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Polymers in Solar Cells

Pedro Pablo Zamora and Klaus Bieger

Abstract

Due to the promising properties of semiconducting polymers they have attracted wide spread interest. During the last decade we have worked on a smart chemistry approach to these substrates and organometallic compounds with special focus on design, synthesis and characterization of materials that could be used in photovoltaic devices. In these materials, one of the most important aspects is high absorbance in the UV-Vis spectrum as a necessary characteristic for high conversion rates of light to electric energy. We were able to show that this can be achieved introducing certain functional groups as, e.g., NO₂-moieties. Another important aspect is the interaction with the buffer layers that also form part of the whole photovoltaic device. Here we show that a double layer of CuI/MoO₃ increased the energy yield for a large variety of organic substrates along with related results from other leading groups reported in literature.

Keywords: polymers, photovoltaics, buffer layer

1. Introduction

Organic photovoltaic devices are often seen as the future of solar cells [1] as they permit energy conversion with much less consumption of material resources than the conventional silicon based semiconductor cells [2]. Additionally they permit the development of flexible devices while the traditional cells are rigid and fragile [3].

Even though since the discovery of the photoelectrical effect in organic substrates large progresses have been achieved [4] to increase yield and stability the organic devices still are much less efficient and present lower lifetimes than the traditional solar cell form [5]. There have also been progresses in developing different cell types. For practical reasons here we center on heterojunction bulk cells as they provide high reproducibility and easy experimental access to poly-layer devices [6].

The construction of heterojunction cells requires several basic elements apart of the proper semiconducting polymer. The polymer has to be linked to a layer—normally fullerene—that accepts the electrons from it. It is also important to count with a “buffer layer” that inhibits the recombination of electrons with the “holes” formed in the same process. Buffer layers are often made of copper-(I)-iodide and molybdenum-(VI) oxide. An appropriate design of this layer can increase the electrical yield in up to 10 times in some cases.

As limits for commercialization 10% of efficiency and 10 years of life expectancy are considered for organic cells. The yield limit already has been reached in some cases due to improvements in the chemical design of donor and acceptor materials [7]. Lifetime is still problematic as degradation of the organic substrate can take place for several reasons as photochemical reactions, interaction with traces of water, encapsulation of the device, thermal instability, etc. Same problems have been found also in other applications and strategies to overcome them are developed [8].

2. Charge transport in polymers

One of the most important aspects in the conversion of light to electrical energy is the electron transport in the semiconductor. It permits the separation of positive and negative charge and prevents the recombination of the exciton known as “quenching” [9]. Therefore a high conductivity in the organic phase as well intra- as intermolecular is desirable and the contact surface among chains in the same layers as well as between layers should be as large as possible to facilitate electron movement. Here homojunction cells have a clear advantage due to the large transition zone between substrates. Anyhow, as mentioned before, it is very difficult to produce this gradient transition in a reproducible manner resulting in larger experimental errors and poorer comparability of results for different materials. Some of the most important aspects are detailed in the following sections:

2.1 Aspects of the material

The backbone of conducting polymers is generally formed by aromatic ring systems with delocalized π -electrons that occupy completely the bonding molecule orbitals. Due to the large amount of orbitals with similar energies they form a completely occupied valence band similar to the situation in classical inorganic semiconductors. The conduction band is made up by the antibonding π^* -orbitals and is generally empty. As in the inorganic counterpart the organic polymers as well can be doped with electron abstracting or electron donating agents leading to p- or n-semiconductors. P-dotation withdraws electrons from the valence band while n-dotation adds electrons to the conduction band increasing the conductivity of the material.

The band gap is defined as the energy gap between valence and conduction band. Generally electrons can be promoted by light energy causing π - π^* -transitions. The electron loss results on the site in a mesomerically stabilized radical cation called “polaron” that can be delocalized in the polymer generally over several monomeric units.

With another bond theoretical focus the band gap corresponds to the difference between HOMO and LUMO as they correspond to the highest occupied bonding and the lowest antibonding orbitals (see **Figure 1**). The electrical conductivity in these terms is due to the excitation of an electron from the HOMO passing to the LUMO and its increased mobility in the delocalized antibonding orbital.

As molecules have a finite extension electrons can only occupy a finite number of discrete energies and normally all bonding orbitals are occupied. Electron

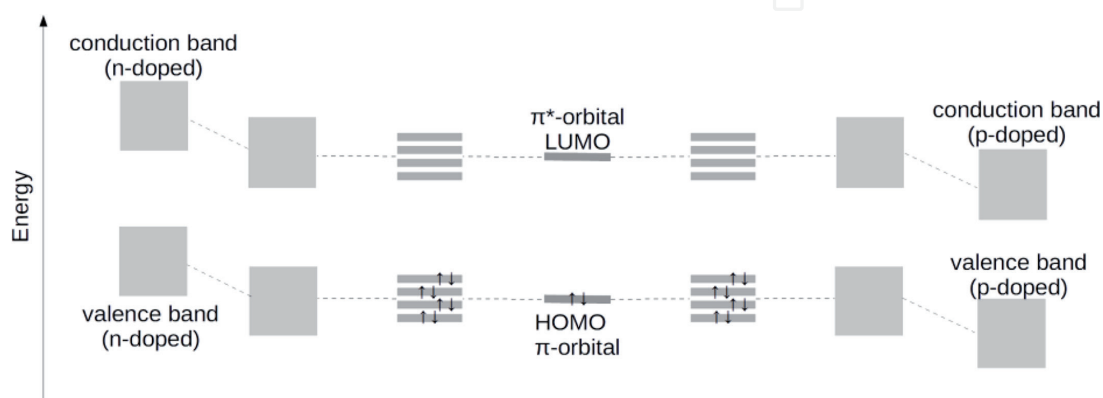


Figure 1. Energy of a simple double bond (center), in a conjugated oligomer (aside) band formation in a polymer and the influence of doping.

mobility is only possible in partly occupied orbitals that can be achieved either by doping the material adding or abstracting electrons with chemical or electrochemical methods. Physically thermal or optical excitation of electrons can be used.

Doping also changes the energies of HOMO and LUMO (or valence-band and conduction band respectively), as these energies are no fixed terms. N-doping—this is adding electrons to the LUMO-orbitals or reduction of the material—will increase the energy level as the electrons will repulse each other while p-doping has the opposite effect and decreases the orbital energy. Additionally doping also alters to a small but significant amount the positions of the atoms as the introduced charges interact with the counter-ions of the doping agent. When the concentration of the doping agent is low it results in the formation of small doped “islands of charge” that can be classified in three types: solitons, polarons and bipolarons. While solitons are wave packets, polaron and bipolaron make reference to quasiparticles.

