Summary

Thesis entitled

"Designing and Studies on Molecular Materials"

Submitted to

THE MAHARAJA SAYAJIRAO UNIVERISTY OF BARODA

By

Mr. Hemant Malhari Mande

DEPARTMENT OF CHEMISTRY

FACULTY OF SCIENCE

THE MAHARAJA SAYAJIRAO UNIVERSITY OF BARODA

VADODARA - 390002, GUJARAT, INDIA

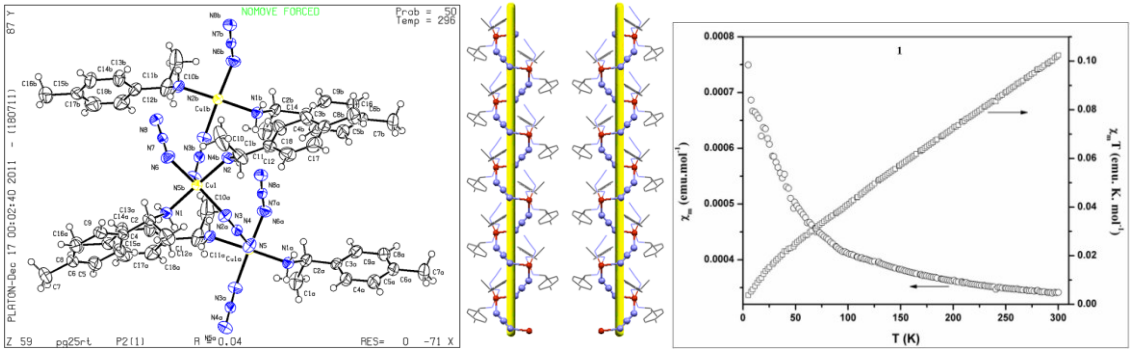
JANUARY 2015

The design of molecular materials is attracting much interest from scientists, probably because it corresponds not only to a natural trend of chemical science and to an economic need of society but also to 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. Molecule-based materials with active physical properties, in particular electrical, magnetic, and optical, are a focus of contemporary materials chemistry research.

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. 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. Keeping all this in mind designing and synthesis of different types of properties of molecular materials is explored in this work. In this thesis "**Designing and Studies on Molecular Materials**", the work is systematically arranged in overall eight chapters, with an introduction to Molecular Materials in Chapter **1** and subsequently conclusion of each chapter.

Chapter 2: Molecular Magnetic Materials

Interplay of chiral auxiallary ligand and azide bridging ligand during the coordiantion network formation with Copper (II)



(a) (b) (c)

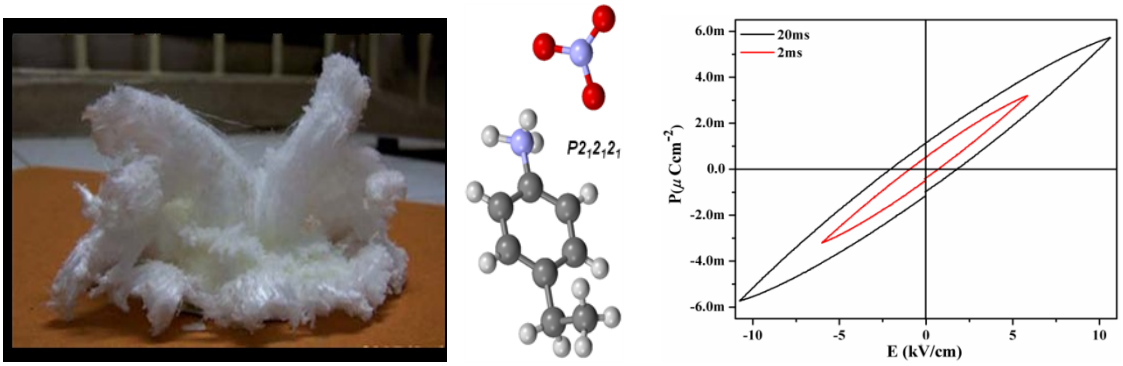
Fig. 1: (a) Molecular view of compound 1 (b) a typical 1-D helical structure of the compound, (b) Plot of χ_M *versus* T and $\chi_M T$ *versus* T for 1

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.

