

Chapter 1
Introduction and Literature Review

1.1.Introduction

Organic semiconducting polymers (OSPs) have received huge scientific interest owing to their striking features of low-cost solution-processing compatibility, easy functionalization, and mechanical flexibility, which means they can be processed on low-cost substrates, such as – plastic, paper, and even on our cloths. These unique properties make OSPs suitable for vast applications- from electronic and photovoltaic to gas sensors, energy harvesting, electrochemical and bio-related applications [1–5]. In the last few decades, among the organic electronic devices, organic field effect transistors (OFET), rectifiers, electrochromic devices (PEC), thermoelectric generators, organic light-emitting diodes (OLED), polymer solar cells, etc., have been fabricated, and extensively researched by various groups worldwide. Among them, only a few devices like PEC and PLED found their way out from the laboratory level to industries owing to exceptional cost-to-performance ratio [6,7]. Other electronic devices still lack performance, stability, reproducibility, and an operational lifetime to compete with commercially available silicon-based devices. Thus, to make OSP-based devices commercially viable, there are two most suitable approaches: one is to reduce the manufacturing cost, and second, to improve device performance.

The major cost in manufacturing these OSP-based devices originated from film fabrication and packaging. Although complex and multistep synthesis and refinement make the active material costly, wastage of these materials while fabricating pin-hole-free, homogeneous, and large-area films increases the fabrication cost significantly. Thus, pronouncing low-cost production of organic electronics suggests that thin-film processing techniques are cheaper compared to inorganic counterparts [8]. Next, a significant cost factor arises from the packaging of these devices. High dependency on stable environment conditions shortens the operational lifetime of OSP-based devices, so high-end packaging is essential.

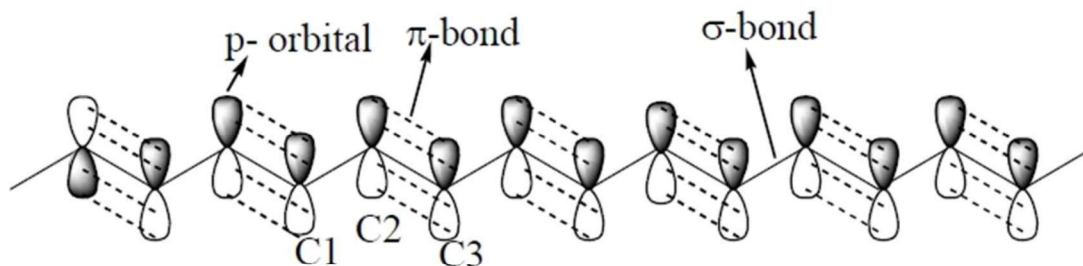


Figure 1.1 π -conjugated backbone system in *trans*-polyacetylene.

The following and equally important criterion for the realization of this technology is the performance of these devices. In terms of mobility that determines the processing speed of a device, OSPs are much behind the highly crystalline silicon because of their relatively slow carrier hopping mechanism [9]. However, the main aim of using organic semiconductors is not to match the speed of crystalline silicon (Si) but to replace the amorphous Si-based devices. To do so, selecting suitable OSPs with promising electronic properties is crucial. Since their inherent chemical structure and intra-molecular interaction is difficult to alter, we can tune the inter-molecular interactions by modifying their crystal packing and orientation [10]. The degree of crystallinity may increase by incorporating filler templates or force-directed self-assembly, which eventually may lead to better device performance by altering their electronic properties. Thus, controlled improvement in materials stability, conductivity, and carrier mobility will open up new possibilities in the field of organic electronics [10,11].

1.2.Organic Semiconductors

Most organic materials do not conduct electricity, but it has been proved that electronic components, typically made from Si, can also be made from organic materials by carefully designing the molecular structure. These organic semiconductors also possess unique optical and electronic properties analogous to those of inorganic semiconductors. The

inception of organic semiconductors was in 1954 by Hiroo Inokuchi through electrical resistance measurement in violanthrone [12]. However, the breakthrough in this field was achieved in the year 1977, when semiconducting trans-polyacetylene (CH)_n were exposed to halogen vapors (chlorine, bromine, or iodine), and the room temperature conductivity ($\sim 3.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$) enhances seven orders of magnitude ($\sim 30 \Omega^{-1} \text{cm}^{-1}$) in (CHI_{0.22})_n [13]. In 1978, (CHI_{0.28})_n, obtained from controlled doping of cis-(CH)_n, exhibited room temperature conductivity $> 500 \Omega^{-1} \text{cm}^{-1}$ [14]. Hideki Shirakawa, Alan G. MacDiarmid, and Alan J. Heeger were the pioneer of these findings, and they were awarded the noble prize in chemistry in 2000. By the end of the 1980s, researchers were able to achieve significant results in organic semiconducting polymer-based devices worldwide.

1.2.1. π -conjugated materials

Organic semiconductors in their pristine form are recognized for their basic electronic structure, i.e., π -conjugated system. This system is formed by carbon p_z orbital overlap in a molecular structure containing alternating single and multiple (double) bonds, sometimes heteroatom in conjugation (for example, an overlap of nitrogen p_z orbitals and aromatic carbon rings in case of polyaniline), where π -electrons delocalize over the entire molecular backbone instead being confined over a single carbon atom (Figure 1.1). This electronic delocalization makes the conduction of electricity possible in these systems.

π -conjugated organic semiconductors can be broadly classified into two categories depending on their molecular weight: small molecules and π -conjugated polymers. Organic small molecules, containing less than ten monomer units, have low molecular weight and

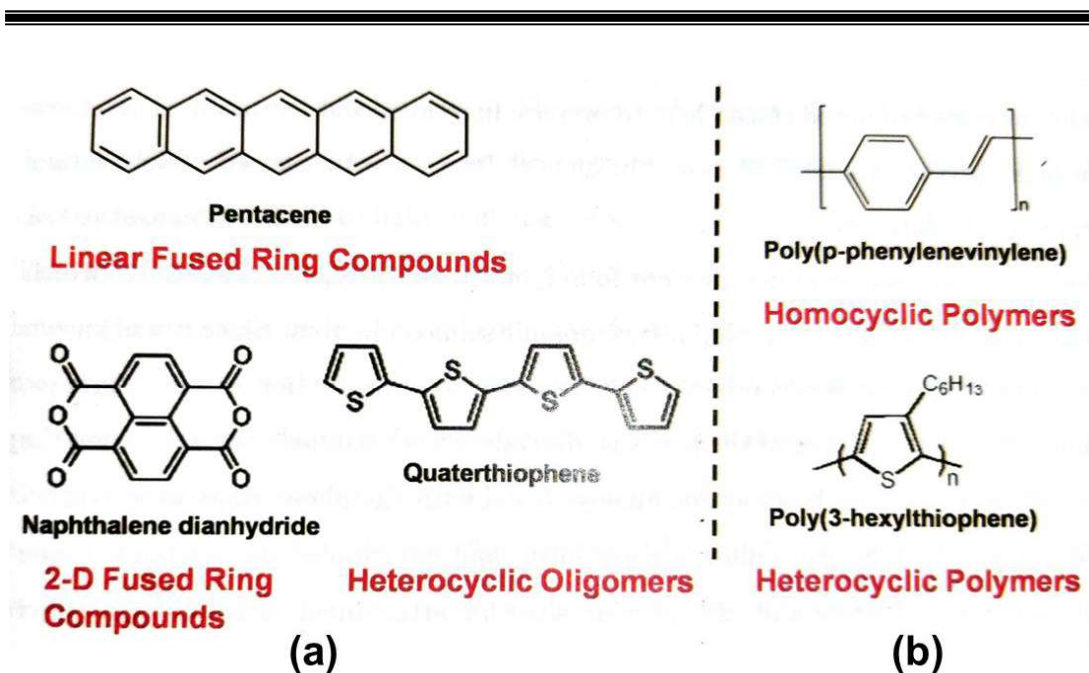


Figure 1.2 Classifications of organic conjugated systems, (a) small molecules, and (b) semiconducting polymer.

generally exist as crystals below their melting point. Thus, small molecules need to be thermally evaporated, thus less suitable for large-area film fabrication. On the other hand, polymers possess monomer units of more than twenty and have higher molecular weight. Organic semiconducting polymers (OSPs) are usually found in a thermodynamically non-equilibrium state and thus may display glass-transition-like behavior. OSPs generally dissolve in common organic solvents like chloroform, toluene etc., thus offering a lucrative option for industry-level large-area film fabrication. Small molecules can be further classified into linear fused ring compounds, 2D fused ring compounds, and heterocyclic oligomers, whereas OSPs are homo- and heterocyclic in nature. Examples of different kinds of π -conjugated organic semiconductors have been summarized in Figure 1.2. Now, besides chemical classification, OSPs (and small molecules also) can be divided into p-type and n-type. Unlike inorganic semiconductors, this classification is based on whether electron or hole transportation is preferred (in terms of mobility) in that system. According to energy

level positions, p-type OSPs show low ionization potential, and n-type materials exhibit high electron affinity.

