Chapter 1

Brief review of the studies in Phthalocyanines
1.1 Introduction

The last decade has witnessed considerable progress in the development of organic semiconductors as an alternative to amorphous silicon for low cost, thin film electronics. Considerable efforts have been made to design synthesis and study molecular materials in particular organic semiconductors.$^{1-6}$ The choice of a molecular material which involves interactions between individual subunits that can be separately synthesized with varying electron affinities and the control of their interactions allow for the design of materials with tunable optical, electronic, and mechanical properties. Organic and metallo-organic derivatives are the basis of most of the molecular materials. Even after many investigations, it seems to be difficult to correlate the molecular structure of these semiconductors with their corresponding electrical properties. Organic semiconductors are capable of being tuned chemically and hence can be used in the fabrication of nanoelectronic device. Basic principles of physical organic chemistry have been employed to modify the characteristics of these materials by incorporating various alkyl chains, and electron-withdrawing groups. On the other hand, the device engineers used synthetic organic chemistry and the material physics as tools to improve the transport properties and device characteristics. Knowledge of the relationship between molecular structure and semiconducting characteristics of the organic compounds, allows the design of new materials that have pre-defined and controlled properties. A vast number of molecular and macromolecular systems have been described which show electrical conductivity in the semiconducting range. However various attempts have been made to optimize their properties. The physico-chemical characteristics of organic semiconductors depend on their molecular structure and on the presence of minute amounts of impurities. The study of the electrical properties of these materials is expected to shed light on these problems.
Future work will involve fabrication of more complex devices for practical applications using organic semiconductors. Above all these organic semiconductors are expected to replace the present semiconductor devices during the coming years and hence the area of large scale integration and device fabrication using phthalocyanines will make drastic changes in the electronic industry in the near future.

1.2 Organic Semiconductors

Modern chemistry enables the synthesis of complex molecules that are comprised mainly of carbon, hydrogen, oxygen and nitrogen atoms. These atoms are linked together by energetically strong covalent bonds of neighboring electrons. In addition, non-covalent interactions such as hydrogen bonding can be used to build complex supramolecular structures. Such bottom-up approaches are at the basis of nanotechnologies.

Organic semiconductors are based on the unusual properties of carbon atoms. Carbon can form four bonds with neighboring carbon atoms or other atoms. In some simple molecules such as methane (CH₄), four valence electrons occupy four sp³ hybridized orbitals and can form four covalent bonds. However, in more complex molecules three of the four valence electrons occupy sp² hybridized orbitals that are in a plane and the fourth electron occupies a Pz orbital which is perpendicular to this plane. A σ bond between two carbon atoms can then be formed by the formation of an orbital overlap of two sp² orbitals. The energy difference between the occupied binding orbitals and the unoccupied anti-binding orbitals is quite large. Correspondingly longer chain of bound carbon atoms would have a large gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) leading to insulating properties. When two electrons which are on adjacent carbon atoms, they form an energetically weak bond that is called a π bond in chain of atoms in the sp²
hybridization. This bond together with a bond formed between two electrons in sp\textsubscript{2} orbitals form a double bond. In molecules that are called conjugated, atoms are linked together by alternating single and double bonds. These bonds have much smaller energetic difference between the HOMO and LUMO, leading to strong absorption in or near the visible spectral range and to semi conducting properties. If carbon atoms form larger molecules, typically with benzene rings as the basic unit, the π-bonds become delocalized and form a π-system which is often has the extensions of the molecule. Benzene molecule which is an example of such a conjugated molecule in which six carbon atoms form a closed loop. This is illustrated in Figure 1.1. The gap between occupied and empty states in this π-systems becomes smaller with increasing delocalization, results in the relocation of electrons thus leading to a significant semi conducting properties. The wave functions associated with these electrons are highly delocalized and provide the molecule with unique properties: first this delocalization leads to high polarizability under the influence of an electric field that is responsible for strong nonlinear optical properties; second the weaker binding energy allows for electron transfer reactions between molecules that allow charge to be transported. The hopping of these π-electrons between molecules confers semiconducting properties to these materials.

These substances can be prepared as molecular single crystals. Due to the close coupling of the π-systems of the molecules in these crystals, they even in a purified form show remarkable electrical characteristics and transport properties. If a long chain of carbon atoms is formed, the π-bonds become delocalized along the chain and form a one dimensional electronic system. This result in a 1D-band with a considerable band width between a filled valence band originating from the HOMOs and an empty conduction band originating from the LUMOs. The transport properties of such organic
semiconductors are usually determined by defects in the 1D-chains or by hopping from chain to chain. Therefore, the samples may not show band transport, but thermally activated hopping. Electronic charge transport in organic molecules does not require perfect single crystals. A regular arrangement of atoms, ions or molecules over a distance of only a few spacing of the structural units is necessary and is usually a sufficient condition for electrical conductivity of the organic systems. Originally, much of the research has concentrated on single crystals, which show mobilities of a few cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature and even much higher values at low temperature, as shown in the pioneering work of Karl.$^7$

