Concluding Remarks and Future Scopes of the Present Work

6.1. SUMMARY AND CONCLUSION

The present thesis incorporates macrocycles and 4,4’–π–conjugated–2,2’–bipyridine derivatives as the major research substrates. The introductory notes on the relevant systems have been summarized in Chapter 1, i.e., this chapter embodies an introduction to the chemistry of macrocycles and bipyridine derivatives while the motivation of the work has been outlined in the last section of the chapter. The major focus of this chapter is only on the significant aspects of the aforesaid materials. Macrocycles are the potential hosts for diverse classes of ionic species whereas the bipyridines are well-known in the area of Coordination Chemistry. Aza-macrocycles and crown ethers are the widely acclaimed building blocks in the area of Supramolecular Chemistry. Although, the two aforementioned classes of substrates have been the subject of various novel research articles till date, many important facets of the interlaying chemical aspects of these two classes of substances are yet to be explored. For instance, the macrocycle Transdiene, has been known since the 1960s and its transition metal complexes are reported to have potential biological and catalytic activities, but the chiral behavior of the pertinent complexes have been paid least attention.

Similarly, the π–extended organic molecules have enticed the scientific community due to their versatile applications in the area of integrated electronics; the Liquid Crystal Display (LCD), Thin Film Transistors (TFT) and Organic Light Emitting Diodes (OLED) being the most common. The heterocyclic organic compounds are promising materials in organic electronics. The 2,2’–bipyridines containing a π–conjugated framework and their transition metal complexes belong to another class of important materials and have been explored in various branches of photosciences e.g., nonlinear optics, dye sensitized solar cells, OLEDs, etc. The spectral feature of these materials is a direct outcome of the nature of substituents in their π–skeleton and their photonic behavior could merely be tuned through judicious selection of the end-capping functionalities. It is thus, worth mentioning that, the design and synthesis of such materials which respond in the longer wavelength region of the electromagnetic spectrum would be an interesting topic of research.
Some queries which cropped up in our minds during rigorous literature survey instigated us to accomplish the present work. A few vital points which have never been emphasized, such as, (i) the chiral resolution of transition metal complexes of the macrocycle, Transdiene; (b) whether supramolecular complexes of crown ethers with angular shaped guests would lead to a helical crystal packing or not and, (c) the difference in photophysical behavior of 2,2’-bipyridines end-capped with hetero-donor functionalities against the known homo-donor derivatives, etc. are the key aspects for which we initiated our work in this direction.

The intermolecular non-covalent association between transition metal complexes of two tetra-aza macrocyclic systems (transdiene and cyclen) and Lindqvist type polyoxometalate (POM) cluster anions has been illustrated in Chapter 2. The various complexes were isolated as their hexametallate salts and their spectroscopic and crystallographic aspects have been illustrated in details. The non-covalent weak interactive forces between various functionalities of the structural motifs are mainly responsible for building the crystals in a three-dimensional array, the hydrogen bonding interactions being the most important due to their directional nature. It is nonetheless important to mention that, hydrogen bonds play a major role in the biological systems, the interaction between the various nucleic bases in the double helical structure of DNA being one of the brightest instances. The double helical architecture of DNA is an excellent example of chiral packing feature, which in most cases, is achieved through hydrogen bonding interactions between the structural motifs in the crystal lattices. The helical packing of the supramolecular building blocks is primarily sub-grouped in two categories: homochiral and heterochiral. In the first case, similar chirality is transmitted through the adjacent helices while in the latter case the adjacent helices of opposite chirality are usually linked by the solvent molecules, anions etc. Each of the crystals containing right and left handed homochiral packing motifs are chiral and they form a bulk condensate with equal distribution, the separation of the individual crystals (i.e. the enantiomers) being known as the Spontaneous Resolution. On the contrary, heterochirality turns the individual crystals optically inactive. The present work aims at understanding as to whether the transition metal complexes of transdiene (racemic form) can be spontaneously resolved or not. The racemic– isomers essentially have a 50:50
distribution of the $RR$– and $SS$– enantiomers which mostly form racemic condensates. However, only the conglomerate formation involves spontaneous resolution of the enantiomers which in turn occurs with 5–10% of the racemates only. Thus, chiral resolution seems to be a very challenging task and this is what is portrayed in Chapter 2.

