BRIEF REVIEW OF THE ELECTRICAL, OPTICAL AND STRUCTURAL STUDIES IN PHTHALOCYANINES

1.1 Introduction

Phthalocyanines, discovered accidentally in 1907 and subsequently described by Linstead, form a series of crystalline compounds which are remarkable for their intense colour and great stability. They comprise both metal-free phthalocyanine (H₂Pc) which contains two hydrogen atoms in the centre of the molecule and metal phthalocyanines wherein the hydrogen atoms are substituted by metal atoms. One of the significant properties of the phthalocyanines is its high chemical and thermal stability. The versatility, architectural flexibility, non-toxicity and ease of processing make them eligible candidates for use not only in electronics but also in photonic technology. These compounds have a long storage life and high read out times, for use in optical storage systems. Phthalocyanine is an important industrial material used in the production of inks, colouring for plastics and metal surfaces. Some of their applications include electrochromic devices, chemical sensors, electrocatalytic and photocatalytic processes and solar energy conversion.
Phthalocyanines are aromatic hydrocarbons exhibiting semiconducting properties and hence come under the class of organic semiconductors. A brief description about the characteristics of organic semiconductors is given below.

1.2 Organic Semiconductors

Semiconductors can be broadly divided into two main groups as inorganic semiconductors and organic semiconductors. Though inorganic semiconductors like germanium and silicon are used extensively in electronic industry, organic semiconductors are only emerging as a new class of semiconducting materials.

Organic semiconductor is a molecular crystal whose energy structure and electronic properties are determined by the molecular structure. It consists of a regular array of closely spaced molecules. The presence of molecular units rather than ions makes their conduction mechanism more complex. A distinguishing characteristic of organic semiconductors is the presence of conjugate bonds. Even though the intermolecular bonding is van der Waals type, the electrons within a molecule are tightly bound. Most of these organic materials are p-type semiconductors. The electrical conductivity and carrier mobility are low in organic semiconductors compared to those of inorganic semiconductors.

The optical absorption in phthalocyanines occurs within the molecule rather than within the entire crystal, as against in inorganic semiconductors. The weaker overlap between adjacent molecules in organic semiconductors makes them narrow valence and conduction band semiconductors.

A comparison of the electrical conduction parameters of the organic semiconductors and those of inorganic semiconductors is given in Table 1.2.1.
A comparison of the electrical conduction parameters for the organic and inorganic semiconductors

<table>
<thead>
<tr>
<th>Electrical parameters</th>
<th>Organic semiconductor</th>
<th>Inorganic semiconductor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobility (cm²/V·sec)</td>
<td>$10^2$-$10^{-6}$</td>
<td>$10^5$-$10^{-3}$</td>
</tr>
<tr>
<td>Carrier concentration (cm⁻³)</td>
<td>$10^8$-$10^{-9}$</td>
<td>$10^{11}$-$10^{06}$</td>
</tr>
<tr>
<td>Trap density (cm⁻³)</td>
<td>$10^{22}$-$10^{28}$</td>
<td>-</td>
</tr>
<tr>
<td>Conductivity (ohm cm⁻¹)</td>
<td>$10^2$-$10^{-14}$</td>
<td>$10^3$-$10^{-9}$</td>
</tr>
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1.3 Molecular Structure

The structure of the planar phthalocyanine molecule was first reported by Dent et al.² The metal free phthalocyanine has the general formula $C_{32}H_{18}N_8$ or $(C_8H_4N_2)_4H_2$. It is chemically designated as 5, 10, 15, 20-Tetraaza-tetrabenzo-azan. The basic molecular structure of phthalocyanine is shown in Figure 1.3.1.
It consists of four isoindole units linked by aza nitrogen atoms and surrounded by two hydrogen atoms. In the metal substituted phthalocyanines, the two central hydrogen atoms are replaced by a single metal atom. The benzene rings at the four corners of the molecule are found to be the projections of regular plane hexagons. The radius of the benzene ring is 1.39Å. The inner system of the molecule consists of a closed system of sixteen carbon and nitrogen atoms, the interatomic distance having constant value of 1.34 ± 0.03Å. This inner system is connected to the four benzene rings by C–C bonds of length 1.49 ± 0.03Å. The carbon links emerging from the benzene rings are strained about 15° from their normal positions. In the crystal, the planes of adjoining rows of molecules are at right angles, and the minimum intermolecular distance is 3.35Å. The perpendicular distance between the molecular planes is 3.38Å.

