CHAPTER 1

Introduction
1.1 MOLECULAR MATERIALS

Materials have played a key role in the evolution of human civilization. The kind of materials developed and used through the course of history, serve as excellent indicators of the progress of science and technology and civilization at large; the stone age followed by the copper, bronze and iron ages have led to the present 'plastic age'. The early utilization of materials was based on their structural, mechanical, optical or thermal properties. Metals and their alloys, metal-based compounds and finally plastics were the forerunners of modern materials. The application of these materials was based primarily on their electrical, magnetic, optical and mechanical properties. Revolutionary developments such as the discovery of superconductivity and the fabrication of the first transistor marked the dawn of a new era in the field of materials. The pace at which the physical and chemical sciences grew was reflected in the appearance of new materials and materials fabrication. Starting with simple mechanical approaches to materials structuring, more sophisticated thermal, electrical, chemical and electrochemical techniques have evolved. Assembly of materials at the atomic and molecular level we witness today is the next link in the logical evolution of materials fabrication.

Molecular materials\(^1\) made up of molecules or molecular ions as their building blocks as opposed to atoms and ions in the traditional solid state materials, form a major class of materials developed over the past five decades. They have attracted considerable attention because of the wide range of properties that can be realized and their potential utility in many technological applications. Because of the relatively weak nature of intermolecular interactions, the properties of molecular materials are generally based on additive contributions from the constituent molecular units. It often occurs that the properties that the molecules exhibit in the materials state are retained in the individual isolated state as well; significant exceptions do however exist. Traditional solids like inorganic salts, metal oxides, covalent solids, metals and alloys, on the other hand, exhibit vastly different characteristics in the bulk state compared to their constituent atoms or ions. Nanoscale materials\(^2\) which are at the focus of extensive scientific and technological research today, show stark differences from the atomic and bulk limits in the case of metals and semiconductors, whereas in the case molecular materials, the supramolecular clusters\(^3\) represent a smooth transition from the molecular to the bulk
materials. The properties of molecular materials are sensitive to the orientations and mutual dispositions of the molecules in the assembly. Molecular materials utilize ionic, covalent and coordinate bonding interactions and in addition, a wide variety of relatively weaker interactions, to organize the molecules in the solid state. Polymeric materials built from macromolecules or metal complexes with extended coordination can also be classified as belonging to the general family of molecular materials. Several classes of molecular materials have been designed and developed over the years to achieve properties such as magnetism, conductivity and optical and nonlinear optical effects. Of late, there is considerable interest in the use of single molecules functioning as active devices for optical, electrical and mechanical functions. Functional molecular scale devices that have been developed include rectifiers, switches, gates, wires, shuttles, brakes, ratchets and gears.

The design and fabrication of molecular materials effectively exploits the enormous power and flexibility of synthetic chemistry to tailor specific molecular structures. The fundamental distinction between the route to molecular materials and the conventional approach to materials is shown in Fig. 1.1. Traditionally, materials are fabricated from suitable precursors, employing techniques such as ceramic methods, melt-quench processes, vapor deposition or sol-gel. In the case of molecular materials, a well defined intermediate stage - the molecule or molecular ion - is involved. The intermediate stage effectively separates the molecule synthesis from the materials fabrication. The property of the molecule is determined by its structure while the property of the fabricated materials depends on the molecules and the way they are organized in the bulk. While the synthetic approach can be fine-tuned to achieve desired molecular structure, the control of organization of the molecules in the bulk state is a considerably more complex problem. Thus, the fabrication of molecular materials with specific organizational motifs is a challenging task that needs to be tackled to realize preferred materials properties. The possibility of dissociating the molecular materials into their constituent units in most instances, facilitates an iterative way of realizing tailored materials (Fig. 1.1) providing a unique handle to control the materials attributes.

Several techniques have been developed for the fabrication of molecular materials. Crystallization from organic or aqueous solvent medium is perhaps the most
Figure 1.1 Schematic representation of the (a) traditional approach to materials fabrication compared to the (b) two-stage synthesis of molecular materials.
common technique.\textsuperscript{14} Electrocrystallization is popular in the case of conductors and superconductors.\textsuperscript{15} In this technique the molecule is oxidized or reduced in the presence of appropriate counterions. Since simple crystallization does not provide facile control on the final bulk organization, alternative techniques which involve directed assembly of molecular materials, are often adopted. They include methods such as electric field poling,\textsuperscript{16} Langmuir-Blodgett technique\textsuperscript{17} and layer-by-layer assembly.\textsuperscript{18,19} Spin and dip coating, sol-gel processing\textsuperscript{13} and chemical or physical vapor deposition\textsuperscript{20} are other approaches resorted to.

\textbf{Molecular magnetic materials}

Molecular magnetic materials are potential candidates to develop magnetic, electromagnetic and magneto-optic devices. For centuries after the discovery of the naturally occurring magnet, Fe$_3$O$_4$, most of the magnets that were fabricated and used were based on the compounds and alloys of elements such as iron, cobalt, nickel and gadolinium, which are themselves ferromagnetic in their pure state. The charge transfer complex of decamethylferrocene and tetracyanoethylene was the first molecular material involving an organic ion radical that showed ferromagnetic phase transition with a $T_C \approx 4.8$ K. Several magnetic materials based on coordination polymers and molecular systems in which metal ion serves as the source of magnetic moment have been developed. The design and fabrication of ferromagnetic solids from simple paramagnetic units and controlling the magnetism using synthetic manipulations is a fascinating problem. The basic idea is to build chains or sheets of paramagnetic metal ions with appropriate bridging ligands so that the desired magnetic interactions between the ions can be achieved. The distance between the ions and their three-dimensional interactions are of profound significance, and optimal design can lead to spontaneous magnetization at ambient temperature.\textsuperscript{21,22} In order to achieve a strong coupling between the metal centers with their unpaired electrons, short bridging ligands such as oxo, cyano, azido, pyrazolate or triazolate have been investigated. The metalloligands are good candidates for the construction of novel bimetallic coordination polymers with spontaneous magnetization.\textsuperscript{23}
Another approach to molecular magnetic materials is to utilize an organic radical ligand which serves as the spin carrier as well as linker to magnetically active metal ions. Different methods have been used to construct coordination polymer based magnetic materials containing organic radical ligands - utilization of an organic radical ligand for a direct linker, generation of a radical on a linking ligand as a result of the formation of the coordination polymer and production of a radical by light irradiation following the construction of the coordination polymer. A strategy using $\pi$-conjugated polynitroxide radicals with high spin ground states as bridging ligands for magnetic metal ions was applied to assemble and align spins on a macroscopic scale. Molecular compounds containing rare earth metal ions coupled with transition metal ions and radical ligands have also been extensively studied.

Even though many organic radical systems are known, obtaining a ferromagnetic coupling in the solid state is a difficult task. Unlike in metal-based systems where the unpaired electron spin are largely confined to the metal center, in organic molecular spin systems the unpaired electron is delocalized over the various atoms that constitute the molecule. Generally, bonding tendencies between orbitals lead to preferential antiferromagnetic coupling of spins. One of the ideas proposed to obtain ferromagnetic spin coupling between molecular spin systems was to achieve a packing of the molecules in such a way that the regions of positive spin densities on one molecule would be in close contact with regions of negative spin densities on the neighboring and vice versa. The ferromagnetic coupling between the unpaired electrons of the $\gamma$-phase crystals of p-nitrophenyl nitronyl nitroxide (p-NPNN) radicals have been extensively studied in the recent past. Combination of structural analysis and specific modification by molecular engineering have led to the preparation of molecular solids that show short range organic ferromagnetism. Molecular magnetic compounds are well developed, and strategies have been worked out to obtain new materials with designed properties, molecular ferro- and ferri-magnets, organic magnets, single molecule magnets and high-spin molecules. Though molecular magnets based on organic polymers and charge transfer complexes continues to attract materials chemists, a well-characterized ambient temperature organic polymer ferromagnet is yet to be realized.
Molecular conducting materials

Most organic solids and polymers are insulators: polymers such as teflon or bakelite are some of the best electrical insulators. However several molecular materials based on charge transfer complexes and doped \( \pi \)-conjugated polymers show appreciable conductivity. They are called synthetic metals,\(^{31} \) as they are prepared through normal organic synthesis protocols. Many molecular crystals and \( \pi \)-conjugated polymers show conductivity similar to semiconductors.

