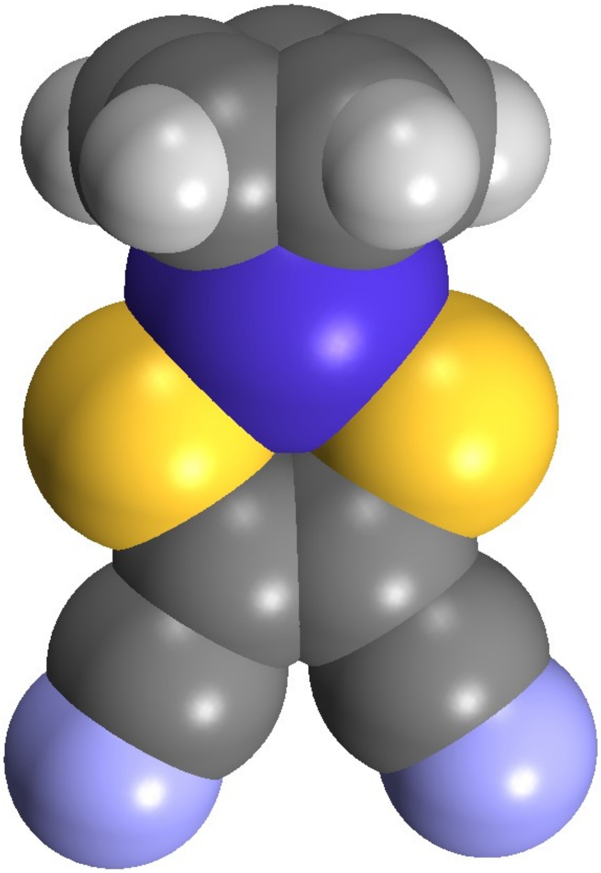
Chapter 1: Introduction of Molecular Materials



1.1 Introduction

Conventional materials, traditionally considered to be solely available from classic atom based inorganic solids such as metals, alloys, or oxides which mostly considered as solid state materials known to exhibit many technologically important properties (e.g., magnetic ordering, conductivity, superconductivity)[1]. The utilization of conventional materials was partly or wholly based on their structural, mechanical, optical or thermal properties. Mostly conventional/solid state materials require high temperature manufacturing i.e. thermodynamically controlled due to which tuning/ addition of properties into it is difficult. Hence, conventional/solid state materials are heavy for today's world. The only positive point about solid state materials, they are robust and long lived in nature.

The word ‘materials’ can conjure up a myriad of interpretations and are broadly defined in dictionaries as ‘substances of value’. The value of a material arises from its associated plethora of chemical and physical properties. Physical limits of the conventional materials generated a scope for the search of new types of smarter materials. Molecular materials found to be suitable alternative for the conventional materials.

Molecular material uses assemblies of individual molecules as basic building blocks to reproduce conventional structures represent the new frontier. A molecule is an entity wherein strong covalent or coordination bonds hold a group of atoms together in a stable state, in solid, in solution/liquid and in several cases, even in the gaseous state [2]. This structural feature creates great opportunities for the modeling of physical properties of materials through the selection of particular molecules. Their relevance in material science is mainly due to the tunability of their physical properties by conventional synthetic methods; molecular materials in fact are obtained through soft routes, traditionally from organic chemistry, coordination chemistry, and supramolecular chemistry, and this opens unprecedented possibilities to the design of molecules with the desired size, shape, charge, polarity, and electronic properties, in response to the changing demands of technology [3].

Molecular Material components consist of an infinite group of substances, and research into the formation and properties of molecule-based materials (MBMs) is a growing contemporary research thrust in chemistry as well as related areas of biology, physics, and engineering. A. P. Alivisatos et al. defined molecule based materials (MBMs) as ‘useful substances prepared from molecules or molecular ions that maintain aspects of the parent molecular framework’ [4]. Thus, an MBM is typically prepared via lower temperature, typical solution-based, organic-synthesis methodologies, organometallic, and inorganic coordination chemistry. These routes provide a means to prepare kinetically and thermodynamically stable materials as well as complex phases that can lead to the improvement of the properties, and lead to the development of materials with a combination of properties that will expand their desirability.

Table 1 highlights the difference between molecular materials and conventional materials.

