CHAPTER 1

Introduction
1.1 MOLECULAR MATERIALS

The latter half of the last century has witnessed a steady growth of the field of molecular materials culminating in their current status as promising candidates for a wide spectrum of technologies in this century. The defining characteristic of molecular materials\(^1\) is their constitution - molecules or molecular ions are their building blocks as opposed to atoms and ions in the traditional solid state. Polymeric materials built from macromolecules can also be classified as belonging to the general family of molecular materials. Molecular materials represent a fundamental and significant departure from the traditional routes of materials fabrication, affording greater flexibility and versatility. They also possess unique electronic, magnetic or optical features opening up the possibility of realizing a vast range of novel applications.

Molecular materials are rather unique in the sense that when dissolved in appropriate solvents, melted or sublimed they break down into their constituents which retain to a large extent the characteristics they exhibited in the solid state. 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. It is natural that 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 of molecular materials, the supramolecular clusters\(^3\) represent a smooth transition from the molecular to the bulk material. Molecular materials utilize, in addition to ionic and covalent interactions, a wide variety of relatively weaker interactions such as H-bonds, \(n\)-stacking and dispersion forces not found elsewhere in conventional solid state materials\(^4\) (Fig. 1.1). The nature of the forces in the molecular materials may however be quite different from that in other solids. For example the electrostatic interactions in ionic solids like sodium chloride are very strong owing to the point charges involved, whereas in ionic molecular solids, such interactions are much weaker due to the smearing out of the charge on the molecular ions. Covalent interactions in solids like silicon or graphite extend throughout the solid, whereas in molecular materials, they are confined to the intramolecular level; polymers\(^5\) represent the state between the two extremes.
Figure 1.1 A schematic diagram describing the organization and functions of molecular materials.
Development of molecular materials

There exists a close parallel between the evolution of materials and human civilization. In fact the nomenclature denoting the progress of civilization is intimately linked to the nature of materials that were developed through the course of history. The stone age was followed by the copper, bronze and iron ages and the period we live in is often called the 'plastic age'. The materials fabrication techniques reflect the progress of technology. Starting with crude 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 therefore represent one of the prime examples of the 'state of the art'.

Liquid crystals discovered in 1888 are perhaps the first examples of molecular materials which found extensive technological application. Discovery of the twisted nematic effect in 1969 in cyanobiphenyls and terphenyls have led to the wide application of liquid crystals in display technology. Their sensitivity towards electric field has been exploited in a variety of ways to fabricate switches and other devices. A variety of luminescent materials were discovered in the 1960’s marking the development of novel optical materials. Since the advent of lasers in the 1960's extensive research has been carried out in the field of optical and non-linear optical (NLO) materials. In 1966 Sorokin and Lankard demonstrated the first dye laser and observed stimulated emission from alcoholic phthalocyanine dye pumped with ruby laser. The development of dye lasers and the role of fluorescent dyes and pigments have been described by Schafer and Maeda. The demonstration of the nonlinear optical phenomenon of second harmonic generation (SHG) in single crystal quartz by Franken and co-workers, and phase matched SHG in KDP crystals by Geordamine and Maker and co-workers laid the basis for modern nonlinear optics. Rentzepis and Pao in 1964 observed SHG in benzopyrene, the first instance in a molecular system. The potential of organics was revealed by studies on hexamethylenetetramine, hippuric acid, benzil and urea. In 1968 a systematic approach was developed to quantify and classify SHG in organic and inorganic compounds by Kurtz and Perry. In the 1970’s the analysis of nonlinear interference pattern in crystals was developed by Jerphagnon et al and electric field
induced second harmonic generation was developed by Hauchecorne and coworkers\textsuperscript{18} which showed the possibility of measuring individual molecular nonlinearities in solutions.\textsuperscript{19} Several books and reviews have appeared which deal with the theory, structural characteristics and applications of nonlinear optical molecules and materials.\textsuperscript{20-3} Organic molecules and polymers are of great importance in the area of optoelectronics and photonics.\textsuperscript{23,24} 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{22} and photoconductive\textsuperscript{6} materials are actively being explored for various applications in information processing and technology.

Fabrication of the first transistor in 1948, discovery of superconductivity\textsuperscript{27} in 1911 and the explanation of the amazing phenomenon in 1957 marked the development of a new era in the history of materials. The pace at which new developments took place in fundamental physics and chemistry was reflected in the fabrication of novel materials. The growth of electronic industry propelled primarily by the advances in semiconductor physics\textsuperscript{28} made unprecedented and challenging demands on the specificity and precision of materials properties. In the latter half of the twentieth century emergence of electronic information technology led to new requirements of materials for application such as transistor based information processing, semiconductor based signal transmission, optical storage devices, fast optical switches and sensors which have also contributed to the progress of communication devices.

The first molecular conductor was synthesized in 1842 by Knop by oxidizing the metal complex $K_2(\text{Pt(CN)}_4)$\textsuperscript{29} with bromine, though the conducting property of this material was perhaps not realized at that time. The development of purely organic conductors containing no metal atoms/ions is quite fascinating. In the early 1950’s Japanese researchers observed that perylene-bromine complex\textsuperscript{30} showed a low electrical resistivity of about 8 $\Omega\text{cm}$, a rather unexpected property for an organic solid. After the synthesis of tetracyanoquinodimethane (TCNQ) in 1962\textsuperscript{31} many of its salts were shown to exhibit electrical conductivity. Following the synthesis of tetrathiafulvalene (TTF) in 1970,\textsuperscript{32} many of its halides yielded conducting materials.\textsuperscript{33} TTF-TCNQ prepared in 1973, exhibited a room temperature conductivity of $10^3$ S/cm. Several metal complexes and phthalocyanines show metallic conductivities.
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In 1980 Bechgaard and coworkers demonstrated superconductivity in molecular materials based on bis(tetramethyltetraselenafulvalene) hexafluorophosphate (TMTSF)$_2$PF$_6$ under 6.5 kPa pressure. (TMTSF)$_2$ClO$_4$ was the first molecular material to show superconductivity at ambient pressure. In 1984, another chemical modification of TTF, bis(ethylenedithiotetra(thiafulvalene) (BEDT-TTF) led to superconductors of the type (BEDT-TTF)$_2$X, where X$^-$ is I$_3^-$ or inorganic anions. Alkali metal salts of buckminsterfullerene, such as K$_3$C$_{60}$ entered the world of superconductors in 1994. Conjugated polymers form an important class of semiconductors today. Starting from the early study of aniline black in the year 1834, the modern era began with the discovery of conduction in doped polyacetylene in 1977. Currently, it is an area of intense basic research and technology development.