The first molecular conductor was synthesized in 1842 by Knop by oxidizing the metal complex \( \text{K}_2(\text{Pt(CN)}_4)_2 \)\(^{32} \) with bromine, though the conducting property of these materials was perhaps not realized at that time. In the early 1950's Japanese researchers observed that perylene-bromine complex\(^{33} \) showed a low electrical resistivity of about 8 \( \Omega \) cm, a rather unexpected property for an organic solid. The synthesis of strong \( \pi \)-electron donor/accepter organic molecules such as tetracyanoquinodimethane (TCNQ) in 1962\(^{34} \) and tetrathiafulvalene (TTF) in 1970,\(^{35} \) marked the development of a large number of conducting or semiconducting charge transfer complexes. The conducting bands in molecular charge transfer complexes are expected to be generally narrow and best visualized as an intermediate regime between band and molecular orbital limits.\(^{36} \) The most popular example of an ‘organic metal’ is the complex between TTF and TCNQ first prepared in 1973. TTF-TCNQ exhibits a room temperature conductivity of \( \sim 10^3 \) S/cm. Advances related to TCNQ based acceptor molecules and other cyano compounds have been reviewed recently.\(^{37} \) TTF and related molecules have been the prime focus of a majority of organic conductors and superconductors research.\(^{38} \) Several molecular conductors based on metal complexes have been developed. The halogen-bridged binuclear metal mixed-valence complexes exhibit metallic conduction above room temperature.\(^{39} \) One-dimensional coordination polymers constructed from stacked porphyrin and phthalocyanine complexes have been studied extensively because of their electrical conductivity.\(^{40} \)
Molecular optical materials

Over the past several decades, various classes of optical materials including dyes, pigments, luminescent and electroluminescent (EL) materials have been developed. Molecules with delocalized $\pi$-electron systems, often with donor-acceptor (push-pull) structure, possess interesting optical and nonlinear optical characteristics. Organic dyes have attracted considerable attention in the field of diodes and laser optical storage devices. The use of cyanine and phthalocyanine dyes in commercial recordable compact discs (CD-R) have facilitated the use of shorter wavelength (635-650 nm) laser beams in place of traditional 780 nm lasers. Dye lasers have contributed greatly to the progress in laser spectroscopy and laser chemistry. A wide variety of organic compounds with complex chemical structures are used as the active medium in current dye lasers. Quinacridine, coumarins and polypyrroles are some of the famous industrial pigments.

Luminescent molecules and materials are potential candidates for display devices and sensor applications. Molecular recognition events that trigger fluorescence response are effectively exploited in chemical and biological applications. Families of molecules which exhibit efficient fluorescence include aromatic hydrocarbons and their derivatives, azomethines, azines, several five and six membered heterocyclic derivatives, carbonyl compounds and metal complexes with a wide range of organic ligands. Several strongly intercalating metal complexes of platinum and ruthenium can act as luminescent markers for DNA and foot print applications. A variety of nanomaterials, polymers and sol-gel systems also display strong fluorescence. Molecular materials which display electroluminescence could be (i) organic dyes (ii) chelate metal complexes or (iii) conjugated polymers. The most widely used metal complexes for electron transport and emitting materials are hydroxyquinoline based compounds. The conjugated polymer, poly (p-phenylenevinylene) (PPV) shows high fluorescence and can be used as the active material in single layer organic light emitting diodes. The potential of molecular and polymeric EL devices for extensive commercial application is bright indeed. Coordination polymers have also been studied for luminescence applications owing to their higher thermal stability compared to pure organic materials and the facility of tuning the emission wavelength of the ligand moiety by metal coordination. The combination of organic spacers and transition metal centers in coordination polymers is seen as an
efficient method for obtaining new types of EL materials for potential applications as light emitting diodes.\textsuperscript{47} Recently, the observation of polarized photoluminescence from molecular materials have suggested the possibility of using them in flat panel displays and other optoelectronic applications.\textsuperscript{48}

**Molecular nonlinear optical materials**

Considerable progress has been made in recent times in using light (photons) as carriers of information. Optical telecommunication using optical fibers and optical displays using liquid crystals or polymeric light emitting materials are significant developments in these fast growing areas. It is expected that optical information technology will expand rapidly at a rate that roughly doubles transport, processing and storage capacity in every three years.\textsuperscript{49} It is believed that a large fraction of the elements for these technologies will use light as the information carrier. Nonlinear optical (NLO) materials interact with the intense electromagnetic fields of laser beams and produce alterations in the properties of light such as the phase, frequency, amplitude, polarization and other propagation characteristics.\textsuperscript{50} NLO materials are the key agents for the fast processing of information and for dynamic or permanent storage applications. The field of research and development of nonlinear optical materials has progressed impressively since the invention of laser in the late 1960’s. Demonstration of the nonlinear optical phenomenon of second harmonic generation (SHG) in single crystal quartz by Franken and coworkers,\textsuperscript{51} and phase matched SHG in KDP crystal by Geordamine\textsuperscript{52} and Maker and coworkers laid the basis for modern nonlinear optics. Parametric oscillation\textsuperscript{53,54} in KDP single crystal and lithium niobate (LiNbO\textsubscript{3}) crystal were discovered in 1965. Rentzepis and Pao\textsuperscript{55} in 1964 observed SHG in benzopyrene, the first instance in a molecular system. The potential of organics was revealed by studies on hexamethylenetetramine,\textsuperscript{56} hippuric acid, benzil\textsuperscript{57} and urea.\textsuperscript{58,59} In 1968 a systematic approach was developed to quantify and classify SHG in organic and inorganic compounds by Kurtz and Perry.\textsuperscript{58}

In the 1970’s the analysis of nonlinear interference pattern in crystals was developed by Jerphagnon and Kurtz\textsuperscript{60} and electric field induced second harmonic
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generation in solution was demonstrated by Hauchecorne and coworkers\textsuperscript{61} which showed the possibility of measuring individual molecular nonlinearity in solution phase.\textsuperscript{54} Several books and reviews have appeared which deal with the theory and structural characteristics and applications of nonlinear optical molecules and materials.\textsuperscript{62-65} Organic molecules and polymers are of great importance in the area of optoelectronics and photonics.\textsuperscript{65,66} It is believed that future information technology will be largely based on photonics, wherein photons instead of electrons will be used to acquire, transmit and store information. Photorefractive\textsuperscript{67} and photoconductive\textsuperscript{68} materials are actively being explored for various applications in information processing and technology.

The efficiency with which materials can carry out nonlinear optical processes is controlled primarily by its nonlinear electric susceptibility. In the traditional semiconductors and other inorganic materials, nonlinear responses are related to individual nuclei or bond polarizabilities. Nonlinearity in molecular materials arises primarily due to electronic polarization effects controlled by the molecular electronic structure. The nonlinearity is highly dependent on the geometrical arrangement of the molecules in the condensed medium in the case of second order nonlinear processes, but much less so for third order nonlinearities. Molecular materials are increasingly being recognized as the materials of the future because of their fast and strong nonlinear responses and the versatility of synthetic chemistry which can be used to alter and optimize molecular structure to maximize the nonlinear responses.

