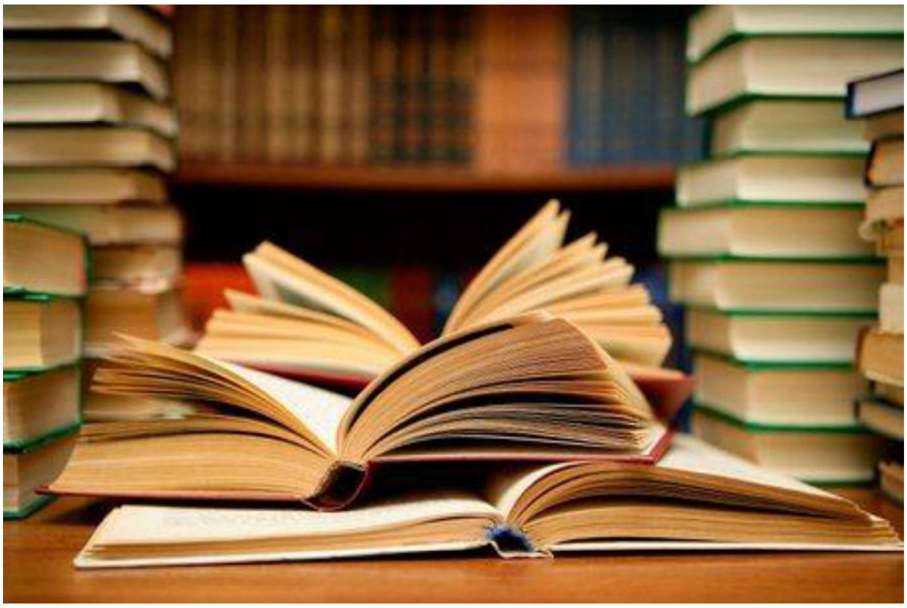
Chapter 1

Introduction and Literature Survey



This chapter covers the essential fundamentals of organic semiconductors and provides a review of relevant literature to frame the thesis. It outlines key concepts, foundational studies, and recent advancements that guide the research focus.

1.1. Introduction:

Organic semiconducting polymers have emerged as excellent candidates for future electronics/optoelectronics devices because of their several unique features, such as solution-based processing at minimal cost, ease of functionalization, and inherent mechanical flexibility[1, 2]. These advantages make possible OSP's integration onto an entire spectrum of low-cost substrates ranging from plastic, paper, and textiles. Such versatility makes them perfect for a verities of applications ranging from electronics and photovoltaics to sensors, energy harvesting, and biomedical technologies[3]. In the last few decades, major efforts have been focused on developing and researching a range of organic electronic devices including organic field-effect transistors (OFETs), rectifiers, polymer electrochromic devices (PECDs), thermoelectric generators, organic light-emitting diodes (OLEDs), and polymer solar cells[1, 4]. Despite very significant efforts, only a few of them, such as ECDs and OLEDs, have found their way from the lab to industries mainly because of their attractive cost-performance ratios[5].

Instead of large development, organic electronics/optoelectronics are still hindered by performance issues, lack of stability, low reproducibility, and short-term operational lifetimes, which prevent them from demonstrating their superiority over their silicon-based counterparts in the commercial market[6]. Reducing manufacturing costs and improving performance are the two most commonly considered cost-effective strategies that can facilitate the improvement of the commercial viability of OSP-based devices. Of all these manufacturing costs, the costliest part involves the film fabrication process and the packaging requirements. Although the synthesis and purification of the active materials are complicated and costly, the serious material wastage in the fabrication of pinhole-free uniform large-area films during production adds more to costs. Thus, the low-cost production of organic electronics bears an intimate relation to the establishment of inexpensive thin-film processing methods[7]. As a matter of fact, even while the films remain consistent and high-quality and material waste is reduced by extremely highly evolved techniques, the devices still do not match up to what was decided for stability, efficiency, and operational life.

Besides, organic semiconductors have intrinsic limitations in charge carrier mobility and also environmental sensitivity, which pitted against more well-established silicon-based technology[8]. There is another critical issue in organic electronics and that is performance. The rather slow carrier transport mechanisms of OSPs mean that these materials operate at slower charge carrier mobility than highly crystalline silicon, thus prescribing the processing speed of a device. However, the whole concept of using organic semiconductors is to offer a competitive route for devices based on amorphous silicon, not compete with crystalline silicon. This will involve selection of promising OSPs with suitable electrical characteristics. While it is hard to change OSPs' intrinsic chemical structure as well as intra-molecular interactions, their inter-molecular interactions may be controlled by manipulating crystal packing and orientation as one potential path forward. Incorporation of filler templates or force-directed self-assembly techniques can increase the degree of crystallinity that have a potential to enhance the performance of devices through betterment of their electronic properties[9]. Hence, controlled increments in material stability, conductivity, and carrier mobility become important precursors unlocking new chances to organic electronics.

1.2. Conducting Polymers:

Conducting polymers are one class of unique materials so different from conventional materials, which are often insulators with extremely low electrical conductivities, often in the order of 10^{-10} to 10^{-12} S/cm. This realization that some polymers can conduct electricity came as a revolution where it was found that a long-held belief regarding all polymer types was actually wrong-that all polymers were merely insulators. It was discovered in the late 1970s when scientists doped polymer chains of polyacetylene with iodine. The conductivity of these materials was highly improved. The reported conductivity values were as high as 10^3 S/cm[10]. It was similar to the capability in metal-based conductors like copper. For these researches, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa were awarded the Nobel Prize in Chemistry in the year 2000. There are other conducting polymers such as polyaniline, polypyrrole, and polythiophene with conductivities of 10^{-1} to 10^2 S/cm depending on the degree of doping and processing conditions[11]. These polymers exhibit both metallic electrical properties as shown in ***Figure 1.1*** and plastic flexibility and processability, hence playing a critical role in a wide variety of applications including organic electronics, sensors, and energy storage.

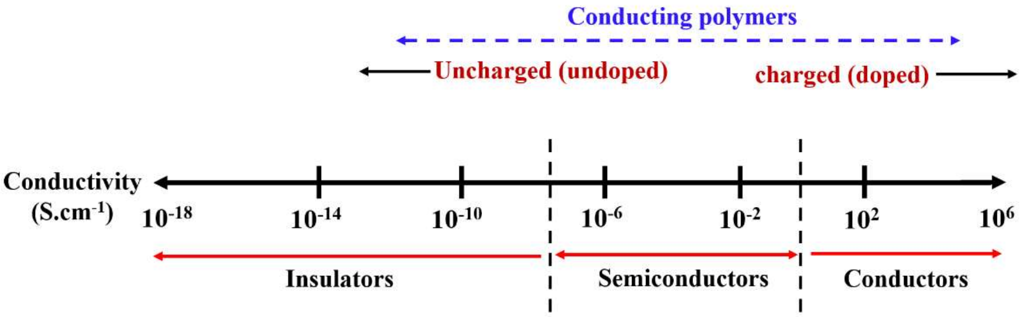


Figure 1. 1 *Represents the log scale of conductivity range of the conjugated polymers.*

1.2.1. π-Conjugated Organic Semiconductors:

Organic semiconductors, particularly those containing π-conjugated systems, constitute an interesting class of materials endowed with unique electronic properties. Organic semiconductors have a structure composed of conjugated systems where the single bonds and double bonds are intercalated within the backbone of the molecules, thus allowing for the delocalization of π-electrons. Such delocalization occurs along a chain of carbon atoms or even sometimes heteroatoms, like nitrogen or sulfur, which are included in the π-system, thus increasing electrical conductivity in the material. The extended clouds of π-electrons spread over the molecular structure allow for quick movement of charge carriers and, therefore, its applicability in electronic devices [11].

Organic semiconductors can be broadly classified into small molecules and conjugated polymers based on their molecular structure as shown in ***Figure 1.2***. Small molecule semiconductors have fewer than ten repeatable units and have well-defined crystalline structures, but usually require vapour phase deposition methods due to the nature of their low molecular weight and more rigid π-conjugated structure that doesn't allow them to dissolve in any solvent which is a significant challenge for industrial scaling. In contrast, conjugated polymers have longer chains, often more than twenty monomer units long, and commonly dissolve in different solvents. Therefore, higher molecular weight conjugated polymers have more flexible processing options. Since, these polymers could be processed from a solution, it makes them particularly attractive for large-scale and flexible electronic applications. Thus, both the small molecule and conjugated polymers have their respective advantages and disadvantages; small molecules are not restricted to well-defined, highly ordered structures, but polymers provide potentially more versatile processing routes. Organic semiconductors can be broadly classified as p-type and n-type materials based on the type of charge carriers they possess. P-type materials preferentially transport holes because of their relatively lower ionization potentials. However, n-type materials prefer electron transport because of their higher electron affinities. These electronic properties make organic semiconductors suitable for a variety of applications, including organic thin-film transistors (OTFTs), organic photovoltaics (OPVs), and other optoelectronic devices.

