Chapter-1

An Introduction to the Chemistry of Macrocycles and Bipyridine Derivatives: Supramolecular and Photophysical Aspects and Motivation of the Present Work

**ABSTRACT:** The present work is mainly subdivided into two broad categories, (a) supramolecular chemistry, and (b) photophysical chemistry. The Chapters 2 and 3 essentially describe the non-covalent intermolecular interactions of macrocyclic cations with external anions whereas, the Chapters 4 and 5 correspond to the syntheses and photophysical properties of 2,2′-bipyridine-based donor–acceptor systems and their transition metal complexes. An important class of inorganic materials namely, polyoxometalates, has been introduced as the anionic counterparts to the supramolecular complexes depicted in Chapter 2. Alternatively, it can be said that, the thesis represents three types of important molecular systems viz., the macrocycles, polyoxometalates and 2,2′-bipyridines, the chemistry of which, has been briefly reviewed in this “Introduction” chapter. Although, an elaborate discussion about the concerned systems is beyond the scope of the thesis, we have made an attempt to focus on the significant aspects of the aforesaid materials relevant to our work. The basic chemistry of the pertinent systems i.e. the synthetic procedures, structural features and their applications etc., has been emphasized in this chapter. On the basis of this background information, we have put across the motivating features behind the present work at the end of this chapter.

● 1.1. INTRODUCTION

The research in experimental chemistry was probably initiated by the Alchemists long before Christ. The integral parts of experimental research or ‘wet’ research lies in the design of molecules with desired properties, synthesis of the target molecules using appropriate synthetic strategies and eventually, characterization of the synthesized compounds via available analytical tools. The ‘modern chemistry’ research was however, fueled up and accelerated with the important inventions such as X-ray, LASER, etc. which paved the way to manufacture various sophisticated instruments for easy characterization and data analyses.

Supramolecular chemistry is a broader subject of modern chemical research which was first brought in by Jean-Marie Lehn in 1978 and was defined as *the chemistry of molecular assemblies and of the intermolecular bond.* Supramolecules are considered as
aggregates in which, a number of components come together, either spontaneously or by design, to form a larger entity, whose properties are generally derived from its precursors. The field of supramolecular chemistry has produced several instances of chemically attractive and aesthetically pleasing self-assembled structures with greater complexity than molecules themselves. The distinction between large molecules and supramolecular species is based on interactions involving the independent molecular parts, i.e., systems where the individual parts or molecules are held together by coordination or covalent bonds are termed as large molecules whereas those, in which intermolecular forces come into play, are termed as supramolecules. Supramolecules are administered by virtue of intermolecular non-covalent forces such as hydrogen bond, dipolar interaction, π-stacking, Van der Waals interaction, donor–acceptor interaction etc. The stabilizing energy of non-covalent complexes is generally said to comprise, contributions from an attractive (e.g. electrostatic, induction, charge transfer, dispersion etc.) as well as a repulsive (exchange-repulsion) term. These two forces work in harmony, thereby bringing stability to such supramolecular complexes in which the existence of the repulsive force prevents the subsystems from drawing too close together. Furthermore, it is worth mentioning that supramolecular chemistry forms the basis of life, which is quite evident from the intensive hydrogen bonding interactions between the nucleic bases which are prevalent in the double helical structure of DNA. Therefore, the study of non-covalent interactions is crucial to comprehend many biological processes from cell structure to vision that rely on these forces. In a nutshell, it can be aptly said that the biological systems are often the inspiration for supramolecular research.

Spectroscopy is another broad subject of modern research, the basis of which relates to the interaction between matter and electromagnetic radiation. The electronic nature of the substrates called chromophores can be comprehended from the UV-visible and emission spectroscopy. The molecular processes, Fluorescence and phosphorescence are well-known emission processes that occur upon electronic excitation of a chromophore. A substantial growth in the electronics market in the past few decades have aided in devising ultra sensitive detectors for gaining information, even up to the single molecular level. Lately, the design and syntheses of new organic chromophores with tunable photophysical properties are drawing immense notice due to their fascinating applications.
in the optoelectronic devices. The work carried out in the present thesis mainly accentuates two broad subjects of chemical research i.e. supramolecular chemistry and synthetic photochemistry. Aza-macrocycles and oxy-crown ethers are the supramolecular synthons used in Chapters 2 and 3, to build various network structures. The other part of the thesis (Chapters 4 and 5) involves syntheses and photophysical aspects of the 2,2’-bipyridine derivatives along with their transition metal complexes. The related chemistry of the focused substrates of the present work is briefly discussed before delving into the main contents of the thesis.

1.2. SUPRAMOLECULAR CHEMISTRY AND THE MACROCYCLES

The formation of supramolecular aggregates or supramolecules is generally governed by molecular recognition of a guest component (substrate) by a host (receptor) through non-covalent intermolecular forces. Thus, the supramolecules are also termed as host-guest complexes. Several types of host molecules have been reported so far, some common representative examples being cyclodextrins, calixarenes, cucurbiturils, porphyrins, metallacrowns, crown ethers, zeolites, cyclophanes, aza-macrocycles etc.

As the non-covalent interactions in supramolecules are usually weak, therefore the only way to achieve strong and specific complexation (recognition) of a guest molecule is the presence of several binding sites in the host or receptor molecule. Though the principle of multi-site complexation is very familiar in biological systems, the same can also be viewed from the generalized chelate effect. Macrocycles are regarded as excellent building blocks for providing multi-complexing sites and the whole cavity for guest encapsulation through non-covalent interactions. An important prerequisite for multi-site binding is that, the binding sites of host and guest molecules must be complementary, i.e. complexation is most efficient when the shapes and arrangements of binding sites in host and guest molecules match each other in congruence with the general lock and key principle by Emil Fischer.

In the present work we have chosen tetra-aza macrocycles and crown ethers as components (see Chart 1) to derive the target supramolecular complexes. A brief overview of the concerned macrocycles will be given in the next few sections of this chapter. The interlaying supramolecular chemistry of the synthesized compounds will be discussed in the respective chapters.
1.2.1. Chemistry of transdiene

The 14–membered aza-macrocycle 5,7,7,12,14,14–hexamethyl–1,4,8,11–tetraazacyclo tetradeca–4,11–diene (commonly known as transdiene) was first synthesized by N. F. Curtis. The master thesis of Curtis described a yellow diamagnetic solid, that was prepared from the reaction between paramagnetic [Ni(en)$_3$]$^{2+}$ and acetone. In 1961, the yellow solid was recognized as the square planar Ni$^{II}$ complex of transdiene (hereafter L). After the discovery of synthetic routes for obtaining the protonated form of the free macrocyclic ligand, coordination complexes of L were extensively explored in terms of electron transfer reactions, as model systems towards understanding the active sites of some biologically active metallo–proteins (e.g. vitamin B$_{12}$), in terms of catalysis (e.g. H$_2$O and CO$_2$ reduction) etc. The macrocycle, L is generally characterized by two NH($^\text{sec}$) protons and based on their orientation, the ligand L generates two chiral centers when it coordinates to a metal atom. Thus, the relevant coordination complexes exist as two diastereomers viz. racemic– (RR– or SS–) if both the NH($^\text{sec}$) protons are on the same face of the macrocycle and meso– (RS–) if they project to different faces as shown in Scheme 1. This macrocycle is mostly isolated as its perchlorate salt in which N(amine)–H···N(imine) hydrogen bonding between the two ethylenediamine type

Chart 1. List of the macrocycles used in the present work.
fragments stabilize the system. It is evident from Scheme 1 that, there are two types of nitrogen atoms in the molecular structure of L and its metal complexes: (a) the amine nitrogen atoms and (b) the imine nitrogen atoms. The amine (\textgreater NH) and imine (\textgreater C=N–) functionalities can be clearly distinguished by IR spectroscopy. Therefore, two types of C–N bonds exist in the molecular structure of L and its complexes i.e., the longer C–N(amine) and shorter C=N(imine) bonds. Similarly, there are three different types of peripheral methyl groups in L: (a) axial, (b) equatorial and (c) directly attached with the imine functionality. Although, the structure of L resembles a Schiff base, it has been found to be highly stable even in acidic or basic media in contrast to the conventional Schiff bases which are prone to hydrolysis in these media.

Scheme 1. Molecular structure of L and its coordination complex, showing two diastereomers of the M–L complexes.