- Five new 1D helical compounds were synthesized and thoroughly characterised.
- Single crystal X-ray studies showed helicity in these compounds is driven by enantiomeric chiral building blocks.
- By a proper substitution in a molecule, away from chiral centre, one can enhance or trigger chiral ligand-chiral ligand interaction (CAL) in a self-assembly driven one pot crystal formation reaction to design multifunctional molecular magnets.
- CD spectroscopy confirms helicity in chiral ligand is expressed in final compound.
- SQUID magnetometric studies reveal that all these compounds showed antiferromagtic interaction due to *end-to-end* azide bridging between metal ions.
- The CAL- CAL interactions will not only play important role in crystal growth or dimensionality, but might help in tuning other physical behaviour. Detailed investigation in this direction is required.

Chapter 3: Molecular Ferroelectric Materials

Generating polar space group in nitrate salts of Anilinium and its derivatives



(a) (b) (c)

Fig. 2: (a) Hair like crystal growth of $AnHNO_3$ (1a) from gel (b) Molecular view of compound 3 (c) PE Loop in compound 3a

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

- We successfully designed, synthesized and characterized series of 4-alkyl substituted aniline nitrate salts using IR, ^{1}H NMR and Single crystal XRD.
- All compounds are investigated for structural phase transitions using TG/DTA, DSC, single crystal XRD and Variable Temperature IR.
- DSC measurements showed solid-solid reversible phase transition for all compounds except compound **4b**.
- Ferroelectric measurement showed hysteresis loop at room temperature for compounds **1a** ($P_S = 1.71\mu Ccm^{-2}$) and **3a** ($P_S = 2.09\mu Ccm^{-2}$).
- Single crystal study showed presence of helical chain in **2b** and **3a/3b** due to H-bonding.

- Compound **3b** crystallizes in two forms with distinctly different helical chains. The separated crystals have left handed (3b-M) and right handed (3b-P) chains.
- CD spectra confirm the enantiomeric nature of the optically active compounds i.e. compounds **3b-M** and **3b-P**.
- Symmetry lowering of the NO_3^- ion from D_{3h} to C_{2v} was found in the compound **1a** confirm by room temperature FT-IR.
- **3a/3b** was found to undergo solid–solid phase transitions: Ferroelastic ($P2_12_12_1$) I 295 K →paraelectric II (*Pbca*) second-order type.
- The single crystal x-ray and calorimetric studies suggest an 'order–disorder' mechanism for the ferroelectric phase transition.
- The ferroelectric phase transition (II →I) mechanism is due to the dynamics of 4-ethyl anilinium cations contributing predominantly to the spontaneous polarization.
- Loss of domains during phase transition in **3b** confirms Ferroelastic character confirmed by polarizing microscope.
- Variable Temperature dependent IR and SXRD study confirmed the change in modes of NO_3^- ion as well ring at phase transition temperature confirming the changes in structure is of order-disorder structure.
- The crystal structure of **3b** at HT, phase II, has highly disordered cations distributed over two sites (occupancy 0.50/0.50). At low temperature (RT), in phase I all the cations are fully ordered.
- By destructing the regular planar arrangement between nitrate anion and ammonium cation to allow latter to act as a stator we designed room temperature ferroelectricity in a KNO_3 type molecular compounds, a true '**Molecular Ferroelectric**'.