Figure 1.1   Delocalized π electrons of the benzene ring forming a π bond
Organic semiconductors have advantages due to their various properties determined by their chemical structures. Consequently, it appears the possibility to synthesize organic semiconducting compounds with properties exactly matched to the requirements of specific applications such as semiconductor devices, solar cells, biosensors and nonlinear optical materials.\textsuperscript{8-17} A knowledge of the relationship between molecular structure and semiconducting characteristics of the organic compounds, allows the design of new materials that have pre-defined and controlled properties.\textsuperscript{18-21} The significant properties of organic semiconductors include efficient electroluminescence, reasonable charge carrier mobility, ease of preparation and low cost have led to expectations of a new ‘plastic’ electronics with applications ranging from flexible flat panel displays,\textsuperscript{22} organic light emitting diodes\textsuperscript{23} and low cost solar cells.\textsuperscript{24} The ultimate penetration of organic electronics into the commercial applications, however, depends upon creation of additional nanoelectronic devices and field effect transistors which require further improvements in its transport properties. While very promising with regard to processing,
cost, and weight considerations, organic compounds generally have a number of disadvantages, including poor mechanical stability and lesser life span. Further the electrical conductivity and carrier concentrations of organic semiconductors are lower compared to those of inorganic semiconductors. In organic solids the molecules interact by relatively weak Van der Waals or London type forces\(^\text{25}\) so that the intermolecular separations are longer compared with the separations between atoms or ions of inorganic substance. Consequently there is only a weak overlap of the molecular orbitals and hence the intermolecular exchange is small. A huge number of molecular and macromolecular systems have been described which show electrical conductivity in the semiconducting range. However various attempts have been made to optimise their properties. The physico-chemical characteristics of organic semiconductors depend on their molecular structure and on the presence of minute amounts of impurities.\(^\text{26}\) Controlled and stable doping is a prerequisite for the realization and the efficiency of many organic based devices.\(^\text{27-29}\) If we succeed in shifting the Fermi level towards the transport states, this could reduce ohmic losses, ease carrier injection from contacts and increase the built-in potential of Schottky or p-n junctions. Since organic semiconductors consist of molecular structures with saturated electron systems, the number of intrinsic defects in disordered systems is much lower than in inorganic amorphous semiconductors, where a large number of dangling bonds exist. The achievement of improved transport properties and higher carrier mobilities necessitates a comprehensive understanding of the connection between molecular structure, intermolecular interactions of the organic material and also the metal-semiconductor contacts. The study of the electrical properties of these materials is expected to reveal the possibilities of organic semiconductors for the enhanced use in the various electronic devices and in the rapidly expanding field of molecular electronics.
There is considerable scientific and technological interest in the design, synthesis and characterization of organic materials that possess unusual solid-state properties. Organic semiconductors are used in the following applications.

- The use of organic semiconductors as active layers in thin-film transistors has raised a large interest in the recent years, both for the fundamental understanding of the charge transport processes in organic materials, and also for the potential applications of these devices in the new field of flexible electronics.

- The physical and chemical properties of organic semiconductors make them good candidates for sensing elements in semiconductor gas detectors\(^{30,31}\) as most of the requirements of an ideal sensor are attained with organic-based devices.

- Organic semiconductors have several properties desirable for low cost solar cells. Many of these materials have high optical absorption coefficients and can be deposited by vacuum evaporation so that large area cells may be produced at modest costs. Although organic solar cells are at present not achieved the efficiencies of silicon-based cells, a modest improvement in efficiency may enable organic solar cells to be used in applications with low land cost and harsh environments, potentially requiring disposable cells. Organic solar cells can also be inexpensive to install if made with flexible substrates so that they can be unrolled and glued onto frames, much like roofing material.

- There are many potential organic materials for Organic thin film transistors (TFTs) that are of interest for a wide range of low-cost, large-area electronic applications. Such applications may include active-matrix liquid-crystal displays, active-matrix emissive displays, active-matrix flat panel imagers, smart cards, smart price and inventory tags, and large-area sensor arrays. Organic TFTs
provide two principal advantages over TFTs based on inorganic semiconductors. They can be fabricated at lower temperature and, potentially, at significantly lower cost. Low process temperatures in particular may allow organic TFTs to be integrated on inexpensive plastic substrates, rather than glass, and the prospect of flexible, unbreakable, extremely low-weight flat panel displays at low cost has spurred significant commercial interest.

- Recently, other organic materials have received considerable attention as potential replacements for their inorganic counterparts in flat-panel-display driver circuitry and light-emitting elements. Organic materials have the key advantage of simple and low-temperature thin-film processing through inexpensive techniques such as spin coating, ink-jet printing, or stamping. In addition, the flexibility of organic chemistry enables the formation of organic molecules with useful luminescent and conducting properties.