1.2.2. Ionization and generation of polaron, bipolaron, and solitons in conjugated polymers

It is well-known that, just like inorganic crystals, the orbital overlap between adjacent organic molecules causes the formation of electronic bands. The highest occupied electronic levels form an electronic band called Highest Occupied Molecular Orbital (HOMO), analogous to the valence band in the inorganic case. The lowest unoccupied electronic levels constitute an electronic band called Lowest Unoccupied Molecular Orbital (LUMO), which is analogous to the conduction band. And the energetic gap between HOMO and LUMO, i.e., band-gap (E_g) regulates the intrinsic electrical properties of these organic semiconductors.

Now, most conjugated polymers are found to have a non-degenerate ground state; thus, an interchange between single and double bonds leads to variations in polymer energy. For example, in polythiophene, two configurations are possible: one is the aromatic form, and another is the quinoid form, and the aromatic form is the low-energy configuration compared to its quinoid form (Figure 1.3 (a) & (b)) [10]. Generally, the ionization process, i.e., charge addition (reduction) or charge subtraction (oxidation) from π -conjugated systems, originates positional as well as electronic distortions. Thus, upon ionizing, the molecule first reorganizes its electron density, whereas the nuclei change its bond length in response to the new electron density (reduction leads to additional electron density among the nuclei: shorter bonds; oxidation causes less electron density: longer bonds). In the case

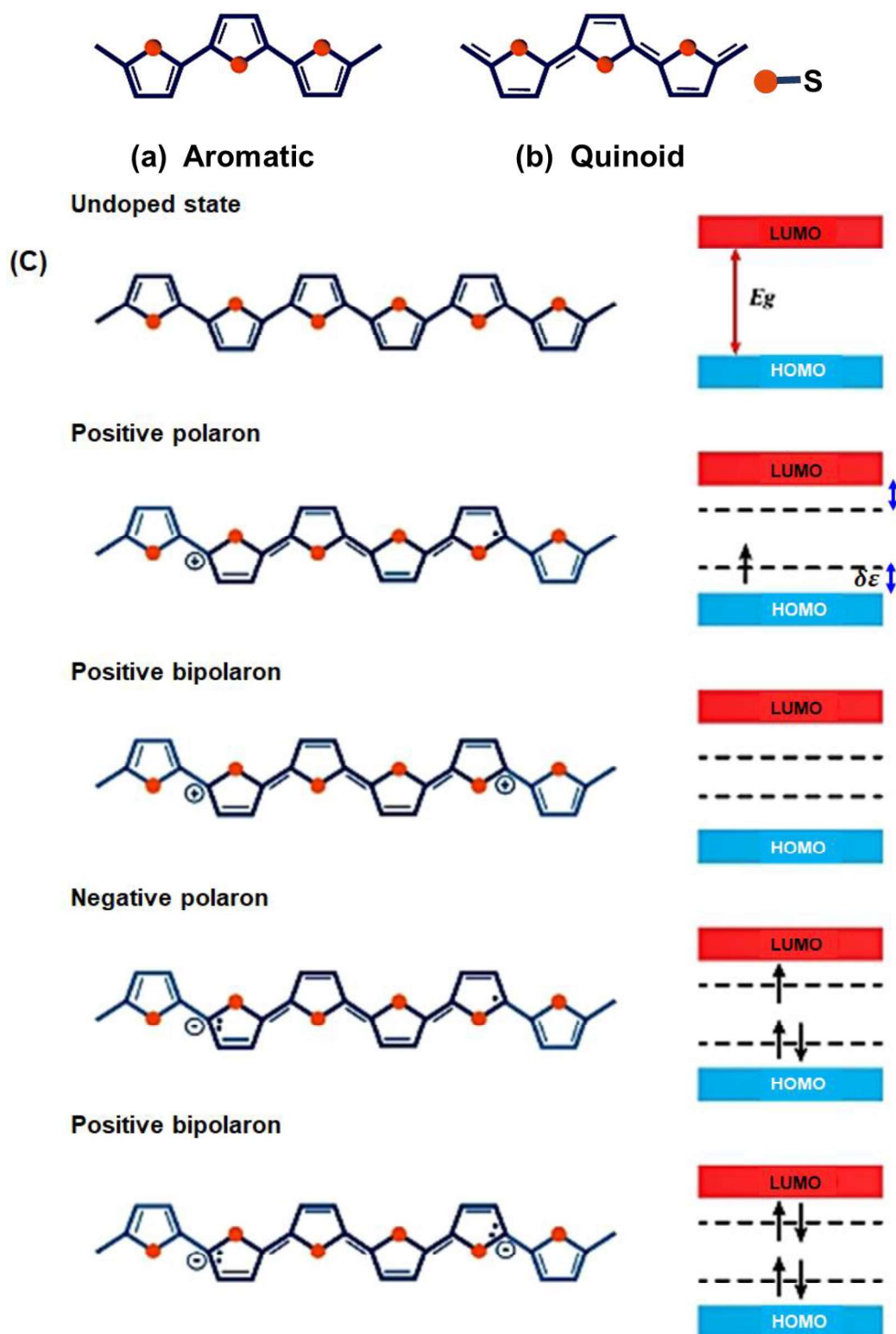


Figure 1.3 (a) Aromatic and (b) Quinoid form of polythiophene, (c) positive and negative polaron and bipolaron formations in polythiophene (Image credit [10])

of polythiophene, oxidation leads to a conformational change from an aromatic structure to a high-energy quinoid structure. These distortions cause a potential well that can travel along the chain at the cost of some additional energy. Thus, a charge combined with an associated potential well or lattice disorder is a quasi-particle called a polaron, and they are intrinsically confined in space, naturally on a single organic molecule or part of a conjugated backbone [15]. Polaron (spin: $1/2$; charge: $1e$) formation causes the injection of electronic states through a local $\delta\varepsilon$ shift from the top of the HOMO and bottom of the LUMO into the forbidden band gap, as shown in Figure 1.3 (c). It should be noted that HOMO levels remain full, and LUMO levels remain empty in forming polarons. Next, second ionization causes the formation of bipolarons through the dimerization of two interacting polarons having the same charge, as shown in Figure 1.3 (c). Bipolaronic defects are energetically more favorable than two individual polarons in a system. As polaronic states appear within the HOMO-LUMO gap, the effective ionization potential (IP) is thus reduced in positive polarons, and the electron affinity (EA) is increased in negative polarons, compared to the intrinsic organic molecules [10,15].

Next, some conjugated semiconductors have degenerate ground states, i.e., two equivalent resonance forms, e.g., trans-polyacetylene (PA). As shown in Figure 1.4 (a), two geometric configurations of trans-PA, formed by the exchange of the single and double bond pattern, possess exactly the same total energy, and thus they have an equivalent probability of occurring, and they can coexist in two parts of the same 1D chain. As a result, two charges which were about to form a bipolaron through dimerization can further lower their energy by separating into two solitary quasi-particles (Figure 1.4 (b)). As this process does not increase overall energy or cause any lattice distortion, it is energetically favorable. Thus, two domains with two different carbon-carbon bond alternations contain a transition region

