CHAPTER 4

ORGANIC SOLAR CELLS

Organic solar cells, which use organic polymers or small organic molecules to convert sunlight into a useable form of energy, are a promising new tool for providing inexpensive, environmentally friendly energy. To date organic solar cells have demonstrated comparatively low rates of efficiency, stability and strength. However, there is much room for improvement before the theoretical efficiency limits are reached. Polymer solar cells are a type of flexible solar cell. They can come in many forms including: organic solar cell (also called plastic solar cell), or organic chemistry photovoltaic cell that produce electricity from sunlight using polymers. There are also other types of more stable thin-film semiconductors that can be deposited on different types of polymers to create solar cells.

An organic photovoltaic cell (OPVC) is a photovoltaic cell that uses organic electronics; a branch of electronics that deals with conductive organic polymers or small organic molecules for light absorption and charge transport. The plastic itself has low production costs in high volumes. Combined with the flexibility of organic molecules, this makes it potentially lucrative for photovoltaic applications. Molecular engineering (e.g. changing the length and functional group of polymers) can change the energy gap, which allows chemical change in these materials. The optical absorption coefficient of organic molecules is high, so a large amount of light can be absorbed with a small amount of materials. The main disadvantages associated with organic photovoltaic cells are low efficiency, low stability and low strength compared to inorganic photovoltaic cells.

The first generation of organic photovoltaic solar cells was based on single organic layers sandwiched between two metal electrodes of different work functions. The rectifying behavior of single layer devices was attributed to the asymmetry in the electron and hole injection into the molecular Π* and Π-orbitals, respectively, and to the formation of a Schottky-barrier between the *p*-type (hole conducting) organic layer and the metal with the lower work function. The power conversion efficiencies reported were generally poor but reached remarkable 0.7% for merocyanine dyes in the early days. In this case, the organic layer was sandwiched between a metal–metal oxide and a metal electrode, thus enhancing the Schottky-barrier effect [metal-insulator semiconductor (MIS) devices].

The next breakthrough was achieved by introducing the bilayer heterojunction concept, in which two organic layers with specific electron or hole transporting properties were sandwiched between the electrodes. About1% power conversion efficiency was reported for two organic materials (a phtalocyanine derivative as *p*-type semiconductor and a perylene derivative as *n*-type semiconductor) sandwiched between a transparent conducting oxide and a semitransparent metal electrode. This result was for many years the outstanding benchmark. A bit later, scientists introduced the concept of an organic tandem cell structure by stacking two heterojunction devices. They also developed a three layer *p-i-n* like structure with a co-deposited interlayer between the *p*-type (hole conducting) and *n*-type (electron conducting) layers. In the meantime, the field of conjugated polymers grew mature, and the first single layer devices based on these newly developed materials were presented. But also, these polymer single layer devices were showing only power conversion efficiencies of less than 0.1%. A further approach was lamination of two polymer layers, leading to a diffusive interface between D and A moieties, and calculated power conversion efficiencies approaching 2% were reported.

The organic solar cell development has gained momentum in the recent years. Conversion efficiencies between 1.5 and 4% have been achieved for evaporated bilayer devices, bulk heterojunction polymer–fullerene Conceptually similar to the bulk heterojunctions, there is a wide research field of dye sensitized, electrochemical solar cells. The early steps in the development were largely improved by the Graetzel group. However, in recent years, by the introduction of organic hole conductors as replacement for the liquid electrolytes in electrochemical solar cells and by the exchange of the electron conducting acceptor materials in organic heterojunction devices with inorganic nanocrystals, electrochemical and organic photovoltaic research directions are gradually merging together.

4.1 STRUCTURE AND DESIGN OF ORGANIC SOLAR CELLS

A photovoltaic cell is a specialized semiconductor diode that converts visible light into direct current (DC) electricity. Some photovoltaic cells can also convert infrared (IR) or ultraviolet (UV) radiation into DC. A common characteristic of both the small molecules and polymers (Fig 1) used in photovoltaic is that they all have large conjugated systems. A conjugated system is formed where carbon atoms covalently bond with alternating single and double bonds, in other words these are chemical reactions of hydrocarbons. These hydrocarbons electrons pz orbitals delocalize and form a delocalized bonding π orbital with a π* antibonding orbital. The delocalized π orbital is the highest occupied molecular orbital (HOMO), and the π* orbital is the lowest unoccupied molecular orbital (LUMO). The separation between HOMO and LUMO is considered as the band gap of organic electronic materials. The band gap is typically in the range of 1-4 eV.

When these materials absorb a photon, an excited state is created and confined to a molecule or a region of a polymer chain. The excited state can be regarded as an electron hole pair bound together by electrostatic interactions. In photovoltaic cells, excitons are broken up into free electrons-hole pairs by effective fields. The effective fields are set up by creating a heterojunction between two dissimilar materials. Effective fields break up excitons by causing the electron to fall from the conduction band of the absorber to the conduction band of the acceptor molecule. It is necessary that the acceptor material has a conduction band edge that is lower than that of the absorber material.

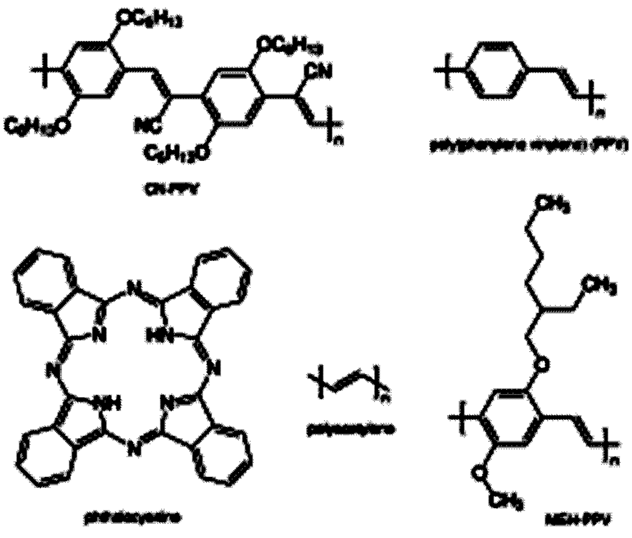


Fig 4.1 Example of organic photovoltaic materials

A typical solar cell structure using organic bulk heterojunctions materials looks such as the one shown below.