1.2 NONLINEAR OPTICS

Basic concepts

Nonlinear optics is the study of phenomena that occur as a consequence of the interaction of the strong electromagnetic field of intense light such as laser beams with materials and the resulting modification of the optical properties of the materials. The strong oscillating electric field of the laser beam creates a polarization response in the material that is nonlinear with respect to the electric field. The electric field of an electromagnetic radiation typically in the range of optical frequencies induces electronic
polarization in a molecule or material, with which it interacts. The dipole moment
induced per unit volume is called polarization. At low electric fields, the polarization, $P$
induced per unit volume is called polarization. At low electric fields, the polarization, $P$
is linearly related to the field $E$ by the proportionality constant $\chi^{(1)}$, the linear electric
susceptibility tensor (Fig. 1.2). At high fields typically those associated with lasers,
contribution of the nonlinear (second and higher order) terms become significant and $P$
varies nonlinearly with $E$. Higher order susceptibilities $\chi^{(n)}$ ($n > 1$) are inherently
smaller than $\chi^{(1)}$ and their magnitudes get smaller with increasing $n$. The polarization in
a bulk material along the direction $i$ can be represented as:

$$ P_i = \chi^{(1)}_{ij} E_j + \chi^{(2)}_{ijk} E_j E_k + \chi^{(3)}_{ijkl} E_j E_k E_l + \ldots $$

(1.1)

In Eqn. 1.1 the indices $i, j, k$ and $l$ refer to the coordinates of the bulk material. The
polarization at the molecular level, $\rho$, similarly depends on the molecular polarizability, $\alpha$
and hyperpolarizabilities, $\beta, \gamma$ etc as given in Eqn. 1.2.

$$ \rho_i = \alpha_{ij} E_j + \beta_{ijk} E_j E_k + \gamma_{ijkl} E_j E_k E_l + \ldots $$

(1.2)

The coefficients $\chi^{(n)}$ in Eqn. 1.1 as well as $\alpha, \beta, \gamma$ etc in Eqn. 1.2 are tensorial quantities.
The phenomenon of frequency doubling or second harmonic generation, a quadratic
nonlinear optical (NLO) effect can be visualized as follows. If the applied electric field
has frequency, $\omega$ and is represented as $\sin(\omega t)$, the quadratic term will have a $2\omega$
dependence as seen in Eqn. 1.3.

$$ E = \alpha \sin \omega t $$

$$ E^2 = \omega \sin^2 \omega t = \frac{1}{2} (1 - \cos 2\omega t) $$

(1.3)

Eqns. 1.1 and 1.2 show that there is an important symmetry constraint for observing
second harmonic generation or any other even order NLO effect. In systems having a
center of inversion symmetry, reversal of the electric field would exactly reverse the
polarization, ie, $P(-E) = -P(E)$. From Eqn. 1.1 it can be seen that this is possible if and
only if all terms with even powers of $E$ become zero. This implies that the even order
coefficients such as $\beta, \delta$ etc and $\chi^{(2)}, \chi^{(4)}$ etc. are strictly zero. In a noncentric system, no
such equality exists and generally, $P(-E) \neq -P(E)$. This implies that quadratic or any other even order effects are possible only in noncentrosymmetric molecules or materials.

![Diagram](image)

**Figure 1.2** Nonlinear polarization at high electric fields; the linearity at low fields is shown using the dashed line.

**Materials for second harmonic generation (SHG)**

Materials developed initially for NLO applications were based on inorganic systems. Ferroelectric materials lacking center of symmetry were prime candidates for observing quadratic effects. Materials extensively used for second order NLO applications are inorganic crystals such as potassium dihydrogen phosphate (KDP),\(^6^9\) lithium niobate (LiNbO\(_3\))\(^7^0\) and β-barium borate (BBO).\(^7^1\) NLO effects in inorganic materials based on ionic solids arise primarily due to the ionic polarization and hence are relatively slow. Since the responses are due to bulk effects, decomposition of the NLO coefficients in terms of atomic/ionic contributions is not straightforward. Molecular
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materials on the other hand with their relatively low refractive indices, exhibit faster NLO responses. Further, the NLO effects can be conveniently analyzed in terms of the molecular contributions and the impact of the molecular organization. If molecules, with large hyperpolarizabilities values are aligned so that their hyperpolarizabilities add up constructively, the assembly leads to noncentric materials with appreciable NLO response.

Organic π-conjugated molecules and polymers have been extensively studied for the past two decades and continue to be an active field in second order nonlinear optics. There is increasing activity in the area of metal-organic systems like coordination complexes and coordination polymers which show many advantages over the pure organic as well as inorganic systems for NLO applications. Considerable effort is being made to develop materials with good thermal and mechanical stability, so that they can compete with traditional inorganic materials which at present dominate the area of technological applications. The physical mechanism of charge transfer that leads to the nonlinear optical effect in a ‘donor - conjugating unit - accepter’ (D-π-A) framework, can be understood in terms of Mulliken resonance structures illustrated in Fig. 1.3. When a molecule is subjected to an applied field parallel to the dipole axis, the electronic polarization response will be unsymmetric as a result of the cooperative influence of the donor and accepter groups; this can be contrasted with the symmetric response of an unsubstituted structure (broken line). The asymmetry in the polarization gives rise to the harmonic frequencies of the field radiated by the molecular dipole oscillations. These simple considerations have led to the developments of a vast number of molecular crystals and polymers as candidates for NLO applications.

Various classes of quadratic NLO molecules have been developed based mostly on donor-acceptor substituted aromatics. Some of the extensively studied classes of NLO chromophores of this type are 1,4-substituted benzenes and stilbenes, 4-nitroanilines and 4-(N,N-dimethylamino)-4′-nitrostilbene (DANS). Dulcic and Sauteret were the first to study the substituent effect in para disubstituted benzene derivatives and Oudar and Leperson reported on the effect of conjugation length by using stilbene in the place of the benzene system. Since then several systematic investigations have been carried out on the structure-property relationship of NLO chromophores. Compounds with
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conjugating bridges such as tolans,\textsuperscript{75} diazostilbenes,\textsuperscript{79} polyenes,\textsuperscript{80,81} polyphenylenes,\textsuperscript{82} as well as heteroaromatic 5- or 6-membered rings like thiophenes and azoles\textsuperscript{83} have been investigated. In order to overcome the problem of absorption in the organic compounds, Mignani and coworkers have developed an interesting approach of linking donor and acceptor groups through s-p conjugative units, such as silanes, oligo-silanes and polysilanes.\textsuperscript{84} A variety of salts especially with pyridinium and stilbazolium cations have been studied for their second order NLO properties. Organometallic and coordination complexes form another class of materials that have been studied for the quadratic NLO properties.\textsuperscript{85} Extensive investigations have been carried out to understand the role of metal ions, oxidation state of the metal, donor/acceptor substituents on the ligand, and length of conjugation in the ligand on the quadratic NLO properties of the metal complexes. The metal complexes generally show an enhancement of molecular hyperpolarizability compared to the free ligand. The transparency - nonlinear response trade-off problem in the metal-organic materials could be overcome by using d\textsuperscript{10} metal ions.\textsuperscript{73} In several instances, octupolar metal complexes have shown better nonlinearity

\begin{itemize}
  \item \textbf{Figure 1.3} \textit{Origin of nonlinear polarization in a 'donor - conjugating unit - acceptor' system. The broken line represents the response of unsubstituted system.}
\end{itemize}
and transparency compared to the dipolar counterparts. Other systems studied include ferrocene, metallocene compounds and calixarenes. We discuss more about metal-organic systems in Sec. 1.5.

Since D-π-A type systems often tend to prefer centrosymmetric organization in the bulk, there has been considerable interest in exploring octupolar molecules. Recently there have also been reports on novel NLO chromophores with through space or through σ-bond (as opposed to π conjugative) interactions between the donor and acceptor groups which show improved absorption characteristics. There is also growing interest in chromophores organized as mesoscopic and crystalline superstructures; the significance of helical organization for enhanced nonlinearity has been investigated.

**Molecular hyperpolarizability**

The first hyperpolarizability, $\beta$ quantifies the second order NLO response at the molecular level. The simplest model to take into account the contribution of charge transfer within a molecule to the first hyperpolarizability is the two-level model proposed by Oudar and Chemla. Red shift in the absorption spectrum due to an increase in the conjugation length or lower energy charge transfer between the donor and acceptor substituents leads to increased $\beta$. Several theoretical methodologies are available to compute molecular hyperpolarizabilities. Two general approaches are often employed: (i) methods in which the perturbation due to the field is explicitly included in the Hamiltonian (the finite field (FF) and coupled perturbed Hartree-Fock (CPHF) method) and (ii) perturbative schemes in which the calculations are carried out on the free (independent of field) molecules and the response involves the coupling of excited states (the sum-over-states (SOS) method). The CPHF method is equivalent to the time dependent Hartree-Fock approximation (TDHF) for static calculations. The semiempirical AM1/TDHF method incorporated in the MOPAC93 programme package provides a convenient means for the prediction of $\beta$ of organic molecules.
Experimental determination of molecular hyperpolarizability is often carried out in the solution phase. Since molecular motion in solution leads to an average center of inversion symmetry, high electric fields are applied to break the symmetry of the isotropic solution in the approach called electric field induced second harmonic generation (EFISHG). In another technique called the harmonic light scattering or hyper-Rayleigh scattering (HRS), local anisotropy within the solution is used to produce incoherent harmonic scattering which allows determination of the \( \beta \). The latter technique is applicable to charged and octupolar compounds that are not amenable to EFISHG studies. Molecular \( \beta \) values can be related to the bulk crystal NLO coefficients through the oriented gas model.