The phthalocyanines normally belong to C2/c space group in the metastable α form and P2₁/a space group in the stable β form. The symmetry of H₂Pc corresponds to the D₂h point group and that of metal phthalocyanine is D₄h. The unit cell of a β-phthalocyanine contains two molecules. The base centred arrangement of the two molecules and their crystal axes in the unit cell are given in Figure 1.3.2.

![Figure 1.3.2 Unit cell of a base centred phthalocyanine molecule](image)

In phthalocyanines, the orbital overlap is diminished by the interspersing of the π-orbitals of parallel pairs of molecules. However, in the
metalophthalocyanines the central metal atom is in a position of nearest approach with nitrogen atoms in parallel molecules which increases the overlap. The molecules lying in parallel, inclined at an angle to the ac plane and the orthogonal projection of one molecule on to another parallel plane does not superimpose as is given in Figure 1.3.3.

![Diagram showing the normal projection of two molecules of the metal substituted phthalocyanine](image)

**Figure 1.3.3**  Normal projection of two molecules of the metal substituted phthalocyanine

A major property related to this structure is that generally the molecules are thermally stable and can be sublimed to form thin films without decomposition. Therefore, in contrast to many other organic compounds, the preparation of phthalocyanine thin films by vacuum sublimation is feasible.
1.4 Earlier Studies on Phthalocyanines

The early history of the synthesis and production of phthalocyanines is described by Moser and Thomas. Metal free phthalocyanine (H₂Pc) was first synthesized in 1907 by Braun Tcherniac, and copper substituted phthalocyanine (CuPc) was originally synthesized in 1927 by De Diesbach and Von der Wied. Following this, many other metal-substituted phthalocyanines were synthesized and a comprehensive study of their properties was initiated by Linstead in 1934.

Some of the selected aspects of the electrical, optical and structural properties of the phthalocyanines are described below.