Polarons and bipolarons can be seen as the polarization of a material due to the presence of charges moving through it. A moving electron, for example, will attract positive charges of the nuclei and push back the negative charges of the electrons in its environment. The polaron is the result of a quantum mechanical treatment of this phenomenon. Bipolarons result from the fact that close polarons may lower their respective energies similar to what happens in Cooper-pairs in superconductors. As the polarization of the surroundings stabilizes the electron lowering the energy of its fundamental state the presence of polarons will result in the formation of new energy bands in the material known as “polaron bands” and new electron transitions may be observed corresponding to this new state could be observed, too. The effect could also be interpreted as a band gap reduction in the semiconducting material [10]. Normally in organic semiconductors polarons and bipolarons are formed due to positive charges found in the polymers. A polaron will correspond to a radical cation while a bipolaron would be formed by a bi-cation. The corresponding energy scheme can be found in **Figure 2**. In organic conducting polymers the presence of various bipolarons at the same time can even lead to the formation of bipolaron bands [11].

The polaron/bipolaron effect has been widely studied on organic semiconducting polymers of different types [12–14]. The effect on bond length has even been confirmed by X-ray diffraction on model substrates with a thiophene backbone similar to the motive found in polythiophenes described later on [15].

While charges are bound to islands where linear parts of molecular chains located in parallel the electron mobility is still relatively low. Anyhow when increasing the doping concentration the charge islands start to overlap giving rise to partly

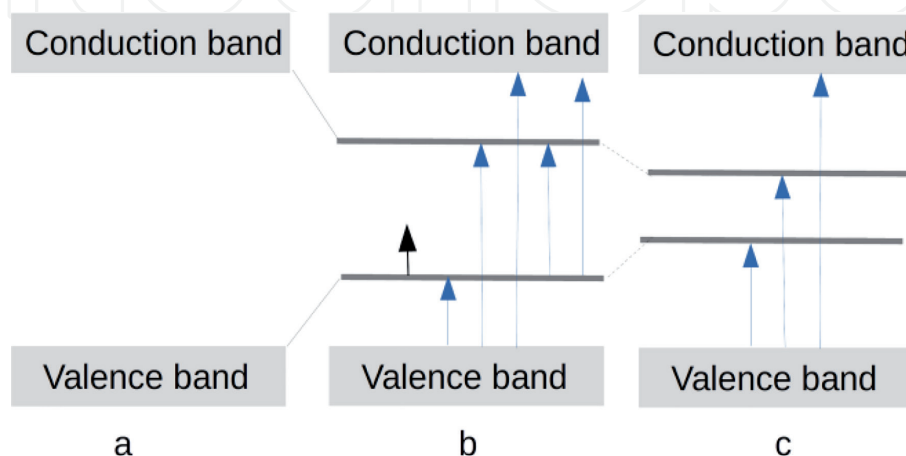


Figure 2. Energy scheme without polarons (a), in presence of polarons (b) (the black arrow represents the radical electron) and in presence of a bipolaron (c). Blue arrows represent possible electron transitions.

occupied bands. In these bands charge mobility increases drastically as electrons can move freely along the whole macromolecule and it becomes an electrical conductor. The overall conductivity depends on the electron mobility in an electrical field within the macromolecular chains as well in their “charge islands” as in the intermolecular charge transport. The step that represents the mayor resistance will limit the overall charge mobility and therewith the conductivity.

The electron transport between polymer chains is linked directly to the degree of order that present molecules. The larger the order the more likely it is that polymer chains are located in parallel and with little distance between each other and this favors the electron transfer. When chains enclose an angle or are even located in perpendicular the jump of an electron from one molecule to the other is much more difficult. In long chain polymers it is not even necessary that a charge is transported along the whole molecule but can jump in part to another nearby unity. The shorter the polymer chain the more important is ordered chain morphology as here inter-chain transport has to occur more often. Unfortunately the general tendency of this type of polymers is to present more disorder or have the chains disposed in a perpendicular manner (see **Figure 3**).

For these reasons long chain per-conjugated polymers are desirable targets for highly conducting materials. The larger the polymer backbone is the larger is the probability to find some ordered region with easy inter-chain electron transport. This is the case even when the crystalline parts are interrupted by amorphous regions. Anyhow chain defects that interrupt the electron delocalization through the chain can make it more appropriate to treat this type of material as an accumulation of several short chain structures. These structures form island-like regions with high conductivity while electron transport between islands is more difficult.

Reasons for the loss of per-conjugation could be torsion between substructures or the formation of neighbored single bonds that do not allow the π -system to extend across the affected site.

2.2 Morphology

Morphology describes the form of the material employed in the construction of a photovoltaic device. It can make reference to the form in which the molecules are present in the substrate or on the physical form of the substrates surface.

Polymer can be present as unordered glass-like phases with the polymer chains in random orientations or as crystalline regions where the chains are ordered in

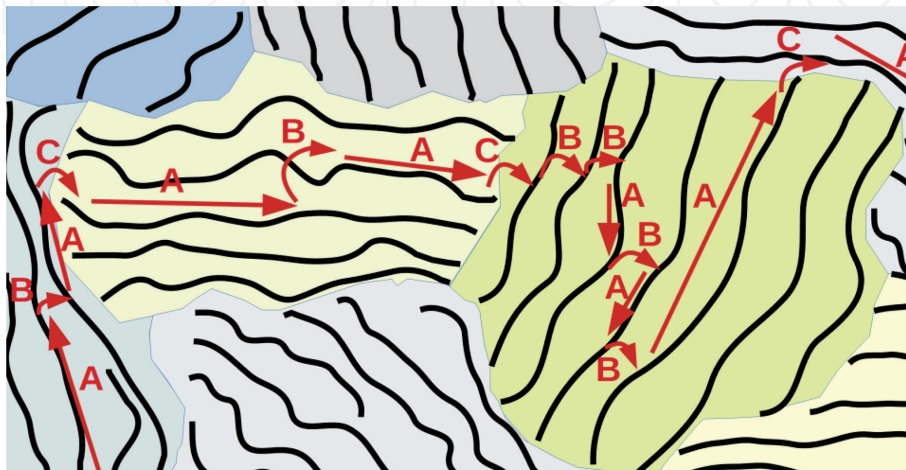


Figure 3. Schematic electron transport in polymers with conductivity islands within the same chain (A), between chains (B) and between islands (C).

