

CHAPTER-1

OVERVIEW

1.1 Introduction

Generation of energy has become the fundamental need of the modern life along with food, water, etc. The world population and scientific developments are growing at faster pace and so the energy need. Hence, the conventional energy resources based on fossil fuels are depleting more rapidly. This emergency has led to the search of a new source of energies which are having low carbon content and converges to the use of nuclear technology, and renewable energies such as geothermal, wind, and solar power. But the catastrophic events happened in the past due to the nuclear power, limit us the extensive use of it.¹ The wind, tidal, hydrothermal, and geothermal are the alternative sources specific to the location and timing. On the other hand, solar energy is abundant and present everywhere.² So, the solar energy has drawn an attention in the scientific community for both grid-connected and off-grid power applications. Although solar cells have the prodigious capability to produce clean energy and meet the world's demand, two major bottlenecks as low-cost production and poor storage capacity restricted the developments. In spite of these problems, solar power research has much attention due to the major limitation of other techniques.

The solar cells are basically categorized into two sections as per their use; one is grid application and other is off-grid energy demand. The silicon solar cell technology has taken over the grid application by in large due to its high efficiency and durability. The silicon and other inorganic solar cells (CdTe, CIGS, GaAs) solar cells have reached 24% lab efficiency till now. But inorganic solar cells require high vacuum processing and hence unable to compete the pricing based on fossil fuels. In spite of being efficient, inorganic solar cells are limited to the mechanical stability. On the other hand, organic photovoltaic (OPV) devices are solution processable, made of cheaper materials, and moreover, mechanical stability is better than inorganic solar cells. With the much lower cost of production, the power conversion efficiency (PCE) of organic solar cells reached up to 10%.³ Also the Shockley Queisser PCE limit for single junction bulk heterojunction (BHJ) OPV devices is 23%, much lesser than their inorganic counterparts.⁴ In spite of all the limitations, OPV devices research has significantly increased in the last two decades. It is mainly because of mobile and laptop industry revolution. The off-grid energy demand increases enormously. The flexibility of OPV devices has opened up the application for building integrated photovoltaics (BIPVs) such as power generating windows.

Organic solar cells have made significant development and reached to the state of commercialization. Especially, BHJ OPV devices have reached close to 13% efficiency with

the help rigorous research in materials, device architecture, and interface engineering.⁵ Still, a lot of challenges persist with OPV devices to reach the Shockley Queisser PCE limit.

1.2 Fundamentals of organic semiconductors

The organic solar cells consist of organic semiconductors of hygroscopic nature. The organic semiconductors turn out to be interesting organic material due to high absorption coefficient and less expensive with low-cost processability.⁶ These organic materials are defined by carbon-based compounds and its derivatives. The basic element used for the synthesis of functionalized organic semiconductors in the lab is carbon atom (C). The organic semiconductors constitute alternate carbon-carbon double and single bond (conjugation) along with some electronegative elements such as Sulphur (S), Oxygen (O), and Fluorine (F) etc. The most common isotope of carbon atom is ${}^6\text{C}^{12}$ and the ground state configuration has four valence electrons. The atomic orbitals $2s$, $2p_x$, and $2p_y$ with similar energy have the tendency to form chemical covalent bonds through sp , sp^2 and sp^3 hybridization and converted into molecular orbitals. By sharing of an electron between sp^2 hybridized atomic orbitals of two carbon atoms results in $\text{C}=\text{C}$, shown in figure 1.1.

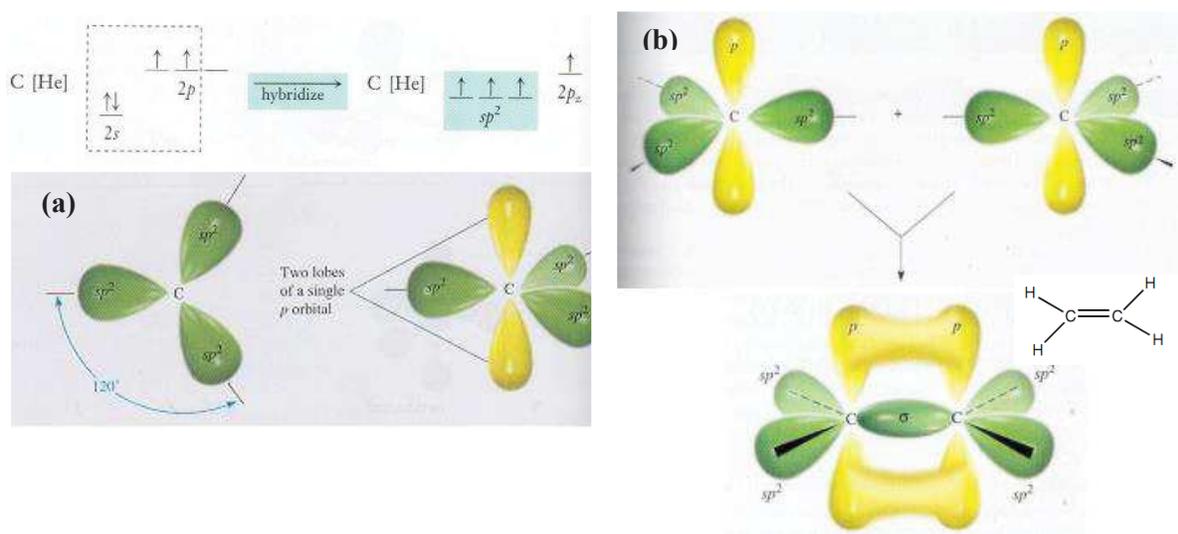


Figure 1.1. Pictorial representation of (a) Carbon atomic orbitals and hybridization process, and (b) $\text{C}=\text{C}$ formation through the overlapping of atomic orbitals.⁷
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The molecular orbital formation takes place when atomic orbitals come closer to each other to make bond. When the atomic orbitals overlap each other in phase, constructive interference leads to the stable bonding orbital. However, when they overlap out of phase, destructive

interference leads to the relatively unstable anti-bonding orbitals. The small molecule (< 1000 amu)⁸ and polymer with semiconducting properties can be realized by the combination of alternate conjugated C=C bonds.⁹