A. Electrical studies

Investigations on the electrical conduction mechanisms in phthalocyanines has attracted great attention because it shows relatively high conductivity among the molecular crystals and is the only material in which the magneto-resistance effects of dark current has been observed. Semiconducting behaviour was originally observed in bulk phthalocyanines in 1948 by Eley and Vartanyan. In due course these measurements were repeated in 1963 by Heilmeier and Warfield on single crystals of H₂Pc, which showed space-charge-limited conductivity (SCLC). Enhancement in the electrical conductivity of MgPc was observed by Vartanyan in 1948. Aoyagi et al. made the electrical conductivity studies and the magnetoresistance studies in H₂Pc, ZnPc, CuPc and NiPc single crystals. They observed the activation energies of these phthalocyanines and concluded that the central metal ion strongly influences the activation energy as well as the mobility. Barbe and Westgate studied the temperature dependence of the SCLC densities in H₂Pc single crystals and proposed the electron trapping models. They also observed that oxygen and hydrogen affect the electrical conductivity by diffusing into the
crystals and thereby introducing additional trapping levels near the middle of the band gap. Harrison and Ludewig\textsuperscript{13} have performed studies on the electrical conductivity and crystal phase changes in phthalocyanines and explained that the intrinsic conductivity of the $\alpha$ and $\beta$ phases does not change in the intermolecular interactions due to rearrangement of molecules in going from $\alpha$ to $\beta$ phase. They observed that the stronger propensity of the $\alpha$ phase to absorb oxygen is the cause of the higher conductivity of $\alpha$ phase compared to $\beta$ phase. According to Helfrich\textsuperscript{14} and Blagodarov et al.\textsuperscript{15}, two types of traps are found in phthalocyanines: (1) traps with discrete energy levels in the forbidden energy gap of the material and (2) traps with a quasi-continuous distribution of energy levels, usually having maximum density at the edge of the conduction or valence band. Ray et al.\textsuperscript{16} made d.c. and a.c. conductivity studies in thin films of phthalocyanines and interpreted the conduction mechanism in terms of bipolaron hopping. But they were unable to explain the origin of defects at hopping sites. The temperature dependence of the electrical resistivity and crystal structure of PbPc was studied by Ukei et al.\textsuperscript{17} and has suggested that it is a one-dimensional conductor. Hassan and Gould\textsuperscript{18} performed studies on annealed CuPc thin films in an oxygen environment. They measured the thermal activation energy and found that the oxygen impurities play a dual role of acceptors and traps. The hole concentration in annealed samples was found to be lower than that in unannealed samples. Hamann\textsuperscript{19} has determined the mode of trap distribution in CuPc films by SCLC measurements. Sadaoka et al.\textsuperscript{20} observed that in the presence of oxidising gases, conductance is increased and activation energy is decreased for H$_2$Pc and ZnPc systems. Abdel-Malik et al.\textsuperscript{21} showed that the electrical measurement results on $\beta$-NiPc film can be interpreted using an exponential trap distribution. They also obtained the electron mobility, density of states, total trap density and the characteristic temperature of the trap
distribution. It was suggested that polycrystalline thin films have larger defects than single crystals of phthalocyanines. The effect of annealing on trap distribution in CoPc thin films was discussed by Gravano et al.\textsuperscript{22} and observed a significant reduction in current density within the ohmic region and interpreted the results as due to the removal of oxygen molecules. Hole mobility and thermal activation energy were also calculated. The dependence of the evaporation pressure to deposition rate ratio on the electrical properties of CuPc thin films were investigated by Gould.\textsuperscript{23} A decrease in mobility and increase in trapping concentration of two orders of magnitude were observed in the pressure range $2.6 \times 10^4$–$1.3 \times 10^9$ Pa m$^{-1}$s. These variations are ascribed to the scattering and trapping effects of incorporated ambient gas molecules. Twarowski\textsuperscript{24,25} has studied the temperature dependence of the schottky barrier capacitance in ZnPc and MgPc. He observed that oxygen molecules could diffuse into the film and act as acceptor sites. Many workers\textsuperscript{26,27} indicated that the change in ambient gas molecules affect the conductivities of both phthalocyanine crystals and films. Dahlberg and Musser\textsuperscript{28} reported that the adsorbed oxygen is present in an undissociated form above the central metal atom in the phthalocyanine ring. Abdel-Malik et al.