Chapter 4: Molecular Nonporous Compounds for Adsorption-desorption

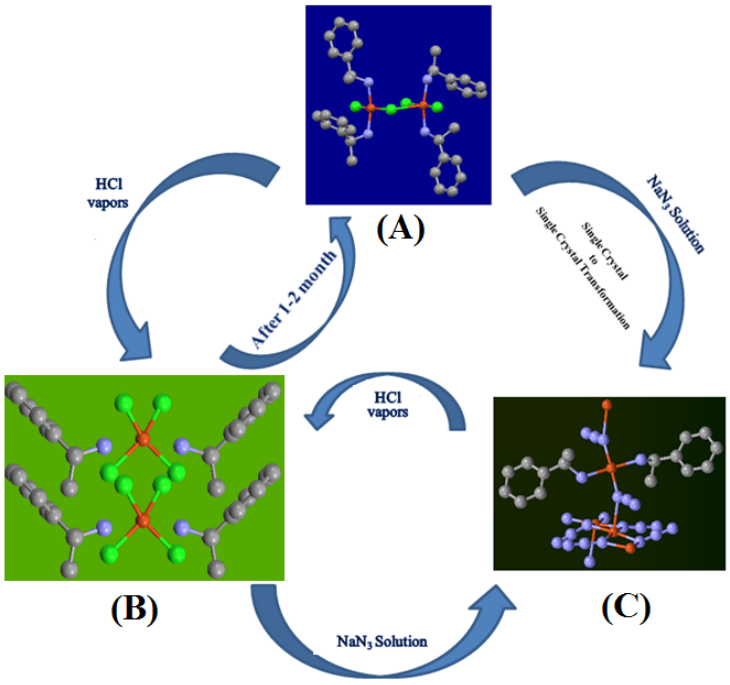


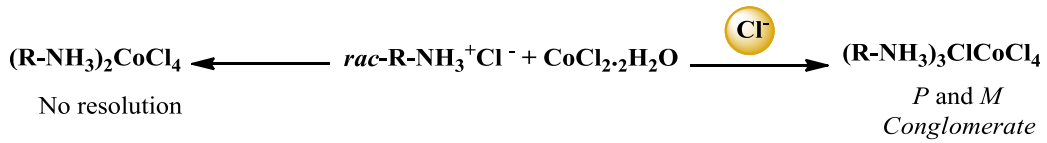
Fig. 3. Molecular Accommodative Chemistry : Non-porous complex exists in dimeric form (A). when exposed to HCl gas (solid-gas reaction) reversible changes to (B), (A) transform at solid-liquid interface with Single-Crystal to Single Crystal conversion in azide bridged coordination network (C). (B) transforms to reversibly to (C).

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.

Chapter 5: Racemic Resolution in Molecular Materials

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.