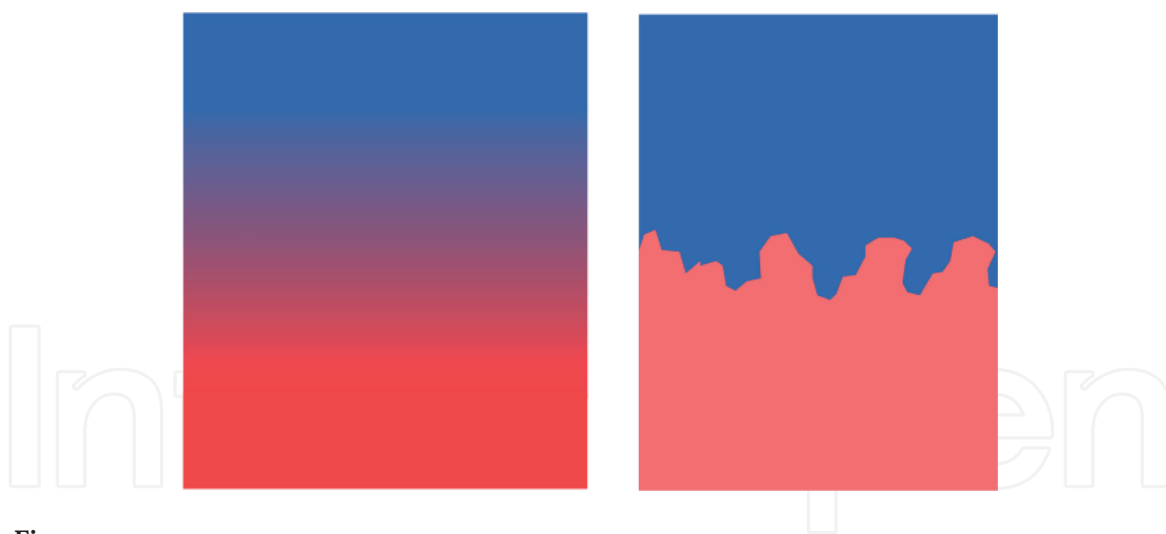


Figure 4. Gradual transition in heterojunction cells (left) and hard interphase in heterojunctions (right). Larger contact reduces the electrical resistance.

parallel. This order or the lack of it will also be related to electronic properties of the substrate as polyconjugation is related to co-planar stretched structures that are lead more easily to crystalline regions while disorder requires generally more flexible structures. These are obtained when the π -system is interrupted due to larger torsion angles and the lack of overlap. Conjugation on the other hand is crucial for electron mobility and transport. Thus crystalline ordered regions will exhibit lower electrical resistance than the glass like zones and are the preferred form for high overall yields.

Morphology reflects to some extent the chemical properties of the molecules. Rigid annulated aromatic ring systems are more likely to form rigid rod-like structures than other open chain backbones. On the other hand, it can be controlled to a certain extent by the conditions used in the deposition of the layers. When deposited by sublimation slow deposition rates at relatively high temperatures favor that the polymer reaches the thermally most stable perconjugated form while fast deposition at relatively low temperatures fixes the higher disorder.

In homojunction devices various substrates have to be deposited at the same time forming a determined gradient. This adds several new parameters and complications to the manufacturing process as diffusion rates, inter-material interactions with the possibility of phase separation, differences in vapor pressure and different requirements for the formation of crystalline phases have to be controlled at the same time over the whole substrate surface. For these reasons results obtained are very difficult to reproduce.

While in homojunction cells charges can pass from one “layer” to the next along the whole gradient that exists between both, in heterojunction cells charges have to pass through the layer-layer-interface. This interface acts as an electrical resistance. Therefore increasing the contact surface with rough surfaces will help to increase the electrical yield. On the other hand, if grooves are too large in comparison with the layer thickness, there exists the risk of hole-formation and direct contact formation of layers that should be separated by the intermedium layer (see **Figure 4**). Surface morphology also depends on substrate and on deposition conditions. A review on morphology of thin film transistors that can be applied in large extent to solar cells can be found in [16].

3. Operational principles of organic photovoltaic cells (OPVCs)

OPVCs use the internal photoelectrical effect that liberates electrons and is used to transform light into electrical energy. The energy generation depends on the

absorbed light. The higher the absorption rate the more electrical energy is produced [17] in form of excitons. This makes it clear that the conversion rate is linked to the absorption coefficient of the substrate in the UV-Vis spectrum. The maximum is also indicative for the band gap. The higher the wavelength of the absorption maximum the lower is the band gap and the higher can be the theoretical photovoltaics yield. On the other hand too low band gaps favor the recombination of the electrical charges as the substrate becomes a conductor and inhibit the proper work of the cell. Therefore values of 1–2 eV are desirable what would correspond to an absorption maximum at about 1200–600 nm [18]. Absorbed energy is used to promote an electron from the HOMO to the LUMO. In a first moment the electron stays close to the positive charge produced in the same process (see **Figure 5**). The electron-hole pair is known as “exciton.” It has to be taken to the polymer—electron acceptor interface where it is separated and the electron is guided to the electrode. An exciton blocker layer (EBL) between the acceptor layer and the electrode inhibits that positive charges migrate to the electrode as this would result in direct charge recombination and no electrical current could be obtained from the device.

The distance an exciton could migrate in a layer is of the order of several 100 nm [19, 20]. The polymer donor layer should therefore have a thickness that is inferior to the migration distance to avoid that excitons recombine on their way to the acceptor-layer. Better conductivity of the polymer allows building thicker layers as it increases the maximum migration distance. Thicker polymer layers are desirable as they lead to higher absorption rates. The same accounts for the acceptor layer.

Typical dimensions found in cells using phtalocyanine-copper as donor and fullerene as acceptor, are some 20 nm for the fullerene and some 40 nm for the phtalocyanine layer for largest possible negative charge transfer.

For charge transfer also a high contact surface is desirable. Double layer and interpenetrated layer devices have been developed. Interpenetrated devices present at least theoretically higher conversion rates due to the large contact surface. Anyhow their construction is difficult and often cannot be reproduced easily.

Double layer devices on the other hand are easily obtained and their structure can be controlled with little effort but have small contact surfaces and herewith lower yields. At least for comparison reasons, the benefits of the high reproducibility compensate the lower yields as they permit detecting promising materials with more accuracy. For real world applications the thus found substrate can later still be used to produce interpenetrated devices.