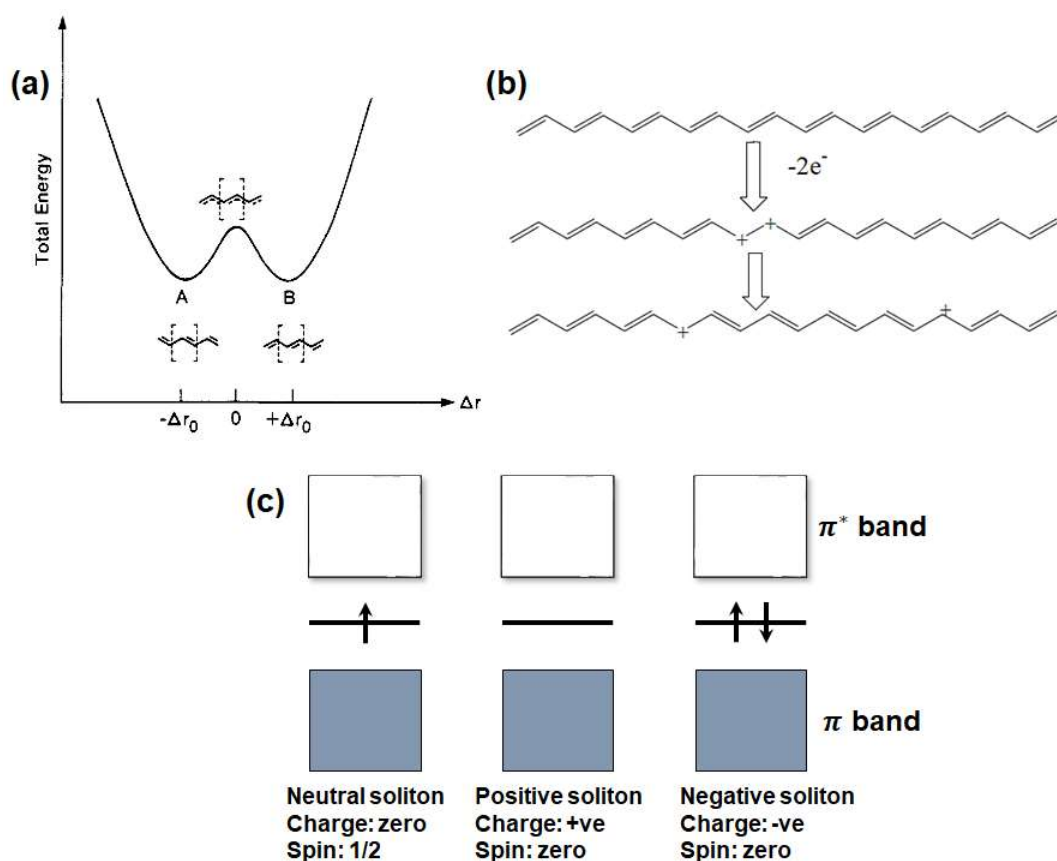


Figure 1.4 (a) Total energy curve corresponding to *trans*-polyacetylene chain with respect to the degree of bond length alternation Δr (image credit [15]), (b) soliton formation on *trans*-polyacetylene chain (image credit [15]), and (c) three different solitons with band structure illustration.

associated with an isolated charge, which can propagate without any dissipation or lattice deformation, like a solitary wave accompanying a domain boundary or wall. Such quasi-particles are known as solitons, which signify the excitation of the conjugated system from one potential well to another with the same energy [15]. When a pristine *trans*-PA contains an odd number of conjugated carbons, a π - electron remains unpaired, giving rise to a neutral soliton. The spin density (or charge density) in a neutral soliton (in a charged soliton) does not remain confined over a single carbon atom; instead, they delocalize over several carbon atoms, corresponding to the width of a soliton. The double bonds in a long *trans*-PA chain gradually elongate, and single bonds shorten from one edge of the soliton

towards the other edge, so the bond pattern reversed while arriving at the other side. It signifies that the bond lengths become equal in the middle of the soliton. Soliton formation causes a localized electronic level to appear at the mid position of the HOMO-LUMO gap, which is half-occupied for a neutral soliton, empty for a positively charged soliton, and doubly occupied for a negatively charged soliton, as shown in Figure 1.4 (c). Unlike polarons, neutral soliton has a spin $\frac{1}{2}$, and charged ones are spinless [10,15].

1.2.3. Charge injection mechanisms

The performance of any organic electronic device generally depends on two factors: charge injection efficiency through the contacting electrodes into the semiconducting layer and effective carrier transport through the bulk semiconductor. Generally, electrons (or holes) can reach the LUMO (or HOMO) level through three different approaches:

- a. chemical doping,
- b. optical excitation, and
- c. carrier injection from electrode

However, thermal excitation in organic semiconductors is very unlikely because of the relatively larger HOMO-LUMO gap (>1.5 eV).

1.2.3.1. Chemical doping:

The free movement of π -electrons over the conjugated backbone is not enough for charge conduction in organic systems, as they are tightly packed/confined over the single conjugated chain. Thus, some of the π -electrons need to be added or removed from the polymer chain to make them conduct electricity. This ionization can be achieved through chemical doping (e.g., with bromine, iodine, etc., as discussed in section 2) or

electrochemical doping. Thus, doping can form charge carriers like polaron, bipolaron, and soliton in conjugated backbones, which facilitates charge conduction [1,13–15].

1.2.3.2.Optical excitation:

Absorbing light with energy greater than the HOMO-LUMO gap, electron-hole pairs are generated in π -conjugated systems, which are bound to each other through the coulomb force of attractions, which is known as an exciton. Usually, Frenkel-type excitons are found in organic semiconducting systems having exciton binding energy in the range of 1 eV. Excitons are also quasi-particles that are created throughout the bulk of the semiconductors upon photoexcitation and tend to diffuse over regions of low dielectric constant. The exciton population gradient is also responsible for the excitons to drift over the bulk. The effective exciton diffusion length is very crucial for optical-to-electrical conversion efficiency in organic optoelectronic devices. Exciton diffusion length also depends on the degree of structural coherence, effective conjugation length, and intrinsic molecular structures [16,17].

1.2.3.3.Carrier injection from electrode:

Charge injection in a device includes electron transfer from the HOMO level of a conjugated system to the Fermi level of the contact electrode, i.e., hole injection, or electron transfer from the contact electrode Fermi level to the LUMO, i.e., electron injection, creating polaronic species in both cases. Suppose the electrode work function is such that charge transfer from the contact electrode to the semiconductor is energetically favorable. In that case, electrode Fermi energy is larger than the positive polaron formation energy or smaller than the negative polaron formation energy, and spontaneous charge transfer will occur until system equilibration is reached. This type of contact is known as an ohmic

contact (Figure 1.5 (b)). On the other hand, if the electrode work function is such that it does not allow spontaneous charge transfer, and offers a barrier for charge injection, then it is said to be a blocking contact (Figure 1.5 (a)). A device having two ohmic contacts, one for injecting electrons and another for holes, is called a basic diode. Under forward bias condition, that means both contacts will inject charge carriers for which it is ohmic, and the forward current in the device will exponentially increase with applied potential. And under reverse bias conditions, both the contacts will block/resist charge flow, and thus a negligible amount of current (due to minority carrier) is found flowing through the device, giving rise to a non-linear diode characteristic. For the devices with only one ohmic contact, current will still flow through it. However, since only one carrier type is injected, the current flowing through the device will be limited by the built-up space charge. Even if there is no ohmic contact, current can still flow through the device at the expense of some additional energy to overcome the so-called injection barrier, φ_b . Energy-level alignment at the electrode-semiconductor interface will be very important to improve the overall device performance [11,19–21].

1.2.4. Charge transport in semiconductor bulk:

In contrast to inorganic crystals, organic conjugated systems are kept organized through weak van der Waals bonds between adjacent molecules. Thus, electronic interactions between neighboring molecular orbitals in a lattice are weak, leading to narrow bands with bandwidth <500 meV. Moreover, with increasing temperature, intra- and inter-molecular vibrations destroy the energetic coherence in the lattice, and then the scattering-dominated mean free path of the charge carrier will approach the distance between adjacent sites. Thus,