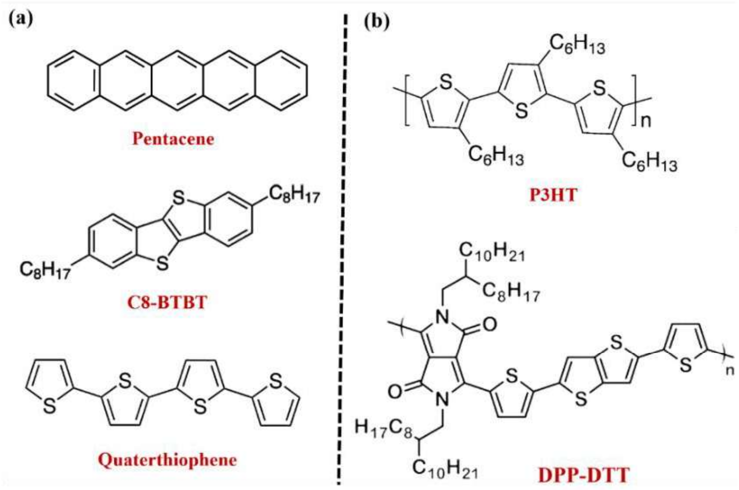


Figure 1. 2 *Types of organic conjugated semiconductors* ***(a)*** *small molecules, and* ***(b)*** *semiconducting polymers*

1.2.2. Charge Transport in Organic Semiconductors:

Organic semiconductors vary significantly from their insulating polymer analogues that are not conjugated and do not transport charge with any measure of note. The mechanism for transport of charge in this material are alternating single and double bonds between the carbon atoms, resulting in sp^2 hybridization: This type of arrangement enables π-bonds that result in the delocalization of the electrons all along the backbone of the polymer, forming an associated "cloud" of delocalized electrons. An electron cloud is a high-density state supporting charge movement. Organic semiconductors, in their intrinsic state, are poor conductors of electricity because they do not carry free charge carriers. Organic semiconductors are doped, and the type of doping determines whether it is an n-type doping through the addition of an electron or p-type doping through the removal of an electron. This doping modifies the electronic structure of the material so that either holes or electrons are charge carriers. The highest occupied molecular orbital (HOMO) is called the valence band, and the lowest unoccupied molecular orbital (LUMO) is known as the conduction band. The gap between HOMO and LUMO is called the bandgap (Eg), that describes to what extent a material can transport charge. Unlike the situation in metals, wherein the overlap of valence and conduction bands leaves no bandgap, the organic semiconductor possesses a small finite bandgap. In addition, doping leads to modulation of the band gap, making the easier transition of electrons between the HOMO and LUMO[12]. Charge carriers injected into the material move through the delocalized electron cloud either by hopping or band-like transport; this is determined by the degree of order in the polymer chains. Charge transport in such materials may be band-like in the ordered domains but tends to be a hopping process from state to state in the disordered regions. The organic semiconductors' dual charge transport mechanism varies linearly with the structure, morphology, and the level of doping of the material.

1.2.3. Doping in Conducting Polymers

Doping is a critical process in enhancing the electrical conductivity of conducting polymers. Unlike conventional semiconductors, where doping involves adding impurities, doping in conducting polymers typically involves chemical or electrochemical processes that alter the electronic structure of the polymer. The process introduces additional charge carriers, either by removing or adding electrons, leading to significant changes in conductivity. Conducting polymers in their intrinsic form are usually semiconductors or insulators, and doping can convert them into highly conductive materials[12, 13].

1.2.3.1. Chemical Doping

(a) In p-type doping the conducting polymer is oxidized that involves removal of electrons from the polymer chain. This results in the formation of a positive charge carrier along the polymer backbone. Oxidation often follows the mechanism of using an electron accepting dopant, which includes iodine (I_2), ferric chloride ($FeCl_3$), and other oxidizing agents. Doping polarons or bipolarons are formed according to the degree of doping, which act as mobile charge carriers. For instance, doping iodine into polyacetylene removes electrons from the polymer backbone and increases its conductivity enormously as described by the ***equation (1.1)***.

$$(\boldsymbol{\pi - polymer})_{\boldsymbol{n}} + \frac{3}{2}\boldsymbol{ny}(\boldsymbol{I_2}) \rightarrow \{(\boldsymbol{\pi - polymer})^{+\boldsymbol{y}}(\boldsymbol{I_3^-})\boldsymbol{y}\}_{\boldsymbol{n}} \qquad \textbf{(1.1)}$$

(b) n-type doping is a process where reduction occurs, which means adding electrons to the polymer chain. In this form of doping, negative charge carriers (electrons) are introduced along the polymer backbone. During reductive doping, an electron-donating dopant like sodium (Na) or an alkali metal donates an electron to the polymer. The polarons or bipolarons carried by n-type doped polymers have increased electron conduction through the polymer by negative charge enhancement as described by the ***equation (1.2)***.

$$(\boldsymbol{\pi - polymer})_{\boldsymbol{n}} + \{\boldsymbol{Na}^{+}(\boldsymbol{Naphthalid})^{-}\}_{\boldsymbol{y}} \rightarrow \left\{(\boldsymbol{Na}^{+})_{\boldsymbol{y}}(\boldsymbol{P})^{-\boldsymbol{y}}\right\}_{\boldsymbol{n}} + (\boldsymbol{Naphth})^{\boldsymbol{0}} \qquad \textbf{(1.2)}$$

1.2.3.2. Photo Doping:

Photo doping is the generation of charge-carriers in polymers under the influence of light. Photons impart energy to excite the electrons that may result in promotions from the valence band which is known as HOMO to the conduction band which is LUMO. Here, chemicals need not be a kind of doping agent; rather the absorption of energy from photons changes the electronic characteristic of the polymer as described by the ***equation (1.3)***[14].

$$(\boldsymbol{\pi - polymer})_{\boldsymbol{n}} + \boldsymbol{h}\upsilon \rightarrow \{(\boldsymbol{\pi - polymer})^{+\boldsymbol{x}}(\boldsymbol{\pi - polymer})^{-\boldsymbol{x}}\}_{\boldsymbol{n}} \qquad \textbf{(1.3)}$$

Here ‘x’ represents the number of electrons or holes generated. In photoabsorption, applied potential excites the absorbed photons to develop electron-hole pairs, which then become separated due to applied electric field[15]. Due to separation of charge carriers, conductivity increases; phenomenon is termed as photoconductivity.

1.2.3.3. Electrochemical Doping:

Electrochemical doping is whereby a potential from the outside is applied to the polymer that is dipped in the electrolyte solution. This makes the process of either removing or adding electrons to the polymer chain now determined by the applied potential[16]. Indeed, this process is very common in devices such as organic transistors and electrochromic displays. This is because in electrochemical doping, one can reverse control the conductive value of the polymers by altering the voltage that they are given to the polymer.

1.2.4. Charge Carriers in Conducting Polymers:

Charge transport in conducting polymers is associated with the formation of quasi-particles like polarons, bipolarons, or solitons, and each of which brings about a specific kind of interaction between charge carriers and the polymer lattice[17].

(a) **Polarons:** The polaron formation in a polymer takes place due to the ionization process: either oxidation, which is the removal of electrons; or reduction, which is the addition of electrons. An electronic distortion that goes on to distort the lattice itself constitutes the transference of the charge within the polymer chain. This redistribution of electron density changes the bond lengths of the polymer as shown in ***Figure 1.3***. In the case of reduction, it shrinks these bonds due to increased electron density, whereas in the case of oxidation, it stretches the bonds due to decreased electron density. This distortion leads to a localized well of potential associated with the charge, thus quasi-particles known as polaron [17]. A polaron has a spin of 1/2 and a charge of ±1e[18]. A polaron introduces new energy states inside the bandgap of the polymer, thus enhancing charge mobility since the polaron can move along the polymer chain.

(b) **Bipolarons:** As the process of ionization proceeds, once two polarons bear the same charge, they can then combine to give a bipolaron as shown in ***Figure 1.3***. The system is more energetically stable than two isolated polarons since it lowers its energy due to the mutual interaction of the two charges. The bipolaron, therefore, indicates an additional reorganization of the electronic states within the HOMO-LUMO gap and lowers the ionization potential for positive charges as well as raises the electron affinity for negative charges. Bipolaron is spin less by nature as the spin of the two polarons adds up to cancel out in combination. Like polarons, bipolarons are mobile within the lattice of the polymer, acting effectively as charge carriers, though it would usually require more energy in a greater distortion of the lattice for bipolarons [17].

Conducting polymers exhibit reversible redox behavior that governs their electrical, optical, and mechanical properties as shown in ***Figure 1.3 (b)***. The polymer backbone undergoes drastic electronic and structural changes upon the redox process, directly influencing conjugation and charge transport. During the oxidation process, electrons are removed from the π-conjugated system of the polymer, resulting in the formation of polarons and bipolarons. This process tends to decrease bond lengths between carbons along the backbone due to increased delocalization and partial quinoid character, which enhances planarity and conjugation. Upon reduction, the addition of electrons will tend to populate anti-bonding orbitals, which elongates some of the bond lengths, disrupts conjugation, and adds increased torsional disorder to the polymer chain. These redox-driven interconversions between benzenoid and quinoid structures common for instance in the polymers polyaniline or polythiophene—can profoundly alter the electronic band structure and, as a result, the material's conductivity.

