Chapter 1

A REVIEW OF ELECTRICAL, OPTICAL, STRUCTURAL AND SURFACE MORPHOLOGICAL PROPERTIES ON TTBNc, ZnTTBNc AND VTTBNc THIN FILMS

1.1. Introduction

Scientific advances and technological progress are often proceeding with different time constants. While the former is often higher than the latter, they nevertheless march forward in a coupled rhythm. This is perhaps nowhere better illustrated than in thin film science and technology. Scientists have made rapid and significant advances in the field of semiconducting thin film physics due to their numerous practical applications. Studies of this subject have also provided a fundamental insight into the electronic process involved, optical properties and of course the structure and surface morphology of thin films. Many new materials and devices which possess specific properties for special purposes are now available, but material limitations are often the major deterrent to the achievement of new technological advances. Engineers and materials scientists are now particularly interested in developing materials which maintain the required properties even under extreme environmental conditions. The relationship between utility and fundamental materials science is now considerably developed making efficient optimum use of organic materials also possible due to their improving quality and increasing productivity and reduced manufacturing costs.

Semiconducting nature coupled with transparency featuring organic materials increase their demand in molecular electronics and optoelectronic industries for thin film device fabrications. One of the most important fields of current interest in materials science is the fundamental aspects of thin films that escalate the application value of the material. Further betterment of thin film techniques will make these technologies more fruitful and substantially expanding the use of thin film in versatile areas.
1.2. Thin films

Thin film technology is one of the oldest arts of the newest science. Involvement of human beings in thin film technology began in the metal ages of antiquity with the efforts on precious metals like gold and silver for coating applications on vessels [1]. Thin film may be arbitrarily defined as a layer of material in solid, liquid or in gaseous phase whose thickness varies from a few nanometers to about several micrometers. In an ideal case, thin film is a homogenous solid material contained between two parallel planes and extended in X and Y directions but restricted along Z axis, which is perpendicular to X-Y plane. The dimension along Z-direction is known as thin film thickness [2].

The factors such as thin film thickness, post deposition annealing treatments, substrate temperature and irradiation with high energy electromagnetic radiations can change certain physical and chemical properties of thin films. A transition from bulk materials to thin film states may cause a drastic change in its properties as macro molecules in bulk powder form are reduced into micro level nano structures in thin film [3]. The phenomenal rise in thin film researches is due to the extensive application of thin film in diverse fields like electronics, optics, defense, medical sciences and space sciences. Development of most complex instrumentation in the above mentioned fields is, of course, due to numerous inventions in active and passive components of basic electronics, piezo electric devices, solar energy devices, magnetic memories, superconducting thin films, interference filters and antireflection coatings [4].

Thin film devices and components are preferred to their bulk counter parts due to compactness, better performance, reliability coupled with low cost of production and low packing weights. The demand for the development of smaller devices with higher speed makes it essential to concentrate on fundamental properties of thin films whether they are semiconducting, transparent or both. Semiconducting nature and optical transparency are generally regarded as two converse ideas. Combining both enhances its application in materials sciences up to future Giga Scale Integration (GSI) technology as well [5].
1.3. Organic semiconductors

Thin film technology interest in the field of organic semiconductors, has been there since decades, due to their high thermal and chemical stability. During the past few years, researchers are mainly concentrating on the device fabrication using organic semiconductors in gas sensors, solar cells, heat reflectors, protective coatings, luminescent painting applications and in the fabrication of inexpensive medical equipments [6]. Due to the high impact of nano technology and molecular electronics in common man, both developing and developed countries pay much attention to basic research in the area of organic semiconductors in order to increase their research output. Organic semiconductors are more generally defined as organic materials or compounds whose electrical conductivity lies between metals and that of insulators. Organic and metallo-organic derivatives are the basis of most of the molecular materials [7].

There are two major classes of organic semiconductors: one is organic charge transferring complexes and other is the linear backbone polymers derived from polyacetylene. Organic charge transfer complexes are similar to inorganic semiconductors in their conducting mechanisms and they possess hole/electron conduction layer with a typical band gap [8, 9]. Quantum mechanical tunneling, localized states and phonon assisted hopping are responsible for electrical conduction in polyacetylene derivatives. Several kinds of carriers mediate conductivity in organic semiconductors such as Π electrons and unpaired electrons. Even though most of the organic solids are insulators, Π conjugate systems in constituent molecules help the electron to move as Π electron cloud overlaps. Phthalocyanine class of organic semiconductors possesses this type of conduction mechanism [10].

Early reports on organic semiconductors appear in 1963 by Weiss et al. for passive high conducting iodine-“doped” oxidized polypyrrole [11]. Likewise an organic electronic device is reported in 1974 by John McGinness and his co workers on State and hallmark negative differential resistances in DOPA Melanin [12]. Analogous rigid-backbone organic semiconductors are now used as active
elements in optoelectronic devices such as organic light emitting diodes (OLED), organic field effect transistors (OFET) and recently in bio sensing applications due to their advantages such as easy fabrication, mechanical flexibility and low cost. Processing of organic semiconducting materials is more important since most of the organic materials are insoluble in universal solvent like water. So chemical methods are not viable for industrial manufacture. Most of the \( \Pi \) conjugated organic molecules are expensive in powder form and they decompose at very large temperature. Hence it is more suitable to transform powder into thin film form by room temperature evaporation techniques for large area thin film production. This approach yields amorphous or polycrystalline films with a moderate degree of disorder [13].

Organic semiconductors differ from their inorganic counter parts in many ways. The physical and chemical properties of organic semiconductors depend on their molecular structure and on the presence of impurities. In order to design and model the organic semiconductors, one should be aware of its electrical, optical structural and surface morphological properties [14]. Even though the electrical conductivity and carrier concentration are low compared to inorganic semiconductors, it gives negative temperature coefficient of resistance on annealing and substrate heating. Electrical conductivity of organic semiconductors can be measured using two probe and four probe conductivity measurements. Optical spectra for this class of materials can be obtained using UV-Visible absorption spectrometer and photoluminescence spectrometer [15]. Chemical composition and structure of organic semiconductors are determined by Carbon Hydrogen Nitrogen Sulphur (CHNS) analysis and X-ray diffractogram techniques (XRD). Semiconductor film appearance and morphology can be studied with Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) [16].

In addition to experimental characterization, there has been some theoretical study in electrical conductivity due to the application of low electric field. Li et al. observed that the conductivity of organic semiconductor is proportional to \( T^{-1/4} \) and in high electric filed it is proportional to \( e^{-\Delta E/aT} \), where “a” is a constant of material. From the above studies low temperature parameters
like Fermi energy and hopping distance can be calculated [17]. Optical absorption and reflection spectra also give light towards theoretical studies like that reported by Lenski et al. on different optical parameters like refractive index, various energy losses and optical conductivity of organic semiconductors. Knowledge of the relationship between molecular structure and semiconducting properties of organic compounds, allows the design of novel materials with pre-defined and controlled properties [18].