Part I: Chloride anion assisted Resolution of chiral cobalt compounds

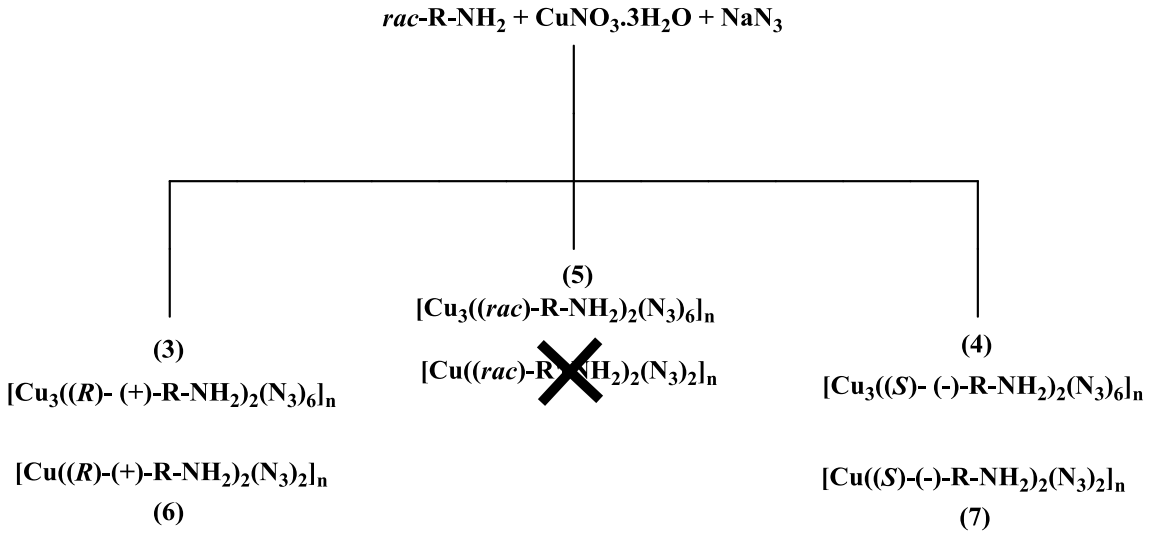


Scheme 1: Schematic representation of compound formation

- Synthesized four different Cobalt based complexes of general formula (R-$NH_3)_nCl_xCoCl_4$, [where, R-NH_3 = (*R*)- (+)-4-chloro methyl benzylamine (**1*R***) and (*S*)- (-)-4-chloro methyl benzylamine (**1*S***), (±) 4-fluro methyl benzylamine (**2**), (*R*)- (+)- methyl benzylamine (**3*R***),; x= 0, 1 and n=2, 3]
- All the compounds were characterized using elemental analysis, FT-IR, thermal analysis and single crystal X-ray diffraction.
- Isolated structures were observed in complexes, where $CoCl_4^{2-}$ exists in distorted tetrahedral geometry.
- Single crystal studies shows racemic((*R/S*)-(+/-) 4-F-$C_6H_4CH(CH_3)NH_3$, **2**, react with $CoCl_2$ to form two separate anti-parallel helical chains of Cl···NH hydrogen bonding originated in one $[CoCl_4]^{2-}$ tetrahedra with synthon B.

- Single crystal studies on compound **3*R*** [(*R*)-(+)-$C_6H_4CHCH_3NH_3]_3ClCoCl_4$ and **1*R*/1*S*** [(*R/S*)-(+/-)-4-Cl-$C_6H_4CH(CH_3)NH_3]_3ClCoCl_4$ showed presence of free anion Cl^- driving $Cl^{\cdots}N$ interaction in the form of synthons A and C, for separation of racemic amines with conglomerates.
- Due to 'inclusion' of free Cl^- in the structures **1*R*/1*S*** stabilization and continuous formation of helical chains resulted in separation of isomers and hence resolution of racemic mixture of ligand.
- Present work of Cl^- inclusion, leading to novel synthon formation, will help in revealing 'molecular' aspect of controlling helicity and resolution of chiral amines.

Part II: A case study of Cu-azide bridged compounds with *racemic* auxiliary ligand



Scheme 2: Schematic representation of compound formation

- Racemic auxillary ligands, *racemic* methyl benzylamine **1** and *racemic* 4-chloro methyl benzylamine **2** gives 2D and 1D copper azido complexes respectively.
- All compounds were characterized using elemental analyses, FT-IR, CD spectroscopy and Single Crystal X-ray Diffraction.
- Spontaneous resolution of auxillary racemic ligand **1** results in to formation of conglomerate crystals (**3** and **4**) having chiral space group $P2_12_12_1$ as well as racemic crystal (**5**) having non chiral space group *Pbca*.

- In all compound (**3**, **4** and **5**) copper was found to exist in three different crystallographically environments (two square pyramidal and one square planar).
- Crystallization of racemic compound **5** (copper azido complex) happens due to square planar geometry around copper and phenyl rings twist.
- Only conglomerates (**6** and **7**) formation occurred in case of spontaneous resolution of auxillary ligand **2**.
- Compound **6** and **7** crystallized into chiral space group $P2_1$ in which copper having only square pyramidal geometry.
- Strong hydrogen bonding and supramolecular interactions (Cl---N) prohibit the crystallization of opposite isomer in **6** and **7** and hence resulting into conglomerates only and not racemic complex.
- CD spectra confirm the enantiomeric nature of the optically active compounds i.e. compounds **3**, **4**, **6** and **7**.
- Compound **5** showed silent CD spectra confirm the crystallization of both isomers.