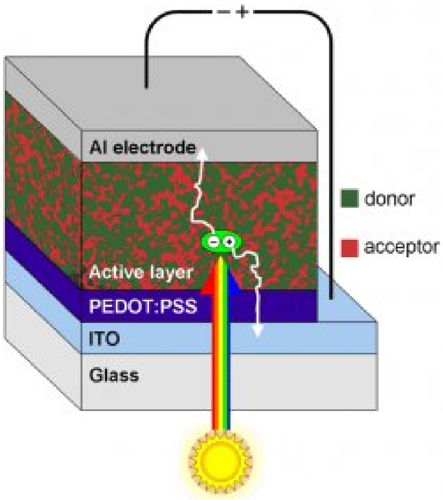


Fig 4.2 Architecture of an organic photovoltaic device. The negative electrode aluminum, indium tin oxide (ITO) is a common transparent electrode, and the substrate is glass. The schematic depicts a bulk heterojunction (BHJ) active layer where the donor and acceptor blend forms phase segregated domains within the active layer. The structure of the BHJ is critical to the performance of the solar device.

ITO coated glass or any flexible plastic substrate is spin coated with 4-(ethylene dioxythiophene) –poly (styrenesulfonate) (PEDOT:PSS) to a thickness of about 100 nm to facilitate hole conduction and also to smoothen the relatively rough ITO layer, which prevents short circuits in the solar cell. Next, a bulk heterojunction polymer-fullerene blend containing poly (3-hexylthiophene) (P3HT) in its regioregular form as electron donor and a fullerene derivative ([6,6]-Phenyl C61-butyric acid methyl ester)(PCBM) as electron acceptor is deposited to a thickness of about 100nm. Finally aluminum (100 nm) is vacuum evaporated onto P3HT: PCBM to form the back layer electrode to complete the solar cell device fabrication.

The asymmetry of the work functions between the cathode and the anode creates an internal electric field such that the holes move toward the ITO layer and the electron towards the aluminum cathode. By externally connecting the electrodes a current can be generated.

Single layer organic photovoltaic cell

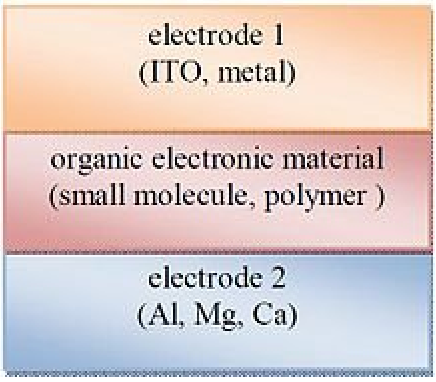


Fig 4.3 Sketch of a single layer organic photovoltaic cell

Single layer organic photovoltaic cells are the simplest form among various organic photovoltaic cells. These cells are made by sandwiching a layer of organic electronic materials between two metallic conductors, typically a layer of indium tin oxide (ITO) with high work function and a layer of low work function metal such as Al, Mg and Ca. The basic structure of such a cell is illustrated in Fig 4.3.

The difference of work function between the two conductors sets up an electric field in the organic layer. When the organic layer absorbs light, electrons will be excited to Lowest Unoccupied Molecular Orbital (LUMO) and leave holes in the Highest Occupied Molecular Orbital (HOMO) forming excitons. The potential created by the different work functions helps to separate the exciton pairs, pulling electrons to the positive electrode (an electrical conductor used to make contact with a non-metallic part of a circuit) and holes to the negative electrode. The current and voltage resulting from this process can be used to do work. Using electric fields is not the best way to break up excitons, heterojunction based cells which rely on effective fields are more effective

Bilayer organic photovoltaic cells

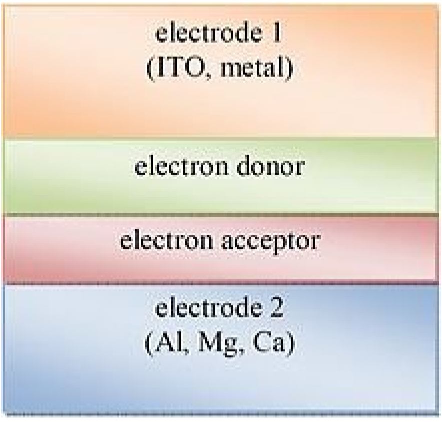


Fig 4.4 Sketch of a multilayer organic photovoltaic cell

This type of organic photovoltaic cell contains two different layers in between the conductive electrodes (Fig 4.4). These two layers of materials have differences in electron affinity and ionization energy, therefore electrostatic forces are generated at the interface between the two layers. The materials are chosen properly to make the differences large enough, so these local electric fields are strong, which may break up the excitons much more efficiently than the single layer photovoltaic cells do. The layer with higher electron affinity and ionization potential is the electron acceptor, and the other layer is the electron donor. This structure is also called planar donor-acceptor heterojunctions.

Bulk heterojunction photovoltaic cells

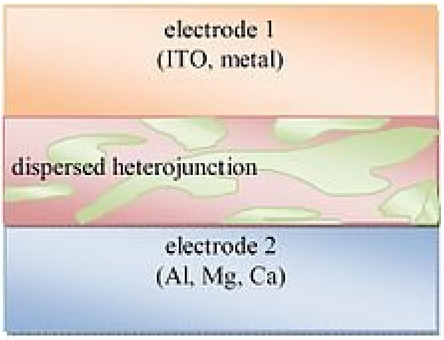


Fig 4.5 Sketch of a dispersed junction photovoltaic cell

In this type of photovoltaic cell, the electron donor and acceptor are mixed together, forming a polymer blend (Fig 4.5). If the length scale of the blend is similar with the exciton diffusion length, most of the excitons generated in either material may reach the interface, where excitons break efficiently. Electrons move to the acceptor domains then were carried through the device and collected by one electrode, and holes were pulled in the opposite direction and collected at the other side.