Organic semiconductors are highly disordered system and charge transport in these systems are the primary concern. Many efforts have been done in order to get highly pure and ordered molecules in organic crystals. In early 1960, hopping transport in disordered inorganic semiconductors was described by Miller and Abrahams.¹⁰ Later, Scher and Lax presented the theoretical description of charge transport via hopping mechanism in disordered materials in the mid-1970s.¹¹ Further, Bäessler and co-workers have done the simulations as well as experiments and successfully measured charge transport in the disordered organic semiconductors.¹²⁻¹⁴ The two popular models were proposed to understand the charge transport mechanism namely, Polaron and Disorder models. As per Polaron model, the total mobility was expressed in terms of tunneling mobility and hopping mobility¹⁵⁻¹⁶ (only dynamic disorder due to electron-phonon coupling is considered) and given as;

$$\mu = \mu_{tun} + \mu_{hop}$$

Where, μ_{tun} is the mobility due to coherent electron transfer (electron tunnelling) and μ_{hop} is the mobility due to incoherent electron transfer (related to hopping motion). Tunnelling mobility in disordered systems dominates transport at low temperature while at higher temperatures, hopping mobility dominates.

On the hand, in the disorder model, the disorder due to physical and chemical defects (static disorder) has been considered for the explanation of charge transport in organic semiconductors. The static disorder has a tendency to localize the band states in the ordered materials. The disorder in the material can be treated as the measurement parameter for the localization of band states. The weak disorder means that only tail states are localized in the system, while more the disorder, more will be the localized states. In case of strong disorder, the charge transport mechanism is governed by hopping of charges across the localized states (nearest interacting molecules).¹⁷

Based on the above background, several works have done for the experimental determination of charge carrier mobility, transport and lifetime in organic semiconductors using various methods with respect to organic solar cell application. Bisquert and co-workers have introduced the impedance spectroscopy for the OPV devices which became an important method to determine transport properties.¹⁸⁻²⁰ The closest calculation of charge dynamics

parameters is observed with the help of space charge limited current (SCLC) method, and impedance spectroscopy (IS).

Most organic semiconductors are prone to degradation in presence of oxygen and moisture. In order to resolve these limitations, research is progressing towards material and device design. Few materials are already developed with improved stability in the ambient condition. For the development of this technology, the development of organic semiconductors is an important aspect.

1.3 Applications of organic semiconductor in solid state electronics

In the beginning, organic semiconductor materials were used only in the domain of pure research because of their interesting optoelectronic properties and ability to modify the chemical structure in ways that it could directly have an impact on physical properties in its thin film form.^{21,22} In the 1980s, Ching Tang et al. at Kodak demonstrated organic thin film based a low voltage light emitting diode (LED).²³ It led the foundation to utilize the organic thin films for the new generation of optoelectronic devices.

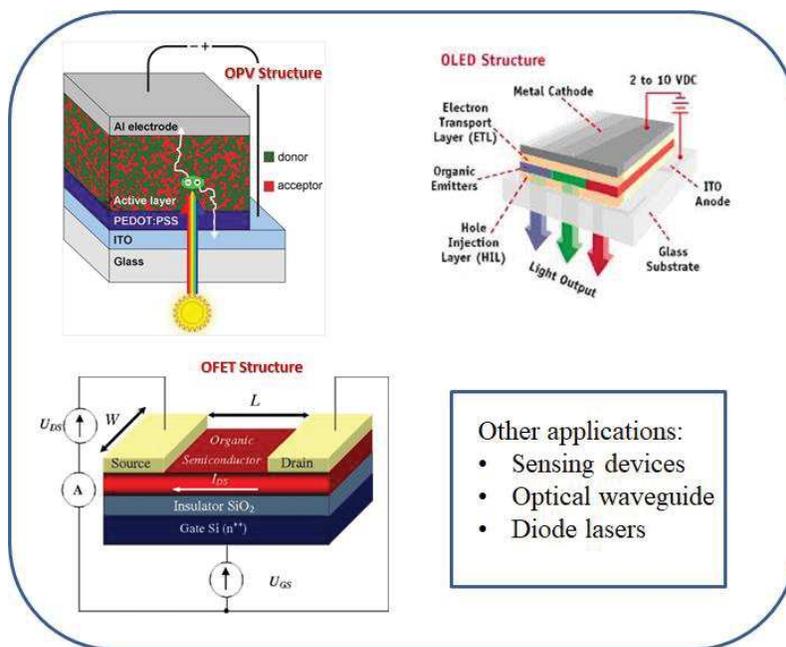


Figure 1.2. Applications of organic semiconductors in organic electronic devices.²⁴⁻²⁶

The most successful organic electronic devices are OLED devices which have successfully hit the market. The OLED devices are used nowadays in long-lasting and highly efficient colour displays in its basic structure as shown in figure 1.2. The progress of OLED

devices is inspiring to explore the other organic materials based optoelectronic devices extensively for their potential applications.

With the developments of organic semiconductor materials, small molecule and polymers have emerged as a potential candidate for energy harvesting applications in organic photovoltaic devices (the structure is shown in figure 1.2). The OPV devices have reached to its commercialization owing to gap high performing organic materials and device design. Recently, OPV devices found an application in mobile and laptop chargers, remote power applications etc.