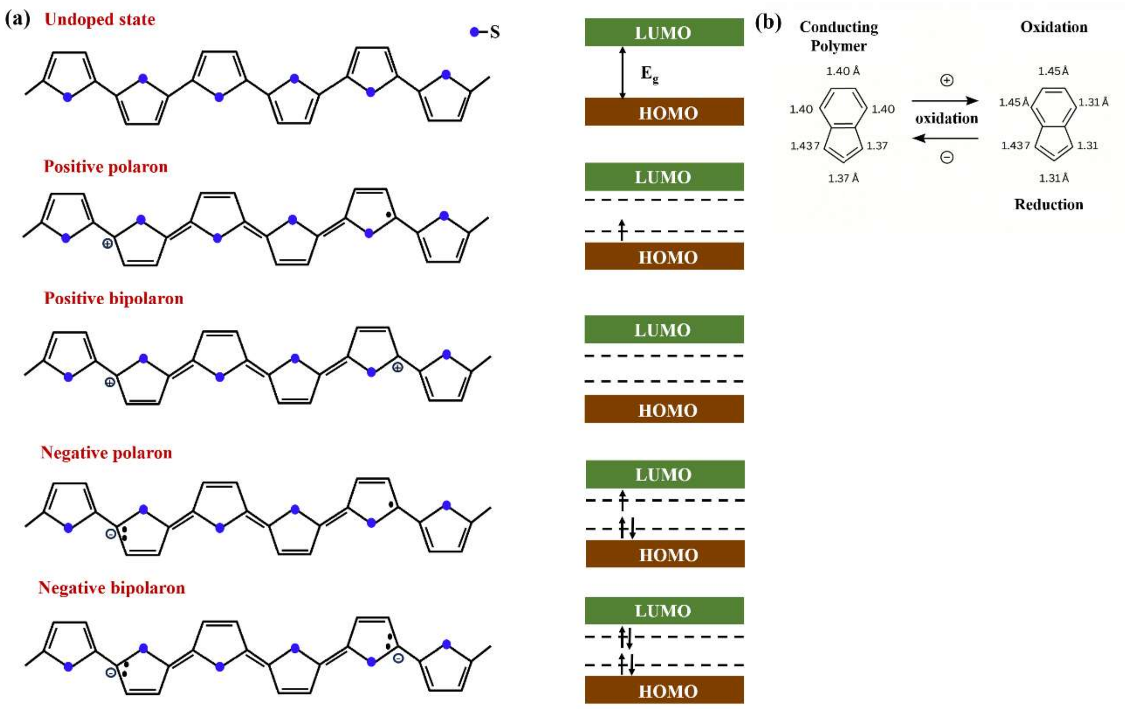


Figure 1. 3 (a) *Illustrates the formation of both negative and positive polarons, as well as bipolarons, in polythiophene.* ***(b)*** *schematic for bond length alteration during oxidation and reduction.*

(c) Solitons: In some conjugated polymers, such as trans-polyacetylene, which has degenerate ground states-meaning, there are many configurations of equal energy-another type of quasi-particle called a soliton as shown in ***Figure 1.4***. Solitons differ from polarons and bipolarons in that they introduce little distortion to the lattice due to the fact that the formation of these quasiparticles represents a sort of transition between the two equivalent resonance forms of the polymer. A soliton is a boundary of one domain with another where the pattern of single and double bonds is reversed. Solitons may have charge or spin, based on the configuration. A neutral soliton carries a spin of 1/2, while the charge-carrying solitons have no spin[19]. Solitons play a strange role in charge transport as they move down the polymer chain with little loss of energy to the surroundings or even deformation of the lattice; they essentially act like solitary waves. That makes them very efficient charge carriers, particularly in polymers having degenerate ground states, through which solitons allow seamless transitions among various geometric configurations of the polymer[20].

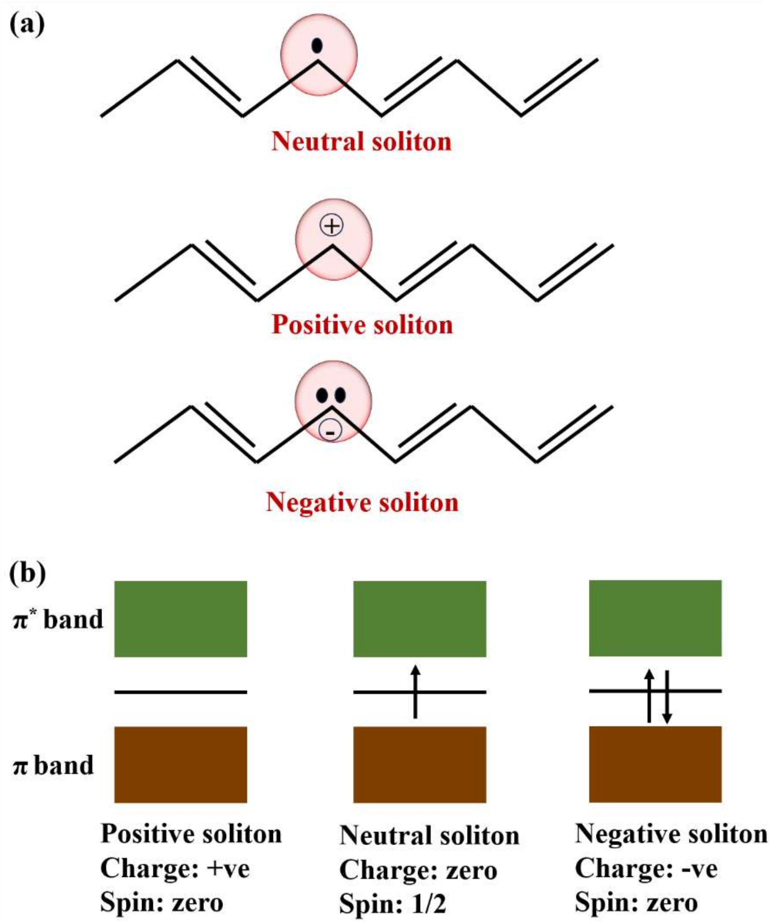


Figure 1. 4 ***(a)*** *Depicts soliton formation along a trans-polyacetylene chain, while* ***(b)*** *presents an illustration of three distinct solitons and their associated band structures.*

1.3. Organic Electronic Devices:

Organic electronic devices encompass a diverse variety of organic semiconductors, all prepared using organic, carbon-based materials with defined electrical characteristics. Examples of these devices include organic diode, organic photodiode, OLEDs, organic solar cells, OTFTs, and a few more devices which display the flexibility of their structures, low-cost production, and more. My PhD research work involves mainly the planar organic devices like OFETs and OPTs. This work is a dissertation about the design, fabrication, and performance analysis of OFETs as an attempt to improve the performance of devices[21].

1.3.1. Organic Schottky Barrier Diode:

A Schottky barrier diode (SBD) is a majority carrier device formed by the metal-semiconductor junction. Unlike conventional p-n junction diodes, the application of Schottky diodes does not involve minority carrier injection, which minimizes charge storage significantly and enables a greater rate of switching. The metal-semiconductor junction results in the formation of a Schottky barrier whose height depends on the difference between the work function of the semiconductor and the metal.

The electrical characteristic of SBDs, prepared by sandwiching an organic semiconductor layer (considered p-type) between two contact electrodes, with one junction of the ohmic type (ITO/Polythiophene) and the other of the Schottky type (Al/polythiophene), can be used to study out-of-plane carrier mobility if the charge transport is bulk limited and not contact limited. When the Schottky junction is formed, e.g., when the work function of the metal is less than the p-type semiconductor, then electrons start migrating from the metal to the semiconductor side until Fermi levels are equilibrated. Holes in the metal side will generally be confined to the surface because of high carrier density in metals whereas a very low charge density in the semiconductor side will cause the depletion region to extend up to a certain depth. Electronic bands will bend in this depletion region/space-charge layer along the direction of the electric field and it is generally called 'band-bending'. The built-in contact potential (V_{bi}) developed because of this charge dipole layer, defined as the difference in metal-semiconductor work functions, which will offer a barrier for further charge migration. Under reverse bias, the applied potential will increase the barrier, and thus ideally, no current will flow through the device. However, in forward bias condition, the applied potential will reduce the potential barrier by an amount eV_F. Therefore, carrier migration will again begin across the junction and device current will start to rise with applied voltage. Here, the carrier mobility will depend upon the intrinsic properties of organic semiconductor. We may use the standard Mott-Gurney law [9,31] to estimate the carrier mobility given below in ***equation 1.4.***

$$J = \frac{9}{8}\varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \qquad \textbf{(1.4)}$$

Where, ε_0 is the free-space permittivity, ε_r is the relative permittivity of the organic semiconductor, and d is film thickness.