The higher stability of the coordination complexes of L as compared to that of an open chain chelating ligand e.g. ethylenediamine is a direct consequence of the macrocyclic effect. An accepted explanation for this phenomenon is the intricacy in detaching the first donor atom from the metal ion in what is probable to be a stepwise dissociation of the polydentate ligand. A polydentate chelate can be dissociated from a metal ion in the course of successive S_N1 replacement steps, commencing with a terminal donor. However, a macrocyclic ligand cannot be dissociated in a similar way as because there is no end group. Therefore, some sort of ligand rearrangement has to occur so as to weaken one M–L bond prior to its dissociation, thereby eventually impelling the rest of
the ligand to dissociate. Since such type of a rearrangement exacts a cost in energy, hence the dissociation step is found to be very slow. Even though similar problems might be expected to slow the rate of formation reaction as well, experimental database have suggested that the macrocyclic effect arises primarily from the dissociation step, signifying that dissociation is more delayed than is binding. Moreover, the macrocyclic effect is expected to be associated with more favorable entropy of complexation. This is for the reason that upon coordination, a linear ligand tends to lose free rotations around its single bonds to some degree while in a macrocycle, these rotations are already partially lost (although macrocycles possess a considerable degree of conformational flexibility). Thus, the primarily dissociative effect in addition to this highly associative chelate effect leads to a large increase in stabilization for macrocyclic complexes.

**Scheme 2. Two synthetic procedures to obtain the macrocycle, L.**

Two different synthetic procedures to obtain the macrocycle have been individually reported by (a) Curtis and Hay,\(^6\) and (b) Endicott and Sadasivan.\(^6\) In fact, both the aforementioned routes can be used for the synthesis of the dihydroperchlorate salt of L (see Scheme 2). Curtis and Hay (1966) synthesized the title compound by a simple Schiff condensation between ethylenediamine and acetone in presence of perchloric acid.\(^6\) In the same year (1966), Endicott and Sadasivan followed metal-template condensation
procedure to synthesize \( L\cdot2\text{HClO}_4 \). The concerned synthetic methodology involved condensation between \( \text{Fe(en)}_3(\text{ClO}_4)_2 \) and acetone at room temperature. Although the same reaction was tested with various other transition metals (copper, nickel, cobalt, zinc etc.), it was finally established that only iron could template the desired compound in good yield. However, the synthetic route (b) has some major drawbacks such as, (i) the synthesis is complex as compared to route (a) and special care has to be taken to avoid moisture, (ii) the desired compound gets contaminated with colored impurities, metal oxides, hydroxides etc., (c) repeated recrystallization of the isolated solid is required for its purification, etc.

Scheme 3. Synthetic routes to obtain some of the \( \text{Co}(L)X_2 \) complexes; \( L = \text{transdiene}, \ X = \text{axial ligand} \).

Previously, Endicott and co-workers synthesized a series of cobalt complexes of \( L \) and studied their spectral properties. In the pertinent study, the coordination geometry around the metal center in the \( \text{Co}^{\text{III}} \) complexes, was found to be octahedral in which the four nitrogen atoms of the macrocycle provided the basal coordination and two additional ligands (halide, nitro, isothiocyanato etc.) occupied the axial positions. The relevant complexes were formulated as \( \text{Co}^{\text{III}}LX_2 \) in which \( X \) was the axial ligand. It was shown that a diverse class of macrocyclic compounds could be synthesized through simple wet-syntheses as schematized in Scheme 3. The pertinent compounds were synthesized using \( \text{[Co}^{\text{III}}(L)\text{Cl}_2(\text{ClO}_4) \) as the starting precursor which was obtained by the reaction between
L·2HClO₄ and Na₃[Co(CO₃)₂]·3H₂O, followed by acidification with HCl. Thus, it is quite evident that the lability of the Co–Cl bonds renders the replacement of cobalt bound axial chloride ligands by several other nucleophiles (NO₂⁻, N₃⁻, SCN⁻, CN⁻ etc.) easy. Infact, all the complexes differ in their color, based on the axial ligands. For example, the precursor complex, [Co₃(III)(L)Cl₂](ClO₄) is green in color while replacement of the axial ligands by nitro leads to the isolation of [Co₃(III)(L)(NO₂)₂](ClO₄) which is orange-yellow. A simple crystal field model for the relevant cobalt complexes was also established by Endicott _et al._ on the basis of UV-visible spectroscopic data. The absorption spectra of Co₃(III)LX₂ complexes, in the pertinent study, were found to consist of three low-intensity absorption bands in the visible and near-ultraviolet spectral regions which were assigned to the Bands IA, IB and II based on the convention of Linhard and Weigel. The same convention has also been used to explain the absorption spectra of the cobalt complexes presented in Chapter 2. The structures of the aforementioned Co₃(III)LX₂ compounds were unambiguously elucidated later after the invention of X-ray diffractometer. At this point, it is interesting to note that the crystal structures of Co₃(III)–L and Co₂(II)–L complexes were found to be remarkably different. The Co₃(III) complexes were found to be low–spin and octahedral in which the macrocycle provided the basal coordination and two auxiliary ligands occupied the apical sites. In contrast, the Co₂(II) complexes were found to be tetra–coordinated (square planar).

It has already been mentioned that, transition metal complexes of L have been heavily used for the study of electron transfer reactions. Endicott and co-workers investigated the electron transfer reactions of dihalogen radical anions (2X₂⁻→ X₂ + 2X⁻) with Co₃(III) and Co₂(II) complexes of transdiene. The relevant study was very crucial as only few reactions of dihalide radical anions with transition metal substrates were known during that period. It was observed that the tetradeutate ligand, L remained coordinated to Co₂(II) for long periods in aqueous solutions. As such, radical recombination reactions were expected to be particularly important for charge transfer photochemistry of the Co₃(III)LX₂ species (X = axial ligand). In addition to this, it was also observed that the Co₂(II)–L species was weakly reducing and low–spin, and thus, it was suggested that such systems could act as good model systems for examining the reactivity of low–spin Co₂(II) complexes with simple radicals.
Besides, cobalt complexes of the macrocycle, L are also used as model systems of vitamin B\(_{12}\). The octahedral complexes of the type [Co\(\text{IIILX}_2\)]\(^-\) (where X is anionic axial ligand) exist as two diastereomers *viz.* racemic– and meso–. Interestingly, the symmetry of such type of complexes is further reduced when the two axial positions are differently substituted. Creutz and co-workers reported an organo-cobalt complex with the axial positions of the Co\(\text{III}\) center being occupied by a methyl and an aquo substituent.\(^ {13}\) The general structural feature of the complex is presented in Scheme 4, which reveals the possibility of three isomeric forms of the concerned Co–L complex. The two vertical lines in each of the cartoon representations denote the orientation of the axial methyl groups of the macrocycle. They project to the same face of the macrocycle in case of the *racemic*– isomers while the reverse order is followed in case of the *meso*– diastereomers.

**Scheme 4.** Molecular structure of the [Co(L)(CH\(_3\))(OH\(_2\))]\(^{2+}\) cation along with the cartoon representation showing the three possible isomers of the cobalt complex.

Accordingly, if the open face of the macrocyclic complex is denoted as "primary" and the face toward which the axial methyl groups point is denoted as "secondary", then the two isomers of the *racemic*– diastereomer are termed primary X, aquo and secondary X, aquo. The determination of crystal structure of the compound, [Co(L)(CH\(_3\))(OH\(_2\))]\((\text{CF}_3\text{SO}_3)_2\), in the pertinent study, pointed out that the stereochemistry of the coordination complex was *trans-sec, rac*–.\(^ {13}\) The macrocycle in the title crystal structure was found to
be twisted so that the two “axial” methyl groups of the macrocycle were swept back away from the axially coordinated methyl ligand. This configuration was thought to be stabilized by the hydrogen bonding interactions between the macrocycle amine hydrogen atoms and the trifluoromethane sulfonate anions. The system was further stabilized by hydrogen bonds between the axial aquo ligand and the trifluoromethanesulfonate anion. These hydrogen bonding interactions, as well as the methyl–methyl repulsion on the secondary face of the macrocycle, were considered to be responsible for the folding of the macrocycle towards the axial water ligand and away from the axial methyl ligand.\(^{13}\)