The construction of a double layer device starts with a transparent and conducting substrate. Normally this is glass or poly ethylene terephthalate (PET) with an

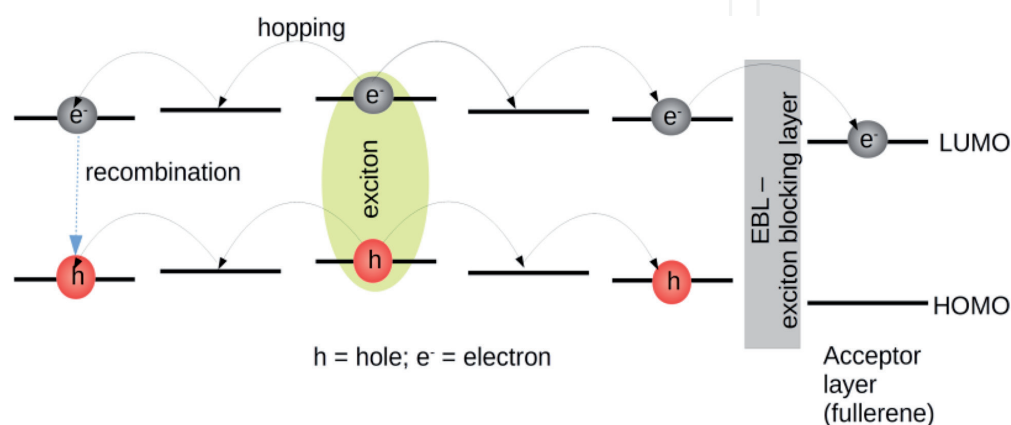


Figure 5.

Excitons can travel along the organic semiconducting material and are separated to electrons and holes on the exciton blocking layer. Long diffusion length favors recombination and efficiency loss [23].

indium-tin-oxide (ITO) layer as transparent conductor. On this generally commercially available substrate an anode buffer layer (ABL) of some 20 nm is deposited. In our work we use molybdenum-(VI)-oxide and copper-(I)-iodide. In spite of their high band gap (>3 eV) characteristic for electrical insulators they help to extract cations as ITO has a high barrier to hole collection. The ABL reduces the barrier matching the energies of the involved bands. In some cases and depending on the ABL substrate it also induces higher crystallinity and improved morphology in the following polymer layer [21]. In our work with polyaniline and polyaminothiophene we observed an increase of the photoelectrical yield of some 10 times due to the proper design of the ABL using MoO_3/CuI . An explication could be the interaction of copper ions with the nitrogen atoms present in the polymer. Optimization of these interactions forces the polymer chains in a parallel direction to the polymer-ABL-interface and herewith leads to an increased order close to the interface. A prove for higher degree of orientation is given by X-ray diffraction where polymer deposits on CuI layers show more and sharper peaks than polymers grown on other substrates. The higher crystalline degree lowers the electrical resistance and this leads to the observed yield improvements. Further investigation shall show if other elements known to show high tendency to form interactions with nitrogen as cobalt, nickel or zinc have similar or even better effects on the polymer growth. After the polymer is deposited as electron donor it follows an electron acceptor layer, normally 40 nm of fullerene for best electron mobility [22].

It follows a thin layer of bathocuproine (BCP). As in the case of the ABL it is a substrate with a relatively high band gap (about 3.5 eV). Its purpose is to avoid the pass of the positive holes to the cathode and herewith recombination of holes with electrons. Therefore the layer is also known as exciton blocking layer (EBL). On the other hand the insulating properties of the material that are necessary for the exciton blocking will decrease the yield of the solar cell. Thus it is necessary to find a balance that optimizes both effects looking for an improved layer thickness. In most applications this is about 4–5 nm.

Finally on the EBL follows aluminum as cathode and selenium as protecting material that prevents oxidation of the organic molecules involved in the sandwich structure.

As shown above buffer—and blocking layers play an important role in the optimization strategy of organic photovoltaic devices and have to be treated along with the organic substrate used as electron donor. The combined tuning of all parameters has allowed designing photovoltaic cells that reach already 13% [24].

When looking for improved electron donor materials at least two important features should be taken into account:

- A high absorption coefficient in the UV-Vis and the near IR spectrum is essential. Only the absorbed light can be transformed into electrical energy and this is the most intense part of the solar spectrum that permits to reach usable electrical tensions by exciton formation.
- For long term stability the material has to be resistant to photochemical degradation as well as to high temperatures as in real world applications it will be exposed to high UV-light densities and temperatures above 100°C .

Additional optimization can be done in all other involved layers. Thus molecules with higher electron acceptor capacities and better stability than fullerene are investigated [25].

Apart of this more chemical part also the electrical behavior of the solar cell is important. Generally it can be seen as a serial circuit. All layers act in this case as

serial resistors (R_s). The electrical resistance especially of the donor—and acceptor layers will diminish the current density (J_{sc}) in the solar cell. Additionally due to the cell construction and its electrical contacts some parallel resistances (R_{sh}) can be observed. The resistances increment also when quenching (coQ) occurs as it lowers the quantity of charges present in the valence- and conduction band.

There also exists a phenomenon known as “dark current.” It consists in the flow of electrons that have already passed to the fullerenes as electron acceptors back to the HOMO of the electron donor. This effect is increased by the polarization observed in the working solar cell as here the negative charge produced in the cathode attracts the positive charges still present in the donor material and increases its density close to the electrode. The dark current could be seen as an “indirect quenching” and also lowers the obtained electrical current. To diminish the dark current, an electron blocking layer (EBL) is applied with an E_g sufficiently high as to prevent the migration of positive charges to the cathode.

As one can deduct from the previous chapters after the exciton formation charge separation is a key step of the whole photo-electrical process. Whatever substrate is used as donor- and acceptor, ionization potential (HOMO) and electron affinity (LUMO) have to match in the way that it permits the exciton dissociation. The electron affinity of the donor has to be less than that of the acceptor and the ionization potential of the acceptor has to be considerably higher than that of the donor molecule. Otherwise no exciton separation corresponding to the crossing of electrons from the LUMO of the donor to the LUMO of the acceptor will occur [26]. The whole construct can be seen in **Figure 6**.