### 1.3 Phthalocyanines

Phthalocyanines was first obtained by Broun and Tcherniac in 1907 as a byproduct of the preparation of o-cyanobenzamide from phthalamide and acetic anhydride. Since then, there has been tremendous amount of research on their remarkable electrical and optical properties. Later the basic syntheses and characterization methods of these materials were also thoroughly investigated. The term ‘Phthalocyanine’ was first used by Linstead in 1930, have properly determined the molecular structure of metal-free and metallophthalocyanine and fitted the earlier observation into systematic scheme showing that a vast range of phthalocyanines were all based on a single structure. Phthalocyanines
are aromatic hydrocarbons which exhibit a significant semi conducting property and come under the class of organic semiconductors. The word phthalocyanine originates from the two Greek words naphtha and cyanine. As an alternative to inorganic semiconductors, organic materials have recently gained much attention because of its significant semiconducting properties. Generally phthalocyanines are classified as p-type semiconductors characterized by low mobility and low carrier concentration. The versatility, architectural flexibility, and low cost of preparation make them eligible candidates for not only in electronic industry but also in photonic technology. These materials are thermally stable and can be evaporated to form thin films of suitable thickness without any decomposition. Therefore in contrast to many other organic compounds the preparation of phthalocyanine thin films by vacuum evaporation is viable. The semi conducting property of phthalocyanines have attracted significant interest during the past few years because of its incredible potential as a p type organic semiconductor. They comprise of both metal free phthalocyanine, which contain two hydrogen atoms in the centre of the molecule and the various metal substituted forms where the hydrogen atoms are replaced by a single metal atom. Some of the applications include their use as sensing elements in gas sensors, photovoltaic cells, solar cell elements, data storage device and dyes. During this decade, their commercial utility in the manufacture of semiconductor devices is expected to have significant ramifications.

1.4 Molecular structure of phthalocyanines

J.M. Robertson made the first investigations on crystal structure of relatively large organic molecules by X-ray diffraction studies and the first studies of semi
conductivity in solid phthalocyanines were reported by Eley\textsuperscript{45} and Vartanyan\textsuperscript{46} in 1948. The studies on electrical measurements were stimulated by the similarity between phthalocyanines and the biologically important porphyrin molecules, so that studies of charge carrier generation and transport in phthalocyanines might provide a model for electronic processes in biological systems. This similarity together with the high stability of phthalocyanines has led to their adoption as one of the principal model compounds in the study of molecular crystals as a class of solid state materials.\textsuperscript{47} Consequently a vast number and range of studies of all manner of chemical and physical properties of phthalocyanines have been reported, and there are several extensive reviews and books which provide a perspective of this broad field.\textsuperscript{48-50}

The structure of the planar phthalocyanine molecule was first reported by Dent et al.\textsuperscript{51} The metal-free phthalocyanine has the general formula C\textsubscript{32}H\textsubscript{18}N\textsubscript{8} or (C\textsubscript{8}H\textsubscript{4}N\textsubscript{2})\textsubscript{4}H\textsubscript{2}. It is chemically designated as 5,10,15,20-Tetraaza-tetra benzoporphyryin or Tetra benzoporphyrazin. Phthalocyanine consists of a symmetrical 18 π-electron aromatic macrocycle, closely related to the structure of naturally occurring porphyrins. It consists of four isoindole-class [(C\textsubscript{6}H\textsubscript{4})C\textsubscript{2}N] units linked by four nitrogen atoms to form a conjugated chain. Like porphyrins, phthalocyanine macrocycle can play host to different metal ions in its centre by coordinate bonds with the four isoindole nitrogen atoms. The phthalocyanine molecule is also able to coordinate hydrogen atoms to form metal free phthalocyanines. The central atoms can carry additional ligands. Most of the elements have been found to be capable of coordinating to the phthalocyanine macrocycle. This macrocyclic structure shows a striking feature as a colorant like porphyrins (biopigments) in nature. The basic molecular structure of phthalocyanine is as shown in Figure 1.3.
Phthalocyanine is a large planar molecule\textsuperscript{52-54} with an extensive delocalized $\pi$-electron system. Although most of its metal complexes are also planar, those with metals such as lead which are too large to fit into the space between the four central nitrogen atoms show significant non-planarity.\textsuperscript{55} In the solid state the intermolecular forces between these large polarisable molecules are predominantly attractive dispersion forces, which are not strongly directional in nature, and short-range repulsion forces. As in many molecular crystals, this leads to the occurrence of polymorphism, several different molecular packing arrangements being possible with similar overall lattice energy. The planar metal phthalocyanines have common polymorphic forms $\alpha$, $\beta$ and $\gamma$ phases,\textsuperscript{56} where $\alpha$ and $\beta$ structures are both monoclinic with the characteristic “herring bone” packing of molecules in stacks. These structures are given in Figure 1.4. The principal difference between $\alpha$ and $\beta$ phases is the angle between the stacking axis and the normal to the molecular plane, which is about 25$^\circ$ for the $\alpha$ phase and about 45$^\circ$ for the $\beta$ phase.\textsuperscript{57} The $\beta$ phase is more stable than the $\alpha$ phase, by 8.4 kJ/mol. for H$_2$Pc\textsuperscript{58} and by 10.3
kJ/mol for CuPc. Sublimation of phthalocyanines at low pressures onto substrates maintained at temperatures around 450K generally yields the metastable $\alpha$ phase\textsuperscript{59} which may be converted to the $\beta$ phase by heating\textsuperscript{60} or by solvent treatment.\textsuperscript{61}

In the case of a simple metal phthalocyanine such as Magnesium phthalocyanine (MgPc), the central metal atom is Mg which is in +2 oxidation state. A main property related to this structure is that generally the various phthalocyanine molecules are thermally stable and can be sublimed without decomposition. Therefore in contrast with many other organic compounds, the preparation of phthalocyanine thin films by vacuum evaporation is feasible.