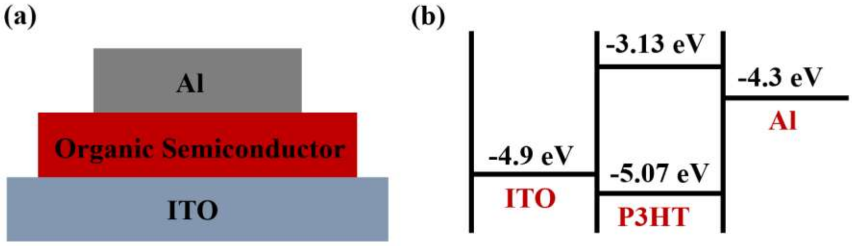


Figure 1. 5 *Schematic of* ***(a)*** *organic diode* ***(b)*** *band positions of Al/P3HT/ITO Schottky diode.*

1.3.2. Organic Field Effect Transistor:

The basic layout of an OFET is an ultra-thin layer of organic semiconducting polymer deposited over a gate dielectric with three electrodes: source, drain, and gate. OFETs are fabricated in four major configurations: bottom gate-top contact (BGTC), bottom gate-bottom contact (BGBC), top gate-top contact (TGTC), and top gate-bottom contact (TGBC) as shown in ***Figure 1.6 (a)***. All the four have some particular advantages and disadvantages depending on the aim of usage and kind of fabrication. The charge transport mechanism in OFETs is understood by the operation of the device under the influence of the applied gate voltage V_G and drain-source voltage V_{DS} as depicted in ***Figure 1.6(b)***. Depending upon the type of semiconductor used, the device could operate in either p-type (hole transport) or n-type (electron transport) mode.[22].

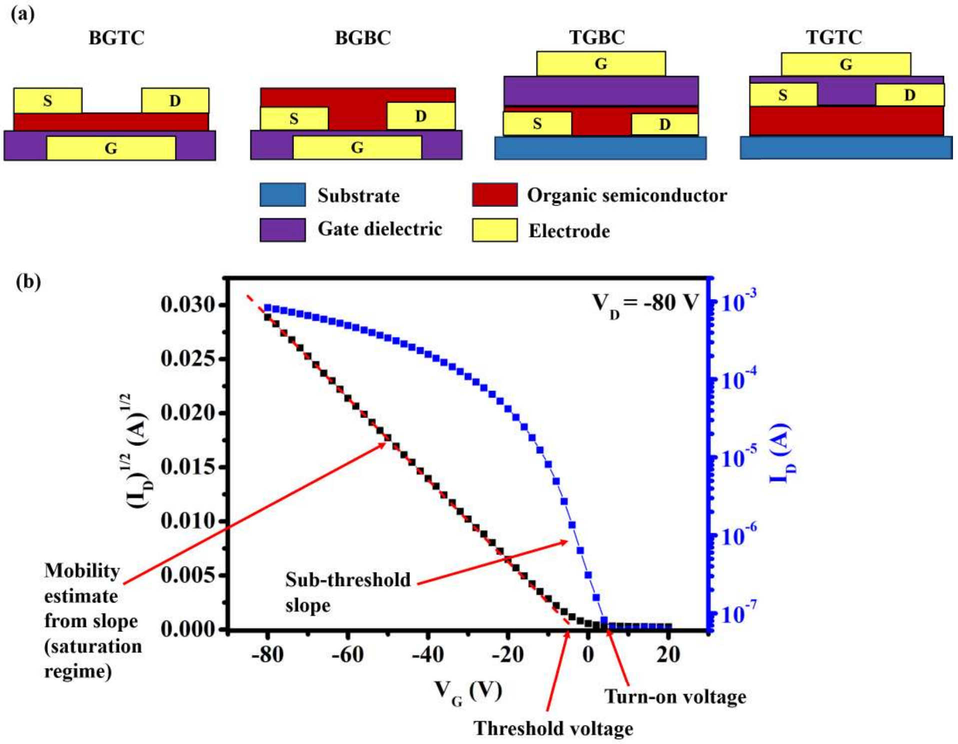


Figure 1. 6 *Illustrates **(a)** different configurations of OFETs, and **(b)** presents the corresponding transfer characteristics.*

1.3.2.1. Working Mechanism of Organic Field Effect Transistors:

When a voltage V_G is applied to the gate, an electric field arises across the gate dielectric. This electric field induces charge carriers; in the case of the p-type material, holes are induced while in the case of n-type materials, electrons are induced within the organic semiconductor at the semiconductor-dielectric interface that forms a conductive channel. If V_{DS} is applied between the source and drain electrodes, the induced charge carriers are transported through the channel based upon the electric field created by V_{DS}[23]. The flow of these carriers is referred to as the drift current and is given by the following ***equation (1.5).***

$$\boldsymbol{I_D = \mu C_i (V_G - V_{th}) V_{DS}} \tag{1.5}$$

Where, I_D is the drain current, μ the charge carrier mobility, C_i is the capacitance per unit area of the gate dielectric, V_G is the applied gate voltage, V_{th} is the threshold voltage (the minimum gate voltage required to induce a conductive channel) and V_{DS} is the applied drain-source voltage. The mobility μ is a critical parameter that determines how efficiently the carriers move through the channel. In organic semiconductors, charge transport occurs via hopping between localized states in the material, which can result in lower mobility compared to crystalline inorganic semiconductors.

The charge transport can be categorized into two operational regimes based on the magnitude of V_{DS}[24]:

(a) **Linear Region:** When V_{DS} is small ($V_{DS}<V_G-V_{th}$), the drain current I_D increases linearly with V_{DS}. This region is characterized by ***equation (1.6).***

$$\boldsymbol{I_D = \mu C_i(V_G - V_{th})V_{DS}} \tag{1.6}$$

(b) **Saturation Region**: When V_{DS} is large enough that the channel near the drain pinches off ($V_{DS}\geq V_G- V_{th}$), the drain current saturates and becomes independent of V_{DS}. The current in this regime is given by ***equation (1.7).***

$$\boldsymbol{I_D = \frac{1}{2}\mu C_i(V_G - V_{th})^2} \tag{1.7}$$

In this region, the transistor behaves like a voltage-controlled current source, and the current is primarily controlled by the gate voltage V_G.

Charge carrier mobility $\boldsymbol{\mu}$ is a key figure of merit in OFETs, as it dictates how easily carriers can move through the semiconductor channel under an applied electric field. The mobility depends on the quality of the organic semiconductor, the molecular ordering, and the interface between the semiconductor and the dielectric. Mobility can be extracted from the transfer characteristics of the transistor. In the saturation regime, the mobility is derived using the ***equation (1.8).***

$$I_D = \frac{W\mu_{sat}C_i}{2L}(V_G - V_{th})^2 \tag{1.8}$$

In the given equation, I_D represents the saturated drain current, C_i corresponds to the areal capacitance of the dielectric oxide, V_{th} denotes the threshold voltage, while L and Wrefers to the channel length and width, respectively.

1.3.3. Organic Phototransistor (OPT) Configuration:

An OPT is a light-sensitive device based on organic semiconductor materials, which integrates the properties of both a photodetector and a transistor as shown in ***Figure 1.7***. OPTs are widely used in applications such as light sensors, imaging devices, and flexible optoelectronic circuits[25].

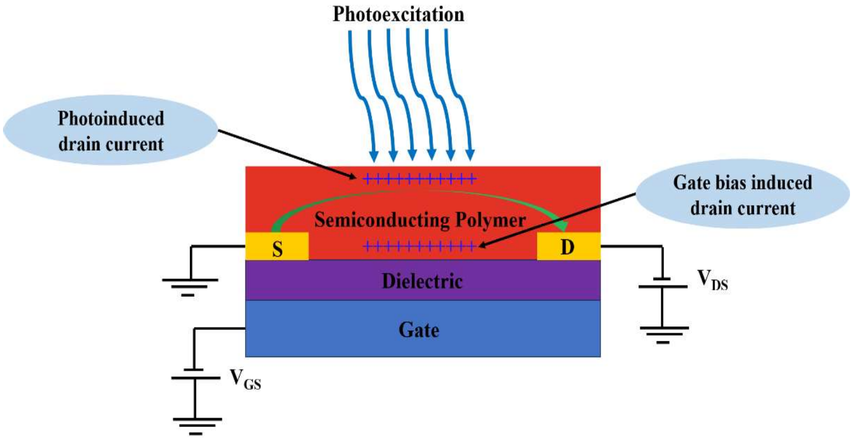


Figure 1. *7 Schematic representation of the operational mechanism of a phototransistor.*

1.3.3.1. Working Mechanism of Organic Phototransistor:

The basic operating principle of an OPT is that it modulates electrical conductivity under light exposure. As soon as light is absorbed by the organic semiconductor, it generates electron-hole pairs, which can be split into free charge carriers. Thus, under illumination additional electrons and holes are also transported through organic semiconductor material, and can be modulated using gate voltage. Overall, the net current of an OPT under illumination is the sum of dark current in absence of light and current due to generation of the photocurrent caused by incident photons. It further emphasizes the importance of the role played by the gate voltage in regulating both the dark and the photocurrent for OPT to operate in either accumulation or depletion modes[26].