The already mentioned need for high absorption rates makes it clear that the design of solar cell materials and the design of dyes have to be intimately related. In fact a part of the here mentioned bulk layer solar cells there exist other designs as the “dye-sensitized solar cell” (or Grätzel-cell) where the relation becomes even more evident [27]. One of the best known dye-precursor is aniline. Already its discoverer Wöhler mentioned that wood treated by aniline turned to several colors of a while. Anyhow it was Perkin some years later who patented the first synthetic dye also based on aniline—the mauveine [28]. Since then a whole family of colored compounds known as “aniline dyes” has been synthesized. It is also known that aniline can be polymerized under oxidating conditions forming a green semi-conductive polymer known as “emeraldine” due to its intense green color. Further oxidation would lead to blue-violet pernigraniline. The difference is the presence of varying quantities of hydrogen on the nitrogen atoms. Higher hydrogen-content is related to a reduced leuco-form with only amino groups while oxidation and hydrogen abstraction leads to a large proportion of quinoid structures that allow better perconjugation and herewith lowers the energy of the LUMO-orbitals. The result is a semiconducting organic material with low band gap and high absorption coefficient—perfect for applications in organic solar cells.

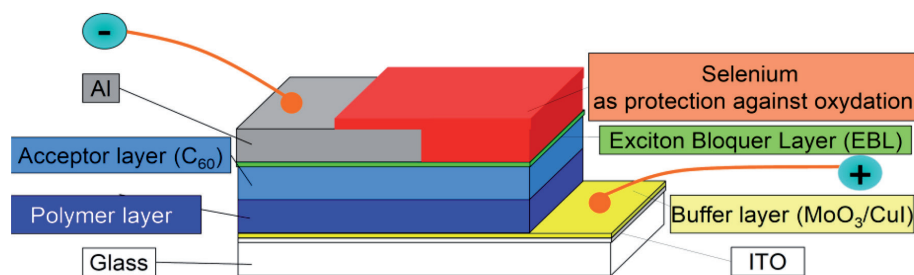


Figure 6.

Typical disposition of the elements that belong to a bulk heterojunction solar cell made of organic polymers as electron donor material.

Another substructure known to lead to good properties as organic semiconducting material is thiophene. The thienyl-system is in many aspects equivalent to a benzene moiety but has an even higher “aromatic” character. Additionally due to the presence of the sulfur heteroatom it undergoes easier oxidation reactions. For this reason we became interested in aniline-analog polymers based on thiophene systems. The natural precursors in this case are 2- and 3-aminothiophenes. Unlike aniline in an amino substituted thienyl system all carbons are different leading to a larger amount of possible isomers formed in the polymerization reaction that is formally an additional substitution.

3.1 Photoelectrical parameters important for the yield of an organic photovoltaic devices

In **Figure 7** a classical J/V-diagram is shown. The characteristics of an OPVD depend mainly on four factors:

- V_{OC} or open circuit voltage
- J_{SC} or short circuit current density
- ff or form factor/fill factor
- η or photovoltaic yield

Here we explain briefly the meaning of these concepts and how they are related to the photoelectrical behavior of the solar cell.

3.1.1 The open circuit voltage V_{OC}

The open circuit voltage is the electrical potential between anode and cathode of an OPVD when illuminated and the circuit is left open. This means that no electrical current passes between the electrodes. Chemically the V_{OC} is related to the energetic difference between the LUMO of the acceptor and the HOMO of the

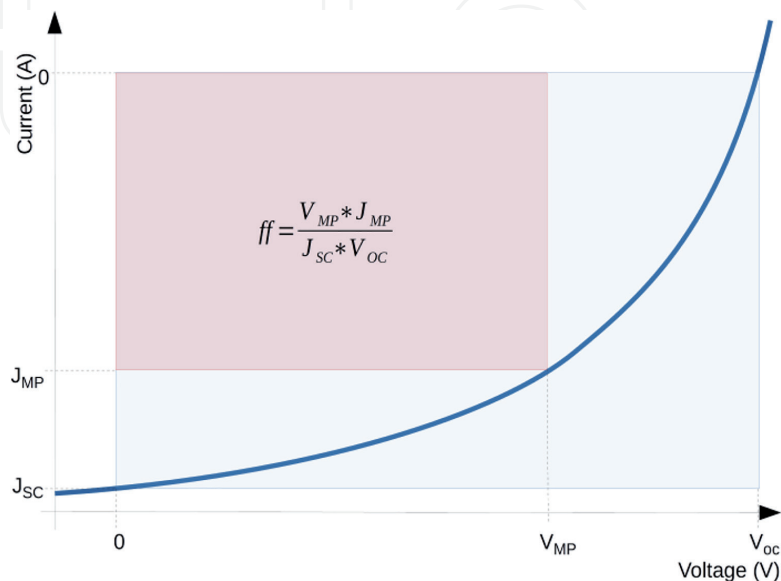


Figure 7. J/V-diagram with the graphical representation of the form factor ff as relation between the light blue and violet areas.

donor material. The larger the difference between both orbitals the higher is the voltage that can be achieved in the solar cell. In **Figure 7** you can see that V_{OC} can be determined graphically as the point where the curve passes through the x-axis of the diagram as here the current displayed on the y-axis is zero.

3.1.2 Short circuit current density J_{SC}

The short circuit current density is the photoelectrical current that can be observed when the OPVD is irradiated with light and a direct contact between both contacts forces the potential difference to be 0 V. Practically you produce a short circuit of the photoelectrical cell.

It has been demonstrated that the current density observed in these conditions is related to the interaction between the electron donor and the ABL as well as the light absorption by the donor material. In this sense a molecule with a large absorption rate over large parts of the electromagnetic spectrum contributes to increase the photoelectrical yield. Anyhow you also need a large efficiency for passing positive charges to the anode through the buffer layer. Increase in efficiency will lead directly to higher short circuit currents and as consequence to higher photoelectrical yields. As a third factor also the electrical resistance of the organic substrate is important here as resistance and electrical current in a DC device are directly related by ohms law.

3.1.3 Form factor (or fill factor) ff

The form factor of a solar cell is defined as the relation of the measured maximum electrical power that is provided by the cell and the product of J_{SC} and V_{OC} . Thus you can use the form factor as an indicator of how close the electrical behavior of the cell is to an ideal device.

In the figure you can see J_{mp} and V_{mp} as current and voltage delivered by the cell at maximum power. The product of both will give directly the maximum power that can be obtained from the device.