Chapter 6: Molecular Thermochromic Materials

Synthesis and Studies on Thermochromic Compounds A_2CuCl_4 : [(naphthyl ethylamine)$_2$CuCl$_4$]

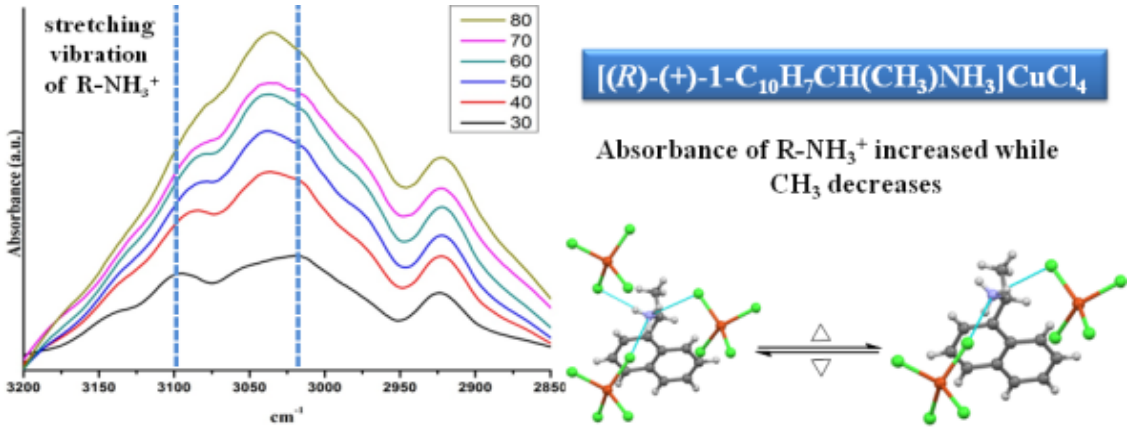


Fig. 4: Variable temperature FT-IR spectra of compound 3 and different and Hydrogen bonding pattern of compound 3 at different temperature

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.

- Synthesized and characterized two copper based compounds **3** and **4** using FT-IR, CHN and single crystal X-ray diffraction.
- Compounds were investigated for structural phase transitions using TG/DTA, DSC, single crystal XRD and Variable Temperature IR.
- TG-DTA showed endothermic transition, with possibility of solid-solid structural phase transition. DSC measurements showed 'reversible' nature of these transition for both the compounds in the range of 350-371K.

- Single crystal X-ray studies on both the compounds showed $CuCl_4^{2-}$ dianion remain in distorted tetrahedral geometry irrespective of change in temperature. There in also no observable change in Cl-Cu-Cl bond length and angles.
- Distinct synthons in the form of NH···Cl hydrogen bonding are observed in both the compounds. These synthons form different motifs with change in temperature.
- Different Hydrogen bonding pattern between two ligand molecules attached to same center leads to thermochromic and fluorescence behavior.

- Thermochromism in compounds can be tuned at molecular level using proper NH---Cl synthons or motifs, and should not be confined to geometry change around metal polyhedra.
- Thermochromism is not thought to result from a gross geometry change of the Cu-(II) chromophores, but rather a variation of the ligand field strength due to a change in the (*R)*-(+)-napthyl-1-ethylamine and (*R)*-(+)-2-napthyl-1-ethylamine conformation with temperature.