1.4. Phthalocyanines

Among different organic semiconductors, a class of macro cyclic hydrocarbon compounds having an alternating hydrogen atom carbon atom ring structure is predefined as phthalocyanines exhibiting semiconducting properties. Most of the simple phthalocyanines are P-type materials, their complex molecules and derivatives having large carrier concentration make them act as N-type materials. The versatility and architectural flexibility make them eligible for electronic industries and photonic device technologies. The name Phthalocyanine is derived from Greek terms naphtha (rock oil) and cyanine (dark blue) [19]. The term Phthalocyanine was first used by Reginald P. Linstead of Imperial College of Science and Technology in the year 1933 to describe the class of organic compounds [20]. Phthalocyanine class of compounds consists of metal derivatives of Phthalocyanine. The two hydrogen atoms in the center of the molecule can be replaced by metals from every group in the periodic table to form the group of compounds known as metal phthalocyanines. Also, from 1 to 16 of the peripheral hydrogen atoms in the four benzene rings in the Phthalocyanine molecule can be replaced by the halogen atoms and by numerous organic and inorganic groups. More than forty metal phthalocyanines have been prepared and several thousand different Phthalocyanine type compounds have been synthesized [21].

All Phthalocyanine compounds absorb light on both sides of the blue-green portion of the visible spectrum. Therefore, “Phthalocyanine” is an apt nomenclature for all members of the Phthalocyanine class. Not only are the phthalocyanines a new class of organic compounds but also they constitute a new
class of colouring matter having moderate cost, good stability and functional properties, in the region of visible spectrum. Absorption spectra of phthalocyanines lies in ultraviolet region are however sparse, since the Phthalocyanine dispersion media are commonly aromatic in nature [22]. Assuming the \( \Pi \) electrons in the phthalocyanines are a one dimensional free-electron gas, each contains two electrons, in accordance with Pauli’s exclusion principle and they resonate between two equivalent limiting structures of the Phthalocyanine ring with constant potential energy along its length. The absorption maxima value of Phthalocyanine lie between 6000 and 7000\( \text{Å} \). The spectra of metallic derivatives of phthalocyanines and addition of different aza group to metal free Phthalocyanine ring changes the absorption maxima to 1000-2000\( \text{Å} \) towards the right or left with respect to the above mentioned region of absorption [23, 24].

The electrical conductivity in Phthalocyanine was first observed by Eley and Vartanyan in 1948 and they measured the unusual temperature dependence of resistivity of phthalocyanines and its metal derivatives. They measured the specific conductivity of Phthalocyanine to be about \( 5 \times 10^{-5} \text{ohm}^{-1} \text{cm}^{-1} \) and they found that it decreases in the case of metal phthalocyanines and with no change in conductivity due to low energy beams (visible and ultra violet light) irradiation [25]. Heating of magnesium Phthalocyanine in oxygen can increase its conductivity by \( 10^2 \) fold with respect to prepared powder [26]. The semiconducting nature of thin films of Phthalocyanine also shows a tremendous increase in conductivity; that is Zinc Phthalocyanine thin films show \( 10^{-12}-10^{-13} \text{ohm}^{-1} \text{m}^{-1} \) in its conductivity with activation energy of 1.7-1.8eV [27]. The semiconductivity of phthalocyanines is considered to be intrinsic although the variation of results indicates that impurities, anisotropic strains, crystal imperfections, contacts and surface conditions may influence the observed values [28].

The structural and surface morphological properties of phthalocyanines include X-ray structure determination, polymorphism and different electron microscopical studies. In his work on Phthalocyanine, Robertson accomplished the first direct X-ray analysis of an organic molecule, not even involving the assumption of the presence of discrete atoms due to the molecular arrangement
having centers of symmetry, at which different metal atoms can be inserted by means of chemical reactions without appreciable alternation in the chemical structure [29]. In metal phthalocyanines, the dimensions of molecules are very similar for several compounds examined with slight variation in nitrogen-metal distances due to the differences in the radii of atoms. The similarity of crystal structure in X-ray analysis of different phthalocyanines accounts for their unaltered large rigid framework which is not altered in size or form by the entrance of metal atom in its center or addition of any organic group in basic benzene ring [30].

Surface morphology of phthalocyanines may vary in accordance with annealing temperature, thickness, substrate temperature and irradiation treatments. The change in its topology is mainly due to the phase transformation from $\alpha$ to $\beta$ in simple phthalocyanines while the re-arrangements of $\Pi$ conjugated atoms occur on surface levels in complex phthalocyanines. Most commonly needle/wire type patterns are observed in powder phthalocyanines and whisker surface patterns in thin film form [31]. There are also reports on nano structures on Phthalocyanine materials such as nano flowers, rods, ribbons and wire like patterns formed due to agglomeration of Phthalocyanine seeds due to thin film formation and temperature application on films [32].

High energy electromagnetic radiations like gamma ray irradiation on different Phthalocyanine thick films can change their optical and electrical properties. Ebraheem et al. reported that high gamma irradiation dosage on organic dyes can change their optical properties making them the best candidate for dosimetric applications [33]. Gamma ray irradiation effects on Phthalocyanine thin films are studied by Abu El-Fadl et al. The study reveals that electrical conductivity is affected by high energy electromagnetic radiation [34].

Commercial application of Phthalocyanine can be enhanced by combining various properties of phthalocyanines. The oldest application of Phthalocyanine is as dyeing agent and colourant. Textile industries, paint manufacturing, printing ink preparation, applications in plastic materials, miscellaneous colourant fields are benefited for Phthalocyanine colourants applications. No major colourant application of Phthalocyanine lies in the area of catalysts, lubricating greases,
applications in analytical chemistry as oxidizing agents and acts as good medical components \textit{in vivo} cancer treatments. Metal Phthalocyanine is used in electrical industries for insulating coatings of conductors and multi layered coils. The addition of 0.1 to 10\% of Phthalocyanine to poly phenyl coolants for nuclear reactors improves their resistance to deterioration induced by exposure to neutron irradiation at high temperatures. Nowadays the choice of Phthalocyanine type materials are adequate for research since the novelty of such materials in molecular electronics is increasing day by day and the electrical studies of most of its derivatives are not even reported by the basic researchers for the device fabrications \cite{35}.

1.5. Phthalocyanine-type compounds: Naphthalocyanines

Phthalocyanine-type compounds are defined as porphin derivatives with one, two, three or four aza groups joining the pyrrole nuclei, with one or more inorganic-organic groups replacing the $\beta$ hydrogen atoms, and with any suitable metal replacing the two hydrogen atoms in the center of the molecule. From 1 to 8 of the $\beta$ hydrogen atoms may be replaced. Phthalocyanine-type compounds, like the phthalocyanines, are pigments, being insoluble in aqueous solutions and common organic solvents. Replacement of at least 40 different central metal atoms are possible in naphthalocyanines for one to three aza links on methane links and an array of substitutions in various inorganic-organic groupings. Eight available positions along the periphery of the porphin molecule, it would appear possible to synthesize several hundred thousand Phthalocyanine type compounds \cite{36}.

One of the first Phthalocyanine-type molecules to be synthesized was Naphthalocyanine with 56 conjugated $\Pi$ electrons. 1,2-Naphthalocyanine (tetra-3,4 benzo Phthalocyanine) and 2,3-Naphthalocyanine have been synthesized by Linstead and co-workers from 1,2 and 2,3 dicyanonaphthalene. Their stability and optical properties investigated at the end of 1960s. Naphthalocyanines also have been made by Farbenindustrie in the same period of Linstead \cite{37}. The properties of naphthalocyanines are almost similar to the properties of phthalocyanines. The compounds are dark green with a blue to purple luster; sublimable; and they may
be purified by crystallization from high-boiling solvents. Naphthalocyanines (NPc) are more stable to heat and are more inert chemically than the corresponding Phthalocyanine counterparts; however both of them are equally stable in concentrated sulphuric acid. In synthesis, naphthalocyanines turn to form a greenish blue solid, which is kept in the form of an aqueous paste for the purpose of diazotization and coupling with azo coupling components and it turns greenish yellow when it forms thin film under room temperature. Since it was found that the solubility of unsubstituted metal-free and transition-metal 2,3 NPc is very low in common organic solvents, early efforts on substituted 2,3 NPcs were focused on the preparation of soluble 2,3 Naphthalocyanine derivatives. This led to the preparation of tert-butyl added ligands on 2,3 Naphthalocyanines at the beginning of seventeens. The major substitution reactions for the ligands addition on 2,3 naphthalocyanines are Diels-Alder reaction and high temperature catalytic transformations [38].

