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A brief review on the electrical properties of organic phthalocyanine thin films

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Abstract

Phthalocyanines (Pcs) are a class of organic semiconductors with unique electronic, optical, and chemical properties. Their inherent stability and adaptability render them fundamental constituents in a diverse array of electronic and optoelectronic apparatuses. This review explores the direct current (D.C.) electrical properties of phthalocyanine thin films, covering structural aspects, deposition methods, temperature effects, charge transport models, and potential device applications. The impact of dopants, film thickness, and substrate type are also discussed. Emphasis is placed on recent advancements in understanding the relationship between structure and conductivity, supported by theoretical models and experimental data. Insights into device performance, challenges, and future directions are also presented.

Keywords: Organic Semiconductor; Phthalocyanines; Thin Films; D.C. Electrical properties

1. Introduction

Phthalocyanines (Pc's) are macrocyclic compounds with a large delocalized π-electron system, structurally related to porphyrins. Their metal coordination versatility and thermal stability have attracted attention in organic electronics, especially in thin film applications [1,2]. Among various physical properties, their D.C. electrical behaviour plays a significant role in determining their effectiveness in devices such as gas sensors, photodetectors, and field-effect transistors (FETs) [3,4]. Over the past decades, extensive research has been conducted to understand and manipulate their conductivity through synthetic modifications and processing techniques [5,6].

2. Molecular Structure and Electronic Configuration

Phthalocyanines consist of a conjugated macrocyclic ligand composed of four isoindole units connected via nitrogen atoms, forming a planar structure. The cavity in the center can accommodate various metal ions, drastically altering the compound's electronic structure [7,8]. The electrical conductivity is influenced by the central metal ion (M), and peripheral substituents. Metal-free phthalocyanine (H_2Pc) tends to exhibit lower conductivity compared to its metalated counterparts such as CuPc, ZnPc, FePc, and CoPc [9,10]. Fig. 1. shows the general structure of metal phthalocyanine (MPc) with central metal ion. Electronic delocalization within the conjugated π-system enables charge mobility, which can be modulated through metal ion selection and film crystallinity [11]. Transition metals contribute d-orbitals that participate in charge delocalization, affecting conductivity and transport mechanisms.

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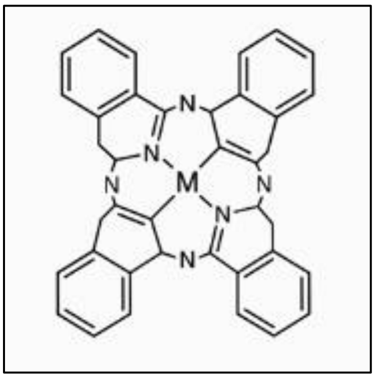

Figure 1 General structure of Metal Phthalocyanine molecule

3. Deposition Techniques and Film Morphology

The D.C. electrical behavior of Pcs is closely linked to film morphology, which in turn depends on the deposition technique. Common methods include:

- **Thermal evaporation**: Produces uniform, crystalline films with good reproducibility [12, 13].
- **Spin coating**: Suitable for soluble derivatives, yielding amorphous or polycrystalline films [14].

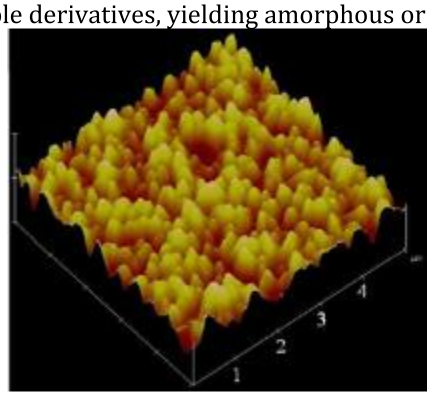

Figure 2 AFM image of ZnPc thin film deposited by Thermal Evaporation

- **Organic molecular beam deposition (OMBD)**: Allows precise control over film thickness and orientation [15].
- **Langmuir-Blodgett (LB) technique**: Facilitates mono-layer-by-layer deposition with oriented molecular packing [16]. Fig. 2. shows the surface morphology of ZnPc films prepared via thermal evaporation [4], Crystallinity and grain boundaries affect carrier mobility and charge trapping. Evaporated films often exhibit higher conductivity due to enhanced crystallite alignment and reduced interfacial defects [17].