Table 1.1: Difference between molecular materials and conventional materials

	Molecular Chemistry	**Solid- state Chemistry**
1	Low reaction temperature	High reaction temperature
2	Kinetically controlled	Thermodynamically controlled
3	At equilibrium all the reactants are present in infinite amount	Not necessary
4	Conservation of molecular framework, i.e., reaction takes place at functional group	Destruction of molecular framework
5	Diffusion coefficient ~10^{-5} cm^2/sec	Diffusion coefficient ~10^{-10} to 10^{-14} cm^2/sec
6	Transport distance ~ 5-10 Å	Transport distance ~ 10^4 to 10^6 Å
7	e.g., Organic superconductors (BEDT-TTF), NLO	e.g., Present electrical, magnetic metals/alloys/oxides

It is also a challenge for developing new synthetic methods that would make it possible to control the directional arrangement of molecules in the space crystal lattice. The design of molecular materials is attracting much interest from scientists, probably because it corresponds not only a natural trend of chemical science and an economic need of society, but also a clear and aesthetic aspect of the professional activity of chemists. Certainly, one reason for this interest has been the realization that these materials can exhibit cooperative properties [5].

A current development in the general area of molecule-based materials is to design, from a wise choice of the constituent molecules, new materials that combine properties not normally associated with a single material. Current methods in chemical synthesis allow for the construction of virtually any molecular architecture, allowing chemists to focus on the properties and function of molecules rather than only on their structure. These materials have properties that depend on their exact structure, the degree of order in the way the molecules are aligned and their crystalline nature. Small, delicate changes in molecular structure can totally alter the properties of the material in bulk. Combined with X-ray crystallography, this strategy has been used to uncover structure–property relationships and to study the underlying principles that govern required properties [6]. These bottoms up molecular approaches are also particularly well suited for the construction of low to high dimensional species designed to test the predictions of theoretical models that have been examined by physicists. The field thus represents an area that is intrinsically interdisciplinary and multifaceted, melding organic and inorganic synthesis with physical measurements and modeling. The complexity of these materials makes the design of the molecular building blocks, the control of the intermolecular interactions, and the crystallization techniques crucial for obtaining functional materials exhibiting technologically useful physical properties.

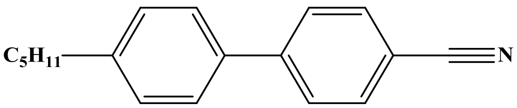
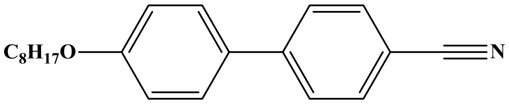
Representative technologically important physical properties (structural, electrical, electronic, magnetic, and optical) along with examples of materials (both MBMs and MDMs) exhibiting these properties are presented in Table 2 [7].

Table 1.2: Examples of conventional inorganic network and molecule-based functionally active materials

Property	Conventional inorganic Materials	Molecule Based Materials
Conductivity	Cu, Au	[TTF] [TCNQ]
Piezoelectric	Quartz	Poly (1,1-difluoroethene)
Pyroelectric	$BaTiO_3$	$KNa(O_2CC(OH)H)_2.4H_2O$
Ferroelectric	$BaTiO_3$	9-hydroxyphenalenone
Dielectric	Al_2O_3, SiO_2	Teflon, nylon
Photochromic	AgX glasses	Fulgides, spiropyrans
Thermochromic	Cu_2HgI_4, Au/Zn alloys	Liquid crystals
Ferrimagnetic	Fe_3O_4	Mn^{II}/Cu^{II} chains
Ferromagnetic	Fe, CrO_2	$[Fe^{III}(C_2Me_5)_2]^{+\cdot}$ $[TCNQ]^{-}$

Technologically important MBMs are, in fact, already in use in a variety of commercial applications; examples utilizing the physical properties are summarized in Table 3.

Table 1.3: Representative commercially used Molecule Based Materials (MBMs)

Molecule	Commercial Product
7,7,8,8-Tetracyano-p-quinodimethane (TCNQ)	*N*-n-Propyl-I-quinolinium $(TCNQ)_2$ - based electrolytic capacitors
A mixture of 4'-substituted 4-cyanobiphenyls 	Liquid crystal display 
Triglycine sulfate	IR detectors (pyroelectric)
KNa (tartarate). $4H_2O$ (Rochelle salt)	Electronic oscillators, filters, etc., (Piezoelectric)
VOPc (Pc = pthalocyanine)	Photoreceptor sensitizer

Keeping all this in mind designing and synthesis of different types of properties of molecular materials is explored in this work. The work is systematically arranged in overall eight chapters, with an introduction to Molecular Materials in Chapter **1**.

