Preface

The discovery of ferroelectricity in molecules, possessing chiral or asymmetric carbon, by Robert Meyer in 1975 motivated several scientists across the globe to realize the materials exhibiting liquid crystalline phases at ambient temperatures, with large spontaneous polarization, and chemical stability to atmosphere and other external stimuli. Subsequently the next two decades has seen several interesting phenomena from ferroelectricity to antiferroelectricity and their possible applications in display devices. However in 1996 the reported discovery of ferroelectricity in achiral bent or V or banana shaped molecules by Takezoe at the sixth international liquid crystal conference has opened a new subfield in liquid crystal research. In these bent or banana or V-shaped molecules the layer order, molecular tilt order and polar order are realized at the isotropic- liquid crystal phase transition because of the unique shape of the molecules and the spatial constraints associated in the molecular arrangement. The materials exhibit ferro- and/or anti- ferroelectricity, large spontaneous polarization, chirality, second harmonic generation (SHG) and non linear optical properties and hence are considered future materials with potential applications in LCD industry.

The synthesis and characterization of novel molecule-based second order nonlinear optical (NLO) materials (figure 1a) have recently become one of the frontier areas of research not only because of exciting prospects or new scientific phenomena but also of possible potential applications in emerging opto-electronic technologies. Recently transition metal coordination compounds (figure 1b) have emerged as potential building blocks for second order non-linear optical materials suitable for electro-optical devices. However none of these materials do exhibit liquid crystalline behaviour. Liquid crystalline behaviour is particularly attractive since they are easily deposited for device construction and are able to form thin films instantaneously.

A review of literature in the last few years quickly envisages that of all the molecular based materials synthesized thus far, the vast majority contains Schiff base linkage and usually V-shaped or bent shaped molecules possessing C_{2v} symmetry. The synthesized NLO materials can be broadly classified into two categories viz., non-mesogenic organo-metallic compounds and organic compounds exhibiting liquid crystalline behaviour. The crucial prerequisite for achieving large bulk second order NLO response in any of the above materials is that the individual constituent possessing large first order molecular hyperpolarizablity, β response and then arranging in non-centrosymmetric architecture. Such molecular engineering for material optimization at the microscopic scale has been realized in the recent reports on the metal complexes of a new Schiff base ligand (figure1b) based on the condensation of diaminomaleonitrile (or 1,2-phenylenediamine or its substituted ones) and 4-(diethyl amino) salicylaldehyde. These metal complexes exhibit large values of hyperpolarizability, β but do not exhibit liquid crystalline behaviour. Further these metal complexes are not derived from rod like molecules i.e. possessing long alkyl chains to exhibit any liquid crystalline behaviour. Hence there are many of the aliphatic or aliphatic-aromatic end groups, which can be added to extend the molecular length without foregoing the pre-requisites for NLO materials, thereby possibly lead to liquid crystalline behaviour. It is a subtle problem to match the requirement of bent shaped molecule possessing structural anisotropy with the inevitable disruption, which will be caused by the introduction of shape factor (one of the prerequisite for promoting NLO characteristic) to such anisotropy, to exhibit liquid crystalline behaviour. However selective molecular engineering of such structures with the proper interplay of molecular structural anisotropy and shape factor with required polarizability anisotropy has been achieved in banana or bent shaped liquid crystals (figure 1c) with large spontaneous polarization, P_s (350-700nC.cm^2) values matching the organo-metallic chromophores.