Magnetic materials are largely based on the compounds and alloys of elements such as iron, cobalt, nickel and gadolinium which are themselves ferromagnetic in the pure state. Later, magnetic materials based on coordination polymers and molecular systems in which metal ion serves as the source of magnetic moment were discovered. The charge transfer complex of decamethylferrocene and tetracyanoethylene (TCNE) was the first molecular material that showed ferromagnetic phase transition with a $T_C$ ~ 4.8 K. $p$-nitrophenylnitronylnitroxide was the first purely organic ferromagnet to be synthesized. Molecular magnetic materials are potential candidates to develop magnetic, electromagnetic and magneto-optic devices. Though molecular magnets based on organic polymers and charge transfer complexes continues to fascinate materials chemists, a well characterized ambient temperature organic polymer ferromagnet is yet to be realized. Currently there is considerable excitement about the development of the so-called single molecule magnets.

Multidisciplinary activities involving chemists, physicists, biologists and engineers have led to the emergence of a wide spectrum of novel materials with desired properties. The quest for miniaturization appears to be heading to its logical conclusion through the development of molecular devices. There are several reports of single molecules functioning as active devices carrying out a wide variety of optical, electrical, and mechanical functions. The fantastic list of functional molecular scale devices include rectifiers, switches, gates, wires, shuttles, brakes, ratchets and gears.
**Fabrication of molecular materials**

The design and fabrication of molecular materials effectively exploits the enormous power and flexibility of synthetic chemistry to tailor specific molecular structures and hence the desired molecular materials. The fundamental differences between the route to molecular materials and conventional approaches to materials is schematized in Fig. 1.2. Traditionally materials are fabricated from suitable precursor materials employing techniques such as ceramics methods, melt-quench processes, vapor deposition, sol-gel and so on methods. In the case of molecular materials on the other hand a well defined intermediate stage is involved which is simply the molecule or

![Figure 1.2](image-url)
molecular ion and which effectively separates the chemical reaction from the material fabrication process. The property of the molecule is determined by its structure resulting from the chemical reactions employed for its synthesis while the property of the fabricated materials depends on the property of the molecules and the way they are organized in the bulk. The molecules can be identified and studied using a variety of spectroscopic and analytical tools. This provides a synthetic approach for the design of molecular materials. Design of molecular materials involves molecular recognition and organization thus leading to the construction of supramolecular systems. The iterative way of realizing the property of tailored molecular materials provides a unique handle to fine tune the materials properties.

Crystallization from organic or aqueous solvent medium is perhaps the most common technique for the fabrication of molecular materials. Electrocrystallization is popular in the case of conductors and superconductors. In this technique the molecule is oxidized or reduced in the presence of appropriate counterions. Since simple crystallization does not provide much 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, Langmuir-Blodgett technique and layer by layer assembly. Spin and dip coating, sol-gel processing and chemical or physical vapor deposition are other approaches resorted to. The intermediate stage involved in the synthesis of molecular materials provides a systematic control in the assembly of the bulk material and the realization of the materials properties.

1.2 MOLECULAR OPTICAL MATERIALS

Dyes and pigments

Substances that are used to color materials are broadly divided into two classes—dyes and pigments. Dyes are soluble substances commonly used to color items such as utensils, paper, plastic and leather. Certain classes of dyes are made insoluble by a chemical process after they penetrate into the material being dyed. Pigments are colored
solids, practically insoluble in most of the solvents and exist as particles when dispersed in paints, lacquers, inks, paper, plastics and rubber. Triphenylmethane dyes are some of the early synthetic dyes developed and form an important class of commercial dyes and pigments. Photophysical and photochemical properties of triphenylmethane dyes in solid state and solution have been discussed by Duxbury and coworkers. In recent years carbides, nitrides and carboxynitrides of transition metal compounds as well as diamond-like carbon films have been extensively investigated for decorative applications. Organic dye-metal oxide composite thin films possessing good mechanical properties and showing strong selective absorption in the visible range are important candidates for future applications. Bottcher and coworkers were the first to report on the preparation of mixtures called norganics of organic merocyanine dye and inorganic materials for spectral sensitization in photography. 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 the traditional 780 nm lasers. Metallized thiazolyl dyes are often used as recording materials. Optical fibre based chemical sensors exhibiting strong optical response have attracted increasing interest in recent years owing to their immunity to electrical noise, ease of miniaturization and possibility of application in real time monitoring and remote sensing. Some ultra violet dyes incorporated in solid polymer electrodes (PVA/H₃PO₄) and certain NIR dyes are promising candidates for optical humidity and integrated optical sensing.

The prime concerns in dye chemistry are color control (tuning the wavelength of absorption and emission) and thermal and photostability. Dyes find application in electronic devices, lasers, liquid crystal displays, electrochromic systems, optical switches, solar cells and nonlinear optical devices. Crystal violet, cyanine, molecules based on squarine templates, benzolothiazolium and salts of N-methylpiridinium, several of them in the form of LB films, have demonstrated stronger upconversion of fluorescence emission than common organic dyes such as rhodamine. Several of them also exhibit strong nonlinear optical responses due to the large molecular hyperpolarizabilities. Phthalocyanine base dyes have attracted considerable attention due to the ease of synthesis.
Quinacridone, coumarines and pyrrolopyrroles are some of the famous industrial pigments. Quinacridone and pyrrolopyrroles belong to the group of carbonyl pigments and are some of the oldest known and most important colorants. Fluorescent pigments for paints are commonly dyes embedded in a plastic matrix. Zinc oxide is the most common, one of the longest known and widely used white inorganic pigment. New colored compounds have now been prepared using zinc oxide as the base and these can be used as pigments for coloring plastics and paints. Colored oxides produced through solid state reaction with mixed oxides are potential inorganic pigments which are environmentally friendly.