Chapter 7: Molecular Dual Fluorescent Materials

Synthesis and Studies on Dual fluorescent 4-Thiocyanato aniline and its derivatives

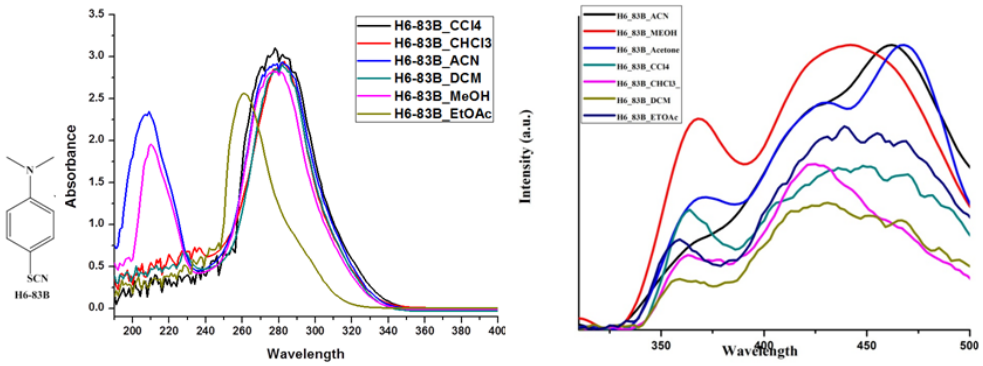


Fig. 5: UV-Vis. and Fluorescence study of N, N-dimethyl-4-thiocyanato aniline in different solvents.

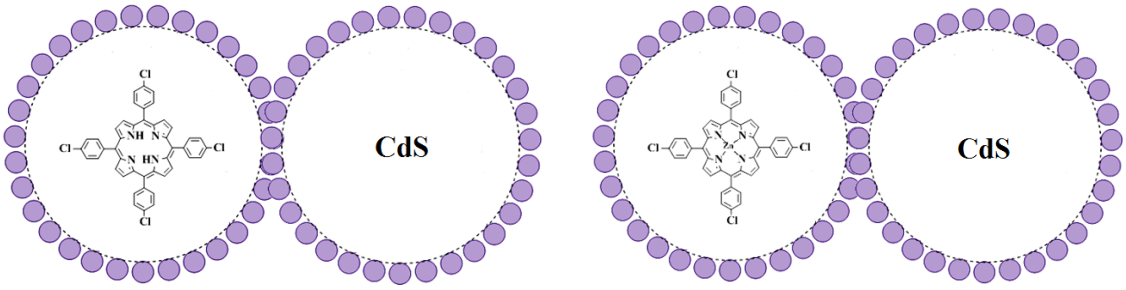
Chapter **7** introduces 4-thiocyanato aniline and its derivatives as a class of molecular dual fluorescent material. Rotation of an electron donor (ED) group or the wagging of electron acceptor (EA) group played an important role in observing dual fluorescence in this molecular compound. Thus, designed 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.

- We successfully synthesized and characterized four new compounds of 4-thiocyanato substituted anilines and two salts using IR, ^{1}H NMR and Single crystal XRD.
- Designed a series of smallest aromatic electron donor-acceptor molecules.
- Single crystal XRD showed the rotation of thiocyanato group is dependent on substituent present on amine group and phenyl ring.
- Fluorescence study shows the presence of Dual Fluorescence ($\boldsymbol{F_A}$ and $\boldsymbol{F_B}$ bands) for all compounds.
- Non polar solvent and Polar aprotic solvents, increase intensity of $\boldsymbol{F_A}$ band was observed.
- Time Dependant Fluorescence at ***nano second*** does not show the signal for fluorescence decay confirms the *pico second* fluorescence decay can reveal the correct information about decay, presently under investigation.

- As per our understanding Dual fluorescence behavior is observed due to rotation of -SCN moiety.
- In direct proof for our hypotheses is confirmed by the single crystal XRD of **4-Thiocyanato aniline salts** (compound **5** and **6**) and their single fluorescence spectra.
- In present set of compounds, TICT Mechanism and charge separation both are playing the important role for Dual Fluorescence although our conclusions is based on liquid state fluorescence study.

Chapter 8: Interaction of Molecular Nanoparticles and CdS nanoparticles

Fluorescence quenching of nanoparticles of porphyrins [T(*p*-Cl)PP] and nanoparticles of metal-porphyrins [Zn-T(*p*-Cl)PP] in colloidal CdS



(a) **(b)**

Fig. 6: CdS colloids surface interaction with (a) 1NC, (b) Zn-1NC

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.