1.3.3.2. Photoexcitation and Photocurrent Generation:

When the organic semiconductor absorbs light with energy higher than its band gap, excitons (electron-hole pairs) are generated. The applied gate voltage helps dissociate these excitons into free charge carriers, which then contribute to the total current. This photocurrent can be described as ***equation (1.9)*** [27].

$$\boldsymbol{I_{total} = I_{dark} + I_{ph}} \qquad \textbf{(1.9)}$$

Where I_{total} is the total current, I_{dark} is the dark current (in the absence of light), I_{ph} is the photocurrent. The photocurrent depends on the light intensity and the ability of the device to separate and transport photogenerated carriers.

1.3.3.3. Operation Mode of Phototransistor: The OPTs works the two modes of operation like; accumulation and depletion mode.

(a) Operation in Accumulation Mode:

In accumulation mode, the gate voltage enhances the concentration of charge carriers in the organic semiconductor. For example, in a p-type organic semiconductor, a positive gate voltage attracts holes into the channel, increasing the carrier density. This results in a higher photocurrent because more charge carriers are available to transport the photogenerated charges. The drain current in accumulation mode can be described as ***equation (1.10)***.

$$\boldsymbol{I_D = \mu C_0 \frac{W}{L}(V_G - V_{th})V_{DS}} \qquad \textbf{(1.10)}$$

Where μ is the mobility of the carriers, C_0 is the gate capacitance per unit area, $\frac{W}{L}$ is the width-to-length ratio of the channel, V_G is the gate voltage, V_{th} is the threshold voltage,$V_{DS}$is the drain-source voltage.

(b) Operation in Depletion Mode:

In depletion mode, the gate voltage depletes the carrier concentration in the channel. For p-type semiconductors, a negative gate voltage repels holes from the channel, reducing the number of available carriers. This leads to a lower dark current, as the conductivity of the channel is reduced in the absence of light. However, under illumination, the photocurrent becomes more pronounced because the photogenerated carriers dominate the transport.

1.3.3.4. Key Parameters of Organic Photodetectors:

The performance of an OPT can be evaluated through several key parameters, including responsivity, sensitivity, and detectivity[28].

(a) Responsivity:

Responsivity represents the ability of the phototransistor to convert incident light into photocurrent. It is defined as the ratio of photocurrent to the incident optical power as given in ***equation (1.11)***.

$$\boldsymbol{R = \frac{I_{ph}}{P_{light}A}} \qquad \mathbf{(1.11)}$$

Where $I_{ph}$is the photocurrent, P_{light} is the incident optical power, A is the active area of the phototransistor.

(b) Sensitivity:

Sensitivity quantifies the device's ability to differentiate between dark and illuminated states. A higher sensitivity means that the phototransistor can detect weak light signals more effectively, which is crucial for applications such as low-light imaging. It is given by the ratio of photocurrent to dark current as given in ***equation (1.12)***.

$$S = \frac{I_{ph}}{I_{dark}} \quad \textbf{(1.12)}$$

(c) Detectivity:

Detectivity measures the ability of photo detection of the phototransistor. Higher detectivity indicates better performance in detecting low- intensity light, making the device suitable for sensitive photodetection applications. It is expressed as given ***equation (1.13)***.

$$D^* = \frac{R}{\sqrt{2qI_{dark}}} \quad \textbf{(1.13)}$$

Where R is the responsivity, q is the elementary charge, I_{dark} is the dark current.

1.3.4. Charge Transport in Organic Electronic Devices:

In organic devices, charge carriers (electrons and holes) play a crucial role in device operation. In OLEDs and OFETs, these carriers are injected from the electrode into the organic semiconductor. In contrast, in devices like organic solar cells (OSCs) and organic phototransistors (OPTs), charge carriers are generated within the active layer by exciton dissociation at the donor-acceptor interface, driven by photon absorption. Once generated or injected, the efficiency of the device is largely determined by the ability of these carriers to move efficiently through the organic semiconductor, which is heavily influenced by the material's π-conjugated system. The key parameter for assessing charge transport is the charge carrier mobility, which quantifies how easily charges can move under an applied electric field as ***equation (1.14)***.

$$\langle x^2 \rangle = nDt \quad \textbf{(1.14)}$$

In this equation, $\langle x^2 \rangle$ represents the mean-square displacement of charge carriers, while t denotes time and D is the diffusion coefficient. The parameter n takes values of 2, 4, or 6 for one-dimensional, two-dimensional, and three-dimensional systems, respectively.

Carrier mobility (μ) can be described using the Einstein-Smoluchowski ***equation (1.15)*** [29].

$$\mu = \frac{eD}{k_B T} \tag{1.15}$$

In this equation, e denotes the electronic charge. When an external electric field is applied, charge carriers experience a drift, with their average position shifting along the direction of the electric field. The drift velocity (ʋ) of these carriers is determined by the magnitude of the applied field, F. Consequently, carrier mobility can be characterized as ***given equation (1.16)***.

$$\mu = \frac{\upsilon}{F} \tag{1.16}$$

This mobility is typically reported in cm²/V. s, reflecting how well carriers travel under a given voltage[29]. Several experimental techniques are used to measure mobility, TRM-SHG, and field-effect transistor configurations[30-32]. The thesis investigates charge transport across various fabricated thin films, focusing on anisotropy and the effects of nanofillers on mobility, using time-resolved second harmonic generation. This approach provides valuable insights into how charge transport dynamics are influenced under different conditions, offering a detailed understanding of the variations in mobility within these thin films.

1.3.5. Time Resolved Microscopic Second Harmonic Generation (TRM-SHG):

To explain the directional transport of charge in thin films, a highly advanced TRM-SHG technique has been utilized which is capable of actual mapping pathways of carrier movement in the vectorial presentation form within organic semiconductor films. The traditional methods of I–V curve tracing and Time-of-Flight (TOF) measurements yield sufficient information of mobility anisotropy, but because of their inherent limited angular resolution cannot focus on the directions of maximum and minimum carrier mobility precisely[31]. However, this limitation can be overcome by this TRM-SHG technique as it provides an overall view of carrier mobility, which enables the identification of directions of superior and inferior mobility along with magnitude directly from the captured images. TRM-SHG provides the transport phenomenon with further detailed insight, so that it is possible to evaluate the inherent anisotropy of mobility together with its corresponding activation energies. Carrier distribution in thin film devices was further investigated using the electric-field-induced second-harmonic generation (EFISHG) technique. In this technique, if a static electric field E(0) is applied and the material is simultaneously irradiated with a powerful laser beam, a second-order nonlinear polarization P(2ω) response is induced [33]. This response is described by the ***equation (1.17).***

$$P_{(2\omega)} = \epsilon 0\chi^{(2)}E(\omega)E(\omega)+ \epsilon_0\chi^{(3)}E(0)E(\omega)E(\omega) \qquad \textbf{(1.17)}$$

Here $\chi^{(2)}$ is the second order nonlinear susceptibility, $E(\omega)$ is the electric field, $\chi^{(3)}$ is the third order nonlinear susceptibility and $E(0)$ is the local electrostatic filed. This formulation relates the first term to the standard SHG effect, which is irrelevant in materials with inversion symmetry because all the tensor components vanish in such symmetric conditions. The second term is due to the effect of the static electric field E (0), being the major contribution for the SHG signal in centrosymmetric materials. Such interaction is at the heart of the EFISHG effect, in which the static electric field E(0) consists of an imposed external field E_{ext} and an intrinsic space-charge field E_{sc}[34]. The observation of a EFISHG signal provides a comprehensive mapping of electric and carrier distributions and, therefore, enlightens spatial properties of carrier dynamics. The upgrading of this method to time-resolved measurements finds a doorway for live tracking of transient phenomena of carrier distribution. One of the powerful nonlinear optical techniques applied to probe the dynamics of charge transport in organic thin films, especially in devices such as transistors, is time-resolved second harmonic generation (TR-SHG). This technique provides a non-invasive probe for the spatial and temporal evolution of charge carriers within the active layer in organic transistors, thus providing crucial insight into anisotropy and mobility in the devices. TRM-SHG is very useful in studying how nanofillers or other changes to the thin-film structure affect charge transport behavior. Second Harmonic generation is a nonlinear optical process in which two photons of the same frequency (ω) interact with a material that is not centrosymmetric to produce one photon having twice the frequency (2ω). In the time-resolved SHG, the sample is excited by ultrashort laser pulses, and the generated second harmonic signal is monitored as a function of time. This technique thus enables one to observe real-time dynamics of charge transport in organic transistors. The SHG signal strongly depends on changes in the local electric field, which emerges due to motion of charge carriers in the active layer of the device. Indeed, upon an external bias applied to the organic transistor, charge carriers-instances, electrons or holes-are injected into the active layer, and their motion modifies the local electric field. The modulation is detected as a change in the intensity of the SHG signal over time. Analysis of the time evolution of the SHG signal can yield important information about the mobility and dynamics of charge carriers within the transistor. Charge transport efficiency is very sensitive to anisotropy in organic thin films. Charge transport can be directional due to the molecular orientation and the presence of nanofillers or other structural modifications. Hence, it provides a very unique way to study the anisotropic charge transport behaviour of materials, since the SHG signal is individually sensitive to both the orientation of the material's molecular structure and the direction of the electric field. In the case of charge transport, the second harmonic signal intensity I_{SHG} is related to the electric field E generated by the moving charge carriers as follows ***equation (1.18)***.

$$\boldsymbol{I_{SHG}} \propto \left|\boldsymbol{P}^{(2)}\right|^2 = \left|\boldsymbol{X}^{(2)}\boldsymbol{E}^2\right|^2 \qquad \textbf{(1.18)}$$

Here, $P^{(2)}$ is the second-order polarization, $X^{(2)}$ is the second-order nonlinear susceptibility tensor of the material, and E is the local electric field induced by the charge carriers. The anisotropy of the film can be deduced by examining how the SHG signal varies with the polarization direction of the incident laser beam or by studying the spatial distribution of the SHG signal in different regions of the thin film.