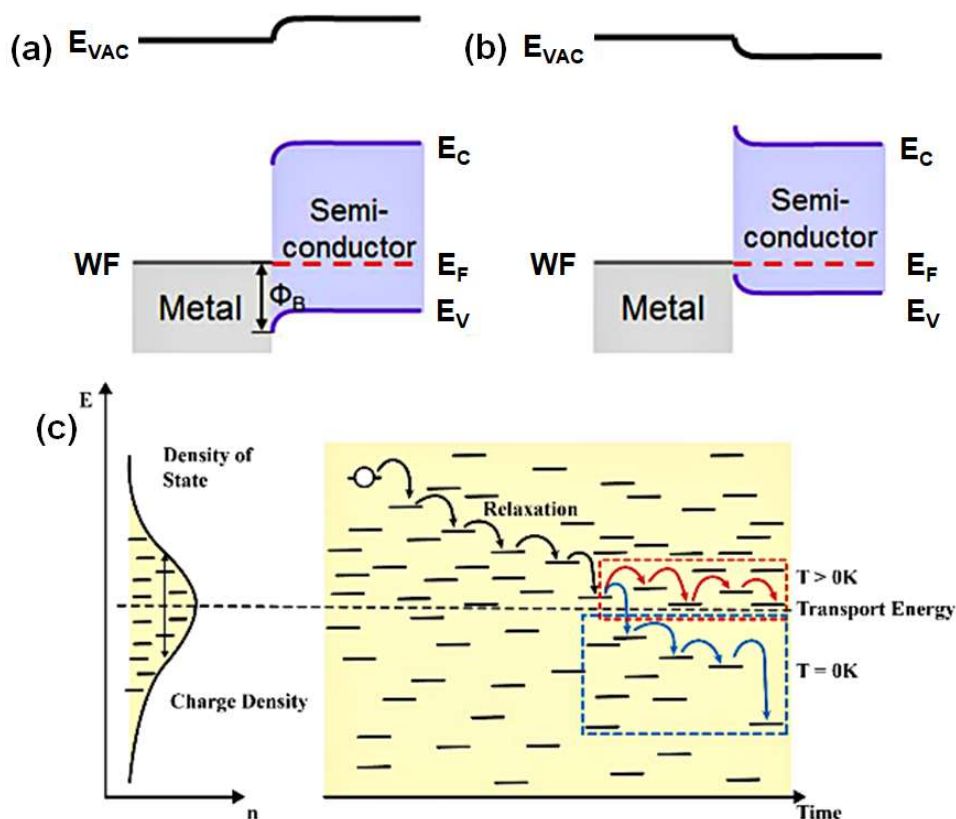


Figure 1.5 Energy level arrangement at the metal-semiconductor interface after the formation of (a) Schottky contact and (b) ohmic contact (image credit [18]); (c) Density of states and carrier transport mechanism based on Gaussian disorder model (image credit [10]).

except for some highly pure molecular crystals (e.g., naphthalene, perylene), which show a bandlike transport at low temperatures, charge carriers in organic conjugated polymers move through a ‘hopping’ mechanism [9,22]. The charge carriers in OSPs, polarons, bipolarons, and solitons can move along the conjugated backbone and hop/jump between adjacent conjugation segments. As charge conduction in conjugated polymers occurs through a perturbation of the intrinsic molecular electronic levels, charge carriers must overcome an energy barrier during each intermolecular hopping; thus, charge transport is a prolonged phenomenon in organic systems (Figure 1.5 (c)). Several factors strongly affect

charge transport, like polaron formation energy, degree of orbital overlap between adjacent molecules, and local energetic and spatial disorders [9,15,22,23].

Now, according to one of the successful models of charge transport in disorder systems with localized states by Mott [24], charge transport happens through a variable range hopping (VRH) from one localized state to another by thermal activation or tunneling, and the conductivity is described as follows:

$$\sigma = \sigma_0 \exp\left(\frac{E_c - E_{eq}}{K_B T}\right) \quad (1.1)$$

Where σ_0 is a pre-exponential factor, E_c is the mobility-edge energy, and E_{eq} is the systems equilibrium energy (or Fermi energy), T is the absolute temperature and K_B represents the Boltzmann constant. The hopping probability between two adjacent states with energetic and spatial separation of ΔE and, Δx respectively, is given by the Miller-Abrahams theory [25] as follows:

$$p \propto \exp\left(-2\alpha \cdot \Delta x - \frac{\Delta E}{K_B T}\right) \quad (1.2)$$

Here, α is the inverse localization radius. The total conduction by hopping can be estimated by integrating p over all the energy states and spatial separations.

1.2.5. Charge transport within organic devices:

Charge carriers (electrons and/or holes) are either inserted from the contact electrode into the organic semiconductor (for OLEDs or OFETs) or generated within the active layer in case of organic phototransistors (OPTs) or organic solar cells (OSCs) through photoinduced exciton generation and charge separation at the donor-accepter interface. After that, the performance of organic conjugated material-based devices critically depends on the efficient charge transport within the π -conjugated systems. The key quantity to study

the charge transport efficiency in the conjugated systems is the charge carrier mobility. Without applying any external biasing potential, carrier transport is purely diffusive in nature and can be described as,

$$\langle x^2 \rangle = nDt \quad (1.3)$$

here, $\langle x^2 \rangle$ signifies mean-square displacement of charge carriers, t denotes time, D is diffusion coefficient, and $n = 2, 4,$ or 6 for 1D, 2D, and 3D systems, respectively. The carrier mobility (μ) can be expressed using the Einstein-Smoluchowski equation [9] as:

$$\mu = \frac{eD}{k_B T} \quad (1.4)$$

Here, e represents the electronic charge. As charge carriers also drift under an external electric field, the average position of the charge carriers displaces according to the electric field direction at a velocity (v) depending on the amplitude of the applied field, F . Thus, carrier mobility can also be defined as:

$$\mu = \frac{v}{F} \quad (1.5)$$

The drifting effect dominates the carrier migration across the organic active layer, and thus $\text{cm}^2/\text{V}\cdot\text{s}$ is the unit used to express mobility [9]. There are several experimental techniques available to determine the effective carrier mobility, for example, the time-of-flight (TOF) method [26,27], electric field-induced second-harmonic generation (EFISHG) method [28], pulse-radiolysis time-resolved microwave conductivity (PR-TRMC) method [29], field-effect transistor configuration [30], diode configuration [9,11], etc. In this thesis, we have focused on the Schottky barrier diode (SBD) configuration and OFET configuration to study electrical mobility in the dark and OPT configuration to explore mobility in the dark and light.

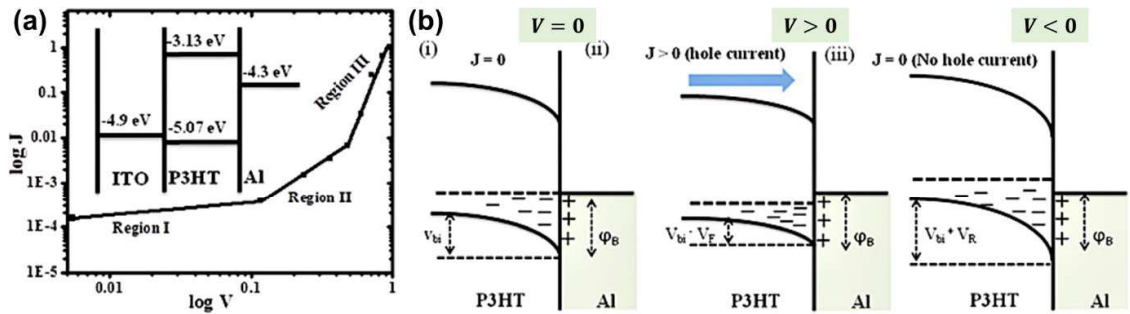


Figure 1.6 (a) $\log J$ vs. $\log V$ plot in an Al/P3HT/ITO Schottky diode [31], and (b) energy level alignment of P3HT/Al junction at three different bias potential, $V=0$, $V>0$ and $V<0$ volts (image credit [31]).

1.2.5.1. Schottky barrier diode configuration:

The out-of-plane carrier mobility can be studied from the electrical characteristic of SBDs (provided charge transport is bulk limited and not contact limited), developed by sandwiching an organic semiconductor layer (p-type is considered) between two contact electrodes, where one junction is ohmic type (ITO/Polythiophene), and another one is Schottky type (Al/polythiophene). When the Schottky junction is formed (i.e., the work function of the metal is less than the p-type semiconductor), electrons start migrating from the metal to the semiconductor side until Fermi levels are equilibrated. Now, holes in the metal side will typically be contained on the surface due to high carrier density in metal; however, a low charge density in the semiconductor side will lead to the formation of a depletion region extending up to a certain depth. And electronic bands will bend within this depletion region/space-charge layer along the electric field direction, typically 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 .

Thus, carrier migration will again start across the junction, and the device current will start increasing with applied voltage (Figure 1.6 (b)).

