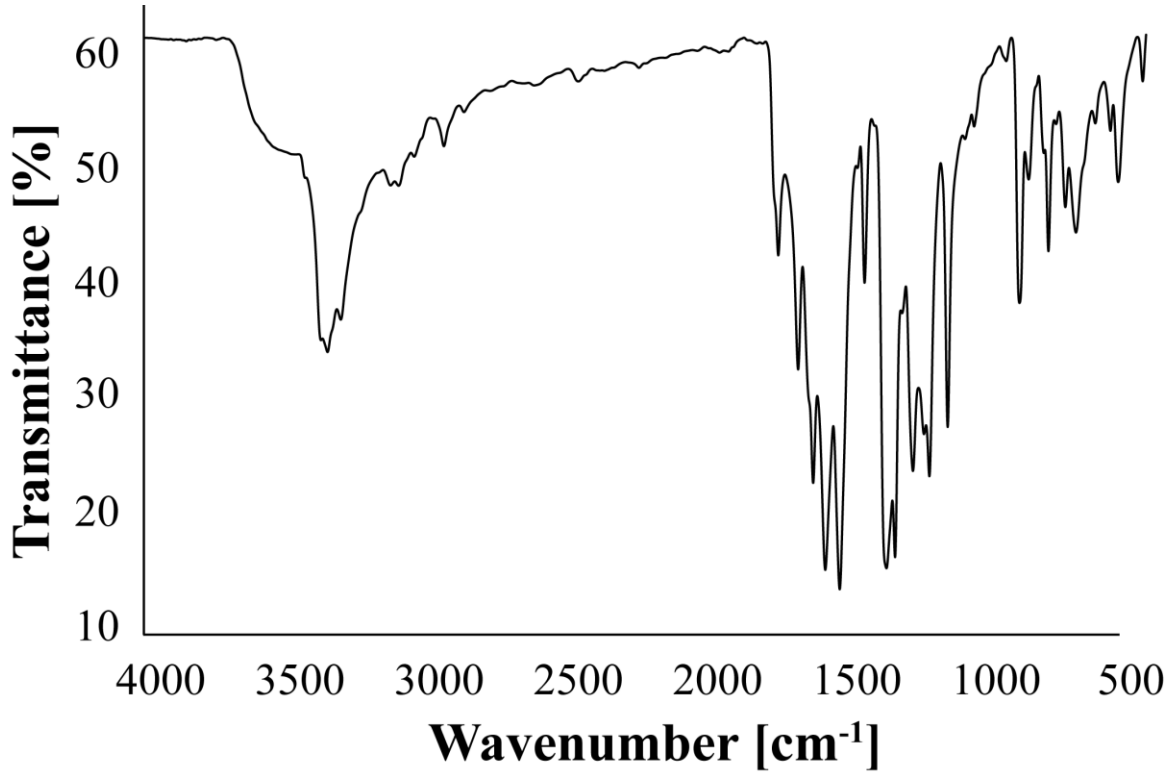


Fig. A2.19 FT-IR spectrum of receptor $\mathbf{L_5}$ recorded in KBr pellet at 25ºC.

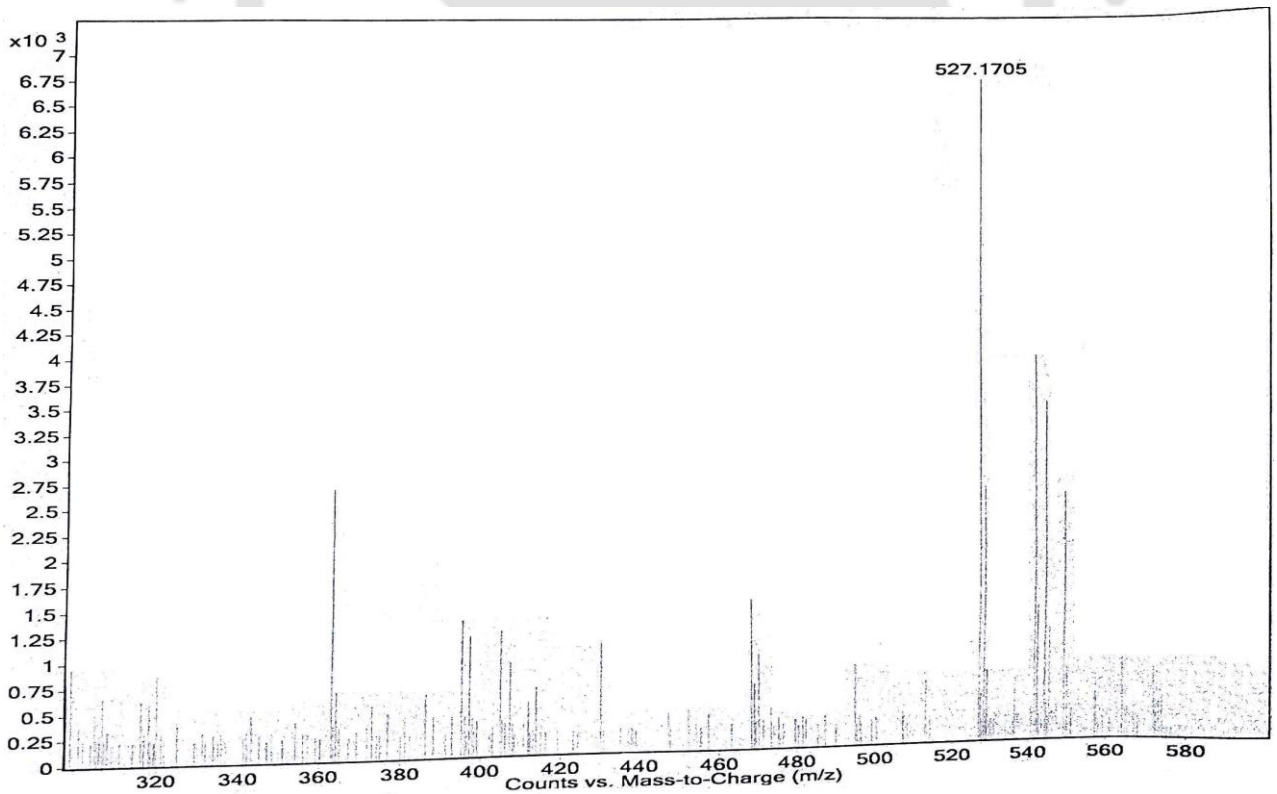


Fig. A2.20 ESI-Mass spectrum of receptor $\mathbf{L_5}$.

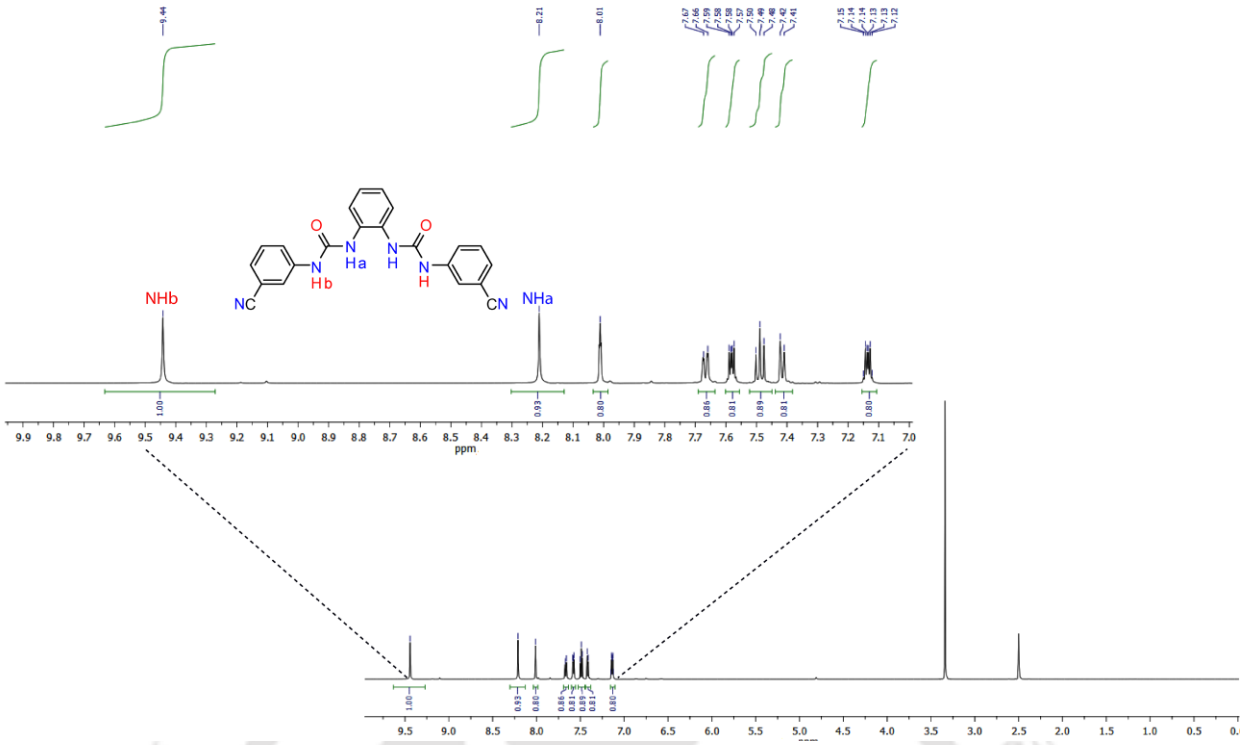


Fig. A2.21 ^{1}H-NMR spectrum of receptor $\mathbf{L_6}$ at 25ºC.

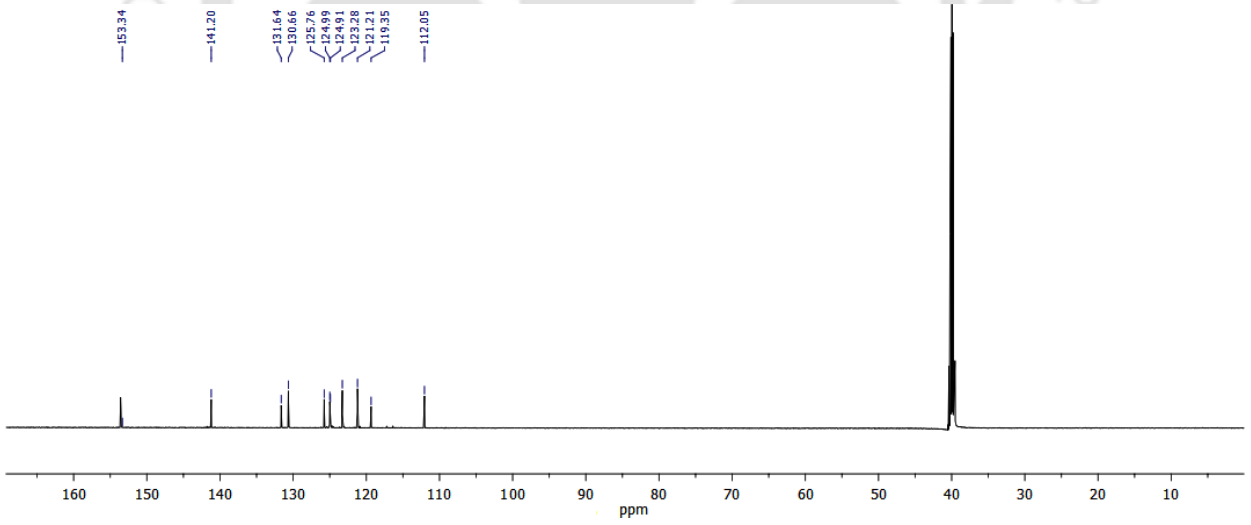


Fig. A2.22 ^{13}C-NMR spectrum of receptor $\mathbf{L_6}$ at 25ºC.

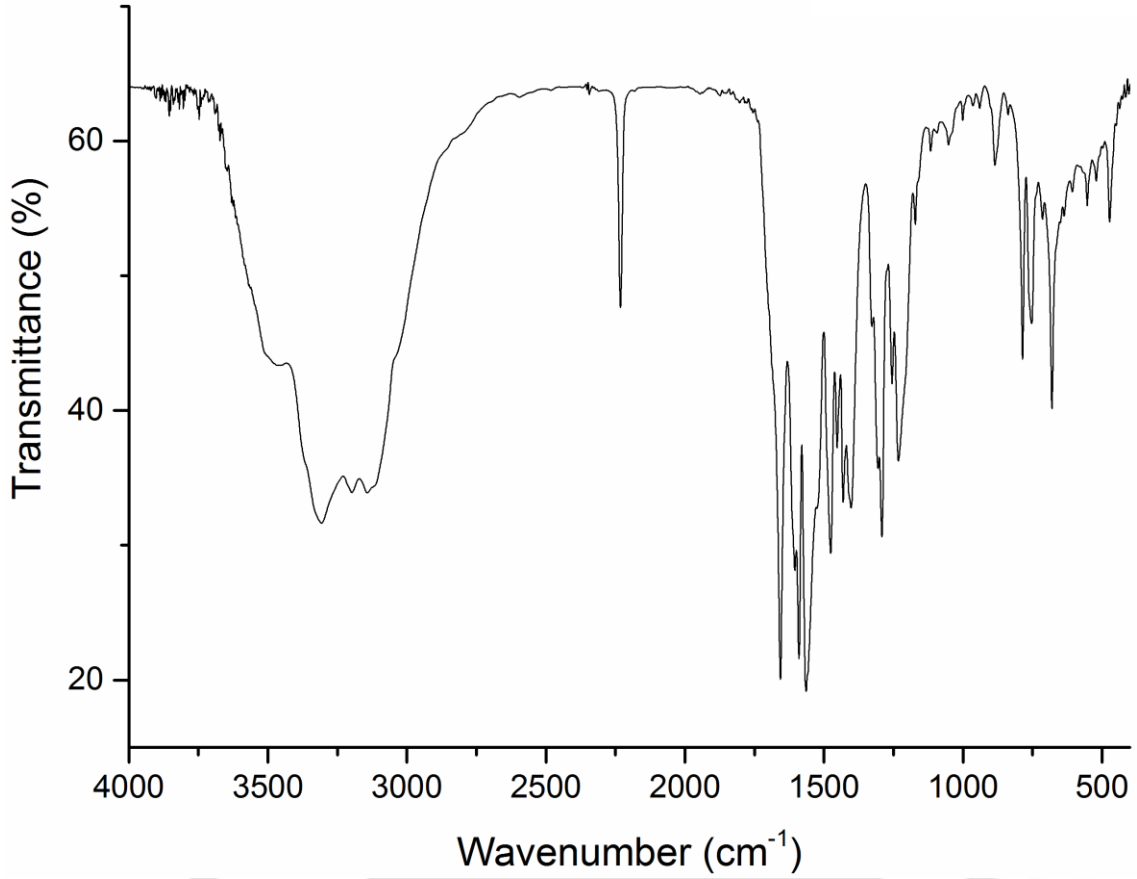


Fig. A2.23 FT-IR spectrum of receptor $\mathbf{L_6}$ recorded in KBr pellet at 25ºC.

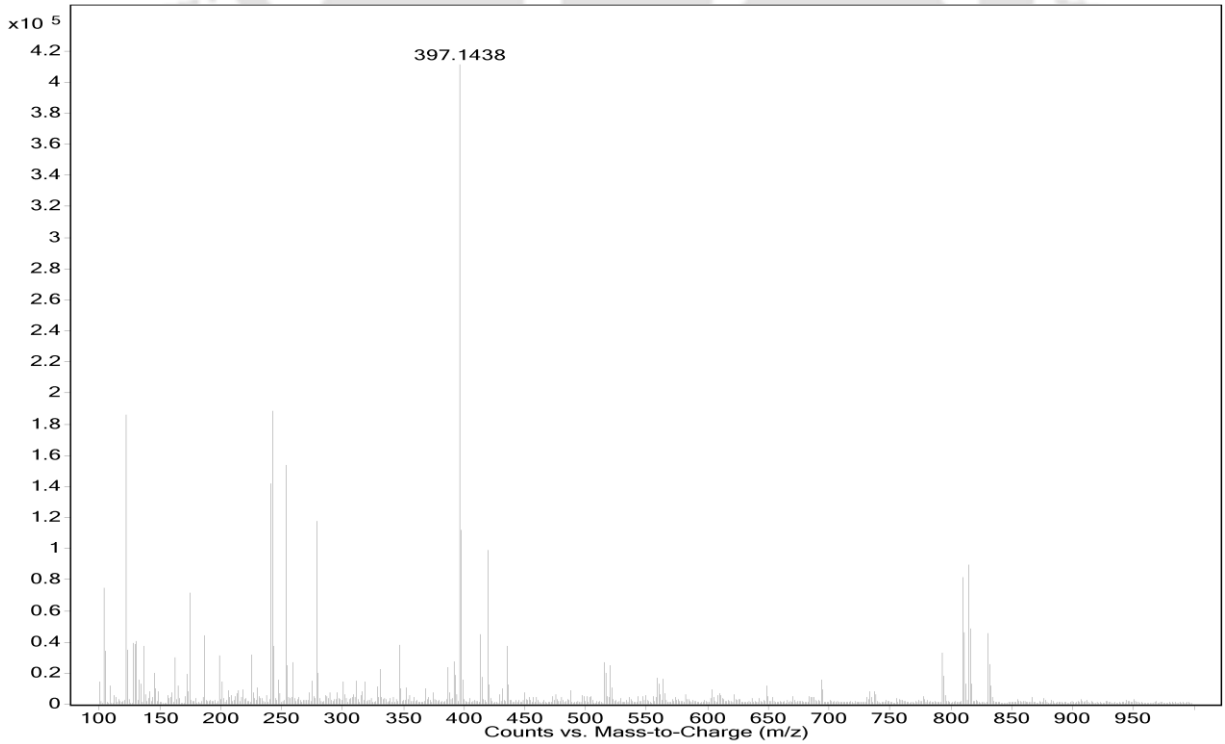


Fig. A2.24 ESI-Mass spectrum of receptor $\mathbf{L_6}$.

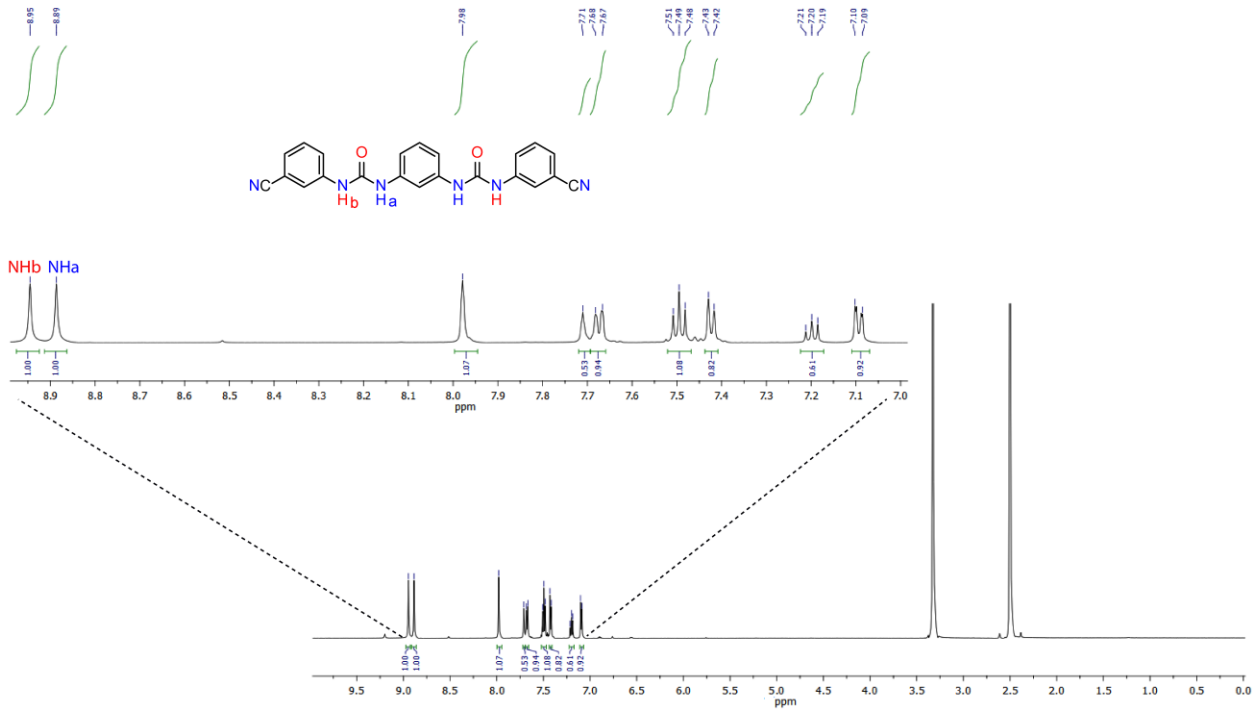


Fig. A2.25 ^{1}H-NMR spectrum of receptor $\mathbf{L_7}$ at 25ºC receptor.

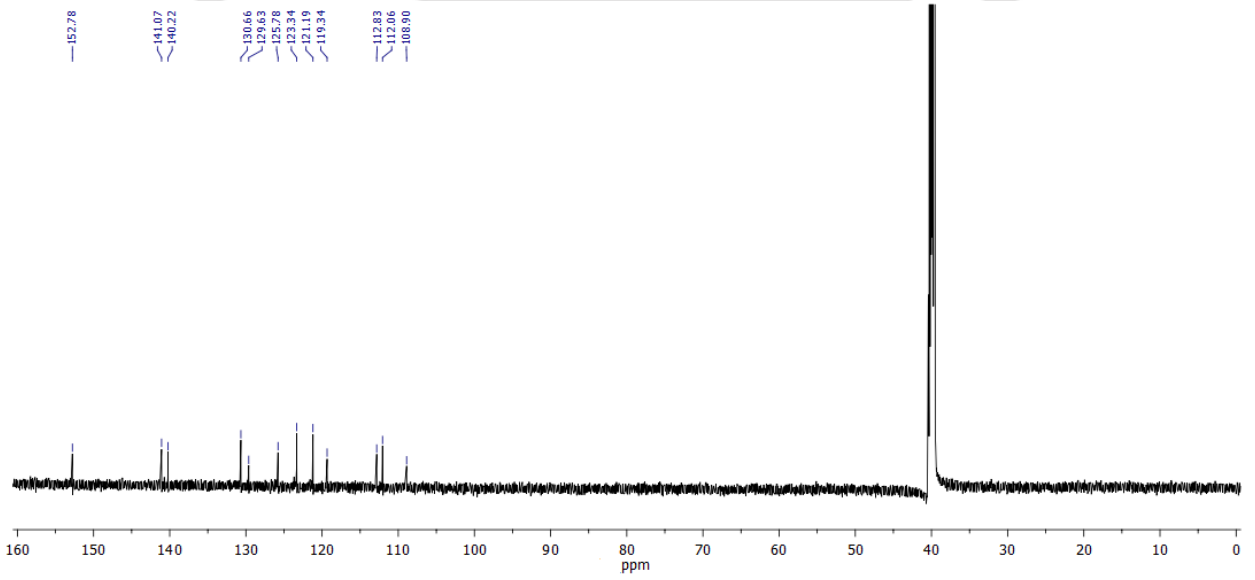


Fig. A2.26 ^{13}C-NMR spectrum of receptor $\mathbf{L_7}$ at 25ºC.

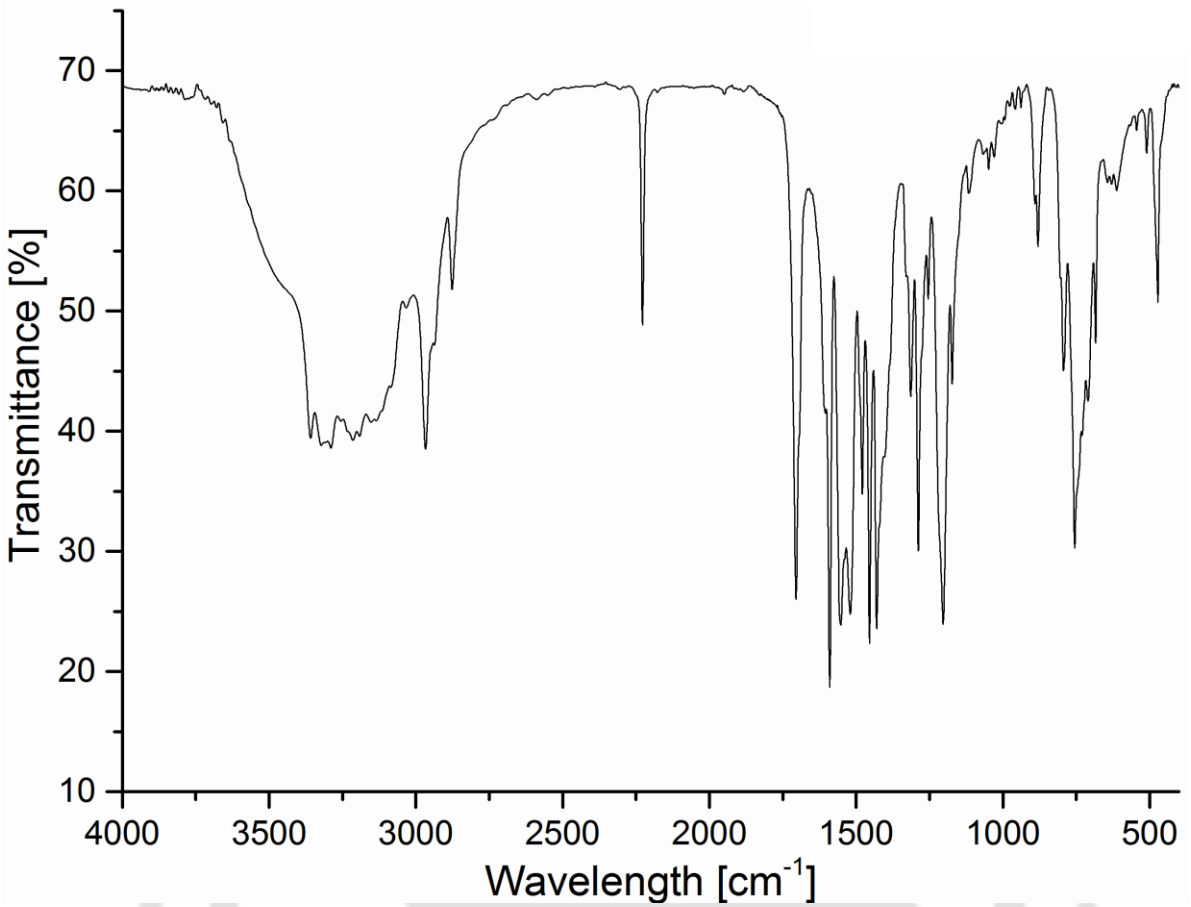


Fig. A2.27 FT-IR spectrum of receptor $\mathbf{L_7}$ recorded in KBr pellet at 25ºC.

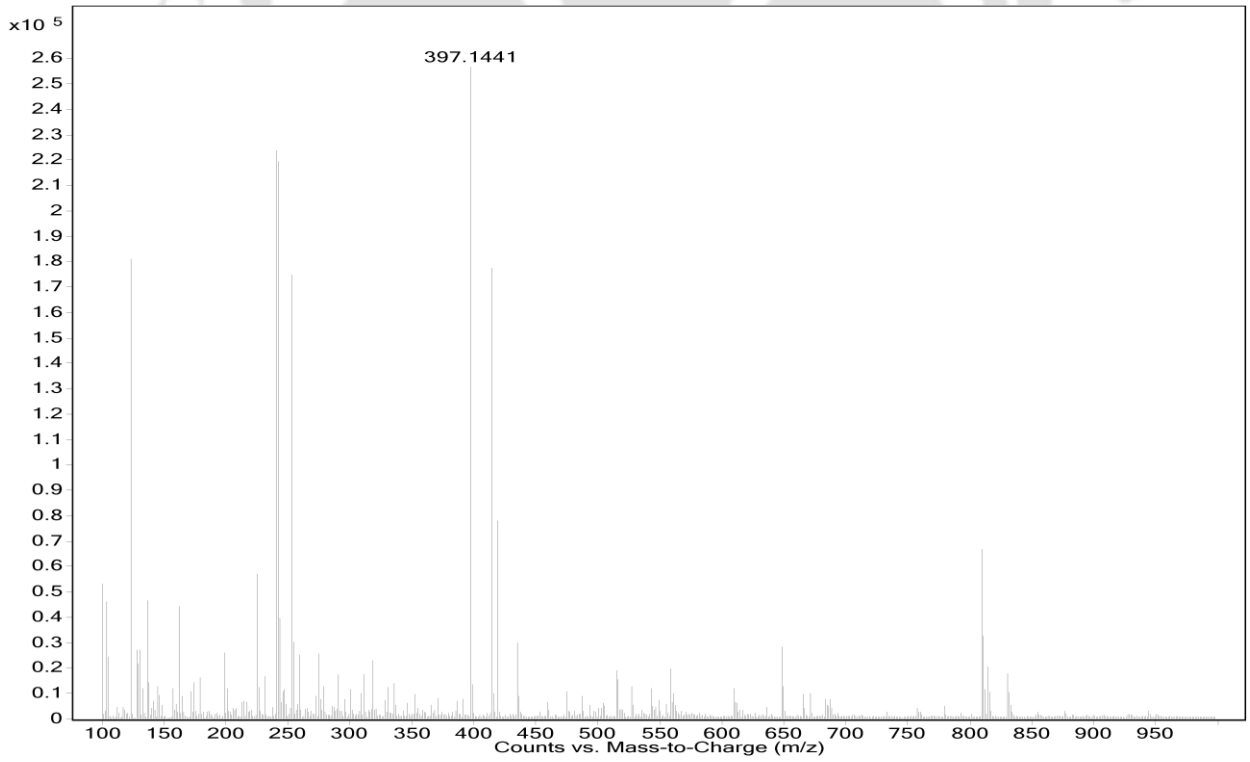


Fig. A2.28 ESI-Mass spectrum of receptor $\mathbf{L_7}$.

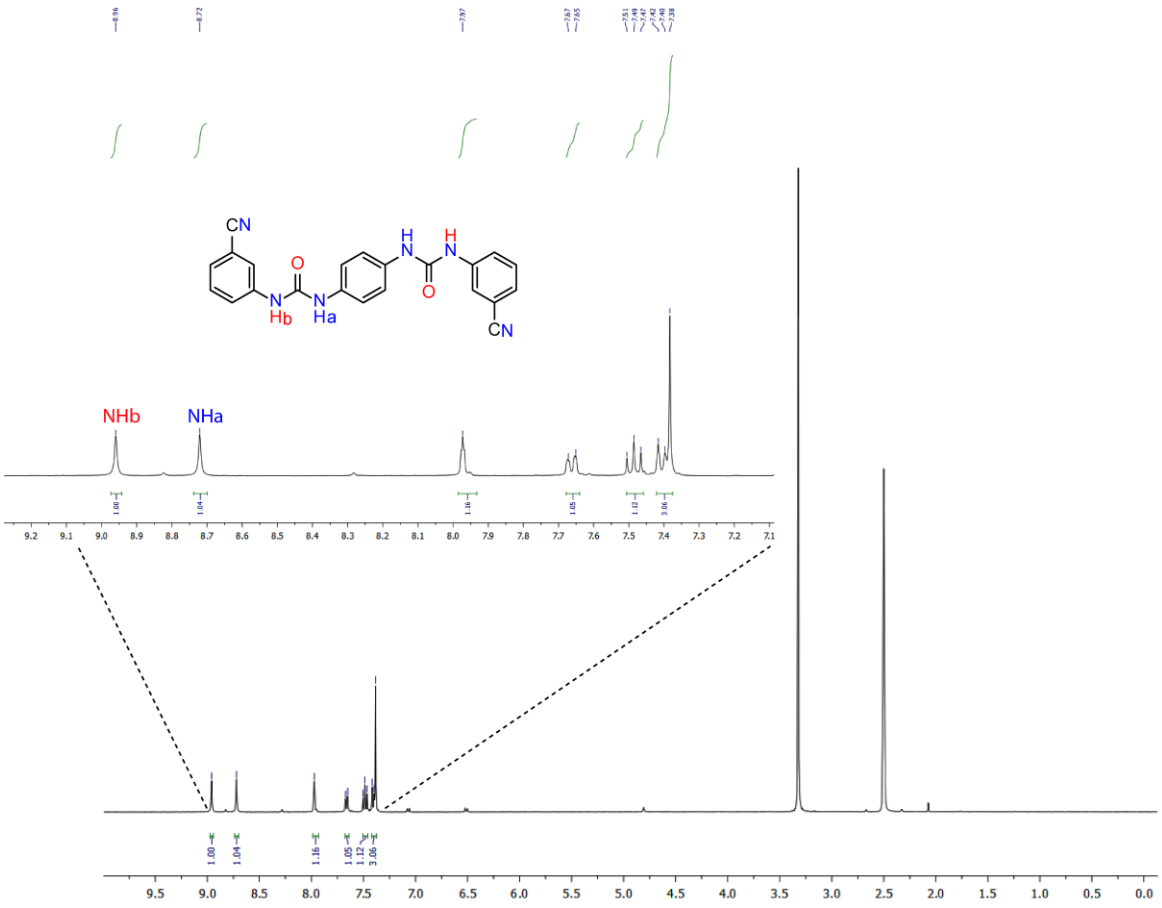


Fig. A2.29 ^{1}H-NMR spectrum of receptor $\mathbf{L_8}$ at 25ºC.