**Organization of molecules in materials for SHG**

Noncentrosymmetric arrangement of molecular chromophores in the crystalline state is a prerequisite condition to have a nonvanishing macroscopic second order nonlinear optical response from the materials. Even though ground state dipole moment of the dipolar molecules are not having direct correlation to the formation of centrosymmetric lattices, dipole-dipole interactions between dipolar molecule generally promotes centrosymmetric organization in the bulk. Search of the Cambridge crystallographic database shows that typically 70-80% of the molecular crystals belong to centrosymmetric space groups. Different strategies have been developed to obtain noncentrosymmetric organizations, (i) inclusion of chirality, (ii) exploitation of weak as well as strong intermolecular forces and (iii) incorporation of alkyl chains of appropriate length are some of the approaches developed for molecular crystals. Other strategies include, (i) electric field poling of polymer films containing the NLO-phores, (ii) fabrication of X and Z type LB films, (iii) formation of host–guest systems, (iv) sol-gel synthesis and (v) salt formation. Crystal engineering strategies have also been utilized to generate acentric metal-organic polymers based on asymmetric bridging ligands. Recently remote functionality and complexation strategy was explored to obtain noncentrosymmetric organization. Even though noncentrosymmetry is an essential condition for quadratic NLO materials, optimum molecular organization required for efficient SHG is not guaranteed by the noncentrosymmetric assembly alone.
Very often noncentrosymmetric structures depart only slightly from the centrosymmetric one. The oriented gas model developed by Zyss and Oudar provides a basis to determine the optimal molecular orientation of dipolar chromophores which can give rise to efficient SHG.

![Figure 1.4](image)

**Figure 1.4** The dependence of SHG intensity on the average particle size, \(<r>\) for phase-matchable and non phase-matchable materials; \(<l_c>\) is the average coherence length.

The Kurtz-Perry powder technique is a convenient and simple method for screening large sets of microcrystalline materials for SHG activity. It involves the determination of the variation of SHG intensity with the average particle size of the microcrystalline powder as illustrated in Fig. 1.4 for phase-matchable and non phase-matchable materials. The salient feature to be noted here is that for particle sizes much greater than the average coherence length (i.e. to the right of \(<r> = <l_c>\)), the SHG intensity, \(I_{2\theta}\) for phase-matchable materials reaches a saturation value and is independent of the particle size whereas \(I_{2\theta}\) for non phase-matchable materials decreases with increasing particle size and becomes negligible or undetectable at large sizes. Materials that are phase-matchable include LiNbO\(_3\), urea, 4-nitrophenyl-S-prolinol (NPP) and 2-
methyl-4-nitroaniline (MNA). The powder technique is often employed as a simple tool to probe for the presence or absence of center of inversion symmetry in the crystal lattice. However one should exercise caution in using this technique, since factors such as changes of chemical composition on powdering the crystals (for example by loss of solvate molecules) and modification of surface features are known to cause artifacts. Detailed characterization of the SHG coefficient of crystals and their correlation to the molecular hyperpolarizability tensor components is possible by measurements on large size single crystals. Such measurements are essential to investigate the phase-matching direction in the crystals.

**Fabrication of molecular materials for SHG**

The main approaches to the fabrication of materials for second order nonlinear optical studies are: (i) crystal growth, including inclusion and host-guest complexes, (ii) growth in confined structures such as wave guides and fibres, (iii) poled polymer systems and polymer crystal composites, and (iv) thin films formed by the Langmuir-Blodgett (LB), self-assembly (SAM) and vapor phase deposition techniques.

Crystallization is the most common technique for the purification and fabrication of molecular materials. Different kinds of approaches have been developed to grow good quality crystals. The advantages of crystals lie in the highly specific arrangement of molecules and the improved density of packing in the crystalline state. The specific arrangement of molecules leads to high levels of bulk nonlinearity, provided that optimal geometrical arrangements and crystal symmetries are achieved. The high packing density also contributes to the magnitude since bulk nonlinearity depends on the chromophore density. In favorable cases, crystals can be cut, polished and shaped into devices for various applications. In poled polymers, considerable flexibility exists in the choice of molecular and polymeric constituents, allowing for systematic design and optimization. Polymer films deposited from solutions lend themselves well to planar fabrication approaches so that waveguide and integrated optical devices can be fabricated.
In general, thin films can be grown from solution or deposited from the gas phase. The solution-based techniques are easy to setup and are extensively used. Langmuir-Blodgett (LB)\textsuperscript{17} and self-assembled monolayer\textsuperscript{18,19} techniques are capable of forming noncentrosymmetric films with molecular alignment perpendicular to the surface with well-defined thickness. Rational design through synthesis of suitable chromophores and the use of appropriate templates, have resulted in considerable progress towards increasing the quality and stability of the films. Vapor phase deposition\textsuperscript{20} technique offers the advantages of layer thickness control of the thin films with very high chemical purity, \textit{in-situ} growth monitoring and high growth rates. The materials should be stable to sublimation processes and temperatures. Noncentrosymmetric thin films were prepared by vapor deposition on to lattice-matched inorganic crystals or oriented substrates. Recently hydrogen-bonding approach was utilized in the preparation of noncentrosymmetric thin films by organic molecular beam deposition technique.\textsuperscript{107} We discuss more about thin films for SHG in the next section.

\subsection*{1.3 THIN FILMS FOR OPTICAL SECOND HARMONIC GENERATION}

Thin films and nanostructures have attracted increasing interest because of their potential applications in a variety of advanced technologies, including nonlinear optics, microelectronics, nanotechnology, light emitting devices, field-effect transistors, liquid crystals, sensors, and solar cells.\textsuperscript{18,19,44,108} For many of these applications, the device performance is crucially dependent on the orientation of the functional molecules in the film or the nanostructures.\textsuperscript{109} Therefore, methods for alignment of molecules in the structures are of great technological interest. The alignment can be centrosymmetric or noncentrosymmetric. Thin films with noncentrosymmetric ordering of molecular dipoles are attractive for a multitude of information processing and photonics applications, such as high speed electro-optic modulation, optical switches, terahertz wave generation, holographic storage, anisotropic charge transport, self-assembled molecular nanowires, or NLO wave guides for integrated frequency conversion using low-power semiconductor lasers.\textsuperscript{42,108,109}
Several techniques have been developed for the growth of anisotropic thin films, including electric field poling,\textsuperscript{16} Langmuir-Blodgett transfer,\textsuperscript{17} self-assembling monolayer\textsuperscript{18,19} and vapor phase deposition\textsuperscript{20} techniques. The classical poling method consists of heating the polymer close to its glass transition temperature ($T_g$), so as to increase the molecular mobility in the polymer matrix and application of a DC electric field which results in statistical polar orientation of the molecular dipoles along the field direction. Cooling to room temperature while keeping the orienting field on, freezes the chromophores in the polar orientation. Adjustment of the electrode configuration, can in principle, be used to obtain any desired direction of the orientation axis imprinted inside the materials.\textsuperscript{110} Even though the poled polymers offer many advantages as materials for second order nonlinear optical applications, the dilution of the NLO chromophore in the matrix, the broad orientational distribution and the temporal instability of the dipole orientational ordering often limit their utility.