On the other hand, consistent improvement in charge carrier mobilities in organic materials led to the faster evolution of organic field effect transistors (OFETs). An improved charge carrier mobility in organic semiconductors is shown in figure 1.3. In the last 10 years, organic semiconductors used for OFET have made rapid progress with the increase in mobility much higher than that of amorphous silicon ($0.1\text{-}1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).²⁷ The OFET devices find their application in operating display devices, low-cost logic circuits and sensors.²¹

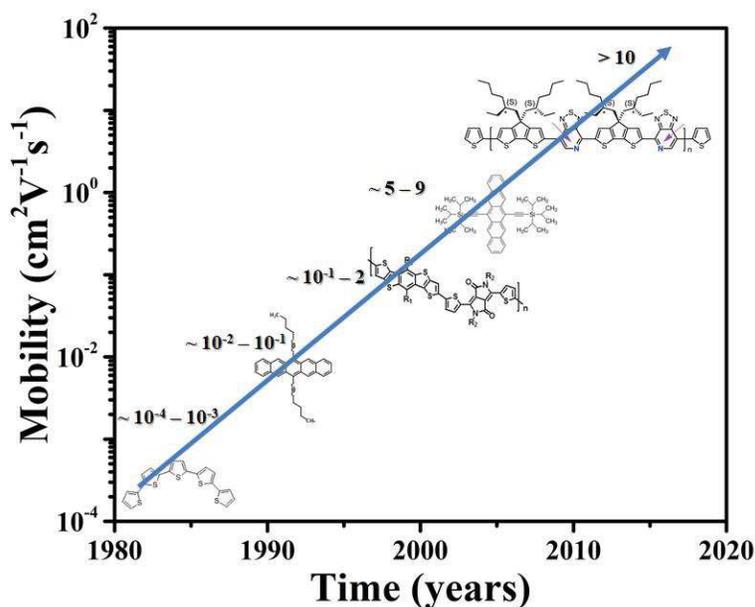


Figure 1.3. Progress of charge carrier mobility in organic semiconductors.

In other applications of organic materials, dye laser, optical communication, optical memories, biomedical testing, sensing devices and many more are emerging fields and extensive investigations are required to commercialize them. In this thesis, my focus will remain to OPV devices, in particular, interface engineering in order to improve charge extraction.

1.4 Progress of organic photovoltaic (OPV) devices

The OPV devices are the power generating devices based on disordered organic semiconductors. These devices are having its evolution way back since the emergence of inorganic counterparts. The first organic semiconductor-based solar cell was demonstrated by Kalvin et al. in 1958.²⁸ It was single layer solar cell made of Magnesium phthalocyanine with efficiency $\sim 10^{-3}$ %. After several years of research in this direction, a major breakthrough was shown by C. W. Tang (an inventor of the donor-acceptor heterojunction in OSC) in 1986.²⁹ He made a bilayer OSC using Copper phthalocyanine and perylene tetracarboxylic derivative, and demonstrated a revolutionary improvement in the efficiency of 1 %. Later, in 1992, Heeger et al. mixed the donor polymer with the acceptor molecules homogeneously, to design bulk heterojunction photoactive layer in OSC devices.³⁰ In this way, they were able to overcome the limitation of the diffusion length of excitons at the certain extent and demonstrated high-efficiency solar cells.³⁰ A systematic evolution of organic solar cells is shown in figure 1.4.

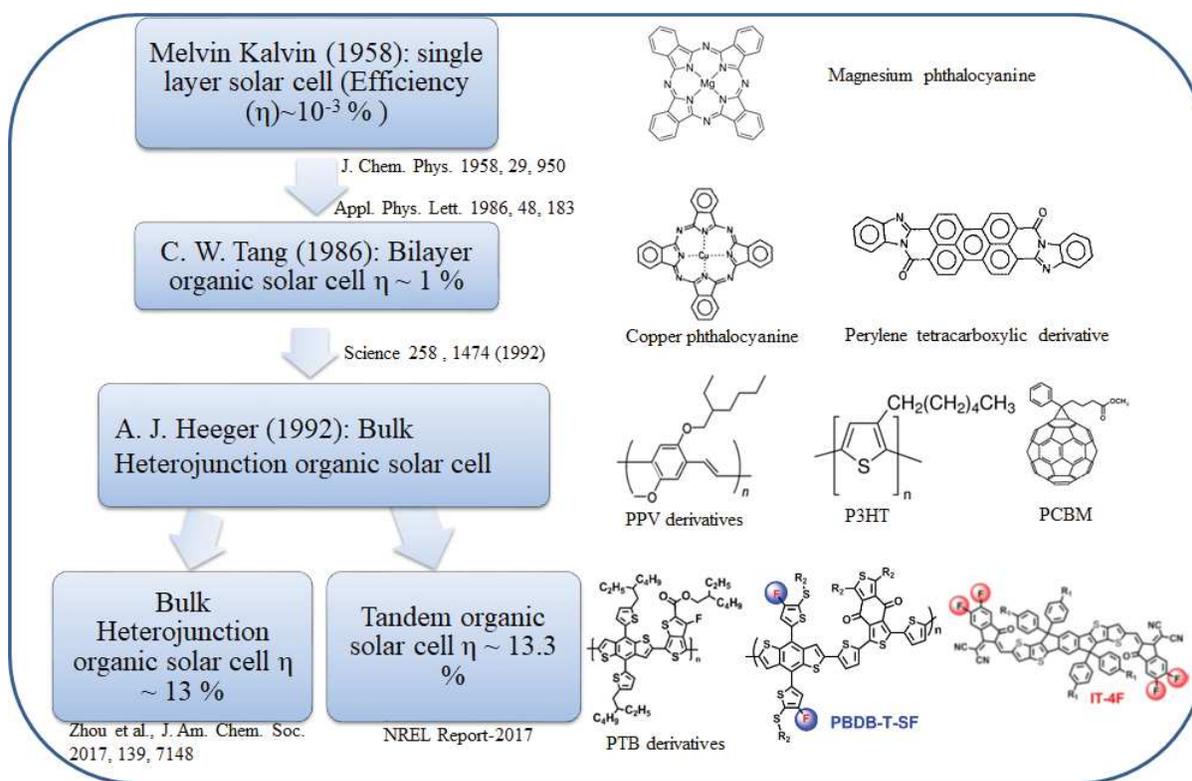


Figure 1.4. Breakthrough progresses in organic photovoltaic devices.²⁸⁻³²

Recently, OPV devices have reached up to 13% efficiency.⁵ The development of OPV devices till now evolved due to the basic research in the three major areas namely, high

performing organic semiconductor materials (electron donors and acceptors), device architecture, and interface engineering.