![Figure 1.4 Schematic representation of the three main molecular stackings found for metallophthalocyanines](image)

\textsuperscript{59}Phase $\alpha$.

\textsuperscript{60}Phase $\beta$.

\textsuperscript{61}Solvent treatment.
Large size nanocrystals are mostly of β-type. They are generally grown by sublimation under a stream of nitrogen at temperatures 600K-800K. The crystals are needle shaped, typically 1cm long, 0.1cm wide and 0.01cm thick. Metal phthalocyanines crystallizes in a base centered monoclinic lattice. Figure 1.5 shows the basic parameters of the lattice of β-phthalocyanine. The large area surfaces are along (001) and the needle direction is (010) axis (b-axis). In phthalocyanines, the orbital overlap is diminished by the interspersing of the π-orbitals of parallel pairs of molecules. However, in the metallo-phthalocyanines, the central metal atom is in a position of nearest approach with nitrogen atoms which increases the overlap. Metal phthalocyanines form thin films of the α-type when evaporated under vacuum (10^{-5}–10^{-6} Torr) on to a substrate maintained at room temperature. The phthalocyanine normally belongs to C2/c space group in the metastable α-form and P2_{1}/a space group in the stable β-form. During the past decade both types of phthalocyanines particularly metal phthalocyanines have gained considerable attraction of scientists and technologists owing to their unique optical and electrical properties. Not only the easily adaptable structure but also the electronic and morphologic characteristics that are highly favorable for semiconductive or conductive properties have let phthalocyanines in finding a comfortable place among the organic semiconductors. Since its discovery a variety of phthalocyanine complexes have been synthesized. Moreover, the
chemical versatility of phthalocyanine makes it possible, the introduction of different types of metals in their central cavity and their peripheral functionalization with electron-withdrawing groups, thus allowing the modulation of their electronic properties. Superior to many other conducting and semiconducting organic compounds such as charge-transfer complexes, doped poly-acetylene, poly-pyrrole, poly-thiophene and poly-aniline, metal substituted phthalocyanines possess substantially strong chemical and thermal stability. Recent progress in nanotechnology and nanoscience have facilitated both experimental and theoretical study of the electrical characteristics of various metal substituted phthalocyanines. The versatility, architectural flexibility, and low cost of preparation make them eligible candidates for not only in electronic industry but also in photonic technology. Some of the applications include their use as sensing elements in gas sensors,\textsuperscript{65,66} light emitting display devices,\textsuperscript{67} solar cell elements,\textsuperscript{68} and photovoltaics\textsuperscript{69,70} organic field effect transistors\textsuperscript{71,72} and in medical applications.\textsuperscript{73,74} It is possible to form Schottky type contact between phthalocyanines and metal electrodes when suitable electrode materials are employed.\textsuperscript{75,76} In addition, the electrical properties of phthalocyanine-based devices are also known to be critically dependent not only on the electrode material employed but also upon the ambient conditions.

Apart from their intrinsic use as dyes the metallophthalocyanines (MPc) show the following remarkable and unique physical properties, in which the scientists and researchers were always fascinated.

- Phthalocyanines are easily sublimed and, crystallized resulting in materials of high standard of purity unparalleled with many substances in organic chemistry except a few anthracene type materials which are purified to a similar extent.
Phthalocyanines show an exceptional thermal and chemical stability. In air Phthalocyanines are stable up to 700 K without any degradation and in vacuum most of the metal phthalocyanine are firm up to 1100 K.\textsuperscript{77} There is no evidence of any reaction of phthalocyanine complex to strong acids or bases. But with very strong oxidizing agents like dichromate or ceric salts, phthalocyanine molecules can be broken to phthalimide or phthalic acid.\textsuperscript{34,60}

Phthalocyanines are showing a strong absorption in the visible region of the optical spectra. The optical properties and the strong absorption of phthalocyanines in the visible region are of significant importance in the conversion of solar energy to electrical energy. The conjugated $\pi$ system, containing 18 electrons in the macrocyclic ring, leads to very intense absorption bands. The extremely high absorption coefficients in the visible range of some dyes offer the possibility to prepare very thin photo detectors and photovoltaic cells.\textsuperscript{78}

They provide an astonishingly versatile chemical system. Most of the elements of the periodic table can combine with the phthalocyanine ring and more than seventy different metal phthalocyanines are known to exist. The nature of the sequestered metal ion has a profound influence on the physico-chemical properties of metal phthalocyanines.