The LB technique is the first technique that provided the chemist with the capability to construct ordered molecular assemblies. This technique in the most general form, consists of forming monolayer of amphiphilic molecules (composed of a hydrophobic tail and a hydrophilic head group) at the air/water interface and transferring them onto a suitable substrate, preserving the monolayer organization to a large extent. Repeating the process allows the growth of multilayers. The advantages provided by the LB technique for the growth anisotropic thin films include, the possibility of easily modifying the environmental parameters of a monolayer, the flexibility and range of strategies available in the design of NLO chromophores and the homogeneity of the film thickness that can be achieved. In most of the cases, the multilayer films adopt a centrosymmetric head-to-head or tail-to-tail arrangement, the so-called Y-layer deposition. However, the technique has been used to obtain noncentrosymmetric thin films displaying a herringbone arrangement,\textsuperscript{111} with the direction of the herringbone structure parallel to the dipping direction. The X and Z-type depositions lead to noncentrosymmetric organization of the multilayers. The second harmonic intensity varies linearly with the square of the film thickness, when the multilayers are well-ordered, and NLO waveguides using such films have been successfully demonstrated.\textsuperscript{112} While the LB technique is relatively successful in obtaining noncentrosymmetric thin films consisting of up to ~100 monolayers, it has the disadvantage that it is very time
Chapter 1

consuming. In many cases, the structures are also thermally unstable; the thermal instability has been attributed to the weak nature of the intermolecular forces within the layers.

Self-assembled monolayers (SAM) and molecular self-assembly provide an attractive alternative approach to second order NLO materials. One of the successful methods is based on the construction of covalently linked, intrinsically acentric superlattices containing molecular chromophoric subunits. SAMs are molecular assemblies that form spontaneously by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent. One obtains films consisting of densely packed long chain organic molecules which are chemisorbed, usually on inorganic substrates, through a head group which has specific affinity for the substrate. These materials offer higher net chromophoric alignment, larger number densities and greater stability and structural control than LB films. In the first step, the substrate is thoroughly cleaned, washed and dried to produce a well-defined surface. In the second step the coupling layer is formed. This layer will provide the binding specificity of the NLO chromophore. The next step involves the introduction of the chromophore layer. In the last step a capping layer is added to promote structural stability. Recently the method has been used to produce robust, densely packed thin films and further extended to produce multilayered films with strong NLO properties. The major disadvantage afflicting this technique comes from it being a solution based technique were side reactions and several intermolecular interactions can interfere with the deposition processes. In addition, the rates at which films can be grown with this technique are not sufficient for practical purposes.

In the vapor-phase deposition method, two kinds of method such as organic molecular beam epitaxy (OMBE) and organic molecular beam deposition (OMBD) have been developed to fabricate thin films. Organic thin films can in principle be grown by epitaxy on a lattice-matched substrate. Such an OMBE procedure needs good film-substrate interactions for the achievement of single domain crystalline organic thin films that are required for NLO applications. This is a major limitation of the technique. Epitaxial growth of a specific class of organic compounds have been demonstrated, but ordered growth on inorganic substrates could not be achieved due to incompatibility of
lattice parameters and the weak forces between the substrates and the organic films. In order to overcome the problems of lattice-matching of the substrate and epitaxial growth, another approach called OMBD has been developed. In this technique, thin films are fabricated by the evaporation of molecules onto a thermally stabilized substrate under high or ultra high vacuum conditions. OMBD technique is interesting because it has many advantages over the solution-based techniques, such as greatly reduced contamination in the ultra-high vacuum condition, a solvent free environment, superior control over growth parameters, and reasonably high growth rates. In addition, mask-designed microstructures, such as strip waveguides and integrated hetero-layered structures, can be easily fabricated using this technique. Günter et al. have demonstrated the utility of the OMBD technique to fabricate organic thin films with hydrogen bond directed preferred orientation of molecular dipoles on amorphous glass substrate. Other methods like rubbing and dragging techniques have also used to fabricate oriented thin films. Kim et al. have demonstrated a new strategy using a supramolecular device technique, for the spontaneous self-assembly of NLO chromophores with directional order and enhanced polar stability. In this approach, the chromophore is uniaxially included in the helical cavity of amylose as receptor, which preferentially accommodates hydrophobic guests, forming a helical rigid-rod supramolecular complex. The various thin film techniques allow the fabrication of large area NLO materials and devices and hence hold great promise from the point of view of practical application. The small dimensions perpendicular to the film plane also facilitates the utilization of small voltage to achieve large electric fields when required.

1.4 POLAR ASSEMBLY OF DIPOLAR MOLECULES IN CRYSTALS

The bulk properties of molecular materials are intimately linked to the relative orientation and organization of the constituent molecules. For example, the electrical transport in organic molecular conductors based on charge transfer complexes critically depends on the interplanar distances and π-orbital overlaps of the donor/acceptor molecules. Magnetic interactions and hence the cooperative magnetism in molecular magnets can change drastically when the mutual disposition of the molecular radicals is altered. Molecular materials that crystallizes in acentric space groups are of
general interest to studies of solid state properties such as pyroelectricity, piezoelectricity and second order nonlinear optical responses such as SHG, frequency mixing, linear electro-optic effect and photorefractive effects.\textsuperscript{62,66} Polar solids in particular, are an important class of materials for pyroelectric, piezoelectric and second order NLO applications, especially for the linear electro-optic (EO) effects. Parallel alignment of dipolar molecule with large $\beta$ leads to high values of bulk nonlinearity. The linear electro-optic (EO) effect, the electric field induced change of the refractive index, of several organic and inorganic materials have been extensively investigated and is a technologically important phenomenon which is currently employed in electro-optic modulators. Therefore, developing acentric materials wherein the chromophores are aligned in a parallel fashion, is an interesting as well as challenging problem.\textsuperscript{120} Parallel orientation of the molecular dipoles can be achieved by electric field poling technique in doped polymer films; however as discussed in Sec. 1.3, the temporal instability and the dilution of the nonlinear chromophores in the polymer matrix are major handicaps for device applications.\textsuperscript{16}

The crystalline state is, in principle, the best medium for generating NLO phenomena because of the high packing density of the active components. In the past, several design strategies have been attempted to achieve parallel molecular dipole orientations in NLO crystal (Table 1.1). Marder \textit{et al}\textsuperscript{105,121} have developed a ‘salt methodology’ wherein the anion sheets provide the shielding required to achieve net polar alignment of the NLO-phore cations and lead to materials with large SHG capability. Bosshard \textit{et al} demonstrated a cocrystal approach, in which careful selection of the molecular units, led to one of the first examples of a geometrically and electronically optimized electro-optic crystal.\textsuperscript{122} Crystal engineering strategies have also been used in the development polar supramolecular assemblies of molecular dipoles.\textsuperscript{123,124} Approaches to obtain polar supramolecular host-guest systems by incorporating NLO molecules in a parallel fashion is an interesting strategy and are relatively more successful compared to the other approaches. Starting with $\beta$-cyclodextrin\textsuperscript{125} a number of clathrate-forming compounds\textsuperscript{126} such as urea and thiourea, cyclophosphazien, deoxycholic acid and perhydrotriphenylene (PHTP)\textsuperscript{127} were examined with respect to the formation of inclusion compounds with small organic as well as
Table 1.1  Routes developed in earlier work towards parallel molecular dipole alignment in NLO crystals