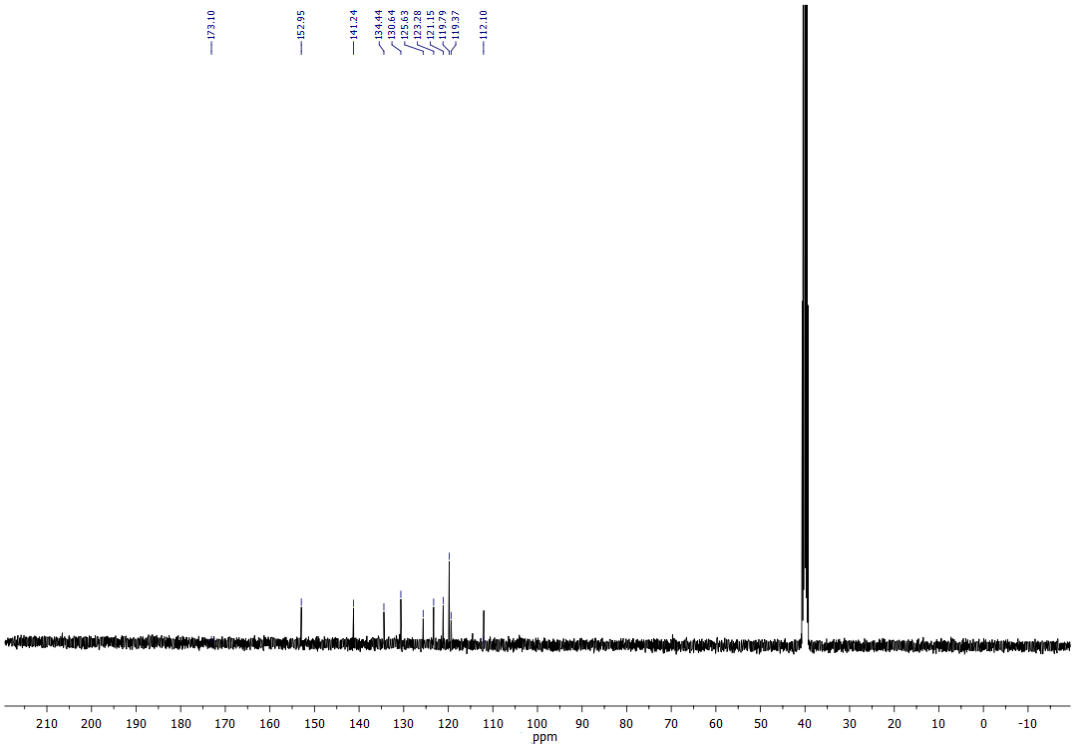


Fig. A2.30 ^{13}C-NMR spectrum of receptor $\mathbf{L_8}$ at 25ºC.

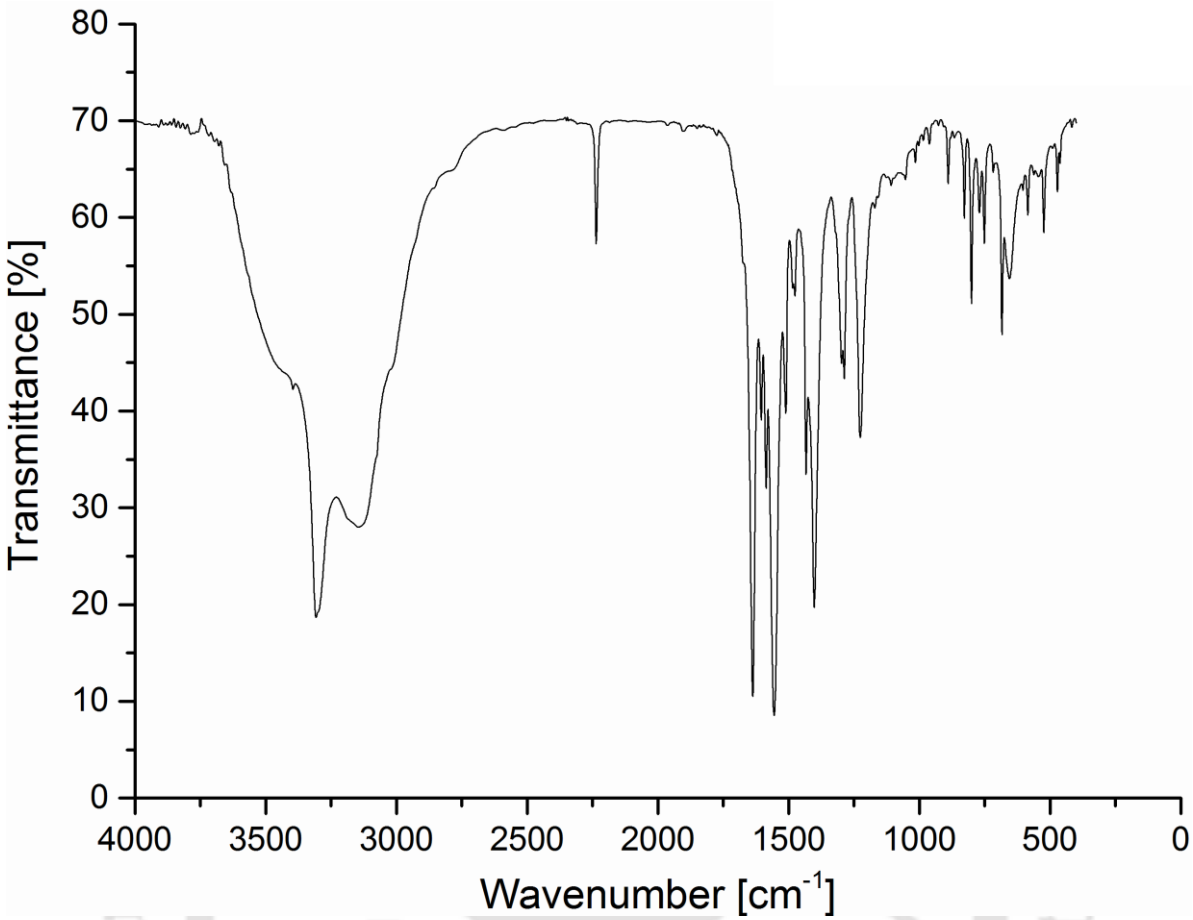


Fig. A2.31 FT-IR spectrum of receptor $\mathbf{L_8}$ recorded in KBr pellet at 25ºC.

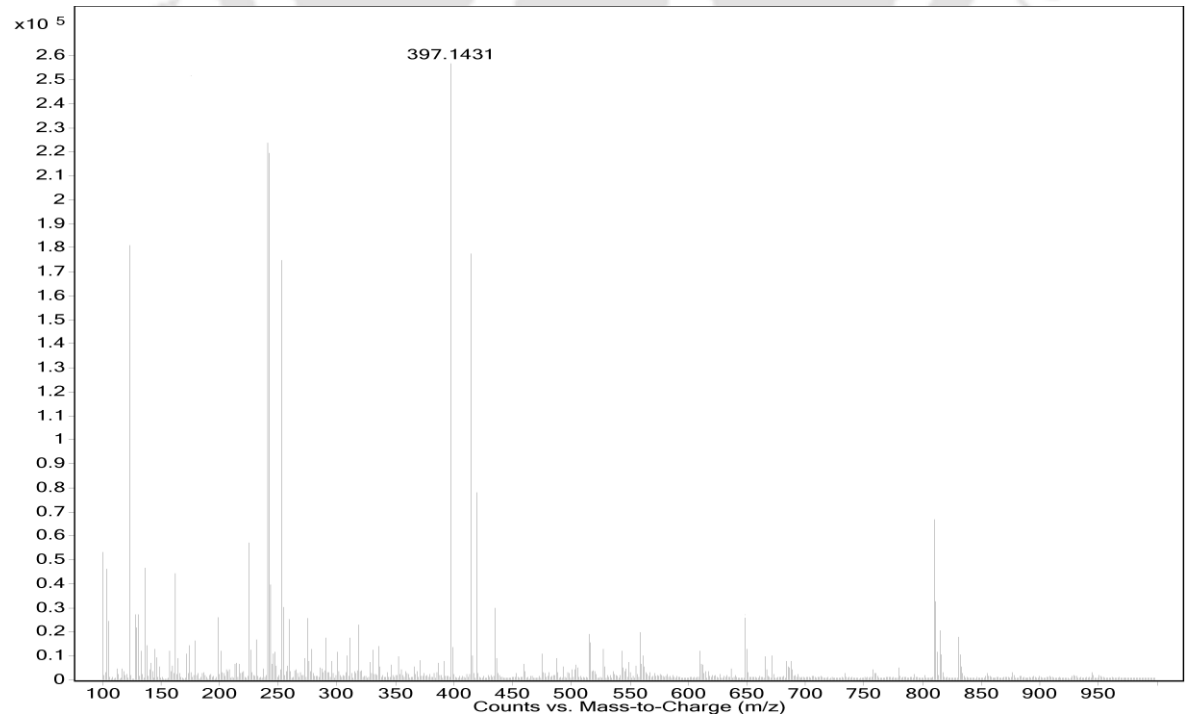
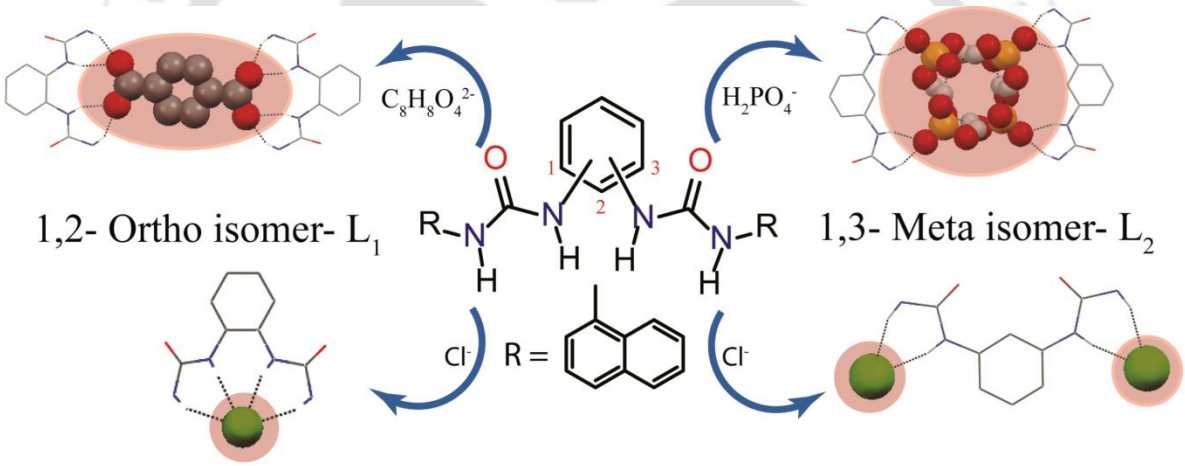


Fig. A2.32 ESI-Mass spectrum of receptor $\mathbf{L_8}$.

Chapter 3

Naphthyl Substituted Electron-Rich Bis-Urea Neutral Receptors: Halides and Oxyanions Binding via Cooperative vs. Non-Cooperative Modes

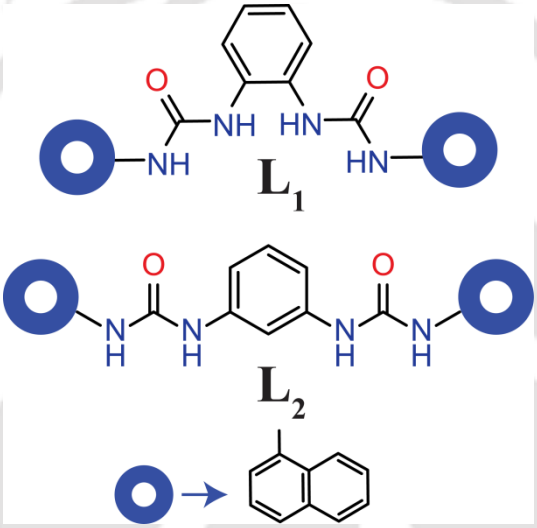


3.1 Background and Focus of the Chapter

Anion coordination by hydrogen bonding platforms within the broad area of supramolecular chemistry has emerged into active field of research.[1] As anions play critical and important roles in living organisms as well as in a range of biological, medical, industrial and environmental processes,[2] the entrapment of anionic guests by a variety of non-covalent interactions within the multi-armed abiotic host receptor scaffolds have emerged as topics of prime importance in supramolecular chemistry.[3] For binding of various anionic guests, neutral receptors comprising of specific binding sites from amide,[4] urea,[5] pyrrole,[6] and indole[7] functionalities, as in natural system protein can bind anions efficiently and selectively *via* non-covalent interactions, therefore researchers get motivated to develop multi-armed abiotic host receptor. Encapsulation of chloride within the cleft diammonium receptor, which were essentially the first anion complexes was reported by Park and Simmons in the year 1967.[8] Over the past few years, the field has grasped much more consideration and it is well established that anion complexes display double valance as transition metal complex and there anions behave as the "primary valence" while "secondary valence" is satisfied by H-bonds between the receptor and guest anion which offer a coordination number.[9] On this basis, based on accomplishment of overall coordination saturation of anions the design of prospective receptors are constructed. Thus synthetic design of a receptors proficient of strong biding towards anions of different dimensionality (tetrahedral, planar, spherical) is an area of enormous interest.[10] Most of the commonly reported urea receptors consists of electron-withdrawing group making the receptor more electron deficient in nature to assist the binding of anion.[11] Hence, in contrary our challenge is to design and syntheses of urea functionalized receptor comprising electron rich group. Recognition of tetrahedral oxyanions among the several oxyanions, mainly phosphate by entrapment inside the appropriate neutral receptor has been the focus of research interest, especially in sulfate and phosphate binding proteins[12] because of their roles in physiological and biological processes.[13] $H_2PO_4^-$ is most abundant amongst all of the Inorganic phosphate that occurs in three different forms ($H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}). Self-complementary H-bonding in cluster chemistry among $H_2PO_4^-$ anions under certain circumstances create self-aggregated anion assemblies, called as "anion clusters" in solid-state. $H_2PO_4^-$ anion shows both H-bond donor and acceptor properties similar to water molecules. Distinct oligomeric structures of $H_2PO_4^-$ anions having cyclic dimers, trimers, tetramers, hexamers, and octamers are well defined in the literature.[14]

This chapter describes anion coordination behaviour of two electron-rich naphthyl ring containing bisurea receptor resulting from *ortho* (**L_1**) and *meta* (**L_2**)-phenylenediamine. Receptor

L_1 self-assembled in presence of organic terephthalate anion into a dimeric pseudo-capsular host assembly sealed by tetrabutylammonium counter cation (Complex **1c**). However, **L_2** self-assembled in 2:4 host-guest fashions (Complex **2d**) with H-bonded dihydrogenphosphate tetrameric anionic guest in the presence of excess n-TBA (H_2PO_4). Further, receptor **L_1** has been found to self-assembled into unimolecular cooperative 1:1 complex in presence of spherical chloride anion (Complex **1a**) and planar acetate anion (Complex **1b**). Moreover, receptor **L_2** forms similar kind of non-capsular host-guest assembly in presence of spherical halides like Cl^-, Br^-, and F^-. The results obtained in the solid state studies were validate by ^{1}H-NMR titration experiments have also been performed using n-TBA salts of anions to inspect the solution state anion binding behaviour of isomeric receptors **L_1** and **L_2**.



Scheme 3.1 A comprehensive representation of molecular receptor structures.

3.2 Design aspects of anion binding receptors L_1-L_2

Two isomeric bis-urea receptors **L_1** and **L_2** having *ortho* and *meta*-phenylenediamine base were synthesized in great yield. In acetonitrile medium, by the reaction of one equivalent of *o*-phenylenediamine and *m*-phenylenediamine using two equivalents of 1-naphthyl isocyanate, bis-urea receptors **L_1** and **L_2** (Scheme 3.1) have been produced respectively. To coordinate with the anions of different sizes, an appropriate artificial receptor should have possessed a particular rigid or flexible supramolecular structural design. Both the receptors **L_1** and **L_2** hold their rigid structural design keeping the neighbouring urea moieties of two aromatic moieties which can accept guests of diverse dimensionality either in cooperative syn-fashion or in non-cooperative anti-mode of urea groups, so thus having various interacting possibilities depending upon the guests as well as positional aromatic functionalization of hosts. X-ray analyses of receptor anion

complexes have given the detailed structural information which demonstrates the divergences of binding with a particular receptor with the particular anion. Traditionally, crystallization has been the main focus in anion-recognition chemistry to understand the structural insight of receptor-anion. Structural information obtained from single crystal X-ray analyses of the isolated crystals provides insight into the proper binding topology of anions with the neutral receptor molecules. Efforts were made to explore the solid-state binding properties of $\mathbf{L_1}$ and $\mathbf{L_2}$ with various anions in different crystallization conditions, by charging excess quaternary ammonium (*n*-TBA/TEA) anion salts to the individual solutions of receptors in aprotic solvents such as MeCN, DMF and DMSO.

3.3 Cooperative vs. non-cooperative binding of spherical halides: Structural diversity in chloride complexes

Structural elucidation of complex **1a** [($\mathbf{L_1}$.TBACl)] revealed the unimolecular self-assembly of $\mathbf{L_1}$ in presence of spherical chloride guest assemblage within its complementary cavity (Fig 3.1a) suitably sealed by two n-TBA cations (Fig. 3.1a). X-ray analysis exposes the occurrence of cis-orientation adjacent urea -NH moieties of particular receptor which help in the 1:1 host-guest assembly formation by cooperative H-bonding interactions of urea N-H group and chloride ion through four N–H···Cl interactions. Additionally, the non-capsular assembly of chloride and $\mathbf{L_1}$ receptors are stabilized by two C–H···O, C–H···Cl and two weak C–H···π supportive interactions between the two exterior n-TBA units with chloride and receptor, respectively. The stoichiometry of the complex **2a** is 1:1.5 and it is confirmed by the asymmetric unit of the crystal structure. In DMSO solution, receptor $\mathbf{L_2}$ in the presence of excess chloride ions forms 1.5:2 host-guest complexations in non-cooperative way through different number of H-bond sharing of urea groups from two symmetrically identical receptor units. Single crystal X-ray structure of complex **2a** reveals that two symmetrically independent chloride anions receive six strong N–H···Cl bonds [2 for Cl1 and 4 for Cl2] amongst which one receptor unit donated four H-bonds and rest of the H-bonds are contributed by the urea moieties of other identical receptor unit of the non-capsular 1.5:2 assembly (Fig. 3.1c). Additionally, the $\mathbf{L_2}$-chloride complex is stabilized by three C–H···O and three C–H···π interactions of receptors and tetrabutyl ammonium counter-cations. In case of ortho substituted ligand all the N–H groups of the both the arms are pointed inward and converged towards the same chloride anion. However in *meta* substituted ligand, N–H groups of both the arms of the dipodal ligand are pointed in the opposite direction and bind two different chloride ions simultaneously. Thus, each arm of complex **2a** is more planar in comparison to complex **1a** (torsion angle between the naphthalene ring and the

urea NH is ~1718 in complex **1a** and ~1758 in case of complex **2a** respectively). This is also reflected in the relative bond distances of both the complexes. Stronger binding is observed in complex **2a** (N–H···Cl) bond distances are 2.478A^{o} and 2.333A^{o}) in comparison to complex 1a (N–H···Cl) bond distances are 2.609A^{o} and 2.511A^{o}.

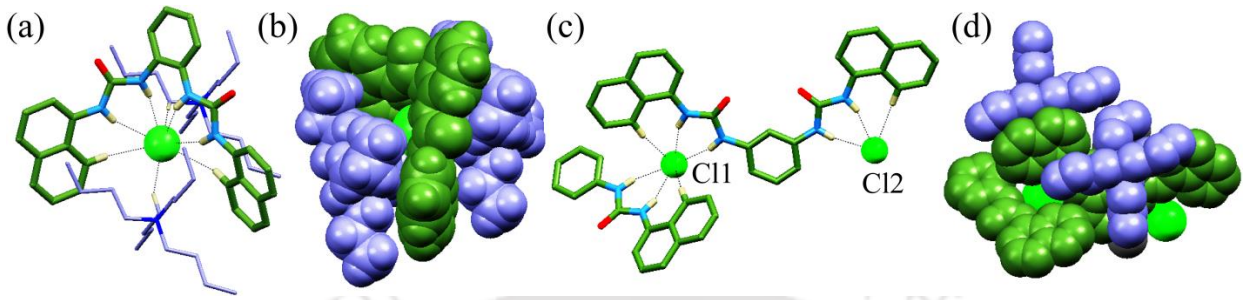


Fig. 3.1 Single crystals X-ray structure of complex **1a** and **2a** illustrating (a) H-bonding interactions of the chloride with receptor $\mathbf{L_1}$ and n-TBA cations, (b) space-fill view of the complex **1a** (entrapment of the guest inside dimeric cavity), (c) H-bonding interactions of the chloride with receptor $\mathbf{L_2}$, (d) spacefill view of isomeric receptor $\mathbf{L_2}$ with chloride anion.

In the solid-state towards chloride anion, the deviation of binding of two isomeric receptors $\mathbf{L_1}$ and $\mathbf{L_2}$ is possibly attributed to the isomeric variation of *ortho* and *meta*-diamine. The closer proximity of the urea groups of receptor $\mathbf{L_1}$ assisting in cooperative chloride binding, whereas in contrary, receptor $\mathbf{L_2}$ displays non-cooperative halide binding of urea groups because of greater distance among the urea groups of an individual receptor moiety along with the less coordination number of halides as witnessed from solid-state study. Two symmetrically diverse bromide ion is bound by two symmetrically equal $\mathbf{L_2}$ receptor through six strong N–H···Br (complex **2b**) and three C–H···Br interactions (Fig. A3.1) conforming 1.5:2 non-capsular host-guest assembly similar to the chloride complex. However, larger bromide anion forms relatively weaker complex (N–H···Br) bond distances are 2.664A^{o} and 2.471A^{o}. Two urea groups from one ligand bind one bromide ion, while the one urea groups of other receptor coordinate another bromide ion. Supportive interactions like three C–H···O and two weak C–H···π interactions between the two external n-TBA and receptors stabilized the non-capsular assembly of bromide and $\mathbf{L_2}$ receptors. Correspondingly the single crystal X-ray structure of fluoride complex **2c** visibly demonstrates that among the two symmetrically dissimilar fluoride ions, F_1 and F_2 are coordinated *via* three and six H-bonds respectively and hence conforming the non-capsular host-guest assembly parallel to Cl and Br complex (Fig. A3.2). Moreover, between receptors and the two external n-TBA, complex **2c** gets stabilized by one weak C–H···π and one C–H···O supportive interactions. The distance between urea NH and guest in the complex **2c** is 1.954A^{o}

and 1.880A^{o} and it is shorter than bromide complex as size of fluoride is much smaller than bromide ion.

3.4 Structural divergence in cooperative acetate and terephthalate complex: Cation sealed complexes

Through cooperative H-bonding, the acetate complex **1b** of $\mathbf{L_1}$ forms 1:1 host-guest assembly, where the urea N–H group of the receptor $\mathbf{L_1}$ interacts with acetate ion (Fig. 3.2a) *via* four N–H···O interactions, forming 1-D coordination polymer like structure (Fig. A3.3).

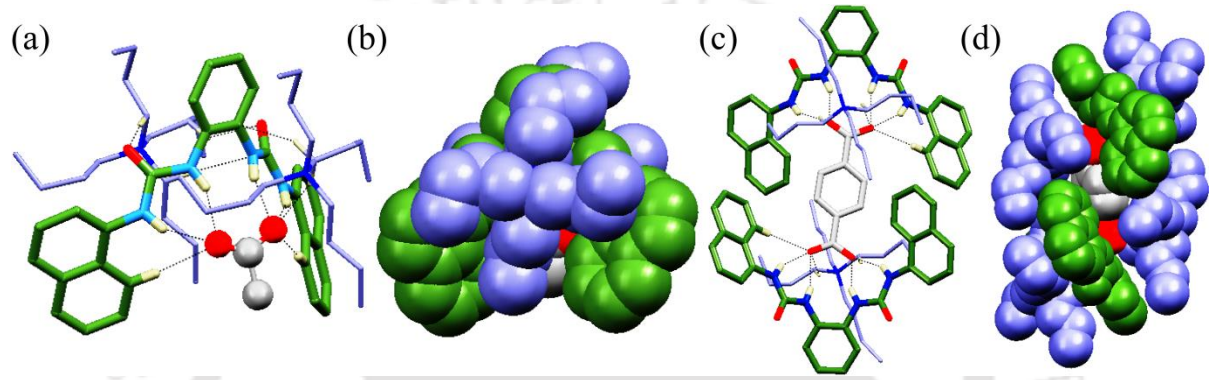


Fig. 3.2 Single crystals X-ray structure of complex **1b** and **1c** describing (a) hydrogen bonding interactions of the acetate with receptor $\mathbf{L_1}$ and tetrabutyl ammonium cations, (b) spacefill view of entrapment of the guest inside dimeric cavity in case of complex **1b**, (c) interaction of terephthalate anion with the receptor $\mathbf{L_1}$ and n-TBA counter cation (d) space fill view of receptor $\mathbf{L_1}$ with terephthalate.

The receptor-acetate self-assembly is also stabilized by seven C–H···O and one weak C–H···π supportive interactions between the two peripheral n-TBA units with respective acetate and receptor. DMF solvated 2:1 host-guest complex **1c** forms in presence of organic terephthalate ion which is coordinated by two symmetrically identical $\mathbf{L_1}$ receptor units and four n-TBA cations *via* eight strong N–H···O and six C–H···O interactions conforming 2:1 (Fig. 3.2c) pseudo-capsular cation-sealed host-guest assembly Each carboxylate group of a terephthalate dianion is coordinated to a receptor molecule by four N–H···O hydrogen bonds to the two urea functions. Two identical-symmetric receptor molecules are flipped inward towards each other in face to face fashion and so generate a pseudo molecular capsule engulfing a terephthalate dianion. The packing motif of acetate complex (Fig. 3.3a) forms a wave like structure while complex **1c** forms a stair case alike (Fig. 3.3b) packing arrangement. Furthermore, complex **1c** also gained strength by intermolecular C–H···O interaction and π–π stacking with the neighbouring receptor moieties. The orientation of naphthalene ring in complex **1b** is out of plane with respect to the central core (benzene ring), however in case of complex **1c** it is in plane with respect to the central benzene ring. The angle between the two planes bisecting the

naphthyl ring in both of the complexes is different. Both the urea NH and central benzene ring of receptor $\mathbf{L_1}$ in presence of two different anions was found to be 62.058^o in case of complex **1b** where as in complex **1c** it was about 71.968^o.

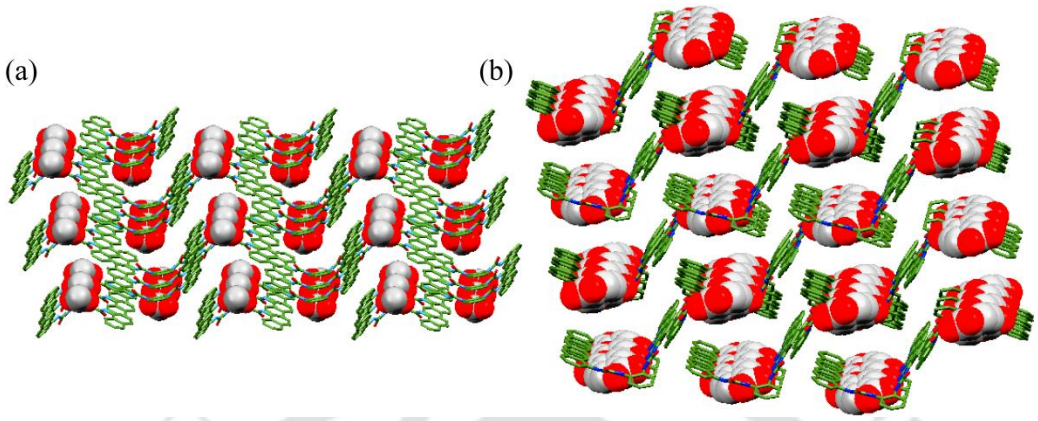


Fig. 3.3 Molecular packing of (a) complex **1b** (wave like) and (b) complex **1c** (staircase) viewed along crystallographic b-axis.

Comparative structural analysis of complex **1b** and **1c** of respective planar acetate and terephthalate of receptor $\mathbf{L_1}$ demonstrates the non-capsular 1:1 host-guest assembly of acetate ion by cooperative binding of urea groups (Fig. 3.2a) whereas, terephthalate anions are pseudo-encapsulated into the dimeric cavity $\mathbf{L_1}$ receptor in 2:1 host-guest fashion (Fig. 3.2c) which may be attributed to the large size of organic terephthalate dianion compared to smaller inorganic acetate anion.

3.5 Cooperative cation sealed phosphate tetramer complex

In complex **2d,** the dihydrogen phosphate cluster comprises of symmetry-independent two receptor $\mathbf{L_2}$ molecules, four dihydrogen phosphate anions, and tetrabutylammonium counter cations presented in Fig. 3.4a. The existence of four tetrabutylammonium cations specified the only potential combination of monovalent dihydrogen phosphate anion. Captivatingly, a cyclic tetramer (Fig. 3.4d) is formed by the interaction of four symmetrically dissimilar dihydrogen phosphate anions with each other. The X-ray crystal structure of the complex **2d** evidently demonstrates that two symmetrically distinct $\mathbf{L_2}$ receptor units coordinated to four independent monovalent dihydrogen phosphate anion by eight strong N–H···O and four *ortho*-aryl C–H···O interactions which is presented in Fig. 3.4a conforming a 2:4 host-guest assembly. Four pair of symmetrically diverse tetrabutylammonium cations is fully sealed the cyclic tetrameric dihydrogen phosphate cluster. The tetrameric cluster host-guest assembly of monovalent dihydrogen phosphate and $\mathbf{L_2}$ receptors gets additional stability five weak C–H···π and seven C–H···O interactions from the tetrabutylammonium cations unit.