C_{60} and its derivatives are also used as electron acceptor in the dispersed heterojunction photovoltaic cells. Yu et al. fabricated a cell with the blend of MEH-PPV and a methano-functionalized C_{60} derivative as the heterojunction, ITO and Ca as the electrodes. This cell showed a quantum efficiency of 29% and a power conversion efficiency of 2.9% under monochromatic illumination. Later they replaced MEH-PPV with P3OT, which obtained a cell with a quantum yield of 45% under a 10V reverse bias.

Polymer/polymer blends are also used in dispersed heterojunction photovoltaic cells. Halls et al. used a blend of CN-PPV and MEH-PPV, fabricated a cell with Al and ITO as the electrodes, whose peak monochromatic power conversion efficiency is 1% and fill factor is 0.38. Dye sensitized photovoltaic cells can also be considered as important ones of this type.

4.2 CONDUCTIVE POLYMER

Conductive polymers or, more precisely, intrinsically conducting polymers (ICPs) are organic polymers that conduct electricity. Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not plastics, i.e., they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show mechanical properties as other commercially used polymers do. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Types of Conductive polymers

The linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers are the main class of conductive polymers. Historically, these are known as melanins. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.

Synthesis

There are many methods for the synthesis of conductive polymers. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation:

$$n\ H\text{–}[X]\text{–}H \rightarrow H\text{–}[X]_n\text{–}H + 2(n-1)\ H^+ + 2(n-1)\ e^-$$

The low solubility of most polymers presents challenges. Some researchers have addressed this through the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water. These include polyaniline nanofibers and PEDOT:PSS. These materials have lower molecular weights than that of some materials previously explored in the literature. However, in some cases, the molecular weight need not be high to achieve the desired properties.

Molecular basis of electrical conductivity

The conductivity of such polymers is the result of several processes. E.g., in traditional polymers such as polyethylenes, the valence electrons are bound in sp^3 hybridized covalent bonds. Such "sigma-bonding electrons" have low mobility and do not contribute to the electrical conductivity of the material. However, in conjugated materials, the situation is completely different. Conducting polymers have backbones of contiguous sp^2 hybridized carbon centers. One valence electron on each center resides in a p_z orbital, which is orthogonal to the other three sigma-bonds. The electrons in these delocalized orbitals have high mobility when the material is "doped" by oxidation, which removes some of these delocalized electrons. Thus, the conjugated p-orbitals form a one-dimensional electronic band, and the electrons within this band become mobile when it is partially emptied. The band structures of conductive polymers can easily be calculated with a tight binding model. In principle, these same materials can be doped by reduction, which adds electrons to an otherwise unfilled band. In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction silicon atoms are replaced by electron-rich (e.g., phosphorus) or electron-poor (e.g. boron) atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

The most notable difference between conductive polymers and inorganic semiconductors is the electron mobility, which until very recently was dramatically lower in conductive polymers than their inorganic counterparts. This difference is diminishing with the invention of new polymers and the development of new processing techniques. Low charge carrier mobility is related to structural disorder. In fact, as with inorganic amorphous semiconductors, conduction in such relatively disordered materials is mostly a function of “mobility gaps” with phonon-assisted hopping, polaron-assisted tunneling, etc., between localized states. Recently it has been reported that Quantum Decoherence on localized electron states might be the fundamental mechanism behind electron transport in conductive polymers.

The conjugated polymers in their undoped, pristine state are semiconductors or insulators. As such, the energy gap can be > 2 eV, which is too great for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes only have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping (< 1%), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported up to now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyactetylene are delocalized along the chain, pristine polyacetylene is not a metal. Polyacetylene has alternating single and double bonds which have lengths of 1.44 and 1.36 Å, respectively. Upon doping, the bond alteration is diminished in conductivity increases. Non-doping increases in conductivity can also be accomplished in a field effect transistor (organic FET or OFET) and by irradiation. Some materials also exhibit negative differential resistance and voltage-controlled "switching" analogous to that seen in inorganic amorphous semiconductors.

Despite intensive research, the relationship between morphology, chain structure and conductivity is poorly understood yet. Generally it is assumed, that conductivity should be higher for the higher degree of crystallinity and better alignment of the chains; however, this could not be confirmed for PEDOT and polyaniline which are largely amorphous.

Properties and applications

Conductive polymers enjoy few large-scale applications due to their poor processability. They have been known to have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process. Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly provide fresh air to this field with their higher surface area and better dispersability.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

- **Electroluminescence**

Electroluminescence is light emission stimulated by electrical current. In organic compounds, electroluminescence has been known since the early 1950s. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Barriers to applications

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis. Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can processed only by dispersion.

Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. To date, there remains to be discovered an organic polymer that is *intrinsically* electrically conducting.

4.3 MATERIALS USED IN ORGANIC SOLAR CELLS

New materials have been integrated into organic solar cells that double its open-circuit voltage and demonstrate the potential to make highly efficient photovoltaic cells much less expensively than with silicon. The research boosted the power output of photovoltaic cells, which in turn reduces their cost per kilowatt-hour. The researchers achieved an open-circuit voltage of 0.97 V, while surpassing the power output of a control organic solar cell by over 50 percent. A high-efficiency organic solar cell typically has a open-circuit voltage of 0.54 V. Silicon solar cells can have an open-circuit voltage as high as approximately 0.71 V. This latest research demonstrates that we can achieve high open-circuit voltages in small-molecular organic solar cells while also making gains in power output. Traditionally, photovoltaic or "solar" cells have been constructed of an inorganic semiconductor like silicon. Efficient silicon-based devices, especially of large surface area, are difficult and expensive to produce. Silicon cells are fragile, heavy and opaque, limiting applications and potential uses. Cost is a critical factor in the solar cell industry as solar generated power is still four to six times more expensive to consumers than coal-generated power.