Phthalocyanine (Pc) and NPc, as close relatives of naturally occurring Porphirin, are notable for their strong tendency for co-facial association and self-aggregation, which results in poor solubility, especially in polar protic solvents, and greatly influences the intrinsic nature of the macro cycles, including their spectroscopic, photophysical, electrochemical, and conducting properties. Naphthalocyanine dendrimers, bearing eight BHT-derived Fréchet type dendrons on the periphery and NPc as the core, have been synthesized to address the aggregation issues. The study of anti-aggregative properties of NPc dendrimers by UV-Visible spectroscopy demonstrated that the second generation of NPc dendrimers exhibit non-aggregating property in both DCM solution and thin film. Synthesis of asymmetric Pc/NPc by “Capture-ROMP-Release” method has also been investigated as a different approach to control self-aggregation pattern. The asymmetric Pc, tagged with an acid-labile and cross linkable norbornene, was synthesized by a statistical condensation between two different phthalonitriles. Ring-opening-metathesis-polymerization on the norbornene tagged asymmetric Pc has yet to be investigated [39].
A detailed and complete study on properties and structural features of 2,3 Naphthalocyanine thin film was first undertaken by Kaplan et al. They mention that 2,3 naphthalocyanine thin films are strong absorbers in near infrared region and thus make them potentially useful as optical data recording media. Metal free, Magnesium, Vanadyl, Copper and Tin Naphthalocyanines are used by Kaplan et al. to show different properties and applications. The absorption studies on naphthalocyanines reveal that most of the Naphthalocyanine thin films have absorption maxima ranging from 6000Å\textsuperscript{0} to 8500Å\textsuperscript{0}. The absorption coefficients of thin films of several phthalocyanines are similar to NPcs and the value is about 3x10\textsuperscript{5}. The electrical properties of room temperature Naphthalocyanine thin films show the semiconducting region in electrical conductivity with a significant lower resistance for metal free Naphthalocyanine thin film as compared to the metal NPcs [40].

Analysis of the structural properties, like X-ray analysis of the above mentioned Naphthalocyanine thin films has revealed that Vanadyl Naphthalocyanine thin films have the highest degree of crystallinity and broadened diffraction peaks than the others. There is only standard JCPDF data for Zinc 2,3 naphthalocyanines (ZnNPc), so the others get compared with ZnNPc. Kaplan et al. also mention that the full structural determination, must await for the preparation of single crystals of these naphthalocyanines. Surface morphological studies on naphthalocyanines have drawn much attention of the scientists from the end of last century. In the scanning electron microscopy of heat treated Vanadyl naphthalocyanines thin films, there is gross particle compared to the smooth surface pattern of as deposited sample [40]. Recently nano tubes fabricated from nickel Naphthalocyanine thin films by a template method are well explained by the SEM and TEM image. In addition to finding the difference in surface morphology, the variation in particle size is also measured using atomic force microscopic image (AFM) of Zinc and Vanadyl NPc thin films deposited on glass and NaCl substrates [41].

The main application of naphthalocyanines, especially Silicon NPc, is in the medical field, in the area of photo sensitizers for pharmacokinetic and in tissue distribution [42]. In photonics, Gallium naphthalocyanines are used for optical
limiters of intense light and are useful for varying their nonlinear optical properties [43]. In optoelectronic applications, naphthalocyanines accounts for the fabrication of organic light emitting diodes, in solid state lasers and as photo sensitizers [44]. Recently Nickel Naphthalocyanines (NiNPs) are used as nano tubes in nano electronics with walls consisting of well ordered NPC molecular disk. Thermal treatment of Nickel Naphthalocyanines with Graphenes at 600°C produced carbonized nano tubes containing ordered columnar, graphitic wall structures. These nano tubes of NiNPC are suitable for application of nano device fabrication [45].

1.5.1. Metal free 2, 11, 20, 29 Tetra Tert-Butyl 2,3 Naphthalocyanine (TTBNc)

Tert-butyl addition to the fourth position of benzene ring in 2,3 naphthalocyanines with aza groups on different positions form 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanine (TTBNc) with an empirical formula C_{64}H_{58}N_{8}. Tert-Butyl addition to the NPCs enhances the synthesis of materials, improves its stability which in turn causes a pronounced shift of Q-bands towards the longer wavelength due to the increase of fundamental benzo units. This results in the extra stability of tetra tert substituted naphthalocyanines apart from NPCs. The molecular weight is 939.20 with 97% dye content and possesses absorption maxima near 784nm [46]. The molecular structure of TTBNc is as shown in Figure 1.1.

The main difference of TTBNc from the basic Phthalocyanine ring is due to the additional benzene ring in each branch. Like that of metal free Phthalocyanine, the central hydrogen atom is co-ordinate with the nitrogen in aromatic ring structure. In the figure "t-Bu" represents “tert-butyl” group and can be seen in each branch of benzene rings in the fourth position of outermost unit. Like that of metal free phthalocyanines, TTBNc also have melting point greater than 300°C. So, in order to make thin film of TTBNc using physical vapour deposition, a higher temperature (> 300°C), as sublimation temperature is needed [46].
Figure 1.1 Molecular structure of Tera Tert-Butyl 2,3 Naphthalocyanine (TTBNc)

Physical Vapour Deposition (PVD) technique can be used for the preparation of TTBNc thin films with varied thickness ranging from 10nm to several micro meters. The basic physical and chemical properties of TTBNc thin films are listed in Table 1.1.

Freyer et al. [47] compared TTBNc solution with thin film in absorption bands. Particularly Q-band region are shifted and broadened to longer wavelength region 797-718nm in their studies. Intensity of B-band around 300nm is independent of the material nature. As the thickness of TTBNc thin films increases, there is a splitting of Q-bands into Q_x and Q_y transitions. Absorption spectra of low thickness (<100nm) TTBNc films attributed to the reduction of D_{2h} symmetry close to D_{4h} symmetry. Large \Pi system connected TTBNc thin film thickness influences both absorption pattern and position of maxima. Annealing effects also arise in the broadening of Q-bands and increase the intensity of B-bands with a blue shift in the intense peaks.