3.1.4 Photovoltaic yield η

$$\eta (\%) = \frac{J_{SC} [mA\,cm^{-2}] v_{OC} [V] ff}{I_0 [mW\,cm^{-2}]} \quad (1)$$

The photoelectrical yield η is defined as the relation between the maximum electrical power delivered from the photoelectrical device calculated as the product of short circuit current J_{SC} , open circuit voltage V_{OC} and form factor ff divided by the power it receives in form of light energy I_0 by the formula:

As one can see from an electrical point of view J_{SC} , V_{OC} and I_0 have to be optimized together in order to obtain high yields. As we have seen before they are related to the chemical nature of the substrates that are used to build up the cell. This explains why until now improvements of the cell yields always implied the design of optimized molecules. The improvement has to imply the donor and acceptor molecules as well as the material employed in the ABL as only an optimized hole extraction work will lead to a high short circuit current. Thus an intelligent cell design will take into account that:

- The electron donor interacts with the anode in that way that allows to extract the highest possible percentage of positive charges possible.

- The donor material has a high absorption coefficient in the part of the spectrum important for electrical energy generation (near IR to UV).
- The interaction between donor and acceptor is as large as possible and an EBL has to be applied to avoid the recombination of holes with the already separated charges (dark current).

On a molecular level these needed photophysical and electrochemical properties can be achieved designing molecules with a high degree of order and preferably π -stacking interactions that bear functional groups able to optimize the interaction with the anode material and herewith the energy transference. The functional group design has to take into account the affinities that exist towards the elements involved in the ABLs. When copper is used in ABL—construction good candidates will be thio- and nitrogen(-III) containing groups as copper is known for his high affinity towards this kind of moieties. For molybdenum-(VI) also oxygen groups could be important as the small size of the element in this oxidation state fits well to the small orbitals of oxygen.

3.2 Conducting polymers in solar cells

There is a large number of monomers that lead to a variety of conducting polymers. Modifications can lead to an even increased amount of derivatives that could be employed in solar cells. Some of them have been used in our investigation group as derivatives of aniline, pyrrole, thiophene or furane.

3.2.1 Polypyrroles

Polypyrroles (**Figure 8**) can be obtained via electrochemical deposition using cyclovoltic techniques [29]. During the synthesis different solvents could be employed as THF, acetonitrile chloroform, etc. The solvent is important for the morphology of the deposited polymer. Using acetonitrile a product is obtained than from chloroform. The solvent is therefore selected according to the needs of the desired application and in function of the employed oxidating agent.

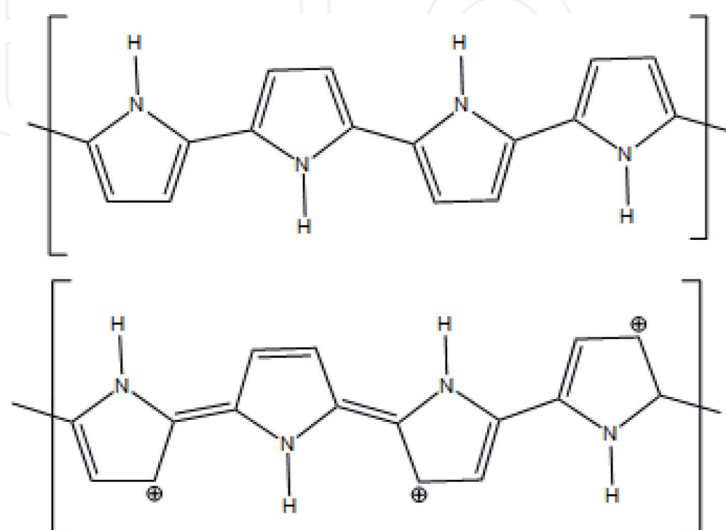


Figure 8. Polypyrrole in the ideal reduced form (above) is normally obtained as partially oxidized (p-doped) form (below). Charges are compensated by anions trapped in the polymeric material.

This way and controlling current and cycle number the layer thickness can be determined. Anyhow the polymer obtained this way has some disadvantages that limit its use in photovoltaic devices. First of all doping is only reversible in very thin layers. This limits the available charges as well as the mechanical stability of the polymer film. Second polypyrroles have shown to be very sensitive to excessive oxidation as it leads to chain degradation especially by reactions through positions 3 and 4 of the pyrrole system [30]. Blocking these positions with substituents or forming copolymers with aniline this type of degradation can be prevented leading to electrochemical more stable polymers.

These substituents according to their electron donor or acceptor characteristics will also alter the color of the polymer as they influence the HOMO and LUMO energy levels. There is also an influence due to steric hinderence as this will force the rings to present torsion angles and interrupt the perconjugated π -system. Less conjugation on the other hand will lead to decreased electron mobility and increased electrical resistance. So these effects have to be taken into account when designing a polymer more resistant to oxidative degradation.

3.2.2 Polythiophenes

Polythiophenes (**Figure 9**) are among the best studied and most promising conducting polymers [31]. Similar to polypyrroles polythiophenes can be obtained by electropolymerization from acetonitrile solutions at potentials between 0 and +1 V. The polymerization process starts with the generation of a cation radical. Due to the high reactivity of this species anhydrous conditions are crucial. The larger attention received by polythiophenes compared to polypyrroles is due to its higher chemical stability. Additionally it can be more easily processed and it is easy to obtain derivatives of the monomer. This allows tuning optical and mechanical properties of the polymeric materials and converts thiophenes in one of the most valuable starting materials for tailor made organic semiconductors.

The influences of the substituents on the properties of the polymer chain depend largely on their positions in the chain. For example, the reduced form of poly-3-methyl-thiophene shows a large variety of colors as small changes in conjugation will lead to large effects on optical- and redox properties and morphologies.

Introducing an electron withdrawing group instead of the methyl moiety will help to stabilize the radical anion when n-doping the polymer material.

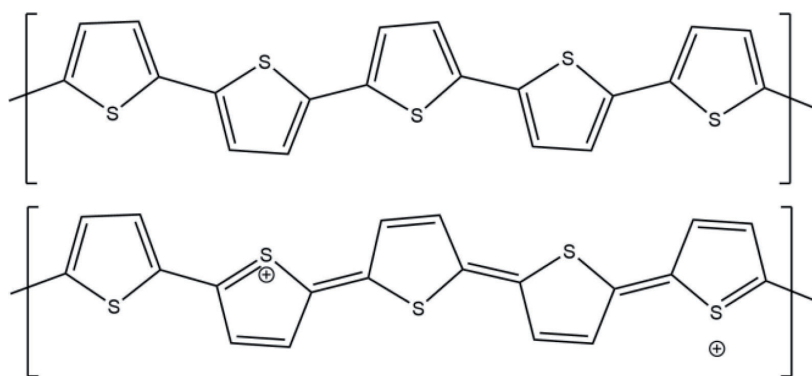


Figure 9. Polythiophene in the “normal” reduced form (above) and in the partially oxidized p-doped form presenting two charges in form of a bipolaron (below).