**Laser dyes**

After the demonstration of the dye laser in 1966 by Sorokin and Lankard, Schafer and coworkers and Spaeth and Bortfeld observed the dye laser action in cyanine dye. In 1967 a flashlamp-pumped dye laser was developed and both xanthene dyes and coumarin derivatives showed efficient laser action. Various classes of laser dyes have been developed to cover the wide spectral range from IR to UV. A continuous wave rhodamine 6G dye laser using an argon ion laser as a pumping source was demonstrated in 1970. The first experiment on tuning and condensation of lasing spectrum of a dye laser was made by Soffer and McFarland. 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. Although dyes usually imply colored substances, many colorless, but fluorescent organic materials are also used for dye lasers. The lasing compounds are classified according to their chemical structure. A compilation of 30 famous dyes have been published by Kauffman.

Until recently liquid dye lasers were the main systems used to achieve tunability in the visible range and the only choice for commercial lasers. But in the last few years intensive efforts have been devoted to produce embeddings of organic dyes in various solid materials such as polymers, silica gels, xerogels, alumina gels, ormosils and composite glass with a view to replace liquid dye lasers. Solid state dye lasers are
attractive due to their nonvolatile, nonflammable and nontoxic nature, the compact size and stability. Photostability is a feature of prime importance in selecting a laser dye. Pyrylimide dyes,\textsuperscript{74} spiro type molecules,\textsuperscript{75} electroluminescent oxadiazole dimers\textsuperscript{76} and polyurethanes with pendant nitrostilbene units\textsuperscript{77} are important candidate systems.

**Photoluminescent materials**

Organic luminescent materials have been surveyed in various books.\textsuperscript{78,79} Fluorescent molecules and materials are of great interest in a wide variety of applications. They are potential candidates for display devices and are some of the most popular choices for sensor applications. Molecular recognition events which 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 heterocycle derivatives, carbonyl compounds and metal complexes with a wide range of organic ligands. A variety of nanomaterials, polymers, sol-gel systems etc. also display strong fluorescence.\textsuperscript{78,79} A wide variety of molecules used as fluorescent and phosphorescent probes in biological applications are listed below since they can form the basis for the development of novel luminescent materials.

Well known phosphorescent molecules include proteins such as hemeprotein, probes like tryptophan and erythrosine, 4,4'-dimethoxybenzophenone (DMOBP), 2,2,2-triphenylacetophenone (TPAP) and heavy metal complexes such as 2,3,4,7,8,12,13,17,18-octaethyl-12H,23H-porphine platinum (II) (PtOEP) and \textit{fac}-tris(2-phenylpyridine)iridium (Ir(PPy)\textsubscript{3}).\textsuperscript{80} Fluorescence probes are useful in the trace analysis of substances in biological systems and therefore have become very useful in the detection of drugs in blood or other fluids. Extensive research in biology and medicine make use of fluorescent materials. 1-dimethylaminonaphthalene-5-sulfochloride (DANSYL chloride)\textsuperscript{78,79} is used as a tracer for proteins. Fluorescamine is an even better tracer since it fluoresces only after combining with amino acids and proteins and not as isolated species in solution. Fluorescein and its derivatives are the most widely used diagnostic tools which can be injected into the body; their luminescence demonstrates the
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patency of blood vessels, blood supply to various parts of grafted skin, the boundaries of
affected area etc. Fluorescein and rhodamine derivatives were used as antibody tracers;
recently, substituted stilbenes, derivatives of dichlorotriazine and pyrene are also being
used for this purpose. In addition to acridine orange, ethidium bromide, quinacrine and
mithramycin are capable of binding to DNA; hence they find application in staining
nucleic acids. DANSYL chloride and fluorescamine are used in quantitative
determination of proteins and amino acids. Acridine orange is the most popular
fluorophore used in determining the DNA to RNA ratio within a single cell as well as in
the study of the activation of chromatin in various processes. Acridine orange, rivanol,
proflavine, primulin and many other fluorophores are used for direct tracing of antibodies
and labeling of cells. Proflavine and ethidium bromide have been used as probes of
nucleic acid structure. Thiazole orange is used in the characterization of long
wavelength probes for DNA sequencing. Photodynamic therapy is a new modality for
the treatment of cancer and current research in this field is also concerned with the
design of molecules which potentially bind DNA and cleave the duplex under
illumination with visible light. DNA intercalators such as adriamycin and daunomycin
and complexes such as cis-platin are strongly mutagenic in nature which stop the
replication and transcription of the DNA resulting in promising chemotherapeutic
activity. NIR dyes are used for clinical sensing. Fluorescent probes are extensively
used in the study of cell membranes; their charge, potential and viscosity give us an idea
about the presence of cholesterol and the mobility of cancer cells. In addition to the
above described systems several strongly intercalating metal complexes of platinum and
ruthenium can act as luminescent markers for DNA and foot printing applications.

Electroluminescent materials

Electroluminescence (EL) is a phenomenon with wide application in the areas of
illumination and display technology. It shares some similarities with the familiar process
of photoluminescence. In photoluminescence, light (typically in the ultraviolet range)
excites a molecule or material which in turn relaxes by emission of visible light. In
electroluminescent materials, an applied electric field generates the excited state or
exciton which decays emitting the visible light. This phenomenon was first discovered in
inorganic materials in 1936 when Destriau et al observed high field electroluminescence from a zinc phosphor powder dispersed in an insulator and sandwiched between two electrodes. In the early 1960’s General Electric introduced commercially available light emitting diodes (LED) based on the inorganic semiconductor GaAsP. Since the energy of the emitted photons and therefore the color of the LED is determined by the energy gap of the semiconducting material in the active region, early LED’s emitted only red. The development of new materials granted access to colors other than red and made blue, orange, yellow and green as well as infrared accessible. Electroluminescence in organic compounds was first demonstrated by Pope et al, Helfrich and Schneider and Mehl and Bucher. In the late 1980’s Tang and Van Slyke as well as Saito and Tsutsui, revived the search on electroluminescence of molecular materials, developing a new generation of LED with organic fluorescent dyes. Organic light emitting diodes (OLED) are obtained by placing charge-transporting and electroluminescent material between two electrodes (one of them being transparent) and applying a suitable bias.