1.4.1 Evolution of organic semiconductor materials for OPV devices

Organic semiconductors can be categorized into two types: π -conjugated molecules and polymers. These materials are far from its inorganic counterparts (Si-based solar cells) in many aspects such as charge carrier mobility, device lifetime, the power conversion efficiency etc. According to NREL, organic solar cells can be commercialized if the efficiency crosses to 15% mark and device lifetime > 5 years.³¹ The development of small-molecule and polymer semiconductors are observed together.

Tang and Albrecht, in 1975, demonstrated the potential of small-molecule organic material for solar cell devices using chlorophyll-a as the semiconducting material.³² First observed was having very low power conversion efficiency (PCE). After almost 10 years, Tang et al. demonstrated a bilayer heterojunction device of 1% efficiency using copper phthalocyanine (CuPc) as the donor layer and 3,4,9,10-perylenetetracarboxylic-bis-benzimidazole (PTCBI) as the acceptor layer.²⁸ The same donor and acceptor material has shown an efficiency of 1.5% when they have been used as a bulk heterojunction. In order to increase open circuit voltage (V_{oc}) and electron mobility, sub-phthalocyanine (SubPc) and buckminsterfullerene (C60) small molecules were introduced by Mutolo et al. in 2006 and found the PCE of 2.1%.³³ Since then a significant progress has happened for both donor and acceptor small molecules. The breakthrough efficiency ($\sim 8\%$) was demonstrated by Sun et al. in 2012 only after the emergence of a donor material, 5,5'-bis{(4-(7-hexylthiophen-2-yl)-[1,2,5]thiadiazolo[3,4-c]pyridine)-3,3'-di-2-ethylhexylsilylene-2,2'-bithiophene (DTS(PTTh₂)₂), and an acceptor material, PC70BM.³⁴

Heeger, Shirakawa, and MacDiarmid have discovered the unique electronic properties of polyacetylene in 1970.³⁵ Polyacetylene was an important finding in the field of semiconducting organic materials, and was critical for the understanding of semiconducting properties in disordered systems.³⁶ Polymer materials have many advantages over small molecule semiconductors because of better phase segregation when two polymers are mixed. The ordered bulk heterojunction and exciton dissociation can be achieved easily in case of polymers.³⁷ In 2004, Alam and Jenekhe reported a bilayer polymer-polymer device with efficiency 4.6%, which was only obtained at a lower intensity of solar radiation.³⁸ The polymers used for these device were poly(benzimidazobenzophenanthroline ladder) (BBL) and poly(1,4-

phenylenevinylene) (PPV). A further high efficiency was reported by these type of device, in 2005 by Kietzke *et al.*, by using (poly[2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylene-1,2-ethenylene)]) (M3EH-PPV) as the donor and (poly[oxa-1,4-phenylene-1,2-(1-cyano)ethenylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano) ethenylene-1,4-phenylene]) (CN-PPV) as the acceptor.³⁹ The most researched donor polymer, in OSC devices, is poly(3-hexylthiophene) (P3HT) and acceptor small-molecule is phenyl-C61-butyric acid methyl ester (PCBM). PCBM has provided ease of solution processability.⁴⁰⁻⁴⁶ Later, the focus of material research has shifted to the development of low band gap polymers to increase the absorption of solar insolation in the wide wavelength range. A successful approach to devise such polymers is mainly by putting donor and acceptor moiety in a single skeleton of molecular structure (D-A-D-A type). In this way, the charge carrier mobility has been improved significantly. On the other hand, PCBM derivatives such as PC71BM, PC81BM, and ICBA have been explored in the attempt to increase the electron mobility as well as an increase in light absorption at lower wavelengths. The most successful low band gap polymers are PTB derivatives.⁴⁷⁻⁴⁹

Polymer solar cells has shown ease of fabrication using solution process compared to the small molecule solar cells, generally processed by physical vapour deposition. Recently, single layer polymer solar cell efficiency has reached 13%. However, more than 12% efficiency has been achieved using small molecule semiconducting materials in tandem architecture.⁵

1.4.2 Evolution of OPV device architecture

A conventional OPV device consists of a D:A BHJ based active layer sandwiched between hole transport layer (HTL)/ transparent metal electrode (ITO) and electron transport layer (ETL)/an opaque metal electrode, shown in figure 1.5 (a). In most of the devices, the front hole collecting layer is used to be poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and the low work function metals (Al, Ag, Ca, Mg etc.) are used as electron collecting layer. The PEDOT:PSS layer is acidic in nature and it corrodes ITO layer with the time.⁵⁰⁻⁵¹ The low work function metal can be easily oxidized and hence OPV devices need to be processed in an inert environment, a high-cost approach. The devices are encapsulated from sophisticated materials to prevent exposure to air.

In the attempt to make OPV devices environment-friendly, several efforts had been done until the inverted architecture comes into the picture, shown in figure 1.5 (b). In the

inverted architecture, materials are chosen in such a way that the role of HTL and ETL reversed. Inverted OPV device consists of ETL on top ITO electrode. While air sensitive low work function metals at counter electrode have been changed with high work function metal oxide/metals.⁵²⁻⁵⁴ The solution processable ETL of metal oxides, such as ZnO, TiO₂, NiO, etc., can be deposited in ambient condition on ITO surface. Such oxides are non-corrosive for ITO surface. Also, high work function metals can be deposited on polymer active layer by non-vacuum techniques such as screen printing. The introduction of inverted architecture for OPV devices offers potentially low cost, lightweight, and easy to fabricate method.