With copolymers obtained from nitrothiophenes and linked to carbon nanotubes yields of about 2% have been obtained [32]. They have an open circuit potential superior to polythiophenes without nitro group [33]. Other devices from polythiophenes with electron attracting groups equally have shown yields of up to 3% with an open circuit voltage of close to 1 V [34]. This shows that the groups help to stabilize the electron in the LUMO and the band match with the electron acceptor entity increases the yield [35].

Alkoxy groups as donor substituents will increase the electron density in the polymer chain and help to decrease the HOMO-LUMO-band gap leading to a red shift of the corresponding absorption band in the UV-Vis spectrum. Variations in the length of the alkyl chains however have little or no influence on the properties and no changes in conjugation or band gap values have taken place. When formed the alkoxy modified polymers are colorless and do not show absorption in the visible spectrum but turn dark blue on electrochemical reduction.

As an example 3,4-ethylenedioxi thiophene (see **Figure 10**) and its polymers have a low oxidation potential, high chemical stability even at elevated temperatures and high conductivity. The copolymer with polystyrenesulfonate is one of the best organic candidates to substitute ITO as electrode material as it is at the same time highly transparent and has a very high ductility. It is already used as antistatic coating [36].

3.2.3 Polyanilines

Like polythiophenes, polyanilines (PANI) can be obtained by electrochemical oxydation via cationic radicals in a complex oxidation and reduction process as it goes along with protonation and deprotonation reactions. In acid media a typical voltamperogram of PANI shows two redox processes that correspond to the conversion of two oxidation stages present in this polymer that go along with electrochromatism. The completely reduced form is colorless and therefore known as leucoemeraldine, from Greek “leucos” = white. In this form only phenylic systems are present that are linked by secondary amino groups.

A partially oxidized form, known as emeraldine due to its green color, is formed by alternating quinoid and phenylic structures with one quinoid structure every four ring systems. The end product of oxidation known as pernigranile, presents only quinoid structures and can be distinguished by its dark blue to black color (see **Figure 11**).

Chemically all polyanilines are basic due to the presence of trivalent nitrogen. Hydrogen of secondary amino groups can also become slightly acidic, especially when the polymer is p-doped and thus positive charges are introduced to the chain.

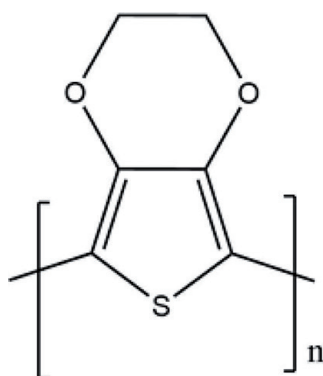


Figure 10.
Motive of poly-3,4-ethylenedioxi thiophene.

Deprotonation will reduce charge density in the polymer and limits its conductivity. Otherwise it is of the same magnitude as that of other polymeric aromatic systems.

3.2.4 Aniline copolymers

In previous works we have synthesized aniline-thiophene and aniline-pyrrole copolymers to improve conductivity, conductivity and optical properties. The obtained materials show—as expected—optical and electrical properties in between the pure polymers obtained from aniline and thiophene respectively. Anyhow solubility in all cases is higher for the copolymers than for the simple separated substrates.

In the UV-Vis spectrum of the aniline-thiophene-copolymer various absorption maxima could be observed: benzenic π - π^* transitions at around 350 nm; π - π^* transitions of the thiophene systems at 450 nm and quinoid transitions at about 700 nm. Additionally in the 650–800 nm range n - π^* transitions could be detected that correspond to the transitions of non-bonding sp^2 nitrogen electrons present on quinoid ring systems [37].

When photovoltaic devices were built from this copolymer the ABL material did not have any influence on the light absorption of the polymer neither in presence of MO_3 nor CuI with no change in absorption rates and position of the peaks in the UV-Vis spectra. As consequence the band gap also remains unaltered. On the other hand the copolymer had a higher red shift than any of the pure substrates. This means that conjugation rate had increased and the band gap diminished when compared to polyaniline and polythiophene. Herewith the copolymer is a better candidate for photovoltaic devices. Effectively unlike polyaniline it shows photovoltaic yield as electron donor when used with MO_3 , CuI or mixtures of both as ABL layers with a modest yield of 0.2–0.5%. A possible explication could be the interaction of the polymer with the copper metal centers that only leads to crystallinity close to the

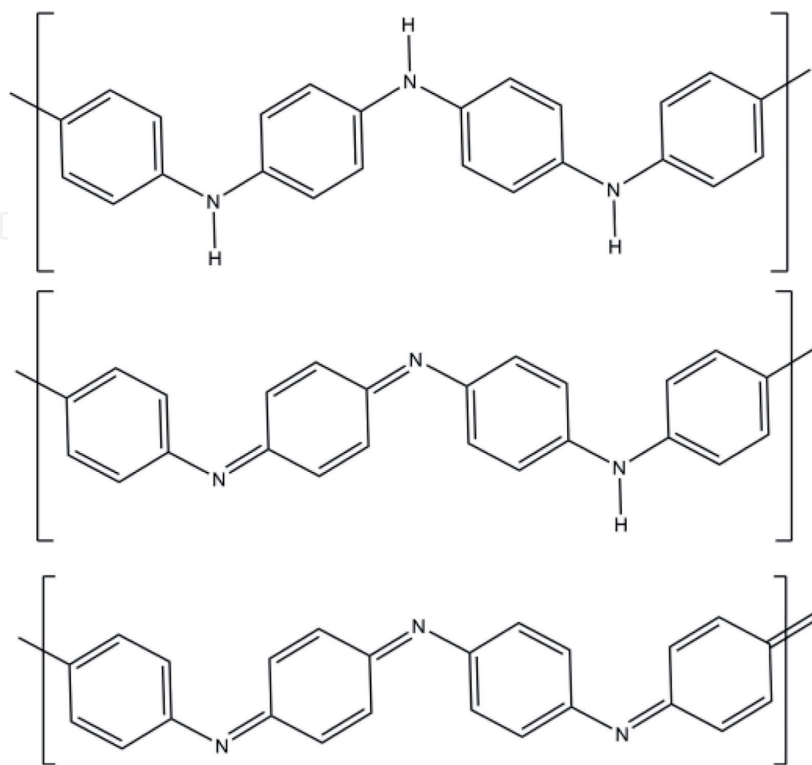


Figure 11. Polyaniline in the completely reduced (leuco) form (above), the partially oxidized (emeraldine) form and the completely oxidized (pernigraniline) form (below).

polymer-buffer layer interface while the rest of the polymer has low crystallinity. The polymer has also only a modest conductivity and a medium light absorption coefficient at about 700 nm. Thus the few polarons generated by light absorption have little mobility and most of them recombine before reaching the next layer [18, 38].