Apart from the cobalt complexes, coordination complexes of transdiene with Ni\(^{II}\), Fe\(^{III}\), Cu\(^{II}\), Zn\(^{II}\) etc. as the metal centers, have also been synthesized. Endicott and Sadasivan prepared a series of \(M–L\) complexes (\(M = \text{Ni}^{III}, \text{Cu}^{II}, \text{Zn}^{II}\)) using dihydroperchlorate salt of \(L\) and appropriate transition metal precursors.\(^6g\) However, structures of the synthesized complexes could not be affirmed at that time. It was only after the introduction of X-ray diffractometer in 1970s, that geared up research in structural chemistry. The determination of the crystal structures of the relevant nickel complexes revealed that, unlike the hexa–coordinated Co\(^{III}\) complexes, the Ni\(^{II}\) center was rather tetra–coordinated and in square planar geometry. Surprisingly, it was also observed in the pertinent study that the square planar Ni\(^{II}\) complexes were very robust to coordination enhancement to hexa–coordination even in presence of highly coordinating ligand e.g. CN\(^−\). This observation was interpreted by several plausible explanations e.g. (a) strong tendency of the amine protons to hydrogen bond with the counter anions in both the solid and solution state, (b) tendency toward decreased coordination in the axial positions of six–coordinate Ni\(^{II}\) complexes containing strong inplane fields, (c) steric crowding of the axial ligating sites etc.\(^6g\) Although, the Ni\(^{II}\)–\(L\) complexes are mostly tetra–coordinated and square planar, exceptions are also known. For instance, Liao and co-workers reported a penta–coordinate complex, \([\text{Ni}(L)(\text{NCS})]\text{ClO}_4\) about a decade ago, with a thiocyanate ligand bound to one of the apical sites leading to a square pyramidal geometry around the metal center.\(^{14}\)

The nickel complexes of \(L\), have also been found to exhibit catalytic oxidation activity, wherein the host-guest nanoscale nickel complex, (Ni\(^{II}\)–\(L\)) is formed by the encapsulation of the macrocycle into the zeolite matrix. For example, cyclohexene is
catalytically oxidized to 2–cyclohexene–1–ol and 2–cyclohexene–1–one in the presence of $O_2$ and $[\text{Ni(L)}]^{2+}–\text{NaY}$ in a solvent-free medium at 70 °C.\textsuperscript{15}

Till date, several crystal structures associated with the transition metal complexes of L have been reported. All the structures exhibit some general features, for instance, longer M–N(amine) bonds compared to shorter M–N(imine) bonds, the five–membered ring bite angles are 4–8° less than 90° and the six–membered ring bite angles are 4–6° greater than 90° etc. In case of the racemic– diastereomers, the two axial methyl groups of the macrocycle project towards the same face of L whereas; they are observed in opposite projection in case of the meso– isomers. The stereochemistry of the M–L complexes can therefore, be unambiguously assigned on the basis of projection of the axial methyl groups even if the amine hydrogen atoms are not located from the X-ray diffraction data. Apart from the strong intermolecular non-covalent interactions such as N–H···O, O–H···O, O–H···N etc., the C–H···O hydrogen bonding interaction has been observed in several crystal structures which play a pivotal role in constructing multidimensional supramolecular frameworks. It is nonetheless, important to mention that, the periphery of the M–L complexes comprises many methyl and methylene groups which might participate in intermolecular C–H···O interactions with an exterior hydrogen bond acceptor. The metal oxo–cluster anions or polyoxometalates (POMs) have been used as the hydrogen bond acceptors to the macrocycle donors in the present study. A brief introduction to this supramolecular building block is made at a later stage in this chapter. The key reason behind pairing up of the two important classes of materials viz. the transition metal complexes of transdiene and the POMs is described in a separate section (\textit{vide infra}).

\textbf{1.2.2. Cyclen}

The tetra-aza crown ether 1,4,7,10–tetraazacyclododecane, commonly named as cyclen, is another important macrocycle, widely known both in the areas of supramolecular and coordination chemistry. Cyclen readily forms complexes with transition metals, lanthanides and actinides. However, only few instances are known where this macrocycle binds alkali and alkaline earth metals. The selectivity of cyclen towards the $d$- and $f$-block elements over the $s$- and $p$- block elements is evidently a consequence of the HSAB principle. The most significant aspect of this macrocycle lies in the fact that the
gadolinium complexes of cyclen and its derivatives are promising contrast agents for Magnetic Resonance Imaging (MRI).\textsuperscript{16a–d} A few important derivatives of cyclen are exemplified in Chart 2. It has been found that the attachment of hydrophilic side chains to cyclen noticeably increases the tolerability of the corresponding Gd\textsuperscript{III} complexes.\textsuperscript{16a–d}

**Chart 2. Some important derivatives of cyclen.**

Furthermore, such types of macrocyclic polyamine systems have proven to be extremely valuable as scaffolds for encapsulating metal ions into larger molecular fragments. As a result, derivatized forms of cyclen are becoming increasingly popular as typical building blocks in the applications requiring highly selective metal ion chelation\textsuperscript{16e–j}. Thus interestingly, aza-crown macrocycles have the potential to reduce the toxicity of toxic metal environment/surrounding through their strong coordination with concerned metal ions. However, such supramolecular complex species are generally soluble in common laboratory solvents, as a result of which, separation of the concerned metal ions from solution becomes difficult. As such, heavy anions, such as polyoxometalate cluster anions can act as useful candidates in the sense that, they can easily be associated with such soluble supramolecular complex cations (ion–pair association/adduct formation) to form insoluble precipitates. This is a handy way of separating specific metal ions (depending on cavity size of the aza-crown ethers) from an aqueous solution by precipitation method.\textsuperscript{16j–k}
1.2.3. Crown ethers as supramolecular building blocks

Crown ethers are the paradigms in supramolecular chemistry which have been investigated heavily as a host for various organic and inorganic guests. This important class of macrocycle was serendipitously discovered by C. J. Pedersen. Till date, a large number of crown ethers have been reported, in which the heteroatoms are mostly oxygen, nitrogen, sulfur, mixed oxygen and nitrogen or sulfur atoms, and they are bridged by aliphatic or aromatic carbon spacers. Among the several derivatives of crown macrocycles, the all oxygen, all nitrogen and mixed oxygen–nitrogen heteroatom containing derivatives are mostly used to recognize neutral or ionic organic and inorganic species. The oxygen atom is the predominant heteroatom in the crown ether chemistry. The general structural feature of such macrocyclic hosts, being saturated and repeating glycolic units (–O–CH₂–CH₂–O–), confers structural elasticity or conformational mobility to the crown ethers, whereby the nature of guest incorporation is largely governed by their cavity sizes and the most stable complexes are formed with the closest match between host cavity and cation size. As for example, the ionic radii of the alkali metal cations along with the approximate diameter of complementary crown ethers in idealized binding conformations are shown in Scheme 5. This remarkable selectivity of metal cation binding to macrocycles in fact illustrates the principle of molecular recognition and in a broader sense, the “lock and key” principle and is the basis for many applications. This size fit argument, as a basis for solution selectivity patterns has undergone much revision and addition at a later stage. Though the smaller crown ether, 12–crown–4 has no selectivity towards any metal cation, there are instances where it binds Li⁺ or Na⁺ cations with the crown being distorted because of the size mismatch. A similar trend of deviation from the hole–size concept has also been observed for the complexes of transition metal cations with azamacrocycles. Thus, it can be concluded that the hole–size concept apparently works better for more rigid systems which exhibit a size–match selectivity for both small and large cations.

The crown ethers possess a hydrophobic ring surrounding a hydrophilic cavity, which enables them to form stable complexes with metal ions and also to be simultaneously incorporated in the lipid fraction of the cell membrane. Natural and synthetic ionophores are capable of forming stable, most often lipophilic complexes with charged hydrophilic
Scheme 5. A comparison of the ionic radii(Å) of alkali metal cations with the cavity diameter(Å) of crown ethers.

species. They can transfer ions into the lipophilic phases and can therefore, be used as trans-membrane carriers. As a rule, the complexation demands that the process is quite specific and thus, the ionophores get a fair chance to discriminate between metal cations of different charge and different size. Ionophores behave as host molecules for the simplest guests of spherical shape, e.g. alkali and alkaline earth cations, and encapsulate them within their cavities through electrostatic forces. Most often, the majority of ionophores which have been used for elimination of metal ions are neutral crown ethers. Anions generally accompany these macrocyclic complexes to maintain electrical neutrality when these are used to mediate metal cations.