According to the recent surveys, electricity demand will nearly double by 2025, requiring an additional 11.7 trillion kilowatt-hours of capacity, and solar energy must play a major role in meeting this demand to mitigate greenhouse gas effects and meet global emission standards. Global solar cell production has grown 25 percent annually for the last 20 years. This accelerating growth has resulted in a worldwide shortage of semiconductor silicon, driving solar cell prices higher. Recent efforts have focused on the use of "organic" semiconductor materials. Organic semiconductors contain the ubiquitous element carbon and have the potential to achieve ultralow production costs and high power output. Organic materials are ultrathin, flexible and can be applied to large areas, including curved or spherical surfaces. Because the organic layers are so thin, transparent solar cells can be fabricated creating power-generating windows that retain their basic function. The researchers have focused on organic "small-molecule" devices that are assembled literally a molecule at a time in highly efficient nanostructures. Organic materials can be applied to virtually any surface using a low-temperature method akin to spray painting. These kind of production methods are easily adaptable to continuous and so-called "roll-to-roll" manufacturing processes and hold the promise of dramatically reduced production costs. Organic materials also can be used in flexible applications, or even be used to create photovoltaic cells that act as window tinting in buildings.

Though common materials used for photovoltaics (i.e., the conversion of sunlight into electrical energy) are inorganic, there has been a tremendous effort to develop organic solar cells within the last three decades. The fields started by the application of small organic molecules (pigments), and since the development of semiconducting polymers, these materials were incorporated into organic solar cells resulting in remarkable improvements within the past years. The potential of semiconducting organic materials to transport electric current and to absorb light in the ultraviolet (UV)-visible part of the solar spectrum is due to the sp^2-hybridization of carbon atoms. For example, in conducting polymers the electron in the p_Z-orbital of each sp^2-hybridized carbon atom will form π-bonds with neighboring p_Z electrons in a linear chain of sp^2-hybridized carbon atoms, which leads then to dimerization (an alternating single and double bond structure, i.e., Peierls distortion). Due to the isomeric effect, these π-electrons are of a delocalized nature, resulting in high electronic polarizability.

Besides the absorption of sunlight and (subsequent) creation of photogenerated charge carriers, a second requirement for solar cell materials is the ability to transport these charge carriers. Both properties are commonly found for materials that have an extended delocalized π-electron system. Phthalocyanine is a representative of the *p*-type, hole-conducting materials that work as electron donor. The perylene and its derivatives show an *n*-type, electron-conducting behavior, and they serve as electron acceptor material. Both of these molecules were often incorporated into evaporated solar cells. Because the optical bandgap of most organic materials is around 2eV, the thermally excited, intrinsic charge carrier concentrations are rather low. Due to disorder and limited overlap of electronic wave functions (van der Waals interactions), also the charge carrier mobility of organic materials are relatively small and hence they can nearly be regarded as insulators. However, there are possibilities to increase the charge carrier concentration, mostly done via molecular or electrochemical doping.

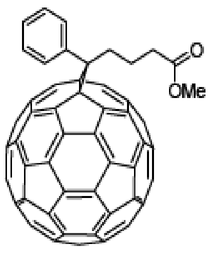
Donor type materials show a doping effect when exposed to oxygen or other strong oxidizing agents such as iodine. This doping is achieved by transferring an electron from the ground state S_0 of the organic semiconductor to the oxidizing agent, resulting in increased charge carrier concentrations in the hole conductor.

As an example for *n*-type doping, perylene was doped upon exposition to hydrogen. Due to these doping effects, the formerly rather insulating materials possess free charge carriers and bilayer devices can work like classical *p-n* junctions. However, doping with gases is not very well controllable. A more controlled approach of doping is achieved by the co-evaporation of materials, matrix and dopant. Among others, the Buckminster fullerene C_{60} (and derivatives) is a strong electron acceptor. Blended with hole-conducting materials, it does not improve charge transport in the dark, but leads to a large increase in photoconductivity under illumination. This is a result of the photo induced charge transfer, and hence this process can be viewed as photodoping.

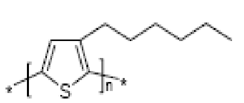
The chemical structures of some molecular materials are depicted in Fig.4.6. P3HT (poly(3-hexylthiophene-2,5-diyl) ,a soluble derivative of C_{60}, namely PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C_6 and C_{60}. Some commonly used conjugated polymers are shown.

To display the fraction of the sunlight, which can contribute to energy conversion in these materials, absorption coefficients of films of some materials are shown in comparison with the air mass (AM) 1.5 standard solar spectrum. Though the silicon absorption spectrum extends up to 1100 nm, the organic materials use only the blue side of the solar spectrum. Charge carrier mobilities in films of molecules and conjugated polymers often depend on the nanoscopic order, which can be manipulated by the preparation conditions.

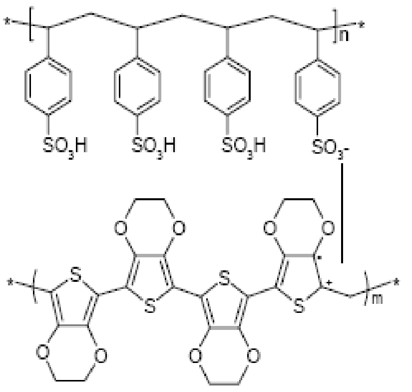
For example, a preferential orientation of polymer backbones parallel to the substrate gives rise to an anisotropic charge transport. For bulk heterojunction solar cells, it was observed that the charge transport in such blend structures is a sensitive function of the nanomorphology of the mixture.