<table>
<thead>
<tr>
<th>Design Principle</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability (ca. 25% crystal structures in CSD are acentric)</td>
<td><img src="image1.png" alt="Image" /></td>
<td>High density of NLO active component; parallel alignment rare</td>
</tr>
<tr>
<td>Minimum ground state dipole moment</td>
<td><img src="image2.png" alt="Image" /></td>
<td>Large $\beta$ values possible</td>
</tr>
<tr>
<td>Co-crystallization or salt formation</td>
<td><img src="image3.png" alt="Image" /></td>
<td>Greater synthetic flexibility, Dilution of NLO component</td>
</tr>
<tr>
<td>Supramolecular synthons (strong, directional interaction)</td>
<td><img src="image4.png" alt="Image" /></td>
<td>Parallel alignment of polar molecular ‘strings’. Antiparallel alignment possible</td>
</tr>
<tr>
<td>Inclusion in inorganic zeolites</td>
<td><img src="image5.png" alt="Image" /></td>
<td>Small guests preferable small crystal, dilution</td>
</tr>
<tr>
<td>Inclusion in $\alpha$- or $\beta$-cyclodextrins</td>
<td><img src="image6.png" alt="Image" /></td>
<td>Limited to few guests, Dilution effect</td>
</tr>
<tr>
<td>Inclusion in organic, channel-forming host molecules</td>
<td><img src="image7.png" alt="Image" /></td>
<td>Applicable to many rod-like NLO active guests, Dilution</td>
</tr>
<tr>
<td>Inclusion in organic open frameworks</td>
<td><img src="image8.png" alt="Image" /></td>
<td>Applicable to few NLO guests, Dilution</td>
</tr>
</tbody>
</table>
organometallic species. The host-guest systems provided a high proportion of polar structures for the inclusion compounds. Zeolite channels have also been utilized to include the NLO chromophore in a parallel arrangement. Hulliger et al successfully demonstrated the inclusion of polar guest molecules into the PHTP host channels with parallel alignment of the dipoles. They have developed a model based on the Markov’s theory of stochastic processes to understand the mechanism of spontaneous polarity evolution of the guest molecules in the PHTP channels. They have concluded that the polarity in supramolecular materials is a tunable property and that the polar structure formation in three-dimensions results from a subtle balance of intermolecular interactions, between donor/acceptor groups of the push-pull molecules and along/perpendicular to the molecular dipole axis. In the open framework strategy, the polar host frameworks enforce the alignment of guest molecules into a polar organization.

Most of the strategies developed so far, to obtain parallel alignment of the molecular dipoles in the crystals require the involvement of a supporting structure based on host polymer or framework lattice, counterion or cocrystallization partner. This invariably leads to a lower density of the NLO active component in the bulk materials (dilution effect mentioned in Table 1.1) and hence reduces the effective utilization of the materials to achieve desired solid state effects. Further, multicomponent systems in many cases pose difficulties with crystallization. It is therefore desirable to develop single component crystals with a perfectly polar alignment of the constituent molecular dipoles. Hulliger et al proposed a theoretical concept for designing geometrically optimized, single component crystals for electro-optic effects. The idea relies on the mechanism responsible for the spontaneous evolution of polarity in channel-type inclusion compounds consisting of non-polar hosts. They envisaged that elongated, rod-like molecular chromophoric structures, which incorporate both a strongly hyperpolarizable core and peripheral, non-polarizable groups and carefully optimized intermolecular interactions have a high probability to form polar single component NLO crystals. Some of the single component polar supramolecular systems that have been reported recently are the following. Weak intermolecular interactions in 2,6-diethynylpyridine lead to the parallel arrangements of the molecular dipoles in the supramolecular assembly and a chiral, parallel alignment of one-dimensional coordination polymer using the chiral
system, the molecule assembled in a noncentrosymmetric parallel alignment in the three-dimensional lattice. Parallel arrangement of molecules have been observed in the crystal lattice of tetrahedral and square pyramidal zinc coordination compounds. Azines were shown to form parallel alignment of molecular dipoles in crystal. Recently, a new strategy for the design of polar organic solids have been demonstrated on the basis of intermolecular interactions in the crystal lattice. Hydrogen-bonded sulfamide sheets lead to the formation of polar assembly of molecules in the crystals of N,N'-Bis(4-substituted benzyl)sulfamides. The single component perfectly polar crystals we have developed will be discussed in Sec. 2.3 and 2.4.

1.5 METAL-ORGANIC SYSTEMS AS SECOND ORDER NLO MATERIALS

Ever-expanding areas such as information technology, image processing and data transmission and storage as well as the advances in applications like optical switching, optical frequency conversion and optoelectronics lay heavy demands on new and more efficient materials. Several classes of materials have been developed based on inorganic crystals and semiconductors, organic crystalline materials, metal-organic systems and polymers with delocalized π-electrons. However, each type of materials is superior in one aspect but of limited merits in another. Inorganic materials generally show relatively weaker and slower nonlinear optical responses than π-conjugated organic molecules, but possesses superior crystal attributes. Organic materials with strong optical nonlinearities often suffer from poor thermal and mechanical stability. In spite of these drawbacks, however, the correlation between the molecular structure and materials properties for molecular second order NLO materials is well developed. Therefore, the synthesis of optimized molecules and fabrication of the molecular materials with appropriate arrangement of the building blocks to achieve efficient second order NLO materials, continues to be an active field of research.

Investigations were initially focused on purely inorganic systems, and some of the first solids to demonstrate second order NLO properties were inorganic crystals (e.g. quartz, lithium niobate and potassium dihydrogen phosphate), in which photo-induced change in refractive index and later, photorefractive effect were observed.
Inorganic semiconductors followed, such as gallium arsenide and indium antimonide which displayed large optical nonlinearities. Multilayer semiconductor materials that were synthesized using new crystal growth techniques exhibited special optical properties not apparent in the bulk materials. These materials are commercially being used as frequency converters, electro-optic modulators and optical switches. However, problems such as 'trade-off' between response time and magnitude of optical nonlinearity and cost of fabrication persist with these materials.

In later years, organic systems were investigated as an alternative to inorganic materials because of their low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and intrinsic tailorability. Particular attention has been paid to the development of discrete organic molecular NLO chromophores. In such molecule-based NLO materials, the optical properties can be readily fine-tuned through subtle changes in the molecular structure using the tools of synthetic organic chemistry. However, in spite of extensive investigations, organic materials are yet to find practical NLO applications. Molecular materials in general are fragile and brittle, and have relatively low thermal stability and low damage thresholds under laser irradiation. Large, optically clear crystals are difficult to grow; for specialized applications, the crystals must be large enough to cut and polish. Good transparency of the materials at the operating frequencies is essential and several organic compounds with large \( \beta \) absorb visible light making NLO applications at these wavelengths inefficient. Recently, investigations of coordination complexes and organometallic systems have intensified considerably. Incorporation of metals into NLO systems gives a new dimension of study and introduces several new variables that can be optimized.

**Metal-organic Materials**

We use the general term metal-organic systems to denote the class of materials including coordination complexes of metal ions, organometallics and coordination polymers. Metal-organic systems are of special interest because of the relatively higher thermal and mechanical stability they possess and the utility of metal centers in the
construction of various one, two and three-dimensional architectures for NLO application. The metals can have a large diversity of oxidation states and ligand environments, and due to the polarizable d-electrons, a number of interesting effects and greater nonlinear optical effects are likely to be observed. Molecular configuration also plays a significant role on second order NLO properties of coordination compounds. The reasons for studying the NLO properties of metal complexes have been expounded in several reviews. The salient features of metal-organic systems as NLO materials are the following.

a) Metal-organic systems often exhibit metal-ligand or ligand-metal charge transfer bands in the visible region of the spectrum. These optical absorption bands are usually associated with large $\beta$, although they can lead to transparency problem.

b) Transition metal centers can undergo redox changes, which can lead to electron-poor or electron-rich situations depending on the oxidation state and ligand environment. Facile redox ability can be envisaged as leading to large $\beta$, in view of the metal center being stronger donor or acceptor in comparison to conventional organic systems.

c) Chromophores, such as porphyrins and phthalocyanines, containing metal ions are amongst the more intensely colored materials known. The strength of the optical absorption band is also associated with large optical nonlinearities.

d) Many metal-organic compounds have low-energy excited states with excited-state dipole moment significantly different from the ground-state dipole moment. Many of the excited states involve transfer of electron density between the central metal and one or more of the associated ligands. Such excited states usually provide a substantial contribution to $\beta$.

e) Metal-organic compounds also have important advantages in the range of non-aromatic ligands that can be attached to the metals. These ligands can shift the occupied and unoccupied metal d-orbitals that interact with the $\pi$-electron of the conjugated ligand system. This provides a mechanism for fine-tuning and optimizing $\beta$ or the crystallographic arrangements that control the bulk nonlinear susceptibility.

f) Additionally, the metal centers in these molecules can be used to generate chiral species so that if resolvable, they can crystallize as noncentrosymmetric lattices, essential to observe quadratic NLO effects.
A general problem is the low energy d-d transitions present in most of the coordination compounds, normally observed in the visible region. This gives rise to what is termed as the nonlinearity/transparency trade-off. If a material is to be used for frequency doubling, then obviously, the absorption of the second harmonic light that is produced will limit the usefulness of the material. Depending on the location of these bands, the ‘transparency window’ can be large or small; larger a materials’ transparency range the greater its potential applications. These considerations suggest that d\(^{10}\) metal ions such as Zn(II), Cd(II), Cu(I) and Ag(I) are potentially important candidates for the fabrication of metal-organic materials for NLO applications.