Crown ethers have been extensively used in the area of crystal engineering. In the relevant crystals, these macrocycles play two major roles; (i) act as hydrogen bonding acceptor through the involvement of D–H···O interaction between the guest donor and the electronegative oxygen acceptor of the host and, (ii) act as hydrogen bonding donor through weak C–H···A interaction with another acceptor fragment in the crystal. The excellent review article by Steed in 2001 brings to light a sound overview of the alkali metal–crown ether chemistry. Their complexation with organic ammonium, arenediazonium, guanidinium, tropylium, and pyridinium cations has also been studied. Though various research groups including Nangia, Atwood, Zaworotko, Fonari,
Nakamura, Stoddart, Braga, Steed, Rogers, etc., have been working on diverse classes of crown ether based host-guest systems with simple to complicated topologies, research incorporating organic ammonium ions (RNH₃⁺, ArNH₃⁺ etc.) as guests with crown ethers still reigns the field of supramolecular chemistry. The organic ammonium ions generally perch into the oxy–crown ether cavity through the N–H···O hydrogen bonds. Very recently, our group has reported ammonium–crown ether complexes in supramolecular association with metal–oxo cluster anions.²³a In the pertinent study, it was observed that the crystal packing feature was dependent on the size of the crown ether and shape/symmetry of the anions. The substitution of one of the hydrogen atoms of ammonium ion by a phenyl ring generated an anilinium ion, which resembled the ammonium ion as far as the nature of guest geometry was concerned. In most of the cases, it was observed that this Ar–NH₃⁺ group (i.e. anilinium) lay in the perching position rather than in the nesting position of the crown ether cavity.²³a The perching position is usually around 1 Å out of plane from the oxygen atoms of the crown ring. For instance, even the ammonium ion which has a diameter of 1.48 Å perches about 1.19 Å out of plane from the 18–crown–6 cavity.²³b–c

Another feature of host-guest complexes incorporating the crown ethers is that the size of the crown ether and the nature of the ammonium cation (NH₄⁺, RNH₃⁺ etc.) are responsible for the stoichiometry and stability of such complexes. Though numerous studies on 18–crown–6 (18C6) and its derivatives revealed a 1:1 stoichiometry of the crown ether with both NH₄⁺ and RNH₃⁺ cations, but with the smaller crown ether, 15–crown–5 (15C5) and its derivatives, a different stoichiometry (2:1) was observed. These complexes of 15–crown–5 were found to exhibit a sandwich structure with the NH₄⁺ cation in between two almost parallel 15C5 residues.²⁰c,²⁴a–c The same type of coordination was also observed for the oxonium ion in the crown ether complex, [(H₅O)(B15C5)₂]⁺, the oxonium ion being isoelectronic with RNH₃⁺²⁴d

In general, anilium ions are known to lie in perching positions of the crown ether cavity. However, Trueblood and co-workers reported that the ammonium or substituted ammonium ions could move nearly to the center of the ring, if their stabilities in such positions were somewhat enhanced by other interactions. As such, a 1:1 crystalline complex, [(NH₂–NH₃)⁺···(18–crown–6)](ClO₄), was examined, in which the −NH₃⁺ group
Figure 1. Crystal structures of some of the ammonium···crown ether complexes adopted from reference 25b.

was found to be almost in plane with the crown ring.\textsuperscript{25a} In order to investigate this contradiction and the underlaying chemistry, two other complexes, $[(\text{OH}–\text{NH}_3)^+···(1\text{8–crown–6})](\text{ClO}_4)$ and $[(\text{CH}_3–\text{NH}_3)^+···(1\text{8–crown–6})](\text{ClO}_4)$ were also synthesized. In the latter two complexes, the ammonium nitrogen atoms were in intermediate positions, about 0.68 and 0.83 Å from the oxygen plane. In the pertinent study, it was found that, in all the three structures, the oxygen atoms of the crown were found to be displaced alternately above and below the plane of the ring. Also, the $–\text{NH}_3^+$ nitrogen atom in the hydrazinium···crown complex was positioned in between the two three-oxygen planes, with a mean deviation of only 0.11 Å from the plane of all six oxygen atoms, whereas in the other two structures, they were positioned above both the oxygen planes. In the hydrazinium···crown structure, weak hydrogen bonding interactions between the $–\text{NH}_2$
group of hydrazinium ion and the crown oxygen atoms were observed, though these bonds were about 0.2 Å longer than the other N–H···O bonds. Moreover, one of these hydrogen bonds was weakly bifurcated and so was also involved in hydrogen bonding with one perchlorate oxygen atom. The –NH$_3^+$ group was however, involved in hydrogen bonding interactions with the oxygen atoms of one plane of the crown ether ring. In contrast, the hydroxylammonium···crown complex was found to encompass interactions of the –NH$_3^+$ group with the ring, in addition to the hydrogen bonding interactions from the –OH group to a water molecule and from that water molecule to two perchlorate ions. Both the O–H···O hydrogen bonds in this structure was found to be almost linear and the orientation of the water molecule was such that the line from the hydroxylammonium oxygen atom, to itself was just ca. 16° from a tetrahedral direction defined by the positions of the hydrogen atoms of H$_2$O.

Another study which emphasized alkylammonium···crown ether interactions was reported by Akimova and co-workers in which three complexes of benzo–15–crown–5 (B15C5) with protonated primary amines were synthesized.$^{25b}$ It was observed that in all the three complexes studied, [PhCH$_2$NH$_3$(B15C5)](ClO$_4$) (a), [p-C$_6$H$_4$(CH$_2$NH$_3$)$_2$(B15C5)$_2$] (ClO$_4$)$_2$ (b), and [H$_3$N(CH$_2$)$_4$NH$_3$](B15C5)$_2$](SCN)$_2$ (c), only 1:1 stoichiometry was formed (see Figure 1). The complex (a) was formed due to the hydrogen bonding interactions between the protonated amino group of the ammonium fragment and two of the oxygen atoms in the crown residue. Apart from these, the RNH$_3^+$ cation also formed hydrogen bonding with the perchlorate anion. A skew conformation was adopted by the crown ether and the nitrogen atom of RNH$_3^+$ group was displaced by ca. 1.842(4) Å from the mean plane of the crown ether. It was put forward that such short ammonium···crown separation was typical of unconstrained 1:1 adducts and was in fact, attributed to additional interactions that might be present in the host-guest adducts. An additional instance having such short separation, was observed in the complex [(H$_3$O)(B15C5)$_2$][Me$_2$NH$_2$]$_2$[PMo$_{12}$O$_{40}$]$\cdot$2(B15C5) in which the cations and crown ether molecules were packed in a 1:1 ratio in the voids of the crystal lattice formed by large polyoxometalate anions.$^{24e}$ Thus, it was argued that alkylammonium cations typically formed 1:1 adducts with 15C5 derivatives and the formation of sandwich complexes was precluded because the alkyl substituent blocked access to any second crown ether.
molecule. This feature was in contrast to the NH$_4^+$-based sandwiches which are generally formed by the ‘sharing’ of the singly charged guest and the electronegative regions of two equidistant host molecules. The other two complexes (b) and (c) crystallized in the centrosymmetric space group, $C_i$. Each ammonium group in complex (b) registered itself with three hydrogen bonds; two with the crown ether and the third with the perchlorate anion. Furthermore, it was observed in the pertinent study that, the geometry and nature of the host-guest interactions was not altered on substituting the p-xylylenediammonium cation with the less bulky tetramethylenediammonium cation in complex (c).$^{25b}$

![Figure 2](image_url)

**Figure 2.** (a) Crystal structure of [Ph$_3$CNH$_3$(12C4)](NCS) and (b) packing topology of the concerned compound adopted from reference 25d.

Fonari and co-workers reported the selective interactions of some triphenylmethane derivatives with crown ethers, such as triphenylmethaninium thiocyanate···12C4 (see Figure 2a). In the pertinent study, this compound was found to crystallize in the centrosymmetric space group, $P2_1/c$, with the crown residing at the center of inversion. In It was also portrayed that the R–NH$_3^+$ group participated in three charge assisted hydrogen bonding interactions, *viz.* one with the crown ether and the other two with the two inversion-related NCS$^-$ anions, thereby giving a tape-like topology. The adjacent tapes were found to pack in an anti-parallel arrangement in the aforementioned compound and the packing topology is shown in Figure 2b.$^{25c}$

In order to better understand the host-guest complexation between crown ether derivatives and ammonium cations, simple systems incorporating guest units with hydrogen bonding sites in angular fashion were chosen in the present work. Also, the cavity dimension of the crown ethers was varied from 12C4 to 21C7. The underlaying
supramolecular chemistry in the resulting host-guest systems have been discussed in Chapter 3.