There are reported optical and photo electron spectroscopic studies based on TTBNc thin films. Electrical conductivity studies on TTBNc, both in bulk form and in the area of molecular electronics, are not done yet. Structural and surface morphological studies are limited in TTBNc thin films since it is a complex level molecule suitable for opto-electrical device fabrications. The \Pi conjugated molecules in TTBNc find it suitable for irradiation studies even though it is not
Table 1.1 Physical and chemical properties of TTBNc

<table>
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<tr>
<th>Material</th>
<th>Physical properties</th>
<th>Chemical properties</th>
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<tbody>
<tr>
<td>Metal free, 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanines (TTBNc)</td>
<td>Colour: dark green</td>
<td>Chemically inert</td>
</tr>
<tr>
<td></td>
<td>Melting point: 375°C</td>
<td>Photoluminescent material</td>
</tr>
<tr>
<td></td>
<td>Sublimation temperature: 500°C</td>
<td>Insoluble in water and soluble in CHCl₃ &amp; CCl₄</td>
</tr>
<tr>
<td></td>
<td>Absorption maxima: 784nm</td>
<td>Structural variations due to the difference in the number of peripheral substitutions and adatoms like axial ligands</td>
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<td></td>
<td>Maximum conductivity in room temperature: 4.5x10⁻³ ohm⁻¹m⁻¹</td>
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reported. General application of TTBNc mainly resides in the medical fields especially in vivo cancer treatments, electronic device fabrication such as solar cells, holographic storage applications by making use of spectral and hole-burning properties and act as good IR functional dyes. Metal free TTBNc is also a good luminescent material for coating applications [47].

1.5.2. Zinc 2,11,20,29 Tetra Tert-Butyl 2, 3 Naphthalocyanine (ZnTTBNc)

Hydrogen co-ordination with nitrogen at the center of TTBNc is replaced by zinc metal to form ZnTTBNc and all the peculiarities like axial ligands, number of benzene ring remain similar to TTBNc. It is having empirical formula C₆₄H₅₆N₈Zn with a dye content of 90%. Its melting point is greater than 300°C with UV-Visible absorption maxima near the IR region of electromagnetic spectrum around 769nm. It is a heavier aromatic compound than TTBNc with a molecular weight of 1002.57amu. It also comes under the region of IR functional dyes with wide applications in organic electronics and in photonics [48]. The basic molecular structure of ZnTTBNc is shown in Figure 1.2.
The general properties of ZnTTBNc are enlisted in Table 1.2. ZnTTBNc thin films can be prepared under physical vapour deposition technique with a suitable sublimation temperature. The Zinc atom has a full 3d shell in the ground state of these molecules. Therefore, the absorption spectra of ZnTTBNc show no ligands to metal and metal to ligands charge transfer bands, and it possesses the electronic states of the reduced symmetry ($D_{4h}$) ring [49].

For ZnTTBNc thin films, the optical absorption Q bands are blue shifted with respect to Phthalocyanine counter parts and annealed samples. Photoelectron spectroscopical and UV-Visible absorption studies are reported in the area of ZnTTBNc thin films and in solution form while the structural and surface morphological studies are limited. Homogenous distributions of agglomerated spherical protrusions are obtained for the surface morphology pattern from atomic force microscopic analysis of ZnTTBNc thin films having lower thickness (60nm). Main application of ZnTTBNc thin film resides in photo emission field due to the satellite features. It is also a best candidate for holographic storage device preparation like that of TTBNc thin films [50].
Table 1.2 Physical and chemical properties of ZnTTBNc

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<tr>
<th>Material</th>
<th>Physical properties</th>
<th>Chemical properties</th>
</tr>
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<tbody>
<tr>
<td>Zinc 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanines (ZnTTBNc)</td>
<td>Colour: dark green&lt;br&gt;Melting point: 360°C&lt;br&gt;Sublimation temperature: 500°C&lt;br&gt;Absorption maxima: 769nm&lt;br&gt;Maximum conductivity in room temperature: 0.99x10^{-3} ohm^{-1}m^{-1}</td>
<td>Chemically inert&lt;br&gt;Photoluminescent material&lt;br&gt;Insoluble in water and soluble in pyridine, dichloro methane&lt;br&gt;Photo chemically active</td>
</tr>
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1.5.3. Vanadyl 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanine (VTTBNc)

In TTBNc, co-ordination of nitrogen atom with two hydrogen atoms at the center is replaced by “V=O” to form VTTBNc. The addition of an unsaturated double bond link towards the central metal atom changes its properties to an extend from metal free and Zinc TTBNc. VTTBNc possess a larger atomic weight of 1004.12amu compared with the other two materials mentioned above. The molecular structure of VTTBNc with an empirical formula C_{64}H_{56}N_{8}OV is shown in Figure 1.3. Its compositional dye content is about 95% with a melting point greater than 300°C. The basic physical and chemical properties are enlisted in Table 1.3. VTTBNc thin films can also be prepared under vacuum evaporation technique and the thickness can vary between 10nm to several micro meters [51]. It is having high yield of nonlinear optical properties due to the generation of third harmonic optical susceptibility.

Figure 1.3 Molecular structure of Vanadyl Tera Tert-Butyl 2,3 Naphthalocyanine (VTTBNc)
Major physical and chemical properties of VTTBNc are listed in Table 1.3. There is a very small splitting of Q bands for as deposited VTTBNc thin films and it gets broadened by changing its physical conditions due to the symmetry for the material thin film close to $D_{4h}$. It leads to small splitting between D levels. This material is electrically and optically more active apart from metal free and ZnTTBNc thin films due to the presence of unsaturated double bond apart from the $\Pi$ conjugated system and bulky appearance of tert-butyl group [51]. This material is absolutely novel and there are few valuable early reports on different properties and application level aspects apart from the patent company reports.

Table 1.3 Physical and chemical properties of VTTBNc

<table>
<thead>
<tr>
<th>Material</th>
<th>Physical properties</th>
<th>Chemical properties</th>
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<tbody>
<tr>
<td>Vanadyl 2,11,20,29 Tetra Tert-Butyl 2,3 Naphthalocyanines (VTTBNc)</td>
<td>Colour: dark green</td>
<td>Chemically inert</td>
</tr>
<tr>
<td></td>
<td>Melting point: 315°C</td>
<td>Electroluminescent material</td>
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<tr>
<td></td>
<td>Sublimation temperature: 500°C</td>
<td>Insoluble in water and soluble in benzene and dichloro methane</td>
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<tr>
<td></td>
<td>Absorption maxima: 808nm</td>
<td>Nonlinear optical material</td>
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<td></td>
<td>Maximum conductivity in room temperature: $7.4 \times 10^{-4}$ ohm$^{-1}$ m$^{-1}$</td>
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</table>