PCBM



P3HT



PEDOT:PSS

C_{60}

Fig 4.6 P3HT (poly(3-hexylthiophene-2,5-diyl), a soluble derivative of C60, namely PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C6 and C60. Some commonly used conjugated polymers are shown

4.3.1 ITO Coated Glass

Fig. 4.7 ITO Glass Substrate

Indium tin oxide (**ITO** or **tin-doped indium oxide**) is a solid solution of indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2), typically 90% In_2O_3, 10% SnO_2 by weight. It is transparent and colourless in thin layers while in bulk form it is yellowish to grey. In the infrared region of the spectrum it is a metal-like mirror.

Indium tin oxide is one of the most widely used transparent conducting oxides because of its two chief properties, its electrical conductivity and optical transparency, as well as the ease with which it can be deposited as a thin film. As with all transparent conducting films, a compromise must be made between conductivity and transparency, since increasing the thickness and increasing the concentration of charge carriers will increase the material's conductivity, but decrease its transparency.

Thin films of indium tin oxide are most commonly deposited on surfaces by electron beam evaporation, physical vapour deposition, or a range of sputter deposition techniques.

ITO can be used in nanotechnology to provide a path to a new generation of solar cells. Solar cells made with these devices have the potential to provide low-cost, ultra-lightweight, and flexible cells with a wide range of applications. Because of the nanoscale dimensions of the nanorods, quantum-size effects influence their optical properties. By tailoring the size of the rods, they can be made to absorb light within a specific narrow band of colours. By stacking several cells with different sized rods, a broad range of wavelengths across the solar spectrum can be collected and converted to energy. Moreover, the nanoscale volume of the rods leads to a significant reduction in the amount of semiconductor material needed compared to a conventional cell. Typically the conductivity is lower for conducting polymers, such as polyaniline and PEDOT:PSS, than inorganic materials, but they are more flexible, less expensive and more environmentally friendly in processing and manufacture.

ITO is a heavily-doped n-type semiconductor with a large bandgap. Because of the bandgap, it is mostly transparent in the visible part of the spectrum. In the ultraviolet, it is opaque because of band-to-band absorption (a UV photon can excite an electron from the valence band to the conduction band). In the near infrared, it also opaque, because of free carrier absorption (an infrared photon can excite an electron from near the bottom of the conduction band to higher within the conduction band).

The main concern about ITO is the cost. ITO can be priced at several times that of aluminium zinc oxide (AZO). AZO is a common choice of transparent conducting oxide (TCO) because of cost and relatively good optical transmission performance in the solar spectrum. However, ITO does consistently defeat AZO in almost every performance category including chemical resistance to moisture. ITO is not affected by moisture and it can survive in a CIGS cell for 25–30 years on a rooftop. While the sputtering target or evaporative material that is used to deposit the ITO is significantly more costly than AZO, consider that the amount of material placed on each cell is quite small. Therefore the cost penalty per cell is quite small too.

ITO is mainly used to make transparent conductive coatings for liquid crystal displays, flat panel displays, plasma displays, touch panels, electronic ink applications, organic light-emitting diodes, solar cells, antistatic coatings and EMI shielding. In organic light-emitting diodes, ITO is used as the anode (hole injection layer).

4.3.2 PEDOT: PSS

PEDOT:PSS or **Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)**

Optoelectronic devices, such as liquid crystal displays (LCDs), light-emitting diodes (LEDs), solar cells, and touch panel displays, have been attracting intense attention, due to their strong application in many aspects. The market for optoelectronic devices has been rapidly expanding. At least one electrode is required to be transparent for the purpose of emitting or harvesting light in optoelectronic devices. Traditionally, indium tin oxide (ITO) is the material as the transparent electrode of optoelectronic devices. However, ITO has some drawbacks, such as high mechanical brittleness, poor adhesion on organic and polymeric materials, and the limited availability of indium that has resulted in a skyrocketing in price. Therefore, new conductive materials are urgently needed to replace ITO as the transparent electrode. Many materials, including conducting polymers, carbon nanotubes, and graphenes, have been investigated as the transparent electrode of optoelectronic devices. Among these materials, poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (chemical structure shown in Figure 4.8) is quite promising as a next-generation transparent electrode material. PEDOT:PSS is the most successful conducting polymer in terms of the commercial application. It can be dispersed in water and some organic solvents, and its films can be readily fabricated through conventional solution processing, such as spin coating. PEDOT:PSS films have a high transparency in the visible range, high mechanical flexibility, and excellent thermal stability. However, PEDOT:PSS suffers a problem of low conductivity. An as-prepared PEDOT:PSS film fabricated from aqueous solution usually has a conductivity below 1 S cm_1, which is remarkably lower than ITO. Hence, it is important to significantly enhance the conductivity of the PEDOT:PSS film to be comparable to that of ITO.

It is a polymer mixture of two ionomers. One component in this mixture is made up of sodium polystyrene sulfonate which is a sulfonated polystyrene. Part of the sulfonyl groups are deprotonated and carry a negative charge. The other component poly(3,4-ethylenedioxythiophene) or PEDOT is a conjugated polymer and carries positive charges and is based on polythiophene. Together the charged macromolecules form a macromolecular salt. It is used as a transparent, conductive polymer with high ductility in different applications. For example, various companies coat photographic films with a thin, extensively-stretched layer of virtually transparent and colourless PEDOT:PSS as an antistatic agent to prevent electrostatic discharges during production and normal film use, independent of humidity conditions.