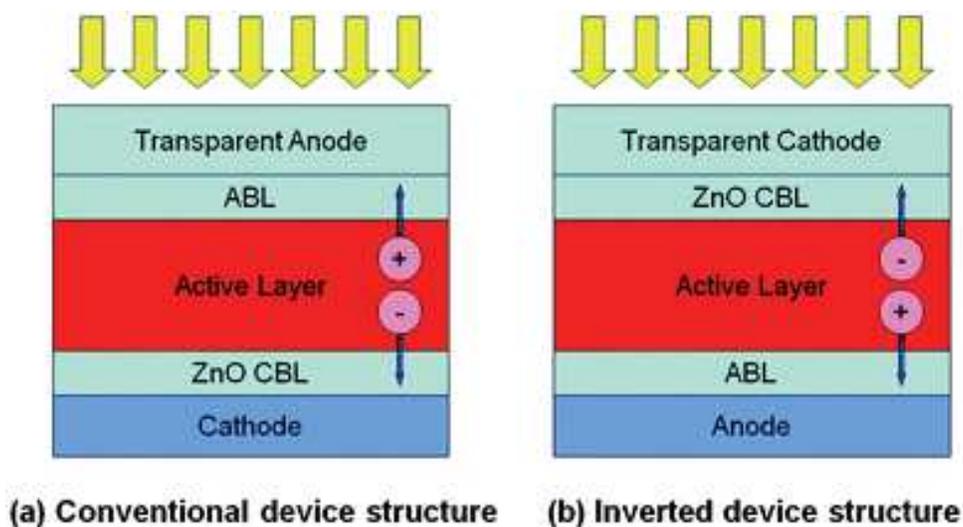


Figure 1.5. (a) Conventional device architecture, and (b) Inverted device architecture of organic solar cell.⁵⁵

In 2006, Ginley *et al.* demonstrated the fabrication of inverted OPV devices using ZnO as an electron-collecting interlayer between ITO and the active layer, and Ag as a hole-collecting electrode.⁵⁶ They had shown 2.5% efficiency for P3HT:PCBM based devices with solution processed ZnO in inverted architecture, and it was a comparable performance to its counterpart conventional OPV device. The electron mobility of solution-processed ZnO was found sufficiently large. Due to which, electrons transported from PCBM to ITO electrode via ZnO layer very quickly. Also, high diode rectification in the dark indicated that the ZnO layer is efficient to block holes. Further, Krebs *et al.* have shown better lifetime for inverted OPV devices than the conventional devices.⁵⁷ The inverted BHJ polymer solar cells have reached close to 10% efficiency with the help of efficient interface modification at both the electrode surfaces.

On the other hand, the scientific groups working with small molecule-based organic semiconductors have proposed the tandem architecture for OPV devices, shown in figure 1.6.⁵⁸ In this case, the active layers, having light absorption in the different region of wavelengths, are connected with electronic binder layers monolithically. Thus tandem solar cells are able to absorb a wide range of solar spectra and hence provide high current density devices. The tandem devices have shown enormous improvement and provided more than 12% efficiency.⁵⁹

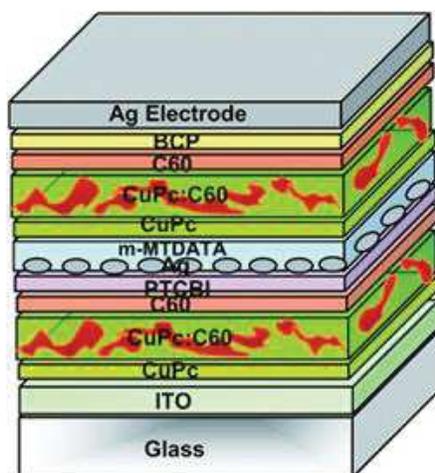


Figure 1.6. Image of tandem structure of organic solar cells⁵⁸

1.4.3 Interface engineering in OPV devices

In the previous section, we discussed the conventional, inverted, and tandem organic solar cells based on the architectural development of the OPV devices in order to improve efficiency and lifetime. But device engineering is required to overcome the inherent limitations of molecular semiconductors. The organic semiconductors show the inability in inter-molecular charge conduction. The electron and hole mobilities are exhibited $\sim 10^{-3}$ to 10^{-9} $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$.⁶⁰ Also the diffusion length of the charge carriers are found to be in the range of 10-20 nm because of high binding energy as π -conjugated molecules are low dielectric materials.⁶¹ Although the material development took place to overcome charge mobility issues in these devices, much research has happened to provide facilitator in charge transport and extraction. Hole and electron transport materials were identified and developed. In OPV devices, HTL and ETL are inserted just before the electrodes on each side. HTL has energy level alignment with the HOMO level of donor materials, while ETL with LUMO level of acceptor materials. In this way, HTL restricts the transport of electrons towards hole collecting electrode, and ETL

restricts the transport of holes towards the electron collecting electrode, thereby reducing the recombination losses.

Interface engineering in the OPV devices involves the modification of interfaces between active organic layer and electrodes by inserting an organic/inorganic buffer layer. PEDOT:PSS thin film, a conductive hole transport layer, is most commonly used buffer layer between ITO and active organic layer in conventional OPV device. It planarizes the ITO electrode and escalated its work function for effective hole extraction.⁶² But, the acidic nature, limited electron blocking capability, and electronic inhomogeneity in PEDOT:PSS layer which acted as catalyst for the further development of HTL/ETL.⁶³⁻⁶⁵ Li et al. have reported the use of self-doped conducting polymer as hole transport layer with an enhanced efficiency.⁶⁶ Several works have been reported about the use of carbon nanotubes (CNTs) as the replacement of PEDOT:PSS for OPV devices.⁶⁷⁻⁶⁹ Further, the research in this area led to the use of the self-assembled monolayers (SAMs) with different end units (-CH₃, -CF₃, -NH₂) having permanent dipole moment for tuning the ITO work function.⁷⁰⁻⁷¹ Hydrophobic character of SAMs provided the much-needed crystallinity in P3HT:PCBM devices.⁷¹