1.6. Survey of earlier studies on TTBNc, ZnTTBNc and VTTBNc

The first known report on Tetra Tert-Butyl 2,3 Naphthalocyanine (TTBNc) is by Kobayashi et al. and the U.S. patent regarding the material corresponding to Baumann et al. [52, 53]. TTBNc is a novel Phthalocyanine type material which got commercialized a few years back. Thus review papers regarding this material are comparatively lesser in number. Considering the fact that most of the properties of Phthalocyanine repeats in Naphthalocyanine, it is more apt to go through the recent progress in Phthalocyanine materials. Phthalocyanine is an intensely blue-green coloured macro cyclic compound that is widely used in dyeing and is now used in nanotechnology as colour pigments. Phthalocyanines form co-ordination compounds with most elements of the periodic table. These complexes are also intensely coloured and are also used as dyes and pigments. First study on metal free Phthalocyanine came in the year 1907. Further the metal substituted phthal
and naphthalocyanines were first synthesized in the year 1927 in Sweden [54, 55]. They remarked on the enormous stability of these complexes but did not further characterize these blue complexes. Many Phthalocyanine compounds are thermally stable over a wide range of temperature and they do not melt but can be easily sublimable as reported by Unni et al. [56]. Unsubstituted phthalocyanines and its complexes are studied by Seoudi et al. who record the difficulty to dissolve them in organic solvents even though metal free and copper Phthalocyanine is easily soluble in sulphuric acid due to the protonation of the nitrogen atoms bridging the pyrrole ring. Metal free Phthalocyanine strongly absorbs light between 600-700nm. Thus, these materials are seen to be blue or green in colour. Substitution can shift the absorption towards longer wavelengths, changing the colour from pure blue to green (when the absorption is in the near infrared) [57]. From the year 2000, there has been a huge development in the area of producing Phthalocyanine class of thin films for basic research purpose as well as in the area of device fabrication. The electrical conductivity in semiconducting region of this class of compounds makes them attractive candidates in the area of electronic industries. The first report on semiconducting behaviour of bulk Phthalocyanine was by Eley and Vartanyan [58]. In due course, these measurements have been reported by many workers on metal Phthalocyanine films. Abdel-Malik made D.C measurements in FePc dispersed in a polymer binder and obtained the activation energies of both $\alpha$ and $\beta$ phases [59]. Annealing effects on metal Phthalocyanine thin film has drawn much attraction since it causes a negative temperature coefficient of resistance and decrease in energy for activation due to the creation of more trapping levels as suggested by Fu Ren Fan et al. [60]. Thickness variation in metal Pc thin films reduces the activation enthalpy. Heating on glass substrate can also influence both metal free and metal substituted phthalocyanines establishing more interesting results in electrical and optical properties. In addition to the above mentioned parameters, there is an impact of high energy radiation like gamma ray on the surface of Phthalocyanine thin films. This will lead to an increase in D.C electrical conductivity due to defect level conduction mechanism and a decrease in band gap
energy due to the creation of more and more trapping levels between the major bands as obtained by Rejimol et al. [61].

During the past decades, most of the Phthalocyanine and its complexes were mainly used for organic colour pigments. Patent reports from Shuji et al. describe that Copper Phthalocyanine (CuPc) dyes are produced by introducing soluble groups, such as one or more sulphonic acid functions. These dyes find extensive use in various areas of textile dyeing (Direct dyes for cotton), for spin dyeing and in the paper industry. Direct blue 86 is the sodium salt of CPC-sulfonic acid whereas direct blue 199 is the quaternary ammonium salt of the CPC-sulfonic acid. The quaternary ammonium salts of these sulfonic acids are used as solvent dyes because of their solubility in organic solvents (e.g. Solvent Blue 38 and Solvent Blue 48). The dye derived from cobalt Phthalocyanine and an amine is Phthalogen Dye IBN. 1,3-Diiminoisoindolene, the intermediate formed during Phthalocyanine manufacture, used in combination with a copper salt affords the dye GK 161 are some examples of Phthalocyanine for their use as dyes and pigments [62]. In addition to that, classically, most of the metal phthalocyanines are used as catalysts for redox reactions and the sweetening of gas streams by removal of hydrogen sulfide by patent reports of Kaufman et al. [63]. From the end of 1900s, Phthalocyanine class of materials has been a part of electronic industry for the fabrication of active components like Schottky diode fabrication, thin film transistors, gamma ray dosimeters etc. like that mentioned by Mclaughlin et al. [64]. Phthalocyanine materials are known for their potential application in molecular electronics and in nano technology and are clubbed recently in hot research publications with bukky balls such as Fullerene (C\textsubscript{60}) due to the establishment of perfect partner for photo and electro active molecular systems as per the reports of Lof et al. [65]. Studies based on nano solar energy device fabrication and nano sensor are going on for future aspects as suggested by Kroon et al. [66].

Medical application of Phthalocyanine and Naphthalocyanine retains its importance from decades back to the present century. Notable properties of phthalocyanines for its medicinal use are their intense colour and incredible stability
to light, acid, and oxygen and their very low solubility in all solvents. Generally, most of the dyes derived from the phthalocyanines are aggregates. Constituents on the aromatic ring produce water-soluble complexes. Metalated phthalocyanines and naphthalocyanines have been studied most extensively for use in Photo Dynamic Therapy (PDT), an effective method for cancer treatments. Because of the interest in phthalocyanines as catalysts and photo catalysts, a large amount of literature has been released about their photochemical triplet lifetimes exists [67, 68]. Bio distribution studies by Chang et al. utilizing fluorescence of the disaggregated tissue showed that the chloroaluminum sulfonated phthalocyanines were taken up preferentially by tumors over normal tissues such as muscle and skin. Another area of interest is the photo radiative therapy with gamma irradiated phthalocyanines. In Morgan’s studies on gamma irradiation therapy, Phthalocyanines and its 6 complexes are injected into the blood of tumorous rats that continuous gamma irradiation for 4 to 24h treatment, it is found that tumor blood flow is significantly reduced. No large inherent toxicity has been found for most of the phthalocyanine’s use in medical field. However, some toxicity of cell lines maintained in the dark has been indicated in vitro for the aluminum nonsulfonated and sulfonated phthalocyanines at rather high dosage ranges. These lie well beyond those used for therapy. Because of their ease of synthesis and their general effectiveness, the future looks good for these compounds as agents for PDT [69].

As an important derivative of phthalocyanines, naphthalocyanines receive much attention as a component in the development of IBM’s single- molecule logic switch as suggested by Liljeroth et al. [70]. There are so many wiki patents regarding the different methods of preparation, types and general formulae and various application like electrophoresis display, optical recording medium and radiation sensitive coating films for naphthalocyanines and its complexes. Most of the physical properties like optical, electrical and thermal properties of phthalocyanines duplicate in naphthalocyanines. Its chemical nature is apparently different as it is having dark green colour and is soluble in concentrated acids and other organic solvents like carbon tetra chloride and benzene. Borodkin and Smirnov have first reported the chemical synthesis of Naphthalocyanine and its
analogs [71]. Photo conductivity studies and photo thermal sensitization process are mainly dealt with different naphthalocyanines. This makes the class of naphthalocyanines as active components in bio distribution of several photo dynamical efficient elements for PDT therapy in cancer treatments. Another application in photo physics, regarding naphthalocyanines, especially halogenated (metal-group (III)) Naphthalocyanine for their optical power limiting properties. It is due to the higher ratio of excited state absorption cross section to the ground state absorption cross section. Silicon 2, 3 naphthalocyanines are enormously used in pharmacokinetics and tissue distribution studies as a good photo sensitizer in medical field as per the study of Biolo et al. [72].

One of the initial reviews by Sigma Aldrich Co. on Functional infrared (IR) dyes, the metal substituted and metal free Tetra Tert-Butyl 2,3 Naphthalocyanines classify themselves as class of materials which perform like organic dyeing agents. Materials property also includes complete transparency near IR region of absorption spectrum. Tert-Butyl addition on the fourth position of benzene ring enhances the ease of synthesis and stability improvement which in turn causes a pronounced shift of Q bands towards the longer wavelength region due to the increase of fundamental benzo units. Sens et al. has obtained the patent regarding TTBNc as a functional organic dye for the application of optical data storage devices by making use of diode lasers [73]. They performed the storage media by fixing of TTBNc colouring matter onto the transparent substrate and had most preferably performed by a coating method.