One of the major advantages of using phthalocyanines in the nanotechnology is their ability to readily modify the molecular structure allowing the molecular engineering of their physical properties accordingly. By varying the constituents on the ring the range of properties of the metal phthalocyanines can be changed. It is possible to tailor materials with an infinite number of such variations.
The electrical conductivity of these compounds is much altered by the addition of impurities to the pure phthalocyanines. This may be donor or acceptor impurities. Controlled and stable doping is a prerequisite for the realization and the efficiency of many organic semiconductor based devices. If we succeed in shifting the Fermi level towards the transport states, this could reduce ohmic losses, ease carrier injection from contacts and increase the built-in potential of Schottky or p-n-junctions.

1.5 Electrical studies

In recent years the electrical properties of organic semi conducting materials are rapidly making an impact in the area of electronics and optoelectronics. The possibility of using organic thin films in electronic devices has been successfully demonstrated by Forrest and coworkers. They have investigated the use of thin organic films prepared from a range of organic compounds. The organic compounds were sublimed and deposited on the various substrates including semiconductor substrates. Diodes prepared in this way exhibited excellent current-voltage (I-V) characteristics which were similar to those of a conventional p-n junction but with electrical breakdown voltages of the order of 250V. During the last ten years, phthalocyanine (H2Pc) and its metal derivatives (MPcs) have undergone intensive investigation because of their interesting properties and technological importance. Among their many properties, electrical conductivity is the one which attracted a great deal of interest since 1948. The highly extended conjugated π bonds of phthalocyanine structure seem to be a good model for understanding many properties of these organic compounds. The semi conducting behaviour of H2Pc and CuPc was reported by Eley. He proposed that the mobile π-electrons are responsible for the effective conduction mechanism in the phthalocyanines. Since the present work is related with the
metal phthalocyanines the electrical properties of such materials are only highlighted. The basic electrical conduction processes observed in these materials depend on many factors including the phthalocyanine species, the film thickness, the film deposition conditions and the electrode materials.\textsuperscript{87-89} The study of thin film hetero structures of the metal-organic semiconductor type gives useful information concerning the electrical conduction mechanism, transport properties, characteristics of metal–organic semiconductor interfaces.\textsuperscript{90-92} Such information is of particular importance in the development of viable thin film devices. Charge transport through metal-substituted phthalocyanine as prototype organic semiconductor has been one of the controversial matters that have attracted a growing interest in their study. Several conduction mechanisms have been proposed; each would largely depend on the type of metallic contact and would also depend on the strength of the applied electric field across the specimen as well as the temperature range of interest. Considerable effort has been devoted to the investigation of the junctions between metal and conjugated organic semiconductors for many physical measurements and for their use as active components in electronic devices. Gold, silver, aluminium, indium, lead, copper, indium tin oxide (ITO) etc are some of the materials used as electrodes which have different effects on the conductivity of phthalocyanines.\textsuperscript{93,94} The nature of the conductivity with these electrode materials are to be investigated for the successful fabrication of thin film devices. There is a need for best electrode materials in the device fabrication with respect to linearity, reversibility and reproducibility.

Hassan and Gould used indium electrode in CuPc thin films which were characterized by non-uniform field distribution throughout the sample leading to asymmetric D.C conduction properties.\textsuperscript{93} Tunneling through potential barriers of an estimated height of 0.3 eV was dominated for one direction of applied field polarity while
trap-controlled space-charge-limited conduction (SCLC) was observed for the reverse polarity. Trap concentration of about $10^{24} \text{ m}^3$ was found and those was similar to values determined using gold electrodes but have modified energy distribution due to interface defects at the indium electrodes. Gould and Hassan$^{95}$ used gold and lead combination to form a sandwich structure of Copper phthalocyanine thin films established a polarity effects leading to diode-type current density–voltage characteristics. Gold was shown to provide ohmic contact to CuPc when it was positively biased with respect to lead, whereas Schottky and Poole-Frenkel effects were the prevailing conduction processes under reverse bias when the lead electrode was positively biased. The electrical conductivity of Copper phthalocyanine with gold aluminium electrodes has been investigated by Abdel-Malik.$^{96}$ He reported the enhanced conductivity after oxygen doping and the effect of annealing in the electrical conductivity. The charge injection processes and their limitations were reported by Reis$^{97}$ et al. in the Copper phthalocyanine with indium tin oxide (ITO) and aluminium electrodes. Tang and Lee$^{98}$ has investigated the various electrical and photoelectrical parameters of Copper phthalocyanines and reported that strong local chemical bonding is a primary factor determining molecular level alignment at metal–CuPc interfaces.

Anita and Tripathi$^{99}$ reported the electrical behaviour of tin and copper electrodes with Cu Pc thin films. The variation of current with voltage for the three electrode materials have been studied on pellets of copper-phthalocyanine It has been reported that the variation of current with varying voltage is a maximum for a tin electrode and is a minimum for a copper electrode.