Now, the forward characteristic of the current density (J) vs. voltage (V) response consists of three regions, as shown in Figure 1.6 (a). In region I, at a small applied voltage, no significant charge injection is possible through the junction, and thus thermally generated intrinsic carriers will contribute most to the current. In region II, at an increased bias potential, carrier injection will start from the electrode to the semiconductor, and initially, the bulk traps will start filling up, and current will increase rapidly because of carrier density increment, causing a trap limited space charge limited conduction (TLSCLC). Finally, in region III, with further increase in applied bias, all the bulk traps will be filled up, and the current will start saturating because of charge accumulation at the injecting electrode, which blocks further carrier injection, and a trap-free space charge limited current (TFSCLC) will be found to flow in the device. In this region, carrier mobility will depend on the intrinsic properties of the organic semiconductor. Therefore, in the TFSCLC region, neglecting the diffusion contribution, we can utilize the standard Mott-Gurney law [9,31] for the estimation of carrier mobility, as follows:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \quad (1.6)$$

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

1.2.5.2.Organic field effect transistor configuration:

The basic OFET structure is made of a thin OSP layer coated over a gate dielectric layer and three contact electrodes, source, drain, and gate. There are four types of OFET configurations possible, bottom gate-top contact (BGTC), bottom gate-bottom contact

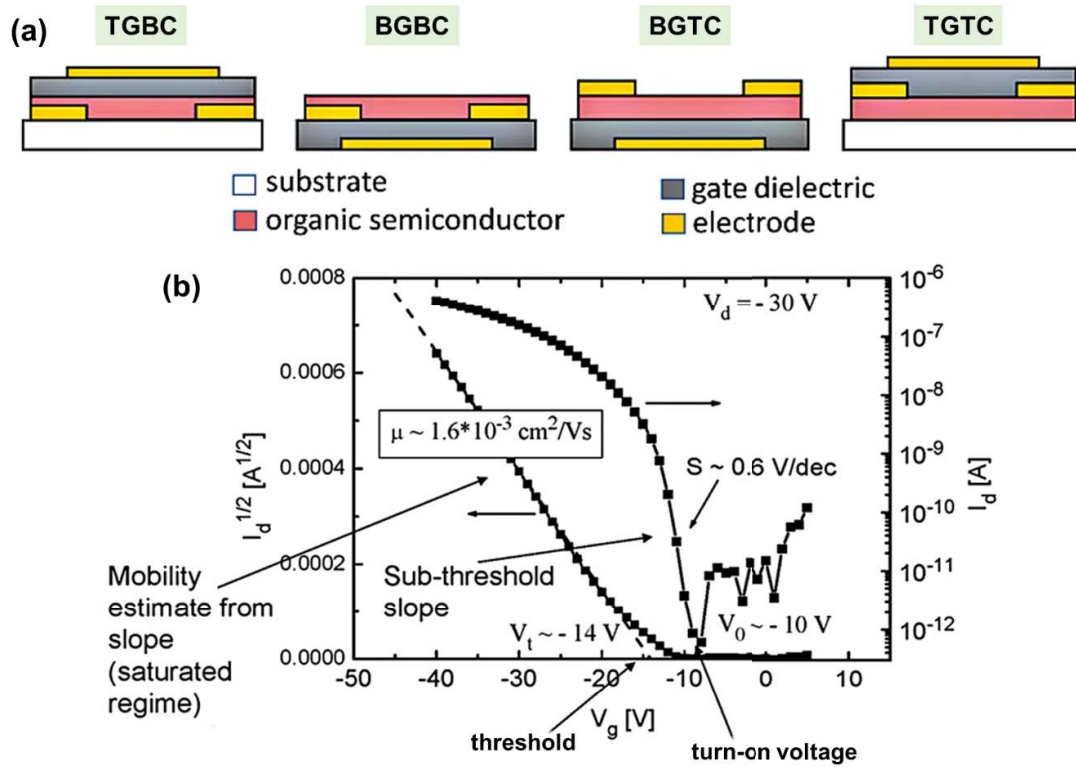


Figure 1.7 (a) Four different types of OFET configurations (image credit [32]), (b) OFET transfer characteristics (adapted from [33]).

(BGBC), top gate-bottom contact (TGBC), and top gate-top contact (TGTC), as shown in Figure 1.7 (a). Among them, bottom gate-top contact architecture is mostly studied OFET structure, as it provides less contact resistance without damaging the gate-dielectric [34]. Source and drain electrodes have a fixed width, also called the channel width (W), and they are separated by a distance L , called the channel length. While the gate electrode is electrically isolated from the active layer by a dielectric layer of thickness, d_i . Usually, the bias voltage is applied between the gate and drain with respect to the source, and current is measured across the source and drain, called the drain current (I_{DS}), for the identification of different transistor operating regimes. OFETs usually operate in the accumulation mode, which means that, on applying appropriate gate bias, carrier accumulation takes place at the dielectric/semiconductor interface (although accumulated carrier type depends on the

gate bias polarity). The accumulated carriers will then form a conducting channel from source to drain that causes an increase in drain current with the applied bias voltage. Thus, as reviewed by Horowitz [30], approximating channel length, $L \gg$ insulator thickness, d_i , current-voltage relationships used for inorganic-based FET can also be used for OFETs to estimate the basic device parameters (Figure 1.7 (b)). Thus, current-voltage relationships are expressed as,

$$\text{in linear regimes:} \quad I_{DS} = \frac{W}{L} \mu C_i [(V_{GS} - V_{th}) V_{DS}] \quad (1.7)$$

$$\text{in saturation regimes:} \quad I_{DS} = \frac{W}{2L} \mu C_i (V_{GS} - V_{th})^2 \quad (1.8)$$

Here, C_i represents the per unit area capacitance of the gate dielectric, V_{GS} , V_{DS} , and V_{th} corresponds to the gate-to-source bias, drain-to-source bias, and threshold voltage, respectively.

Now, as the channel length in OFET is very small (a few μm wide), the carrier migration at the semiconductor/dielectric interface is strongly affected by the microstructural disorders present in the thin-film, surface topology, dielectric polarity, and interfacial defects. Even contact resistance at the electrode/semiconductor interface becomes very significant for OFETs with narrow channel lengths and operating at a low voltage [9,35]. The effective saturation mobility of OFETs is usually found to be higher compared to the linear mobility because of different electric field distributions. Carrier mobility sometimes shows gate-bias dependency owing to the presence of localized trap states and impurities in the active organic layer. The gate dielectric is also found to affect mobility in some cases, for example, in rubrene single crystals [36] and polytriarylamines [9]. These materials have shown a decrease in carrier mobility with the increase in the dielectric constant of the gate

insulator due to a polarization effect, and this charge transport can be explained by the Frölich polaron model [37–39].

1.2.5.3. Organic phototransistor configuration:

In general, photodetector operation consists of three steps, photoinduced carrier generation in the organic semiconductor layer, transport of those photogenerated carriers, and finally, carrier collection by the contact electrodes. Photodetectors include photoconductors, photodiodes and photovoltaic devices (e.g., solar cell), and phototransistors [40,41]. Organic phototransistors (OPTs) are basically OFETs that combine the effect of photovoltaic and photoconduction. The

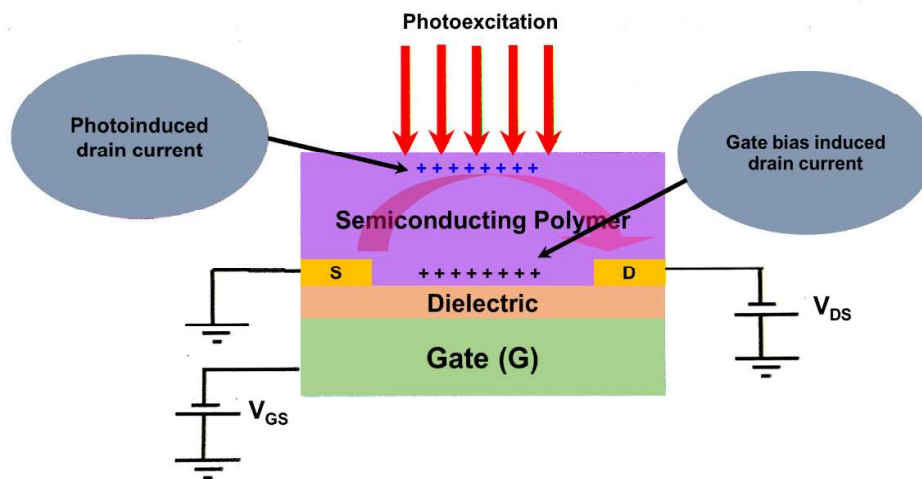


Figure 1.8 Schematic illustration of organic phototransistor operation.

photoconductive effect depends on the photogenerated excess carrier concentration that alters the effective mobility of the majority of carriers. In contrast, the photovoltaic effect (shift in threshold voltage) happens due to the existence of a potential barrier (work function mismatch) at the electrode/semiconductor interface [40–42]. Thus, the output photocurrent in OPTs relies on the gate bias and the light intensity.