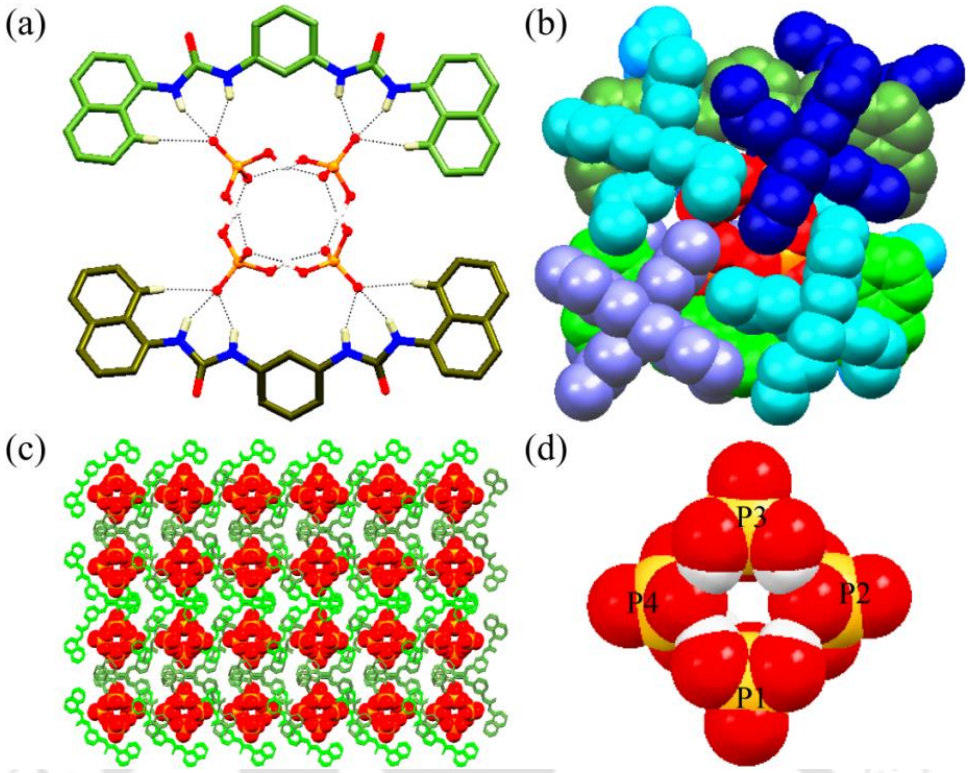


Fig. 3.4 Single crystals X-ray structure of complex **2d** showing (a) H-bonding interaction of the dihydrogen phosphate with receptor $\mathbf{L_2}$, (b) space fill exemplary of 2:4 host-guest assembly, (c) packing arrangement of complex **2d** observed down the crystallographic b-axis, (d) interaction of symmetrically different monovalent dihydrogen phosphate anions with one another to form cyclic tetramer.

3.6 Study of free receptors by density functional theory (DFT)

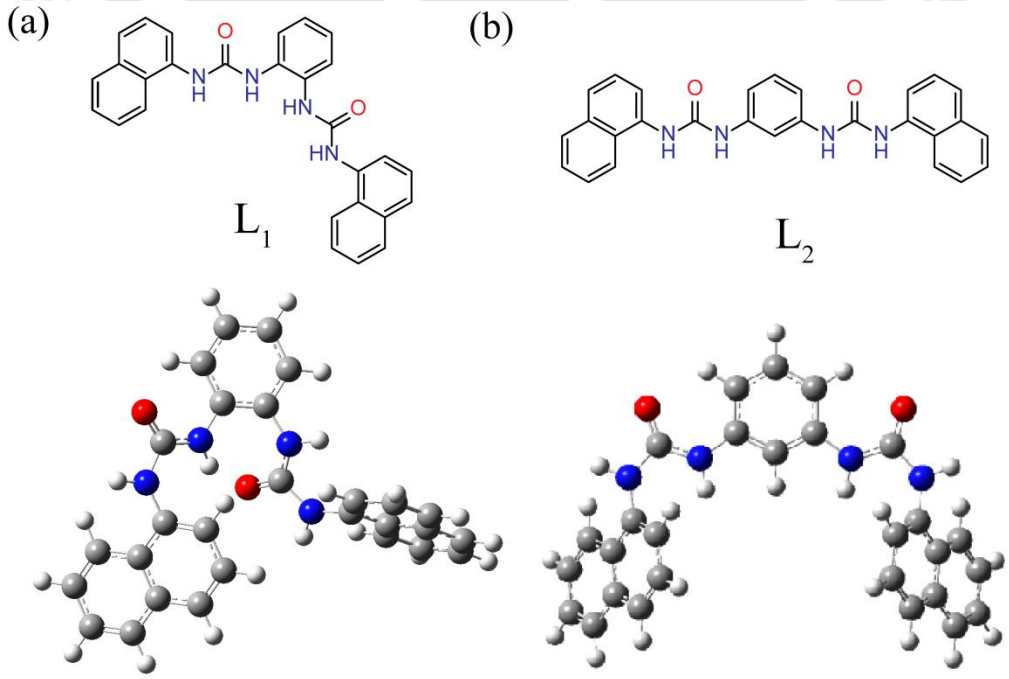


Fig. 3.5 Structural design of the receptors (a) $\mathbf{L_1}$ and (b) $\mathbf{L_2}$ and optimized geometry of the free receptors $\mathbf{L_1}$ and $\mathbf{L_2}$.

We have carried out the DFT studies for the structural explanation of the free receptors because we are unable to grow good quality crystals receptors **L_1** and **L_2**. The DFT study exposes the trans-orientation of first urea NH neighbouring to the central benzene ring in case of receptor **L_1**, while in case of receptor **L_2** the cis orientation of first urea N–H adjacent to the central aromatic ring has been observed which is presented in Fig. 3.5(a, b). DFT optimizations of the receptors were carried out with the B3LYP/6-31+G (d, p) basis set.

3.7 Solution-state anion binding studies

The solution-state anion binding properties of receptors **L_1** and **L_2** were studied through qualitative as well as quantitative ^{1}H-NMR experiments in DMSO-d6 using the quaternary ammonium (n-TBA) salt of the AcO^-, F^- and $H_2PO_4^-$ as recognized from the solid-state. Receptor **L_1** with relative ^{1}H-NMR stack plots (Fig. 3.6) with increasing concentration of tetrabutylammonium acetate anion exhibited a huge downfield shift of NH_a and NH_b and comparatively less shift of *ortho*-aryl CH proton of **L_1** because in solution state the receptor forms complex with a anion. The acetate complex (**1b**) in Fig. 3.6 displayed an average downfield shift of ~1.353 ppm and ~1.125 ppm of –NH protons respectively. Though in solid-state, complex **1c** exhibited an average downfield shift of ~0.691 ppm and ~0.333 ppm.

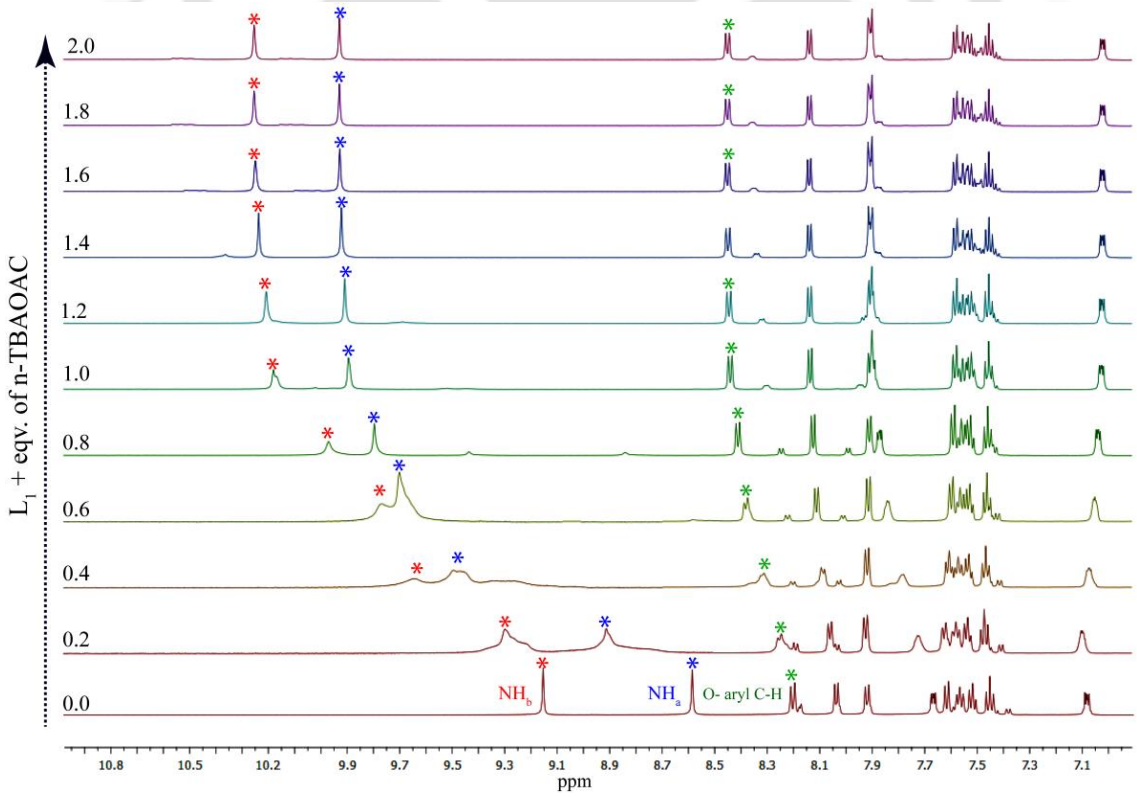


Fig. 3.6 ^{1}H- NMR (600 MHz, DMSO-d6) titration spectra of receptor **L_1** with the evident shifts of urea –NH upon the addition of n-TBACH_3COO.

Afterwards the fluoride complex (**2c**) and phosphate complex (**2d**) revealed an average downfield shift of 1.945 and 2.054 –NH protons for complex (**2c)** and a shift of 1.955 and 2.02 ppm for complex (**2d)** respectively. However, after gradual addition of respective n-TBAF and n-TBAH_2PO_4 anion to the receptors $\mathbf{L_1}$ and $\mathbf{L_2}$, in the ^{1}H- NMR titration, an average shift of –NH protons with a chemical shift of 2.512 and 1.926 ppm for fluoride complex and 1.923 and 1.527 ppm for H_2PO_4 complex (Fig. 3.7 and Fig.3.8) were witnessed respectively.

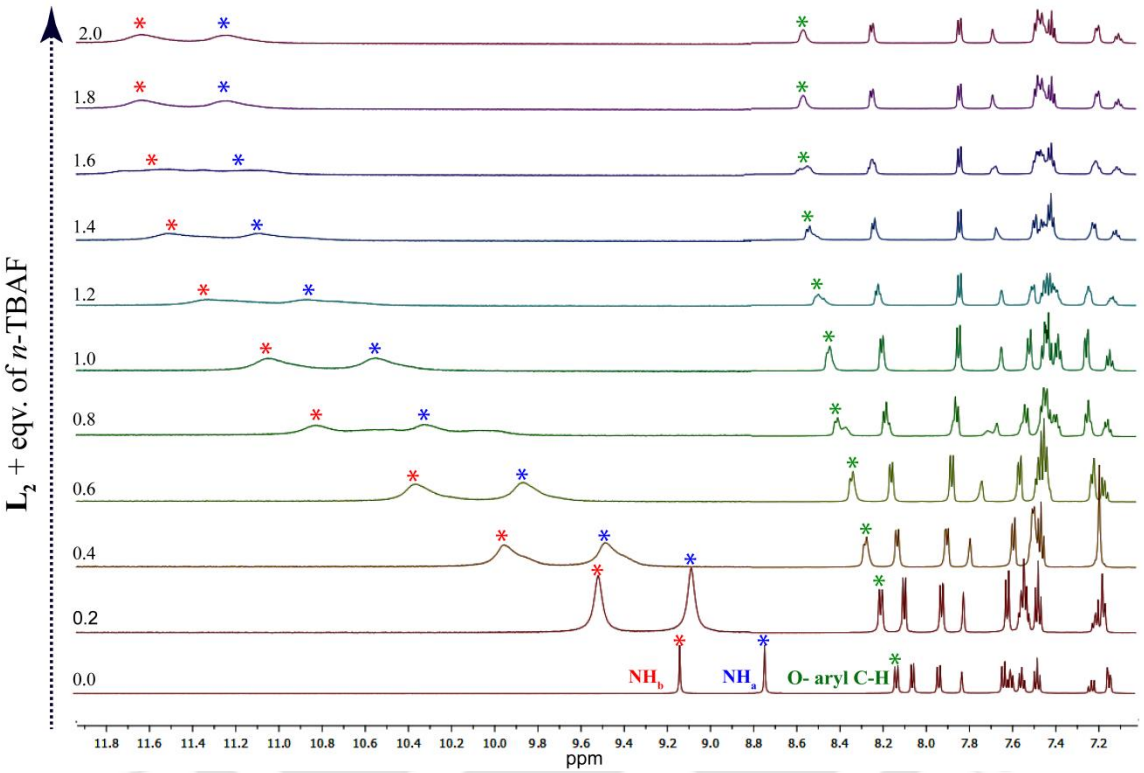


Fig. 3.7 ^{1}H- NMR (600 MHz, DMSO-d6) titration spectra of receptor $\mathbf{L_2}$ with the evident shifts of urea –NH upon the addition of n-TBAF.

We observed a huge downfield shift of NH_a protons than that of NH_b protons in case of titration spectra of complex (**2d**), confirms that the $H_2PO_4^-$ anion binds to NH_a protons strongly and an average downfield shift of *ortho*-aryl CH proton validate the solid-state binding. A mixed equilibrium stoichiometry between 1:2 and 1:3, host-guest of receptor $\mathbf{L_1}$ with aliquots of standard tetrabutylammonium acetate ion in solution has been given by the Job's plot (Fig. A3.6a). However, with aliquots of a standard n-TBAF solution, proton NMR titration data of receptor $\mathbf{L_2}$ resulted in a mixed equilibrium between 1:2 and 1:1 host and guest (Fig. A3.6b), which is more common in literature. From Job's plot (Fig. A3.6c), NMR titration data of aliquots of a standard n-TBAH_2PO_4 with receptor $\mathbf{L_2}$ providing the mixed stoichiometry between the host and guest (2:1 and 1:1 equilibrium). In both solid and solution state, the inconsistency in the binding of anions is common. At this point, in the solution state, the

variation of binding of one or two F^- ions compared to one chloride ion in solid-state is probably attributed to the more rigid and systematized receptor arrangement in solid-state related to more loose coordination in solution-state.

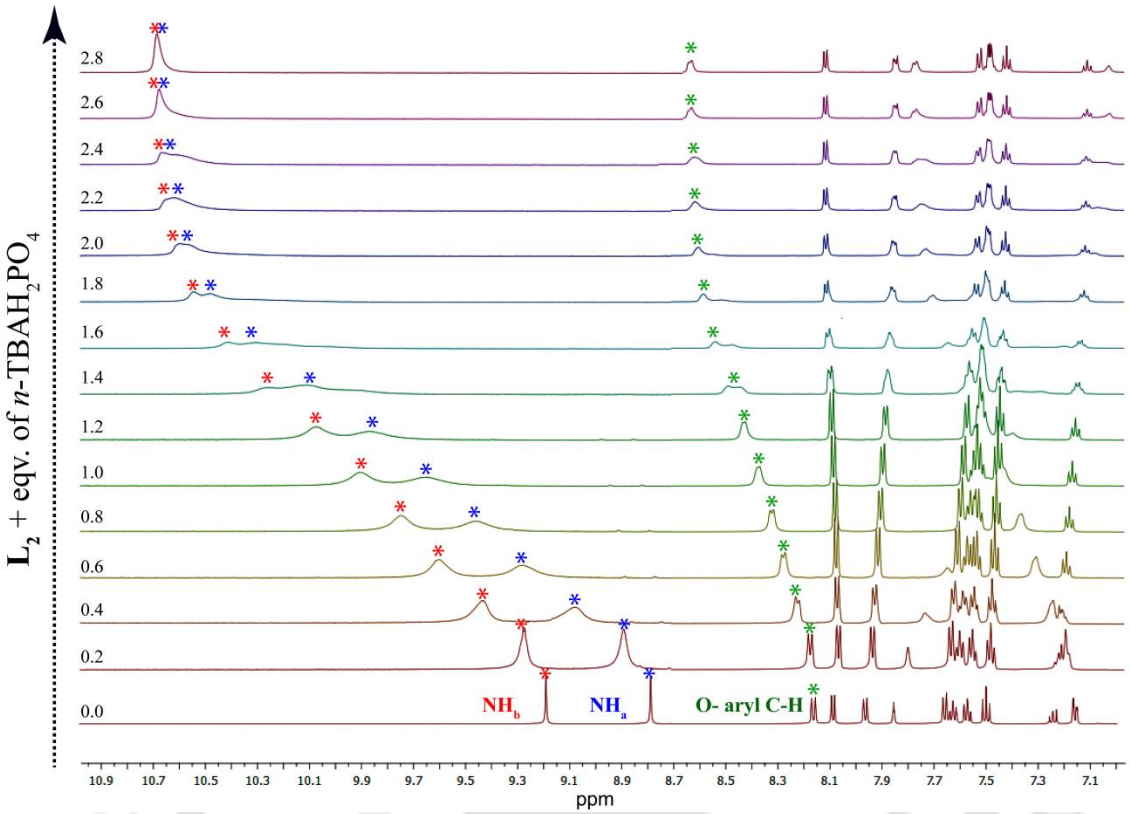


Fig. 3.8 ^{1}H- NMR (600 MHz, DMSO-d6) titration spectra of receptor $\mathbf{L_2}$ with the evident shifts of urea –NH upon the addition of n-$TBAH_2PO_4$.

3.8 Conclusion

The rational and purposeful design of electron-rich naphthyl ring containing two bis-urea receptors resulting from *ortho* ($\mathbf{L_1}$) and *meta* ($\mathbf{L_2}$)-phenylenediamine moieties we're showing the effect of positional isomerism in both solid and solution-state anion binding. Single crystal X-ray structural elucidation revealed that the receptor $\mathbf{L_1}$ having *ortho*-phenylene base has the ability to self-assemble with spherical halide along with the planar organic and inorganic oxyanions. On the other hand, receptor $\mathbf{L_2}$ having *meta*-phenylene base has the capability of trapping of monovalent inorganic $H_2PO_4^-$ in a cooperative way. In contrary, receptor $\mathbf{L_2}$ self-assembles with spherical halides (Cl^-, Br^- and F^-) in an identical non-cooperative fashion. And the reason behind this is maybe due to the less coordination number of halides compared to oxyanions. As a result of the report of well-organized unparalleled terephthalate dianion complex and cyclic tetrameric $H_2PO_4^-$ complex within the dimeric cavity of neutral organic receptor $\mathbf{L_1}$ and $\mathbf{L_2}$ irrespectively, delivers an excellent case of understanding the significance of supramolecular neutral host-guest assembly.

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Annexure 2

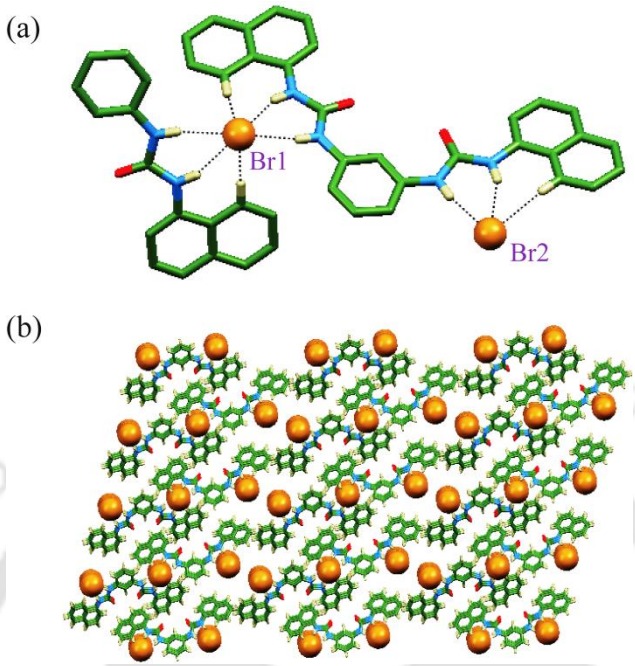


Fig A3.1 X-ray structure of complex **2b** (partial) representing (a) hydrogen bonding interactions of the bromide with receptor $\mathbf{L_2}$ and (b) molecular packing of complex **2b** observed down the crystallographic b-axis.

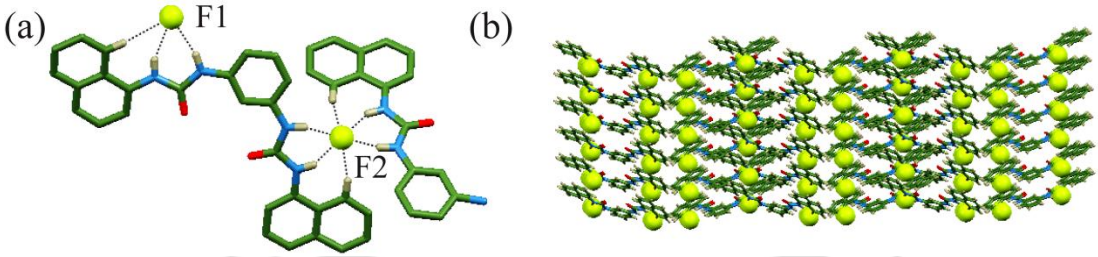


Fig A3.2 X-ray structure of complex **2c** (partial) representing (a) hydrogen bonding interactions of the bromide with receptor $\mathbf{L_2}$ and (b) molecular packing of complex **2c** observed down the crystallographic b-axis.

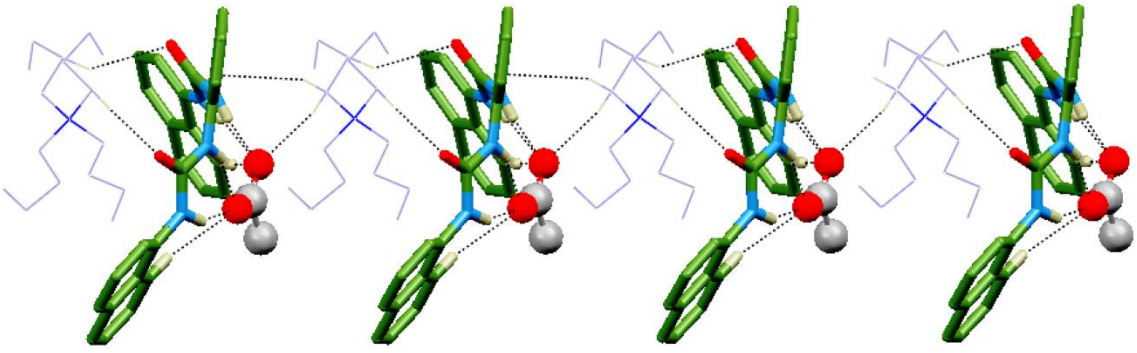


Fig A3.3 X-ray structure of complex **1b** (partial) representing formation of 1-D polymer like structure.

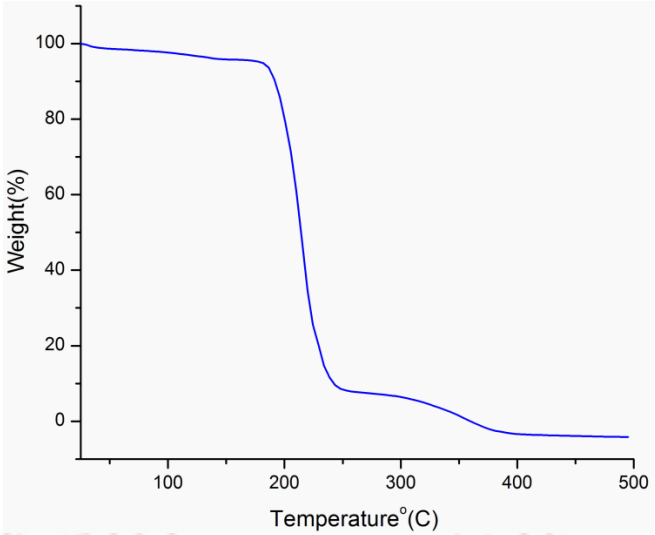


Fig A3.4 Thermogravimetric analysis (TGA) curve of complex **2a** at a heating rate of 5 °C per min

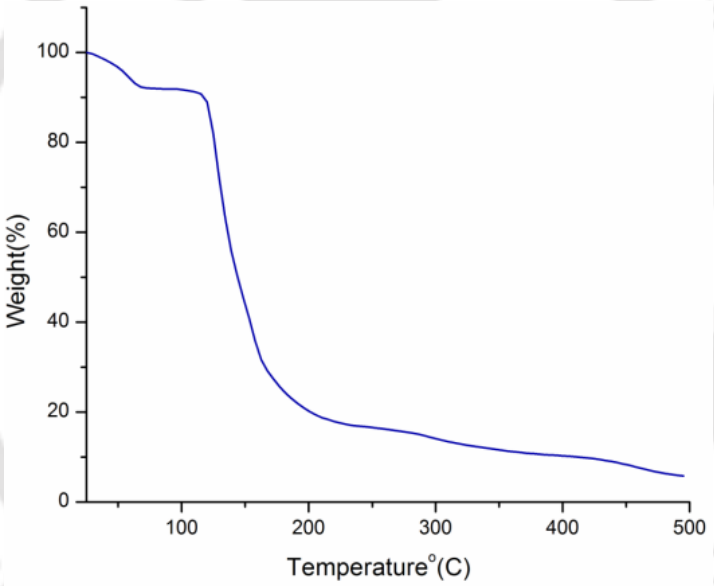


Fig A3.5 Thermogravimetric analysis (TGA) curve of complex **2d** at a heating rate of 5 °C per min

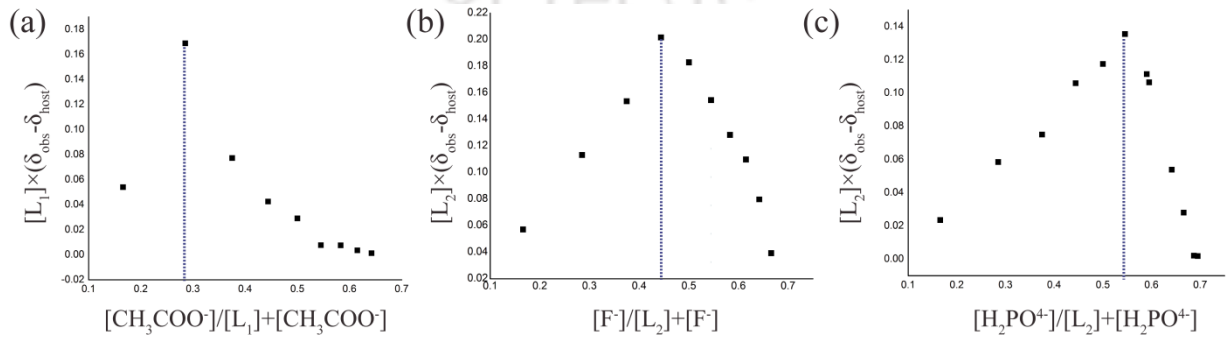


Fig A3.6 Job's plot diagram of (a) $\mathbf{L_1}$ with acetate, (b) $\mathbf{L_2}$ with fluoride, and (c) $\mathbf{L_2}$ with dihydrogen phosphate as obtained from proton NMR titration studies.

Table A3.1 Crystallographic parameters and refinement details of anion complexes of receptors $\mathbf{L_1}$-$\mathbf{L_2}$

Parameters	1a	1b	1c	2a	2b	2c	2d
Formula	$C_{44}H_{58}ClN_5O_2$	C46 H61 N5 O4	C48 H60 N5 O	C104 H152 Cl3 N11 O6	C104 H152 Br3 N11 O6	C104 H152 F3 N11 O4	C120 H196 N12 O21 P4
Fw	724.40	743.81	771.01	1758.72	1892.07	1677.37	2266.77
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	P 21	P -1	P 21/c	C 2	C 2	C 2	P b c 21
a/Å	8.9836(8)	8.9025(7)	13.1506(12)	23.4981(14)	23.4337(18)	23.3251(9)	28.7573(18)
b/Å	18.2157(16)	12.2632(8)	19.4158(19)	8.9382(5)	9.0642(8)	8.8564(4)	16.9017(15)
c/Å	13.1192(10)	20.6201(15)	17.5882(15)	25.2548(15)	25.5491(14)	25.1866(9)	26.789(2)
α/°	90	95.400(6)	90.00	90.00	90.00	90	90
β/°	107.109(9)	101.587(6)	102.689(10)	105.147(7)	105.348(7)	102.099(4)	90
γ/°	90	98.685(6)	90.00	90.00	90.00	90	90
V/Å^3	2051.9(3)	2161.9(3)	4381.1(7)	5120.0(5)	5233.3(7)	5087.4(4)	13020.5(18)
Z	2	2	4	2	2	2	4
D_c/g cm^{-3}	1.173	1.149	1.169	1.141	1.201	1.095	1.156
μ Mo K_α/mm^{-1}	0.135	0.074	0.072	0.146	1.212	0.070	0.125
F000	780.0	808.0	1660.0	1904.0	2012.0	1824.0	4912.0
T/K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
θ max.	22.4850	26.0370	20.2490	21.6130	21.3210	19.7060	21.5770
Total no. of reflections	9134	17852	20838	11775	14663	12376	40507
Independent reflections	6538	9741	9941	8247	9554	8424	23480
Observed reflections	4175	4256	3758	4527	4615	3926	10441
Parameters refined	473	502	518	567	566	558	1444
R_1, I > 2σ(I)	0.0501	0.0797	0.0892	0.0687	0.0600	0.1091	0.0695
wR_2, I > 2σ(I)	0.0788	0.1899	0.2664	0.1709	0.1376	0.2776	0.1614
GOF (F^2)	1.059	1.131	1.046	1.065	0.854	1.174	0.956
CCDC No.	1567646	1567647	1567648	1567649	1567650	1567651	1567652

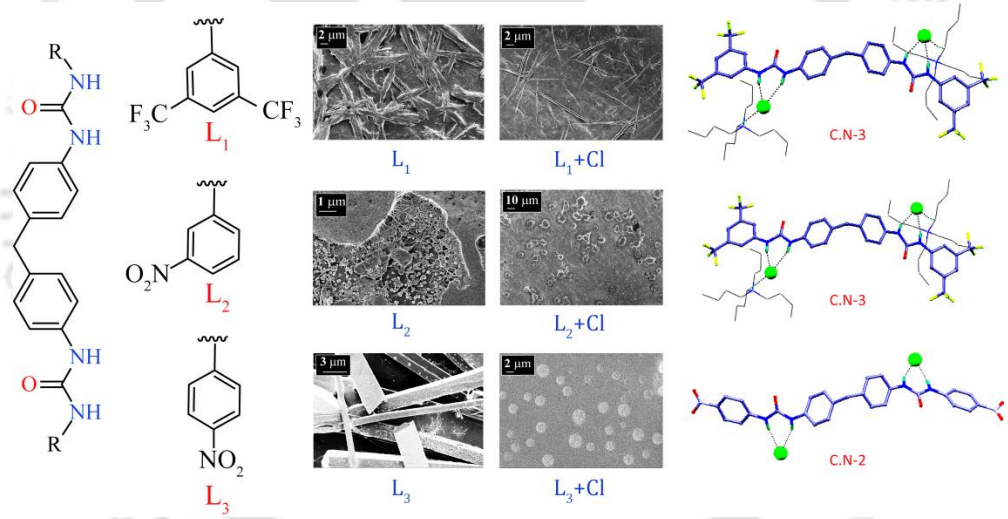
Table A3.2 Details of Hydrogen bonding contacts in anion complexes of receptors L_1-L_2