The electronic conduction in thermally evaporated thin films of Zinc phthalocyanine has been investigated by Saleha et al.$^{100}$ in a broad temperature range using gold ohmic
contacts. Electronic conduction by charge carrier hopping was dominated at low
temperatures and for all applied voltages. At higher temperatures and at higher voltages
space-charge-limited conduction (SCLC) is the dominated mechanism, which is controlled
by hole-trapping states distributed exponentially within the band gap. Shafai and
Anthopoulos\textsuperscript{101} investigated the D.C electrical properties of Nickel phthalocyanine with
gold-indium electrode combinations. At low voltages, current density in the forward
direction is found to obey the diode equation, while for higher voltage levels; conduction
is dominated by a space charge limited conduction mechanism. Sandwich structures of
Indium phthalocyanine chloride with gold-aluminium electrodes on glass substrates were
investigated by Mammen and Menon.\textsuperscript{94} Device characteristics showed rectification
properties. Conduction at lower voltages is ohmic whereas at higher voltages a space
charge limited conductivity controlled by an exponential trapping distribution above the
valence edge is observed.

Wilson and Collins\textsuperscript{102} have studied thin film interdigital metal-phthalocyanine-
metal devices using H\textsubscript{2}Pc and CuPc, with regard to gas sensitivity. Devices utilizing both
CuPc and H\textsubscript{2}Pc with Au, Ag, Ni, and In electrodes were prepared with Pc layers. They
reported that sublimed CuPc with gold electrodes offers the best material combination
with regard to linearity, reversibility and reproducibility.

Conduction in the evaporated Lead phthalocyanines thin films with aluminium
electrodes were investigated by Gould\textsuperscript{103} and reported the conduction as Schottky
behaviour. Sussman\textsuperscript{104} has shown that both the position of the Fermi level and energy
distribution of the trap levels is altered during annealing of Cu Pc The value of the
intrinsic conductivity and mobility were reported to be relatively independent of
preparation and subsequent treatment.
Electrical conductivity and magneto resistance effect in NiPc, CuPc, ZnPc and H$_2$Pc single crystals have been investigated by Aoyagi$^{105}$ et al. They observed that the central metal ion in the phthalocyanine is responsible for the changes in the activation energy. Fan and Faulkner$^{106}$ have studied the dark conductivity in rectifying cells using H$_2$Pc with indium and gold electrodes. They hold the view that most phthalocyanines are p-type semiconductors. Abdel-Malik and Cox$^{107}$ have obtained ohmic conduction and SCLC in NiPc crystals and determined the statistically important energy levels and the density of states.

Gould$^{108}$ has conducted a D.C electrical measurement on the evaporated thin films of CuPc with thicknesses up to 10μm and observed that room temperature J-V characteristics show ohmic conduction in the lower voltage range and space charged limited conduction controlled by an exponential distribution of traps above the valence band edge for higher voltages. Collins and Mohammed$^{109}$ have studied the dark conductivity of Zinc phthalocyanines as a function of material purity, crystal phase transformation and temperature. From the conductivity temperature data, they have observed a transition from extrinsic to non-extrinsic conduction and the conductivity is found to be dependent on the presence of oxygen. Westphalene et al.$^{110}$ have examined the influence of excited plasmons in small silver clusters placed directly in a photovoltaic active Schottky-contact formed at the interface of indium tin oxide and Zinc phthalocyanines films. Peisert et al.$^{111}$ reported the ionisation potential and the energy level alignment at the organic-metal interface. Nahass et al. $^{112}$ measured the dark electrical resistivity and the thermoelectric power of Copper phthalocyanine at different temperatures in the range 300-450 K. Room temperature current density-voltage characteristics showed ohmic conduction in the lower voltage range and space charge limited conductivity in the relatively higher voltage range.
The Schottky energy barrier and the charge injection metal/CuPc/metal structure was studied using electrodes of various work functions by Mahapatro and Ghosh.\textsuperscript{113}

1.6 Effect of doping on the electrical properties of phthalocyanines

The electrical properties of intrinsic phthalocyanines can be much altered by the addition of impurities. However electrical properties of doped phthalocyanines, has been relatively scarcely investigated, in spite of the considerable impact it could have on device performance and new functionalities. The basic principle of doping in organic semiconductors is similar to that in inorganic materials. Due to weak intermolecular interaction in phthalocyanines, charge carriers are strongly localized and the variable range hopping is the dominant charge transport mechanism in disordered organic solids. Since the mobility and charge carrier concentrations are low in the organic semiconductors achieving a high conductivity requires high concentrations of charge carriers. At variance with crystalline semiconductors, doping of an energetically disordered hopping system not only produces free charge carriers but also creates (relatively deep) localized states in addition to the intrinsic density of states. Therefore, increasing charge carrier density will strongly increase the mobility with moderate doping levels. By adding impurities which either transfer an electron to the electron conducting (LUMO) states (n-type doping) or remove an electron from the hole conducting (HOMO) states to generate a free hole. It has been reported\textsuperscript{114} by Yamamoto that very high conductivities can be achieved when organic materials with a weak donor character like the phthalocyanines are exposed to strongly oxidizing gases like iodine or bromine. Such small dopants can easily diffuse in the layers
which significantly changes the electrical characteristics of these materials. However, systematic investigations into the influence of doping on fundamental semiconductor parameters like the Fermi level or the carrier density are still rare. A proper thermodynamic description of the doping process is still a challenge. Apart from that, only a few attempts have been described in the literature to apply molecularly doped dye layers in semiconductor devices.\textsuperscript{115,116} Collins and Abass\textsuperscript{117} investigated the infrared response of the Lead phthalocyanine films to the chlorine and iodine doping and reported the generation of additional acceptor levels within the band gap and led to a splitting of the valence band.

