



JOHANNES KEPLER  
**UNIVERSITÄT LINZ**  
Netzwerk für Forschung, Lehre und Praxis



# TANDEM SOLAR CELLS

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**eingereicht von**

**Hans-Jürgen Prall**

**unter der Betreuung von**

**o. Univ. Prof. Dr. Serdar N. Sariciftci**

**Co-Betreuung:**

**Dr. Gilles Dennler**

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**Johannes Kepler Universität Linz**

**A-4040 Linz • Altenbergerstraße 69 • Internet: <http://www.jku.at> • DVR**

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## Zusammenfassung

Ziel dieser Arbeit war es zu zeigen, dass das Konzept einer „Tandem - Solarzelle“ auch mit organischen Polymeren umgesetzt werden kann.

Grundproblem hierbei sind die Lösungseigenschaften der verwendeten Materialien, die ein einfaches Übereinanderschichten von Strukturen nicht möglich machen. Durch neue Methoden bei der Auftragung von Schichten sowie Oberflächenbehandlungen konnten signifikante Steigerungen der Photospannungen erreicht werden.

Weiters wurden Tandem - Solarzellen aus einerseits lösungsprozessierten und andererseits aufgedampften Einzelzellen hergestellt. Hierbei kam es zur Addition der Spannungen der beiden Zellen, Einbusen im Photostrom konnten aber nicht verhindert werden.

Messungen wie zum Beispiel die Charakterisierungen der Strom – Spannungskurven der Zellen bei bestimmten Wellenlängen unterstreichen die theoretischen Grundlagen und zeigen, dass eine Optimierung der Parameter zu einer Effizienzsteigerung führen kann.

## Abstract

This work aims to show that the concept of stacked solar cells can be achieved with spin-cast organic polymers, paving the route to conjugated polymer based tandem solar cells.

The main problem thereby is the solving properties of the used materials, which tend to hamper the stacking of several layers onto each other. Using new methods of layer casting as well as surface treatments, significant increases in the overall photovoltage of the devices could be achieved.

Further, real tandem solar cells consisting of solvent processed and evaporated single cells have been produced. An addition of the voltages of both cells was observable, yet losses in the photocurrent could not be prevented. Spectroscopic current – voltage curves at certain wavelengths are shown to follow the theoretical basics of tandem cells and indicate the possibility of optimizing parameters to improve efficiency.

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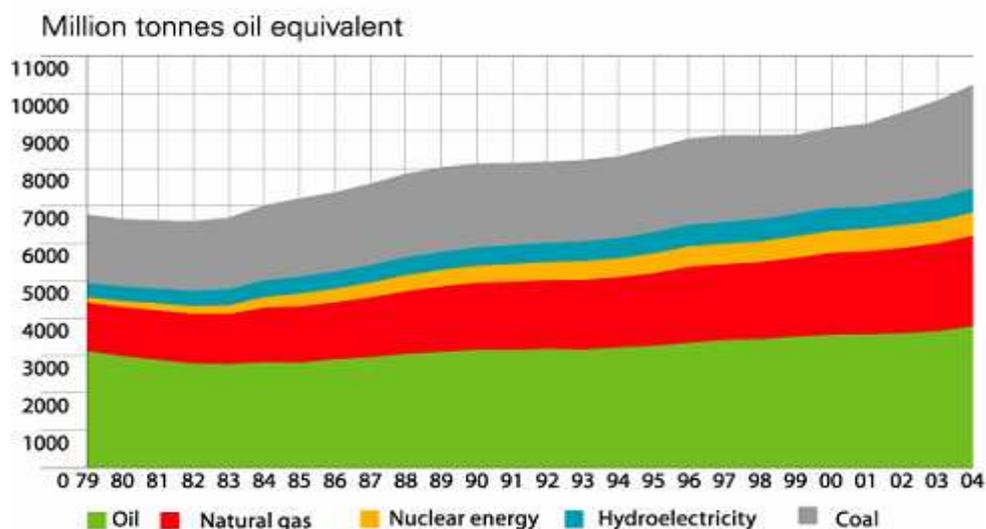
# 1 Introduction

Supply of energy is one of the main concerns of our society. Because of growing economy and modern lifestyle, consumption of energy rises drastically.

The world's fossil energy resources are still ample for the next coming years – yet, the extraction costs for this kind of energy is still under debate.