Complex	D−H···A	*d*(D···H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	<D−H···A/°	Symmetry codes
1a	N1-H1N···Cl	0.86	2.49	3.317(3)	160	x,y,z
	N2-H2N···Cl	0.86	2.51	3.275(2)	148	x,y,z
	N3-H3N···Cl	0.86	2.45	3.203(3)	146	x,y,z
	N4-H4N···Cl	0.86	2.60	3.382(3)	150	x,y,z
	C2-H2···Cl	0.93	2.91	3.771(5)	154	x,y,z
	C25-H25···Cl	0.93	2.88	3.743(4)	153	x,y,z
	C29-H29A···Cl	0.97	2.83	3.691(4)	147	x,y,z
	C37-H37B···Cl	0.97	2.90	3.845(4)	164	x,y,z
	C18-H43A···Cl	1.20	2.64	3.776(4)	155	x,y,z
	C18-H30A···Cl	1.20	2.52	3.119(5)	108	x,y,z
1b	N1-H1N···O3	0.86	2.06	2.844(4)	151	x,y,z
	N2-H2N···O3	0.86	2.04	2.840(4)	155	x,y,z
	N3-H3N···O4	0.86	1.99	2.803(3)	158	x,y,z
	N4-H4N···O4	0.86	2.15	2.240(3)	153	x,y,z
	C10-H10···O1	0.93	2.46	2.889(4)	108	x,y,z
	C13-H13···O1	0.93	2.50	2.904(4)	106	x,y,z
	C16-H16···O2	0.93	2.57	2.950(4)	105	x,y,z
	C20-20···O2	0.93	2.25	2.864(4)	123	x,y,z
	C21-21···O2	0.93	2.58	3.307(4)	135	-x,1-y,-z
	C41-41···O4	0.97	2.51	3.423(4)	156	x,y,z
1c	N1-H1N···O4	0.86	2.13	2.912(4)	151	1-x,-1/2+y,1/2-z
	N2-H2N···O4	0.86	1.95	2.755(4)	155	1-x,-1/2+y,1/2-z
	N3-H3N···O3	0.86	2.04	2.846(4)	156	1-x,-1/2+y,1/2-z
	N4-H4N···O3	0.86	2.09	2.895(5)	155	1-x,-1/2+y,1/2-z
	C7-H7···O2	0.93	2.59	3.517(6)	172	1+x,y,z
	C9-H9···O1	0.93	2.36	2.881(5)	115	x,y,z
	C13-H13···O1	0.93	2.47	2.947(5)	112	x,y,z
	C20-H20···O2	0.93	2.22	2.856(6)	125	x,y,z
	C27-H27···O3	0.93	2.54	3.437(6)	163	1-x,-1/2+y,1/2-z
	C33-H33B···O1	0.97	2.52	3.476(1)	167	x,y,z
	C37-H37A···O4	0.97	2.56	3.423(6)	148	1-x,1-y,-z
2a	N1-H1N···Cl1	0.86	2.59	3.401(6)	158	x,y,z
	N2-H2N···Cl1	0.86	2.39	3.238(6)	168	x,y,z
	N3-H3N···Cl2	0.86	2.33	3.173(5)	165	x,y,z
	N4-H4N···Cl2	0.86	2.48	3.291(6)	158	x,y,z
	C2-H2···Cl1	0.93	2.76	3.682(8)	173	x,y,z
	C9-H9···O1	0.93	2.21	2.829(8)	124	x,y,z
	C17-H17···O1	0.93	2.28	2.881(7)	122	x,y,z
	C17-H17···O2	0.93	2.27	2.868(7)	121	x,y,z
	C20-H20···O2	0.93	2.23	2.834(7)	122	x,y,z
	C25-H25···Cl2	0.93	2.81	3.704(9)	163	x,y,z
	C33-H33A···O2	0.97	2.21	3.177(9)	176	x,1+y,z
	C38-H38B···O2	0.97	2.53	3.395(12)	149	x,1+y,z
2b	N1-H1N···Br1	0.86	2.76	3.576(8)	163	x,-1+y,z
	N2-H2N··· Br1	0.86	2.51	3.364(7)	164	x,-1+y,z
	N3-H3N··· Br2	0.86	2.47	3.318(6)	158	x,-1+y,z
	N4-H4N··· Br2	0.86	2.64	3.458(8)	154	x,-1+y,z
	C2-H2···Br1	0.93	2.85	3.778(10)	173	x,y.z
	C9-H9···O1	0.93	2.23	2.849(9)	123	x,y,z
	C17-H17···O1	0.93	2.28	2.878(9)	121	x,y,z
	C17-H17···O2	0.93	2.29	2.829(9)	120	x,y,z
	C20-H20···O2	0.93	2.24	2.829(9)	120	x,y,z
	C25-H25···Br2	0.93	2.92	3.815(12)	163	x,-1+y,z
	C30-H30B···O2	0.97	2.53	3.388(15)	147	x,y,z
	C33-H33B···O2	0.97	2.22	3.187(11)	178	x,y,z

2c	N2-H2N···F1	0.86	2.40	3.237(7)	166	x,y,z
	N3-H3N···F2	0.86	1.88	2.689(5)	156	1/2+x,-1/2+y,z
	N4-H4N···F2	0.86	1.96	2.752(6)	154	1/2+x,-1/2+y,z
	C9-H9···O1	0.93	2.23	2.833(10)	122	x,y,z
	C17-H17···O1	0.93	2.31	2.895(10)	121	x,y,z
	C17-H17···O2	0.93	2.23	2.844(8)	122	x,y,z
	C20-H20···O2	0.93	2.19	2.830(10)	125	x,y,z
	C25-H25···F2	0.93	2.46	3.369(11)	165	1/2+x,-1/2+y,z
	C33-H33B···O2	0.97	2.27	3.233(11)	171	x,y,z
2d	N1-H1N···O7	0.91	1.98	2.8(6)	156	x,y,z
	N2-H2N···O7	0.78	2.15	2.8(7)	143	x,y,z
	N3-H3N···O19	0.84	2.01	2.8(7)	151	x,y,z
	N4-H4N···O19	0.98	1.99	2.9(8)	153	x,y,z
	N5-H5N···O14	0.89	1.93	2.8(7)	154	x,y,z
	N6-H6N···O14	0.88	2.05	2.9(7)	151	x,y,z
	N7-H7N···O11	0.97	2.09	3.0(7)	152	x,y,z
	N8-H8N···O11	0.92	2.01	2.9(8)	154	x,y,z
	C2-H2···O7	0.98	2.52	3.5(9)	161	x,y,z
	C5-H5···O2	0.88	2.47	3.2(12)	146	-x,1-y,1/2+z
	C9-H9···O1	0.97	2.51	3.0(11)	114	x,y,z
	C113-H11···O7	1.01	2.56	3.4(9)	138	x,y,z
	C13-H13···O1	1.01	2.17	2.8(8)	120	x,y,z
	C15-H15···O2	0.98	2.46	3.0(9)	112	x,y,z
	C20-H20···O2	0.99	2.28	2.9(10)	118	x,y,z
	C25-H25···O19	1.09	2.32	3.4(11)	171	x,y,z
	C28-H28···O3	0.80	2.36	3.1(18)	162	1-x,1-y,-1/2+z
	C30-H30···O14	0.80	2.54	3.2(10)	146	x,y,z
	C37-H37···O3	0.97	2.28	2.7(12)	109	x,y,z
	C41-H41···O3	1.04	2.25	3.0(13)	126	x,y,z
	C43-H43···O4	1.02	2.22	3.0(10)	130	x,y,z
	C48-H48···O4	0.80	2.27	2.8(10)	126	x,y,z
	C56-H56···O1	1.00	2.56	3.5(14)	161	-x,1-y,1/2+z
	C69-H69A···O11	0.98	2.59	3.4(8)	146	x,y,z
	C89-H89B···O30	0.94	2.45	3(2)	169	x,3/2-y,1/2+z
	C97-H97A···O4	0.99	2.57	3.2(11)	119	x,y,z

Chapter 4

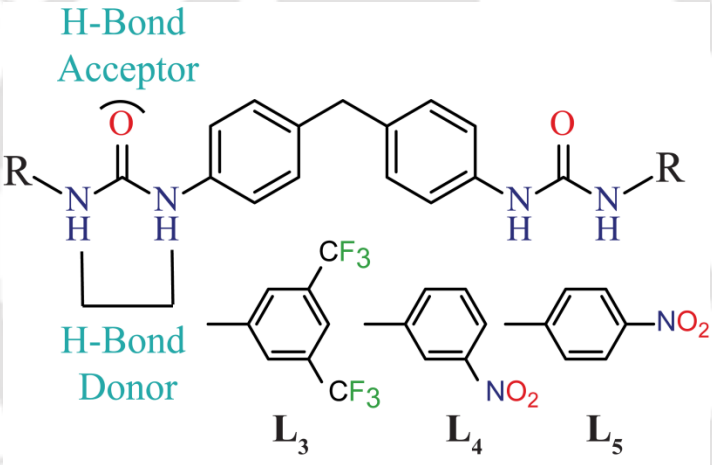
Effect of Terminal Substituent on Flexible Bis-Urea Receptors: A Comprehensive Analysis of Host-Guest Binding



4.1 Background and Focus of the Chapter

Over the years the importance of anion coordination by supramolecular non-covalent interactions with synthetically designed self-assembled neutral abiotic receptors has given rise to an active research field.[1] On a suitable platform, this has been directed to expanding development of studies in the area of molecular recognition with variable binding motifs affixed. Designing the artificial receptor is one of the utmost collective approaches because the −NH function of the receptor interacts via H bonds with anionic guests. In natural systems, several H-bond donor groups and numerous neutral abiotic receptors have been widely used for effective and selective anion coordination.[2] In addition to the recognition of hydrated anions[3], recognition of non-hydrated anion has also been subsequently encouraged due to the impact on frequent biomedical, industrial, and environmental applications as well as the significant role in living organisms.[4] To understand the role of functional groups with different hydrogen bonding abilities in anion recognition, various research groups[5] have studied halide and oxyanion binding by acyclic urea/thiourea receptors derived from various amines. Among the halides, the chloride ion plays a significant role in biological processes, such as transportation of organic solutes through the cell membrane and signal transduction. It is also a dominant anion in biological extracellular fluid and additionally is a major component of oceans.[6] Because of the small size, high hydration enthalpy, and high electronegativity of the smallest fluoride ion along with its roles in biological processes as well as in the drinking water distillation process, fluoride ion recognition is of special importance.[7] In biomineralised materials surrounded by planar oxyanions, one of the major components is carbonate, in particular, working as a buffer in blood and the exoskeletons of a radiolarian.[8] Furthermore, the significant growth in aerial CO_2 concentration is one more major ecological issue instigated by increased consumption of fossil fuels of automobiles, industries, etc., that eventually demands the effectual fixation and activation of atmospheric CO_2 into green chemicals or as carbonate/bicarbonate within the artificial receptors.[9] Lately, many tripodal scaffolds resulting from the aliphatic or aromatic amines having urea functionalization with a structurally preorganized cavity,[10] and some dipodal receptors showing better cooperativity have been commonly used for anion recognition. Due to the relatively less converging receptor conformations, the development of linear flexible dipodal urea anion receptors containing one or more terminal aryl functionalization is very rare in literature. Hence, the systematic investigation of terminal mono-aryl or di-aryl substituted linear flexible bis-urea scaffolds for recognition of anions depending upon the substituents or anion dimension is an exciting area of research to the supramolecular groups.

This chapter describes the design and syntheses of three linear flexible bis-urea receptors (**L_3-L_5**) with different terminal substituents for a comprehensive analysis of host-guest binding propensity in their neutral form. With the existence of electron-withdrawing or π-acidic phenyl substituents, they act as a possible system that can proficiently coordinate with anions of diverse dimensions constantly initiated by the size of the countercations. The 3,5-bis(trifluoromethyl)phenyl-derived isomer **L_3** can readily form cooperative 1:2 neutral self-assemblies with smaller halides to larger halides (i.e., chloride, bromide and iodide anions) and non-cooperative 4:2 neutral self-assemblies with planar divalent carbonate anions. Fascinatingly the *meta* isomer **L_4** binds with spherical halides i.e. chloride and bromide, in orthorhombic space group Pbcn with Z = 4, forming a 1:2 host-guest complex. However, the isomeric receptor **L_5** shows cooperative capture of Cl^- anions, having coordination number 3 in the presence of tetrabutylammonium chloride. Scheme 4.1 shows the molecular receptor structures **L_3-L_5**.



Scheme 4.1 Molecular structure of the receptors **L_3-L_5**.

4.2 Design aspects of anion binding receptors L_3-L_5

To coordinate with the anions of a specific geometry and size, in the design of a specific receptor comprised of various terminal substituents, it should have a preorganized orientation of the functional group capable of forming hydrogen bonds. In dry acetonitrile medium, by the reaction of the diamine with 3,5-bis(trifluoromethyl)phenyl isocyanate, *m*-nitrophenyl isocyanate, and *p*-nitrophenyl isocyanate in 1:2 molar ratios, the three 4,4′-methylenedianiline-based bis-urea isomeric receptors **L_3-L_5** were synthesized in good yield, respectively. With two urea functions, receptors **L_3-L_5** having highly electron-withdrawing groups possess a well-organized dipodal cavity appropriate for anion coordination through hydrogen bonding. The $-CF_3$ electron-withdrawing groups and nitro groups containing highly acidic bis-urea receptors

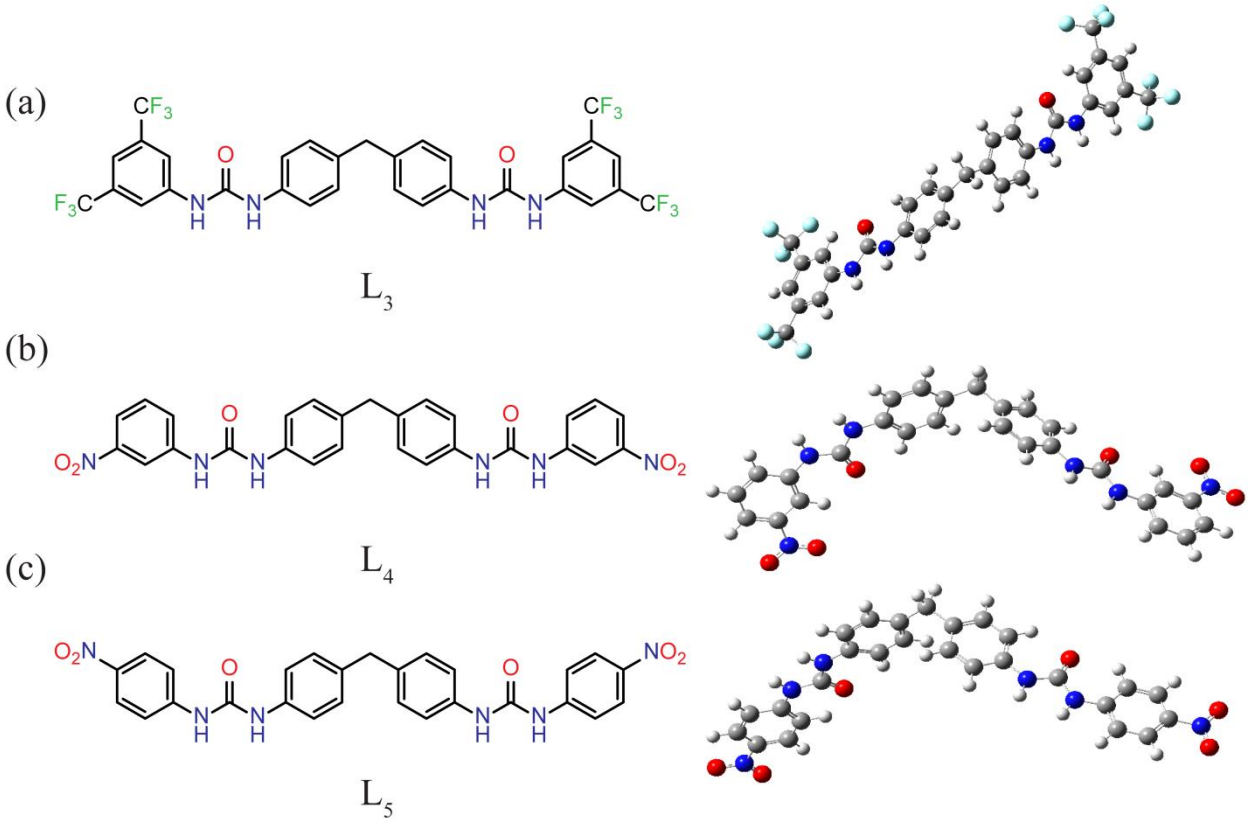


Fig. 4.1 Molecular architecture of the receptors and optimized geometry of the free receptors $\mathbf{L_3}$–$\mathbf{L_5}$ using the B3LYP/6-31+G (d, p) basis set.

in $\mathbf{L_3}$-$\mathbf{L_5}$ orient both of the urea arms toward the recognition of planar and tetrahedral oxyanions along with the halides. The receptors and their corresponding complexes with anions can deliver acuity into the coordination discrepancies of oxyanions and halides with the receptors which can be analyzed by single crystal X-ray studies. The outcomes allied with the formation of the neutral host-guest assembly by the receptors $\mathbf{L_3}$-$\mathbf{L_5}$, which are then related to the coordination environment of oxyanions and halides in neutral anion complexes.

From DMSO, DMF, or a DMF/DMSO solvent mixture, in the presence of π- acidic aromatic terminal species having an electron-withdrawing group, the dipodal scaffold is adept in binding anionic guests in the solid-state. Single crystals of spherical halides (chloride, bromide, and iodide) complexes were easily obtained from their tetrabutylammonium salts. Additionally, the planar carbonate complex is isolated as well from the exceptional host-guest assemblage of a flexible dipodal scaffold. The structural interpretation of chloride (complexes **3a-5a**), bromide (complex **3b-4b**), iodide (complex **3c**), and carbonate (complex **3d**) complexes of receptors $\mathbf{L_3}$–$\mathbf{L_5}$ clearly shows that the interactions (urea)N−H···(anion)A are mostly involved in binding strengthened by some noncovalent intermolecular interactions. It also supports a basis for effective crystallization of complexes that have been unexplored and tempts a structure of a host-guest assembly.

Note that, after several attempts to get crystals of the free receptors **L_3-L_5** under different conditions from various solvents, we were not able to obtain good-quality crystals of bis-urea based receptors. The DFT study reveals that in the case of receptor **L_3** the adjacent urea groups are in syn positions showing complete cooperativity of urea −NH protons, whereas, in the case of receptors **L_4** and **L_5**, the adjacent urea groups are in opposite directions, i.e. anti to each other showing non-cooperativity (Fig. 4.1). Employing the B3LYP method, DFT optimizations were carried out with the 6-31+G (d, p) basis set.

4.3 Comparative structural analysis of the complexes of chloride [(n-TBA){(L_3)(Cl)}] (3a), [(n-TBA){(L_4) (Cl}] (4a), and [(n-TBA){(L_5)(Cl)}] (5a).

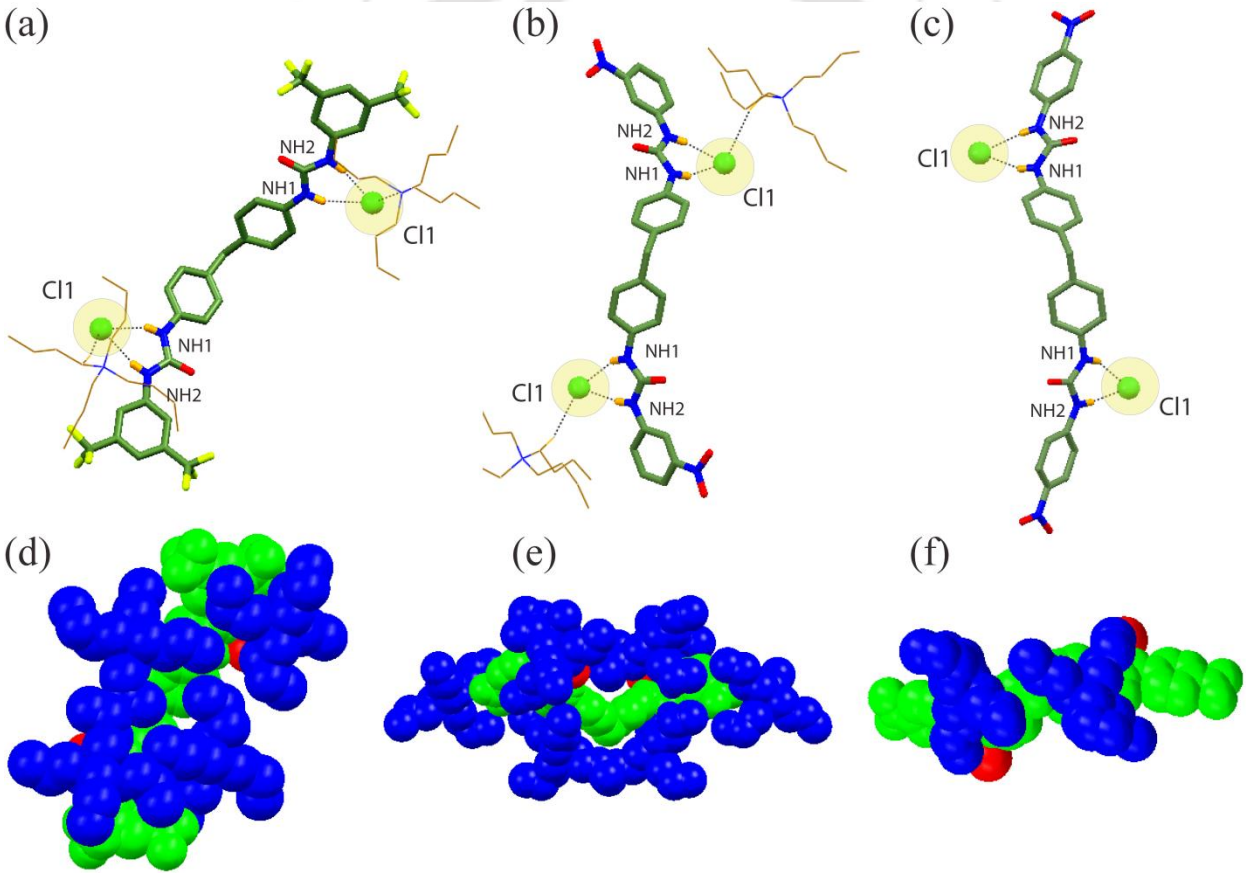


Fig. 4.2 Single-crystal X-ray structures portraying (a) complex **3a** showing an H-bonding coordination environment of chloride-coordinated ligands, (b) complex **4a** displaying H-bonding interactions of chloride-receptor assemblies by receptor **L_4**, (c) environment of hydrogen-bonding coordination of two chloride-coordinated receptors in complex **5a**, (d) space-filling demonstration of TBA cation sealed chloride-receptor complex in **3a**,(e) space-filling depiction of chloride-coordinated complex **4a**, and (f) space-filling illustration of complex **5a**.

From a DMF solution mixture, in the presence of excess tetrabutylammonium chloride salts the 1:2 receptor-chloride complexes **3a-5a** were obtained from **L_3-L_5**, respectively. Complexes **3a** and **5a** develop in the monoclinic crystal system having space group C2/c with Z = 4 and space

group P2/c with Z = 2, respectively, whereas complex **4a** crystallizes in orthorhombic space group Pbcn with Z = 4. Structural elucidation exposes that the asymmetric structural unit of all complexes contains one receptor unit, one chloride (Cl^-) anion, and the corresponding tetrabutylammonium (TBA) counteraction. The flexible receptor $\mathbf{L_3}$ unit coordinates with the two chlorides in a cooperative manner via four urea N−H···Cl interactions (Fig. 4.2a), where the two urea groups are positioned anti to each other in the presence of anion in complex **3a**. Moreover, additionally, the same two Cl^- ions have C_{TBA}−H···Cl hydrogen bonds with two tetrabutyl cations in a face to face manner, respectively. Altogether the two tricoordinated chloride-bound 1:2 neutral receptor-anion assemblies become stabilized by two weak C_{TBA}−H···O_{urea} interactions (Fig. A4.2a). Moreover, unlike complex **3a**, the structure of the complex **4a** reveals that the two urea groups are positioned opposite to each other and each urea group binds to one chloride ion via two urea N−H···Cl interactions and each Cl^- is hydrogen bonded with one tetrabutyl cation via one weak C_{TBA}−H···O_{urea} interaction, forming a 1:2 host-guest assembly (Fig. 4.2b). In comparison to complex **3a,** the 1:2 host-guest assembly of complex **4a** gains extra strength by four C_{TBA}−H···$\pi_{benzene}$ and six weak C_{TBA}−H···O_{urea} interactions. The X-ray crystal structure of complex **5a** shows that the two adjacent urea groups are anti to each other and coordinate to two chloride ions via four urea N−H···Cl anion interactions, forming a 1:2 host-guest assembly (Fig. 4.2c). Additionally, complex **5a** is stabilized by weak forces such as two C_{TBA}−H···$\pi_{benzene}$ and two C_{TBA}−H···O_{urea} interactions. The coordination number of the anion in complexes **3a** and **4a** is 3, whereas that in complex **5a,** it is 2.

4.4 Comparative structural analysis of the bromide complexes [(n-TBA){(L_3)(Br)}] (3b) and iodide Complex [(n-TBA){(L_3)(I)}] (3c).

The spherical bromide and iodide entrapped complexes **3b** and **3c** crystallize in similar the monoclinic crystal system having space group I2/c (Z = 4). The asymmetric structural unit of complexes **3b** and **3c** comprised of a single $\mathbf{L_3}$ receptor unit, a single anion, and its corresponding n-TBA countercation. Structural elucidation reveals that the binding behaviours of the complexes are very different. In the case of complex **3b**, the crystal structure clearly shows that the flexible dipodal receptor $\mathbf{L_3}$ unit coordinates to four bromide ions by different interactions, where the receptor unit binds to two bromide ions via four strong N−H···Br interactions and additionally bromide is coordinated to two tetrabutyl countercations and another two identical receptor units via four C−H···Br interactions (Fig. 4.3a). However, interestingly in the solid-state the receptor unit binds to another two symmetrically distinct bromide ions via aryl

C−H···Br interactions which are supported by four strong N−H···Br interactions from another two similar receptor units and two C−H···Br interactions from two n-TBA cations, forming a very beautiful 1-D polymeric type of network (Fig. 4.3c). Thus, it is difficult to find out the stoichiometry of the complex. Even in the solution state, we have tried to figure out the solution-state binding of Br anion; where there is much less of a downfield shift of NH_a and NH_b protons, but there is no evidence of aryl CH proton shift (Fig. A4.3).

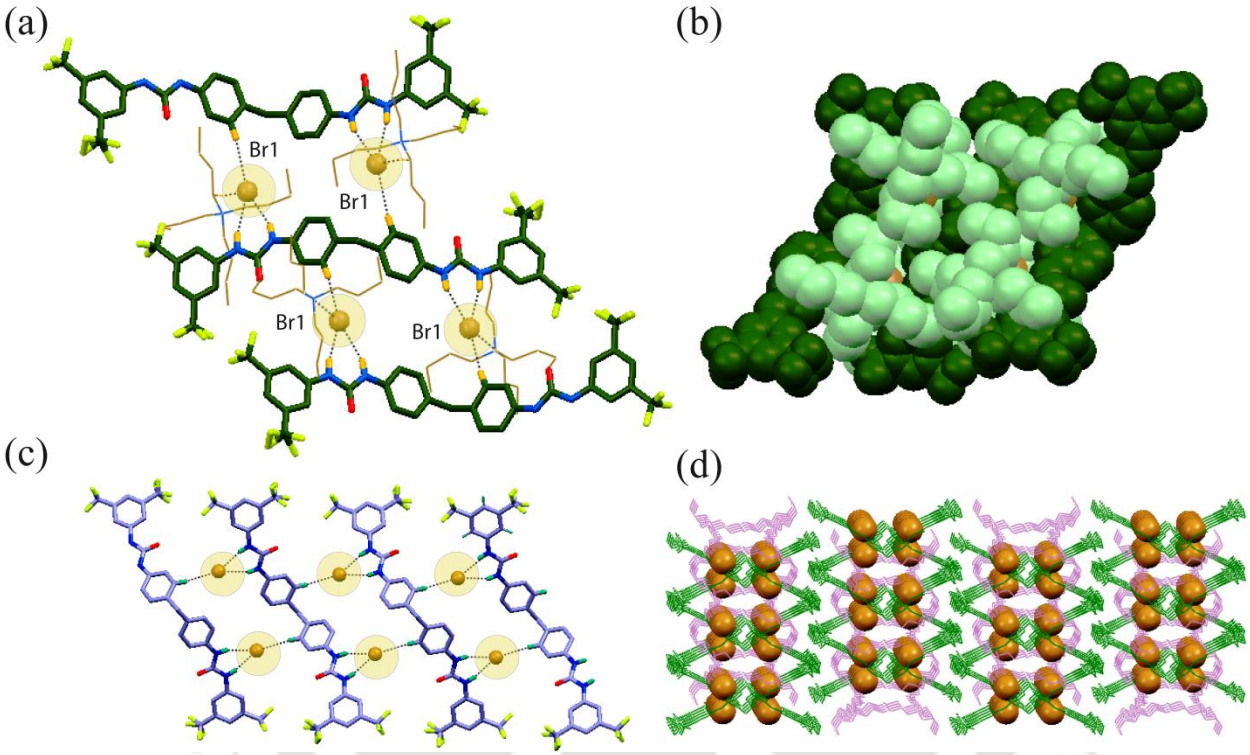


Fig. 4.3 Single-crystal X-ray structures showing (a) H-bonding interaction of cation sealed Br coordinated receptors in complex **3b**, (b) space-filling representation of bromide sealed by four pairs of TBA cations, (c) supramolecular polymeric 1D bromide-receptor network of complex **3b**, and (d) packing diagram of bromide-receptor complex as seen along the crystallographic b axis.

Compared to complex **3b**, complex **3c** binds to iodide involving a simple coordinating environment. In complex **3c** the larger spherical anion binds to the receptor unit via four strong urea N−H···I interactions and two tetrabutyl C−H···I interactions, where the two adjacent urea group binds to one I^- via two N−H···I and one C−H···I interaction constructing a 1:2 iodide-receptor complex (Figure 4.4a). Moreover, the 1:2 monovalent iodide complex gains more stability by two weak C_{TBA}−H···O_{urea} interactions.

4.5 Carbonate complex [(n-TEA){(L_3)(CO_3)}] (3d).

A suitable colourless crystal of the $TEAHCO_3$ salt with receptor $\mathbf{L_3}$ was obtained from DMF, which is basic in nature. The pseudocapsular planar carbonate complex crystallizes in the

triclinic crystal system (space group $P\bar{1}$) with Z = 2, and the asymmetric structural unit of this complex is comprised of two symmetry-independent neutral urea receptor $\mathbf{L_3}$ units, a half occupied divalent carbonate anion, its equivalent two monovalent n-TEA^+ countercations, and two DMF solvent molecules. Interestingly the flexible dipodal receptor cavity containing urea platform $\mathbf{L_3}$ comes slightly closer and the adjacent urea moieties are flipping outward from the cavity in opposite directions.

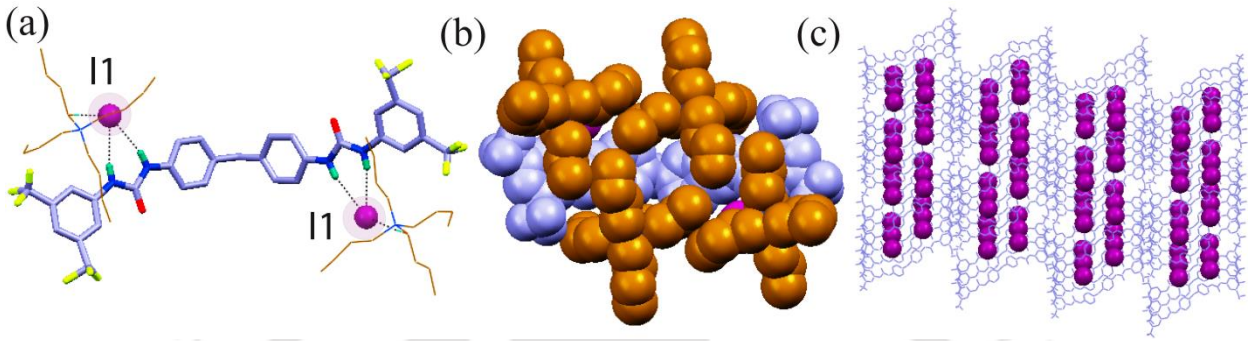


Fig. 4.4 Single-crystal X-ray structures (partial) illustrating (a) hydrogen-bonding interaction of iodide coordinated receptors in complex **3c**, (b) space-filling representation of iodide sealed by four TBA cations, and (c) packing diagram of iodide-receptor complex as seen along the crystallographic a-axis.

Receptor $\mathbf{L_3}$ in the presence of excess HCO_3^- forms a 4:2 complex via different numbers of H-bond sharing of non-cooperative urea groups from two types of symmetrically equivalent receptor units. In complex **3d**, the crystal structure reveals that the two symmetrically identical divalent carbonate anions accept 20 strong N−H···O H-bonding interactions, among which 18 H-bonds are donated by urea −NH groups of the symmetrically distinct receptors (where each O atom accepts three H-bonds) and 2 are contributed by *o*-phenyl −CH groups of the receptor (Fig. 4.5a). Out of the 20 N−H···O hydrogen bonds, 6 H-bonds are donated by two symmetrically identical receptors and the rest of the 16 H-bonds are donated by a urea arm of 4 similar receptor units. Prior to crystallization, in solution, the divalent carbonate anions were not present, and they arise from an H-bonding activated proton transfer reaction in complex **3d** (HCO_3^- anion is deprotonated to form CO_3^{2-}). The divalent carbonate anion coordinated 4:2 host-receptor pseudocapsular assembly gains additional strength by a C_{TBA}–H···$\pi_{benzene}$ and seven weak C_{TBA}–H···O_{urea} interactions.