- Synthesized and characterized *5,10,15,20-tetra* (4-*chlorophenyl)porphyrin* ***(1)*** and *5,10,15,20-tetrakis*(4-*chlorophenyl)porphyrin*-Zn(II) - (**Zn-1**) using elemental analyses, FT-IR, ^{1}H NMR, UV-Visible spectroscopy and fluorescence spectroscopy.
- Nanoparticles of ***1,*** **Zn-1** and CdS (**3**) have been synthesized and characterized using UV-Visible, Emission Spectroscopy and DLS.
- *In situ* nanocomposite formation was carried out using polyacryalmide as stabilizer been successfully synthesized and characterized by using DLS, UV and fluorescence spectroscopy.

- Total fluorescence quenching of **1NC/Zn-1NC** is due to excited state (exciplex) complex ((**1NP**/**Zn-1NP**) **--- CdS)** formation.

Annexure I: Home Built Variable Temperature based Infra Red Spectroscopy Attachment.

Annexure II: Undergraduate Experiment

Nitration of Phenol using $Cu(NO_3)_2$: Green Chemistry Laboratory Experiment.

Annexure III: Synthesis of strong electron acceptor compounds

Synthesis of electron acceptor compounds 2, 3, 5, 6-tetracyanodithadiene and 2, 3, 4, 5-tetracyano thiophene.

In short, the work has been divided into 8 Chapters. Thesis also contains description of Home Built Variable temperature IR assembly, Undergraduate Experiment and Synthesis of strong electron acceptor compounds as Annexure I, II and III respectively.

References:

(1) Train C.; Gruselle M.; Verdaguer M.; *Chem Soc Rev*, **40 (**2011), 3297.

(2) (a) Chorazy S.; Nakabayashi K.; Imoto K.; Mlynarski J.; Sieklucka B.; Ohkoshi S-I.; *J. Am. Chem. Soc.,* **134** (2012), 16151.

(3) (a) Crassous J.; *Chem.Soc.Rev.*, **38** (2009), 830.(b) Crassous J.; *Chem.Soc.Rev*., **48** (2012), 9669.

(4) (a) Harris M.J.; *Solid State Communications*, **84** (1992),557. (b) Ismail M. A., Jayasooriya U. A., Kettle S. F. A.; *J. Chern. Phys.* **79** (1983), 4459.

(5) Vishwakarma *A*., Ghalsasi P.; *J. Therm. Anal. Calorim.*, 2012, **107**, 155.

(6) Adams C. J., Colquhoun H. M., Crawford P. C., Lusi M., Orpen A. G.; *Angew. Chem. Int. Ed,.***46** (2007), 1124.

(7) (a) Cai S.-L., Zheng S.-R., Wen Z.-Z., Fan J., Zhang W.; *Cryst. Growth Des.*, **12 (**2012), 2355; (b) Lacour J., Hebbe-Viton V.; *Chem. Soc. Rev.*, **32** (2003) 373.

(8) (a) Willet R. D., Haugen J. A, Lebsack J., Morrey J.; *Inorganic Chemistry*, **13** (1974), 2510; (b) Bloomquist D. R., Willett R. D.; *J. Am. Chem. Soc.,* **103** (1981) 2615.

(9) Grabowaski Z. R., Rotkiewics K.; *Chem. Rev.* **103** (2003) 3899.

(10) (a) Gong, X., Milic, T., Xu, C.; *J. Am. Chem. Soc.,* **124** (2002), 14290 (b) Nitschke, C., Flaherty S.M., Kroll M., Blau W.J.; *J. Phys. Chem. B,***108** (2004), 1287 (c) A.C.S. Samia, X. Chen, C. Burda; *J. Am. Chem. Soc*., **125** (2003),15736 .

(11) Yadav U., Mande H., Ghalsasi P.; *J Chem Educ.*, **89** (2012), 268.