This compound is generally applied as a dispersion of gelled particles in water. A conductive layer on glass is obtained by spreading a layer of the dispersion on the surface usually by spin coating and driving out the water by heat. Special PEDOT:PSS inks and formulations were developed for different coating and printing processes. Water based PEDOT:PSS inks are mainly used in slot die coating, flexography, rotogravure and inkjet printing. If a high viscous paste and slow drying is required like in screen-printing processes PEDOT:PSS can also be supplied in high boiling solvents like propanediol. Dry PEDOT:PSS pellets can be produced with a freeze drying method which are re-dispersible in water and different solvents, for example ethanol to increase drying speed during printing. Finally, to overcome degradation to ultraviolet light and high temperature / humidity conditions PEDOT:PSS UV-stabilizers are available.

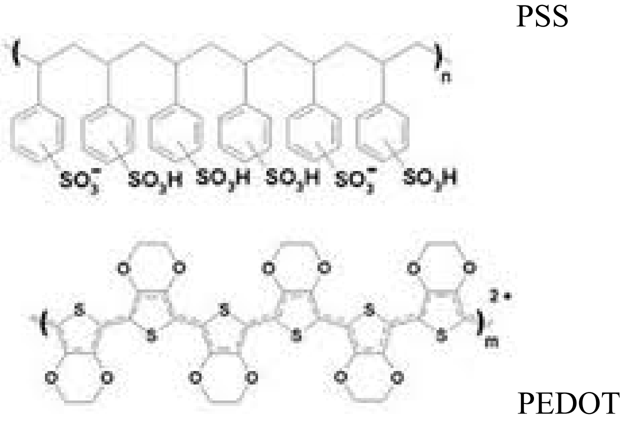


Fig. 4.8 Chemical structure of PEDOT:PSS

4.3.3 P3HT.PCBM

Fig. 4.9 Chemical Structure of P3HT.PCBM

PCBM is the common abbreviation for the fullerene derivative the C_{60} buckyball [6,6]-phenyl-C_{61}-butyric acid methyl ester of that was first synthesized in the 1990s. It is being investigated in organic solar cells. It is an electron acceptor material and is often used in plastic solar cells or flexible electronics in conjunction with electron donor materials such as P3HT or other polymers. It is a more practical choice for an electron acceptor when compared with fullerenes because of its solubility in chlorobenzene. This allows for solution processable donor/acceptor mixes, a necessary property for "printable" solar cells. However, considering the cost of fabricating fullerenes, it is not certain that this derivative can be synthesized on a large scale for commercial applications.

The dispersion of CNTs in a solution of an electron donating conjugated polymer is perhaps the most common strategy to implement CNT materials into OPVs. Generally poly(3-hexylthiophene) (P3HT) or poly(3-octylthiophene) (P3OT) are used for this purpose. These blends are then spin coated onto a transparent conductive electrode with thicknesses that vary from 60 to 120 nm. These conductive electrodes are usually glass covered with indium tin oxide (ITO) and a 40 nm sublayer of poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(styrenesulfonate) (PSS). PEDOT and PSS help to smooth the ITO surface, decreasing the density of pinholes and stifling current leakage that occurs along shunting paths. Through thermal evaporation or sputter coating, a 20 to 70 nm thick layer of aluminum and sometimes an intermediate layer of lithium fluoride are then applied onto the photoactive material.

Organic polymers have wider gap than semiconductors. Thus they give an efficient absorption at near UV part. So is PE3H:PCBM blend. The gap of the blend is approximately 1.8eV. So the longest absorption wavelength should be around 650nm as Figure 4.10 indicates below.

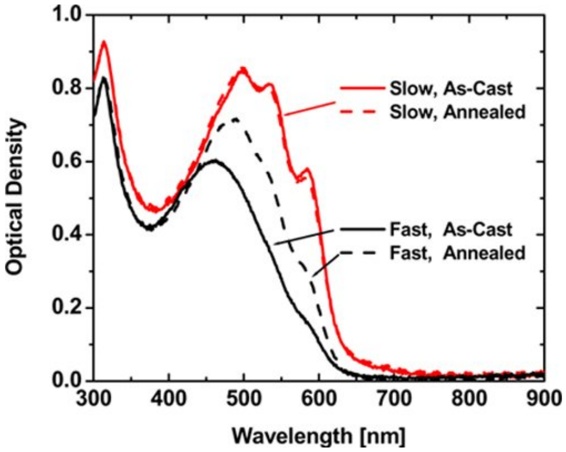


Fig. 4.10 Absorption Efficiency vs Wavelength curve

One of the interesting features of organic polymer is that the band gap can be easily altered without changing its chemical components. It has been discovered that a Head-Tail alignment of P3HT has narrower gap than a Head-Head alignment. It has also been discovered that in some materials, the different arrangement in lateral chains can also result in different band gap structure. Moreover, changing the ration of P3HT:PCBM can change the gap as well. In the presence of P3HT, the PCBM excitons are effectively split quite fast and produce $P3HT^+$ and $PCBM^-$.

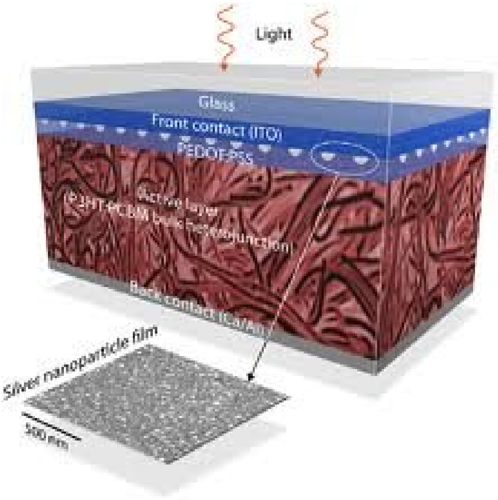


Fig. 4.11 Structure of Organic Solar Cell

4.4 DIFFERENCE BETWEEN CONVENTIONAL AND ORGANIC SOLAR CELLS

The differences between conventional (inorganic) solar cells are usually based on silicon or other inorganic semiconductors, and organic solar cells. Charge carriers (electrons and holes) are generated in the bulk of the material and the electrons and holes are not tightly bound to each. The charge carriers are separated from each other by the built-in electric field of the device and travel to their respective electrode where they are transported out of the semiconducting material. Devices made from organic semiconductors do not operate this way. In contrast to the free carriers in inorganic materials, the charge carriers in organic semiconductors are tightly bound to each other in the form of excitons. The excitons only dissociate at interfaces, such as at electrodes or, as in the case of heterojunction devices, at the interface between donor and acceptor organic materials.