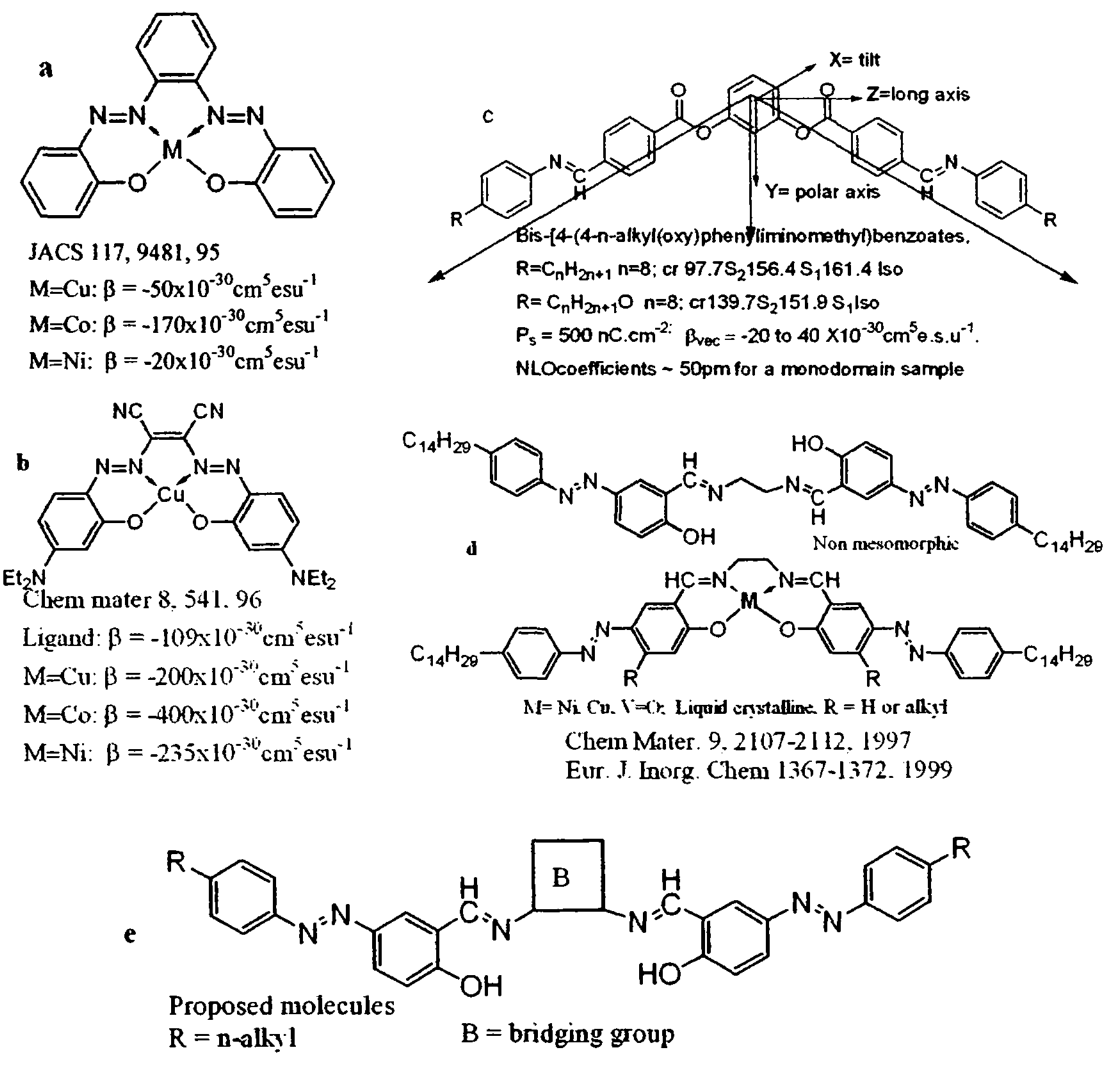

Figure 1

Recently Ghedini et al synthesized bis[4-(n-alkoxy)-5-(p-n-alkylphenylazo)]-substituted (N,N'-Salicylidenediaminato)Nickel (II) complexes (figure 1d), The ligand molecules despite the two mesogenic alkyl phenol azo fragments, do not result into a material to exhibit liquid crystalline behaviour. The possible explanation for such behaviour may be from the transoid N,N$'$ conformation which stabilizes a stepped molecular geometry that discourage mesomorphism. Moreover the development of liquid crystalline materials for optical switching has recently emphasized the role of photoisomerizing (azo group) species, which exhibit a reversible isothermal phase transition. Diaminomaleonitriles have never been used as building blocks either for mesogenic compounds or metallomesogens even though diamines are used in compounds exhibiting thermotropic liquid crystalline behaviour. Hence condensing the basic building block of diaminomaleonitrile with photochromic mesogenic 4–n-dodecyl alkyl phenylazo salicylaldehyde, presents an interesting problem, which can lead to a molecule with C_{2v} symmetry to result into a material possessing nonlinear optical properties.

In attempting to device a strategy for the synthesis of such bent shaped molecules we reasoned that the organic fragments would need to be sufficiently anisotropic to match the perturbation produced in the form of shape factor by the introduction of such bridging groups between two organic fragments. Earlier attempts by introduction of aliphatic linking groups viz., 1,2 diaminoethane, 1,3 diamiopropane and 1,3 diamino 2,2'-dimethyl propane do neither lead to liquid crystalline behaviour nor any NLO characteristics, with few exceptions. However we believe that the augmentation of longitudinal polarizability along the long axis may conceive the mesomorphic behaviour. Further the compounds, which are synthesized using the above bridging groups are non mesomorphic, upon complexation with either Copper or Nickel or Vanadium exhibit mesomorphic behaviour has lent support to the above hypothesis. Most of the above discussion is compiled in chapter 1 and the general experimental methods are presented in chapter 2.