Bernède et al. have shown that MO_3 helps to increase extraction work achieving a match for the band gap between ABL and polymer. When poly-aniline-pyrrole is deposited over MO_3/CuI as ABL a small red-shift of the absorption maxima in the UV-Vis spectrum is observed compared to other ABL substrates. As in other cases the red-shift in absorption corresponds to a smaller band gap in the electronic characteristics. The photovoltaic behavior is similar to that of aniline-thiophene copolymer on any MO_3/CuI combination as ABL substrate.

3.2.5 Non polymeric organic and organometallic substrates

As already mentioned the use of different tampon layers changes the photovoltaic yield and in the right combination it helps to improve it. The effect has been studied by us and Bernède et al. not only with polymers but also with monomeric species. Copper-phthalocyanines behave similar to polymers when deposited on different buffer layers.

To find out if these or other molecules could be used in organic photovoltaic devices their electrochemical properties play a crucial role and herewith the energy of the frontier orbitals. When these molecules are deposited on an electrode by cyclovoltametry the potentials of oxidation and reduction starts can be determined. These values are related to the energies of the frontier orbitals as in oxidation an electron is withdrawn from the HOMO while during reduction an electron is deposited in the LUMO. Orbital energies are proportional to the corresponding redox potentials. Due to the experimental ease these values can be obtained the technique is used by an increasing number of workgroups.

3.3 Functional groups modifying electron density

3.3.1 Electron withdrawing groups

Electron withdrawing groups lower the energy of the antibonding LUMOs and herewith stabilize charges present in this orbital. For this reason they are used often in the design of material for electron accepting layers. They can also help to improve the electron transition between accepting and donating molecules. This is not only due to the stabilization effect on the LUMO but they also increase the interaction between both molecules. In some cases they can directly bind acceptor and donor units. The most commonly used electron attracting groups are carboxylic acids and their derivatives.

Lately investigations turned to other functional moieties as sulfonates, salicylates pyridine, catechol, etc. that help to fix both parts together [39–41] even so their electron attraction capacity is only moderate. All of these groups have proven useful in the development of devices with higher overall yield. Another new target group is the nitro moiety. It does not only withdraw more electron density, shifts the absorption maximum of the modified substrates to farther red but also has higher stability than the carboxy-derivatives. Its anchoring abilities could be attributed to the formation of π -complexes as these interactions are well known for electron rich aromatic systems and others bearing nitro groups. All these effects even increase when several nitro groups are present. As mentioned earlier this is caused by the fact that the nitro group helps to link to the electron donor and it increases the band gap and with it the open circuit voltage [42, 43].

3.3.2 Electron donating groups

While electron withdrawing groups stabilize electrons in the LUMO or the corresponding conduction band electron donor groups have the opposite effect and achieve a relative stabilization of holes in the HOMO increasing the energy of this orbital. The observed increase is even higher on the LUMO and as a consequence the gap between conduction and valence band becomes larger. When charges are present in both bands the larger energy difference leads electrically to a higher measurable open circuit cell voltage.

Donor groups also diminish the translation energy for holes making positive charge transport more effective. Unfortunately at the same time electron transport is hindered and slows down. For this reason one has to take care to equilibrate the number of electron donor and electron withdrawing groups to guarantee that both speeds are comparable and holes and electrons reach their respective electrodes at about the same time [44–46].

3.4 Buffer layers

Buffer layers also known as interface layers are crucial in organic photovoltaic devices to improve the overall yield. The correct selection and deposition of the materials that form this layer are therefore important decisions that could decide if a new approach has success or not. Changing the construction of the buffer layers up to 10-fold increase in the overall electrical yield has been observed in an extreme case [47] due to rise of the open circuit potential, the short circuit current and the form factor.

Many materials that could be used in buffer layers are permeable as well for electrons as for holes. This lowers the yield as it leads to electron-hole recombination on the electrodes. MoO₃/CuI-layers however let pass selectively positive charges and improve their pass to the anode. As during this step they are separated from the electrons this prevents recombination and herewith keeps the yield high.

The buffer layer material has also influence on the morphology of the material deposited in the next layer. In chemistry the affinity between copper and nitrogen, sulfur or other heteroatoms with free electron pairs is well known. When these elements are present in the substrate used in the next layer the intermolecular interactions will force the molecules in a defined shape and herewith provoke a determined morphology. Generally it increases the degree of order and crystallinity at least close to the interphase. This helps to increase the charge transport to the anode [47–49]. The effect of incorporation of other elements with modified affinities has still to be studied.

4. Conclusions

Photovoltaic devices nowadays represent a fast growing multi-million dollar market that has the potential to provide energy to humanity without contributing to CO₂ emissions. The largest part of it belongs to classical cells based on silicon as inorganic semiconductor. These devices however require a large amount of prime matter that are themselves highly energy consuming in their fabrication. Additionally they are not flexible, a fact that reduces the possible application fields.

A solution can be organic photovoltaic solar cells based on conducting polymers. These devices can be built as thin multi-layer constructions on flexible substrates as plastics or thin glass plates consuming just a little portion of the resources used for silicon devices. Anyhow organic cells still provide much lower conversion yields than the inorganic counterparts.

Organic bulk heterojunction cells are large constructs with various stacked layer. In the stack every layer has a dedicated function and the overall yield depends on the combination and cooperation of all parts. Strategies to improve the device will have to include necessarily not only fine tuning of each of the parts but also take into account the interaction of the layers. We present some viable and proven strategies to ameliorate the properties and interactions of several of the involved materials. These strategies include co-polymerization, the selection of appropriate functional groups understanding the influence they have on the polymer and the construction and interaction of the layers in direct contact with the semiconducting polymer.

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