4. Measurement Techniques for D.C. Conductivity

D.C. conductivity is typically measured using the two-probe or four-probe method under controlled atmospheres to avoid moisture and oxygen interference [18]. Gold or silver contacts are evaporated onto the thin films, and current-voltage (I–V) characteristics are recorded over a range of temperatures. Two-probe or four-probe setup can be used for conductivity measurement. In Two-Probe Setup the same probes carry the current from the DC source and measure voltage via an electrometer. Four probe features four equally spaced probes contacting the thin film. Outer probes source current; inner probes measure voltage drop with a high-impedance voltmeter, effectively excluding contact resistances. The resulting I–V curves often exhibit non-ohmic behavior, indicating the presence of trap states, injection barriers, or field-dependent conduction mechanisms [19, 20].

5. Temperature Dependence of Electrical Conductivity

Temperature-dependent studies provide insight into the activation energy and conduction mechanisms. Phthalocyanine films exhibit semiconducting behaviour with conductivity increasing with temperature, following an Arrhenius-type relationship:

$$\sigma (T) = \sigma_0 \exp (- E_a / kT) \quad \text{----------} \ (1)$$

where, σ_0 is the pre-exponential factor, E_a is the activation energy, k is Boltzmann's constant, and T is temperature [21]. Fig. 3. show the Arrhenius plots for CuPc films annealed at different temperatures. Activation energy values vary depending on film morphology, crystallinity, and dopant levels, typically ranging from 0.2 to 0.8 eV [22,23].

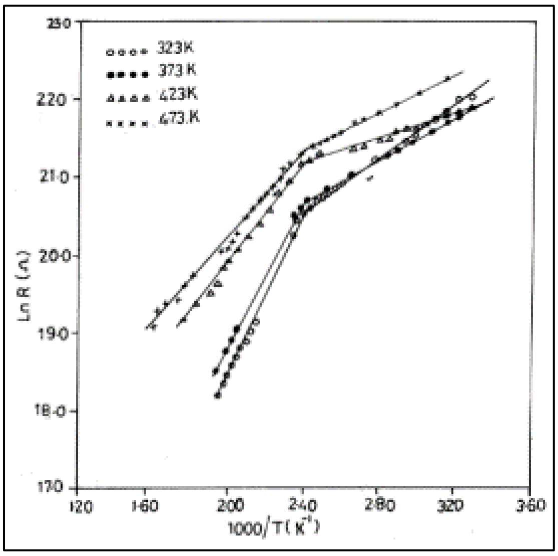

Figure 3 Arrhenius plots for CuPc films deposited at different temperatures

6. Charge Transport Mechanisms

Charge transport in Pc thin films is complex and involves several mechanisms:

- **Hopping transport**: Dominant in disordered or amorphous films [24]. Hopping transport in organic semiconductors refers to a thermally activated mechanism by which charge carriers (electrons or holes) move between localized molecular sites due to thermal energy. This contrasts with the band-like transport seen in crystalline inorganic semiconductors, and it's the dominant conduction mechanism in disordered or amorphous organic materials. In these systems, charge carriers are localized due to disorder and weak intermolecular electronic coupling. Transport thus involves thermally assisted jumps (hops) between neighbouring or even non-nearest localized states. The rate of hopping depends on the overlap of molecular orbitals, energy differences between sites, and thermal energy. As temperature increases, hopping becomes more probable, which will enhance conductivity.
- **Band transport**: Observed in highly ordered crystalline films [25]. Band transport in organic semiconductors refers to a mechanism where charge carriers (electrons or holes) move through delocalized energy bands, similar to what occurs in crystalline inorganic semiconductors like silicon. However, this transport regime is rare in organic systems and typically only occurs under specific structural and thermal conditions. In highly ordered organic crystals with minimal dynamic disorder, charge carriers can achieve partial delocalization, enabling coherent or band-like transport. This is characterized by a decrease in mobility with increasing temperature, due to enhanced phonon scattering—opposite to the behavior seen in hopping transport. Such behavior has been observed in single crystals like pentacene, rubrene, and certain thiophene derivatives [26]. Band transport critically depends on π-π stacking and molecular planarity, which determine the extent of orbital overlap between neighboring molecules. When this overlap is strong and consistent across the crystal, the resulting electronic coupling enables carriers to delocalize over several molecules, forming energy bands. However, any degree of orientational disorder or dynamic fluctuations can disrupt this coherence, pushing the transport mechanism back into the hopping regime [27,28].