Electroluminescence in semiconductor devices arises from the electron impact excitation of luminescent centers, for example the manganese or terbium ions doped in ZnS. On the other hand, EL in molecular systems arises from the recombination of electrons and holes injected into the material from the cathode and anode respectively. The energy gap between the HUMO and the LUMO controls the emission color. Strong EL arises from efficient charge carrier transport and high fluorescence efficiency. Voltage required to drive the luminescence is generally low in the case of molecular materials, especially when fabricated in the form of thin films. Most of the current EL devices run on DC voltage but recent experiments show that some organic polymer EL devices can be run on AC voltage as well, enlarging the scope of these materials for practical applications. The efficiency of electroluminescence goes down if recombination of electrons and holes takes place too close to the electrodes. Special multilayer thin film assemblies are often fabricated to ensure that the recombination takes place away from the electrodes and efficient luminescence occurs. Excellent reviews of organic electroluminescent materials and devices may be found in Refs. 91 and 92. The progress in thin film electroluminescent devices has been reviewed by Tsutsui.
Molecular materials for electroluminescence devices are often classified into three categories according to their structure: (i) organic dyes (no metal atom), (ii) chelate metal complexes, and (iii) conjugated polymers. Fig. 1.3 provides a schematic view of the scope of inorganic and organic molecular EL materials. Some of the common organic EL dyes are based on derivatives of oxadiazole, phthalocyanine, quinacridone, and pyrazoline. Electroluminescence in derivatized organic molecules containing donor-acceptor groups has been reported recently. An interesting family of materials being explored is based on spiro systems such as spirolinked quarterphenyl and higher analogues. They show high quantum yield (nearly 60%) for blue photoluminescence. The spiro linkage apparently leads to high quality amorphous materials with high glass transition temperatures. Important properties of organic dyes include high fluorescent quantum yield, ease of film formation by vapor deposition, possibility of obtaining high levels of purity and flexible molecular design. On the other hand there are several problems with the use of organic dyes such as easy crystallization after film formation and the occasional production of exciplexes. The chelate complexes commonly employed in EL applications include those of aluminium and zinc with ligands such as:

<table>
<thead>
<tr>
<th>Organics</th>
<th>Inorganics</th>
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<tr>
<td>Fluorescent dyes</td>
<td>Conjugated polymers</td>
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<tr>
<td>Doped Semiconductors</td>
<td>Eg. ZnS : Mn</td>
</tr>
<tr>
<td>Eg. GaAs</td>
<td>Semiconductors</td>
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<tr>
<td>Large area application</td>
<td>Small (mm²) area application</td>
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**Figure 1.3** The wider scope of molecular materials over inorganic semiconductor materials in electroluminescent device application (adapted from Ref. 91).
8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, 7-n-propyl-8-hydroxyquinoline, 2-(2-hydroxyphenyl)-5-phenyloxadiazole (ODZ), 1-phenyl-2-(2-hydroxyphenyl) benzimidazole (BIZ)\textsuperscript{76,80} The most widely used electron transport and emitting material is AlQ\textsubscript{3}, as it is easily synthesized and purified, avoids exciplex formations and is thermally and morphologically stable when evaporated into films. Since the functioning of molecular organic devices is affected by crystallization in the amorphous thin films, special efforts have gone into the design of amorphous EL materials.

Polymeric EL materials is a fast expanding field of research.\textsuperscript{1} This fundamental contribution to the evolution of OLED came from Friend and coworkers in 1990.\textsuperscript{96} They replaced the fluorescent dyes and inorganic semiconductors which require expensive and technologically inconvenient vapor deposition methods for fabrication, by the highly fluorescent conjugated polymer, poly(p-phenylenevinylene) (PPV) as the active material in a single layer OLED. Conjugated polymers derive their semiconducting properties from the $\pi$ electrons delocalized along the polymer chain; the delocalized valence $\pi$ and conduction $\pi^*$ wave functions support the mobile charge carriers. PPV and its derivatives are some of the most promising conjugated polymers for EL applications. PPV produces intense yellow green luminescence (> 100 candela/m$^2$) at driving DC voltages typically below 10 V. Doped ZnS on the other hand, normally require voltages of the order of 100 V. Organic EL devices based on polymeric materials have been reported using conjugated polymers such as polyphenylene, polyalkylfluorene, polyalkyl thiophenes and polyvinyl carbazole. The main advantage of polymers is the ease of film formation by casting and the absence of crystallization in the cast films. However their purification is generally not simple. The external quantum efficiency (number of photons per electron injected) of commercial inorganic LED's remains close to 1% after several decades of development whereas in less than a couple of decades, OLED’s have reached comparable or better efficiency. The other advantages they offer are the low threshold voltages, possibility for large area application and the light weight and mechanical properties of plastics. Synthetic manipulations can be easily carried out on conjugated polymers providing control on the HOMO-LUMO gap and hence on the color of the electroluminescence. An important advantage of polymer LED's is the flexibility of fabrication modes.\textsuperscript{98} Polymers can be processed into several forms such as solid films, solutions and gels.\textsuperscript{99} Polyaniline as a hole injecting material
and polyethylene terephthalate as substrate have been used in the fabrication of flexible light emitting diodes. Polymers with substituted diphenylamino groups have been reported to have excellent emissive capability. Several novel benzene derivatives have been synthesized and used as hole blockers applicable in blue-violet emitting fluorescent and green emitting phosphorescent EL devices.

Electroluminescent devices with multilayered structures composed of two or three vacuum sublimed dye films exhibit high device performances. There has been considerable effort to develop efficient hole transport materials for multilayer OLED's since the discovery of triaryl amines with biphenyl center core as hole transport layer which improved the electroluminescence and operational stability of OLED's. Several systems like biphenyldiamine derivatives, amorphous spiro-linked systems, triphenylene derivatives, vanadyl phthalocyanines and crosslinkable polymers have been developed. Conjugated molecules containing cyano substituents are known to achieve desirable luminescence property and good electron injection/transport ability. The potential of molecular and polymeric EL devices for extensive commercial application is bright indeed.