1.2.4. Polyoxometalates as a supramolecular entity

Metal–oxo cluster anions or polyoxometalates (POMs) are giant inorganic anions usually formed by the group 5 or group 6 transition metals. The general structural feature of these macro-anions is linking of the metal centers by oxygen atoms. These cluster anions are usually isolated using external cationic counterparts and possess three dimensional structures depending upon the number of metal centers and nature of linkages. The metal atoms which are typically in their higher / highest oxidation states, build the framework and are termed as addenda atoms. The electronic configuration of the addenda atoms in these higher oxidation states is $d^0$ or $d^1$. Some typical and common instances of addenda atoms include molybdenum (VI), tungsten (VI), vanadium (V) etc. Apart from the ideal ionic radius and charge for favorable combination with oxygen, molybdenum and tungsten, possess empty d–orbitals which render them ideal for participation in metal–oxygen π–bonding. Therefore, even though, other transition metals, like niobium (V), tantalum (V), hexavalent Tc, Re, Ru, Os; pentavalent Cr, Mo, W, Tc, Re, tetravalent Ti, V, Cr, Mo, W etc. are valuable components for cluster formation, molybdenum and tungsten metals take a special note and have become very well-known in the area of POM chemistry.

Based on the constituents, the polyoxoanions are broadly classified into two categories; (a) heteropolyanions and (b) isopolyanions. The popular and major members of the POM family are the heteropolyanions and in these macro-anions, $p$-, $d$- or $f$- block hetero elements are included in addition to the addenda atoms. The heteropolyanions are thus, formulated as $[X_xM_mO_y]^q^−(x \leq m)$ where M is the addenda atom and X is the heteroelement. In contrast to heteropolyanions, the isopolyanions are constituted with only addenda atoms and oxygen atoms and are formulated as $[M_mO_y]^p^-$. The structures of the polyoxoanions are conveniently described in terms of assemblages of metal–centered MO$_n$ polyhedra through corner, edge and (rarely) face sharing. However, all the polyoxoanion structures do not include metal atoms lying at the center of the polyhedron of oxide ions; rather they are strongly displaced towards a vertex or edge of its own polyhedron.
The polyoxoanions can be isolated from both aqueous and non-aqueous solutions. There is no rule of thumb that can explain the systematic and designed rational synthesis of polyoxometalates. The synthesis and isolation of these cluster anions are well controlled by many factors, under confined conditions.

These cluster anions are excellent building blocks to construct multidimensional network structures. Very recently, our research group has demonstrated supramolecular association between ammonium⋯crown ether complexes and polyoxoanions. It was portrayed that, the surface oxygen atoms of the anions were involved in extensive hydrogen bonding interaction with the appropriate donor functionalities. The topology of the resulting supramolecular complexes was found to vary with the size of the polyanion. Two such examples are pictorially depicted in Figure 3 which clearly show the differing packing features of ammonium-embedded crown ether supramolecular complexes with two different polyoxoanions.

Figure 3. Crystal packing feature of (a) \([\text{NH}_4(\text{DB18C6})]_2[\text{Mo}_6\text{O}_{19}]\) and (b) \([\text{NH}_4(\text{B18C6})]_4[\text{SiW}_{12}\text{O}_{40}]\) adopted from reference 23a.

- **1.3. CHEMISTRY OF 2,2′-BIPYRIDINES**
- **1.3.1. General features**

Since its discovery at the end of nineteenth century, the bipyridine ligand (also known as bipyridyl, dipyridyl and dipyridine ligand) has been extensively used as a building block in supramolecular and coordination chemistry, macromolecular chemistry as well as in nanoscience. These ligands are nitrogen containing hetero–biaryl neutral compounds wherein two pyridine rings are coupled together. The bipyridine ligands, well-known as bidentate chelating ligands in the area of coordination chemistry, represent one of the archetypes of polypyridine ligands and exist as six regioisomers, viz. 2,2', 2,3', 2,4', 3,3', 2,5', 3,5'.
Chart 3. Symmetrical and disymmetrical isomers of the bipyridine ligand.

3,4' and 4,4'; the 2,2’-bipyridine ligand being the most common (Chart 3). It is quite feasible to make a distinction between the symmetrical (2,2', 3,3', and 4,4') and the disymmetrical isomers of bipyridine (2,3', 2,4', and 3,4'), with only the 2,3'- and 3,3'-bipyridines being naturally abundant in certain varieties of tobacco.\(^{28}\)

The major characteristic features of the bipyridine ligand are: (i) it is a neutral ligand and can easily chelate metal cations to form charged complexes, (ii) it can be easily functionalized for custom-tailored applications, (iii) metal–bpy ligands with extended π-conjugated frameworks find applications in material science, including nonlinear optics (NLO),\(^ {29}\) and photovoltaics.\(^ {30}\) As a result, the design and synthesis of new bipyridine ligands featuring extended oligophenylenevinylene π-conjugated backbones (OPV bipyridines) are in great demand in the modern scientific community. As the present work aims at synthesizing new bipyridine derivatives and studying their photophysical properties, a brief introduction to the associated chemistry is made in the following sections.

- **1.3.2. Synthesis of bipyridine based ligands**

   Though several synthetic strategies have been devised over the years to improve the formation of bipyridine derivatives, the most extensively employed method is the metal-
catalyzed (Ni and Pd/C catalyzed) coupling of pyridine, substituted pyridines, or 2–halopyridines to form the desired 2,2ʻ–bipyridine products. A meticulous investigation on such type of systems reveal that better yields of bipyridines can be obtained under milder conditions by incorporating several improvements to the Ni-catalyzed homo–coupling of aryl halides rather than the traditional Ullmann coupling. Recently, procedures utilizing directed cross-coupling reactions, such as Stille–type and Negishi–type have come to the limelight for the synthesis of symmetrically as well as unsymmetrically functionalized bipyridines in high yields.

1.3.2.1. Homo-coupling of pyridine
Badger and Sasse used the Raney nickel catalyst to synthesize 2,2ʻ–bipyridine as well as its symmetrically disubstituted derivatives. A key advantage of this coupling procedure is that there is complete recovery of the unchanged starting material and thus, it can be easily recycled. However, in such cases, the conversion is found to be rather poor for each synthetic cycle. In order to exemplify this process, 2,2ʻ–bipyridine was synthesized by simply heating neat pyridine in the presence of active W7 Raney nickel catalyst. Subsequent pyrolysis yielded the desired bipyridine product with traces of an insoluble organo-nickel compound as a side product.

1.3.2.2. Homo-coupling of 2-halopyridines
Recent synthetic methods used for the preparation of symmetrical 2,2ʻ–bipyridine derivatives in high yield involve transition metal-mediated homo–coupling of 2–halopyridines. Though the classic Ullmann reaction can be used to generate 3,3ʻ–dimethyl–2,2ʻ–bipyridine by coupling 2–bromo–3–methylpyridine in high-boiling solvents, utilizing Cu powder, it suffers from some major drawbacks, such as, usage of drastic experimental conditions to procure the desired product and low conversions from reactants to products. However, such a low conversion was improved by using phase transfer conditions, e.g., 2–bromo–6–picoline with 5% Pd/C afforded pure 6,6ʻ–dimethyl–2,2ʻ–bipyridine in 50–68% yield.
In recent times, the Ni-catalyzed homo-coupling of aryl halides has received substantial consideration due to a number of reasons, such as, it permits the incorporation of a number of functional groups, e.g., an aldehyde or ketone; it utilizes milder conditions relative to the Ullmann reaction and finally, it also results in good yields (ca. 75%).

Furthermore, Lemaire et al. brought in a catalytic alternative to the Ullmann reaction to obtain 2,2′–bipyridines and their symmetrical 5,5′–dimethyl derivatives in very high yields (ca. 90%) by employing Pd(OAc)₂ as the catalyst with n-Bu₄NBr and trialkylamine, as a base in 2–propanol. The usage of K₂CO₃ as base instead of trialkylamine, resulted in 70% yield of the 5,5′–dimethyl homo-coupling product.

1.3.2.3. Cross-coupling of 2-halopyridines

Fraser et al. reported an efficient synthetic strategy for the preparation of 4–, 5–, and 6–methyl–2,2′–bipyridines by a Negishi cross-coupling reaction. For instance, an in situ lithium/halogen exchange was carried out by treating 2–bromopyridine with tert-butyl lithium followed by Li to Zn transmetallation. The desired bipyridine product was obtained in 93–98% yield by the subsequent addition of (methyl)pyridyl triflate and the Pd(PPh₃)₄ catalyst generated in situ. Due to the halogen/lithium exchange, this reaction is, however, restricted to the bromo- or iodo- functionalized pyridines.