Initially, Freyer et al. reported the thin film aspect and solution type form of TTBNc for some optical properties [74]. A complete study in optical properties of this material composed of Micro-Raman analysis and luminescence spectroscopic studies based on laser excitation with UV-Visible absorption spectra. Thin film preparation of TTBNc in the above described paper is done by means of vacuum sublimation technique onto quartz cover slides under high vacuum conditions with a sublimation temperature of 500°C. In addition to optical studies, surface morphology studies are also done by atomic force microscopic technique in a contact mode NanoscopeIII, Digital instruments.
Major results arrived from the optical and surface morphological studies on TTBNc thin films show that they exhibit a stronger broad Q bands with a splitting of Qx and Qy components in UV-spectroscopy analysis and exhibit two luminescent bands with different stokes shifts. Raman spectroscopic modes for TTBNc thin film are similar to TTBNc solution and a measure of degree of benzo annealing is obtained from the study [74].

1.6.1. Electrical properties

Most of the phthalocyanines and simple naphthalocyanines are extensively studied for electronic applications. Nowadays, soluble precursors of phthalocyanines and 2,3 naphthalocyanines combinations are converted into insoluble sandwich thin film for transistor applications as explained by Hirao et al. [75]. As TTBNc thin films are derivatives of 2,3 naphthalocyanines, it is more adequate to study the detailed review of 2,3 naphthalocyanines from the earlier reports for the present and future aspects. The first reported electrical studies regarding Ruthenium TTBNc thin film was by Hanack et al. There was only some very sketchy data on 2,3 naphthalocyanines (NPcs) [76]. The activation energy for conductivity in Vanadyl NPc (VNPc) is reported to be 0.35eV, by Thomas et al. and the electrical conductivity of VNPc increases with doping of iodine [77]. Another study regarding naphthalocyanines is the conductivity of amorphous Zn 1,2 NPc, grown directly on a brass substrates by Kuznetsova et al. From this work, the carrier density and mobility at 300K are found to be $3 \times 10^{12}$cm$^{-3}$ and 0.5cm$^2$V$^{-1}$S$^{-1}$ respectively. This result encompasses the clear evidence of polarons as the charge carriers [78]. Kaplan and his co-workers measured the room temperature resistivity of several NPcs together with the resistivity of Metal free Phthalocyanine (H$_2$Pc) for comparison. From the above study, it is revealed that the resistivity of metal free naphthalocyanines is significantly lower than that of metal 2,3 naphthalocyanines [40].

Report on first titanium complex of 2,3 NPcs (TiONPc) was made with its electrical properties by Law et al. [79]. The method of preparation of TiONPc is similar to that employed by Pac and co-workers in the synthesis of unsubstituted TiOPc [80]. The electrical properties of complex TiONPc include the dark
conduction with temperature and activation enthalpy by making use of Arrhenius equation. The semiconducting property of TiONPc in room temperature was in the range of $10^{-8}$-$10^{-9}$Ω cm$^{-1}$ which seems to be higher than the values reported for similar phthalocyanines. There is also an indication of Arrhenius plot for TiONPc thin film that the graph shows two distinct linear regions of different activation energies ($E_1=0.24$eV and $E_2=0.41$eV) with no sign of sharp transition [79].

As compared to single crystals of 2,3 naphthalocyanines, most of its complexes possess stable electrical conductivity. By taking one such case, single crystals of Cobalt 2,3 Naphthalocyanine (CoNPc) is prepared by Naoko Matsumura et al. and electro chemical oxidation is done to transform the material to a complex aceto nitrile- dichloro benzene dicyano 2,3 naphthalocyanato cobalt (III) \{Co(2,3Nc)(CN)$_2$CH$_3$CN\}. In electrical conductivity studies, the single crystals of CoNPc are found to be not as stable as that of its complex counterpart. They reported the temperature dependence of resistivity for the above mentioned complex of Cobalt and its semiconducting nature (conductivity=0.3Scm$^{-1}$) with activation enthalpy 0.11eV. Also they found that the values of electrical measurements for Cobalt complex 2,3 naphthalocyanines are comparable to that of Phthalocyanine neutral radical crystal with three dimensional Π-Π stacking interactions [81].

Yamana et al. noticed that the effect of heat treatment on oxidative gas adsorption causes a change in conductivity of Lead 2,3 Naphthalocyanines (PbNPcs) and that will inturn produce good gas sensors. Thin films of PbNPcs are reported with a change in conductivity due to the exposure of 5ppm NO$_2$ in N$_2$ at 210°C. The results for gas exposure and simultaneous heat treatments are encoded that the amount of NO$_2$ and O$_2$ adsorbed at room temperature increase with prolonging heat treatment time for the film up to 10h, making the desorption in the higher temperature region more prominent [82].

In addition to 2,3 naphthalocyanines, 1,2 Naphthalocyanine metal complexes are known for their conducting phenomena. Similar to the above mentioned result, Gacho et al. reported one dimensional conductor of axially substituted species with C$_{4h}$ isomer of Cobalt 1,2 Naphthalocyanine cyanato
complex \( \text{Co}^{III}(1,2-\text{Nc-C}_4h)(\text{CN})_2 \) anion. The crystal comprises of slipped stacked one dimensional chain and one dimensional array of tetra phenyl phosphonions. The conductivity at room temperature for the above metal 1,2 naphthalocyanato complexes is about \( 0.1 \Omega^{-1}\text{cm}^{-1} \) and the temperature dependence is semiconducting with a small activation enthalpy of 0.05eV [83].

Tetra Tert-Butyl addition to Phthalocyanine ring can cause a drastic change in its conductivity. Michael Hanack et al. reported the electrical properties of Tetra-tert-butyl 2,3 Naphthalocyaninato Ruthenium-II (RTTBNc). They compare the properties with the corresponding Phthalocyanine. The electrical conductivity of RTTBNc is found to be \( 1.2 \times 10^{-5} \Omega^{-1}\text{cm}^{-1} \) and that obtained from Ruthenium tetra tert-butyl Phthalocyanine is \( 3.4 \times 10^{-7} \Omega^{-1}\text{cm}^{-1} \). The explanation for such a high conducting nature of tert-butyl bearing Naphthalocyanine and Phthalocyanine is explained by the dimeric structure in the solid state [76]. In another study of Nickel Tetra Tert-Butyl Phthalocyanine multilayer thin film systems, Rikukawa and his co-workers studied the effect of electrical conductivity in thin films with suitable dopents like I\(_2\) and SbCl\(_5\). Conductivities in range of \( 10^{-2}-10^{-3} \Omega^{-1}\text{cm}^{-1} \) were observed in films containing a 5:1 mole ratio of poly 3-hexylthiopene to Phthalocyanine [84]. Post evaporation annealing treatments on Cu(II) Pc thin films as reported by Wang Ting-Ting et al. gives a valuable result in common Pc thin films that the class of materials shows a negative temperature coefficient of resistance (TCR) and a decrease in activation energy due to annealing effect by showing both A.C and D.C conductivity [85]. Effect of thickness and substrate temperature on different ZnPc thin films as studied by Senthilarasu et al. suggest three distinct linear regions for conductivity and it arise variation in activation energy [86]. High energy irradiation treatments like gamma irradiation effect on electrical properties of Manganese Pc thin films are studied by Arshak et al. They change the dosage of irradiation on MnPc and find them suitable for gamma-radiation sensors by the property of Schottky conduction mechanism in them [87]. Effect of annealing treatments and gamma-radiation on SnPc thin films as reported by Regimol et al. shows both has a direct dependence on activation enthalpy by applying a dark conduction mechanism in them [88]. Studies regarding gamma
radiation treatments on organic materials are limited though its scope is elaborate in inorganic semiconductors like NiO, TeO₂, Fe/Ir super lattices and platinum thin films for the fabrication of gamma ray dosimeters and sensors [89, 90, 91].