In addition to, or as a consequence of, the properties outlined above, there are other differences between conventional and organic solar cells.

Conventional devices are so-called minority carrier materials. The diffusion of the minority carriers in the built-in electric potential (electric field) creates the photovoltaic current. On the other hand, organic cells are majority carriers because holes exist primarily in one phase, electrons exist primarily in the other phase, and their movements result directly in current flow. This is illustrated in Figure 4.12 below.

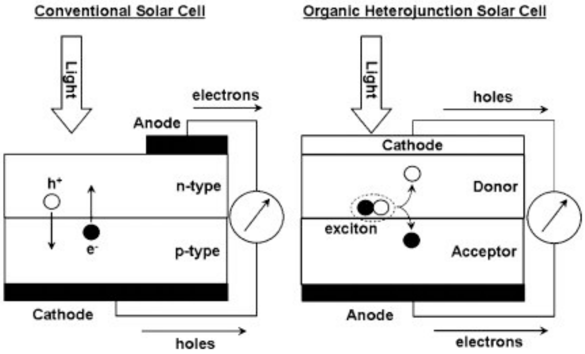


Fig 4.12 Schematic diagrams of a conventional p-n junction solar cell (left) and an organic heterojunction solar cell (right). The diagram highlights the differences in carrier generation between the two types of devices.

Inorganic Solar Cells

Practically all conventional inorganic solar cells incorporate a semiconductor that is doped to form a p-n junction across which the photovoltage is generated. The p side contains an excess of the positive charges (holes), and the n side contains an excess of the negative charges (electrons). In the region near the junction an electric field is formed and the electrons and holes, which are generated through light absorption in the bulk of Si, diffuse to this junction, where they are directed by the electric field towards the proper electrode. Over the years, solar cells have been made from many other semiconductor materials with various device configurations such as single-crystal, polycrystalline, and amorphous thin-film structures. At present, crystalline Si solar cells are by far most dominant PVs used and account for more than 85% of the market.

Organic solar cells

Organic materials bear the potential to develop a long-term technology that is economically viable for large-scale power generation based on environmentally safe materials with unlimited availability. Organic semiconductors are less expensive alternative to inorganic semiconductors like Si; they can have extremely high optical absorption coefficients which offer the possibility for the production of very thin solar cells. Additional attractive features of organic PVs are the possibilities for thin flexible devices which can be fabricated using high throughput, low temperature approaches that employ well established printing techniques in a roll-to-roll process. This possibility of using flexible plastic substrates in an easily scalable high-speed printing process can reduce the balance of system cost for organic PVs, resulting in a shorter energetic pay-back time.

The electronic structure of all organic semiconductors is based on conjugated Π- electrons. A conjugated organic system is made of an alternation between single and double carbon-carbon bonds. Single bonds are known as σ-bonds and are associated with localized electrons, and double bonds contain a σ-bond and a Π- bond. The Π-electrons are much more mobile than the σ-electrons; they can jump from site to site between carbon atoms thanks to the mutual overlap of σ-orbitals along the conjugation path, which causes the wave functions to delocalize over the conjugated backbone. The band gap of these materials ranges from 1 to 4 eV. Many years of research have shown that the typical power conversion efficiency of PV devices based on single (or homojunction) organic materials will remain below 0.1%, making them unsuitable for any possible application. Primarily, this is due to the fact that absorption of light in organic materials almost always results in the production of a mobile excited state (referred to as exciton), rather than free electronhole pairs as produced in inorganic solar cells. This occurs for the reason that organic materials are characterized by low dielectric constant (typically 2-4), compared to inorganic semiconductors, which require an energy input much higher than the thermal energy (kT) to dissociate these excitons. The electric field provided by the asymmetrical work functions of the electrodes is not sufficient to break-up these photogenerated excitons. Instead, the excitons diffuse within the organic layer until they reach the electrode, where they may dissociate to supply separate charges, or recombine. Since the exciton diffusion lengths are typically 1-10 nm, being much shorter than the device thicknesses, exciton diffusion limits charge carrier generation in these devices since most of them are lost through recombination.

4.5 HOLE TRANSPORT MECHANISM OF INORGANIC AND ORGANIC SOLAR CELL

Hole is a positive charge (+1) that can move across a semiconductor. Hole conductivity occurs when positive charges can move, whereas both electrons and negatively charged ions (anions) cannot move easily across a semiconductor. Correspondingly, the negative charges contribute minimally to overall conductivity of the material.

Hole conductivity in inorganic semiconductor (silicon)

Holes can form near the interface of a semiconductor (silicon on the scheme below) and positively charged bias (usually metallic anode). That occurs when an electron from a silicon atom transfers to the metal. Subsequent movement of the hole, thus generated, to the cathode occurs through electron pair transfer form a neighboring bond to the positively charged atom. As a result, the charge appears on the neighboring atom whereas the previously charged atom becomes neutral.

The process continues until the hole reaches the cathode and takes an electron from it. As a result - negative and positive charges from both biases are neutralized and all Si-Si bonds on the hole's pathway are regenerated.

Holes may pre-exist also in a semiconductor that is not connected to the charged electrodes. This type of semiconductors is called **p-conductors** or **p-transporters**.