- **Polaron conduction**: Accounts for electron-lattice interactions, particularly at higher temperatures [29]. Polaron conduction in organic semiconductors is a fundamental mechanism of charge transport wherein a charge carrier—either an electron or a hole—couples with local lattice or molecular vibrations, forming a quasiparticle known as a polaron. This interaction leads to a self-induced distortion of the surrounding molecular environment, effectively "dressing" the carrier and altering its transport behaviour. In organic materials, especially π-conjugated systems, the molecular lattice is soft and disordered. When a charge carrier enters such a material, it locally distorts the molecular structure, lowering its energy and becoming trapped in a potential well created by its own distortion. This composite of charge plus lattice deformation is what defines a small polaron [30].
- **Poole-Frenkel emission**: Field-assisted thermal excitation of trapped charges [31]. Poole–Frenkel (PF) emission in organic semiconductors describes a field-assisted thermionic emission process where trapped charge carriers are thermally excited out of localized trap states under the influence of an external electric field. This mechanism is particularly relevant in disordered semiconductors like organic thin films, where trap states are abundant and often govern charge transport. In a typical scenario, a charge carrier is trapped at a localized state due to imperfections or energetic disorder. When an electric field is applied, the Coulombic potential barrier that holds the carrier in place is effectively lowered. This field-induced barrier lowering increases the probability that the carrier can escape the trap via thermal excitation—a process that defines PF emission. The phenomenon is expressed quantitatively by the Poole–Frenkel equation, which shows a logarithmic dependence of current or mobility on the square root of the electric field [32]. Models such as Mott's Variable Range Hopping (VRH) and Miller-Abrahams models are used to fit the experimental data [33, 34].

7. Effects of Doping and Substituents

Chemical doping is a well-established strategy for tuning conductivity in organic semiconductors. Iodine, bromine, or TCNQ (7,7,8,8-tetracyanoquinodimethane) are common dopants for Pcs, enhancing carrier concentration by charge transfer [35]. Substituent groups on the Pc ring (alkyl, sulfonic acid, carboxyl) modify solubility, film morphology, and energy levels [36]. Doping can reduce activation energy, promote band-like conduction, and improve environmental stability [37].

8. Influence of Film Thickness and Substrate

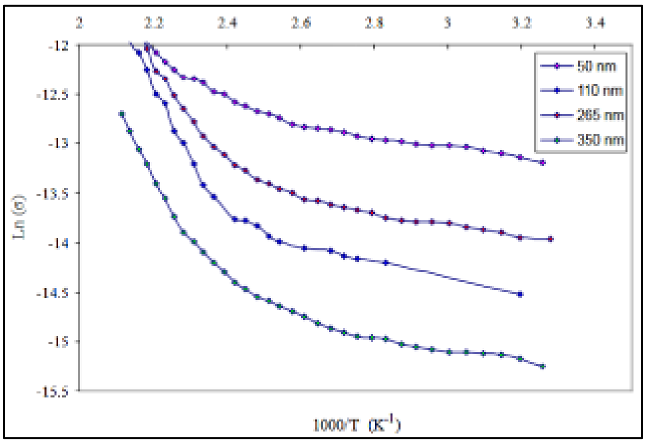

Figure 4 Conductivity (σ) vs Temperature (T) for NiPc thin films for different thicknesses

Conductivity also depends on film thickness. Extremely thin films (<50 nm) may suffer from discontinuity or increased interface resistance, while thicker films (>300 nm) may introduce grain boundaries and defects [38]. Fig. 4. shows the thickness dependence of electrical conductivity in NiPc films [39] . The choice of substrate (glass, silicon, ITO) affects nucleation and growth, influencing orientation and mobility. Substrate temperature during deposition alters crystallinity and film continuity, hence conductivity and activation energy [20,40].