The most important finding of the work carried out in the Chapter 2, is the occurrence of spontaneous resolution of the copper complex of transdiene with the POM anions during crystallization whereas the other six compounds crystallize in centrosymmetric space groups (Chapter 2). The $rac$– diastereomer of [Cu(L)](ClO$_4$)$_2$ has been observed to crystallize as a racemate (space group = $P2_1/c$) from methanol, wherein the perchlorate counter anion acts as a mediator for transferring opposite chirality between the two opposite handed Cu$^{II}$–L helical chains. The same result is also obtained upon crystallization of [Cu(L)](ClO$_4$)$_2$ from acetonitrile. However, replacing the perchlorate counter anion with the hexatungstate anion leads to the occurrence of spontaneous resolution during crystallization in acetonitrile solvent. Both the enantiomorphs of compound [Cu(L)(MeCN)][W$_6$O$_{19}$] (P and M) have been structurally elucidated which clearly reveals that the principal reason behind this occurrence is the transmittance of interstrand chirality through hydrogen bonding interactions throughout the network. In addition, the occurrence of spontaneous resolution has also been firmly confirmed on the basis of CD spectra of the relevant compounds which exhibit opposite Cotton effects. Therefore, the POM anion participation as well as acetonitrile coordination to the copper center is strongly believed to play an important role in this unique spontaneous resolution process. In order to further comprehend whether the macrocycle, the POM or solvent coordination plays the major role in the occurrence of spontaneous resolution, we have also studied another copper macrocycle assisted by a POM cluster anion, [Cu(cyclen)(MeCN)][W$_6$O$_{19}$]. This complex also has a copper coordinated acetonitrile molecule, but it does not crystallize in any chiral space group.

We have also tried to explore if the angular geometry of guest molecules leads to any helical crystal packing. In an endeavour to do so, we have demonstrated in Chapter 3, seven host–guest complexes in which ammonium–type cationic guests are incorporated with various crown ethers. In the pertinent study, we have used doubly protonated 3–amino pyridine (3AmPyH$_2$), diamino diphenyl ether (DADPEH$_2$) and diamino diphenyl
methane (DADPMH₂) that serve the role of anchoring units to the crown ethers. Among all the supramolecular complexes demonstrated in this chapter, only the compound [3AmPyH₂(12C₄)₂][ClO₄]₂ crystallizes in a chiral space symmetry (P2₁). The differing behavior of 12C₄ in this compound (chiral packing) is not very clear to us at this level of investigation. The crystallographic analysis of all the compounds discussed in the Chapter 3 reveals that the crown ethers play a dual role, i.e., hydrogen bonding acceptance as well as donation. The guest integration within the host cavity is mainly governed by the N–H···O hydrogen bridges between the ammonium functionalities and the oxygen acceptor heteroatoms of the crown ethers, while the weak C–H···O interaction between the crown ethers and the perchlorate counter anions in the crystal lattice of the aforementioned compounds concurrently plays an important role in packing the host-guest complexes. However, owing to the failure of crystallization attempts, the complete set of crystal data regarding complexation of the same crown ether with all the three ammonium systems is unavailable. Hence, drawing a straightforward structure-packing correlation is beyond the scope of the present work.