Huanjun and Yongli\textsuperscript{118} experimented doping in Copper phthalocyanines with alkali metal Sodium and Cesium and reported a energy level shift in organic semiconductors. They reported a Fermi level moving in the energy gap as a result of the doping of electrons from the alkaline metal to the phthalocyanine layer which is a function of the doping concentrations, and another stage in which a significant modification of organic energy levels.

Pfeiffer et al.\textsuperscript{119} explained a better pathway to phthalocyanine doping using larger aromatic molecules with strong p-electron donors or acceptors. In his work phthalocyanines have been doped by adding organic acceptor molecules like orthochloranil, tetracyano-quinodimethane (TCNQ) or dicyano-dichloro-quinone (DDQ). The conductivity of doped Zinc phthalocyanine with the strong electron acceptor F\textsubscript{4}-TCNQ is many orders of magnitude higher than the background conductivity of nominally undoped Zinc phthalocyanine. With a variety of polycrystalline and amorphous materials p-type doping was also carried out. Chamberlain\textsuperscript{120} made a review of doping effects in photoconductivity and photovoltaic cells. He revealed that molecular doping is crucial for
efficient carrier photo generation. The mechanism is the result of the formation of charge transfer complexes at specific sites in the bulk of the organic film. Further progress will depend on optimizing the type, concentration and distribution of dopant in the organic film. The effects of phthalocyanines exposure to oxygen and water vapour was also studied by Chamberlain. A systematic study on doping of Vanadyl phthalocyanine and Zinc phthalocyanine by a fully fluorinated form of tetracyano-quinodimethane by controlled doping was studied by Pfeiffer and Beyer. They observed a significant increase of conductivity and a corresponding shift of the Fermi level towards the valence states with increasing dopant concentration. They concluded that doping has the potential of both reducing the series resistance and increasing the photo voltage of organic solar cells.

Craciun et al. discussed the electrical transport measurements performed on thin films of different metal phthalocyanines doped with potassium atoms. They reported that the nature of the molecular orbitals produces observable effects in the doping dependence of the electrical conductivity of the materials. For ZnPc, CuPc, and NiPc, the added electrons are expected to occupy orbitals centered on the ligands and for CoPc, FePc, and MnPc electrons are added to orbitals centered on the metal atom. Further the temperature dependence of the conductivity showed that a metallic state occurs on a wide range of doping concentrations for various metal phthalocyanines. The effect of O₂ doping on Titanyl phthalocyanine thin films was investigated by Toshio et al. and the effect of NO₂ doping in the CuPc was reported by Lozzi et al. Yongli and Li have investigated the doping cesium on Copper phthalocyanine and observed that valence and core level spectra change at different cesium to Copper phthalocyanine ratios, and reported that the doping induces energy level shift due to the Fermi level moving in the
energy gap as a result of the doping of electrons from cesium to Copper phthalocyanine, and also the modification of Copper phthalocyanine energy levels. Weiying and Antoine \(^{126}\) investigated the doping of Zinc phthalocyanine with tetrafluoro tetra cyanoquinodimethane (F\(_4\)-TCNQ). They reported that the large doping induces an increase in hole current due to improved carrier injection via tunneling through the narrow interface space charge layer. Sharma, Sangodkar et al.\(^{127}\) investigated the electrical and photovoltaic properties of the iodine doped Zinc phthalocyanine thin films, sandwiched between indium tin oxide and aluminium electrodes. Doping with iodine brings adequate changes in the characteristics of the device. The depletion layer width and potential barrier height decrease with iodine doping. The position of Fermi level shifts toward the valence band edge, which indicates that I\(_2\) doping increases the p-type conductivity. Perr et al.\(^{128}\) have reported that in the exposure of Lead phthalocyanine thin film to chlorine molecules, followed by diffusion into the bulk, leads to the formation of acceptor sites. They reported the response of Lead phthalocyanine thin film to NO\(_2\) gas exposure and explained as a surface adsorption process coupled with bulk diffusion. Haan et al.\(^{129}\) have investigated the influence of ozone and chlorine on the conductance of phthalocyanine films.

As organic devices are slowly moving toward commercialization, there is therefore a considerable incentive to achieve a better understanding of doping mechanisms and the opportunities that doping offers in terms of device improvement.