The electron blocking ability of above-discussed HTLs are limited. Hence, in order to improve interfacial properties further, transition metal oxides (MoO₃, WO₃, V₂O₅, and NiO) have been used as modifying layer for ITO electrode.⁷²⁻⁷⁵ These are wide band gap materials with good transparency to the visible and near-infrared light. They increase the ITO work function effectively from 4.7 eV to 5.1-5.3 eV, well in aligning the HOMO level of donor polymers. The conduction band lowest energy level of these oxides is much higher than the LUMO level of both generally used donor polymers and acceptor molecules, and so the better electron blocking prospect has been seen. The fill factor (FF) of 70% is achieved using these oxides, clearly far better performance than PEDOT:PSS.⁷³⁻⁷⁵

Till now, we have discussed the improvement at hole collecting interface. The interface engineering at electron collecting interface is equally important in order to have better-performing devices. Thermally evaporated low work function materials such as Ca, Mg, and LiF have used as ETL layer in conventional OPV devices. Brabec et al. have shown higher device performance with sub-monolayer of LiF as ETL between the electrode and active organic layer.⁷⁶ The formation of dipole moment at the interface because of LiF is shown favourable for electron extraction. The solution processable ETLs such as poly(ethylene oxide) and water-soluble polyfluorene derivative (WPF-oxy-F) was reported by Zhang et al. and Na et al. respectively for conventional OPV devices.⁷⁷⁻⁷⁸ The solution process will be helpful in the development of flexible solar cells. The self-organizing property of materials during spin

coating has been utilized in getting modified interface. Wei et al. have demonstrated the migration of fluorinated fullerene, added in P3HT:PCBM BHJ layer, towards film surface during spin-casting.⁷⁹ Due to which interface dipole is formed between migrated fluorinated fullerene and Al cathode, resulted in a better performance with lower series resistance.

Further metal oxides such as TiO_x and ZnO have found much attention to be used as ETL in conventional OPV devices.⁸⁰⁻⁸³ Park et al. have demonstrated 6% efficient device by using the TiO_x interfacial layer for PCDTBT:PC71BM BHJ solar cells.⁸⁴ TiO_x is a multifunctional interface layer because it acts as oxygen barrier along with having hole blocking property. They have improved the electron extraction property of TiO_x by doping it with Cs. The Cs-doped TiO_2 layer reduces the work function further for efficient electron transport.⁸⁵ On the other hand, Jen and co-workers have used the solution-processed ZnO nanoparticles thin film as ETL.⁸⁰ Since the Fermi level of ZnO are quite close to the LUMO level of PCBM, hence it facilitates better charge transport towards the appropriate electrode. It also helps in the effective hole blocking as its valence band is low-lying. ZnO nanoparticle-based thin film shows higher electron mobility and it can be tuned easily by modifying its surface using self-assembled monolayers (SAMs).⁸⁶⁻⁸⁸ Application of SAM layer between ZnO and top electrode provides higher device performances even with high work function electrodes (Ag, Au) due to improved chemical bonding between SAM and metal as well as appropriate dipole direction.⁸⁹⁻⁹⁰ All these competencies make ZnO as a versatile candidate for the interface engineering in OPV devices.

Till now, the role of buffer layers as ETL/HTL is discussed in detail for the conventional OPV devices. But the buffer layers become critical in getting high performing inverted OPV devices. First P3HT:PCBM BHJ based inverted solar cell was demonstrated by Li et al. by utilizing Cs_2CO_3 as ETL and V_2O_5 as HTL.⁹¹ Cs_2CO_3 is most studied out of all alkali metal salts as interface modifier for ITO electrode.⁹²⁻⁹³ On the other hand, Lim et al. have demonstrated the use of PEDOT:PSS as high work function HTL for inverted PSCs.⁹⁴

Later, metal oxides used as ETL has been explored extensively in inverted devices as they have already shown the promising results in the case of conventional OPV devices. Mostly used oxides are TiO_2 , ZnO as ETL and WO_3 , MoO_3 as HTL. Waldauf et al. presented P3HT:PCBM device of 3.1% efficiency by using TiO_x as ETL and PEDOT:PSS as HTL.⁹⁵ Several groups have worked with TiO_x in spite of knowing that amorphous TiO_x thin film has low electron mobility.⁸¹ Although the electron mobility in TiO_x thin film can be increased by annealing it up to 400 °C, which is not suitable for flexible PSCs. While ZnO has higher electron mobility than TiO_2 as well as wide optical band gap. Hence ZnO has evolved more

with the time as ETL in inverted organic solar cells. The efficient P3HT:PCBM BHJ based device has been demonstrated by White et al. by using ZnO as ETL and Ag as HTL.⁵⁶ In this work, ZnO thin film was deposited by sol-gel method. The crystallinity of ZnO has increased after annealing it at 300 °C, thereby increasing conductivity. Due to the high-temperature processing of ZnO, it cannot be suitable for flexible organic solar cells. It led to the evolution of new low-temperature processing of ZnO layer. The ZnO nanoparticles can be deposited by solution method at room temperature and it shows high mobility as well without post-annealing.⁹⁶ Hau et al. have demonstrated high PCE inverted OPV devices using ZnO NPs as ETL.⁹⁷ These devices have shown better life as well.