The basic operation of an OPT is shown in Figure 1.8. When the photogenerated excitons tend to diffuse through the semiconductor bulk, they often dissociate into free charge carriers at the donor/acceptor interface (for donor/acceptor composite material) or near the built-in field of the depletion regime [42], or under the effect of an external applied electric field. Thus, the extra photogenerated charge carriers will drift along with the gate bias-induced accumulated charges at the semiconductor/insulator interface, under the effect of the lateral applied electric field in the channel, and get collected at the source/drain. Thus, a significant increment in drain current can be seen in OPTs after exposure to suitable light. Upon light illumination, the active organic layer in OPTs shows two different effects: photoconductive and photovoltaic effects. During the OFF-state operation, the photoconductive effect dominates the photocurrent, as described by the following equation [42]:

$$I_{ph,pc} = (q\mu nE)Wd = BP_{opt} \quad (1.9)$$

Here, n is the carrier density, E represents the electric field in the transistor channel, W and d are the channel width and active layer thickness, respectively. Thus, photocurrent in OFF-state directly depends on the P_{opt} with a proportionality constant B .

In ON-state operation, photovoltaic effect dominates the photocurrent and can be expressed as following [42]:

$$I_{ph,pv} = G_M \Delta V_{th} = \frac{AK_B T}{q} \ln \left(1 + \frac{\eta q P_{opt}}{I_{pd} h\nu} \right) \quad (1.10)$$

Where, G_M and ΔV_{th} are the transconductance and shift in threshold voltage, A is a fitting parameter, q is the electronic charge, η represents the quantum efficiency, $h\nu$ and P_{opt} represent the photon energy and power of incident light, respectively, and I_{pd} denotes the

dark current. Thus, illumination of the active organic layer in OPTs alters the effective charge carrier mobility, and the change depends on various factors like P_{opt} , the energy of the incident photon, the quantum efficiency of the polymer, and the degree of microstructural perturbations.

1.2.6. Polythiophenes (PTs)

Now, among the π -conjugated polymers, Polythiophenes (PTs) (Figure 1.3 (a) & (b)) have attracted huge interest in the last few years because of their highly functional nature and striking electronic properties. 2-5 coupled polythiophenes, known as p-type OSP, were first synthesized in the year 1980 [43]. Conjugated PTs usually show high conductivity and satisfactory environmental stability. However, because of the highly crystalline molecular packing of rigid backbones, they are insoluble in common organic solvents, limiting their use for solution-processable large-area film fabrication. The insolubility issue was first addressed by Masa-aki Sato et al. (1986) [44,45], where they grafted different alkyl side-chains on the 3rd position of the thiophene ring at the monomer level and then electrochemically polymerized it to synthesize poly (3- alkylthienylenes) (P3ATs). Grafting long alkyl side chains help destroy the symmetry and stops the crystallization of the conjugated backbones, thus making them more easily soluble in common organic solvents. However, random grafting of alkyl side chains causes backbone twisting due to steric hindrance from neighboring alkyl side chains; they cannot adopt a planar conformation and thus “dilute” the conjugated backbones, leading to a decrease in conductivity. To address these issues, researchers adopted several approaches, from regio-regular head-to-tail coupling to engineering in the backbones, making more planar conformation to minimize the steric hindrance and maximize charge conduction.

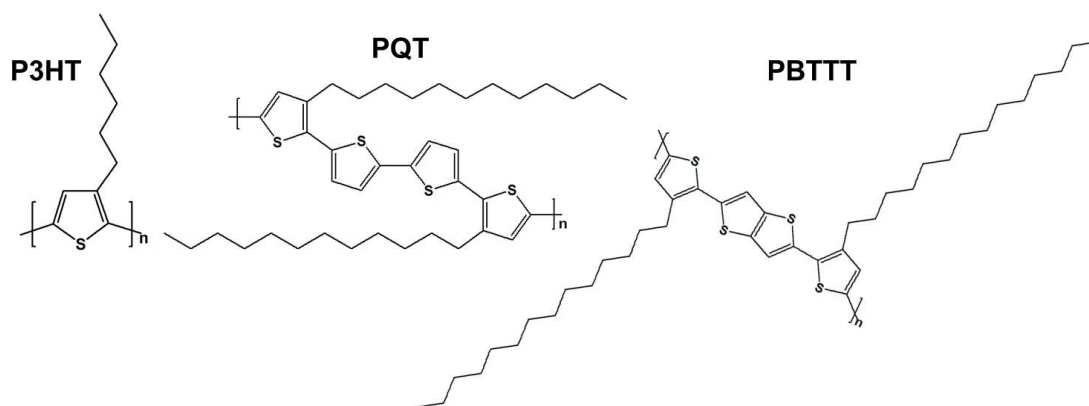


Figure 1.9 Schematic representation of three model polymers, P3HT, PQT, and PBTTT.

Among several conjugated polymers, which have been synthesized utilizing the thiophene aromatic ring, poly(3-hexylthiophene-2,5-diyl) (**P3HT**), poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (**PBTTT**), and poly(3,3''-didodecyl[2,2':5',2'':5'',2''':5''''-quaterthiophene]-5,5''''-diyl) (**PQT**) have gained lots of interest because of their relatively high mobility and tendency to undergo self-assembly, in solution as well as in the solid phase. Their structures have been shown schematically in Figure 1.9. P3HT has 6C-alkyl chain in its backbone, PQT has 12C-alkyl chain, and PBTTT has 14C-alkyl chain, but the density of side-chain in P3HT is nearly twice compared to PQT and PBTTT, making it the most flexible (backbone) one among three. As backbone flexibility and dense alkyl side-chains hinder the formation of a long-range crystalline coherence, researchers modified the flexible P3HT backbone by introducing unsubstituted thiophene units and removing the existence of regioisomers. This kind of backbone modification was shown to improve crystallinity and increase the ionization potential (IP) because of a higher degree of rotational freedom along the backbone [46,47]. However, reducing side-chain density means compromising solubility. Thus, to balance these two factors, the side-chain length was made double, from 6C to 12C in PQT, which retains its solubility and improves the crystalline order in thin film. The organic electronic device using PQT as a

semiconductor was first reported by Ong et al. in 2004 [46], showing high carrier mobility and greater stability than P3HT.

Thus, it was proved that a larger local free volume facilitates the self-organization and crystallization process. Next, to improve the effective carrier mobility by enlarging the crystalline domain size further, researchers combined a linear conjugated comonomer with a fused aromatic ring, thieno[3,2-b]thiophene, within the backbone [48]. A larger resonance stabilization energy of a fused ring compared to a single thiophene ring lowers the highest occupied molecular orbital (HOMO) level by reducing electron delocalization along the backbone. This increases the ambient electrochemical oxidative stability of PBTTT. Furthermore, the rotational invariance of PBTTT backbone helps to adopt a low-energy planar backbone conformation, and a tail-to-tail regiopositioning of 14C-alkyl chains on the bithiophene unit promotes the self-assembly process, minimizes steric hindrance from adjacent side-chains, and enhances the crystalline order. Thus, P3HT, PQT, and PBTTT can be used as model OSPs to study the self-assembly process and their effect on mobility as well as overall device performance.

1.2.7. Molecular packing and orientation

Polythiophenes are basically π -conjugated systems, where, the π -electron clouds are mostly delocalized along the polymer backbone direction, and thus electron density is higher over the backbone. Because of this unique structure, polythiophene derivatives with different backbone structure, having different functionalities, promotes weak but specific local non-covalent interactions (for example, hydrophobic, π - π interactions, H-bonding) among themselves, without any external direction, to form an organized hierarchical architecture [11,49]. Initially, in the solution phase, molecules were randomly oriented in an isotropic manner that did not form any ordered crystalline structure. With the aging or solvent drying

process, when the effective distance between isolated OSP molecules reduces, polymer backbones start organizing or assembling themselves into ordered aggregated structures through intermolecular π - π interaction, which gradually leads to a long-range ordering. This process is known as molecular self-assembly [50,51], and it is essential to have high carrier mobility in organic devices. The self-assembled crystallites in PT thin films can be classified into three categories according to the polymer backbone orientation in the thin films (Figure 1.10 (a)):

- a) ‘edge-on’ stacking, where the π - π stacking lies parallel to the film plane,
- b) ‘face-on’ stacking, having π - π stacking perpendicular to the film surface, and
- c) ‘end-on’ stacking with polymer backbones lying perpendicular to the film plane.