### 1.3 MOLECULAR NONLINEAR OPTICAL MATERIALS

**Basic concepts of nonlinear optics**

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, \( P \) is linearly related to the field \( E \) by the proportionality constant \( \chi^{(1)} \), the linear electric susceptibility tensor (Fig. 1.4). 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)

![Nonlinear polarization at high electric fields; the linearity at low fields is shown using the dashed line.](image)

**Figure 1.4** Nonlinear polarization at high electric fields; the linearity at low fields is shown using the dashed line.

In Eqn. 1.1 the indices $i, j, k$ and $l$ refer to the coordinate framework of the bulk material. The polarization at the molecular level, $\rho_i$, 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 can be represented as $\sin(\omega t)$, the quadratic term will have a $2\omega$ dependence as seen in Eqn. 1.3.

\[
E \propto \sin \omega t \\
E^2 \propto \sin^2 \omega t = \frac{1}{2}(1 - \cos 2\omega t) 
\] (1.3)

Eqns. 1.1 and 1.2 show that there is an important symmetry constraint for observing second harmonic generation or any even order NLO effect. In systems having a centre of symmetry, reversal of the electric field would exactly reverse the polarization, $\text{ie, } P(-E) = -P(E)$. 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 $\beta$, 5 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 effect are possible only in noncentrosymmetric molecules or materials.

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

Materials developed initially for NLO applications were largely based on inorganic systems. Ferroelectric materials lacking a centre of symmetry were prime candidates for the quadratic effects. The popular materials used for second order NLO applications are inorganic crystals such as potassium dihydrogen phosphate (KDP),\textsuperscript{103} lithium niobate (LiNbO\textsubscript{3})\textsuperscript{104} and $\beta$-barium borate (BBO).\textsuperscript{105} 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 materials on the other hand, with their relatively lower refractive indices, exhibit faster NLO responses and the NLO effects can be conveniently analyzed in terms of the molecular contributions and the impact of the intermolecular organization. If molecules with large ($\beta$ values are aligned so that their hyperpolarizabilities add up constructively, the assembly leads to noncentric materials with appreciable NLO response.
There has been a growing interest in developing \( \pi \)-conjugated organic molecules for nonlinear optical application. Considerable effort has gone into overcoming the limitations of organic materials such as low thermal and mechanical stability, so that they can compete with 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 organic molecules possessing a 'donor-conjugating unit-acceptor' (D-\( \pi \)-A) framework, can be understood in terms of the Mulliken resonance structures illustrated in Fig. 1.5. When the molecule is subjected to an applied field parallel to the dipolar axis, the electronic polarization response will be unsymmetric as a result of the cooperative influence of the donor and acceptor groups; this can be contrasted with the symmetric response of an unsubstituted benzene (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 organic molecular crystals and polymers as candidates for NLO applications. The D-\( \pi \)-A system leads to high second order nonlinear optical response.

The quadratic NLO molecules are mostly based on donor-acceptor substituted aromatics. Some of the extensively studied classes of NLO chromophores of this type are 1,4-substituted benzenes and stilbenes,\(^{106,107}\) 4-nitroanilines and 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS).\(^{108}\) Dulcic and Sauteret\(^ {109}\) were the first to

![Figure 1.5](image.png)

**Figure 1.5** Origin of nonlinear polarization in a donor-acceptor substituted benzene. The broken line represents the response of unsubstituted benzene.
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... 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 conjugating bridges such as tolans, diazostilbenes, polyenes, polyphenylenes, as well as heteroaromatic 5- or 6-membered rings like thiophenes and azoles have been investigated. Other systems studied include organometallic compounds and calixarenes. In order to overcome the problem of absorption at 2ω, 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 poly-silanes. A variety of salts especially with pyridinium and stilbazolium cations have been studied for their second order NLO properties.

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 their helical organization for enhanced nonlinearity has been discussed.

Molecular hyperpolarizability

The first hyperpolarizability, β quantifies the second order NLO effect at the molecular level. Several theoretical methodologies are available to compute molecular hyperpolarizabilities. Two approaches are often employed to compute (3: (i) generalized finite field elaborations 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 and quick solution for the prediction of $\beta$ of organic molecules. The simplest model to take into account the contribution of charge transfer resonance within a molecule to the first hyperpolarizability is the two-level model proposed by Oudar and Chemla.\textsuperscript{108,123} An increased $\beta$ is often accompanied by a red shift in the absorption spectrum due to a larger conjugation length or lower energy charge transfer between the donor and acceptor substituents.\textsuperscript{124}

Experimental determination of molecular hyperpolarizability is often carried out in the solution phase. Since molecular motion in solution leads to an average centre of 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).\textsuperscript{125} In another technique called the hyper-Rayleigh scattering (HRS),\textsuperscript{126} 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.\textsuperscript{127}

**Noncentrosymmetric organization of molecules in materials**

As noted earlier, dipolar molecules often show a predilection towards centrosymmetric organization in the bulk. In fact, an examination 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,\textsuperscript{11} (ii) exploitation of weak as well as strong intermolecular forces\textsuperscript{129} and (iii) incorporation of alkyl chains of appropriate length\textsuperscript{130} are some of the approaches developed for molecular crystals. Other strategies include, (i) electric field poling of polymer films containing the NLO-phores,\textsuperscript{51} (ii) fabrication of X and Z type LB films,\textsuperscript{52} (iii) formation of host-guest systems,\textsuperscript{131} (iv) sol-gel synthesis\textsuperscript{53} and (v) salt formation.\textsuperscript{132}
The Kurtz-Perry powder technique\textsuperscript{15} 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. 1.6 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 SHG interaction length (i.e. to the right of $<r> = <l_c>$), the SHG intensity, $I_{2\omega}$ for phase-matchable materials reaches a saturation value and is independent of the particle size whereas $I_{2\omega}$ for non phase-matchable materials decreases with increasing particle size and becomes negligible or undetectable at large sizes. Materials which are phase-matchable include LiNbO$_3$, urea, 4-nitrophenyl-S-prolinol (NPP) and 2-Methyl-4-nitroaniline (MNA). The powder technique is a reliable tool for establishing the presence or absence of centre of 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\textsuperscript{133}) and modification of surface features are known to cause artifacts.
Diaminodicyanoquinodimethanes

Diaminodicyanoquinodimethanes (DADQ) are easily synthesized from tetracyanoquinodimethanes (TCNQ) by treatment with primary or secondary amines. DADQ's are highly versatile push-pull molecules with a strongly zwitterionic structure. (Fig. 1.7). Several families of DADQ's have been investigated in our laboratory over the past few years, because of their interesting quadratic nonlinear optical properties.