\textsuperscript{29} performed electrical transport properties in sandwiched NiPc films and showed ohmic conduction in the lower voltage range and space-charge-limited conduction (SCLC) in the higher voltage range. Wilson and Collins\textsuperscript{30} showed that the gas-surface interactions on phthalocyanine thin films are complex and reported that oxygen in the form of water vapour is adsorbed on the film surface on exposure to atmosphere. The electrode material and purity of the phthalocyanine film affect the dark conductivity. Abdel-Malik\textsuperscript{31} studied the temperature variation of current densities flowing in the c-direction in $\beta$-NiPc crystals in oxygen, air and vacuum. Sussman\textsuperscript{32} has studied the effect of substrate temperature and annealing temperature on the electrical properties of
CuPc thin films and explained the influence of ambients on the conductivity, trap density and mobility. He reported that oxygen causes the Fermi level to move nearer to the valence band. Wilson and Collins\textsuperscript{33} made investigations on the effects of electrode materials in metal-phthalocyanine-metal structures. Frenkel\textsuperscript{34} and Vermilyea\textsuperscript{35} showed that the presence of a strong electric field caused the effective depth of a trap to be reduced. Fan and Faulkner\textsuperscript{36} studied the photovoltaic properties of H\textsubscript{2}Pc and ZnPc. Meir\textsuperscript{37} reported that the bond length between the adsorbed oxygen and phthalocyanine molecules depends on the nature of the central metal ion. Loutfy\textsuperscript{38} and Blagodarov et al.\textsuperscript{15} studied the trap distributions in H\textsubscript{2}Pc films and their results were consistent with the assumption of an exponential trap distribution. Collins and Mohammed\textsuperscript{39} studied the electrical and structural properties of ZnPc thin films as a function of substrate temperature and annealing. Experiments on d.c. electrical conductivity measurements and activation energy measurements on metal phthalocyanine films were performed by Hassan and Gould\textsuperscript{40} and they suggested a hopping type conduction at lower temperatures. Belghachi and Collins\textsuperscript{41} interpreted the thermal activation energy observed in phthalocyanines as the difference between dominant energy levels in the energy band gap. Hamann\textsuperscript{42} suggested that extended annealing causes regrowth of the phthalocyanine layer and the appearance of crystal defects. Eley and Parfitt\textsuperscript{43} indicated that the conductivity of the \( \alpha \) phase phthalocyanine is about 10 times greater than the \( \beta \)-conductivity. Effect of ambients on the electrical conductivity of vacuum sublimed MgPc, FePc and ZnPc thin films were studied by Jones and Bott\textsuperscript{44} and suggested a detailed study into the role played by the central metal atom in this process. El-Khatib et al.\textsuperscript{45} performed d.c. and a.c. conductivity measurements on p and n doped ZnPc films. The position of Fermi level and the value of the activation energy was found to be a function of the doping ratio. Fan and Faulkner\textsuperscript{46}
performed studies on \( H_2Pc \) and \( ZnPc \) and they observed that phthalocyanines are p-type semiconductors. Kearns and Calvin\(^47\) and Fedorov and Benderski\(^48\) investigated the electrical properties of \( MgPc \) and indicated that the properties are governed by a p-n junction formed within the phthalocyanine phase. Assour and Harrison\(^49\) proposed that the interaction of oxygen with each phthalocyanine is not identical and observed an extrinsic-intrinsic cross-over for the activation energy in vacuum and in atmosphere. The applicability of the energy band model for phthalocyanines is demonstrated by Heilmeier et al.\(^50\) Abdel-Malik\(^51\) made d.c. current measurements in \( FePc \) dispersed in a polymer binder and obtained the activation energies of both \( \alpha \) and \( \beta \) phases. Modulation of electrical conductivity upon exposure to oxygen in \( MgPc \) is reported by Vartanyan.\(^9\) Boudjema et al.\(^52\) performed investigations on metal-phthalocyanine-metal sandwich samples of \( ZnPc \) and \( NiPc \). They observed that the microcrystallite size in the \( \alpha \) phase are between 50 and 100 nm. It is reported that oxygen acts as an acceptor in the phthalocyanine lattice through the equilibrium