1.6.2. Optical properties

Optical properties are more significant for 2,3 naphthalocyanines and their complexes since they are considered as photonic materials. There are earlier reports on optical properties of different Tetra Tert-Butyl 2,3 naphthalocyanines (TTBNc) since they belong to the category of infrared functional dyes. Pop et al. observed that like any other IR dyes, TTBNcs commonly possess an absorption peak corresponding to 700-850nm region and its value may vary the limit due to variation of some parameters like molar concentration of solvent and film thickness [92]. In addition to NIR absorption power, good IR transmission with excellent luminescent capability and Raman active nature is supported by Freyer et al. The optical absorption studies of different 2,3 naphthalocyanines were repeated by Kaplan et al. In the study, they noticed the absorption maxima occurred in the near infrared region, about 80-100nm longer wavelength than the maxima for phthalocyanines [40].

Most of the optical studies give us the comparison in optical behaviour of (Metal) TTBNcs with (Metal) TTPcs and with (Metal) 2,3 NPcs. Ken Harada et al. reported such a case, where ZnTTBNc is assimilated with ZnTTPc and found that ZnTTBNc, possesses a complex structure with a prominent blue shifting occurs in absorption spectrum. As far as the absorption studies of highly concentrated Metal free TTBNc solution (1.9x10⁻²M in CCl₄) are concerned, there is a report on maximum absorption peak in 785nm with a shoulder peak at 771nm. Also there is an indication of variations in absorption maxima corresponding to TTBNc thin film having thickness 20nm at 797nm and a shoulder peak at 718nm. Even though the film and solution having a small shift in maxima values Qx and Qy, the full width at half maxima values for both of them remains the same [93, 94]. Spectral and hole burning properties are observed for ZnTTBNc and TTBNc thin films by Turukhin et al. and they mentioned the absorption spectra for calculating the quantum efficiency and it leads to the holographic storage application with diode
lasers [95]. Hayashida et al. reported the optical absorption, non linear optical properties and luminescent properties on account of different TTBNc powders; make them useful as the efficient inhibitors for photodestructive processes in photochemical systems [96]. As per the reports of Wang et al. on optical studies like absorption spectra for different TTBNc thin films with sandwich- type naphthalocyaninato and porphyrinato rare earth complexes, a detailed investigation of change in Sorret and Quscent bands for sandwich layer with respect to single layered TTBNc thin film is explained. Effect of substituent and molecular symmetry are taken as prominent factors for those changes in absorption peaks. Most of the optical transmission spectra related to TTBNc exist in IR region since these classes of materials are good IR functional dyes [97].

The absorption peaks corresponding to most of the metal 2,3 naphthalocyanines are similar to that of metal TTBNc and it is envisaged by the absorption peak of characteristic Silicon 2,3 Naphthalocyanine (SiNPe) in a photo dynamic therapy studies by Brasseur et al. [98]. In another study regarding photoconductivity in SiNPe by Hayashida et al., show the vacuum deposited thin films possess a broad spectrum in Q bands while the splitting of Q bands is prominent in highly concentrated solution of SiNPe with CH$_3$Cl [99]. There is also some reported studies regarding the IR transmission studies related to Zinc 2,3 Naphthalocyanines by Volger et al. and there the most intense band at 1092cm$^{-1}$ with two stretching vibrations like C-C, C-N at 1333 and 1360cm$^{-1}$ respectively [100]. Tokumaru et al. reported on variation in absorption maxima with molar concentration of different ZnTTBNc solution and the effect of thickness variation on change in absorption peaks of class of ZnTTBNc thin films [101]. In addition to optical absorbance, there are some works on optical transmission and reflection studies on Tert-butyl substituted phthalocyanines like CuTTPc thin films done by Emelianov et al. while there are very sketchy data in naphthalocyanines [102]. Meso-phenyl substitution on Naphthalocyanine gives a broad transmittance near green region of visible range and is fully transparent in IR region that makes them suitable for non-linear optical studies as suggested by Mathews et al. [103]. Octa-butoxy substitutions in naphthalocyanines are studied by Huang et al. and in Tin 2,3
NPcs cause a near infrared absorptions (900-930nm) with high extinction coefficients like $1 \times 10^5 \text{M}^{-1}\text{cm}^{-1}$ with a red shifted Q bands due to those substitutions [104]. Studies based on optical constants like refractive index and dielectric constants in tert-butyl substituted phthalo and naphthalocyanines are limited.

There are numerous research reports on Metal free and different metal PCs, regarding optical properties and studies relating various optical constants. Most of the optical studies of PCs describe the optical absorption spectra along with absorption coefficients, extinction coefficients and optical band gap energy. Optical constants like refractive index, dielectric constants and extinction coefficients with photon energy for many Pc thin films are also studied by Verzimakha et al. [105]. Annealing effects on variations in optical transmittance for CuPc thin films as reported by Ambily et al. gives information of nearly 50% transmittance for CuPc thin films near 550nm and the percentage of transmittance remains unaltered on annealing treatments [106]. In addition to simple phthalocyanines, there are reported works in optical properties for hybrid phthalocyanines by Varghese et al. by co-sublimation techniques of different phthalocyanines like CuPc-NiPc combination [107].

1.6.3. Structural properties

Structural studies in most of phthalo and naphthalocyanines cover powder or thin film X-ray diffractogram analysis. Tert-butyl addition to different 2,3 naphthalocyanines makes them complex in structures. Lack of standard JCPDF data for these macro molecules, some additional powder indexing software like CRYSFIRE gives opportunities to researchers for finding structural parameters by assimilating the experimental ‘20’ and ‘d’ values with their built-in values having an error of 20% [108]. On similarities in structural information of simple 2,3 NPcs with TTBNcs, the only available JCPDF file for Zn 2,3 NPc is JCPDF file number 48-2159 [109]. By making use of those available data, Kaplan et al. suggested some structural information on different 2,3 NPcs like metal free, Lead and Vanadyl NPc. They could find no sample correlation with the known crystal structures of PCs [40]. In another study of Photoconductivity in Silicon 2,3 Naphthalocyanines, Shigeru Hayashida et al. reported the X-ray diffractograms of vacuum deposited Si 2,3NPcs with their annealed counter parts. They report some sharp diffraction lines at...
d-spacing from 2.9 to 4.4Å. From their studies, they also find that intermolecular interactions of NPc molecule in thin films decreases with the increase of alkyl chain length in the axial substitutions [99]. By a computational method like PBE/DNP level of theory, Jan Andzelm suggests some structural information regarding Si 2,3NPc, Methyl complex of Si 2,3NPc and SiNc(OH)2. In complexes of Si 2,3NPcs, they applied C1 and C2h symmetries and found that the main structural differences were due to the dihedral angle involving the position of hydroxyl group above the Si 2,3NPc ring with an energy difference of 0.6Kcal/mol [110]. From the epitaxial growth of NPc thin film vacuum deposited on alkali halides by Hisao Yanagi et al. elucidate the structural information from XRD, Electron Diffractogram (ED) and Transmission Electron Microscopic image (TEM). The molecular stacking and orientation of Metal NPc crystals deposited on (001) surface of NaCl, KCl and KBr are divided into two classes: “face-to-face”, “eclipsed” stacking and “P-orientation” for divalent H2NPc and ZnNPc while that of trivalent AlNPcCl, GaNPcF and tetravalent VoNPc possess “eclipsed- slipped” stacking and “l-orientation” [111]. Structural analysis of different Vanadium bearing macro and micro molecules like VOPc, VONPc and V2O5, reveal no direct similarities with VOPc and VONPc, but Kaplan et al. narrates a close similarity of V2O5 with VONPc in its peaks’ orientations. The above result indicates the structural similarity of naphthalocyanines with micro inorganic compounds. Slipped- stacking arrangements in NPc are observed by the crystal structure of Co (III)1,2 NPc with a C4h symmetry and tetragonal crystal system. Apart from Co(III)1,2NPc, Mg1,2NPc possess monoclinic system with C4h symmetry in its X-ray analysis.