In the Chapter 4, we have shown how simple modification of the π–skeleton of donor-acceptor based bipyridine derivatives modulates their fluorescence behavior. In an endeavor to do so, a series of styryl– and bistyryl– 2,2’–bipyridine chromophores functionalized with both the alkoxy and amino functionalities were synthesized and their photophysical properties have been demonstrated. The prototype of the synthesized dyads is of D–π–A–A–π–D (D = donor, A = acceptor) in which the bipyridine moiety acts as the central acceptor core to join the terminal donor functionalities through vinylene linkers. The 2,2’–bipyridine derivatives are generally endowed with an extensive coordination / supramolecular chemistry. This N–heterobiaryl compound has been employed in our study because the pyridine rings can be easily derivatized thereby paving the way for the introduction of an assorted class of donor end-capping functionalities to tune the optical properties of the relevant 2,2’–bipyridine based dyads. The transition metal complexes of the 2,2’–bipyridine based DA systems are of topical interest due to their potential applicability in octupolar nonlinearity and this is what has drawn our attention and motivated us to carry forward our research in this direction. The photophysical properties (absorption and emission) of the synthesized chromophores are
found to be governed by the intramolecular charge separation between the donor end-capping functionalities and the pyridine acceptor heterocycle as depicted by the computational studies. A large solvent sensitive photoluminescent behavior has been observed for the synthesized compounds which clearly indicate that the emitting state of the fluorophores is more polar than the ground electronic state. Furthermore, it has been observed that the conjugation backbone i.e. the nature, position and number of donor functionalities modulate the absorptive and emissive nature of the title chromophores. For instance, among the eight dye stuffs described in the Chapter 4, the compound, MS 5 fluoresce even in the condensed phase which is one of the prerequisite for possible application in light emitting devices. It is thus quite apparent that, variation of the amino donor from open chain dibutylamino in MS 4 to the cyclic pyrrolidine donor in MS 5 results in such differing photophysical behavior. In short, our systematic study on the photophysical properties of the 4,4′–π–conjugated–2,2′–bipyridine based hetero-donor systems in comparison with the parent chromophores bearing alike donor functionalities approaches a structure-function relationship which would be useful for choosing the materials for practical applications (in terms of devising nonlinear optical and solar energy harvesting materials). In view of that, the findings of the current study in conjunction with the photophysics of the earlier reported parent dye molecules construct a library of such systems wherein, the present exploration finds some remarkable diversities in the fluorescence responses compared to the parent molecules functionalized with only one kind of donor sub-chromophores.

As already mentioned, the transition metal complexes of 2,2′–bipyridine based DA systems are useful in various fields, such as, nonlinear optics, photonic devices, etc. As such, in order to check out whether the structural factors would improve the linear and nonlinear optical properties of the extended π–conjugated bipyridyl metal complexes or not, we synthesized a new series of cyclometalated IrIII complexes which has been described in Chapter 5. Since the synthesis of homoleptic Iridium complexes seems to be more intricate and tedious as compared to that of the heteroleptic complexes, therefore, the synthesis of heteroleptic cyclometalated IrIII complexes was preferred in our study. The absorption spectra of the synthesized complexes have been found to display a broad structureless feature in the 350–700 nm spectral region, but in most of the cases, the two
bands are well resolved in this region. These two bands are due to the intraligand charge transfer (ILCT) transitions and due to the involvement of mixed metal and ligand centered transitions (ILCT, LL'CT, MLCT, IL etc.) respectively as depicted by the computational studies. A systematic variation in the nature, position and number of donor groups has been observed to modulate their electronic absorption behavior and a negative solvatochromic effect has been observed on increasing the solvent polarity. A bathochromic shift (ca. 25–35 nm) of the highest energy band has been observed for the cyclic pyrrolidine donors as compared to their acyclic dibutylamino analogues in the title complexes irrespective of the solvent. Also, it has been observed that only two metal complexes containing cyclic donor systems emit in the NIR region. Eventually, the two-photon absorption cross-sections of the synthesized complexes were measured in dichloromethane solvent using the Z–scan technique yielding a moderately good value of $\sigma_2$. Such classes of cyclometalated iridium complexes can herald new and exciting opportunities to have a better control over the photophysical aspects intended to be used for a wide variety of applications.