\[
PcM,O_2 \Leftrightarrow PcM^+,O_2^- \Leftrightarrow h^++PcM,O_2^-
\]

where \( PcM \) is the metal-substituted phthalocyanine and \( h^+ \) is a hole.

A.c. and d.c. conductivity measurements on \( FePc \) grafted Poly(N-vinylcarbazole) were made by Zamora and Gonzalez.\(^53\) Wagner and Loutfy\(^54\) studied the heterojunction properties of \( CdS/MgPc \) films and found that the barrier width is not sensitive to the thickness of \( CdS \). Hor and Loutfy\(^55\), while performing studies using \( MgPc \) and \( ZnPc \) showed that the exact location of Fermi level within the band gap of a semiconductor is affected by impurity concentrations. Saleh et al.\(^56\) obtained the activation energy, capacitance and dielectric loss as functions of temperature and frequency on \( ZnPc \) films. Vidiadi et al.\(^57\)
investigated the a.c. conductivity of preheated samples of MgPc and CuPc in vacuum and concluded that the conduction is mainly of the free band type in the high temperature low frequency region whereas it is of the hopping type in the low temperature high frequency region. Moigne and Even\textsuperscript{58} also arrived at the same conclusion while working on FePc films. Rahmann et al.\textsuperscript{59} suggested that freshly prepared samples may contain different kinds of defects such as vacancies, grain boundaries and dislocations which may be partially annealed out by heat treatment resulting in a decrease in the density of defects and in local structural rearrangements. Martin et al.\textsuperscript{60} measured the junction properties in Au/ZnPc/metal (metal = Au, Cu, Cr, Al, In) both in vacuum and in air and found a diode-type conductivity.

B. Optical studies

Anderson et al.\textsuperscript{61} reported that the central metal of the phthalocyanine molecule influences the optical absorption spectrum. Optical characterisation of FePc complexes using UV-Vis and Mossbauer spectroscopy was done by Hanack et al.\textsuperscript{62} and showed that the strength of π-acceptor bond in phthalocyanine depends on the central metal atom. Feijfar et al.\textsuperscript{63} studied the optical properties of H\textsubscript{2}Pc composite films using UV-Vis-NIR and FTIR spectra. Epitaxial films of ZnPc were investigated by Kaneto et al.\textsuperscript{64} and determined the band gap and thermal activation energy. Gurinovich et al.\textsuperscript{65} calculated the rate constant for fluorescent decay in the singlet-triplet transition of MgPc. Ahmad and Collins\textsuperscript{66} showed that the Q band absorption in phthalocyanines is due to π-π* transition and the soret band absorption is of electronic origin. Freyer and Pragst\textsuperscript{67} and Angh et al.\textsuperscript{68} observed new absorption bands in the green and IR regions of the absorption spectrum in MgPc. Third order non-linear optical properties of FePc were studied by Nalwa and Kakuta.\textsuperscript{69} Lucia and Verderame\textsuperscript{70} performed optical
characterisation in the monoclinic and triclinic phases of H₂Pc and ZnPc and observed absorption doublets below the energy band gap in the monoclinic phase. They have suggested that the Devy dov splitting of the Q band occurs due to dipole-dipole interactions. Ordinary absorption spectra and electro-absorption spectra of ZnPc films were measured by Yoshida⁷¹ to study the charge transfer excitation bands. Asakov and Vartanyan⁷² measured the ESR absorption spectra of MgPc and ZnPc. Hoshi et al.⁷³ investigated the effect of substrate, substrate temperature, thickness of the film and post-deposition annealing on the structure and properties of phthalocyanine films. They suggested a pseudomorphic region that exists at the thin film-substrate interface. They also suggested that the interaction between admolecule and substrate may cause distortion in the electronic structure of the phthalocyanine molecule. Low energy electron diffraction investigations of FePc and H₂Pc films grown in situ on copper substrates showed the existence of pseudomorphic structure which was stable up to a film thickness of 1000Å.⁷⁴ Campbell and Collins⁷⁵ showed that the optical absorption in phthalocyanines could be used to detect the phase of the film. The optical and morphological behaviour of MgPc films in contact with aqueous NaClO₄ medium was studied by Taguchi et al.⁷⁶ Khatib et al.⁷⁷ measured the absorption spectra of ZnPc films and the peaks located at around 700 nm, 360 nm and 210 nm were assigned to be Q band, B band and C band respectively. It was suggested that the broadening of these absorption bands is caused by aggregation of molecules. The investigations by Gu et al.⁷⁸ showed that the absorption region is matched with the wavelength of semiconductor diode lasers. Schoch and Temofonte⁷⁹ determined the IR response of the metal phthalocyanine thin films in dilute NO₂-air mixture and a relationship between free carrier absorption and gas concentration were established.
C. **Structural studies**