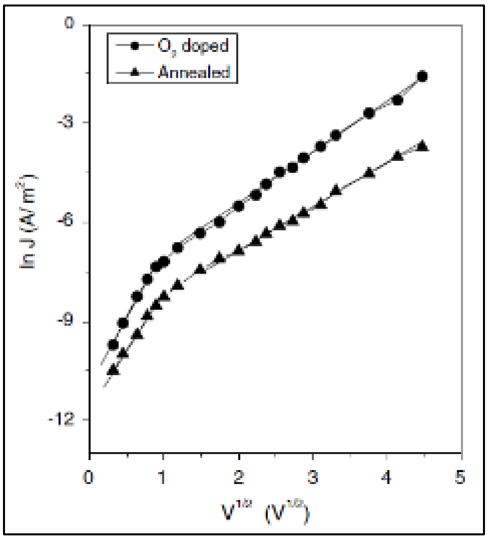

Figure 5 The Current density (J)–Voltage (V) response to Oxygen (O_2)

9. Applications in Electronic Devices

D.C. conductivity of phthalocyanine films is crucial for their implementation in:

- **Field-effect transistors (FETs)**: CuPc and ZnPc used as active layers in organic FETs [41,42].
- **Gas sensors**: Conductivity changes with gas adsorption (NO_2, NH_3, H_2S, O_2), enabling sensing [43]. Fig. 5 show the Current density *(J)*–Voltage *(V)* response to O_2 [44]
- **Photovoltaic cells**: Phthalocyanine as Donor materials in bulk heterojunction or bilayer devices [45].

Improvements in film processing, doping, and device engineering continue to enhance the performance and stability of these applications.

10. Theoretical Modeling and Future Perspectives

First-principles calculations, such as density functional theory (DFT), provide insight into the band structure, density of states, and charge distribution in Pcs [46]. Transport simulations based on drift-diffusion and Monte Carlo methods help understand device behaviour and predict performance.

Future research is expected to explore:

- Hybridization with 2D materials.
- Eco-friendly solvent processing.
- Scalable manufacturing.
- Integration in flexible and wearable electronics.

11. Conclusions

This review work highlights that the direct current electrical properties of phthalocyanine (Pc) thin films are fundamentally linked to their molecular and crystalline arrangement. The choice of metal center and the type of chemical functionalization significantly affect the energies of frontier orbitals and the way molecules pack together. Generally, precise management of the nucleation and growth processes—ranging from vacuum sublimation to solution casting—is essential to customize film microstructure and, consequently, conductivity. Charge transport in phthalocyanine films is often temperature-dependent, exhibiting both trap-limited hopping and space-charge-limited behaviours under varying electric fields and temperature conditions. The thickness of the film also influences transport characteristics – very thin films often display conduction primarily affected by substrate interfaces and traps, while thicker films may demonstrate current limited by the bulk. The dependence on temperature is generally in line with either Arrhenius or Mott-VRH behaviour, indicating the significance of localized states. These observations highlight that conductivity and carrier mobility are highly responsive to film morphology, purity, and external influences (such as doping and exposure to light), as thoroughly discussed in existing literature. Looking toward the future, advancements will rely on sophisticated modelling and materials engineering. First-principles and mesoscale simulations could enhance predictions of charge transport across grain boundaries and through defects, aiding the development of derivatives with higher mobility. In conclusion, the extensive literature verifies that phthalocyanine thin films possess highly adjustable DC electrical properties determined by their molecular structure, film morphology, and history of processing.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

Author contribution statement

"Conceptualization, K.R.R. and C.S.M.; Methodology, K.R.R and C.S.M.; Validation, K.R.R, C.S.M and C.R.I ; Formal Analysis, K.R.R.; Investigation, K.R.R.; Resources, K.R.R and C.R.I.; Data Curation, K.R.R and C.R.I.; Writing – Original Draft Preparation, K.R,R.; Writing – Review & Editing, K.R.R and C.R.I.; Visualization, K.R.R.; Supervision, C.S.M

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