The Stille-type cross-coupling procedure, which involves organotin compounds and palladium catalysts, is the second widely used methodology for the preparation of bipyridines. Initially, (trimethylstannyl)pyridine was cross-coupled with bromopyridines in the presence of a catalytic quantity of Pd(PPh₃)₄ to afford the 2,2′–bipyridine product in 77% yield. Later, the same method was extended for the syntheses of symmetrical as well as unsymmetrical methyl-substituted bipyridines, along with bromo-, trimethyltin-, and...
nitro-, ester-, and hydroxymethyl-functionalized bipyridines.\textsuperscript{39} A valuable feature of this method is that different functional groups, such as protected esters and hydroxy groups, are tolerated in this coupling procedure.

\begin{center}
\begin{tikzpicture}

\node (a) at (0,0) {\includegraphics[width=0.9\textwidth]{reaction1.png}};
\end{tikzpicture}
\end{center}

- **1.3.2.4. Monosubstituted bipyridines**

Monosubstituted bipyridine ligands can effortlessly be synthesized by the traditional Kröhnke procedure, directed cross-coupling of halopyridine derivatives utilizing Negishi-type or Stille type, monosubstitution on bipyridine or by ligand-coupling methodologies like Suzuki-type reactions.\textsuperscript{40a} The functionalization on bipyridines originate from the methyl precursor, which can be oxidized, brominated or halogenated, lithiated and modified under diverse conditions. These mono-functionalized precursors draw increasing interest as building blocks in supramolecular and macromolecular chemistry as well as in nanoscience.

\begin{center}
\begin{tikzpicture}

\node (a) at (0,0) {\includegraphics[width=0.9\textwidth]{reaction2.png}};
\end{tikzpicture}
\end{center}

The usage of a modified Negishi cross-coupling procedure yielded 5–monosubstituted 2,2′–bipyridines in high yields.\textsuperscript{40b} The initial step involved the formation of the lithiated derivative by adding 2–bromopyridine to a \( t\)-BuLi solution in THF and subsequent addition of ZnCl\(_2\) to obtain the respective organozinc derivatives. Finally, the cross-coupling reactions with the respective mono-derivatized chloropyridine were carried out using a palladium catalyst, the observed yields being dependent on the functional group on the chloropyridine.

- **1.3.2.5. \( \pi \)–Conjugated bipyridines**

Apart from simple bipyridine derivatives, interest in synthesizing \( \pi \)–conjugated donor–acceptor bipyridine derivatives has been mounting over the years because of their
potential applications in photonic devices. Although homo-coupling of substituted pyridines is a useful route for synthesizing such molecular systems, they can be effectively synthesized through simpler alternative synthetic protocols. The 4,4’–π–conjugated–2,2’–bipyridine derivatives are very familiar in this aspect and these can be obtained using 4,4’–dimethyl–2,2’–bipyridine as the starting precursor. The olefinic functionalities at the 4,4’– positions of 2,2’–bipyridine can be introduced through various pathways, though the Horner–Wadsworth–Emmons reaction is the most common. The title reaction requires a phosphonate precursor which can easily be synthesized through an Arbuzov reaction with the appropriate halomethyl derivatives. Though the classical method for the synthesis of halomethyl bipyridine precursors includes reaction of dimethyl bipyridine with N–halosuccinimide, these reactions offer a major drawback as they render multiply halogenated products which make the isolation of the desired products complicated. An alternate and very efficient protocol to synthesize the halomethyl derivatives of 2,2’–bipyridine was reported by Fraser and co-workers (Scheme 6). The concerned synthetic pathway incorporated lithiation of 4,4’–dimethyl–2,2’–bipyridine with 2 equivalents of lithium diisopropylamide (LDA) followed by trapping of the carbanion with trimethylsilyl chloride (TMSCl). Subsequent reaction between the silylated bipyridine and the commercially available electrophile, hexachloroethane in presence of a dry fluoride source, CsF finally resulted in isolation of the chloromethyl derivative in excellent yield. The same procedure can be used for mono-chlorination of 2,2’–bipyridine using controlled amount of the base. The chloromethyl derivatives, formed by the aforementioned method, can then be transformed into their triphenyl phosphonium salts for the conventional Wittig reaction with proper aldehydes so as to introduce the double bonds at the 4– or 4,4’– positions of 2,2’–
bipyridine. Alternatively, they can be treated with trialkylphosphites to result in a phosphonate ester of 2,2′-bipyridine which will then undergo a Horner–Wadsworth–Emmons reaction with the appropriate aldehydes to yield the corresponding 4- or 4,4′-π-conjugated products. The better performance and higher E-selectivity of the Horner–Wadsworth–Emmons protocol compared to the conventional Wittig pathway makes it a better choice for synthesizing similar bipyridine derivatives.

Alternatively, the 4- or 4,4′-π-conjugated-2,2′-bipyridine derivatives can be synthesized using the Knoevenagel type reactions between the methyl bipyridine derivatives and appropriate aldehydes in presence of strong bases such as LDA or potassium tertiary butoxide. Both the protocols involve the formation of a carbanion which undergoes addition to the aldehyde electrophiles forming a secondary alcohol. If LDA is used as the base, the corresponding alcohol is isolated from the reaction mixture and is subsequently dehydrated usually, by pyridinium p-toluene sulfonate (PPTS) to obtain the desired olefin functionalized bipyridines. However, in case of potassium tertiary butoxide as the base, the desired product is obtained directly without isolation of the alcohol.

The above synthetic protocols have been used to synthesize a large number of 2,2′-bipyridine derivatives with diverse end-capping functionalities which exhibit tunable optical properties. Le Bozec and co-workers reported a series of p-phenylenevinylene-2,2′-bipyridine in which the π-conjugated backbone varied from styryl, thienylvinyl, phenylimino and phenylazo etc., and the ligands were end-capped with various donor or acceptor functionalities such as –NBu₂, –OOct, –SO₂Oct, –NO₂. Similarly, hydroxyl alkylamino functionalities were also introduced to the 2,2′-bipyridine core using appropriate alcohol functionalized dialkylamino benzaldehydes.

1.3.3. Complexation and applications of π-conjugated-2,2′-bipyridine derivatives

It is worth mentioning that the 4,4′-disubstituted-2,2′-bipyridine ligands with a π-extended skeleton have been grabbing considerable attention of the scientific community due to the very interesting photophysical and photochemical properties exhibited by the ligands as well as their transition metal complexes. When suitable donor end-capping functionalities are introduced into the pyridine rings via π-linkers, then ‘push-pull’ or EDA molecules are formed. These molecules, being synthetically flexible offer easy
tuning of the optical properties (absorption, emission etc.) through simple modification of their π-backbones. A simple compound of such category namely, the 4,4’-bis(2,5–dimethoxy)styryl–2,2’–bipyridine (known as N945L) is well known as a blue organic light emitting diode (OLED).

Very often, such bipyridine derivatives are highly fluorescent and their photophysical properties are simply tuned through proper selection of the donor termini. It has been observed that absorption due to such ligands shifts to longer wavelength upon increasing the donor strength and the π–conjugation. The lowest energy absorption band due to these ligands appears predominantly due to an intramolecular charge transfer (ICT). The absorption maxima of these ligands also depend upon the π–spacers. Moreover, the variation of fluorescence property of such ligands generally maintains a similar trend as that of the absorption behavior. Bozec and co-workers observed a substantial bathochromic shift of the ICT band upon changing the π–spacers in the order of phenylazo > thienylvinyl > phenylimino > styryl > vinyl, in the case of an invariable donor group. However, the introduction of imine functionality instead of the alkene moiety was found to quench the fluorescence of the samples.

Transition metal complexes of extended π–conjugated ligands are promising as new molecular materials for photonic and optoelectronic applications and are excellent building blocks for the construction of dipolar or octupolar (either octahedral or pseudo-tetrahedral) complexes. Ruthenium complexes of similar ligands are well-known as sensitizers for dye-sensitized solar cells (DSSC). Since the present thesis mainly deals with the optical properties of 4,4’–π–conjugated–2,2’–bipyridine derivatives (linear) and their transition metal complexes (linear and nonlinear), therefore a brief introduction to the nonlinear optical properties of such complexes is made in the following section.