Figure 1.7 Structure of diaminodicyanoquinodimethanes (DADQ's).

Semiempirical computational studies have shown that they possess large molecular hyperpolarizabilities in spite of the relatively small size of the chromophore. These studies also provided insight into the influence of the molecular structure on the molecular nonlinear response. Inclusion of chirality and intermolecular H-bonds have been effectively used in developing DADQ systems showing strong SHG in the solid state. Introduction of alkyl chain on the amino end of diaminodicyanoquinodimethanes was shown to be an interesting novel strategy to control centrosymmetric and noncentrosymmetric lattice formation and hence SHG activity. Ampiphiles based on DADQ's and their LB films have also been investigated in our laboratory. We present in Chapters 2 and 3, a variety of novel optical and nonlinear optical materials based on DADQ's, in which the molecular assembly and materials property are strongly influenced by functionalities attached remotely from the \( \pi \)-electron chromophore unit.
1.4 MOLECULAR CONDUCTING MATERIALS

Materials are often classified into the three broad categories of insulators, semiconductors, and conductors based on their electrical conductivity behavior. Substances which offer strong resistance to the flow of electrons are insulators. Their conductivity is typically less than $10^{-6}$ - $10^{-8}$ S/cm. Most organic solids and polymers are insulators; polymers such as teflon or bakelite are some of the best electrical insulators. Those materials which show very low resistance to electrical transport are the conductors. Their conductivity is $10^5$ - $10^6$ S/cm or higher. Metallic conductivity is marked by an increase with decrease of temperature. Metals and their alloys are some of the best conductors. However several molecular materials based on charge transfer complexes and doped $\pi$-conjugated polymers show appreciable conductivity. They are called synthetic metals,\textsuperscript{138} as they are prepared through normal organic synthesis protocols. Materials which show partial resistance to electron transport are the semiconductors. They behave as insulators at absolute zero of temperature, and at finite temperatures show conductivity intermediate between metals and insulators. The room temperature conductivity of semiconductors are typically of the order of $10^5$ to $10^2$ S/cm. Their conductivity increases with increasing temperature. Classic examples of semiconductors include silicon, germanium and gallium arsenide. Many molecular crystals and $n$-conjugated polymers show conductivity typical of semiconductors.

The band theory of solids provides a convenient framework to understand and explain the conductivity behavior of materials. Appreciable overlap between the wave functions of large number of atoms in the solid leads to the formation of energy bands. Depending on the atomic energy levels from which they are constructed and the extent of overlap, the bands would show different widths and forbidden energy regions between them. The resulting band structure and the electron count, leads to the following situations : (i) the highest energy electrons (Fermi electrons) occupying a partially filled band (metals) or (ii) completely filled and empty bands with an energy gap in between. The latter situation leads to insulating or semiconducting behavior depending on whether the energy gap is large or small compared to thermal energy. The bands in molecular charge transfer complexes are expected to be generally narrow and best explained as an intermediate regime between the valence band and molecular orbital limits.\textsuperscript{139} Electronic
structure of conducting polymers are best explained using polyacetylene as a model system.\textsuperscript{138,140} In a regular all trans-polyacetylene, the band picture predicts a half-filled conduction band and hence metallic behavior. However, due to the one-dimensional nature, the polymer undergoes Peierl's dimerization opening up a gap at the Fermi level. This leads to the observed semiconducting nature of pure polyacetylene. Doping introduces a wide range of charge carriers leading to enhanced conductivity in the conjugated polymer.

\textit{Organic charge transfer complexes}

Perylene-bromine\textsuperscript{30} is perhaps the earliest organic material in which enhanced electrical conductivity was observed. As mentioned in Sec. 1.1, synthesis of the strong n-electron acceptor, TCNQ\textsuperscript{31} led to the development of a large number of semiconducting charge transfer complexes. The earliest and the most studied among organic metals is TTF-TCNQ which shows metallic conductivity down to ~ 60 K. The high conductivity of TTF-TCNQ arises due to the segregated stacks of donor and acceptor molecules with short inter-layer distances as well as their partial ionicity. The extent of charge transfer leads to 'neutral' or 'ionic' ground states for the charge transfer complexes. A 'partially ionic' state leading to fractional oxidation state allows unactivated electron transport along the \textit{\pi}-stacked structures and high electrical conductivity.

Some of the well known \textit{\pi}-electron donor and \textit{\pi}-electron acceptor organic molecules which have been used to prepare conducting or semiconducting charge transfer complexes are shown in Figs. 1.8 and 1.9 respectively. Molecules like, N,N,N',N' tetramethyl-p-phenylenediamine (TMPD), tetrakis(dimethylamino)ethylene (TDAE), tetrathiotetraspolyvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)\textsuperscript{141} are very good \textit{\pi}-electron donors and possess ionization potential of ~6-7 eV. Charge transfer complexes based on TMTSF and BEDT-TTF and several of their derivatives show superconductivity at low temperatures. Molecules like tetracyanoethylene (TCNE), tertracyanoquinodimethane (TCNQ) and dicyanoquinodiimine (DCNQI) are very good it-electron acceptors with electron affinities ~ 3-4 eV. Various heterocyclic analogues of TCNQ, generally called as hetero-TCNQ's,\textsuperscript{142} are of interest because they engage in strong intermolecular interactions and
Figure 1.8 Molecular structures of \(\pi\)-electron donors.