The current oil prize instability reveals the vulnerability of our economy towards higher energy prizes, not mentioning the political and economical unrest predominant in several main oil producing countries. Because our Western world highly depends on those supplies, there is a risk of slipping into an energy crisis someday soon.

Figure 1 shows the worldwide primary energy consumption from 1979 to 2004, registering the strongest growth in history.



**Figure 1** Global primary energy consumption recorded the strongest incremental growth ever, rising by 4.3 %. Growth was above the 10 - year average in all regions and for all fuels.<sup>1</sup>

Another major reason for the necessity of a change towards regenerative energy sources is found in the global warming caused by air pollution on account of the carbon dioxide emission using fossil fuels.

One alternative would be to substitute fossil energy by nuclear power, but the disposal of the radioactive nuclear waste is a problematic, unsolved issue until now.

Therefore, the development of alternative energy sources does trigger tremendous research activities these days.

One of the most viable ways to solve the foreseeable world's energy crisis is to utilize the power of the sun. The direct conversion of sunlight into electricity by photovoltaic cells has been examined and developed for several decades - Figure 2 shows the expansion trend of the photovoltaic industry over the last 15 years. One can note that the PV module production grows over 30 % annually, reaching a volume of almost 1200 MWp in 2004.

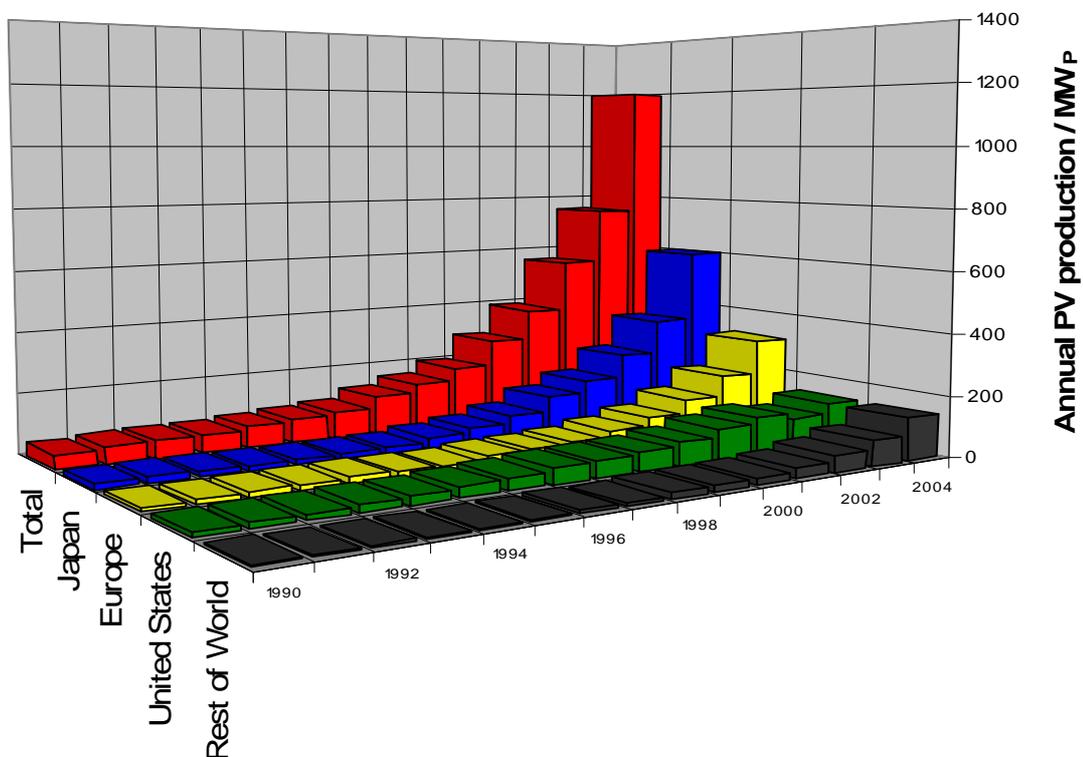


Figure 2 World photovoltaic cell/module production from 1990 to 2004 (data from <sup>2</sup>).

However, the material and production costs of the existing inorganic semiconductor-based technology are still too high for a widespread substitution of fossil energy by economic energy production. Therefore, a widespread attention is currently focused on new types of materials for photovoltaic devices. Among them, organic semiconductors are seriously considered as potential candidates for the next generation of solar cells.