The time evolution of the SHG signal after an applied external bias will, therefore, reflect the carrier mobility using TRM-SHG; charge carrier motion generates a transient's electric field that modulates the SHG signal in time. From the time when the SHG signal changes, one can extract the mobility μ of the charge carriers-the time corresponds to moving charges over the thickness of the active layer. The mobility of the charge carriers can then be linked to the drift velocity υ and applied electric field F as in given ***equation (1.16)***. This allows TRM-SHG experiments to deduce the drift velocity from the time dependence of the SHG signal change, thus providing the real-time capability of obtaining mobility values. Such a measurement is very sensitive to variations of mobility due to incorporation of nanofiller and any structural modification to the thin film structure. Among the quantities so far deduced from TRM-SHG measurements is charge carrier mobility, which can be expressed as in, given ***equation (1.19)***.

$$\mu = \frac{x^2}{2Vt} \qquad \textbf{(1.19)}$$

Here, the mobility of the carrier is denoted by μ where x represents the front of the position of the carrier, V is the applied voltage, and t represents time. Using this equation, the carrier mobility in the transistor is calculated. Studies of how the presence of nanofillers influences charge carrier mobility and anisotropy in organic thin films can be carried out by using TRM-SHG. The differences in anisotropic behavior of charge transport as well as in total device performance might be related to the fact that nanofillers can form local inhomogeneities of electric fields or alter molecular ordering in an organic semiconductor. This information is of paramount importance for optimizing design and performance in organic transistors.

1.4. Limitations of Conducting Polymers in Electronic Devices:

Despite the great potential for application in organic electronic devices, conducting polymers have several significant limitations. Probably, one of the primary limitations is the inherently low charge carrier mobility which originated due to the disorderness of the molecular structures of conducting polymers[35]. This disordered nature of polymers creates inefficient charge transport pathways since charge carriers are bound to move through a maze of poorly aligned polymer chains[36]. This leads to a general lower mobility that also directly affects the speed and efficiency in devices such as OFETs and OLEDs. Besides, environmental sensitivity is another crucial limitation. Conducting polymers degrade sharply upon exposure to oxygen, moisture, or heat. The long-term exposure to such environmental factors can lead to oxidation in the chains of the polymer or induce structural transformations that degrade the electrical properties. This degradation seriously degrades the operation lifetime of devices such as organic solar cells and thus lowers their performance level[37]. Besides, orientation in the molecular level of conducting polymer films is generally random or not very well controlled, such lack of orientation control is a greatest challenge in fabricating high performance organic devices[38]. Charge transport is optimized only when the polymer chains are well-aligned but many times this is not the case as the chains are anisotropic in nature. Charges flow better along the backbone of the polymer chain but if it's not oriented well then it has to move through much less efficient pathways, resulting in reduced mobility. Another point of concern is the interfaces between the polymer and electrodes. Poor contact between the active layer and electrodes usually results in high contact resistance, which reduces the efficiency of charge injection or extraction. This is a particularly challenging problem in devices where efficient flow of charges is essential, such as in OFETs and OLEDs.

1.5. Approaches to Enhance the Performance of Organic Electronic Devices:

To overcome these challenges, several approaches have been taken including control of molecular orientation by solution shearing or solvent evaporation. This significantly helps the alignment of polymer backbones and thus, enhances charge transport subsequently. Other approaches include infusion of dopants or blending with 2D materials like graphene or transition metal dichalcogenides[39, 40]. These 2D materials should offer an avenue for high-efficiency charge transport, but the presence of dopants would enhance carrier density and stability by mitigating the impact of environmental degradation. These strategies, which combine enhanced molecular alignment and blending with advanced materials, are thought to be able to overcome these intrinsic limitations of conducting polymers and push the boundaries of their performance in organic electronic devices.

1.5.1. Molecular Orientation of the Polymer Backbones:

This molecular orientation of polymer chains in conducting polymers has been identified as an important parameter to determine charge transfer efficiency and direct ramifications on the performance of various organic electronic devices, such as OFETs, organic solar cells, or OLEDs. The alignment and the conformation of the polymer backbones indeed, play a pivotal role in how charges move through the material. This is primarily because conjugated polymers are essentially semi-conductive in nature and the delocalized π-electron cloud along the backbone governs charge transport. Keeping this in mind, orienting the backbones at a molecular level ends up being the most basic optimization step in any device[41]. In conducting polymers, the orientation of the backbone relative to the substrate plays a crucial role that determine nature of transport of charge carriers. The backbone of the polymer is an alternation of single and double bonds; therefore, a conjugated system of π-electrons is realized which may potentially contribute to charge transfer. When these backbones are aligned in the same direction, especially unidirectionally oriented, charge carriers can move freely along the backbone. This results in higher charge mobility along this orientation than within any other orientations, including side chains that are non-conjugative and act to insulate. The anisotropy in charge transport therefore yields charge mobility dependent on the direction. The charge carrier mobility is highest along the conjugated backbone of the polymer due to extensive π-conjugation, intermediate mobility in the intermolecular direction of π-π stacking because of orbital overlap between adjacent chains, and lowest carrier mobility is in the direction of insulating alkyl chains side chains, where charge transport is significantly hindered[42]. This results in the control of molecular orientation, which becomes crucial to enhance device efficiency. For instance, in the case of OFETs, it is highly necessary to have the polymer backbones aligned edge-on to the substrate to maximize charge mobility in transporting charges in-plane, further maximizing the device performance. Alternatively, in a device in which vertical transport is predominant, such as OLEDs or organic solar cells, a face-on or end-on orientation should be applied in order to optimize vertical charge transfer.

1.5.1.1. Types of Molecular Orientation:

Mainly, three kinds of polymers' chain conformations have been reported in thin films: edge-on, face-on, and end-on orientations as shown in ***Figure 1.8***. These orientations are mainly distinguished by the relative positions of the backbones and side chains to the substrate[41].

(a) Edge-On Orientation: In this side chain configuration, the polymer backbone is parallel to the substrate, and the alkyl side chains are perpendicular. This orientation would enable efficient in-plane charge transport, which incidentally is favorable for OFETs and other FET-based devices that rely on lateral charge movement.

(b) Face-On Orientation: Here, both the backbone and the alkyl side chains lie in the plane of the substrate, while the π-π stacking is perpendicular to the substrate. This arrangement favors vertical charge transport, making it suitable for devices like organic solar cells and OLEDs that require efficient movement of charge carriers in a direction perpendicular to the substrate.

(c) End-On Orientation: In this less common configuration, the polymer backbone is oriented perpendicular to the substrate, allowing for optimized vertical charge transfer. However, achieving this ideal alignment is challenging with many conjugated polymers, and face-on is typically a more achievable and effective alternative for vertical transport.

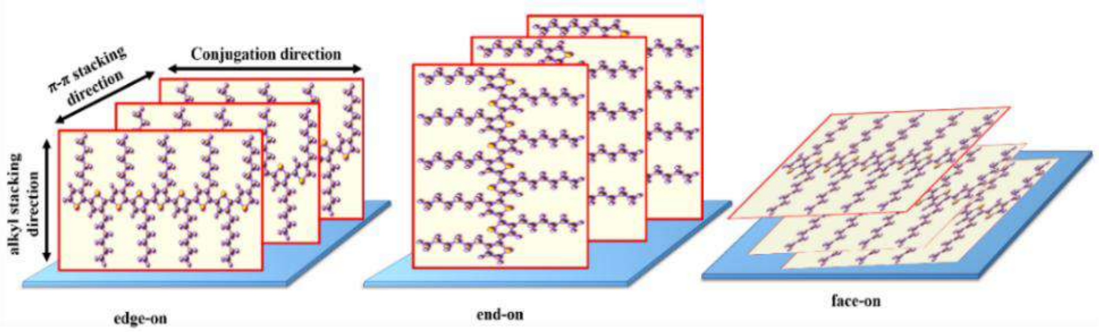


Figure 1. 8 *Represents the schematic for the three different types of orientation occurred in conducting polymer thin films.*

1.5.1.2. Different Approaches for Molecular Orientation:

Different techniques of fabrication have been proven to have effects on the orientation of polymer chains at a molecular level in thin films. Hence, these techniques could be critical in defining the conformation of the polymer that ultimately has an effect on the charge-transport efficiency within the device.