**Coordination complexes with second order NLO properties**

Several classes of coordination complexes have been investigated for second order nonlinear optical properties. The materials that have been extensively studied are those based on pyridyl, Schiff base and thiocyanate ligands. Even though there are some reports on quadratic NLO properties of porphyrin and phthalocyanine complexes, they are better known for their third order NLO effects, which stem from the extended delocalized π-systems and strong absorption. Recently, an excellent review of the NLO properties of coordination complexes has appeared.\(^ {85}\)

**Complexes of pyridyl ligands**

One of the earliest NLO studies involving metal pyridyl complexes was reported by Frazier et al. in 1986 who investigated the SHG from various Group 6 metal pyridyl carbonyls. SHG was observed in a Re(I) complex and inclusion compounds of various metal complexes with thiourea or tris-ortho-thymotide.\(^ {148}\) Following these early solid state investigations, electric field induced second harmonic generation (EFISHG) and theoretical calculations were carried out on several pyridyl complexes; the β values similar to that of 4-nitroaniline were observed in several cases and the values are sensitive to the nature of the pyridyl substituent.\(^ {87,142}\) Kanis et al carried out detailed computational studies on pyridyl complexes that showed excellent agreement with EFISHG data, it was concluded that the β is greatly influenced by the substituents in the
4-position of the pyridyl systems than the phenylene 4-substituents in the stilbazole systems.\textsuperscript{149} The extension of the conjugation length does not lead to sharp increase in $\beta$, in marked contrast to the behavior of purely organic NLO-phores. Generally, pyridine and stilbazole ligands show appreciable enhancement in the $\beta$ upon complexation with the metal centers. Molecular hyperpolarizability enhancements of the metal complexes depend on the $\sigma$-electron withdrawing capability of the metal centers as well as the donor/acceptor substituents on the ligand.

Coe and coworkers have investigated the NLO properties of ruthenium amine complex salts of pyridyl ligands, focusing on the establishment of structure-activity correlations for $\beta$ values derived from hyper Rayleigh scattering (HRS) measurements.\textsuperscript{150} Perhaps the most interesting result to emerge from these studies is the observation that the MLCT absorptions and $\beta_0$ responses of certain complexes can be reversibly and effectively attenuated by Ru$^{II/III}$ redox changes using chemical reagents.\textsuperscript{150} This demonstration of redox-induced switching of NLO responses provides a novel justification for incorporating transition metal centers in molecules with large $\beta_0$ values. The donor ability of the $\{\text{Ru(NH}_3\}_2^{2+}$ has been demonstrated in 4,4'-bipyridine based coordination complex and shows better ability than dimethylamino group as a $\pi$-electron donor. Bimetallic complexes containing pyridyl carbonyl centers with ruthenium $\sigma$-acetylide\textsuperscript{87} or ferrocenyl\textsuperscript{87,147} electron donor groups have also been investigated. Fabrication of ruthenium coordination complexes into thin films by the LB technique and their second order NLO properties have been investigated.\textsuperscript{85} Rapid photoinduced modulation of the SHG from LB films have also been studied.\textsuperscript{151}

Attention has been drawn to octupolar chelate complexes by the work of Zyss \textit{et al.}\textsuperscript{152} Octupolar molecules are non-dipolar species based on two-dimensional or three-dimensional chromophore structures. Metal ions are well suited for building coordination molecules with two-fold ($D_2$) or three-fold ($D_3$) symmetries around the metal center (e.g. tetrahedral, octahedral, or trigonal bipyramidal geometries). NLO systems based on octupolar metal complexes, mainly of bipyridine ligands, have been reported and recently reviewed.\textsuperscript{91} Le Bozec \textit{et al} have incorporated octupolar chromophoric unit into macromolecular structures and measured their $\beta$ by the HRS method.\textsuperscript{153} The enhancement of $\beta$ without significant loss of transparency in octupolar molecules
compared to dipolar molecules makes them attractive candidates for nonlinear optical applications.

**Complexes of Schiff base ligands**

The first observation of SHG in metal Schiff base complexes was reported in 1991.\(^{154}\) The metal-ligand core was used to enhance the NLO response of an apically substituted pyridine ligand. Thami *et al* reported\(^ {155}\) Co(II) complexes of electron donor/acceptor substituted Schiff base ligands with approximate C\(_2\) symmetry. Di Bella *et al* have studied the quadratic NLO properties of various types of Schiff base complexes.\(^ {156}\) The metal center in such complexes behaves like a template in the formation of noncentrosymmetric molecular structures; the thermal stability of the chelate ring structure is enhanced and metal helps to ‘switch on’ and enhance the nonlinear response. A review of these studies including a brief discussion of the complexes incorporated into main chain polymer, has appeared.\(^ {157}\) Recently, a combination of HRS experiments and theoretical calculations have been used to investigate the three-dimensional character of the \(\beta\) of Schiff base complexes. Lacroix *et al* investigated\(^ {157}\) the quadratic NLO properties of Schiff base complexes by substituent modification, doping the complexes in polystyrene thin films followed by poling and by incorporating chirality in the Schiff base ligand. Colorless, tetrahedral complexes based on Zn(II) and Cd(II) metal centers have been prepared and the SHG capabilities of the complexes investigated.\(^ {71}\) A series of octahedral complexes have been reported to show weak SHG, the most active one adopting a helical structure.\(^ {158}\) E\(\text{FISHG}\) and solid state SHG studies have also been carried out on binuclear square planar and square pyramidal Schiff base complexes. Tetrahedral Zn\(^ {\text{II}}\) complexes of chiral ligands substituted with electron donating groups show strong SHG, combined with good transparency in the visible range.\(^ {146, 159}\)

**Complexes of thiocyanate ligands**

The first coordination complexes to be studied for their NLO properties were the colorless thiocyanate bimetallic single crystals, which exhibited efficient and phase-matchable SHG.\(^ {160}\) This early discovery stimulated considerable research into these and
related types of materials. Easy growth of large, high quality single crystals, combination of good thermal stability with relatively high optical damage threshold and efficient SHG at wavelengths such as 380 nm and 404 nm make $\text{[Zn}^{II}\text{Cd}^{II}(\text{SCN})_{4}]$, promising candidates for ultra-violet SHG and related NLO device applications.\(^{161}\) The second order NLO properties of several other thiocyanate complexes have also been reported.\(^{85}\)

**Coordination polymers for SHG**

Coordination polymers, in some cases referred to as metal-organic coordination networks (MOCN) or metal-organic frameworks (MOF), are metal-ligand compounds which form structures extending in one, two or three dimensions via coordinate metal-ligand bonding.\(^{162}\) The use of metal atoms in coordination polymers offers several advantages over purely organic chains, grids or frameworks which are organized by non-covalent interactions.\(^{4}\) Coordinate metal-ligand bonds are stronger and in many instances show more directionality than several other weak interactions, such as hydrogen bonding or $\pi-\pi$ stacking.\(^{163}\) Differences in the size, hardness/softness, ligand field stabilization of the metal ions and the various coordination modes (octahedral, tetrahedral, square planar etc) facilitate a wide range of construction possibilities. The metal atoms in coordination polymers can act as assembling and templating joints for the organic bridging ligands. More interestingly, metal-ligand combination can give rise to two or more different structures, even with the same stoichiometry of all the components. This has been termed as polymorphism or supramolecular isomerism in the context of coordination networks.\(^{162,164}\) Subtle factors of crystallization conditions such as solvents, temperature, time, concentration, anions and pH play significant role in the formation of specific structures.\(^{164}\) Considerable research work has been dedicated towards understanding the self-assembly process between metal ions or secondary building units derived from them and the multidentate ligands.\(^{162,164,165}\) The design and properties of the ligand itself is an active area of research, because the ligand can play a crucial role in the construction of novel structure as well as in the properties of the coordination polymers. The synthesis or self-organization of coordination polymers is often achieved by combining the appropriate metal salt and ligand in a suitable solvent under mild or at most hydrothermal conditions. Even though much effort is still devoted to the preparation and structure
determination of crystalline materials, the final goal is to design properties of the polymeric assemblies of metal complexes with applications in catalysis and conducting, luminescent, magnetic, spin-transition, nonlinear optical or porous materials.\textsuperscript{21}