Figure 1.9 Molecular structures of \(\pi\)-electron acceptors.
possess reduced on-site Coulombic repulsion. In spite of the lack of superconductivity in their salts and complexes, derivatives of TCNQ and DCNQI, have been the focus of extensive synthetic efforts because of the variety of conducting materials that could be fabricated using them. Advances related to these significant acceptor molecules and other cyano compounds have been reviewed recently.\textsuperscript{143} Several charge transfer salts of TCNQ have been investigated for magnetic\textsuperscript{144} and conducting properties.\textsuperscript{145} Functionalized electron acceptor TCNAQ has been utilized in the synthesis of new D-\(\sigma\)-A compounds.\textsuperscript{146} A comparison of TCNQ and TCNQF\(_4\) based complexes and their properties has been presented by Azcondo \textit{et al.}\textsuperscript{147} The clathrate compounds of H\textsubscript{2}TCNDQ are expected to have both electron acceptor and proton donor capability.\textsuperscript{148}

TTF and related molecules have been the prime focus of a majority of organic conductor and superconductor research.\textsuperscript{138,149} Recent developments in the functionalization\textsuperscript{150} of TTF have enabled these units to be covalently linked to macromolecular\textsuperscript{151} systems. New architectures and interesting redox activity have been realized with the synthesis of polymeric TTF’s. Extended \(\pi\)-electron donors are important systems in modern TTF chemistry.\textsuperscript{152} Fused\textsuperscript{153} and halogenated TTF’s\textsuperscript{154} have provided useful input for structure-property relationships. Dimeric and oligomeric TTF’s\textsuperscript{155,156} are also being extensively studied. An excellent review on TTF has been published recently.\textsuperscript{157} In spite of several advantages possessed by conducting charge transfer complexes and ion radical salts, these materials tend to be brittle and unprocessable. In principle this problem can be overcome by incorporating them in polymers where the charge transfer complexes form part of the main chain or the side chains.

\textit{Conjugated polymers}

Prior to the discovery of conducting polymers\textsuperscript{158} in the 1970’s, polymer science and technology was largely based on saturated polymers. Saturated polymers like polyethylene are insulators and consequently do not show any special electronic or optical properties. Conjugated polymers on the other hand possess overlapping \(\pi\)-orbitals leading to extended 71-electron delocalization. The resulting band structure bestows
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semiconducting or metallic properties on these materials. The classic case of polyacetylene \((\text{CH})_n\) has been noted earlier. Conjugated polymers with chain structures and extended \(\pi\)-electron conjugation can be considered as quasi one dimensional conductors.\(^{159}\) The conductivity of the conjugated polymers are usually very sensitive to the extent of electron or hole doping. The structures of some of the common conducting polymers are shown in Fig 1.10. Polymers such as poly vinyl ferrocene, poly vinyl carbazole and tetrathiafulvalene substituted polystyrene\(^{160}\) are called redox polymers and can be subjected to doping. However they are less suitable for electrical conduction.

![Molecular structures of some of the well known conjugated polymers (adapted from Ref.138).](image-url)

Figure 1.10  Molecular structures of some of the well known conjugated polymers (adapted from Ref.138).
Conducting polymers combine many of the electrical and optical properties of metals and semiconductors and the mechanical attributes of conventional plastics. Thus they are unique materials poised for major applications in the current and future technologies. We have discussed in Section 1.2, the electroluminescence of conducting polymers. The electrical conductivity of these polymers arise due to a variety of nonlinear excitations such as solitons, polarons and bipolarons generated by chain relaxation or deformation as well as doping. One of the important features of these materials is the feasibility of fine-tuning the conductivity by controlling the doping levels. This has significant implications for applications of conducting polymers as sensor elements. Conducting polymers find application in other areas as well, such as electromagnetic radiation shields, anticorrosion coatings, smart windows and solid electrolytes.

**Polyanilines**

Polyaniline (PANI) is one of the most easily synthesized, thermally and environmentally stable conducting polymer. Its versatility stems from the possibility of controlling its electrical and optical characteristics through proton doping. PANI is also probably the oldest known conjugated organic polymer. It was prepared in 1834 by treating aniline with concentrated sulfuric acid. The product was an ill-defined, black, amorphous powder, aniline black. From 1980's PANI has been synthesized chemically electrochemically and its electrochromic characteristics in aqueous and nonaqueous solutions have been extensively investigated. It exists in five different forms (Fig. 1.11) ranging from the fully reduced leucoemeraldine to the fully oxidized pernigraniline. Protonation of the emeraldine base yields the famous ‘emeraldine salt’ state which is the conducting form of PANI. Molecular weights of polyanilines generally range from 2500 - 6000 g/mol; high molecular weight polyanilines have also been reported.

Oligoanilines provide useful insight into structure-property relationships. Wudl and Heeger have synthesized phenyl capped octaniline which showed the same conductivity as the normal polyaniline. N-methyl substituted oligoanilines have also been synthesized. Recently Buchwald and coworkers have used palladium catalyzed
coupling of aryl bromides and arylamines in conjugation with protective groups to synthesize oligoanilines of up to 24 units.\textsuperscript{164} Self-doped conducting polyaniline with improved solubility is obtained by sulfonation of the aromatic units with fuming sulfuric acid.\textsuperscript{165} It shows a conductivity of 0.1 S/cm which is independent of the pH. Recently Mullen \textit{et al.} have synthesized hybrid structures\textsuperscript{166} of polyphenylene sulfide and polyaniline which exhibit excellent solubility in various organic solvents. Because of their electron rich character they are being tested as hole transport layers in LED's.
Research on PANI has been extensive and multifaceted. It has been the subject of fundamental studies as well as a wide range of applications. An exhaustive review of all the work on this fascinating material is beyond the scope of this brief overview. We list a few of the recent exciting investigations. Polyaniline has been deposited on self assembled monolayers for micron scale patterning.\textsuperscript{167} PANI-PVA composite films\textsuperscript{168} have been utilized in humidity sensing; at high humidity polyaniline existed in the emeraldine salt form and transformed into a non-conducting base form with decreasing environmental humidity. The conductivity of novel poly aniline-inorganic salt composites\textsuperscript{169} have been analyzed via percolation theory. Nanocomposites with transition metal oxides\textsuperscript{170} prepared by direct intercalation methods possess good electrical conductivity. Nanoscopic polyaniline particles with good crystallinity have been successfully synthesized in water-oil emulsion.\textsuperscript{171} Novel polyaniline nanotubules have been used as second order template\textsuperscript{172} by encapsulating iron nanowires and their magnetic behavior has been investigated. Polyaniline nanowires were obtained by electropolymerization of liquid crystalline phases\textsuperscript{173} and chiral polyaniline nanotubes were obtained by template-free methods.\textsuperscript{174} Polyaniline - metal chelate blends synthesized recently\textsuperscript{175} are promising candidates for cathodes in lithium batteries. Realization of good solubility and processability along with high conductivity continues to be a challenge in the research on polyanilines. Our efforts in this direction will be discussed in Chapter 4.