(a) Off- Centered Spin Coating: Off-center spin coating is commonly used in developing a more controlled molecular orientation and improving the crystallinity of polymer thin films. This is required in order to maximize the performance of OFETs. This is done by making the substrate off-axis from the central point during spinning as shown in

Figure 1.9 (a), thus giving an asymmetric distribution of the material being coated. Such imbalance generates shear forces that contribute towards the alignment of polymer chains, such as P3HT, in a preferred direction. This alignment, therefore, supports π-π stacking and enhances the crystallinity of the polymer, enhancing the mobility of charge carriers, which is crucial to the performance of OFETs. Nevertheless, this process produces charge carrier mobility significantly higher than that obtained in other techniques. However, one of the main disadvantages of this technique is to attain uniform film thickness, which arises because off-centre placement results in variation across the substrate, resulting in large variation of device-to-device performance. Besides, it consumes material wastage since part of the coating material is spun off the substrate during the process[43].

(b) **Solution Shearing:** The shearing process can be further adjusted in such a way that it controls the alignment of the polymer backbones in the desired direction. In this technique, shearing of the polymer solution across a substrate allows the polymer chains to align with the direction of the shearing force as shown in ***Figure 1.9(b)***. This kind of method is successful in producing ordered films with unidirectional alignment, favorable to charge transport. Despite the many benefits offered by solution shearing, such as good control over the film's morphology at the molecular level and the capability of yielding highly crystalline and aligned conducting polymer thin films, there are a few significant drawbacks with the method. One of the major limitations of this method is that the shearing process cannot give uniform film thickness over large areas because in many cases, the solution does not spread homogeneously. This non-uniformity can result in poor performance in large-scale electronic devices. Solution shearing also remains sensitive to processing conditions. The influences of these include shearing speed, solution concentration, and temperature of the substrate. Such tiny differences can, therefore have a large impact on crystallinity and polymer alignment. Thirdly, scaling up the technique to industrial applications is also challenging because maintaining the precision control required for uniform film quality becomes tougher at larger scales. Finally, solution shearing may result in wasting of materials. Sometimes, all the solution may not deposit on the substrate. Such material wastage tends to make the fabrication pricey, especially when using costly conducting polymers[44].

(c) Epitaxial Crystallization: It involves the epitaxial crystallization of semiconducting polymers which is a process by which a polymer film is deposited on a substrate in a manner so that its lattice is aligned with the lattice of the substrate it lies under as shown in ***Figure 1.9(c)***. Such alignment of chains is very crucial for the enhancement of charge carrier mobility in semiconducting applications, such as OFETs and organic photovoltaic cells. Epitaxial crystallization can align polymer chains, and the electronic properties of semiconducting polymers are thereby greatly improved. This approach is considered effective for attaining good use for high-performance organic electronics. However, there are several disadvantages associated with this process such as the choice of materials which is required to be lattice matching between the polymer and the substrate. This severely limits the extent to which epitaxial crystallization may be applied to a more general family of semiconducting polymers. Additionally, the process requires highly rigorous control over conditions pertaining to crystallization, particularly temperature and evaporation rate of the solvent, which can make the fabrication process cumbersome. Scaling up the technique to large-area devices is also an issue, as the ability to obtain reliable crystallinity at large sizes of substrate presents difficulties. Finally, deposition of high-quality films free of defects is also sensitive to a very small change in the parameters of processing and thus quite not very practical in terms of large-scale production[45].

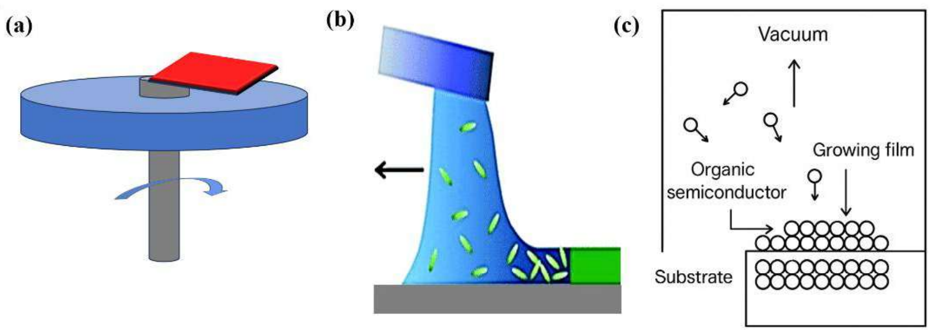


*Figure 1.9 Represents the schematic of **(a)** off-centered spin coating **(b)** Solution shearing **(c)** Epitaxial crystallization for organic thin films.*

(d) Annealing: Thermal annealing is provoked by providing the semiconductor polymers with thermal energy to cause transitions in the orientation of molecular arrangement through the allowance of reorganization of polymer chains. Annealing can induce structural changes, for example, a face-on to edge-on transition, depending upon specific polymers among other substrates used. This process is heavily used as a post-deposition treatment for sharp molecular alignment and for the improvement of the performance of organic electronic devices through their charge transport properties. However, there are many disadvantages associated with thermal annealing. High temperatures would severely degrade the sensitive polymer materials and thus impair the device's performance. Additionally, annealing parameters, temperature and time need to be strictly controlled in order to gain the ideal molecular orientation. Any change in these parameters would cause some irreproducibility. Furthermore, the method is possibly not applicable to every substrate or polymer because some of the temperatures may be beyond the thermal stability of some materials, hence its range of application is limited mainly to flexible devices[46].

(e) Floating-Film Transfer Method (FTM): In collaboration with Japanese researchers, our group have developed a novel, cost-effective technique known as the Floating Film Transfer Method (FTM) as shown in ***Figure 1.9***, which is highly suited for fabricating large-area, highly oriented thin polymer films. FTM allows for the creation of thin solid films of organic semiconducting polymers that float on a hydrophilic liquid substrate, enabling the possibility of layer-by-layer deposition. Various studies have shown that common polythiophene derivatives (such as P3HT, PQT, PBTTT, DPP-TTT, etc.) exhibit a highly beneficial 'edge-on' molecular stacking when processed using FTM, making them ideal for organic field-effect transistor (OFET) applications[47-50].However, this FTM as shown in ***Figure 1.10*** utilizing small circular petri dishes sometimes result in films with unintended circular molecular orientations.

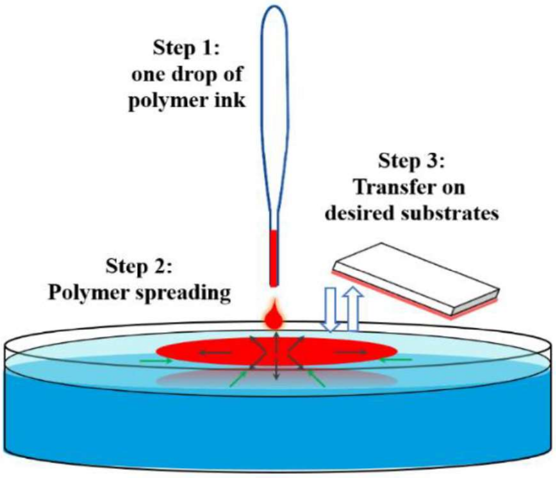


Figure 1. 10 *Schematic of the floating film transfer method.*

To address this, we modified the technique by incorporating a Teflon slider known as Unidirectional Floating Film Transfer Method (UFTM) as shown in ***Figure 1.11***, which ensures that the molecular orientation aligns in a specific direction, either parallel or perpendicular to the film expansion[51]. This refinement not only minimizes material waste but also ensures the production of highly oriented thin films. Furthermore, UFTM offers the advantage of enabling film fabrication directly onto polymer dielectrics without degrading them, as the films contain no residual solvent after processing.

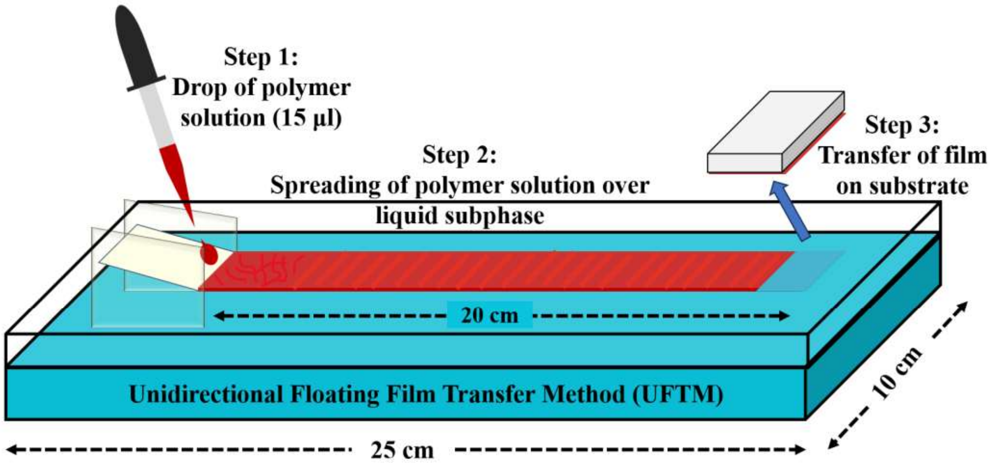


Figure 1. 11 *Schematic representation for the Unidirectional floating film transfer method.*

Therefore, it can be concluded that techniques such as the floating-film transfer method or unidirectional Floating Film transfer method have a large impact on controlling the molecular orientation at the nanoscale. The judicious choice of the modification in the floating Film transfer method allowed us to fine tune the molecular alignment to optimize charge mobility in the appropriate direction for OFETs. Advanced characterization methodologies such as grazing incidence X-ray diffraction and polarized UV-Vis-NIR absorption are very useful to confirm whether these alignment strategies are successful in optimizing molecular orientation that ultimately influences the performance of a device.