The first two types, i.e., ‘edge-on’ and ‘face-on’ are commonly found in regioregular polymer chains. However, the ‘end-on’ type of molecular packing is rarely found without an end-functionalization because of its precarious arrangement [52,53]. Controlling this backbone stacking at a molecular level may help us achieve highly anisotropic charge transport in organic devices.

1.2.8. Electrical anisotropy in π -conjugated polymers:

Improvement in charge transport will lead to better device performance, and thus huge efforts have been made to enhance the charge transport characteristics in OSP thin films by changing the intrinsic molecular structure and film-processing methods. Theoretically, the ordered PT crystallites are able to conduct electricity through their conjugated chain up to the contour length. Thus, an increment in contour length and interconnection between the

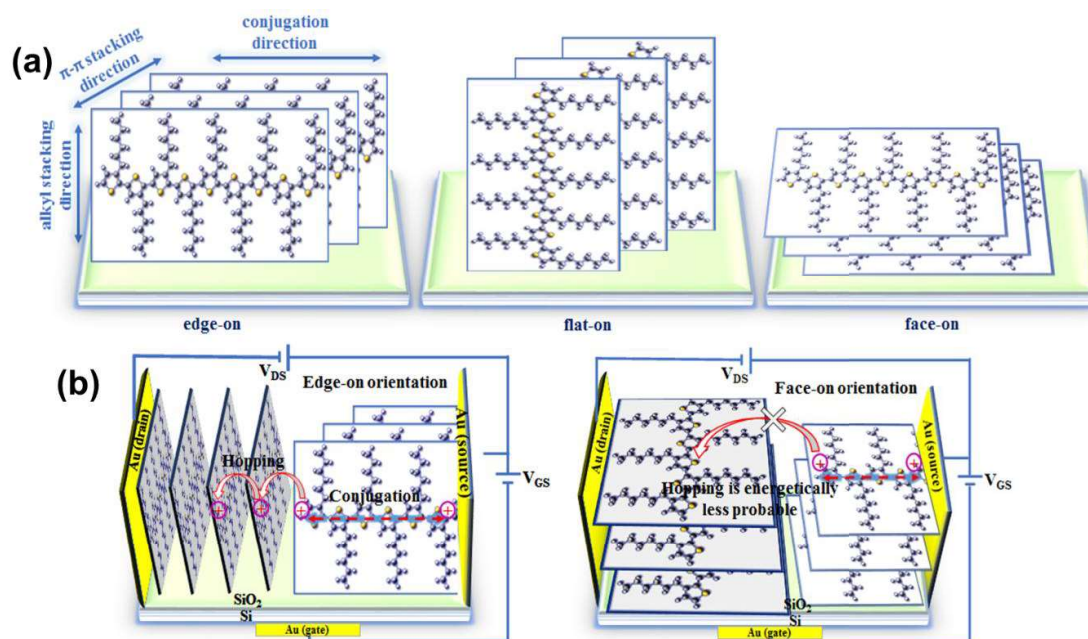


Figure 1.10 (a) Three different backbone arrangements of OSPs found in thin films, (b) charge transport in OFET containing two different backbone stackings in the active semiconducting layer.

crystalline domains will lead to a higher mobility value. Many researchers have explored the high molecular weight (M_w) option [54,55] to increase the effective contour length, as a longer conjugated chain can act as interconnecting ‘tie chains’ between organic semicrystals and prevent carrier trapping at the grain boundaries and disordered interdomain regions. However, long polymer chains are prone to chain folding, and the fold surfaces further restrict the enlargement of ordered domain size, thus limiting a significant mobility enhancement. Uniaxial orientation of these quasi-one-dimensional conjugated backbones like PTs along the source-drain channel direction in an OFET is one of the most effective solutions [56,57] to improve device performance. This is because it has been well-established that stretched PTs show the highest electrical mobility along the conjugated backbone, having the largest charge transfer integral, then along the π - π stacking direction and lowest along the alkyl stacking direction with a very limited π -orbital overlap [55,58]. Thus, charge transport in PT molecular packing is anisotropic in nature. The insulating

nature of the alkyl side chains causes the slowest charge transport through the alkyl interdigitation direction. The intramolecular charge transport depends on the backbone conformational distortions and thus can be enhanced by increasing backbone rigidity, e.g., PBTBT. However, the interchain charge transport is determined in terms of π - π stacking. The charge transport in these systems can be described through Marcus's theory [55,59]:

$$\mu = \frac{ea^2\pi}{K_BTh^2} \tau^2 \sqrt{\frac{1}{4\lambda'\pi K_B T}} \exp\left(-\frac{\lambda'}{K_B T}\right) \quad (1.11)$$

Where, a , τ , h , and λ' represent transport distance, charge transfer integral, Planck's constant, and the molecular reorganization energy, respectively. For any particular polymer, the molecular reorganization energy is fixed, whereas the relative backbone position and frontier orbital shape dominate the charge transfer integral. Thus, a smaller π -stacking enhances the degree of interchain orbital overlap and increases the transfer integral. Moreover, molecular orientation is also important. For example, if the active organic layer of OFETs consists of 'edge-on' type molecular packing, planar charge transport is facilitated by the intramolecular π -conjugation and interchain hopping, as shown in Figure 1.10 (b). However, if a film consists of both 'edge-on' and 'face-on' stacking, as the effective hopping radius between 'edge-on' stacked molecules to 'face-on' stacked molecules is larger compared to the 'edge-on' to 'edge-on' jump, it will offer resistance in charge transport (Figure 1.10 (b)). Thus, the fabrication of 'edge-on' dominated OSP thin films with improved crystallinity and their orientation along the channel direction will help to fabricate highly-efficient OFET-like planar devices. However, a 'face-on' structure or 'end-on' structure is desirable for out-of-plane charge transport in diode-like structures. Thus, precise control over molecular stacking type,

crystallinity improvement, and uniaxial orientation of these conjugated backbones in thin films are essential for the realization of high-performing organic electronic devices.

1.3. Processing of π -conjugated polymers for electronic applications

To achieve the properties as mentioned earlier, considerable research has been done in synthesizing stable and high-mobility polymers. Nonetheless, besides the development of high-mobility OSPs, efforts have been made to utilize process advantages that can facilitate long-range molecular ordering in polymer thin films.

1.3.1. Thin film fabrication methods

Polymer solubility in common organic solvents is the first and foremost criterion for fabricating large-area flexible electronic devices. The key concern for solution processing techniques is how the solvents used for the fabrication will affect the underlying organic features like plastic substrates, organic gate dielectrics etc. Thus, chemical compatibility is essential for utilizing these methods. After making the polymers solution processable, many methods can be adopted for the fabrication of polymeric thin films, for example, spin coating, spray coating, dip-coating, slot-die coating, zone casting, solution shearing, bar coating, strain alignment, doctor blading, mechanical rubbing, and friction transfer method [60]. All these techniques have some advantages and challenges over each other, and they are discussed in TABLE 1.1.

TABLE 1.1 Prospects and challenges with different thin film fabrication methods:

Methods	Prospects and challenges
Spin coating	Easy to handle and can be utilized for both inorganic and organic thin-film fabrication, but material wastage is huge, and the ordering of molecules is not feasible.
Spray coating	Material wastage can be minimized, but unable to prepare homogeneously thick films, molecular ordering is also not possible
Dip coating, slot-die coating, zone casting, solution shearing, bar coating	Limitations in substrates what can be used in these methods, and also not scalable
Strain alignment	Mechanical and compositional damage is very likely, along with a solvent compatibility issue
Doctor blading	It may damage the underlying gate dielectric and also not scalable
Mechanical rubbing	It poses the same challenges of doctor blading
Friction transfer method	Uniaxial ordering is possible; however, it offers only face-on structures suitable for out-of-plane devices. Moreover, it is not scalable.