Holes can roam in these materials whereas their negatively charged counterparts (negative ions) cannot move easily and stay on permanent positions. Concentration of holes may be increased by p-doping, addition of a component with high electron affinity that is called **p-dopant**. This component takes electrons from semiconductor atoms and traps them in a form of static negative ions. Positive charges, holes, roam around unless electrical field is applied. Once it is applied, they start moving in one direction - to the negatively charged cathode.

Hole conductivity in organic semiconductors

Hole conductivity in organic semiconductors occurs when:

1. Molecules of an organic compound/polymer contain long chains of conjugated unsaturated bonds.
2. Molecules of an organic compound/polymer possess electron donating properties, e.g. can 'surrender' one of their electrons easily. Many types of organic conducting polymers are p-type semiconductors. The most widely known are: polyacetylene, polypyrroles, polythiophenes, polyphenylvinylenes (PPVs).

Mechanism of the hole conductance in organic semiconductors is somewhat more complex than that of inorganic materials. Hole conductance may occur along the chain of conjugated unsaturated bonds (simplified scheme see below) as well as between the chains or planes (hopping transport). In any case, the polymers that possess higher order of the chains organization possess also better hole conductivity and, correspondingly, hole mobility. Holes in organic materials may exist and move also together with an unpaired electron, e.g. cation-radical.

In general, hole mobility should be lower than electron mobility, because mechanism of the hole transport requires breakage and formation of covalent chemical bonds, which takes both energy and time to occur. This is always true for inorganic semiconductors, whereas organic semiconductors most often exhibit higher hole mobility than electron mobility. This phenomenon is apparently due to generally higher stability and lower energy of organic cations (carbenium ions) over organic anions (carbanions).

4.6 BILAYER HETROJUNCTION VERSUS BULK HETEROJUNCTION

The simplest structure of an organic polymer solar cell appears to be the superposition of donor and acceptor materials on top of each other, providing the interface needed to ensure the charge transfer. Fig. 4.13 presents the schematic energy diagram of such a bilayer solar cell: the excitons photogenerated in the donor or in the acceptor can diffuse to the interface where they are dissociated; the released electrons are transferred to the fullerene (acceptors); holes and electrons then diffuse or drift in their respective environment to their respective electrode.

The main drawback of this concept resides in the rather short diffusion length of excitons (5–15 nm). Indeed, only those that are created within a distance from the sharp donor–acceptor interface shorter than their diffusion length may contribute to the photocurrent. This limits drastically the photocurrent and hence the overall efficiency of the bilayer solar cells. To overcome this limitation, the surface area of the donor–acceptor interface needs to be increased. This can be achieved by creating a mixture of donor and acceptor materials with a nanoscale phase separation resulting in a three dimensional interpenetrating network: the "bulk heterojunction".

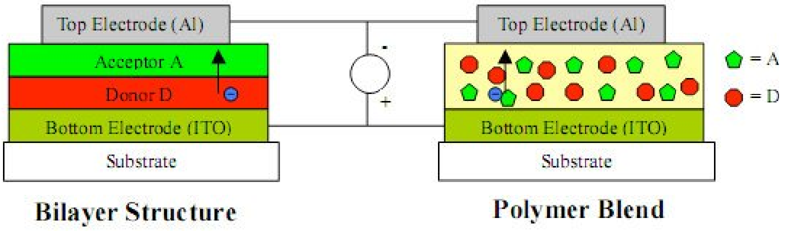


Fig 4.13 Layered structure and polymer blend structure based on an electron donating and an electron accepting polymer

The essence of the bulk heterojunction is to intimately mix the donor and acceptor components in a bulk volume so that each donor–acceptor interface is within a distance less than the exciton diffusion length of each absorbing site.

The bulk heterojunction device is similar to the bilayer device with respect to the D-A concept, but it exhibits a largely increased interfacial area where charge separation occurs. Due to the interface being dispersed throughout the bulk, no loss due to too small exciton diffusion lengths is expected, because ideally all excitons will be dissociated within their lifetime. In this conception the charges are also separated within the different phases, and hence recombination is reduced to a large extent and the photo- current often follows the light intensity linearly or slightly sub-linearly. Though in the bilayer heterojunction the donor and acceptor phase contact the anode and cathode selectively, the bulk heterojunction requires percolated pathways for the hole and electron transporting phases to the contacts. In other words, the donor and acceptor phases have to form a bi-continuous and interpenetrating network. Therefore, the bulk heterojunction devices are much more sensitive to the nano scale morphology in the blend. Generally, bulk heterojunctions may be achieved by co-deposition of donor and acceptor pigments or solution casting of polymer/polymer, polymer/molecule, or molecule/ molecule donor–acceptor blends. The most efficient devices today are based on solution cast P3HT:PCBM blends yielding above 3.5% power conversion efficiency .

4.7 MAJOR ADVANTAGES OF ORGANIC SOLAR CELLS

Comprising conjugated polymers, the organic semiconductors enjoy major advantages as compared to their inorganic counterparts. Indeed, their light weight, mechanical flexibility, and semi transparence opens new opportunities for PV cell design. Moreover most conjugated polymers possess a processing advantage: they are soluble in common organic solvents and hence can be deposited by simple solution processing and printing technologies. Thus, their production can be much easier and consequently much less costly than the inorganic semiconductor devices. Thin films on flexible or nonflexible substrates are achievable by well known and widespread printing methods like screen, ink-jet, offset, or flexo printing. Therefore, mass production by roll-to-roll process can be technologically envisaged. In summary, the conjugated polymer-based PV device production would possess the following advantages:

- Light weight of the product;
- Easy possibility on flexible substrates: flexible product;
- Cost-effective up scaling by roll-to-roll printing techniques;
- Significant reduction of production energy consumption (in respect of the global energy balance);
- Clean processing for environmental considerations.

Nevertheless, to achieve a product viable on the market and competitive with the other available technologies, polymer-based solar cells have to fulfill the Standard requirements: cost, efficiency, and lifetime. Today, conjugated polymer based PV devices have been reported to exhibit efficiencies up to 5%.