1.5 LAYOUT OF THE THESIS

We are interested in the electronic and optical properties of organic molecular and polymeric materials. As discussed in Sec. 1.3, zwitterionic push-pull molecules based on diaminodicyanooquinodimethanes have been investigated previously in our laboratory, because of their quadratic nonlinear optical properties. This family of molecules exhibit interesting structural control of electronic properties which in turn, impact upon their materials properties. We have now focussed on the question of controlling their assembly through functional groups attached remotely from the $\pi$-electron framework that is responsible for their optical characteristics. This led to the discovery of a variety
of interesting phenomena and the fabrication of novel optical and nonlinear optical materials. We have extended this logic to the control of molecular assembly through the utilization of template structures and the fabrication of semiconducting molecular and polymeric materials providing insight into the correlation of molecular organization and materials attributes. The thesis is organized in five chapters. The basic concepts of molecular materials and an overview of optical, nonlinear optical and conducting molecular materials are already covered in the previous sections in this Chapter. We summarize below, the salient features of the remaining chapters.

Chapter 2

In their electronic ground state, the zwitterionic push-pull molecules, diaminodicyanoquinodimethanes (DADQ's), exhibit a large dihedral twist between the diaminomethylene unit and the benzenoid ring plane. The molecular twist has significant impact on the linear and nonlinear optical properties of these materials. After a brief introduction in Sec. 2.1, we present in Sec. 2.2, a semiempirical computational investigation combined with crystallographic examination which we have carried out to model these push-pull quinonoid structures, leading to the concept of a 'molecule-in-a-crystal'. The optimized twist angle, 9 of these molecules are found to sensitively depend on the dielectric constant, ε employed in the solvation subroutine in the calculation. The ε required to reproduce the experimental twist angles from crystal structure analysis could be qualitatively related to conventional intermolecular interactions such as H-bonds and electrostatic forces. This study demonstrates the utility of a standard solvation model in mimicking the molecular microenvironment in crystals. We have used this approach in several instances later in the thesis.

The optical and electronic properties of DADQ's are primarily controlled by the π-electron structure. However molecular assembly can be controlled and fine tuned by remote functional groups such as amines, not in conjugation with the π-electron framework. Sec. 2.3 presents a study on a novel situation involving solid state charge transfer promoted by the remote functionality which acts as an anchoring agent. Charge transfer complex formation observed exclusively in the solid state, between the
**Chapter 1**

**push-pull** molecule 7,7-bis(piperazino)-8,8 dicynoquinodimethane (BPDQ) acid is shown to be a two-component analogue of the Kofler's ternary v. The secondary amine moiety of the piperazine units plays the role of the anchoring agent. Computational studies provide insight into the nature of the charge transfer interaction. Synthesis and investigation of a new family of DADQ molecules possessing remote amino functionalities, exhibiting enhanced fluorescence in the solid state and in polymer films is presented in Sec. 2.4. The critical role of the remote functionality and molecular twist is analyzed through crystallographic and computational studies and the reversible switching of the enhanced fluorescence in a doped polymer film triggered by solvent vapors is demonstrated.

**Chapter 3**

Sec. 3.1 introduces previous studies in our laboratory which have demonstrated the large hyperpolarizability of DADQ's and their potential application as quadratic NLO materials. Subsequently we present novel modes by which noncentrosymmetric SHG active materials were obtained in remote functionalized DADQ's and their derivatives. In Sec. 3.2 we demonstrate a simple approach to the modification of crystal architecture using remote functionalities and the fabrication of noncentrosymmetric and SHG active cocrystals. Structural characterization of centrosymmetric crystals of 7,7-bis(N,N-dimethylethylendiamino)-8,8-dicyanoquinodimethane and its SHG active complex with terephthalic acid, are presented. Sec. 3.3 highlights a novel derivative of DADQ obtained through a simple synthetic modification of remote functionalized systems. 7-(N,N-dimethylpiperazinium)-7-oxo-8,8-dicyanoquinodimethane is found to exhibit spontaneous resolution in crystals. This conformationally chiral molecule engages in strong H-bonding and electrostatic interactions leading to the formation of interesting helical superstructures along the three crystallographic axes. The concomitant formation of the helical motifs expresses the homochirality of the molecular assembly leading to the spontaneous resolution in this material. The moderate SHG exhibited by the microcrystalline material is also presented.
Chapter 4

In the study of remote functionalized DADQ's showing enhanced light emission discussed in Sec. 2.4, we used polyelectrolytes as templates to organize some of the ionic chromophores. We have considered the utilization of polyelectrolyte templates in the fabrication of molecular and polymeric conductors as well. After a brief introduction in Sec. 4.1 we present in Sec. 4.2, the development of a simple and convenient protocol for the synthesis of poly(4-styrenesulfonate) templated polyaniline in the form of practically useful stable aqueous colloidal solutions. Good quality films were fabricated by forming composites with trace amounts of polyvinylalcohol (PVA). Investigation of the submicron and nano level morphological features in the film revealed interesting dependence on the template molecular weight and the amount of PVA additive. The dependence of the film conductivity on the template polymer molecular weight revealed in our studies suggests that the latter is a novel design element for conducting polyaniline. Sec. 4.3 presents the synthesis of a new class of molecular materials which incorporate tetrathiafulvalene (TTF) and polyionic polymers such as poly(4-styrenesulfonate) and poly(vinylsulfate). Enhancement of the conductivity by $\sim 10^2 - 10^4$ over the starting TTF salt based on small anion is demonstrated. We also present a brief investigation of the interesting 'core-sheath' crystal structure and semiconductivity of a TTF complex based on a symmetric counterion.

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) a new methodology to model molecule-in-a-crystal allowing critical solid state effects on molecular geometry and electronic properties to be assessed, (ii) development of a variety of optical materials based on remote functionalized DADQ's exhibiting novel charge transfer complex formation, enhanced fluorescence in the solid state, spontaneous resolution through helical assembly and second harmonic generation, and (iii) fabrication of polyelectrolyte templated molecular and polymeric semiconductors. Directions for further explorations in this area of research are outlined in Sec. 5.2.
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