4.6 Chloride complex [(n-TBA){(L_4)(Cl)}] (4a) and bromide complex [(n-TBA){(L_4)(Br)}] (4b).

In the presence of tetrabutylammonium salt, both bromide and chloride anion coordination inside the flexible dipodal cavity of receptor $\mathbf{L_4}$ has been achieved from a DMSO solution

mixture, to determine the extent of assembly development with large homologous sphere-shaped anions. Structural analysis shows that the 1:2 receptor-anion complexes **4a** and **4b** crystallize in identical orthorhombic crystal systems having space group Pbcn with Z = 4. More fascinatingly, the isostructural nature of complexes **4a** and **4b** were validated by a single crystal study which clearly indicates that the asymmetric unit of both these complexes contains one receptor, one halide anion, and one tetrabutylammonium cation.

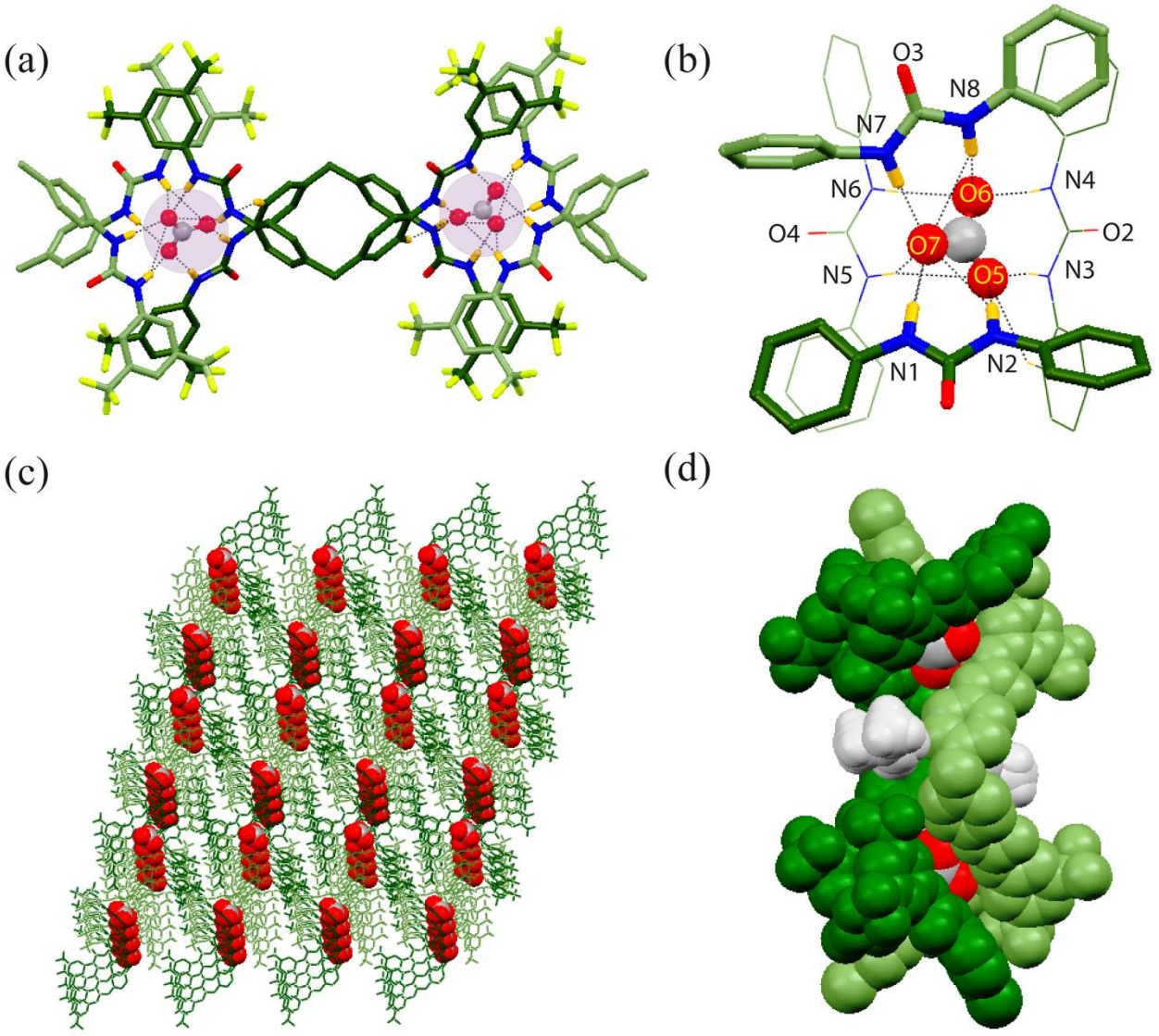


Fig. 4.5 Single-crystal X-ray crystal structures showing (a) the coordination environment of the divalent carbonate anion coordinated 4:2 host-receptor pseudocapsular assembly in complex **3d**, (b) an enlarged view of the hydrogen-bonded carbonate ion and urea −NH protons of $\mathbf{L_3}$, (c) the packing diagram of host-guest complex **3d** as seen along the crystallographic b axis, and (d) the DMF solvated space-filling representation of the divalent carbonate ion with receptor $\mathbf{L_3}$.

As already discussed above for complex **4a**, similar to this in complex **4b** the two urea groups are situated reverse to each other with respect to the substituent and each urea group coordinates to one bromide ion through two strong urea N−H···Br interactions and additionally Br^- is

hydrogen bonded with one tetrabutylammonium cations via one weak C_{TBA}–H···O_{urea} interaction forming a 1:2 host-guest assembly (Fig. 4.6a). In comparison to complex **4a**, the 1:2 bromide-receptor assembly acquires additional stability by two C_{TBA}– H···$\pi_{benzene}$ and six weak C_{TBA}–H···O_{urea} interactions.

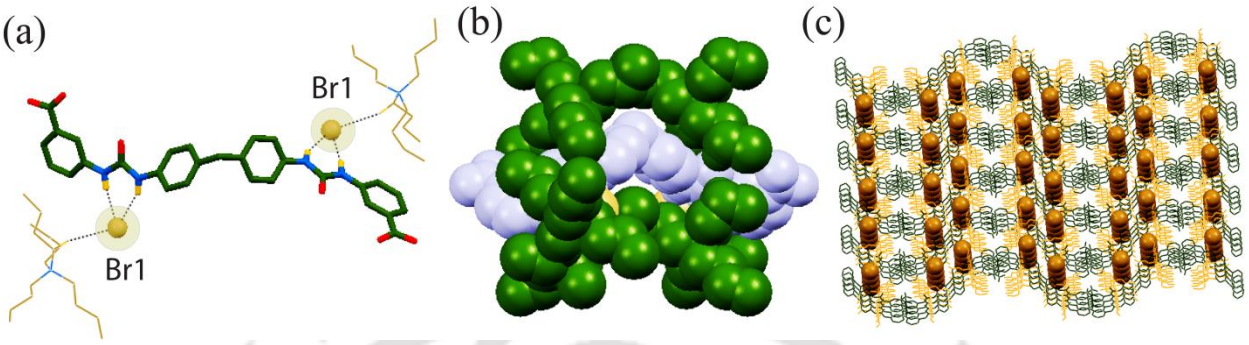


Fig. 4.6 Single crystal X-ray structures portraying (a) hydrogen-bonding interaction of bromide-coordinated receptors in complex **4b**, (b) space-filling representation of bromide sealed by four TBA cations, and (c) complex **4b** showing the wavelike packing diagram of the host-guest assembly as seen along the crystallographic a-axis.

4.7 Solution-state anion binding studies

Anion binding properties of 4,4′-methylenedianiline-based bis-urea receptors **L_3-L_5** in the solution-state are inspected by qualitative as well as quantitative ^{1}H (Proton) NMR experiments in DMSO-d6 using the quaternary ammonium (*n*-TBA) salts of different anions as demonstrated from the solid-state studies. It is reasonably evident that the performance of receptors in dilute solution is indeed quite diverse from their actions in the solid-state. In the preliminary studies of **L_3-L_5**, we found out that for urea −NH protons (−NH_a and −NH_b) the most distinguishable changes have been observed, demonstrating that in solution the interaction between the anion and the receptor is provided by the suitable sites of urea −NH functions. As demonstrated from the solid-state, with individual Cl^- salts we have also executed proton NMR experiments in solution, in a qualitative as well as in a quantitative way, and made a comparison to the free receptors **L_3-L_5**. Fig. A4.5 signifies the maximum recognizable change of urea −NH protons in host-guest complexes in solution. The ^{1}H-NMR spectra of free receptor **L_3** show urea –NH signals at 8.90 and 9.33 ppm, **L_4** shows urea −NH signals at 8.75 and 9.16 ppm, and **L_3** shows urea −NH signals at 8.84 and 9.39 ppm. The ^{1}H-NMR spectra of chloride complexes **3a**-**5a** independently display a huge downfield shift of urea hydrogen in comparison to the peaks of urea −NH of free receptors **L_3-L_5**, which indicates the hydrogen bonding of chloride with the receptors (Fig. A4.5). On the other hand, complexes of the bromide (**3b**, **4b**) and iodide (**3c**) display a slight downfield shift of urea −NH protons (Fig. A4.5), demonstrating that in the

solution state the interactions between these anions is dynamically adverse, which is not a very rare case in the literature.

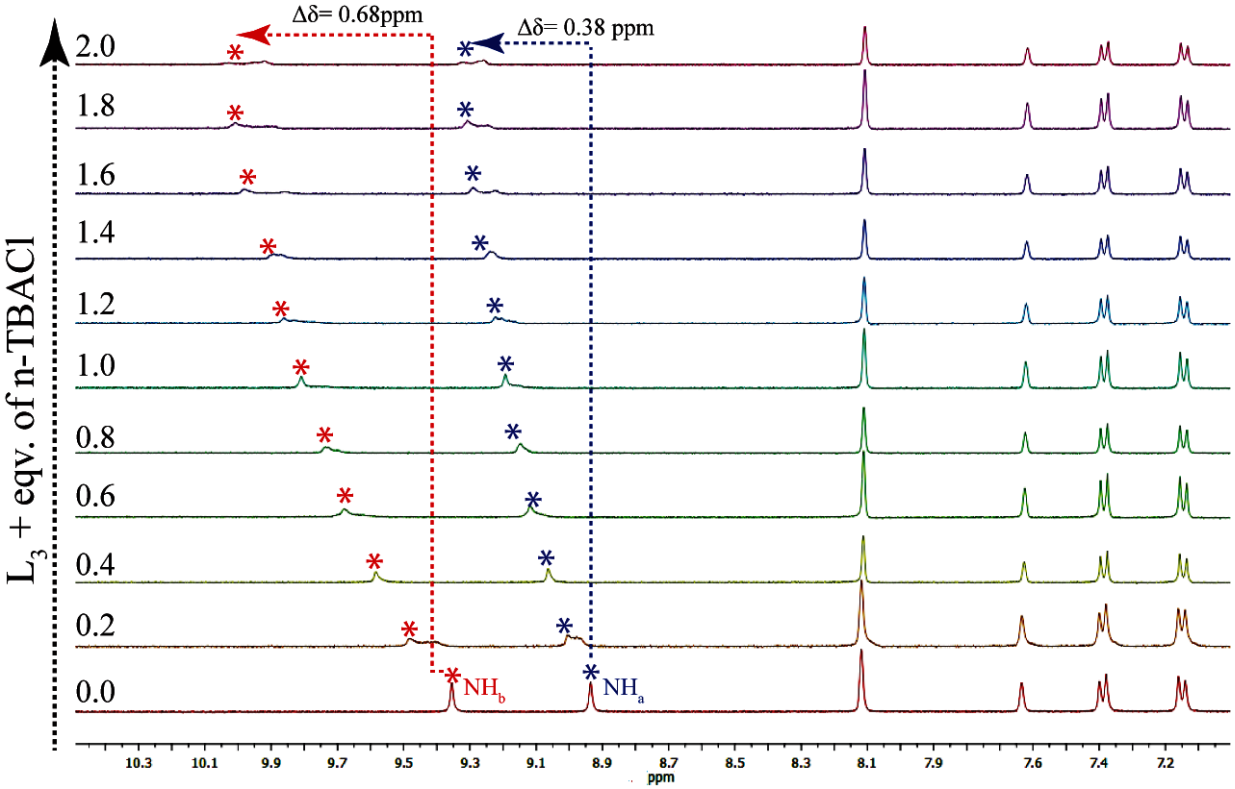


Fig. 4.7 Expanded proton NMR spectra of **L_3** upon titration with n-TBACl and DMSO-d6.

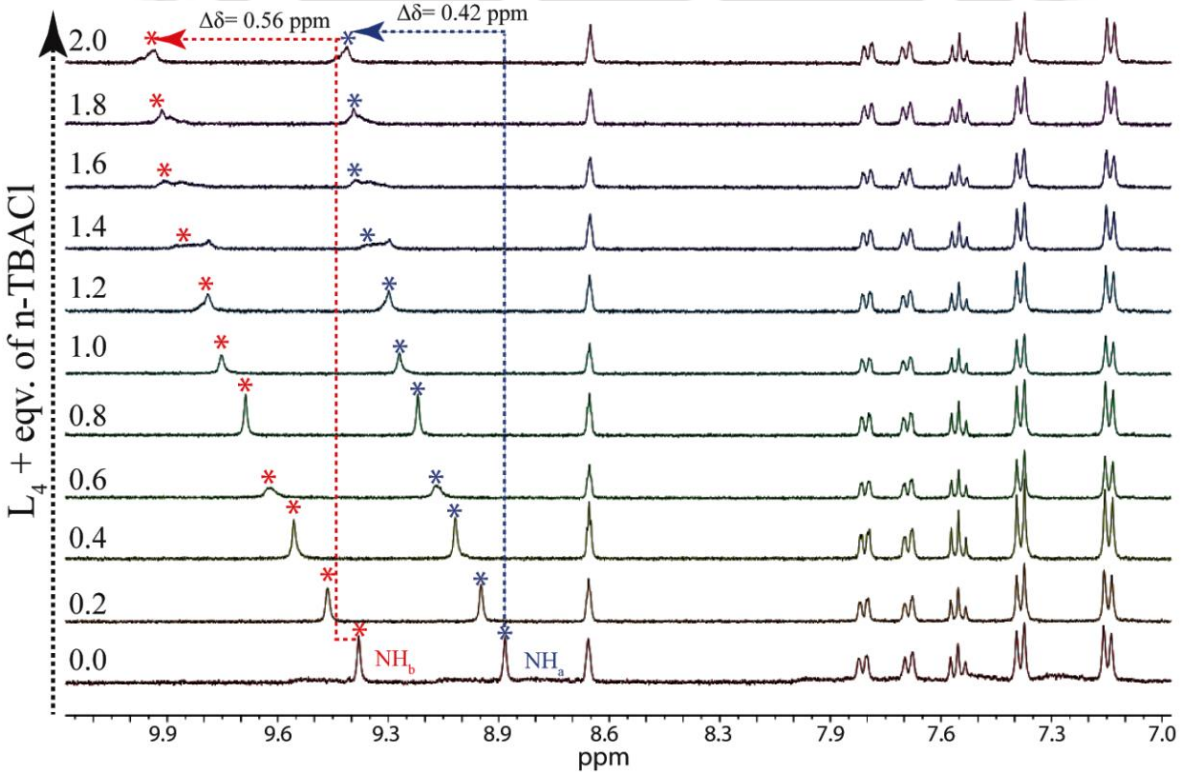


Fig. 4.8 Expanded proton NMR spectra of **L_4** upon titration with n-TBACl and DMSO-d6.

Using aliquots of n-TBACl salt, we have executed a proton (^{1}H) NMR titration investigation of free receptor **L_3** consequently following the qualitative studies, and it shows an immediate huge downfield shift of both urea –NH signals ($\Delta\delta(-NH_a)$ = 0.38 ppm and $\Delta\delta(-NH_b)$ = 0.68 ppm) following subsequent addition of 0.1 equiv of Cl^- ion (Fig. 4.7), which is exactly related to the proton NMR data of the chloride complex (Fig. A4.5).

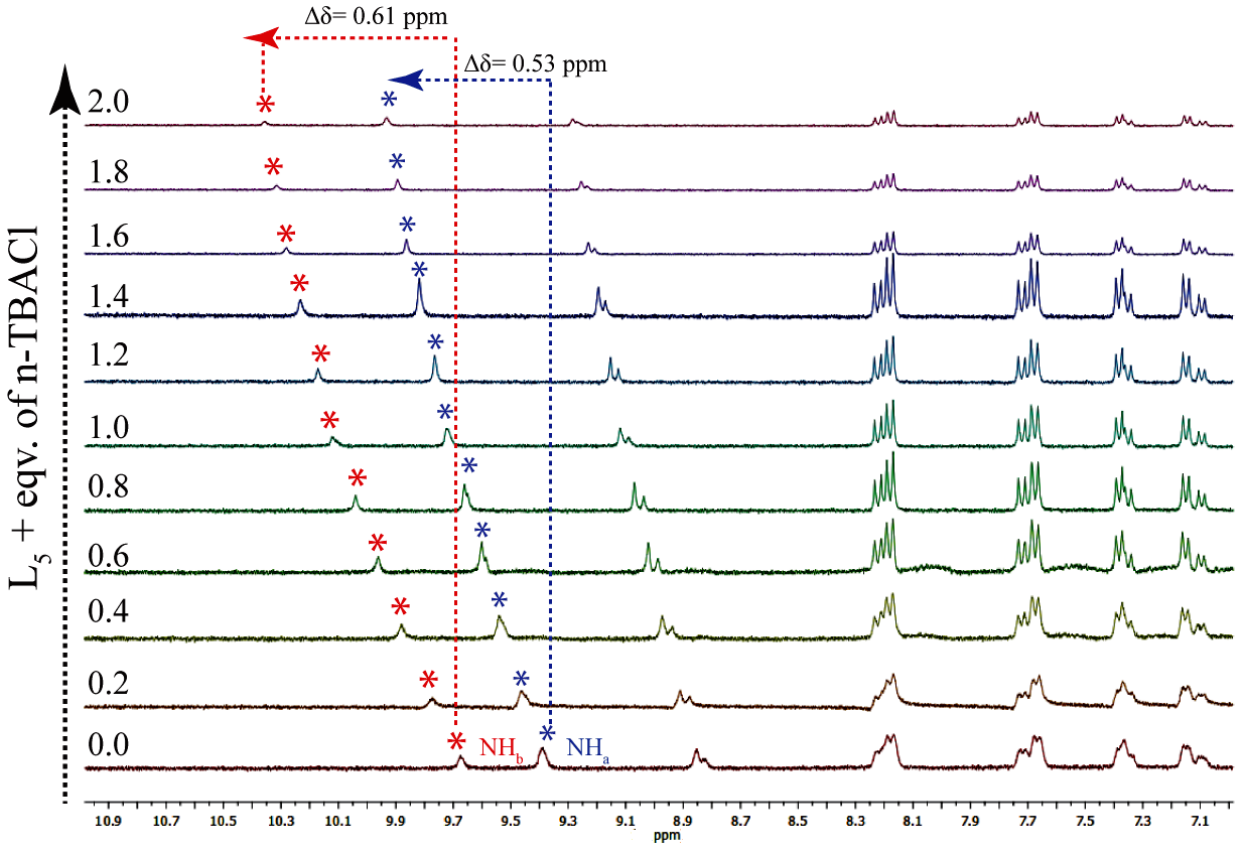


Fig. 4.9 Expanded proton NMR spectra of **L_5** upon titration with n-TBACl and DMSO-d6.

Correspondingly, in titration experiments the slow addition of tetrabutylammonium chloride salts to solutions of receptor **L_4** caused a downfield shift of urea −NH protons ($\Delta\delta(-NH_a)$ = 0.42 ppm and $\Delta\delta(-NH_b)$ = 0.56 ppm) in accord with large broadening (Fig. 4.8), respectively, and that turn out to be very like to the proton NMR data of chloride complex **4a**. Subsequently, in free urea receptor **L_5**, the regular addition of Cl^- salts to the receptor solutions of **L_5** in titration led to an average downfield shift of urea −NH protons ($\Delta\delta(-NH_a)$ = 0.53 ppm and $\Delta\delta(-NH_b)$ = 0.61 ppm) trailed by large broadening (Fig. 4.9) individually. Note that, in chloride titrations experiment, a significantly larger shift of $-NH_b$ protons in comparison to $-NH_a$ protons suggests that in solution the chloride anions are more strongly bound to $-NH_b$ than to $-NH_a$ protons of the bis-urea receptors.

4.8 Self-aggregation microscopic studies of the receptors and their chloride complexes.

A logical solid-state analysis of all chloride complexes exhibited the presence of various noncovalent interactions such as H-bonding and C−H···π anion coordination. Thus, we became fascinated with investigating the morphological behaviour of the free receptor and chloride complexes in solution. To do so, an extensive FESEM imaging study was conducted with a freshly prepared DMF solution to inspect the topographical nature of the supramolecular polymeric assembly among the three receptors **L_3-L_5** as well as deviations in the presence of Cl^-. Interestingly, it was observed that the morphologies of the different complexes were vastly different, even different from that of the free ligand. Excitingly, FESEM for **L_3-L_5** portrayed three totally different kinds of morphologies which in turn were destroyed after treatment with Cl^-.

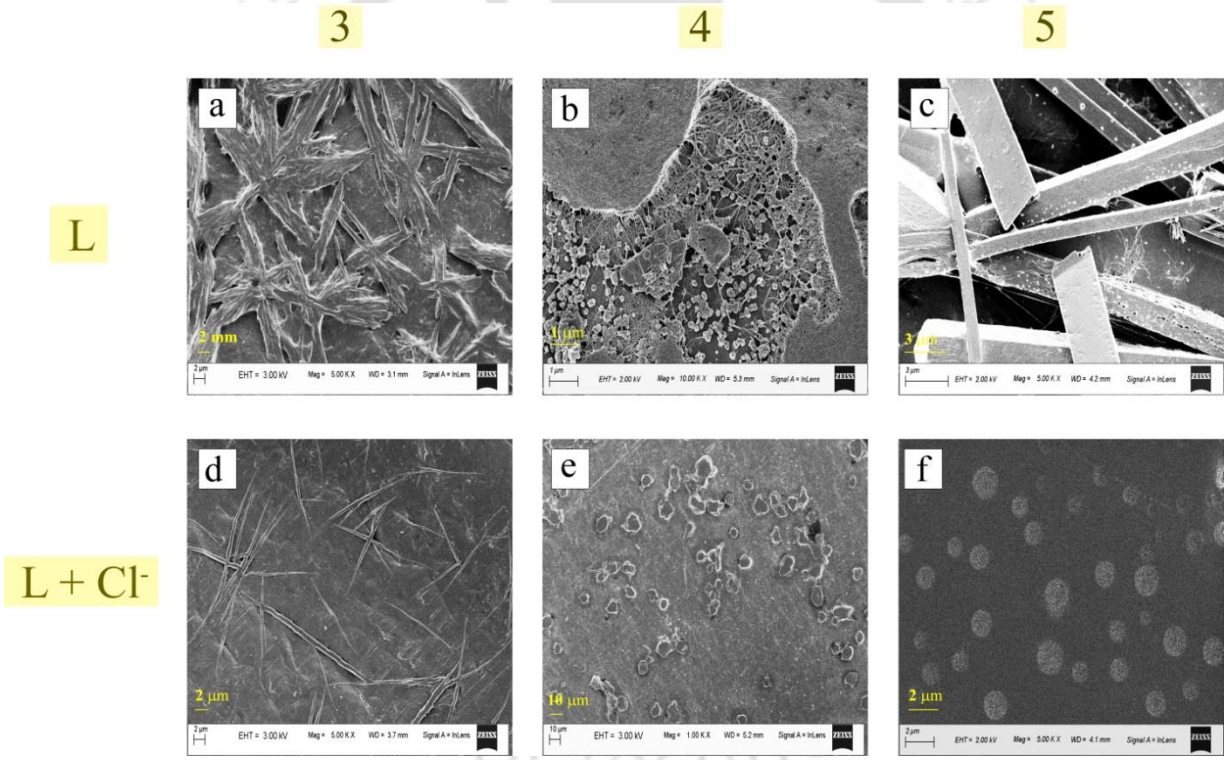


Fig. 4.10 FESEM image of network type assembly of receptors (a) **L_3** and (b) **L_4**, (c) micro plate like assembly of receptor **L_5** and (d-f) FESEM image of receptors after addition of Cl^- at room temperature.

It was observed that the action of Cl^- upon **L_4** and **L_5** was more prominent than that upon **L_3** (Fig. 4.10). The network type morphology for **L_4** and micro-plates for **L_5** disappeared upon interaction with Cl^-, whereas for **L_3**, the dense branched-like structure became thinly distributed. For example, when **L_5** (in an approximately 0.5×10^{-3} M DMF solution) was treated with Cl^- (1:1), the morphologically micro-plate like (Fig. 4.10c) assembly of receptor **L_5** was destroyed (Fig. 4.10f).

4.9 Conclusion

Briefly, in conclusion, the consistent solid-state halides as well as oxyanion binding of substituted neutral dipodal receptors **L_3-L_5**, in the presence of π-acidic, electronegative-containing, aryl-substituted terminals, have expansively established. Single crystal X-ray studies confirm that the bis-urea receptors **L_3-L_5** fully coordinated with the small spherical chloride within its dimeric cavity. The receptor **L_3** can readily form a cooperative neutral self-assembly with smaller halides to larger halides, i.e. chloride, bromide, and iodide, as well as bind with the planar carbonate ion. The *meta* isomer **L_4** forms a 1:2 host-guest assembly with chloride and bromide in the same space group, whereas its isomeric receptor **L_5** forms a cooperative complex only with chloride ion. Anion binding studies in solution accompanied by ^{1}H-NMR titration analysis and a FESEM imaging study also supported the solid-state results, especially for spherical chloride. Successively, the flexible molecular structure of receptors **L_3-L_5** directs the shape along with the preorganized cavity of the receptor to add directionality to the entire coordination and guide the recognition process. In the solid-state, evidence of these types of halides along with oxyanion binding with a highly electron-withdrawing group dipodal moiety specifically would be very helpful to supramolecular scientists to comprehend the neutral receptor-anion assembly development.

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Annexure 3

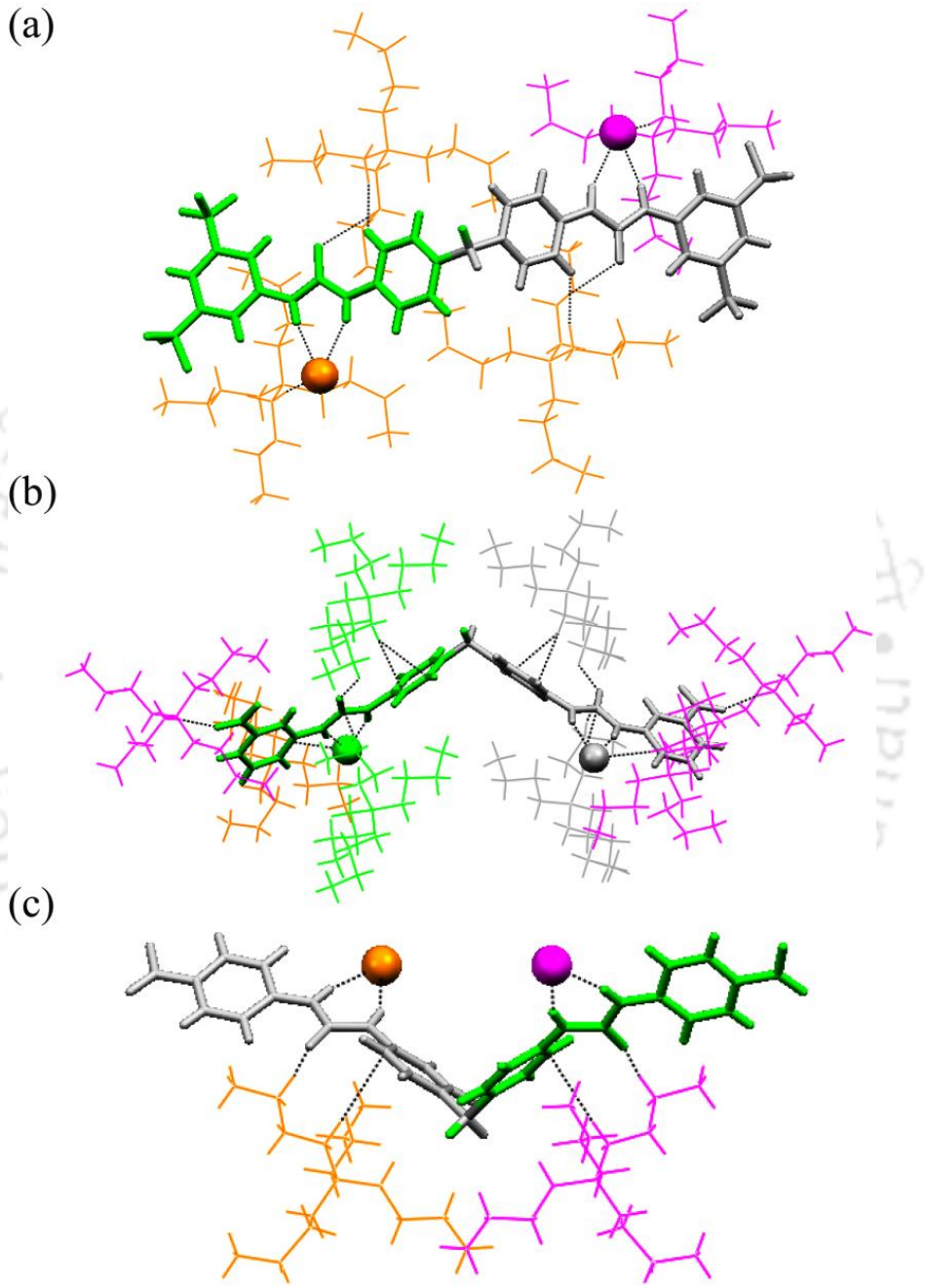


Fig. A4.1 Symmetry operation view of complex **3a,** complex **4a,** and complex **5a** showing all interactions respectively.

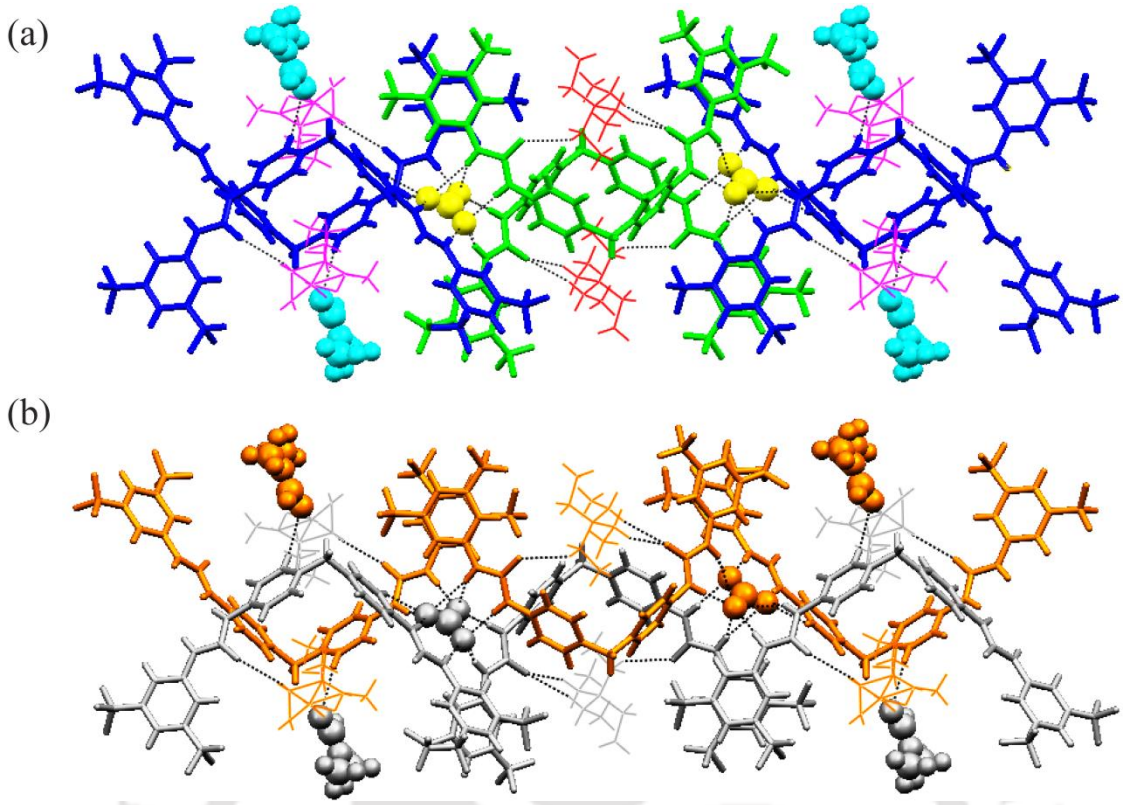


Fig. A4.2 (a) Symmetry equivalence and (b) symmetry operation view of complex **3d**.