Simultaneously, several efforts have been done for the interface between organic active layer and top electrode in inverted devices using metal oxides such as Mo₂O₃, WO₃, AgO_x.⁹⁸⁻⁹⁹ Widely researched HTL layer for inverted OPV devices is Mo₂O₃. Kyaw et al. presented 3.09% efficiency by inserting Mo₂O₃ as HTL between the organic active layer and Ag electrode.¹⁰⁰

There are organic/inorganic hybrid interfaces present in organic solar cells. To improve these interfaces for effective extraction of charge carriers, functional (SAMs) have been utilized especially in inverted OPV devices.¹⁰¹ SAM-modified TiO_x and ZnO layers have used in order to reduce the recombination losses in these devices by passivating the inorganic surface trap states. It also helps in improvement in the morphology of the organic active layer. Hau et al. have shown 3.78% efficient inverted OPV device by using SAM-modified TiO_x.¹⁰² However, 4.9 % PCE was reported by using C-60 modified ZnO NPs layer for ITO planarization.¹⁰³

1.5 Bulk heterojunction organic solar cell

The bulk heterojunction (BHJ) concept was revolutionary in the development of OPV devices. This concept has provided the way to overcome exciton dissociation, diffusion, and low electron/hole mobility in the organic semiconductors.¹⁰⁴⁻¹⁰⁶ The semiconducting molecules and polymers have got much attention for their application in BHJ organic solar cells. The easy synthesis, versatile processing capability, and optoelectronic properties like the inorganic counterparts have made their suitability towards third generation solar cells. These molecules and polymers can be easily tuned to the desired bandgap and can be processed by solution method. The first BHJ solar cell was fabricated by Yu et al. in 1995 using *p*-phenylene vinylene (PPV) derivative as donor polymer and fullerene acceptor.¹⁰⁷ After several works, the focus

has been shifted to polythiophene derivatives for BHJ OPV devices.¹⁰⁸⁻¹¹² The most studied materials are P3HT and PCBM for BHJ solar cells.

1.5.1 Working mechanism of OPV device

The principle mechanisms in BHJ organic solar cells are shown schematically in the figure 1.7. The fundamental steps can be categorized as;

- i. Creation of excitons in conjugated polymer
- ii. Exciton diffusion in conjugated polymers
- iii. Exciton dissociation at donor/acceptor interface
- iv. Charge transport in bulk donor:acceptor blend
- v. Charge extraction and photocurrent generation

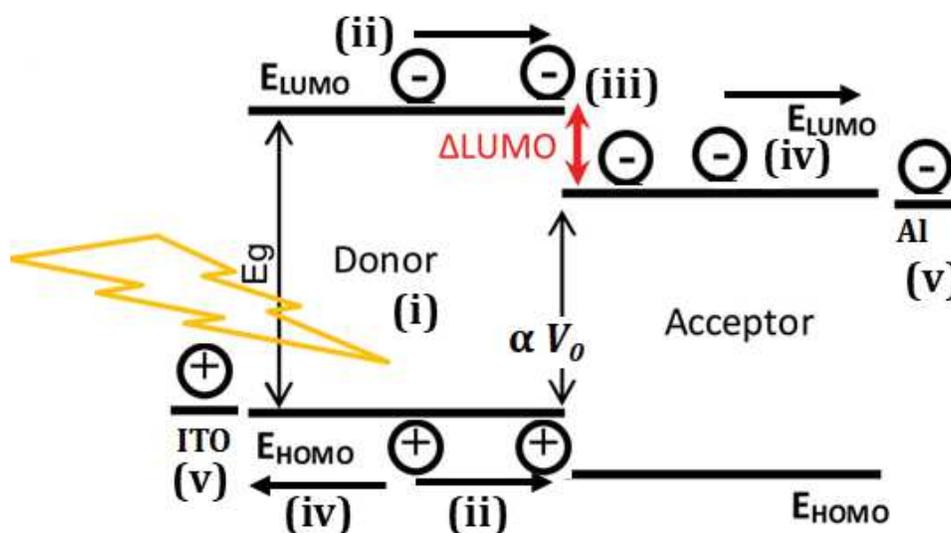


Figure 1.7. Working mechanism of organic BHJ solar cell.

Creation of excitons in conjugated polymer

The creation of excitons depends on absorption coefficient and optical bandgap. The conjugated polymers absorb light efficiently because of high absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$). Due to which, less thickness (\sim few hundred nanometer) is required to absorb all the light in the absorption band. However, the absorption band is determined by the bandgap of the material and the bandgap of common conjugated polymers is much higher than its counterpart inorganic materials. Most common materials like P3HT has a bandgap of $\sim 1.9 \text{ eV}$, which covers approximately 30-40% of AM1.5 solar radiation. Although the development of low bandgap conjugated polymers and small molecules ($\sim 1.6 \text{ eV}$) has provided the way to tap more than 50% of radiation by only 100 nm thick film. When the photon flux having energy above

the absorption edge incident on BHJ active layer the device through the transparent electrode, Coulombically bound electron-hole pairs (excitons) are generated. The Frenkel-like excitons are localized in molecular solids as there is a weak interaction between neighbouring molecules and hence no band to band transition. Now the excitons are required to be separated into free charge carriers. But the exciton binding energy (~ 0.4 eV) in conjugated polymers is much higher than the room temperature thermal energy kT and so, they need an external field.

Exciton diffusion in conjugated polymers

The external field required for the separation of excitons is provided by the acceptor molecules in the BHJ active layer. For this, it is very important to have polymer/acceptor interface near the created excitons. The excitons are generally created in donor conjugated polymers. Before getting an interface, these excitons need to be travel across polymer. The exciton diffusion length becomes a critical parameter in the operation of polymer solar cells. The exciton diffusion length in conjugated donor polymers are found in the range of 5-20 nm.¹¹³⁻¹¹⁸ The concept of bulk heterojunction comes to rescue and circumvent the diffusion length limitation. In this way, most of the photogenerated excitons find the donor/acceptor interface within the limit of diffusion length and encounter the offset potential between polymer and acceptor molecule.