NLO materials based on coordination polymers can be designed so as to contain organic ligands with large hyperpolarizabilities, and possessing noncentrosymmetric structures.\textsuperscript{21,159,166} Molecular hyperpolarizabilities are frequently larger for the metal complex than for the free ligand chromophore, because of the metal-to-ligand or ligand-to-metal charge transfer and due to the involvement of the metal orbitals.\textsuperscript{155,166,167}

Another appealing aspect for the design of NLO properties is that metal centers can serve as pivotal points in the engineering of three dimensional tetrahedral and octahedral structures, giving rise to octupolar molecules.\textsuperscript{90,168} The recent success in the design and synthesis of novel materials based on metal-organic coordination networks has stimulated much interest in the developments of noncentrosymmetric solids for NLO effects by exploiting the strong and highly directional metal-organic coordination bonds. Examples of some systems and direction of research in this area are described below.

The polynitrile lanthanide complex which crystallized in acentric network structures was found to exhibit solid state SHG, 16.8 times that of urea.\textsuperscript{169} Lin et al have demonstrated that noncentrosymmetric solids based on infinite networks can be rationally synthesized by combining unsymmetrical bridging ligands and metal centers with well defined coordination geometries.\textsuperscript{73} Several noncentrosymmetric coordination polymer assemblies with different network topology have been successfully synthesized and their SHG capabilities were explored. An obvious choice of three-dimensional network for realizing noncentrosymmetric solids is the diamondoid network. The connecting points in the diamondoid networks are tetrahedral or pseudotetrahedral.\textsuperscript{170} In fact, the prototypical NLO material, KDP crystallizes as a diamondoid network.\textsuperscript{171} Metal-organic diamondoid structures have a high propensity to interpenetrate in order to fill void space in the network.\textsuperscript{172} Despite the inherent noncentrosymmetric nature of the diamondoid net, an even number of interpenetrations could potentially lead to inversion centers relating pairs of mutually independent nets. On the other hand, an odd number of diamondoid net interpenetrations synthesized from unsymmetrical bridging ligands will lead to the formation of a noncentrosymmetric lattice. Another approach that is
employed to generate acentric diamondoid nets involves the use of low symmetry bridging ligands to link four connecting centers.\textsuperscript{173}

Acentric metal-organic coordination polymers based on two-dimensional network structures have also been synthesized and their solid state SHG investigated.\textsuperscript{174} Octupolar metal-organic NLO materials based on a chiral two-dimensional coordination network has also been reported.\textsuperscript{175} Even though the design of noncentrosymmetric one-dimensional chains can be readily achieved, the construction of a noncentrosymmetric solid based on one-dimensional chains is a more difficult task, owing to the lack of control in the assembly of chains. Teo \textit{et al} have demonstrated a novel approach, in which tetrahedrally coordinated tetraalkylammonium ions control the arrangement and alignment of the cadmium thiocyanate anion chains and leads to the formation noncentrosymmetric structures.\textsuperscript{176} \textit{In situ} synthesis of ligands and the formation novel, acentric metal-organic coordination polymers under hydrothermal conditions have been reported by Xion \textit{et al}.\textsuperscript{177} Metal-organophosphate hybrid frameworks have also been explored for optical SHG.\textsuperscript{178} Helical coordination polymers have been generated using chiral as well as achiral ligands and enhancement of solid state SHG compared to the free ligand and the role of helical chains in the formation of noncentrosymmetric solid have been studied.\textsuperscript{179}

1.6 LAYOUT OF THE THESIS

This thesis describes the development of novel metal-organic systems and the investigation of optical second harmonic generation from them. Observation of perfectly polar organization of molecular dipoles as well as extreme molecular orientation of dipoles in dimorphic structures of new zinc coordination complexes that we have synthesized, are highlighted; the unusual molecular assembly is analyzed and SHG capability of these materials are presented. Thin films of these polar molecular materials fabricated by physical vapor deposition on amorphous glass substrates show uniaxial ordering of crystallites and are of potential interest in electro-optic applications. In addition to being the acceptor moiety in the molecular unit, the metal center is used to assemble C\textsubscript{2}-symmetric chiral ‘push-pull’ ligand into hierarchical network coordination
polymer structures; one-dimensional helical polymers showed the highest second harmonic generation capability among the hierarchical structures. The strong hydrogen bonding capability of some of the ligand molecules was exploited to develop thermally stable organic materials as well as of coordination polymers for SHG applications. A schematic representation of the research work presented in this thesis is shown in Fig.1.5. The thesis is divided into five chapters. Development of molecular materials and its importance as magnetic, conducting, optical and nonlinear optical materials are already discussed in the previous sections of this chapter. We describe below, the salient feature of the remaining chapters.

Chapter 2

After introductory remarks in Sec. 2.1 and synthesis details in Sec. 2.2, we present in Sec. 2.3, the discovery of single component perfectly polar crystals of a family of zinc complexes. The formation of such structures is analyzed on the basis of the molecular structure and the hierarchy of non-bonding interactions in the crystal lattice. The investigation of the effect of solvent polarity and rate of crystallization on the formation of dimorphic structures of a complex, with extreme molecular orientation of dipoles is discussed in Sec. 2.4. Cogrowth of the polar/centric and polar/polar structures as well as the formation of twin polar domains in monolithic crystals are also presented. Semiempirical computational investigations indicate the delicate balance between the solvent polarity control of parallel and antiparallel molecular organizations. Uniaxial ordering of the perfectly polar crystallites in physical vapor deposited thin films, structural and morphological investigations and optical second harmonic generation measurements are discussed in Sec. 2.6.

Chapter 3

We have developed a new C_2-symmetric 'push-pull' ligand with multi-dentate coordination capability and its coordination polymers with Ag(I) and Cu(I) metal ions.
Figure 1.5 Overview of the work presented in the thesis
They show hierarchical structures including helical chain. In Sec. 3.3, we discuss the role of ligand conformations and the mode of ligation on the formation of helical and network structures. Solvent influences on the formation of coordination polymers with different ligand conformations are also presented. Impact of the structural motifs on the optical second harmonic generation capability of these coordination polymers is presented in Sec. 3.4. A simple computational approach that can be used to understand the influence of the ligand conformation and coordination of metal ions on the molecular hyperpolarizability is discussed in Sec. 3.5.

Chapter 4

This chapter presents C2-symmetric molecules possessing bis(amide) functionality and coordination polymers developed based on them. In Secs. 4.3 and 4.4, we present the crystal structure investigations of different derivatives, a variety of extended H-bonded structures including polar ones are observed. The unusual occurrence of the syn conformer of the bis(amide) group and interesting helical assemblies through various H-bonding interactions in crystals are presented. Role of the substituents in the bis(amide) derivatives on the solid state second harmonic generation capability of these organic materials are discussed. Influence of the strong complementary amide hydrogen bonds on the assembly of coordination polymer network structures and their high thermal stability as well as the second harmonic generation capability of these materials are highlighted in Sec. 4.5 and 4.6.

Chapter 5

In Sec. 5.1 we provide an overview of the various investigations presented in the thesis. The highlights of the work include: (i) the development of a class of zinc complexes, which exhibit single component perfectly polar molecular assemblies in crystals, (ii) fabrication of these materials into thin films with acentric uniaxial ordering of the polar crystallites, (iii) utilization of a C2-symmetric ‘push-pull’ ligand in the formation of a range of coordination polymer topologies and the correlation of the
network structure with optical second harmonic generation capability and (iv) structural and solid state second harmonic generation investigations of strongly hydrogen bonded, thermally stable bis(amide) derivatives and hydrogen bond directed coordination polymeric network structures. Directions for further explorations in this area of research are outlined in Sec. 5.2.
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Chapter 1


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