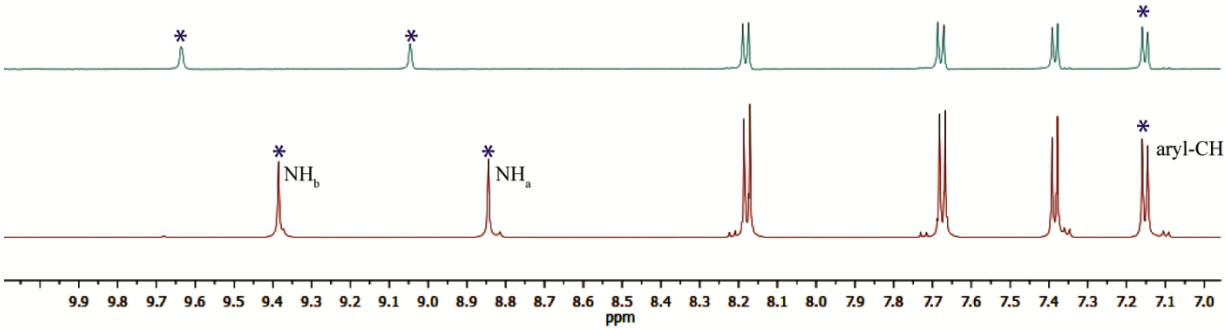


Fig. A4.3 Comparative ^{1}H-NMR spectrum of free receptor $\mathbf{L_3}$ and its bromide complex **3b**.

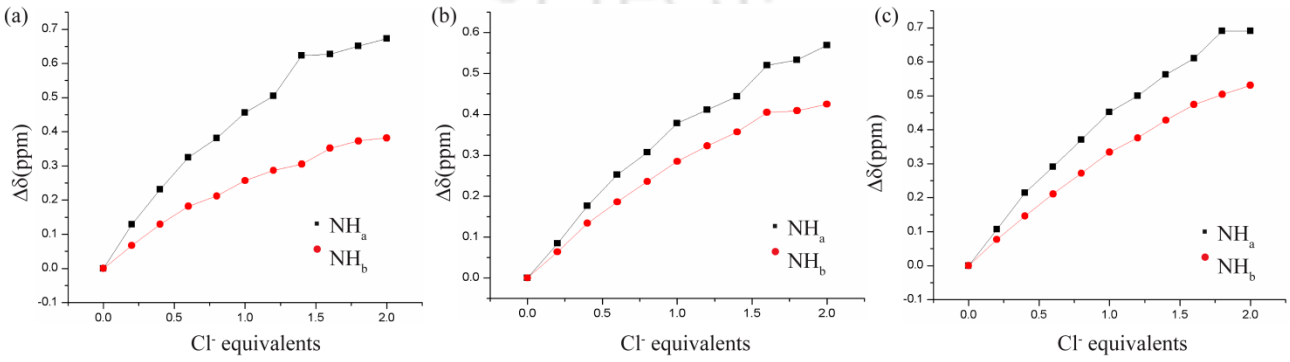


Fig. A4.4 Change in chemical shift of –NH resonances of (a) $\mathbf{L_3}$, (b) $\mathbf{L_4}$, and (c) $\mathbf{L_5}$ (10 mM) with increasing concentration of standard Cl^- solution (50 mM) in DMSO-d6 at 298 K..

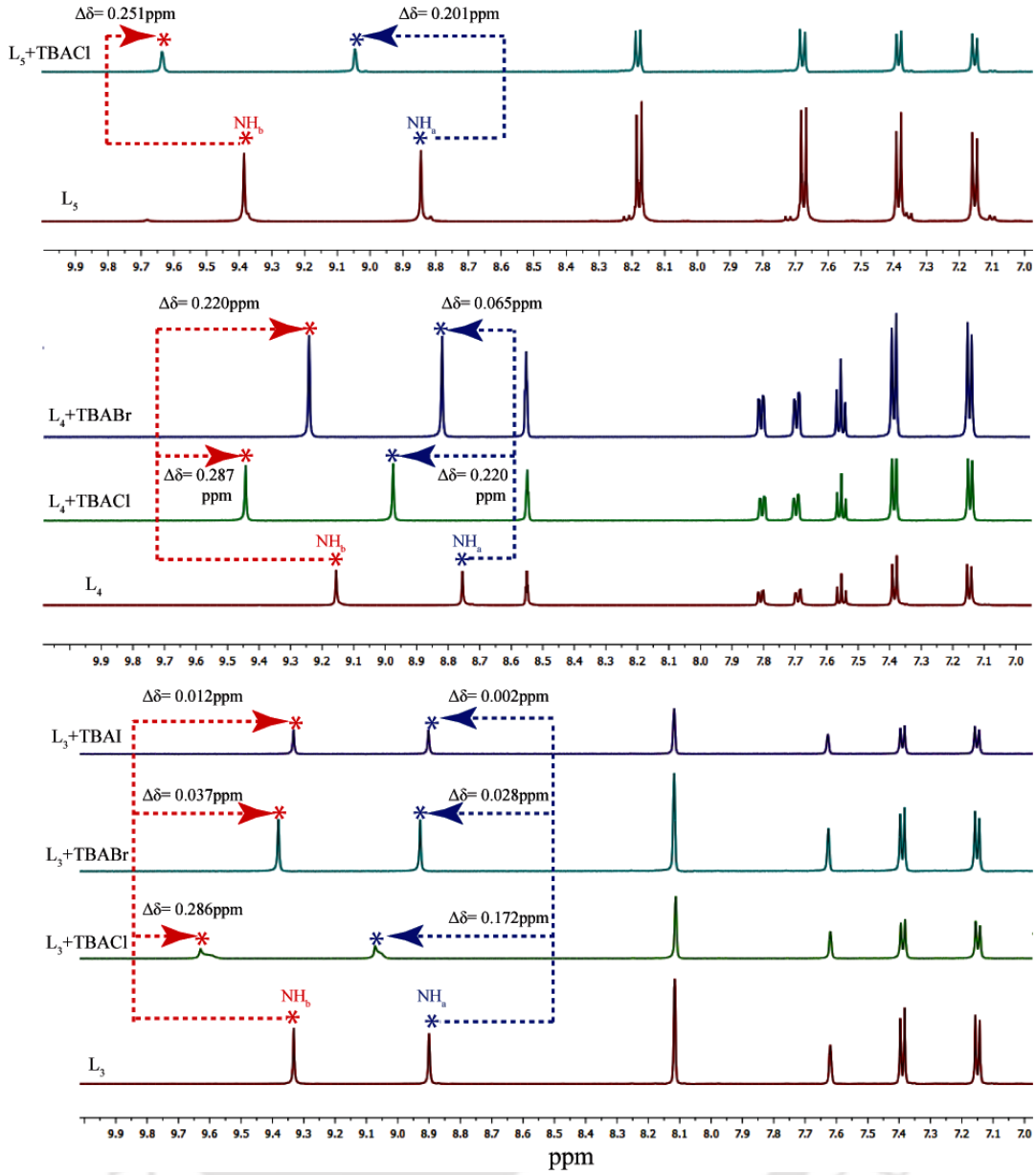


Fig. A4.5 Expanded partial ^{1}H-NMR comparative stacked spectra in the solution phase of bis-urea receptor **L_3**, **L_4**, and **L_5** with halides as observed from the solid-state, displaying the observable downfield shifts of urea $-NH_a$ and $-NH_b$ proton resonances of molecular receptor **L_3**, **L_4**, and **L_5** upon anion complexations.

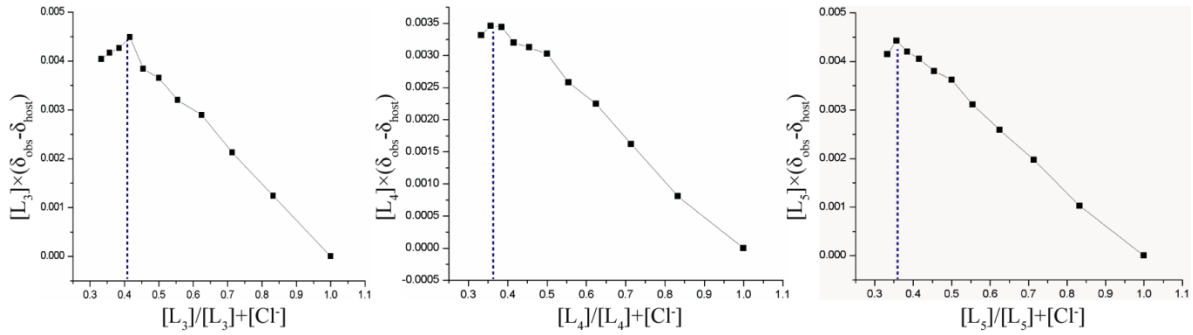


Fig. A4.6 Job's plot diagram of **L_3**, **L_4**, and **L_5** with chloride (1:1 and 2:1 stoichiometry) respectively as obtained from proton NMR titration studies.

Table A3.1 Crystallographic parameters and refinement details of anion complexes of receptors **L_3-L_5**

Formula	$C_{63}H_{92}Cl_2F_{12}N_6O_2$	$C_{63}H_{92}Br_2F_{12}N_6O_2$	$C_{63}H_{92}F_{12}I_2N_6O_2$	$C_{85}H_{93}F_{24}N_{12}O_9$	$C_{59}H_{94}Cl_2N_8O_6$	$C_{59}H_{94}Br_2N_8O_6$	$C_{59}H_{94}Cl_2N_8O_6$
CCDC	1871250	1871249	1871251	1871252	1871254	1871253	1871255
Fw	1264.33	1353.23	1447.23	1882.71	1082.32	1171.22	1082.32
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	orthorhombic	orthorhombic	monoclinic
Space group	*C 2/c*	*I 2/c*	*I 2/c*	$P\bar{1}$	*P b c n*	*P b c n*	*P 2/c*
a/Å	43.914(3)	19.7327(10)	20.3365(9)	12.2455(10)	37.9221(17)	38.047(2)	19.3291(18)
b/Å	8.7711(5)	8.9156(9)	9.0636(4)	17.2779(13)	9.7702(4)	9.7801(12)	9.7601(14)
c/Å	19.3487(13)	40.391(3)	39.9667(19)	23.5317(17)	17.1521(8)	17.2351(16)	16.9098(15)
α/°	90.00	90.00	90.00	99.612(5)	90	90	90
β/°	111.830(4)	95.951(5)	97.865(4)	98.177(4)	90	90	93.717(9)
γ/°	90.00	90.00	90.00	105.591(4)	90	90	90
V/Å^3	6918.2(8)	7067.6(9)	7297.4(6)	4635.6(6)	6355.0(5)	6413.3(10)	3183.4(6)
Z	4	4	4	2	4	4	2
D_c/g cm^{-3}	1.214	1.221	1.317	1.349	1.131	1.213	1.129
μ Mo K_α/mm^{-1}	0.186	0.328	0.934	0.121	0.154	1.315	0.154
T/K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
θ max.	20.0610	20.9020	20.6790	18.90	18.56	24.2690	20.0910
Total no. of reflections	28126	19300	22096	65643	53409	21465	13860
Independent reflections	8165	8172	8461	20997	7321	7393	7255
Observed reflections	6326	2834	4014	6419	2544	3469	2301
Parameters refined	389	397	388	1191	344	344	344
R_1, I > 2σ(I)	0.1012	0.0891	0.0643	0.0926	0.0951	0.0637	0.0985
wR_2 (all data)	0.2489	0.2636	0.2365	0.2165	0.2636	0.2786	0.2570
GOF (F^2)	1.143	1.043	0.971	1.163	1.118	0.864	1.024

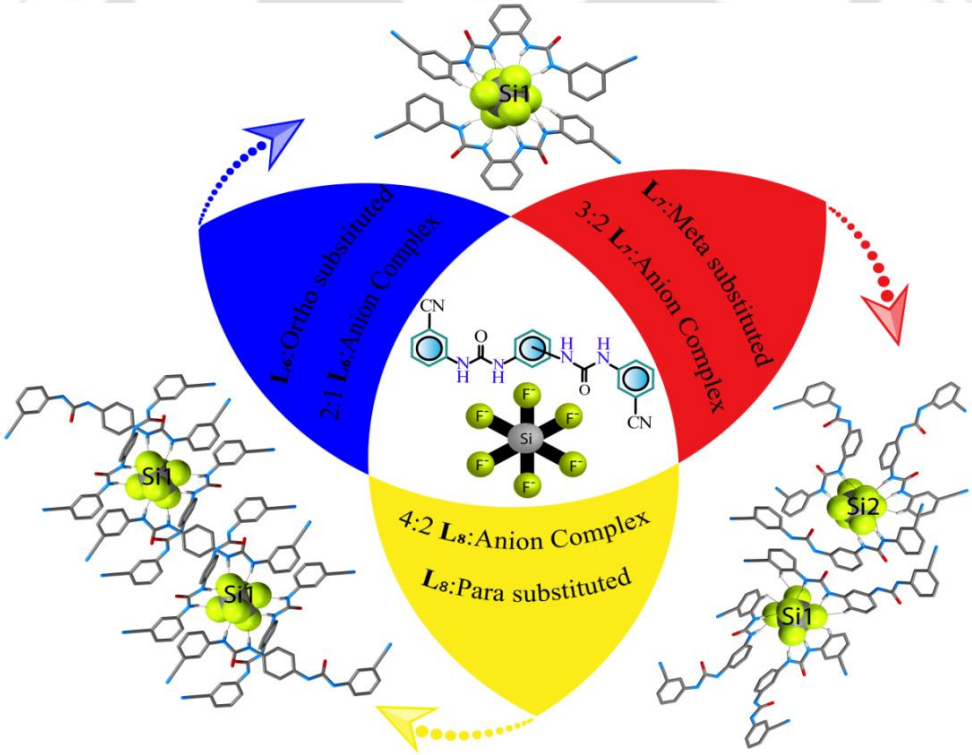
Table A4.2 Details of Hydrogen bonding contacts in anion complexes of receptors $\mathbf{L_3}$-$\mathbf{L_5}$

Complex	D−H···A	*d*(D···H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	<D−H···A/°	Symmetry codes
3a	N1-H1N···Cl1	0.86	2.32	3.156(4)	165	x,1-y,-1/2+z
	N2-H2N···Cl1	0.86	2.43	3.248(4)	158	x,1-y,-1/2+z
	C6-H6···F6	0.93	2.43	2.745(10)	100	x,y,z
	C8-H8···O1	0.93	2.24	2.836(8)	121	x,y,z
	C11-H11···O1	0.93	2.26	2.868(7)	122	x,y,z
	C21-H21B···Cl	0.97	2.83	3.777(6)	166	x,-1+y,z
	C28-H28B···F4	0.96	2.52	3.324(17)	141	1/2-x,1/2+y,1/2-z
3b	N2-H1N···Br1	0.86	2.46	3.301(6)	166	x,y,z
	N1-H2N···Br1	0.86	2.56	3.384(4)	160	x,y,z
	C6-H6···O1	0.93	2.25	2.860(8)	122	x,y,z
	C10-H10···O1	0.93	2.26	2.855(9)	121	x,y,z
	C29-H29B···Br1	0.97	2.93	3.888(8)	170	x,y,z
	C30-30A···O1	0.97	2.58	3.484(10)	156	-1/2+x,3/2-y,z
3c	N1-H1N···I1	0.86	2.68	3.529(6)	167	x,y,z
	N2-H2N···I1	0.86	2.77	3.607(4)	164	x,y,z
	C6-H6···O1	0.93	2.26	2.842(8)	120	x,y,z
	C15-H15···O1	0.93	2.28	2.887(8)	122	x,y,z
	C30-H30A···O1	0.97	2.50	3.432(11)	161	-1/2+x,1/2-y,z
3d	N1-H1N··· O7	0.86	1.86	2.713(10)	174	1-x,1-y,-z
	N2-H2N···O5	0.86	2.21	2.964(10)	146	1-x,1-y,-z
	N2-H2···O7	0.86	2.49	3.216(10)	142	1-x,1-y,-z
	N3-H3A···O5	0.86	1.93	2.783(10)	168	x,y,z
	N4-H4···O6	0.86	1.90	2.757(8)	172	x,y,z
	N5-H5N···O7	0.86	2.54	3.270(11)	144	x,y,z
	N6-H6N···O6	0.86	2.15	3.007(8)	172	x,y,z
	N76-H7N···O7	0.86	1.93	2.793(11)	176	-x,1-y,1-z
	N8-H8N···O6	0.86	2.05	2.848(8)	154	-x,1-y,1-z
	C6-H6···O1	0.93	2.26	2.854(12)	121	x,y,z
	C15-H15···O1	0.93	2.47	2.936(11)	111	x,y,z
	C22-H22···O2	0.93	2.24	2.806(11)	118	x,y,z
	C25-H25···F12	0.93	2.43	2.752(11)	101	x,y,z
	C29-H29···O2	0.93	2.21	2.799(12)	120	x,y,z
	C39-H39···O4	0.93	2.24	2.839(11)	121	x,y,z
	C42-H42···O4	0.93	2.34	2.811(10)	111	x,y,z
	C60-H60···O3	0.93	2.24	2.840(10)	121	x,y,z
	C63-H63A···O4	0.97	2.58	3.331(11)	134	x,y,z
	C65-H65A···O3	0.97	2.33	3.240(11)	156	x,y,z
	C69-H69A···O3	0.97	2.51	3.352(11)	145	x,y,z
	C80-H80A···O8	0.96	2.38	2.73(3)	101	x,y,z
4a	N1-H1N···Cl1	0.86	2.55	3.357(4)	156	x,1-y,1/2+z
	N2-H2N··· Cl1	0.86	2.34	3.184(4)	168	x,1-y,1/2+z
	C3-H3···O1	0.93	2.57	2.956(5)	105	x,y.z
	C13-H13···O1	0.93	2.26	2.850(6)	121	x,y,z
	C18-H18A···O2	0.97	2.42	3.382(7)	171	1/2-x,1/2+y,z
4b	N1-H1N···Br1	0.86	2.55	3.279(4)	168	x,1-y,1/2+z
	N2-H2N··· Br1	0.86	2.64	3.446(5)	156	x,1-y,1/2+z
	C23-H23B···Br1	0.96	3.00	3.938(5)	105	x,y.z
	C15-H15A···O3	0.97	2.38	3.351(8)	174	x,y,z
	C21-H21A···O1	0.97	2.64	3.610(8)	171	1/2-x,1/2+y,z
	C25-H25A···O1	0.97	2.67	3.397(9)	131	x,y,z

5a	N1-H1N···Cl1	0.86	2.43	3.382(5)	155	x,1-y,1/2+z
	N2-H2N··· Cl1	0.86	2.64	3.146(5)	169	x,1-y,1/2+z
	C6-H6B···O1	0.97	2.60	3.299(11)	129	x,-1+y,z
	C18-H18···O1	0.93	2.27	2.870(8)	121	x,y.z
	C24-H24···O1	0.93	2.50	2.906(7)	107	x,y,z

Chapter 5

Aromatic Meta-Substitution Based Positional Isomeric Receptors for Encapsulation of Hexafluorosilicate Anions

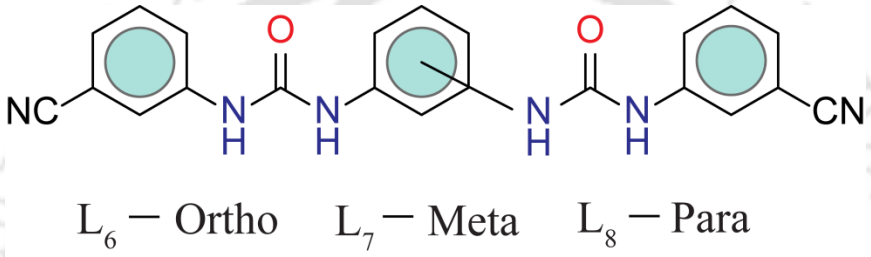


5.1 Background and Focus of the Chapter

Host-guest chemistry has been one of the main compelling fields in the field of supramolecular chemistry.[1] Most of the underlying biological and chemical phenomena in the areas of sensing, catalysis and transport, and molecular recognition of anions play a vital role. So, along with the detailed analysis of the diverse functions of those anions, the area of research for recognition of anions particularly in the solid-state or solution phase has become more exciting and continues to expand.[2] The primary strategy used for anion coordination using abiotic moieties with H-bonding frameworks is noncovalent, reversible interactions and it has become a significant and active field of research in the area supramolecular chemistry.[3] Anion binding proteins like phosphate-binding proteins in Escherichia coli[4] or sulfate binding proteins in Salmonella typhimurium[5] bacteria and their H-bonding environment in a natural system has encouraged researchers to develop multiple H-bond available abiotic receptors for the recognition of anionic guests on suitable frameworks that offer specific binding sites.[6] Usually, anions have very high solvation free energies (e.g., $\Delta G_{hydration}$ of CO_3^{2-}, SO_4^{2-}, and $H_2PO_4^-$ are −1315, −1080, and −465 kJ mol^{-1}, respectively) and substantial standard Gibbs energies of hydration; thus, more than one receptor molecule is clearly required in the whole host-guest system within the internal anion binding components for adequate recognition of one or more higher coordinating oxyanions.[7] Over the last two decades, tren [tris(2-aminoethyl)-amine]- based tripodal receptors having terminal aryl substituents comprising electron-withdrawing or either electron-donating groups have been structured into a distinctive class of anion binding aromatic acyclic ionophores which can recognize one or more anionic guests in pseudocapsular/capsular assemblies.[8] The encapsulation of anions of larger dimensions like planar carbonate and tetrahedral sulfate within the receptor cavity is also quite challenging, as planar carbonate anions work as buffers in the blood, and because of the high charge density of sulfate anions in drinking water, they exist as contaminants as well as act as pollutants in nuclear and radioactive waste.[9] The recognition and binding of fluorosilicate anions are much less explored[10] though lately, selective binding of fluorosilicate anions has drawn the attention of supramolecular researchers due to its biomedical impact and environmental impact[11] along with the application of fluorosilicates for the fluoridation of drinking water[12] noteworthy potential for health damage.[13] The use of fluoride for dental caries[14] and the treatment of osteoporosis[15] along with the ill effects of fluorosis[16] make it significant and biologically relevant amongst the full range of anions.

Hence, in continuing our group's interest in the field of substituent directed host-guest self-assemblies, in this chapter, we demonstrate three positional isomeric bis-urea receptors (**L_6-L_8**) with the cyano group as a terminal substituent have been synthesized for extensive analysis of

host-guest anion binding propensity in their neutral form. The existence of electron-withdrawing or π-acidic phenyl substituents in the receptors **L_6-L_8** supports efficient binding of the octahedral hexafluorosilicate anion within their dimeric cavity. Receptor **L_6** and its cyano-substituted *para* isomer receptor **L_8** have been found to entrap water-free naked SiF_6^{2-}, while the *meta* receptor has been found to trap hydrated SiF_6^{2-} within its cavity. In the presence of excess fluorides, **L_6** self-assembles to form dodeca-coordinated hexafluorosilicate complex **6a** and **L_8** self-assembles to form octa-coordinated hexafluorosilicate complex **8a** in the solid-state *via* cooperative and non-cooperative H-bonding interactions of urea moieties respectively. However, the *meta* receptor **L_7** self-assembles to build a 3:2 host-guest assembly, where the two SiF_6^{2-} units show different coordination environments.



Scheme 5.1 Molecular structure of the receptors **L_6-L_8**.

5.2 Design aspects of anion binding receptors L_6-L_8

Three isomeric bis-urea receptors **L_6-L_8** having electron-withdrawing cyano groups as meta substituents were synthesised in good yield from 3-cyanophenyl isocyanate by reaction with three positional isomeric cores *ortho*, *meta*, and *para*-phenylenediamine in acetonitrile solvent at room temperature, respectively (Scheme 5.1). For anion coordination *via* H-bonding, the receptors having urea functionalities with the highly electron-withdrawing group provided a well-organized cavity, which is highly appreciated. In presence of the electron-withdrawing *meta*-cyano group in receptors **L_6-L_8** with a well ordered dimeric cavity providing the platform for H-bonding to bind with a different dimension of anions. The electron-withdrawing groups in highly acidic bis-urea receptors **L_6-L_8** dependably orient both the urea arms in the direction of the recognition of large oxyanions and halides. The urea moieties from the inflexible receptors can adapt themselves to coordinate guest molecules *via* cooperative or non-cooperative H-bonding interactions either in the syn- or anti-fashion, which depends upon the dimensions of the anionic guest molecules. The binding difference of a distinct receptor with a particular anion is given by the detailed structural information from the single crystal X-ray study. The results we obtained from the coordination selectivity and single crystal X-ray investigation of naked anion complexes of *meta*-cyano substituted bis-urea receptors are confirmed in (Fig. 5.1-5.3).

The chelate effect plays an essential role for anionic guests with different dimensions, because of the favourable assistance from both enthalpy and entropy. Attempts were made by charging excess n-TBA salts of anions to the solution of receptors in glass test tubes in various aprotic solvents like DMSO, DMF, and a mixture of DMF/DMSO and MeCN for inspection of the solid-state binding of oxyanions. Thereby, here, we were able to isolate the fluoride ion-induced very rare hydrated and non-hydrated complexes of hexafluorosilicate with receptors **L_6-L_8**. From the structural explanation of hexafluorosilicate complexes of receptors **L_6-L_8**, it shows that the (urea)N–H···A(anion) interactions are mostly involved in binding additionally strengthened by some non-covalent intermolecular interactions.

5.3 Single crystal X-ray structural analysis of hexafluorosilicate complexes

5.3.1 Hexafluorosilicate complex (6a)

Tetrabutylammonium silicon hexafluoride salt complex **6a** was obtained by the reaction of the bis-urea receptor **L_6** with TBAF in a DMSO/DMF solution mixture. It is important to remark here that the silicon hexafluoride anion (SiF_6^{2-}) was not present in the reaction mixture before crystallization, and complex **6a** is obtained by the reaction of the receptor and TBAF with glass-silica in DMF/DMSO, probably as a result of glass corrosion.

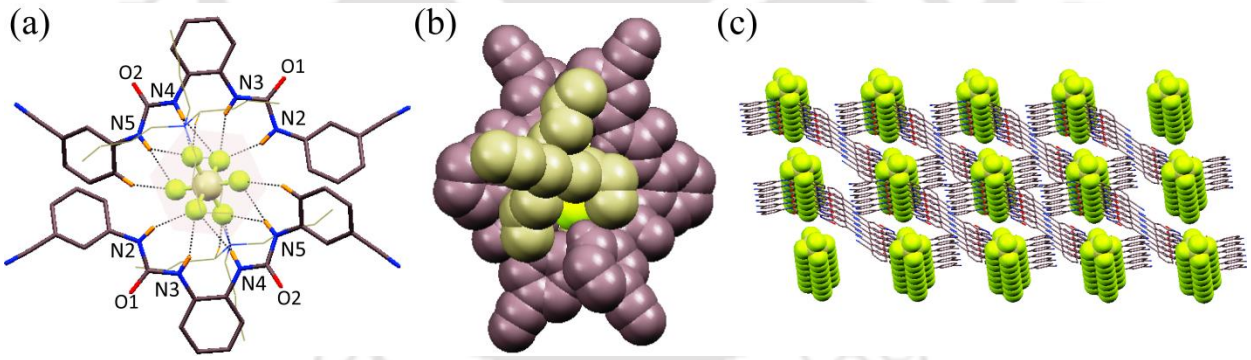


Fig 5.1 Single crystal X-ray crystal structures showing the (a) coordination atmosphere of the divalent SiF_6^{2-} anion coordinated 2:1 host-guest pseudocapsular assembly in complex **6a**, (b) complex **6a** showing C–H···O weak interactions, (c) packing diagram of host-guest complex **6a** as seen along the crystallographic b-axis.

The needle-shaped colourless crystals of the complex crystallizes in the triclinic crystal system of space group $P1^-$ with Z = 1. After the single crystal X-ray study, from the structural explanation, it is clear that the asymmetric structural unit of complex **6a** consists of one receptor unit, a half unit of hexafluorosilicate anion and its corresponding tetrabutylammonium (TBA) countercation. Structural elucidation of the complex revealed that the two symmetrically identical units of the bis-urea receptor are flipped inward towards each other in a face-to-face fashion (distance $Ar_{Benzene}\cdots Ar_{Benzene}$ = 12.317 Å) (Fig. A5.3), where both the receptors

coordinating the octahedral hexafluorosilicate anion exactly in an identical manner creating a caged supramolecular assembly (Fig. 5.3). The arc-type architecture arms of receptor **L_6** create a perfect cavity and the two symmetrically identical molecules of **L_6** with opposite orientations form a capsular cavity that encapsulates a dianionic hexafluorosilicate anion in its centre *via* H-bonds. Receptor **L_6** in the presence of excess F^- forms 2:1 host-guest complexes *via* a different number of H-bond sharing of cooperative urea groups from two types of symmetrically equivalent receptor units. The hexafluorosilicate anion behaves as a bifurcated hydrogen bond acceptor and each arm of receptor **L_6** donate six N–H···F and two C–H···F (one from the *ortho*-aryl hydrogen of the cyano phenyl ring and one from the n-TBA hydrogen) hydrogen bonds resulting in sixteen H-bonds with an average donor-to-acceptor distance of 2.932 Å. In complex **6a**, crystal structural clarification reveals that the two symmetrically identical receptor units donate 16 strong H-bonding interactions in which 12 H-bonds are accepted by one SiF_6^{2-}, two are contributed by the *ortho*-phenyl-CH of the two identical receptors and the remaining two H-bonds are donated by two identical tetrabutyl cation units (Fig. 5.1a). The larger coordinating octahedral hexafluorosilicate anion encapsulated 2:1 host-guest complex **6a** gains extra stability *via* ten C–H···O weak interactions from receptor **L_6** and TBA cations (Fig. A5.2). The packing diagram of neutral complex **6a** shows a beautiful stack of a coin-like arrangement of SiF_6^{2-} anion bound dimeric cages as viewed down along the crystallographic c-axis (Fig. 5.1c). Fig. 5.1b shows the space-fill view of SiF_6^{2-} fully encapsulated by two **L_6** receptor units shielded by two symmetrically identical TBA cations.

5.3.2 Hydrated hexafluorosilicate complex (7a)

Interestingly, another hexafluorosilicate complex with the same cell parameters as receptor **L_7** group $P1^-$ with three symmetrically distinct receptor moieties along with two octahedral hexafluorosilicate anions, four tetrabutylammonium countercations and one water molecule in its asymmetric structural unit which is verified by single crystal X-ray data. Interestingly, the three types of symmetrically different *meta* based receptor cavities containing urea platform **L_7** become a little bit closer, and the adjacent urea moieties flip outward, away from the cavity in the opposite direction. Receptor **L_7** in the presence of excess F^- forms 3:2 host-guest complexes *via* a different number of H-bond sharing of non-cooperative urea groups from the three types of symmetrically distinct receptor units. In complex **7a**, crystal structural clarification reveals that the two symmetrically discrete divalent hexafluorosilicate anions accept a total of 34 strong H-bonding interactions with an average donor-to-acceptor distance of 3.082 Å. Out of the total 34 H-bonds, 17 H-bonds are donated by the urea –NH groups of the three symmetrically distinct

receptors, 5 H-bonds are contributed by the *ortho*-aryl CH of the central benzene ring and cyano phenyl ring, one H-bond is assisted by one water molecule and the remaining 11 H-bonds are donated by two pairs of symmetrically distinct TBA units (Fig. 5.2a).