Nonlinear optics (NLO) generally deals with the interaction of electromagnetic radiation and matter in which the matter responds nonlinearly to the incident radiation. It has been observed that the most extensively studied nonlinear optical phenomena are the second- and third-order effects e.g., second harmonic generation (SHG) and two-photon absorption (2PA) respectively. Second harmonic generation, which is also called frequency doubling, is a second order nonlinear optical process, in which photons interacting with a nonlinear material are combined to generate new photons with twice the energy or frequency and hence, half the wavelength of the irradiated photons. On the
other hand, two-photon absorption is a third order nonlinear optical process which accounts for the simultaneous absorption of two photons of identical or different frequencies so as to excite a molecule from an initial state to a higher energy electronic state. The two-photon absorption differs from linear absorption in the sense that the strength of absorption in the former case depends on the square of the light intensity and hence is several orders of magnitude weaker than linear absorption.

The nonlinear optical phenomenon is generally related to the polarizability of a molecule. For instance, all materials are considered as charged particles in optics. As such, when a dielectric material is considered, the charged particles are bound together even though the bonds are not fully rigid. When an electromagnetic field, $E$ is applied, the charges on the dielectric material are displaced slightly from their mean positions thereby inducing a polarization. This induced polarization ($P$) is represented by the equation:

$$
\vec{P} = \mu_0 + \alpha \vec{E} + \beta \vec{E}^2 + \gamma \vec{E}^3 + \cdots,
$$

where, $\mu_0$ represents the ground state electric dipole moment, $\alpha$ represents dipole (or linear polarizability tensor), $\beta$ represents quadratic polarizability (or first dipole hyperpolarizability) tensor, $\gamma$ represents cubic polarizability (or second dipole hyperpolarizability tensor) and so on.

Thus, the value of the first dipole hyperpolarizability tensor, $\beta$ gives us idea about SHG while the imaginary part of the second dipole hyperpolarizability $\gamma$ is related to the 2PA cross-section ($\sigma_2$). Also, it has been established that apart from excellent octupolar nonlinearities based on extended $\pi$–conjugated systems, coordination chemistry can also be a useful tool in building various branched structures including dipolar and octupolar systems by gathering the coordinating ligands in a pre-designed fashion to yield large values of $\gamma$ and $\sigma_2$.\textsuperscript{44c}

It is worth mentioning that transition metal coordination complexes of functionalized bipyridine ligands are popular as nonlinear optical materials. The metal ion plays some pivotal roles in this aspect, such as; (i) acting as a powerful template to gather ligands in predetermined octupolar arrangements, (ii) inducing a low-energy metal–ligand charge-transfer transition (MLCT) and, (iii) acting as a Lewis acid to induce a strong intraligand charge-transfer (ILCT) transition; thereby contributing to sizable second- and third-order
NLO activity. It can be aptly said that, more the polarization in a molecule, more will be its NLO activity depending on the strength of the donor and acceptor moieties. A majority of the NLO-phores comprise relatively simple dipolar electronic structures, however, octupolar compounds have also enticed scientists, especially for potential quadratic (second-order) applications. Though octupolar molecules have zero net ground-state dipole moments, intramolecular charge transfer (ICT) excitations can lead to large changes in dipole moment thereby imparting substantial values to the first hyperpolarizability ($\beta$) which governs quadratic NLO effects at the molecular level.

**Figure 4.** Derivation of octupolar symmetry from a cubic structure (adopted from reference 45d).

Coordination chemistry is a useful tool in developing octupolar nonlinearity at the molecular level and this concept has been developing since the early 1990s based on group theoretical and quantum mechanical calculations. The octupolar nature of $D_3$ tris-chelate transition metal complexes was first brought to light by Zyss and co-workers to obtain large $\beta$ values for the salts $[\text{Ru}^{II}(\text{bpy})_3]\text{Br}_2$ and $[\text{Ru}^{II}(\text{phen})_3]\text{Cl}_2$, using the hyper-Rayleigh scattering (HRS) measurements and a three-state theoretical model. The octupolar structure can be best described as a cubic structure with alternating donor and acceptor groups at the edges of the cube. Therefore, the pure octupolar symmetries can be derived from this cubic structure either by projection along the 3–fold rotational axis of the cube, resulting in $D_3$ or $D_{3h}$ symmetry, or by fusion of one type of charge at the barycenter of the cube leading to $D_{3h}$, $D_3$, $T_d$ or $D_{2d}$ symmetry (see Figure 4). A large number of NLO–active transition metal complexes of functionalized 2,2′–bipyridine systems have been documented since then in literature, especially from the research group of Bozec.$^{45a-f}$ Apart from the octupolar $D_3$ complexes, the bipyridyl ligands are also used for the design of $D_{2d}$ tetrahedral octupoles by the coordination of two bipyridine ligands to metal ions such as Cu$^{I}$, Ag$^{I}$, or Zn$^{II}$. The incorporation of alkyl or aryl
substituents at the 6,6’– positions of the bipyridyl ligand plays a pivotal role in stabilizing the tetrahedral geometry as well as in protecting the central metal ion against oxidation.\textsuperscript{45g}

In recent times, apart from the second order NLO, the third-order nonlinear optical properties, such as two-photon absorption properties of complexes of $\pi$–conjugated systems, have also come to the limelight. Abbottto and co-workers studied the two–photon absorption properties of Zn$^{\text{II}}$ octupolar molecules and found that the obtained experimental result contradicted the theoretical prediction which estimated an enormous enhancement of the TPA cross-section on complexation of the ligand to a Zn$^{\text{II}}$ center. The experimental cross-section values were found to be much smaller than those predicted for the same theoretically. The lack of TPA cross-section enhancement in the Zn-complex compared to the free ligand was attributed to the inability of the Zn$^{\text{II}}$ center to propagate the intramolecular charge transfer process between the ligands as well as between ligands and the Zn$^{\text{II}}$ metal center.\textsuperscript{46a} Another such surprising result was observed in case of a Ni$^{\text{II}}$–phenanthroline complex reported by Prasad and co-workers, even though coordinating metal ions were expected to act as strong three-dimensional templates for enhancing the TPA cross-section. In this case, it was reported that nickel complexes of phenanthroline ligands, bearing strong electron-donating groups such as a dialkylamino group decreased the TPA cross-section whereas those bearing weaker electron donors such as alkylxy or alkylthio groups enhanced the TPA cross-section.\textsuperscript{46b} In 2007, Le Bozec and co-workers studied the linear properties and second- and third-order nonlinearities of a series of octupolar $\text{tris}[4,4'$–bis[(dialkylamino)styryl]$\text{−}2,2'$–bipyridine]$\text{M}^{\text{II}}$ complexes ($\text{M} = \text{Ru, Fe, Zn, Cu, Ni}$). These compounds exhibited relatively large first hyperpolarizabilities ($\beta$) and TPA cross-section values in the range $650 \text{ GM} < \delta_2 (765 \text{nm}) < 2200 \text{ GM}$. This result pointed out that the role of the metallic core was not only to act as a template, but also to participate in the NLO activity. It was also suggested that the two-photon activity of such metal complexes could be significantly enhanced upon increasing the $\pi$–conjugated backbone in the bipyridine unit.\textsuperscript{46c}

Very recently, phenylpyridine based iridium complexes have attracted our attention, though this class of compounds has been very less explored in terms of nonlinear optics. Beeby and co-workers studied a series of cyclometalated iridium complexes where it was
suggested that if the conjugation of the pyridyl fragment was increased, then the charge separation of the MLCT state would be greater, resulting in larger TPA cross-sections.\textsuperscript{47}

**1.4. MOTIVATION OF THE PRESENT WORK**

The above background information gives a sound overview of the chemistry behind the two important molecular systems of the present work i.e. macrocycles and 2,2′-bipyridines. Based on the information extracted from previous literature reports, we found that a few vital facts have not been addressed yet; (i) chiral resolution of transition metal complexes of transdiene, (b) whether supramolecular complexes of crown ethers with angular shaped guests would lead to helical crystal packing or not and, (c) the difference in photophysical behavior of 2,2′-bipyridines end-capped with hetero-donor functionalities instead of the known homo-donor derivatives.

**1.4.1. Chiral resolution of M–L complexes (L = transdiene)**

The macrocycle, transdiene, readily undergoes complexation with transition metal ions. The coordination complexes of this ligand comprise two stereogenic centers on the two amine nitrogen atoms. In the relevant complexes, based on orientation of the amine hydrogen atoms, two diastereomeric forms are possible i.e. racemic– (RR– and SS–) and meso– (RS–). Similarly, the racemic diastereomers exist as a mixture of two enantiomorphs, \textit{viz.} RR– and SS–. The metal complexes are usually isolated as a mixture of all these isomers from which the diastereomers can easily be separated with the aid of differing solubility. The \textit{racemic}– product which is obtained, is a mixture of RR– and SS– enantiomers in 50:50 statistical ratio. The bulk mixture of these enantiomers is thus achiral but, might be resolved to the individual enantiomers and is consequently, the special attraction of the present work. The working strategy is outlined in Scheme 7.