1.7 Fabrication of phthalocyanine thin film device

Characteristic features of all organic devices are their being based on thin film architectures, which place special emphasis and demands on charge carrier injection and transport through interfaces. In order to enhance the conduction and efficiency of organic semiconductor based devices the design of the device structures is important besides the
material used. These devices often comprise multiple layers of organic materials and contacts for electron or hole injection, making metal–organic and organic-organic interfaces exceedingly important in terms of device performance. These interfaces can at times appear to be difficult hurdles to overcome, or instead present real opportunities for improving device performance. For instance, the large injection barriers often found between metals and large gap organic materials are serious impediments to charge injection, and can cause a variety of problems ranging from high turn-on voltages to device degradation. On the positive side, the advanced architecture of organic light emitting diodes (OLED) and photovoltaic cells has been shown to make successful use of multiple organic layers with different energy gaps in engineering molecular level offsets across organic–organic hetero junctions and blocking unwanted carrier transport or recombination of excitons, thus enhancing quantum efficiency. For obvious importance, these metal-organic and organic-organic semiconductor interfaces have been the subject of multiple fundamental and phenomenological investigations aimed at understanding their electronic and chemical structure, and at controlling interface energy barriers. In 1960 Tollin and co-workers have fabricated a chemiresistor device to detect conductivity changes in phthalocyanine films. Azim et al. have conducted the A.C measurements of sandwich devices fabricated entirely in vacuum using thermally evaporated thin films of Lead phthalocyanine device with gold electrodes. They also have observed that the capacitance and dissipation factor decrease with increasing frequency and increase with increasing temperature. Uwira et al. fabricated a hydrogen sensor with a doped Copper phthalocyanine. The detection limit of the sensor is well below 1 ppm H₂ at an operating temperature of 368K; the response and recovery times are about 1 min, depending on the temperature and gas concentration. Himadri and others used Nickel phthalocyanine, in
data-storage devices. The state of the device has been read by applying a small probe voltage which can be refreshed or erased at will. Hysteresis-type behaviour has been observed in the current–voltage characteristics. The space charges at the metal/semiconductor interfaces, stored under the voltage pulse, have been found to control the charge injection and hence the current in these devices. Valli\textsuperscript{134} fabricated chemical sensors using metal phthalocyanines. The integration of the unconventional electrical and optical properties of phthalocyanines with the potentialities of the Langmuir–Blodgett thin films has generated not only promising expectations, but has given also certainties about the realization of functional sensing devices. Roy et al.\textsuperscript{135} fabricated a thin film Schottky device on an indium tin oxide coated glass substrate having a configuration ITO/FePc/Al which behaves as a radiation sensor. The fabricated device when exposed to gamma radiation the current–voltage ($J$–$V$) and capacitance characteristics of the device showed a remarkable change in its $J$–$V$ characteristics. They reported that the exposure to gamma radiation causes can increase the trap density and also structural disorder. The changes in the $J$–$V$ characteristics bear a linear relationship with adsorbed dose and therefore offer its application as radiation sensor. Arshak et al.\textsuperscript{136} also have investigated the effect of $\gamma$–irradiation on the capacitance of Ag/MnPc/Ag devices. Bouvet et al.\textsuperscript{137} have proposed a new technology in which a molecular field effect transistor is used to titrate quantitatively the ozone in air in the range 0–300 ppb. The static and dynamic characteristics of Copper phthalocyanine thin film organic static induction transistors (SIT) fabricated on fluorinated tin Oxide (FTO) coated glass substrate are reported by Joseph and Menon.\textsuperscript{138} Recently, Chuan and Ham\textsuperscript{139} have devised a chemi-resistor type NO gas sensor based on Nickel phthalocyanine thin films. Kouji Suemori\textsuperscript{140} has fabricated a three-layered organic solar cells incorporating a co-deposited interlayer of fullerene and metal-free phthalocyanine,
whose nanostructure was optimized by controlling the substrate temperature during co-evaporation, showed a photoelectric conversion efficiency of 2.5% under illumination with simulated solar light. Miyata et al.\textsuperscript{141} has succeeded in fabricating a high sensitivity chlorine gas sensor using Copper phthalocyanine thin films. He reported that the properties of the Copper phthalocyanine thin film gas sensors were strongly dependent on the preparation conditions of Copper phthalocyanine thin films. The highest sensitivity for Cl\textsubscript{2} gas was obtained in the gas sensor using Copper phthalocyanine thin film prepared under the optimized preparation conditions: substrate temperature of 443K, evaporation temperature of 748K and film thickness of 50 nm. It was found that Cl\textsubscript{2} gas detection was realized at a minimum concentration of 0.18 ppm. Xiao et al.\textsuperscript{142} have fabricated thin film field effect transistors using Copper phthalocyanine as a semi conductive layer and estimated electrical parameters such as carrier mobility and on/off ratio by field effect measurement. It was reported that FET characteristics are strongly dependent on the ordered film morphology. Lijima et al.\textsuperscript{143} studied the magnetic properties of Iron phthalocyanine after doping with potassium The magnetic properties of the doped sample has been considerably increased.

The gap between solving fundamental materials problems and developing new thin film devices for microelectronic and nano technological applications is quickly increasing. For instance, in many applications the development of thin film systems is accompanied by a variety of materials and fabricating hazards particularly the environmental stability of thin films which require extensive research. Future developments are critical to overcoming obstacles to miniaturization as feature sizes in devices reach the nanoscale. Hence thin film device fabrication and its modeling of will be an absolute necessity in the
next decade in order to utilize the tremendous potential of thin film science and technology.
Reference