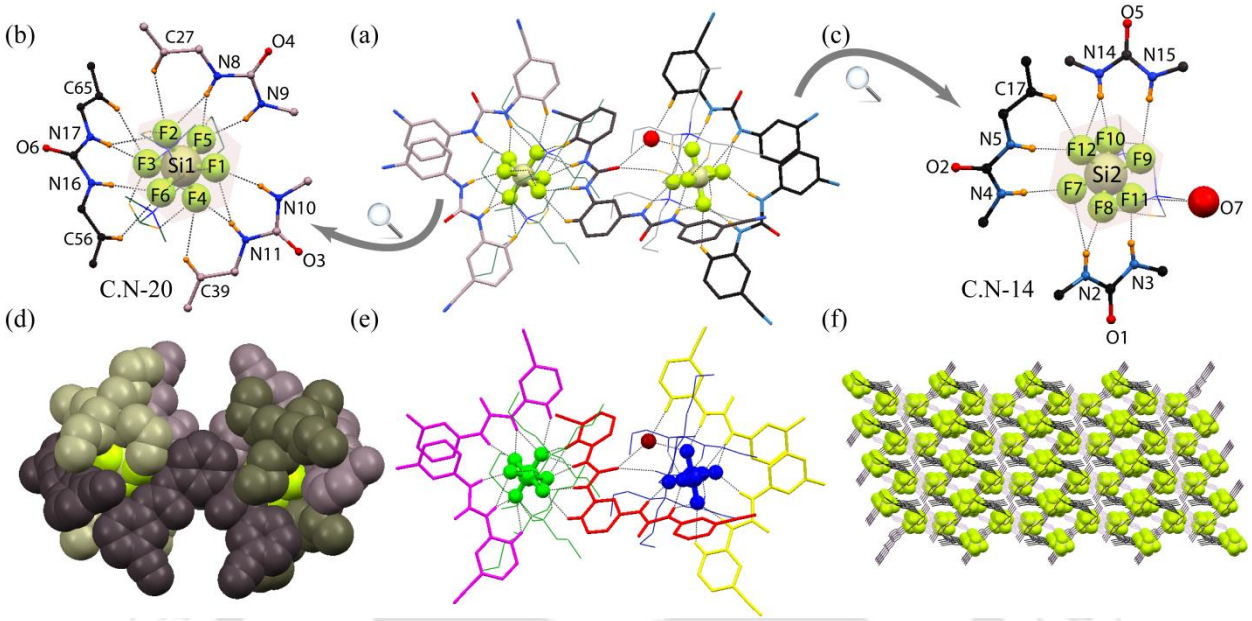


Fig. 5.2 Single crystal X-ray crystal structures showing the (a) binding environment of the divalent SiF_6^{2-}anion coordinated 3:2 host-guest pseudocapsular assembly in complex **7a**, (b) enlarged view of the coordination atmosphere of SiF_6^{2-} , (c) zoomed view of the binding environment of SiF_6^{2-}, (d) space-fill representation of divalent SiF_6^{2-}ions with receptor $\mathbf{L_7}$ shielded by two pairs of TBA cations, (e) symmetry equivalence view of complex **7a** and (f) packing diagram of host-guest complex **7a** as seen along the crystallographic a-axis.

In complex **7a**, from the three symmetrically distinct receptors, interestingly, only one receptor coordinates with the two symmetrically different SiF_6^{2-} and from the other two receptors, one type of receptor binds with only one kind of SiF_6^{2-} (Fig. 5.2e). Here, the most compelling thing is that the binding environments of the two SiF_6^{2-} are totally different, where SiF_6^{2-} accepts 20 strong H-bonds (Fig. 5.2b), out of which 9 H-bonds are strong N–H···F interactions from the urea moieties of the three receptors, 4 are strong C–H···F interactions from the *ortho*-aryl CH group of the aromatic phenyl ring and 7 are strong C–H···F H-bonds contributed by two similar TBA cations. On the other hand, SiF_6^{2-} has a coordination number of 14, out of which the urea arms of receptor $\mathbf{L_7}$ donate eight strong N–H···F interactions, one C–H···F H-bond is donated by *ortho*-aryl CH, 4 H-bonds are contributed by the symmetrically identical two TBA units and fascinatingly, here, the SiF_6^{2-} coordinates with one water molecule which gives one H-bond. The divalent hexafluorosilicate anion coordinated 3:2 host-guest pseudocapsular assembly gains additional strength from several C_{TBA}–H···O_{urea} interactions.

5.3.3 Naked hexafluorosilicate complex (8a)

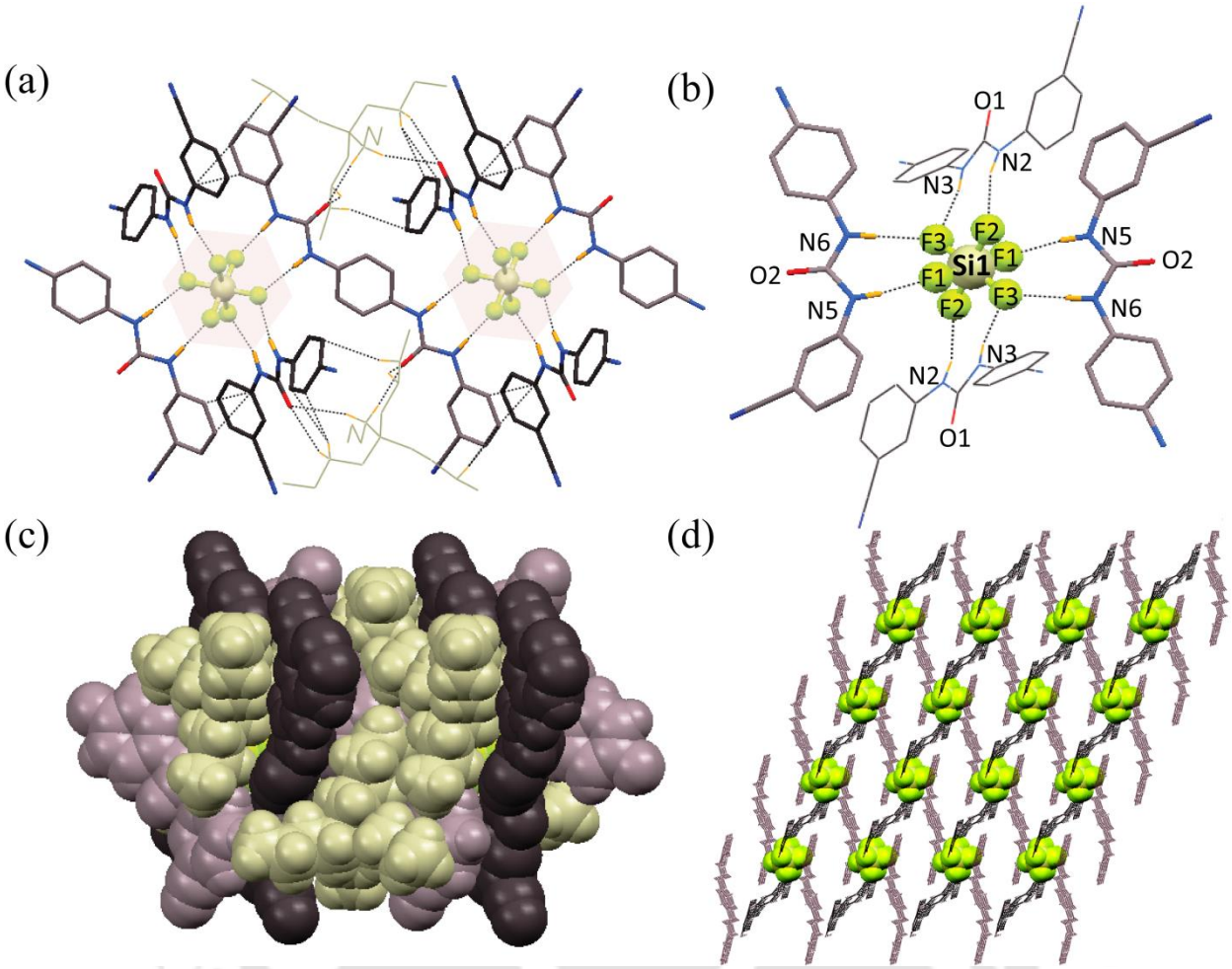


Fig. 5.3 Single crystal X-ray crystal structures showing the (a) coordination atmosphere of divalent SiF_6^{2-} anion coordinated 4:2 host-guest assembly in complex **8a**, (b) enlarged view of a single SiF_6^{2-} anion coordination environment in complex **8a**, (c) space-fill representation of octahedral SiF_6^{2-} ions with receptors and (d) $\mathbf{L_8}$ packing diagram of host-guest complex **8a** as seen along the crystallographic a-axis.

Structural elucidation suggested that complex **8a** crystallises in a triclinic system with the space group $P1^{-}$. Exposition of its crystal structure reveals that the fundamental asymmetric unit of complex **8a** contains two symmetrically distinct receptor units, a half unit of hexafluorosilicate anion and one of its corresponding TBA cation units. From the single crystal X-ray data, it is clear that receptor $\mathbf{L_8}$ orients both the urea arms in the opposite direction to bind with two symmetrically similar anions in a non-cooperative manner forming a 4:2 host-guest complex. Although the urea arms of the neutral receptor are projected in the opposite direction, the receptor is not able to create a C2v symmetric dimeric cavity and the two SiF_6^{2-} anions in complex **8a** are located at opposite sides and stabilized mainly by N–H···F H-bonds from one complete receptor and six half units of the receptor (Fig. 5.3a). The entire coordination environment of divalent SiF_6^{2-} suggests that it has been stabilised *via* sixteen H-bonding interactions with one complete receptor $\mathbf{L_8}$ and half units of two types of symmetrically different

receptors, where the symmetrically identical receptors oriented precisely in the opposite direction having an average donor-to-acceptor distance of 3.025 Å (Fig. 5.3a). In complex **8a**, the coordination environments of the symmetrically identical hexafluorosilicate units are the same, where each SiF_6^{2-} accepts eight hydrogen bonds and the fluoride (SiF_6^{2-}) atoms show mono and bi coordinated nature of hydrogen bonding acceptance. Apart from strong N–H···F H-bonds, the complex gains extra stability from eight π···π interactions, six C–H···π interactions and ten C–H···O interactions (Fig. A5.4).

5.4 Comparative structural analysis of complexes 6a, 7a, and 8a

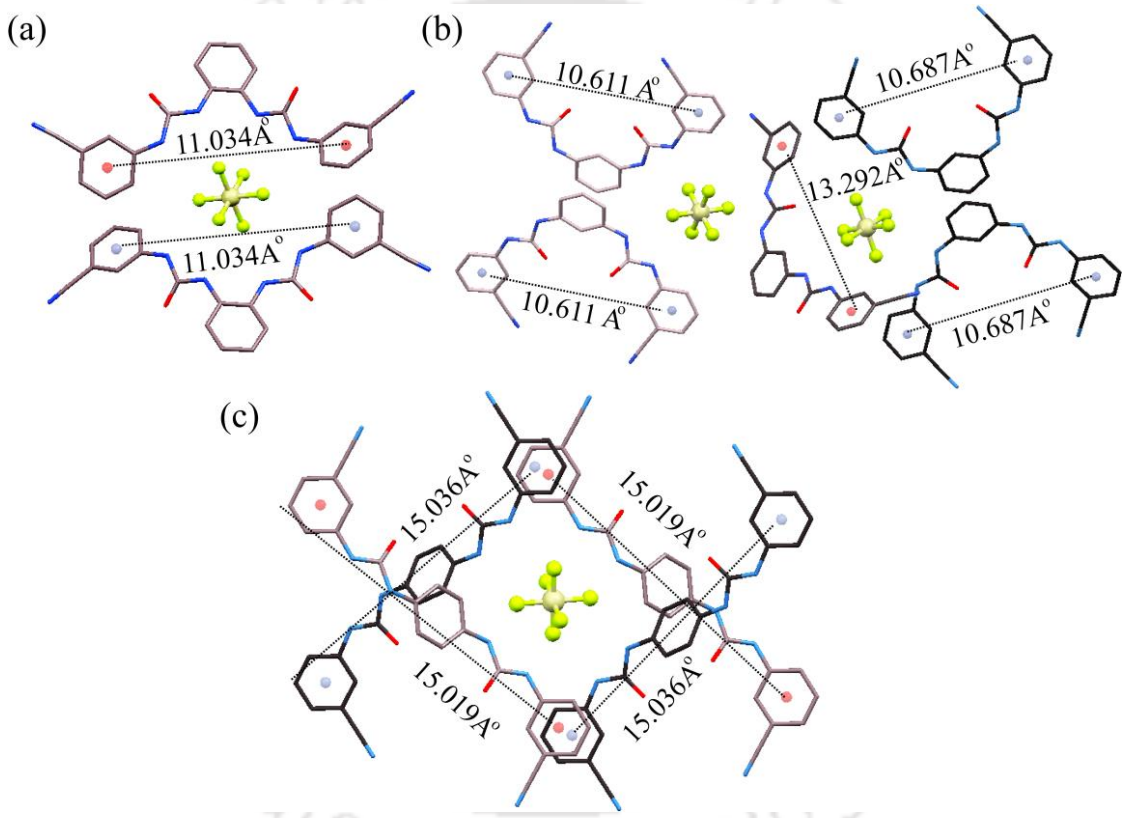


Fig. 5.4 X-ray structures (partial) showing the average pod-distances between the two terminal aryl rings of the bis-urea receptors: (a) complex **6a**, (b) complex **7a**, and (c) complex **8a**.

The isomeric receptors **L_6-L_8** all crystallize in the triclinic crystal system having the space group $P1^{-}$, but are not isostructural. Receptors **L_6-L_8** all assemble in a semi-circular fashion in the presence of excess tetrabutylammonium fluoride salts trapping octahedral anions by cooperative, i.e. two urea N–H groups of a particular receptor bind a particular hexafluorosilicate ion (complex **6a**), and non-cooperative H-bonding interactions of urea N–H groups, i.e. two urea N–H groups of a specific receptor unit bind two different symmetry-identical (complex **8a**) or independent (complex **7a**) hexafluorosilicate ions (Fig. 5.5a-5.5c). Structural clarification

reveals that in complex **6a**, one hexafluorosilicate ion exhibits 12-coordination and in complex **7a**, the two symmetrically different hexafluorosilicate ions show 20-coordination and 14-coordination, while in complex **8a**, each symmetrically identical hexafluorosilicate ion displays octa-coordination. Moreover, all the three entrapped SiF_6^{2-} complexes are stabilized by weaker n-TBA-C–H···O (carbonyl) type H bonds between the n-TBA cation and two carbonyl groups of a specific receptor. It is also significant to remark here that the terminal aryl pod distances of the three receptors in complexes **6a**, **7a**, and **8a** are 11.034 Å, (13.292 Å, 10.687 Å, and 10.611 Å), and (15.036 Å and 15.019 Å), respectively (Fig. 5.4a-5.4c). The terminal aryl pod distances in receptors **L_6-L_8** gradually increase due to the cooperative H-bonding in receptor **L_6** and non-cooperative H-bonding in the case of receptors **L_7** and **L_8**.

5.5 Study of free receptors by density functional theory (DFT)

For a structural description of free receptors, a DFT study was performed, but after numerous efforts to obtain crystals of the free receptors **L_6-L_8** under different conditions, we are not able to nurture good quality crystals of the urea-based receptors. The DFT study reveals that in each case of receptors both the adjacent urea groups are in the syn position showing complete cooperativity of the urea –NH protons (Fig. 5.5). Using the B3LYP method, DFT optimizations were carried out with the 6-31+G (d, p) basis set.

5.6 Solution-state anion binding studies

Solution phase anion binding studies of receptors **L_6-L_8** have also been comprehensively carried out by ^{1}H-NMR experiments (DMSO-d6) to corroborate the binding of SiF_6^{2-} with receptors, as observed from the solid-state investigations. As expected, significant changes have been observed in the case of urea –NH protons of the receptors, being the primary sites for anion recognition with respect to the SiF_6^{2-} complex (Fig. A5.8). ^{1}H-NMR analysis of the free **L_6** receptor shows chemical shift values of δ-NH_a = 8.21 ppm and δ-NH_b = 9.44 ppm, but **L_6** shows an average downfield shift of $\Delta\delta$ = 0.235 ppm ($\Delta\delta$ NH_a = 0.34 ppm; $\Delta\delta$-NH_b = 0.13 ppm) after entrapment of SiF_6^{2-}. Similarly, comparative analysis of ^{1}H-NMR analysis of the free **L_7** and **L_8** receptors and their corresponding SiF_6^{2-} complexes shows an average downfield shift of $\Delta\delta$ = 0.53 ppm and $\Delta\delta$ = 0.026 ppm, respectively. This specifies the efficient binding of hexafluorosilicate anions with the receptors in the solution state, similar to that observed from the solid-state studies.

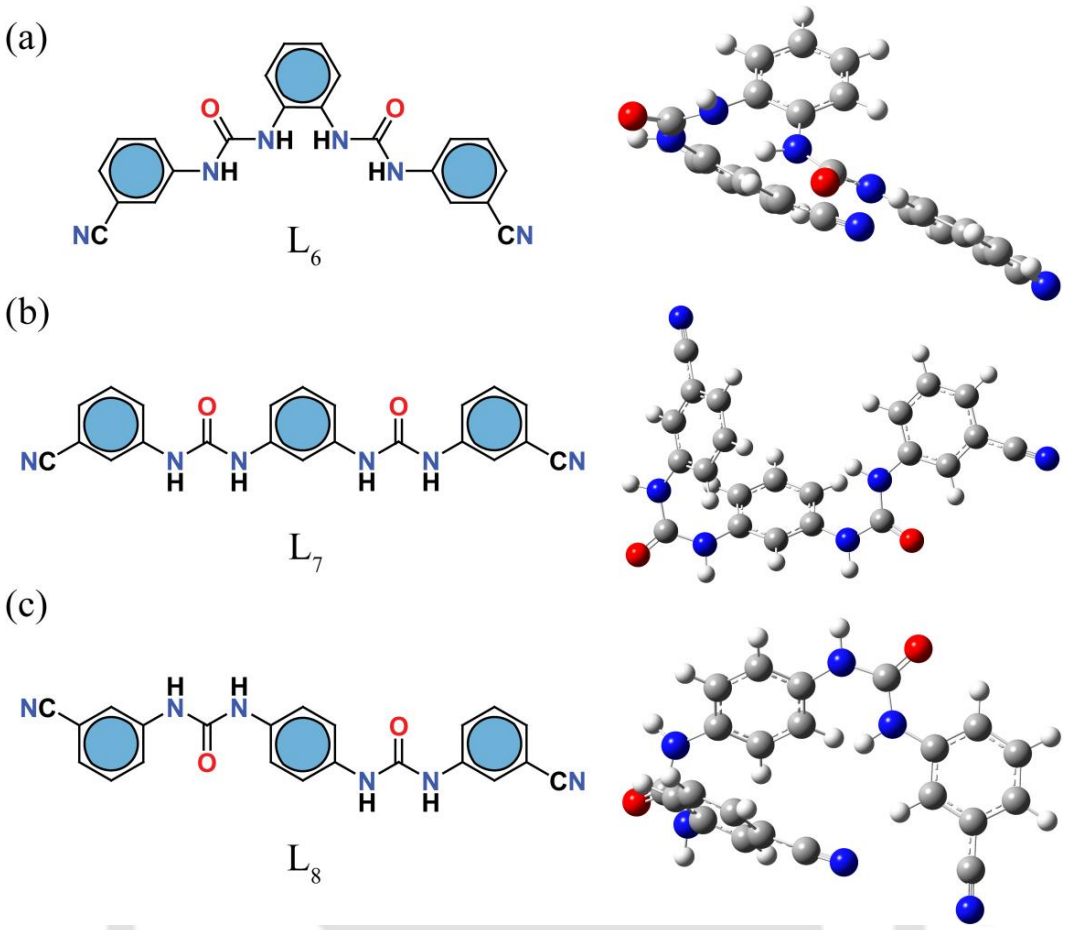


Fig. 5.5 Optimized geometry of the free receptors **L_6**, **L_7** and **L_8** using the B3LYP/6-31+G (d,p) basis set.

5.7 Self-aggregation microscopic studies of the receptors and their hexafluorosilicate complexes

To gain a deeper understanding of the morphological variance between the free receptors and SiF_6^{2-} (obtained from the TBAF solution) complexes, an additional FESEM imaging study was executed by a solution drop-casting method with freshly prepared DMF solutions. The diversity in the topographical nature of supramolecular polymeric assemblies of the three receptors in the absence and presence of SiF_6^{2-} is shown in Fig. 5.6 Interestingly, the morphology of the free receptors varied typically with the type of the isomers and changed after treatment with the anion solution. The flexible micro-fibrils of *ortho* receptor with an average width in the micrometre range did not alter significantly after the addition of anions, whereas the micro-rod like structure of *para* became thinly distributed when treated with the anion solution. However, the change in morphology is the most significant in the case of *meta* due to the action of the SiF_6^{2-} solution as the ill-shaped structure converted entirely into an ordered micro-needle structure. Thus, the isomers differing by substituent position behave differently to develop different morphologies upon interaction with the same anion solution.

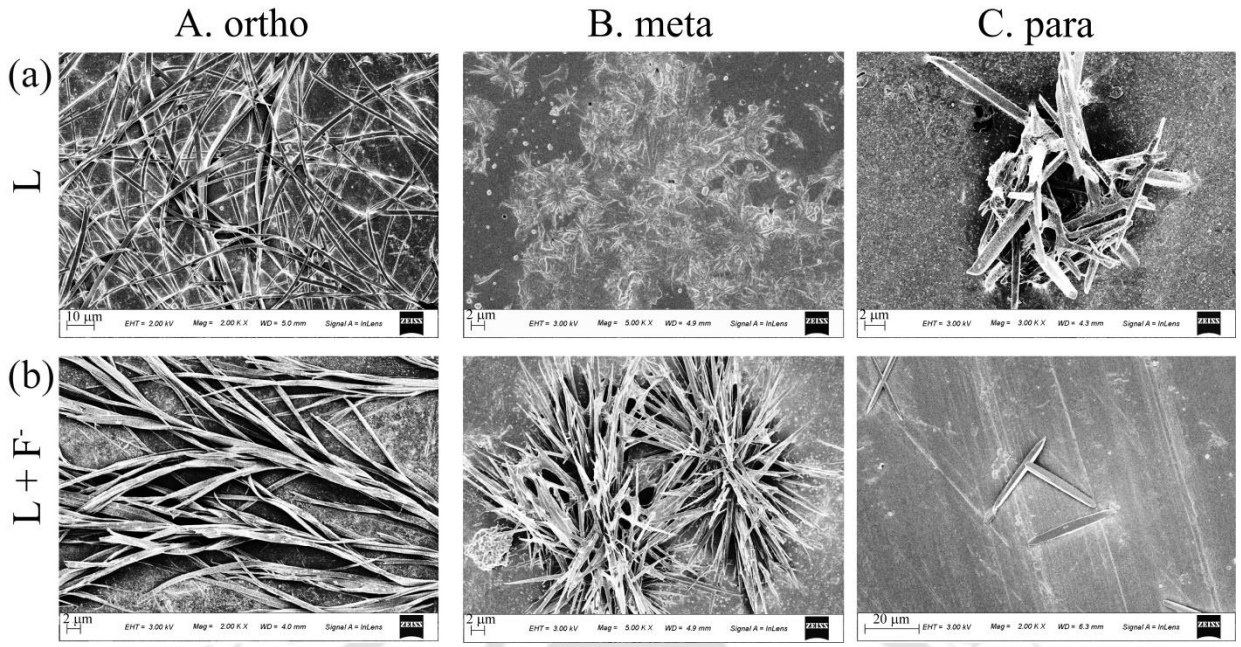


Fig. 5.6 FESEM images of (a) receptors $\mathbf{L_6}$, $\mathbf{L_7}$ and $\mathbf{L_8}$ and (b) FESEM images of receptors after the addition of F^- at room temperature.

5.8 Hirshfeld surface analyses

From the above structural studies, the involvement of strong N–H···anion bonds in the anion complexes in addition to several weak C–H···O and C–H···π non-covalent interactions involved in the changes in the structural conformation of receptors $\mathbf{L_6}$-$\mathbf{L_8}$ upon anion complexations can also be visualized with the Hirshfeld surfaces (HSs). To define the surface characteristics of molecules, Hirshfeld surfaces are contemplated to be a useful tool.[17] By color-coding short or long contacts, HSs offer a unique way of characteristic visualization of intermolecular interactions, where the relative strength of the interactions is described by the colour intensity. The types and nature of intermolecular connections experienced by the molecules in a particular crystal, as "contact contribution", can be quantitatively described by the two-dimensional fingerprint plots (2D FPs) of these Hirshfeld surfaces.[18] Table A5.1 shows the percentage of contact contributions to the d_{norm} surface area of anion bound bis-urea receptor segments of each receptor-anion complex. The Hirshfeld surfaces recorded with the d_{norm} of the SiF_6^{2-} bound neutral receptor segments of 3-cyanophenyl functionalized linear free bis-urea receptors $\mathbf{L_6}$-$\mathbf{L_8}$ are outlined in Fig. A5.6a. The strong N–H···A (SiF_6^{2-}) hydrogen bonds surrounded by the urea N–H donors of the $\mathbf{L_6}$-$\mathbf{L_8}$ receptors and F atom of octahedral hexafluorosilicate in the neutral complexes (**6a**, **7a** and **8a**) are depicted as bright red spots on the surfaces mapped with d_{norm} in Fig. A5.6a. In addition to the strong N–H···A interaction, several weak interactions, like C–H···O, C–H···π, and C–H···F, that exist between the neighbouring receptor fragments, the anion and o-aryl CH of the receptor group or the anion and TBA countercations (Fig. A5.9a) appear as

bright to faint red spots on the Hirshfeld surfaces mapped with d_{norm} of the anion complexes. The H···O close contacts for each anion complex achieved from the corresponding 2D fingerprint plots of HSs (Fig. A5.9b) define the characteristic sharp and soft "spikes" in the plots. On the other hand, the corresponding 2D fingerprint plots for the H···C close contacts display comparatively soft characteristic "spikes" related to those for the H···O close contacts (Fig. A5.9c). From Table 5.1, it is observed that the H···F close contacts of SiF_6^{2-} complexes show contact contributions of ~5–30%. This occurrence is comprehensively attributed to the combined H···F interactions in receptors **L_6-L_8**. Consequently, the H···O close contacts of SiF_6^{2-}complexes exhibit minimal contact contributions (~4-7.5%). On the other hand, the corresponding 2D FPs for the H···C close contacts show contact contributions of ~15-24% (Table A5.1), exhibiting relatively soft characteristic "spikes" in the upper left and lower right of the plots for all of the anion complexes. The results obtained from the HSs and corresponding 2D FPs of the free receptor segments and anion coordinated receptor complexes confirm the solid state results obtained from single crystal X-ray analyses.

5.9 Conclusion

In summary, electron-withdrawing cyano-substituted easy-to-make isomeric bis-urea receptors **L_6-L_8** have rationally developed. Receptor **L_6** has efficiently entrapped SiF_6^{2-} with a total of 12 N–H···F and 4 C–H···F H-bonding interactions within the semi-circular dimeric architecture from primary mixed DMF/DMSO media whereas the isomeric receptor **L_7**, in the presence of excess fluoride, forms a hydrated 3:2 double hexafluorosilicate entrapped complex, where both SiF_6^{2-} units show different coordination behaviour. In mixed DMF/DMSO, receptor **L_8** forms a 4:2 host-guest complex, where one receptor binds with two symmetrically identical SiF_6^{2-} units *via* non-cooperative H-bonding of urea-groups having octa-coordination. The thorough Hirshfeld surface analysis of the hexafluorosilicate anion in the complexes also supports the binding behaviour of the receptors towards SiF_6^{2-} anions. In solution anion binding studies accompanied by a FESEM imaging study also supported the solid-state results. Thus, receptor **L_6-L_8** provides an ideal example of SiF_6^{2-} binding receptor, which has the exceptional ability to change their binding mode towards the SiF_6^{2-}anion in line with the crystallizing environment.

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Annexure 4

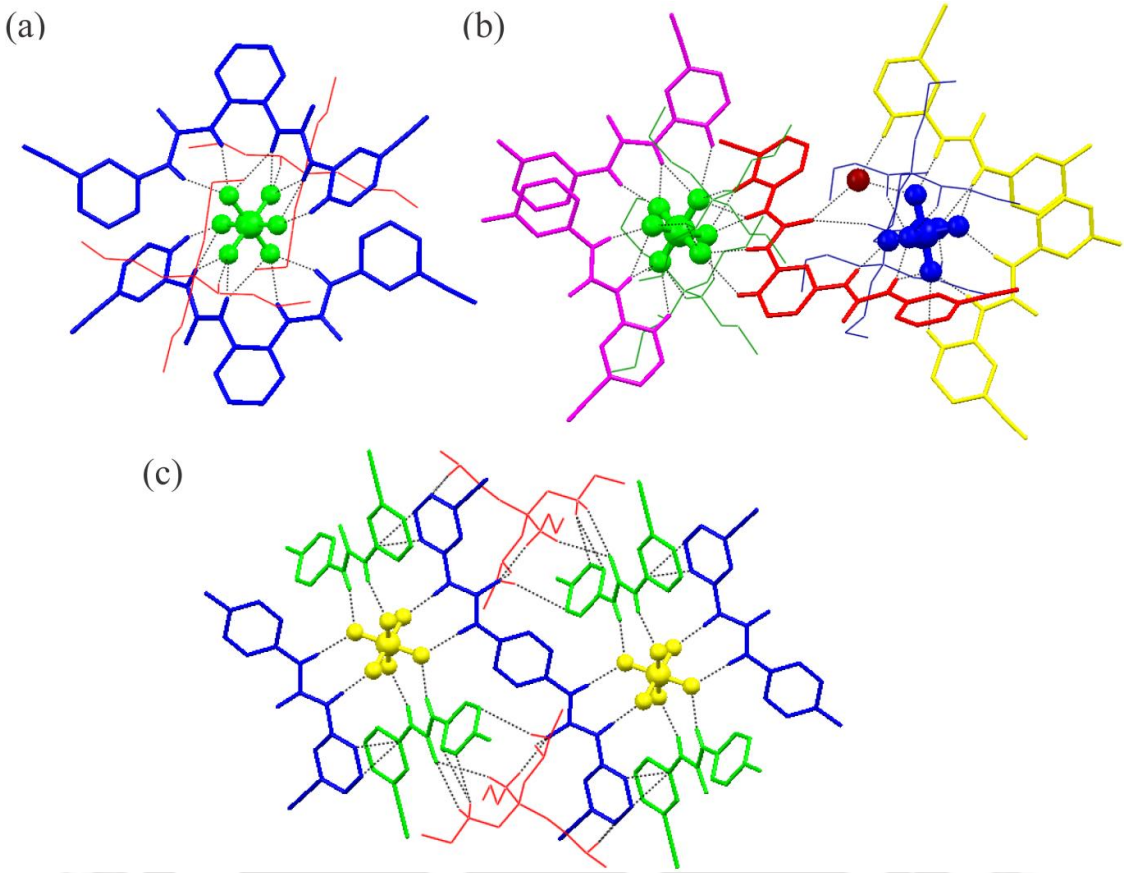

Fig. A5.1 Symmetry equivalence view of (a) complex **6a,** (b) complex **7a**, and (c) complex **8a.**

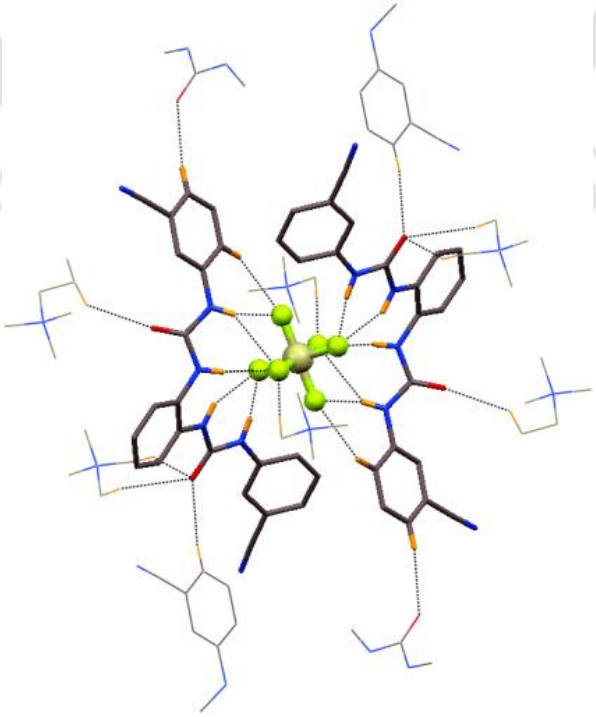

Fig. A5.2 Complex **6a** showing C–H···O weak interactions with receptor unit and n-TBA cations.