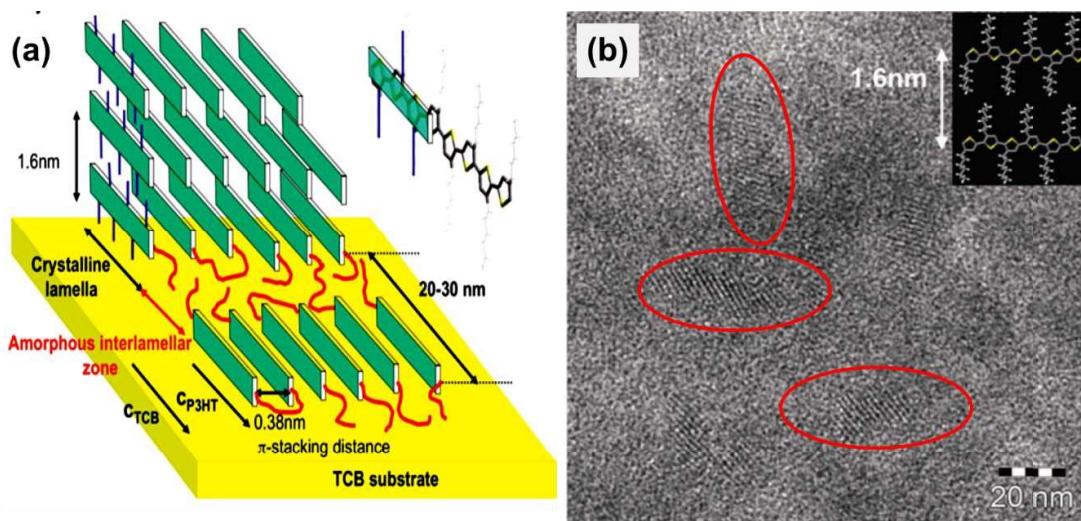


Figure 1.11 (a) Semicrystalline nature of oriented P3HT, and (b) HR-TEM image of P3HT film showing their backbone orientation within crystalline domains separated by amorphous interlamellar regions (image credit [62]).

1.3.2. Molecular ordering enhancement approaches

Given the above-discussed limitations, we shall now discuss various molecular ordering enhancement approaches that have been explored by many research groups worldwide.

The research group led by M. Brinkmann [61] has intensively investigated the orientation of P3HT and its morphology via transmission electron microscopy (TEM), adopting the directional epitaxial crystallization method. In this approach, they used a crystallizable aromatic solvent, 1,3,5-trichlorobenzene (TCB), in which the polymer was dissolved and spread onto PTFE which guided the orientation of TCB on crystallization. The Schematic shown in Figure 1.11 (a) demonstrates the semicrystalline nature of oriented P3HT (backbones shown in blocks) with alternating crystalline zones separated by interlamellar amorphous zones [62]. The same result is shown in Figure 1.11 (b) TEM micrograph in which lattice fringes reveal the π -stacking, and the darker zones containing these fringes are crystalline domains (encircled in red) that are separated by amorphous zones. Igor O. Shklyarevskiy et al. [63] have tried to align a substituted hexabenzocoronene (HBC)

utilizing a high magnetic field and found a 10-fold enhancement in the field-effect mobility in the aligned film, although the actual mobility was found to be around 10^{-3} cm²/Vs. Do Hwan Kim et al. [64] modified the interface between the semiconductor (P3HT) and the gate insulator by different self-assembled monolayers (SAM) containing -NH₂, -OH, and -CH₃ groups and got high field-effect mobility around 0.28 cm²/Vs. However, they annealed the samples at a very high temperature of 240 °C, which is not suitable for plastic electronics, and they did not get any mobility anisotropy. Yeong Don Park et al. [65] mixed functionalized multiwalled carbon nanotubes (CNTs) with P3HT solution and enhanced the overall OFET performance with mobility around 4×10^{-2} cm²/Vs. Jae Won Jeong et al. [66] utilized a good solvent additive with low volatility (high boiling point) for the processing of P3HT fibers, as in fiber formation, the effective ordering enhances through π - π interaction. They utilized the spin coating method to make a film of P3HT fibers (no electrical anisotropy found). R. Mishra et al. [66] tried homogenous dispersion of MoS₂ nanosheets in polyindole (PIn) matrix at an air-water interface, and through the Langmuir-Blodgett technique, they fabricated a large-area thin film with improved forward current, ~9 times higher compared to the pristine PIn, but failed to achieve high mobility. Many similar reports clearly demonstrate that the orientation of organic polymers remains a critical issue for better device performance that needs more attention, particularly in organic thin film-based plastic electronics.

1.3.3. Floating-film Transfer Method

In collaboration with Japanese researchers, our group has also developed a much facile low-cost technique, named '*Floating film Transfer Method*' (FTM), [57] suitable for highly

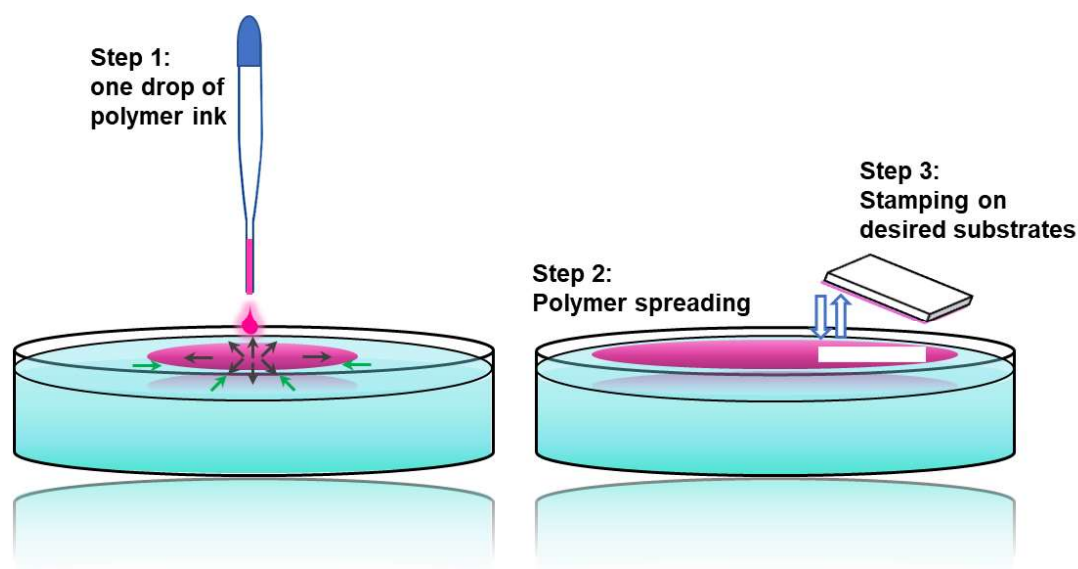


Figure 1.12 Schematic representation of FTM process.

oriented, large-area [67] thin polymeric film fabrication, as shown in Figure 1.12. As FTM provides thin solid films of organic semiconducting polymers floating on a hydrophilic liquid substrate, layer-by-layer deposition [68] is also possible through it. It has been found from various investigations [56,57] that major polythiophene derivatives (rr-P3HT, nr-P3HT, PQT, PBTTT, DPPDTT etc.) form highly ‘edge-on’ type molecular stacking in the films while processed through FTM, which will be beneficial for OFET like planar structures. Even through an interfacial engineering approach, which will be discussed in detail later in this thesis, we have successfully altered the molecular arrangements in PT thin films starting from the air-liquid interface, and this type of molecular packing was found suitable for out-of-plane devices like SBDs.

1.4. Objective of thesis

The successful realization of organic conjugated polymer-based electronic devices depends on developing low-cost and facile processing techniques that facilitate the fabrication of organic devices over large-area substrates without any processing-induced defects. Therefore, such a thin film fabrication methodology is needed, which is not only user-friendly but also provides very good quality crystalline domains. Now, two facets exist in solving such issues: one is understanding the mechanism behind the growth of semicrystals in conjugated polymer thin films through exploring fundamental properties and then utilizing the knowledge to improve the film microstructure and molecular orientation. In view of this, the main objectives of this thesis are as follows:

- Understanding the mechanism behind oriented semicrystal growth in thin films of organic semiconducting polymers self-assembled at the air-liquid interface.
- Development of high-quality active semiconducting layer for planar devices like OFETs harnessing the key advantages of FTM and other molecular order enhancement methods.
- To have precise control over the molecular stacking in OSP thin films self-assembled over a hydrophilic liquid substrate through interface engineering approach
- Further, improve the electronic and optoelectronic device performance through band gap engineering in conjugated polymer/NIR dye hybrid.