Unlike NPcs, most of the phthalocyanines have been structurally analyzed using versatile equipments like XRD, TEM, Scanning Tunneling Microscopy (STM) and Electron Diffraction (ED). In addition to crystal structures and unit cell parameters, there are theoretical works on dislocation density (δ) and strain (ξ) for simple phthalocyanines observed by EL. Nahass et al. [112]. Studies on phase transformation of CuPc thin film from α to stable β phase have been done by Dogo et al. by making use of XRD, Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) analysis. Here the
XRD gives the idea of preferential orientation of peaks in desired position of two different forms while SEM, XPS and AFM analyses, show clearly α→β phase transformation for the CuPc thin film annealed at 250°C for 1h in nitrogen atmosphere [113]. Grain size calculation is also done using Sherrer’s equation implemented on X-ray diffractogram for NiPc thin films by Liu et al. and is equal to nearly 40nm for glass substrates and that of nearly 37nm for Si substrate [114]. Structures of mixed Langmuir-Blodgett films of Tertakis (3,5-di-tert-butylphenyl) porphinatocopper (II) with Cadmium arachidate are studied by Jian Bang Peng et al. using a Grazing Incidence Synchrotron X-ray diffraction study and found out in-plane diffraction Q_{xy} values, d-spacing and miller indices [115]. Bai et al. reported new dimeric super molecular structure of mixed phthalocyaninato and porhyrinato Europium (III) sandwiches with Nuclear Magnetic Resonance (NMR) spectrum in combination with cyclic voltammogram and absorption spectra [116]. X-ray analysis technique is applied by Krishnakumar et al. in FePc thin films to find the variation in grain size due to the annealing effects, substrate temperature variation and change in thin film thickness [117]. Ambily et al. reported the structural properties of PbPc thin films by giving the XRD diagrams of room temperature, 50°C and 100°C air annealed samples [118].

1.6.4. Surface morphological properties

Surface morphological studies in most of phthalo and naphthalocyanines are based on STM analysis. One such study has been reported by Freyer et al. regarding metal free TTBNc thin films by AFM analysis. AFM images for different TTBNc account for a homogenous distribution of small spherical protrusions of similar size and shape having an average root mean square (rms) surface roughness while that of TTPc possess a smooth surface pattern as observed by Souto et al. [47, 119]. Erbium Octa 2,3 NPC monolayer on cleaved mica substrates were analyzed by Chen Yanli et al. using AFM analysis for a scanning range of 500nm x 500nm. A homogenous molecular domains have appeared on the surface of above mentioned mono layers, aggregated forming a supra molecular system [120]. Gopakumar et al. studied the STM studies of planar-metal free NPC and nonplanar-SnNPCs on Graphite (001) substrates. NPC molecules form a close packed adlayer structure while SnNPC forms
a loosely packed adlayer. Further an adsorption of molecule shows a columnar Π-stacking in NPC where as SnNPC molecule shows a non columnar stacking and this feature is apt for single-molecule storage device application [121]. The surface morphology changes in PbNPC thin film are explained through SEM images by Yamana et al. shows that as prepared sample possesses a smooth surface topology while the annealed thin film having a gross particle of about 0.1µm in diameter. It is well speculated by the previous available data. Gas sensing properties of PbNPC films are also explained from SEM due to the porous nature on its topology [82]. In the area of phthalocyanines as well, the surface morphological studies are done with different microscopic analysis techniques. Well defined crystal arrangements in Zinc Hexadecafluoro Phthalocyanine studied by Schlettwein et al. and the columnar growth of CoPc thin films reported by Joseph et al. are some results obtained through AFM and SEM analysis respectively [122, 123].

Nano level regime of Pc and NPC can be easily analyzed through surface morphological microscopic treatments. Recent studies regarding phthalonaphthalocyanines are in their nano level aspects to fulfill nano applications. There are some nano structures reported in case of NPC. Helical Molecular Fibrillar structures of CuNPCOC₄ explained from AFM analysis by Ming Wang et al. and Nano tubes fabricated from NiNPC by a template method explained with the help of SEM and TEM images by the studies of Zhi et al. [124, 125]. Fabrication of composite films is widely acceptable nowadays due to the close similarities of Metal Phthalocyanines (MPc) with carbon nano tubes like Fullerene. Wei Feng et al. studied about the resultant nano composites of NiPc with Multi Walled carbon Nano Tube (MWNT) through SEM and TEM analysis on them. Apart from different nano structures, several nano particles having different dimensions and shape can be elucidated with the help of AFM image [126]. There are reports on NiPc-reconsistuted nano particles (≈ 22nm) for vivo-cancer imaging and treatments in medical field by Liping Song et al. [127]. The article entitled “Phthalocyanines-old dyes, new materials putting colour in nano technology” by Gema de la Torre et al. specifies that most of the phthalocyanines act as versatile building blocks for fabricating materials in nano meter scale and the colour of phthalocyanines make
them apt for fabrication of photovoltaic devices where they function as antennae with a wider absorbing range of the solar terrestrial spectrum [128]. Santanu Karan et al. reported the growth of nano flowers from different metal (nickel, copper, tin, magnesium and zinc) phthalocyanine seeds and nano rods on gold hetero junctions (shown by SEM and TEM images) make them interesting candidates for organic nano rectifiers [129]. There is another report on nano ribbons and nano wires by Tong et al. They specify the particular nano structure of metal (Cu, Ni, Fe, Co and Zn) phthalocyanines as well as F16CuPc through SEM and TEM images and size of nano structures are well calculated [130]. By the new technique like Laser ablation of crystalline powder in poor solvents, Tamaki et al. found out the nano particle formation in VoPc colloidal solution [131]. Suslick et al. reported the power of porphyrins and metallo porphyrins to control materials properties as a building block in nano meter scale. They mentioned the importance of different porphyrins including Pc and NPe materials in the form of thin film, solids and micro porous solids as field-responsive and chemo-responsive materials [132]. Apart from single nano particles, nano nonaggregate Pc are much important in the present research topics like C60-SiPc-C60 system studied by Gomis et al. [133].

The choice of materials like TTBNc, ZnTTBNc and VTTBNc are adequate for thin film fabrication on present scientific outlook due to the following reasons. There are only a few reviews and patent reports for TTBNc, ZnTTBNc, VTTBNc thin films. Though there are early reports on their use in photonic applications, the electrical studies both in high and low temperature region are rare. Lack of available data in the structure and surface morphology of those classes of materials still exists as a hindrance in their applications for constructing single molecular devices and in nano technological applications. In this thesis a modest attempt has been made to study electrical, optical, structural and surface morphological properties on a class of tert-butyl substituted 2,3 Naphthalocyanines by varying different parameters like thickness, post deposition annealing temperature, substrate temperature and irradiation of gamma rays.
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