1.5.2. Blending with Nanomaterials:

Mixing nanomaterials with conducting polymers is an efficient way to enhance organic electronic devices. Nanomaterials, such as graphene and carbon nanotubes as well as 2D transition metal dichalcogenides, result in large improvements to overall charge transport, conductivity, and mechanical properties of the polymer. Such nanomaterials exhibit high electrical conductivities with efficient pathways for charge carrier transport that compensate for the low mobility inherent in conducting polymers. In addition, nanomaterials can improve structural strength in the polymer matrix, thus ensuring stable environmental properties and increasing the life spans of the devices. Under hybrid scenarios, such as OFETs or organic solar cells and OLEDs, this even optimizes electrical and mechanical properties[52-54].

1.5.2.1. Conventional Nanomaterials:

Nanomaterials are those particles whose dimensions are measured in at least one dimension in the nanometre scale, which ranges between 1 and 100 nanometers. Those have properties other than their bulk counterparts mainly because of a large surface area to volume and quantum effects that occur at the nanoscale. Among nanomaterials, there exist various structures for nanoparticles, nanowires, nanotubes, and nanosheets that can be made up of metals, oxides, polymers, or carbon-based compounds. Such end-use applications include electronics, medicine, energy storage, and environmental remediation. It is the electric, optical, mechanical, and catalytic properties present within nanomaterials that allow such technology to be developed, particularly in the production of high-performance devices, which includes sensors, transistors, and energy systems.

1.5.2.1.1. Different types of Conventional Nanomaterials:

(a) Carbon Nanotubes (CNTs): Among the best-known nanomaterials applied in organic electronics, they owe their importance to their structure and their outstanding electrical properties. CNTs essentially consist of rolled-up sheets of graphene structured in cylindrical carbon forms. They can exist as single-walled or multi-walled structures, the latter having multiple concentric layers of rolled-up graphene sheets. The significant advantage of CNTs is their highly conjugated structure, that allows the free motion of π-electrons along the axis of the tube. Such a high level of inhomogeneous electrical conductivity is accompanied by excellent charge-carrier mobility and is therefore very advantageous for the application within OFETs, where the charge transport needs to be fast and efficient. The one-dimensional character of the CNTs creates the possibility of forming continuous pathways for charge carriers, sharply diminishing scattering, and also enhances electron and hole mobility in the polymer matrix[55, 56].

(b) Graphene: It is one of the most widely researched nanomaterials in organic electronics, which finds great appliqué for its superior electrical, mechanical, and thermal properties. Graphene is a two-dimensional material that presents itself through a single atomic layer of carbon atoms arranged in a hexagonal lattice structure. This is therefore one of those materials that boast superlative electrical conductivity due to the delocalized π-electron network. This in turn makes it a suitable candidate for the above applications where very high conductivity and effective charge transfer are required, such as in the case of OLEDs and organic solar cells. The potential possibility of producing thin films of the minimum possible thickness indeed helps in increasing interfacial charge transfer across different layers of the device and so ultimately results in better efficiency. For instance, formation of efficient charge extraction at the interface between the electrode and organic solar cells leads to reduced energy losses[40, 57]

(c) Transition Metal Dichalcogenides (TMDs): Yet another class of nanomaterials has been in the center of attention during the last few years. TMDs, such as MoS_2 and WS_2, are materials that are semiconducting. Differently from graphene, TMDs have an intrinsic band gap, which makes them more viable for on/off switching in devices, including OFETs and photodetectors. The materials belong to the group of two-dimensional materials and feature a layered structure comprising metal atoms between layers of chalcogen atoms (sulfur or selenium). Their composition leads to layered structure, which can be easily exfoliated into ultra-thin sheets that can be integrated into organic electronic devices. The merits of TMDs lies in the fact that electronic properties are readily tunable with the thickness and the number of layers, thus giving freedom in device design[52, 58].

(d) Metallic Nanoparticles: Apart from carbon nanotubes, inorganic metallic nanoparticles, such as gold or silver, act as enhancement of electrical conductivity in organic electronics. Such conductive nanoparticles may indeed form conductive bridges between the polymer matrix; therefore, they exhibit increased charge mobility by means of plasmonic effects. In particular, metallic nanoparticles increase light absorption and enhance charge transport due to localized surface plasmon resonances in organic solar cells and OLEDs. However, it must be said that using metallic nanoparticles will always impose the risk of charge trapping where electrons or holes are trapped at the surface of the nanoparticle and thus create non-smooth current transport. In devices like solar cells, this will lead to recombination losses[59, 60].

1.5.2.1.2. Disadvantages of Conventional Nanomaterials:

Although traditional nanomaterials such as metallic nanoparticles, graphene, carbon nanotubes, and TMDs have greatly improved organic electronics, they still have substantial disadvantages. Although traditional nanomaterials such as metallic nanoparticles, graphene, carbon nanotubes, and TMDs have greatly improved organic electronics, they still have substantial disadvantages. The lack of a band gap limits graphene's use in semiconducting functions, and attempts to modify it typically result in a worsening of its electrical properties. Despite having excellent conductors, CNTs' use is limited by issues with aggregation and contact resistance. Despite being semiconducting, TMDs are often less useful for large-scale applications because to their extensive production needs and poorer charge mobility. Despite improving conductivity, metallic nanoparticles have the potential to create charge trapping sites that impede the efficient passage of charges through the apparatus[60].

1.5.2.2. Organic Graphitic Carbon Nitride (g-C_3N_4) and (C_3N_5):

This opens up new prospects in organic electronics, where new organic 2D materials are becoming available such as graphitic carbon nitride, g-C3N4, and its derivative C_3N_5[61, 62]. Coupling the benefits of the tuneable electrical properties along with enhanced compatibility with organic polymers, these materials overcome most of the deficiencies drawn from traditional nanomaterials. Graphitic carbon nitride, abbreviated as g-C_3N_4, is an ideal organic semiconductor material that encompasses both great conductive and semiconducting properties due to its excellent structural stability along with the tuneable band gap. Whereas g-C_3N_4 has no natural band gap, graphene is a worse material for transistors and other switching devices since its band gap cannot be tuned. This is an emerging compound: a new organic 2D material, a graphitic carbon-nitride derivative known as C_3N_5. The 2D nature of this material gives it special features and benefits for organic electronic devices. The layered material can even act as a template in planar devices in the most effective way, even in the OFETs at high performance. In these devices, C_3N_5 with a 2D structure provides a flat well-ordered surface which maximizes the ordering of conducting polymers that they deposit on it and thus enhances charge transport over the device. This 2D nature also enables better interaction at interfaces, reducing charge recombination and improving carrier mobility. The tunable electronic properties of C_3N_5, including its adjustable band gap, further optimize its performance in OFETs by promoting efficient charge separation and transport while maintaining strong compatibility with organic materials[62]. Thus, C_3N_5's 2D structure not only enhances charge mobility but also plays a crucial role in achieving uniform film morphology, making it highly effective as a template in planar organic devices.

1.6. Existing Problems and Objective of Thesis:

Fabricating devices with low cost and high performance is still a great challenge for the researchers and its operation voltage with the flexibility. So, our motivation is fabricating devices with cost effective fabrication techniques as well as how the fabrication techniques affect the molecular orientation further. I chose the UFTM method which provides the highly ordered crystalline thin film for high performance devices and further tried to fabricate a polymer composite thin film at liquid-air interface and observed how the variation of the filler affects the charge transport of the organic semiconductor. Further I used advanced techniques to study the charge transport as well as anisotropy effects in the devices. Overall, the key objectives of my thesis are;

- Fabrication of cost effective highly oriented organic semiconductor thin film at liquid-air interface using UFTM.
- Fabrication of highly sensitive Flexible phototransistors using polymer dielectric without distorting the dielectric properties of thin film by using UFTM.
- Fabrication of highly sensitive low operated voltage phototransistors using ion-conducting dielectric.
- Investigate charge transport and charge transport anisotropy through the TRM-SHG study.
- Improvement in the charge transport property of the OFETs by band engineering in conjugated polymer by using template assisted 2D materials Polymer/C_3N_5 hybrid device.
- Further investigation of charge transport in OFETs using TRM-SHG focuses on how molecular orientation influences charge transport and how 2D materials enhance charge carrier mobility by facilitating smoother charge flow.