An important and fundamental aspect of structural recognition in this type of supramolecular complexation is chiral recognition, where multidentate organic ligands are mostly used to generate helical structures. In the synthesis of such chiral molecules, two generalized approaches have been established to obtain stacking/packing of the crystallizing substances following a screw symmetry \textit{viz.}, (a) helicity induction through the usage of a chiral substance, and (b) chiral packing motif of the molecular components through spontaneous resolution. The packing of molecular components in chiral space
symmetry is often complicated to predict \textit{a priori} and so, spontaneous resolution through self-assembly without the use of any chiral ligand or chiral auxiliary still remains a challenge and is a growing topic of interest in light of its importance in biology and advanced materials. According to long held views, some sort of well-organized and inevitable asymmetric augmentation process might have operated for generation of enantiomeric excess (ee) thereby paving the way for biomolecular homochirality.

**Scheme 7. Pictorial representation showing the mixture of isomers.**

In general, majority of the chiral molecules crystallize as racemic compounds, but for spontaneous resolution of enantiomers to take place, the formation of racemic conglomerates is a prerequisite (individual enantiomorphs crystallize in different crystals). In fact, when nucleation of crystals takes place from dissolved racemic components, three limiting situations might arise: (a) formation of a racemic crystal in which both the enantiomers maintain opposite chirality/helicity in the same crystal thereby nullifying the overall chirality of the individual crystals (and thus bulk sample), (b) formation of a conglomerate in which 50 : 50 distribution of the crystals containing individual enantiomers makes the bulk sample optically inactive and, (c) formation of a \textit{pseudo}-racemate which maintains inhomogeneous distribution of the enantiomers. However, only the conglomerate formation involves spontaneous resolution of the
enantiomers which in turn occurs with just 5–10% of the racemates and hence, a lot of effort has been undertaken to convert racemic compounds into racemic conglomerates. It is thus obvious that induction of heterochirality through the chirality transport among the helical packing motifs of the crystallizing substances is more common than the maintenance of homochirality in a crystal lattice. Among the various intermolecular non-covalent forces that assemble the adjoining molecules in the crystals in an ordered array, hydrogen bonds are more fascinating due to their strong directional nature and are found to be mostly responsible for controlling homochiral aggregation in the metal complexes thereby causing their spontaneous resolution.

It is thus understood that, isolation of chiral crystals is a rare phenomenon as the inversion symmetry often hinders to do so. The transition metal complexes of transdiene were hitherto isolated as perchlorate, thiocyanate, nitrate, halide etc. salts. Several crystal structures of M–L complexes have been reported so far, none of which encounters the phenomenon of spontaneous resolution. However, in this work, we have introduced a special type of counter anion, namely, polyoxometalate which are excellent building blocks in supramolecular chemistry and are known to be good hydrogen bond acceptors. We were thus, keen to know whether the structural difference between the conventional anions and the polyoxometalates would bring about the isolation of individual enantiomorphs of the M–L complexes through spontaneous resolution or not. The overall investigation has been elaborately discussed in Chapter 2.

1.4.2. Supramolecular complexes of crown ethers

In contrast to aza-macrocycles which are more prone to transition metal complexation, the crown ethers are mostly known to bind alkali or alkaline earth metals. However, they are also known to encapsulate a large variety of cationic guests such as H$_3$O$, \text{NH}_4$, RNH$_3^+$ etc. The encapsulation of these guests usually takes place through non-covalent D–H···X interactions (D = hydrogen bond donor, X = acceptor heteroatom). In addition to the electronegative heteroatoms which act as hydrogen bond acceptors, the donation capability of the peripheral C–H bonds makes them attractive building blocks for generating new supramolecular networks. Thus, in the crystals of the relevant host-guest complexes, the crown ethers play a double role of hydrogen bond donation as well as acceptance. Among the members of the crown ether family, the 18–crown–6 (18C6) and
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its derivatives have mostly been explored as hosts for diverse neutral and cationic guests whereas, the other members are relatively less studied. The ammonium cations are excellent guest species which usually include in the crown ether cavity through three N–H···O supramolecular contacts.


After rigorous literature and crystallographic database survey, we focused our aim at analyzing the crystal structures of crown ether based host-guest complexes in which the guest molecules would possess two hydrogen bonding sites at an angular position. For this purpose, we chose two different types of guest molecules viz., doubly protonated 3–amino pyridine and doubly protonated di-anilines (see Chart 4). The stoichiometry of the host and guests in the resulting supramolecular complexes would depend upon the size of the crown ethers and separation of the hydrogen bonding sites in the guest cations. For example, if the two anilinium sites of a guest are separated by a large distance then, a 1:2 stoichiometry between the guest and the host could be expected and vice versa. The angular geometry of the guest hydrogen bonding sites instead of a linear geometry was chosen so as to comprehend as to whether complexation at an angular fashion would lead to a helical crystal packing or not. The relevant results are portrayed in details in Chapter 3.

● 1.4.3. Hetero-donor functionalized 2,2′–bipyridine ligands and their complexes

The 2,2′–bipyridine based ‘push-pull’ chromophores are important materials in the area of integrated electronics. A variety of functionalities can be introduced with the pyridine rings using proper synthetic strategies. The photophysical properties of the resulting
molecules largely depend upon the strength of the donor functionality, conjugation length and the type of $\pi$-spacer. Dipolar and octupolar metal complexes of such conjugated systems are gaining much more recognition because charge transfer transitions play a pivotal role in augmenting the NLO activity of a material. Hence, an increasing effort has been devoted over the past decade to the design of chromophores with large NLO responses whereby, attention is being progressively moved from the well-known push-pull dipolar molecular structures towards more complex molecular architectures. Therefore, it can be aptly said that, the study of new functionalized bipyridine ligands and their transition metal complexes would be an interesting topic of research.

An ample number of bipyridine based donor–acceptor systems are known till date, the most abundantly used donor functionalities being amino and alkoxy type. Amines are stronger electron donors as compared to the alkoxy functionalities and hence, influence the ICT process to a greater extent. As a result, the chromophores with amine functionalities absorb and emit at longer wavelengths than those with alkoxy substituents. As such, we asked ourselves the question as to whether the outcome of introducing two donor functionalities into the same chromophore would be interesting or not. Accordingly, we synthesized a series of bipyridine derivatives with hetero–donor functionalities which were hitherto unknown and subsequently studied their photophysical properties. The complete study has been illustrated in Chapter 4.

Most of the previous studies involved polypyridine complexes of 3d metal ions, Ru$^{II}$ and Os$^{II}$, though cyclometalated Ir$^{III}$ species have been far less exploited mainly due to difficulties in their synthetic strategies. Two types of complexes, *viz.* homoleptic and heteroleptic complexes can be synthesized, though the latter is the preferred one. For the homoleptic metal complexes, two forms of isomers are known i.e., meridional and facial isomers. It has been observed that $fac$–Ir(C$^\text{N}$)$_3$ (C$^\text{N}$ indicates a phenylpyridine derivative) tends to form at high temperature, whereas $mer$–Ir(C$^\text{N}$)$_3$ forms at low temperature. Therefore, $mer$– isomers can be converted to $fac$– isomers under treatment at high temperatures. The heteroleptic synthetic pathway, on the other hand, cuts down the chance of formation of any isomeric form thereby making its synthesis easy. Thus, owing to their relatively high luminescence quantum yields and their aptitude to behave as photoreductants, such cyclometalated Ir$^{III}$ compounds may preferably replace Ru$^{II}$ and
Os$^{II}$ complexes as building blocks for supramolecular systems designed for specific functions. After the synthesis of a series of new bipyridine ligands, we were interested to study the optical nonlinearity of the cyclometalated Ir$^{III}$ complexes bearing the above mentioned synthesized bipyridine ligands. Infact, we were keen to know whether the nature of donor functionalities at the $\pi$–skeleton of the bipyridine ligands would affect linear and nonlinear optical properties of the relevant complexes or not. The outcome of the overall investigation has been demonstrated in Chapter 5.

1.5. REFERENCES


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