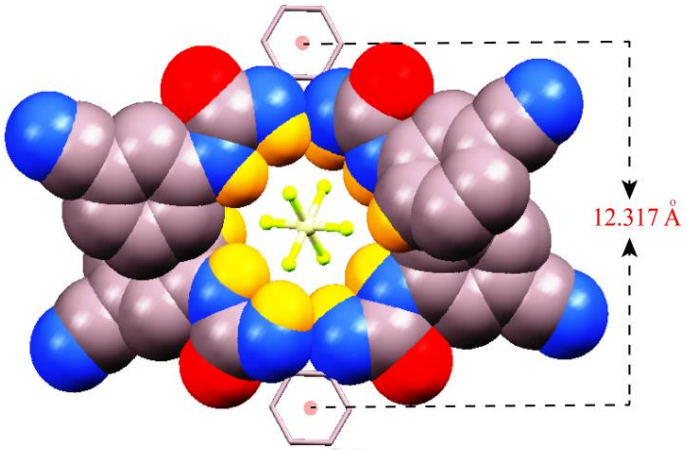

Fig. A5.3 Distance between $Ar_{benzene}\cdots Ar_{benzene}$ of the bis-urea receptor $\mathbf{L_6}$.

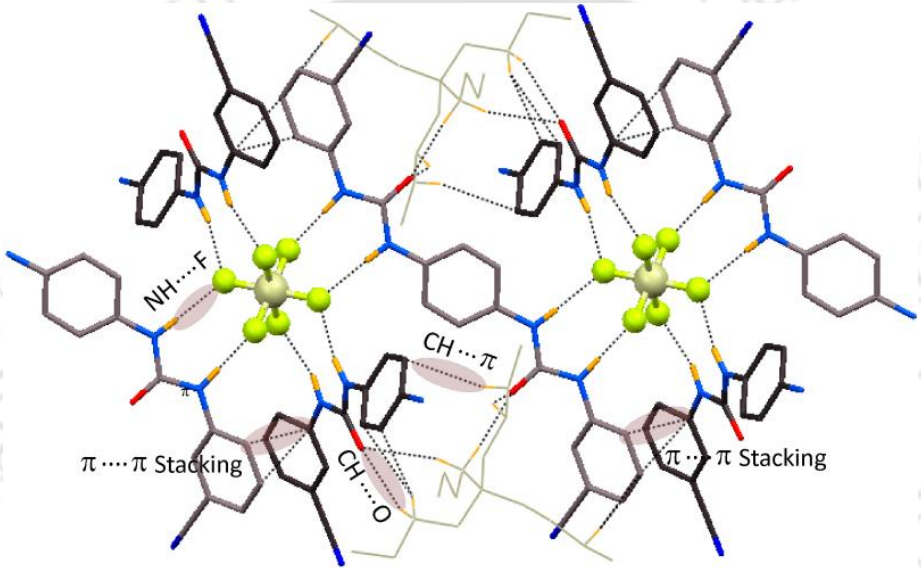

Fig. A5.4 Coordinated 4:2 host-guest assembly in complex **8a** showing different weak interactions.

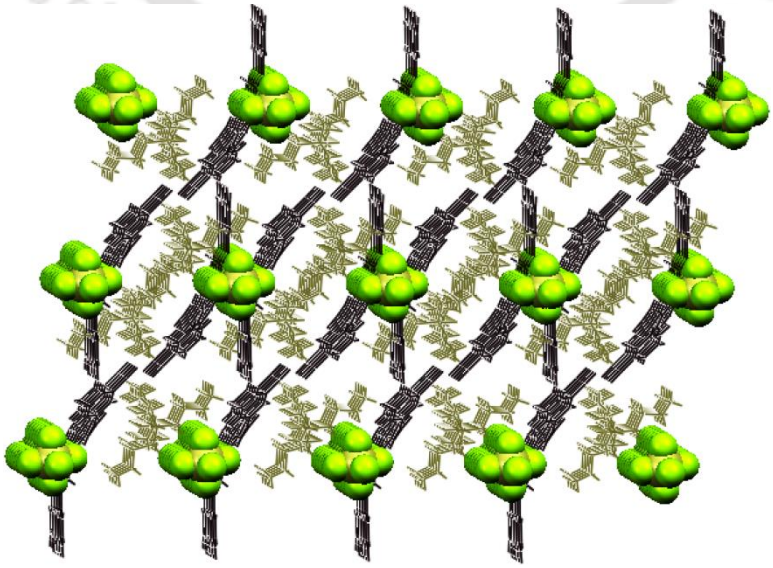

Fig.A5.5 Packing diagram of host-guest complex **6a** as seen along the crystallographic a-axis.

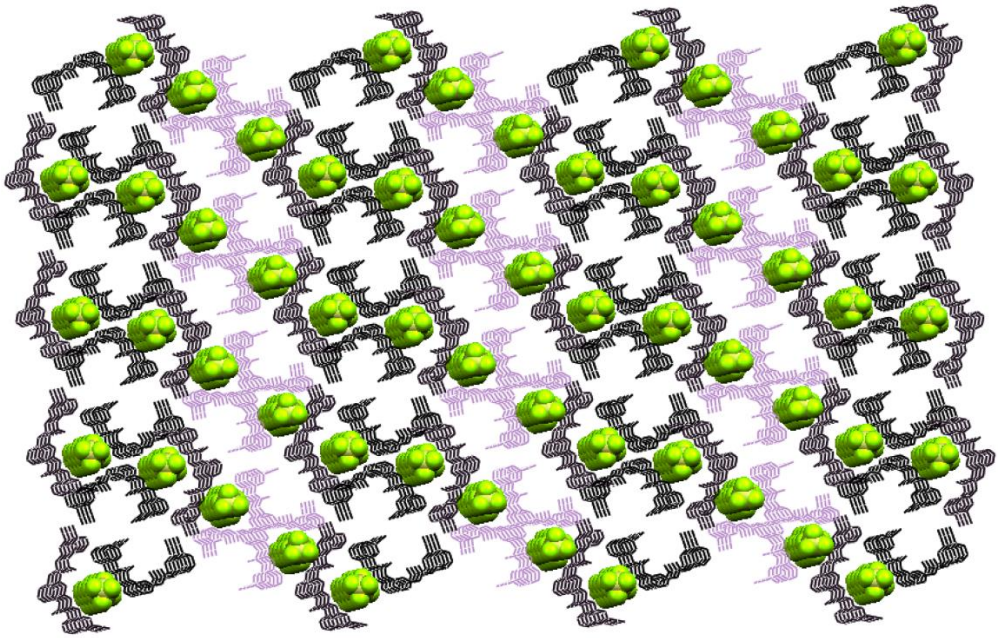

Fig.A5.6 Packing diagram of host-guest complex **7a** as seen along the crystallographic b-axis.

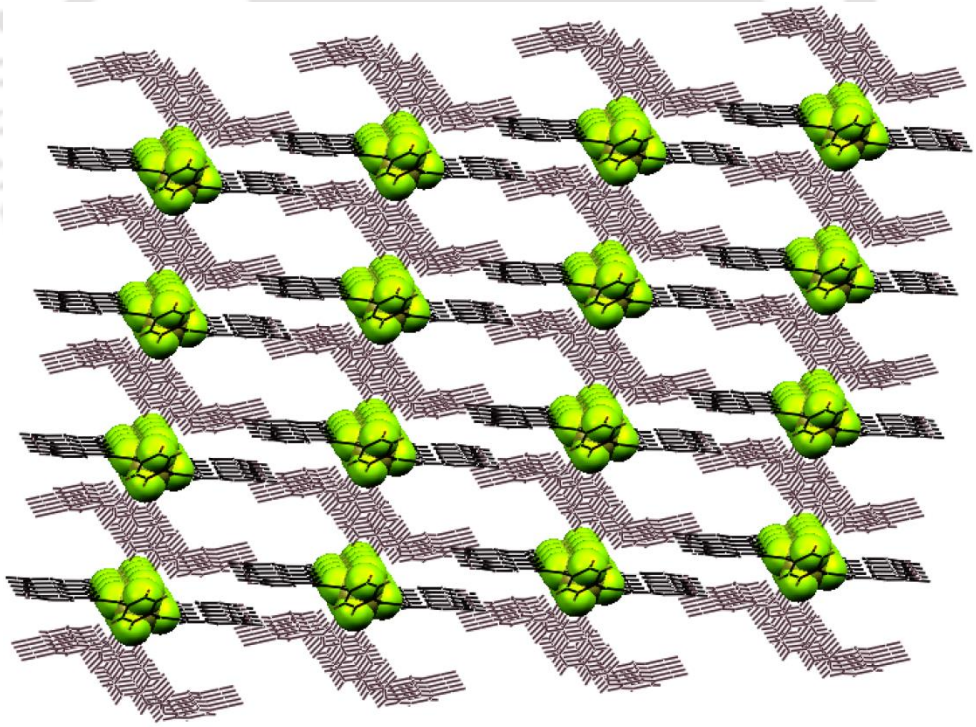

Fig.A5.7 Packing diagram of host-guest complex **8a** as seen along the crystallographic c-axis.

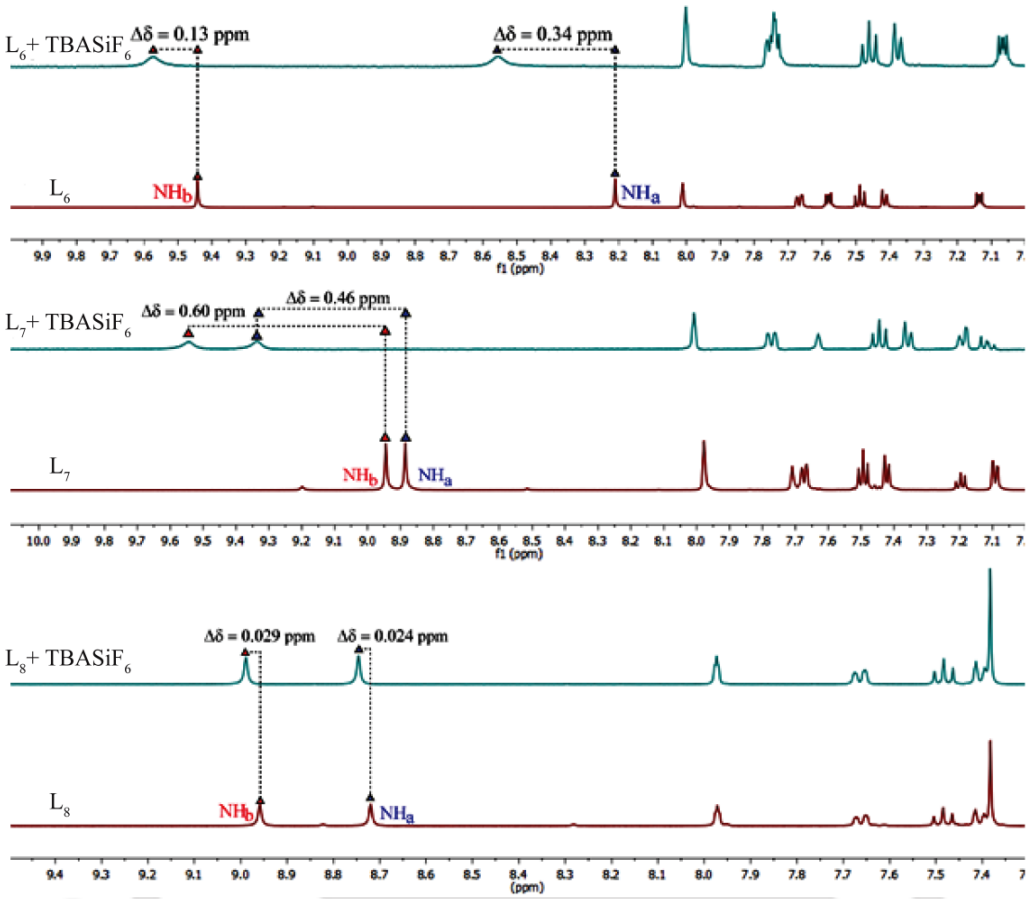

Fig.A5.8 Expanded partial ^{1}H-NMR comparative stacked spectra in the solution phase of receptors **L_6-L_8** with hexafluorosilicate anion as observed from the solid-state, displaying the noticeable downfield shifts of urea –NH_a and –NH_b resonances of a particular receptor upon anion complexations.

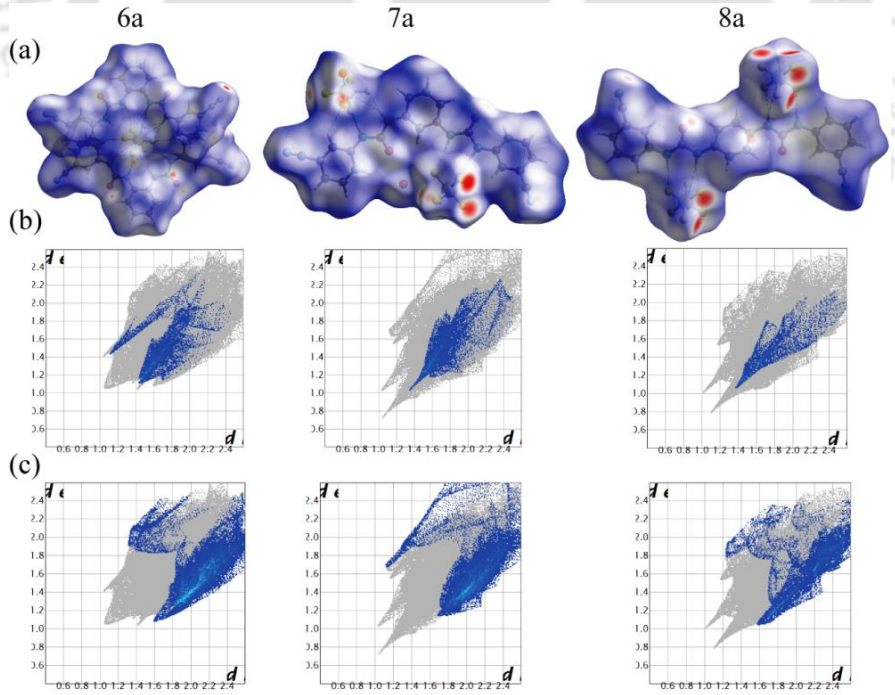

Fig.A5.9 Hirshfeld surface analysis showing the (a) d_{norm} surfaces of anion coordinated receptor fragments of complexes **6a-8a**, (b) corresponding 2D FPs with the O···H interactions highlighted in colour involved in N–H···O or C–H···O close contacts, and (c) corresponding 2D FPs with the C···H interactions highlighted in colour involved in C– H···O or C–H···π contacts.

Table A5.1 Contact contributions from the d_{norm} surface area of segments in the free receptor–anion complexes

Contacts	**6a**	**7a**	**8a**
H···F	5.1	26.7	29.2
H···O	7	7.5	4.4
H···N	19.9	14	13.8
H···C	23.5	19.6	15.4
H···H	40.6	29.5	31.2

Table A5.2 Crystallographic parameters and refinement details of complexes of $\mathbf{L_6}$-$\mathbf{L_8}$

Formula	$C_{76}\,H_{104}\,F_6\,N_{14}\,O_4\,Si$	$C_{130}\,H_{194}\,F_{12}\,N_{22}\,O_7\,Si_2$	$C_{76}\,H_{104}\,F_6\,N_{14}\,O_4\,Si$
CCDC	1937515	1937517	1937516
Fw	1419.82	2461.25	1419.82
Crystal system	triclinic	triclinic	triclinic
Space group	*P -1*	*P -1*	*P -1*
a/Å	11.6125(7)	9.5769(3)	11.3980(3)
b/Å	12.4000(9)	20.4478(8)	11.8157(3)
c/Å	13.7567(10)	37.2350(12)	16.3102(4)
α/°	89.154(6)	92.209(3)	96.1210(10)
β/°	79.572(5)	92.601(3)	96.470(2)
γ/°	87.827(5)	103.469(3)	114.2000(10)
V/Å^3	1946.7(2)	7074.7(4)	1962.28(9)
Z	1	2	1
D_c/g cm^{-3}	1.211	1.155	1.202
μ Mo K_α/mm^{-1}	0.101	0.099	0.100
T/K	298(2)	298(2)	298(2)
θ max.	22.3930	18.1560	18.1650
Total no. of reflections	13769	60575	29413
Independent reflections	6878	25119	6836
Observed reflections	3673	8049	4399
Parameters refined	461	1577	468
R_1, I > 2σ(I)	0.0857	0.0805	0.0724
wR_2 (all data)	0.2315	0.1256	0.1476
GOF (F^2)	1.161	1.052	0.876

Table A5.3 Hydrogen bonding distances (Å) and Bond angles (°) in the neutral anion-receptor complexes

Complex	D−H···A	*d*(D···H)/Å	*d*(H···A)/Å	*d*(D···A)/Å	<D−H···A/°	Symmetry codes
6a	N2-H2N···F1	0.86	2.17	2.960(5)	153	-x,2-y,-z
	N3-H3N···F3	0.86	2.05	2.886(5)	165	x,y,z
	N4-H4N···F2	0.86	2.13	2.923(5)	153	x,y,z
	N4-H4N···F3	0.86	2.39	2.780(5)	108	x,y,z
	N5-H5N···F2	0.86	2.06	2.872(5)	157	x,y,z
	C6-H6···O1	0.93	2.39	2.843(5)	110	x,y,z
	C10-H10···O1	0.93	2.54	2.915(5)	104	x,y,z
	C13-H13···O2	0.93	2.22	2.845(6)	124	x,y,z
	C17-H17···O2	0.93	2.34	2.882(6)	117	x,y,z
	C20-H20···N1	0.93	2.59	3.420(8)	148	x,1+y,1+z
7a	N2-H2N···F11	0.86	1.91	2.761(5)	170	x,y,z
	N3-H3N···F7	0.86	2.52	3.258(6)	145	x,y,z
	N4-H4N···F8	0.86	2.13	2.955(5)	161	2-x,-y,1-z
	N5-H5N···F12	0.86	1.94	2.789(5)	172	2-x,-y,1-z
	O7-H7A···F10	0.85	2.46	3.059(7)	128	-1+x,y,z
	O7-H7A···F11	0.85	2.21	2.975(7)	149	-1+x,y,z
	O7-H7B···O6	0.85	2.03	2.860(8)	166	-1+x,y,z
	N8-H8···F2	0.86	2.34	3.110(5)	150	x,y,z
	N8-H8···F5	0.86	2.21	2.980(5)	148	x,y,z
	N9-H9···F5	0.86	2.02	2.844(5)	160	x,y,z

	N10-H10V···F1	0.86	1.98	2.820(5)	167	1-x,1-y,-z
	N11-H11X···F1	0.86	2.49	3.214(6)	142	1-x,1-y,-z
	N11-H11X···F4	0.86	2.03	2.831(5)	155	1-x,1-y,-z
	N14-H14···F9	0.86	1.95	2.723(5)	149	-1+x,y,z
	N14-H14···F12	0.86	2.53	3.283(5)	148	-1+x,y,z
	N15-H15···F10	0.86	2.33	3.176(5)	166	-1+x,y,z
	N16-H16···F6	0.86	2.06	2.899(5)	167	x,y,z
	N17-H17···F2	0.86	2.48	3.107(5)	131	x,y,z
	N17-H17···F3	0.86	2.03	2.869(5)	165	x,y,z
	C5-H5A···O7	0.93	2.49	3.382(10)	160	1+x,y,z
	C7-H7···O1	0.93	2.35	2.846(6)	113	x,y,z
	C102-H10B··· F9	0.97	2.51	3.362(7)	146	x,y,z
	C107-H10D··· F9	0.97	2.31	3.185(7)	149	x,y,z
	C101-H10G··· F7	0.97	2.47	3.336(8)	149	-1+x,y,z
	C111-H11M··· F7	0.97	2.38	3.344(8)	174	-1+x,y,z
	C119-H11A··· F3	0.97	2.35	3.089(6)	132	x,y,z
	C119-H11B··· F4	0.97	2.44	3.207(6)	136	x,y,z
	C115-H11E··· F2	0.97	2.38	3.344(7)	170	1+x,y,z
	C123-H12H··· F1	0.97	2.50	3.439(7)	164	1+x,y,z
	C130-H13A··· F5	0.96	2.43	3.380(8)	172	x,y,z
	C14-H14A···O1	0.93	2.36	2.877(7)	114	x,y,z
	C14-H14A···O2	0.93	2.44	2.902(7)	110	x,y,z
	C21-H21···O2	0.93	2.21	2.822(7)	122	x,y,z
	C29-H29···O3	0.93	2.24	2.822(7)	120	x,y,z
	C36-H36···O3	0.93	2.22	2.825(6)	122	x,y,z
	C36-H36···O4	0.93	2.47	2.928(7)	111	x,y,z
	C43-H43···O4	0.93	2.33	2.866(9)	117	x,y,z
	C49-H49···O5	0.93	2.30	2.887(7)	120	x,y,z
	C54-H54···O5	0.93	2.26	2.859(7)	122	x,y,z
	C58-H58···O6	0.93	2.31	2.887(6)	120	x,y,z
	C61-H61···O6	0.93	2.32	2.896(7)	120	x,y,z
	C67-H67A···O3	0.97	2.42	3.320(7)	155	x,y,z
	C67-H67B···O4	0.97	2.41	3.283(7)	149	x,y,z
	C71-H71A···O5	0.97	2.57	3.500(8)	162	1+x,1+y,z
	C73-H73B···N7	0.97	2.61	3.520(11)	157	1+x,y,z
	C75-H75B···O4	0.97	2.60	3.441(8)	145	x,y,z
	C87-H87A···O1	0.97	2.33	3.239(7)	157	-1+x,y,z
	C87-H87B···O2	0.97	2.29	3.166(7)	150	-1+x,y,z
	C92H92A···N13	0.97	2.62	3.554(9)	162	-x,-y,1-z
8a	N2-H2N···F2	0.86	2.10	2.930(2)	163	1-x,1-y,1-z
	N3-H3N···F3	0.86	2.04	2.878(3)	165	x,y,z
	N3-H3N···F4	0.86	1.86	2.679(18)	158	x,y,z
	N5-H5N···F1	0.86	2.09	2.897(3)	157	1-x,1-y,1-z
	N5-H5N···F6	0.86	2.17	2.94(2)	149	1-x,1-y,1-z
	N6-H6N···F3	0.86	2.11	2.965(2)	168	1-x,1-y,1-z
	N6-H6N···F6	0.86	2.35	3.04(2)	138	1-x,1-y,1-z
	C7-H7···O1	0.93	2.23	2.821(3)	121	x,y,z
	C11-H11···O1	0.93	2.51	2.913(2)	107	x,y,z
	C14-H14···N1	0.93	2.58	3.362(5)	141	1-x,-y,-z
	C18-H18···O2	0.93	2.39	2.829(2)	109	x,y,z
	C22-H22···O2	0.93	2.24	2.834(2)	121	x,y,z
	C23-H23A···O2	0.97	2.33	3.290(3)	168	-1+x,y,z
	C23-H23B···O1	0.97	2.54	3.443(3)	155	x,1+y,z
	C27-H27B···N4	0.97	2.61	3.569(3)	170	1-x,1-y,-z

In summary, this thesis delivers some significant conclusions in the field of 'anion coordination supramolecular chemistry' where some of linear flexible artificial acyclic receptors coordinate with anions/hydrated anions driven by the size of anion or structural design of host in the solid-state or positional or electronic effect of terminal aryl substituents. The solution state anion binding studies, FESEM imaging studies and Hirshfeld surface analyses of host-guest complexes heavily validated the solid-state results of the anion-receptor complex. Overall, the current outcomes from the experimental studies provide the anionic guest induced polymeric aggregated assembly formation via neutral host-guest associations. Interesting features have uncovered by the individual receptor in the presence of a specific anion/hydrated anions.

The *ortho*-phenylenediamine based receptor **L_1** has the capability to self-assemble with spherical chloride as well as planar organic and inorganic oxyanions in diverse stoichiometries. Receptor **L_1** has been shown to capture organic terephthalate anion into a dimeric pseudo-capsular host-guest assembly sealed by tetrabutylammonium counter cation, while its isomeric receptor isomer **L_2** self-assembled in 2:4 host-guest fashions with H-bonded dihydrogen phosphate tetrameric anionic guest in the presence of excess n-TBA (H_2PO_4). In contrary, spherical halides (Cl^-, Br^- and F^-) self-assembles with the *meta*-phenylenediamine based **L_2** receptor in an identical non-cooperative fashion may be due to the less coordination number of halides compared to oxyanions. The bis-urea receptors **L_3-L_5** fully coordinated with the small spherical chloride within its dimeric cavity. The receptor **L_3** can readily form cooperative neutral self-assembly with smaller halides to larger halides, i.e. chloride, bromide, and iodide, as well as bind with the planar carbonate ion. The *meta*-isomer **L_4** forms a 1:2 host-guest assembly with chloride and bromide in the same space group; whereas it's isomeric receptor **L_5** forms a cooperative complex only with chloride ion. Receptor **L_6** has efficiently entrapped SiF_6^{2-} with a total of 12 N–H···F and 4 C–H···F H-bonding interactions within the semi-circular dimeric architecture from primary mixed DMSO media whereas the isomeric receptor **L_7**, in the presence of excess fluoride, forms a hydrated 3:2 double hexafluorosilicate entrapped complex, where both SiF_6^{2-} units show different coordination behavior. In mixed DMF/DMSO, receptor **L_8** forms a 4:2 host-guest complex, where one receptor binds with two symmetrically identical SiF_6^{2-} units via non-cooperative H-bonding of urea-groups having octa-coordination.

Hence, in the thesis some of the various fundamental and inconsistent concepts of supramolecular chemistry and adaptability of the acyclic receptors as efficient building block through systematic development have been successfully established. Several specialized

applications such as drug delivery, transmembrane anion transport, salt solubilization, extraction, catalysis, stabilizing the anionic reactive intermediates inside the molecular assembly etc. can be achieved by the recognition of anions or hydrated-anions within the molecular assembly or molecular cavity which can expand significantly and bring immense advances in the field of supramolecular chemistry. However, the basic work in tuning the binding of anions/hydrated-anions inside the molecular assembly is highly appreciated for these applications to reach their prospective. From a fundamental lookout, the results included in this thesis are very convenient, but other challenging sides in supramolecular chemistry need to be advanced, mainly from an applicative approach. Based upon the extraordinary anion/hydrated-anion binding molecular assembly, research in these areas with importance on biomedical, environmental, and technological applications, seem to be upcoming.

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Research Interests

- **Supramolecular chemistry of biologically and environmentally important anions:** Solid and solution-state studies of biologically and environmentally significant anions in π–acidic receptors, and anion driven synthesis of supramolecular structural design.

- **Supramolecular capsules and pseudocapsules based on hydrogen bonds or metal-ligand coordination bonds:** From the viewpoint of molecular recognition, the balanced design and synthesis of supramolecular capsules with well-regulated encapsulation and release of a guest molecule remains an important subject in supramolecular chemistry. Moreover plays an impactful role in stabilization of reactive intermediates, catalysis of chemical reactions, and as drug delivery applications.

Publications

1. Consistent binding aptitude of halides and oxyanions *via* cooperative *vs.* non-cooperative binding modes by neutral napthyl bis-urea receptors.
   Biswajit Nayak, Utsab Manna, and Gopal Das ***ChemistrySelect,*** 2018, **3**, 3548.
2. Terminal substituent induced differential anion coordination and self-assembly: case study of flexible linear bis-urea receptors.
   Biswajit Nayak, Senjuti Halder and Gopal Das ***Crystal Growth & Design.*** 2019, **19**, 2298.
3. Binding consistency of anions by the effect of aromatic *meta*-substitution of bis-urea receptors: entrapment of hexafluorosilicate clusters.
   Biswajit Nayak, Senjuti Halder, Sagnik De and Gopal Das ***CrystEngComm*****.** 2019**, 21,** 7172**.**
4. Influence of the cavity dimension on encapsulation of halides within the capsular assembly and side-cleft recognition of a sulfate-water cluster assisted by polyammonium tripodal receptors.
   Utsab Manna, **Biswajit Nayak**, Md. Najbul Hoque and Gopal Das ***CrystEngComm.*** 2016, **18**, 5036.
5. Dual guest [(chloride)$_3$-DMSO] encapsulated cation-sealed neutral trimeric capsular assembly: *meta*-substituent directed halide and oxyanion binding discrepancy of isomeric neutral disubstituted bis-urea receptors.
   Utsab Manna, **Biswajit Nayak**, and Gopal Das ***Crystal Growth & Design***, 2016, **16**, 7163.
6. A benzimidazole-based non-symmetrical tripodal receptor for the ratiometric fluorescence sensing of fluoride ions and solid-state recognition of sulfate ions.
   Nilotpal Borah, **Biswajit Nayak**, Abhijit Gogoi and Gopal Das ***New Journal of Chemistry*****.** 2019, **43**, 16497.
7. Effect of substitution on halide/hydrated halide binding: a case study of neutral bis-urea receptors.
   Asesh Das, **Biswajit Nayak** and Gopal Das ***CrystEngComm,*** 2020, **22**, 2197.
8. Systematic size mediated trapping of anions of varied dimensionality within a dimeric capsular assembly of a flexible neutral bis-urea platform.
   Utsab Manna, Santanu Kayal, **Biswajit Nayak** and Gopal Das ***Dalton Trans.*** 2017**, 46**, 11956.

9. Probing the solvent-tunable aggregation aptitude of neutral naphthyl bis-urea series and their interactions with nitro-aromatics.
   Senjuti Halder, **Biswajit Nayak,** Sagnik De and Gopal Das ***Journal of Molecular Liquids*** 2021, **329,** 115601.
10. Insight into the aggregation prospective of schiff base aiegens enabling efficient hydrazine sensor.
    Senjuti Halder, **Biswajit Nayak** and Gopal Das, Manuscript Submitted.

Conference attended

- Oral presentation in ***ChemCYS 2020 (Chemistry Conference for Young Scientists)*** organized in Blankenberge, Belgium by JONG-KVCV, the youth division of the Royal Flemish Chemical Society.
- Poster presentation in ***20th CRSI National Symposiums in Chemistry 2017***, Gauhati University, Guwahati.
- Poster presentation in ***Frontiers in Chemical Science 2018***, Indian Institute of Technology Guwahati, Guwahati.
- Poster presentation in ***Modern Trends Inorganic Chemistry (XVII) 2019***, Indian Institute of Technology Guwahati, Guwahati.
- Poster presentation in ***ChemCYS 2020 (Chemistry Conference for Young Scientists)*** organised in Blankenberge, Belgium by JONG-KVCV, the youth division of the Royal Flemish Chemical Society.

Workshop attended

- ***'Workshop on Procedures & Applications of XRD, XRF & Single Crystal XRD'*** Gauhati University, Guwahati. (27th July to 1st August, **2018**).
- ***Workshop on Single Crystal X-ray Diffraction Techniques and its Applications'*** Indian Institute of Technology Guwahati. (22nd-23rd January, **2021**).