The magnetic property is the main focus of Chapter **2**. It consists of study of molecular magnetic materials (MMMs). The chapter includes an optical, structural and magnetic study. We are interested in knowing the influence of molecular chirality on the self-assembly, crystallization process and hence bulk properties. Therefore, we used hydrogen bond acceptor group away from the chiral centre in benzylamine derivatives, which results in a change in dimensionality as well as the magnetic properties of the copper complexes.

Chapter **3** deals with ferroelectric property evaluation of aniline and its *para* substituent's molecules. In this chapter, we designed a molecular ferroelectric organic cation for modulating overall crystallization in polar space group to observe room temperature ferroelectricity due to motion of nitrate anion. We show that by the change in substituents at molecular level desired property can be achieved. Synthesis of five of aniline derivatives and structural, optical and electric properties evaluation is presented in this chapter.

Chapter **4** (part I) provides a brief introduction about porous and non porous coordination materials used for adsorption-desorption of gases at the molecular level. The sorption ability of nonporous molecular materials is investigated to design molecular materials for detection at solid-liquid and solid-gas interface. A detailed study description is given for reversible chemisorption of gaseous HCl molecules by a nonporous one-dimensional coordination network having general formula $(R\text{-}NH_2)_2CuCl_2$ that undergoes a facile solid-state transformation process to form salts having general formula $(R\text{-}NH_3)_2CuCl_4$. Chapter includes a thermal, optical and structural study to probe probable mechanism. Part II extends crystal to crystal transformation at solid-liquid interface reaction to detect azide anion from liquid by the same non-porous molecule.

In Chapter **5**, we report the spontaneous resolution of a racemic ligands at molecular level during crystallization (methyl benzylamine ligand and derivatives) in cobalt (part-I) and copper-azido (part-II) complexes. Part I contain chloride anion and NH···Cl assisted spontaneous resolution of chiral cobalt compounds forming conglomerates. Change in substituent on methyl benzylamine ligand molecule showed effects on the spontaneous resolution and hence crystallization. Part II shows crystallization of *racemic* methyl benzylamine ligand in 2D azido based complexes (two of them are chiral crystals i.e. conglomerates (space group $P2_12_12_1$) and one is *racemic* crystals (*Pbca*)) while *racemic* 4-chloro methyl benzylamine crystallizes into 1D azido based complexes (conglomerate only). We performed a detailed structural and spectroscopic study (CD spectra) on the system by systematic characterization of individual single crystals.

Chapter **6** deals with study of thermochromic materials. Thermochromism occurs due to changes in co-ordination sphere around a metal centre or by ligands movement. We sought to study latter effect, molecular in origin not much explored in literature using rigid regio-isomeric ligands. We employed (*R)*-(+)-napthyl-1-ethylamine and (*R)*-(+)-2-napthyl-1-ethylamine ligands and synthesized A_2CuCl_4 compound. The observed thermochromism showed no change in geometry around Cu-(II) and is ligand centric. The chapter includes a detailed optical, thermal, temperature dependant FT-IR and structural study.

Chapter **7** introduces 4-thiocyanato aniline and its derivatives as a class of molecular dual fluorescent material. Rotation of an electron donor (ED) group or the wagging of electron acceptor (EA) group played an important role in observing dual fluorescence in this molecular compound. Thus, designed rotating EA group by addition of –SCN moiety on aniline and its derivatives and studied its effect on dual florescence. Preliminary studies suggest that dual fluorescence depends on the solvent polarity affects and also depend on the rotation of –SCN moiety.

Chapter **8** is about interaction of molecular nanoparticles and CdS nanoparticles. Interaction of inorganic nanoparticles with organic porphyrin/metalloporphyrin counterpart is studied well in literature. Here we study the interaction of both at nano level i.e. inorganic nanoparticles with organic nanoparticles. The chapter begins by synthesis of both inorganic and organic nanoparticles materials using various stabilizers. Absorption and fluorescence spectra of porphyrin/Zn-porphyrin nanoparticles showed distinct change in presence of colloidal CdS nanoparticles. These interactions leads to the quenching of fluorescence. The chapter includes a synthesis process and detailed optical and electrochemical study.

All synthesized compounds were characterized using elemental analyses, FT-IR, NMR, UV-Vis., Fluorescence spectroscopy, CD spectroscopy, Variable Temperature FT-IR (VT FT-IR), PE-Loop tracer, TG-DTA, DSC, Powder XRD, Single crystal XRD, EPR and SQUID Magnetic study where ever necessary.

1.2 References

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