Hence condensing the basic building block of diaminomaleonitrile with photochromic mesogenic 4–n-dodecyl alkyl phenylazo salicylaldehyde, presents an interesting problem, which can lead to a molecule with C_{2v} symmetry to result into a material possessing nonlinear optical properties. Such molecules were synthesized with diaminomaleonitriles, 1,2 diamines and 1,3 diamines as bridging group, analyzed for chemical composition by spectroscopic methods and characterized for the liquid crystalline behaviour using differential scanning calorimetry and thermal microscopy. These results are presented in chapter 3. The highlights of the work are discovery of a new smectic phase, chirality exhibited by some of these compounds and observation of banana liquid crystalline phases in compounds with a bent angle around 60^0.

The search for new hybrid materials with nonlinear optic (NLO) response is one of the thrust areas of research in the last decade, to which both physicists and chemists are devoting with great deal of importance and original effort. Introduction of the o-hydroxy group in N-(4-*n*-alkoxybenzylidene)-4$'$-*n*-alkylanilines has led to the possibility of bidentate coordination of O and N with metals like Cu, Ni, Pd, Re, Mn etc. The transition metal complexes of N-(4-n-alkoxysalicylidene)-4$'$-n-alkylanilines not only afford new pathways to uncommon geometries but their properties are conducive to the production of novel materials with unique features such as large electrical, magnetic and optical birefringence, polarizability, paramagnetism, and color. The introduction of chirality into these structures resulted chiral nematic and chiral smectic (SmC*) phases. The concept of molecular chirality plays an important role in liquid crystal research viz., the ferroelectric properties and applications of liquid crystals in display devices. Three important properties viz., polar symmetry, spontaneous polarization and fluidity when combined uniquely yield a ferroelectric liquid crystal. Metal-containing liquid crystals, popularly known as metallomesogens, are derived either from rod-like molecules or disc-like molecules, which may or may not exhibit liquid crystalline behaviour, incorporated with a metal atom. The salicylaldiminato metal complexes (in particular Ni, Zn) viz., Schiff base complexes exhibit sizeable hyperpolarizabilities and the tendency for crystal centro-symmetry (except two noncentrosymmetric structures for every 25 structures) leads to vanishing NLO response in the solid state. Hence complexation of Schiff bases possessing suitable alkyl chains with different metals leads to several structural possibilities. The results of synthesis and characterization of few mono nuclear and binuclear copper complexes of chiral ligands are presented in chapter 4.

Further recent discovery of ''push–pull'' lanthanide complexes for second-order nonlinear optics due to metal induced NLO activity enhancement opens new perspectives in molecular engineering for NLO studies and for the design of new multifunctional materials combining NLO, luminescence and liquid crystalline properties. Moreover any attempt at the coordination of metals of the lanthanide group with any of the ligands possessing an aryl moiety on the nitrogen atom presents a special experimental challenge because in one of the publications of Binnemans, Bruce and Galyametdinov (different laboratories in Europe) they mentioned

"... However, in whichever laboratory the chemistry was carried out, we were not able to complex N-aryl salicylaldimine to lanthanide centers...."

K Binnemans, DW Bruce, SR Collinson, R Van Deun, YG Galyametdinov, and F Martin, Proc R Soc London A, 357, 3063, 1999

Of particular importance, we attempted to experiment with the synthesis of the lanthanide complexes with *nO(OH).m*, which may promote new molecular structures with possible extension of the molecular length with aryl or aliphatic moieties and different substituents. Our attempts proved to be **successful** and the synthesis and characterization of the first mesomorphic lanthanide complexes with aryl moiety on nitrogen atom of the Schiff base, in particular the dysprosium, terbium and gadolinium compounds of different ligands with an aryl moiety on nitrogen atom of the imine linkage, are present in chapter 4.

The work that is carried out during the last few years is presented in this small thesis with the compilation of the references used in this work in chapter 5.

The highlights of the work are a) discovery of a new smectic phase in a W shaped molecule exhibiting chirality, b) banana shaped liquid crystalline behaviour by a molecule with a bent molecule of around 60^0 c) stable binuclear copper complexes and d) complexation of lanthanides with Schiff bases possessing an aryl moiety on nitrogen atom. The preliminary investigations although inferred the non linear optical characteristics in many of the materials different studies are in progress for further characterization towards their application potential.