● 6.2. FUTURE SCOPES

It has already been stated that isolation of the spontaneously resolved crystals from a bulk conglomerate is a difficult task. The occurrence of spontaneous resolution of the individual enantiomorphs is affected by several factors which lead to the isolation of achiral crystals. The competition between homochirality and heterochirality in the crystal lattice often hinders this process and hence a straightforward prediction about the occurrence of this phenomenon is complicated a priori. As such, it is quite evident that special attention is needed while working in this direction.

Although a large number of publications have demonstrated diverse properties of the transition metal complexes of the macrocycle Transdiene till date, the chirality of the relevant systems have not been depicted yet. Hence, in the quest for isolation of individual enantiomorphs of the pertinent macrocyclic complexes through spontaneous resolution, we have made use of the polyoxometalate cluster anions as described in Chapter 2. In spite of the fact that we were able to isolate individual enantiomorphic crystals of one of the complexes through spontaneous resolution, the interlaying phenomenon responsible for the negative outcome in the rest of the complexes is not very
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clear to us at this level and this issue needs to be resolved in the near future. In a nutshell, rigorous analysis of the structural data of related systems are needed to address a straightforward explanation for the occurrence of this phenomenon in such complexes which has not been hitherto addressed. We anticipate that usage of chiral polyoxometalates in conjunction with the transition metal complexes of Transdiene could make the scenario vivid. Some of the chiral POM structures include \([\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-}\), \([\text{P}_6\text{W}_{18}\text{O}_{79}]^{20-}\), \([\text{P}_2\text{Mo}_5\text{O}_{23}]^{6-}\), etc. The association of the macrocycles (used in Chapter 2) and the host-guest complexes (used in Chapter 3) with chiral POMs have not been explored yet. The work to be accomplished in this direction would be performed in the near future in our laboratory.

While the Chapters 2 and 3 are motivated by single crystal X-ray crystallography, the Chapters 4 and 5 deal with the chemistry associated with the widely acclaimed ligand 2,2’-bipyridine. This ligand and its several derivatives have already been widely studied for a diverse class of applications. However, the scope of the present work was limited to only synthesis and photophysical characterizations of some of the related compounds. We have demonstrated, in this thesis, how simple modification of the conjugated backbone of the relevant bipyridine dyads modulates their photophysical behavior. Nevertheless, it is important to mention that, a series of transition metal complexes of the synthesized bipyridine ligands could be synthesized for custom tailored applications. However due to certain limitations, we had to restrain ourselves to explore only a few numbers of such complexes. However, from the relevant study, we have learnt how to tune the optical properties of the pertinent ligands and their metal complexes. It is a known fact that, coordination of a metal to donor end-capped, extended π–conjugated chromophores such as conjugated bipyridine, phenanthroline or terpyridine ligands produces a significant augmentation of their NLO response. This is for the reason that the metal acts as a Lewis acceptor, thereby causing a red-shift of the intraligand charge transfer transition (ILCT). Though Ir\(^{\text{III}}\) cyclometalated complexes have only recently received attention as NLO materials, they have been characterized as exhibiting one of the highest second order NLO responses ever reported for a transition metal complex. High NLO response for cationic Ir\(^{\text{III}}\) complexes is generally reached without any cost in transparency because these complexes exhibit relatively high energy absorptions, which is a crucial feature in
the design of NLO–phores. We strongly believe that the Iridium complexes demonstrated in the Chapter 5 would exhibit high second order NLO response. Besides the nonlinear optical responses of the related transition metal complexes, their electroluminescent behavior has been a subject of considerable interest in recent times. The photon emission efficiency in response to the electric field is dependent on several parameters. The electroluminescent quantum yield is usually optimized on the basis of several trial and error experimentations. The cyclometalated Iridium complexes of 2,2'–bipyridines are excellent emitters under the influence of electric field. We believe that, in future, we would be able to contribute in this area via the improvement of the photophysical behavior of related complexes.