The initial X-ray diffraction studies were made by Robertson on metal-free, nickel, copper, and platinum substituted phthalocyanines. These measurements were performed on single crystals. Ebert and Gottlieb observed dimorphism in H$_2$Pc, ZnPc, and CuPc. Collins and Mohammed studied the phase behaviour of ZnPc and showed that the growth of α-form microcrystallites into large crystals proceeded from lower temperatures. They also showed that ZnPc remains in α-phase up to 250°C and is fully converted to β-phase at 340°C. Sadaoka et al. also have reported a α to β-phase transition for ZnPc and CuPc. Kobayashi et al. reported that ZnPc forms various crystal phases depending on the dispersion medium. Ashida suggested that the crystal structure of ZnPc film is monoclinic and 1.3 nm spacing is the (200) plane in α-form. H$_2$Pc films evaporated onto rock salt occur in dimorphs and transition temperature is 200°C. Pizzini et al. studied the structure and morphology of ZnPc films in NO$_2$ ambient. Assour indicated that the two polymorphic crystalline phases, α and β, exist for H$_2$Pc and ZnPc. Lucia and Verderame obtained α to β transition temperature as 300°C with preferential orientation (001) at 12.4 Å spacing for ZnPc. Iwatsu et al. studied the phase transition in ZnPc at different alcohol vapour atmospheres and confirmed the existence of an intermediate phase, x-phase with inter lattice spacing of 11.4 Å. They obtained lattice vector $\vec{a} = 3.78$ Å for the α-phase and $\vec{b} = 4.85$ Å for the β-phase. Linstead and Robertson performed X-ray measurements on single crystals of FePc, CoPc and H$_2$Pc. They observed that these phthalocyanines have centro-symmetrical molecules and the metal atom lies in the same plane as the four nitrogen atoms. Kajihara et al. reported that room temperature deposited ZnPc film exhibits only one clear diffraction line at 2θ = 6.8° which corresponds to 1.3 nm spacing of the XRD pattern while powder form showed a complicated pattern with a large number of peaks. Unit cell constants of metastable α-FePc is reported by
Ashida et al.\textsuperscript{91} using high-resolution electron diffraction pattern and are verified with the results obtained by X-ray diffraction. Tada et al.\textsuperscript{92} observed that two factors determine the structural arrangement of metal phthalocyanines on alkali halide substrates. One is the electrostatic interaction between central metal atom of the molecule and a halogen anion of the surface, and another is the van der Waals interaction between each molecule. Debe and Kam\textsuperscript{93} showed that ZnPc possesses three $\alpha$-polymorphs and that H$_2$Pc has two $\alpha$-polymorphs. Mindorff and Brodie\textsuperscript{94} observed phase changes in H$_2$Pc films. Morphology of metal phthalocyanine thin films was studied by Schoch et al.\textsuperscript{95} using TEM and electron diffraction and observed that films deposited at high substrate temperature of 160°C, form $\alpha$-phase. Working on the phase behaviour of ZnPc, CoPc and NiPc, Collins and Mohammed\textsuperscript{81} argued that the transition from $\alpha$ to $\beta$-phase is not a quick process; but a gradual process. The work reported by earlier workers have been given here in such details as may be required for the understanding of the work that follows in the subsequent chapters.

In conclusion, it should be stressed that, although phthalocyanine thin films have been extensively investigated an overall consensus on the relative characteristics is yet to emerge. It is evident that phthalocyanines are considerably less pure than inorganic semiconductors and therefore impurities and traps are likely to be a dominant factor in determining their requisite characteristics. The nature of different conduction mechanisms, mode of photon absorption and electronic excitations and various structural phases in phthalocyanines need a final word since various opinions exist at present. A comparison of the properties between different metal substituted phthalocyanines is desirable for the establishment of a relevant relationship among themselves. A modest attempt has been made in this thesis to study the electrical, optical and structural properties of the metal substituted phthalocyanines MgPc, FePc and ZnPc thin films.
References