Exciton dissociation at donor/acceptor interface

In the molecular solids, the excitons present at donor/acceptor interface either recombine or overcome the Coulomb binding with the help of electric field and temperature.¹¹⁹⁻¹²¹ Onsager theory describes the field dependent charge generation, in which it is described that the diffusive Brownian motion of the bound charges within modified Coulombic potential by an electric field is responsible for their dissociation at the interface.¹²² However, the dissociation is less clear in the case of conjugated polymers. Hertel et al. proposed that free charge generation from excitons involves two steps; Firstly, even after the separation of excitons from a conjugated polymer, the electron and hole polarons are formed which are bound with weak Coulomb force, known as geminate electron-hole pairs and in the second step, the geminate charge pairs are dissociated into free carriers.¹²³ Arkhipov et al. presented the role of donor/acceptor interface towards the dissociation of excitons.¹²⁴ Partial charge transfer before the excitation of the active layer may form a dipole at the donor/polymer interface and it can block the hole transport towards acceptor molecule. Also, the difference in

mobility of the holes and electrons in the organic semiconductors may create an internal field, which can contribute to the dissociation of excitons.¹²⁵⁻¹²⁶

Charge transport in bulk donor:acceptor blend

Once the excitons dissociated, the electrons are localized in the acceptor molecules and holes are localized in the donor polymer chain. The electrons in acceptor molecule should be transported to negative electrode interface and the holes to the anode interface. The electron and hole mobilities in the molecular solids become a critical parameter in order to understand the charge transport in BHJ organic solar cells. For example, the electron mobility in pure PCBM phase was found $2 \times 10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is changed in BHJ environment.¹²⁷ The differential mobility values for electrons and holes alter the internal field and hence there is a significant difference in mobilities in BHJ environment and in pure phase. This change was attributed to charge carrier density in the active layer.¹²⁸ Pacios et al proposed that active layer morphology plays a significant role in enhanced charge transport in the PSCs.¹²⁹

Charge extraction and photocurrent generation

After the successful charge transport in the bulk heterojunction active layer, charge carriers reach their respective electrode interface. For efficient charge extraction in organic semiconductor-based devices, the charge carrier injection at the metal to semiconductor plays an important role. The electron and hole barriers (ϕ_{be} and ϕ_{bh}) at metal/semiconductor interface can be determined from the location of the metal work function, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the organic semiconductor.

1.5.2 Importance of cathode/anode buffer layers in OPV device

In 1960, R. L. Anderson had given a rule, Anderson's rule, for the construction of energy band diagram for semiconductor heterojunctions.¹³⁰ As per that, the electron and hole energy barrier shall be decided after aligning the vacuum energy level of both sides of semiconductors. It was unanimously accepted rule to understand the charge extraction mechanism at the interfaces until in 1998, Kahn *et al.* demonstrated that the vacuum level alignment rule is no more valid at the interfaces of molecular solids and metals.¹³¹ At each metal and molecular solid interface, dipole barrier exists which controls the position of

interfacial Fermi level and hence energy level alignment at these type of interfaces becomes material dependent.¹³²

The organic solar cells require at least one low work function electrode in order to either inject into or collect electrons from LUMO of the organic active layer. The low work function metals are prone to ambient oxygen and water. In the attempt to overcome metal oxidation problem, the fabrication of polymer solar cells has been started in an inert atmosphere of the glove box. Then the devices are encapsulated inside the glove box and taken out for the measurement. All these steps lead to cost enhancement of polymer solar cells. There were many architectural changes have been done and finally, inverted architecture was accepted to curb the problem of low work function electrodes to a certain extent.^{56,95,133}

Several works have been done to replace acidic PEDOT:PSS and extremely low work function electrodes. In the first approach, low work function materials, used for electron injection and ejection, were replaced by ZnO, In₂O₃, Al-doped ZnO, In-doped ZnO, or NiO, which are low work function metal-oxides.¹³⁴⁻¹³⁷ The thin layer (~20-40 nm) metal oxides are then deposited on to ITO surface. They show a lower work function (~ 4.3 eV) than ITO alone. In another approach, the electrodes are passivated with very thin layer of chemically or physically adsorbed materials. These surface modifiers are chosen such that they form strong molecular/interface dipoles, which encourage vacuum-level shift and thus modify the work function of electrodes.¹³⁸

1.6 Technological significance of OPV devices

The OPV devices, in spite of having lower performances, are promising in the applications which cannot be demonstrated by conventional solar cells. The organic materials used in OPV devices used to have high absorption coefficient and hence they have photovoltaic responses even in diffuse light present in houses. Also, the organic semiconductors can have selective absorption wavelengths by the easy tuning the optical bandgap. Such properties, unique to organic semiconducting materials, provides an opportunity to use them in smart applications. The major applications include building integrated photovoltaic (BIPV) using transparent organic solar cells, zero energy building, greenhouse farming, and flexible solar cells for clothing.

1.7 Proposed plan

Solar cells based on organic semiconductors are still far from applicability if compared to silicon solar cells. One of the major obstacles is poor charge transport in the organic solar cells due to primarily hybrid nature of the interfaces. In order to improve the charge transport and hence the charge extraction in these devices, the two-fold research is going on. One of the approaches is to increase the charge carrier mobility and its lifetime in the organic semiconductor materials through new material development. On the other hand, the proper choice of interface layers has shown the new directions for the improvement of the devices.

The questions need to be answered about the role of interlayers (ETL and HTL) in the performance of OPVs. The major points, which has initiated this work, are as follows;

1. What are the appropriate characterization techniques to probe the physical and electrical attributes at the active layer (organic polymers/molecules) and in general, inorganic charge transport interlayers?
2. Why is the impediment in charge transport happening at the respective interfaces?
3. How to rectify the interface events in the attempt to improve the device performance?

In attempt to answer these questions, the following systematic studies have been implied;

1. The electrical and physical characterizations have been done to understand the interfacial phenomenon and their impact on device parameters.
2. The appropriate methods of processing have been utilized to see the interface modification and its impact on device performance.
3. The effect of a change in environment at the interface by modifying the charge transport interlayer has been studied.

The charge transport study in bulk-heterojunction organic solar cells via improvement the in electron transport interlayer is the major content of this thesis.