Conjugated polymers and so-called 'small molecules' are highly absorbing semiconducting dyes, that can potentially be used for energy generation. However, conjugated polymers do possess a tremendous advantage compared to their counterpart: they can be soluble in organic solvents, hence deposited by cost effective solution processing like printing techniques.

Moreover, the softness of conjugated polymers allows their processing on flexible light weight substrates. This offers a considerable freedom for the production and design of solar cells.

Although the efficiency of such photovoltaic cells could not stand yet the comparison with the ones obtained with inorganic semiconductors, the cost factor should be kept in mind: organic solar cells could potentially be produced in a much more cost effective way. The price for the material is quite low, and as mentioned above, the production steps are very simple and considerably cheaper than for inorganic materials, where the steps of purifying and production are extremely energy and cost intensive.

Nowadays, about 90 % of the worldwide solar cell production is based on silicon. However, the market for photovoltaic applications being one of the fastest growing at present time, organic solar cells may have a considerable impact on the market in a couple of years. In order to reach this goal, scientific teams in companies and academia are investigating ways to improve the transport, absorption and stability properties of the materials to further increasing the efficiencies and lifetime of the cells.<sup>3</sup>

Furthermore, the structure of the devices is examined in greater detail. Inorganic and evaporated 'small molecule' solar cells have already proven that an increase of the efficiency can be achieved by stacking single cells on top of

each other. To the best of our knowledge, no such series connected stacked cells have been reported in the case of conjugated polymer so far. The realization of such structure was the very target of this work.

## 2 Conjugated polymers

Reporting the metallic properties in polyacetylene in 1977, Heeger, MacDiarmid and Shirakawa paved the way for a new kind of material: electronically conducting polymers.

They discovered that chemical doping of conjugated polymers results in an increase of electronic conductivity by several orders of magnitude. This work was honored by the Nobel Prize in chemistry in 2000.<sup>4</sup>

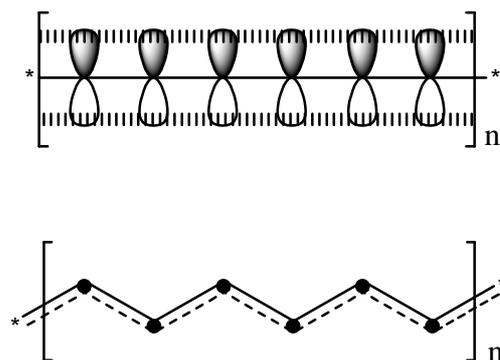
During the last 25 years, a tremendous amount of experimental and theoretical work was been devoted to analyzing the electrical, physical, structural and optical properties of these materials. Consequently, they are today used in various applications, like biosensors, light - emitting diodes, solar cells, photodiodes, transistors, etc....

Conjugated polymers consist essentially of a linear framework of alternating single and double carbon - carbon bonds. In this linear chain, the overlapping  $sp^2$  - hybridized orbitals of the carbon atoms form  $\sigma$  - bonds, and the remaining out - of - plane  $p_z$  - orbitals, each occupied by one electron, overlap with neighboring  $p_z$  orbitals to give  $\pi$  - bonds.

Although the chemical structures of these conjugated polymers propose alternating single and double bonds, the electrons that constitute the  $\pi$  - bonds are not localized but extend over several adjacent atoms due to the isomeric effect [see Figure 3 and 4].



**Figure 3** Isomeric structures of polyacetylen.



**Figure 4** Overlapping  $p_z$ - orbitals, delocalized  $\pi$  - bonds.

This delocalization is also the reason for the conducting properties of these polymers.

The overlap of two  $p_z$  - orbitals forms two molecular orbitals, a bonding  $\pi$ -orbital and an antibonding  $\pi^*$ -orbital. The lower bonding  $\pi$ -orbital is equivalent to the valence band of an inorganic semiconductor, and the higher energetic  $\pi^*$ -orbital forms the conduction band. The difference between these two energy levels is called 'band gap'. The optical and electrical properties of a material are related to this band gap.

Most organic polymers are hole conductors. This means that charge carriers are mostly empty states (holes) in the valence band. They are referred as 'p - type'.

On the other hand, materials with electrons as charge carriers in the conduction band are called 'n - type'. In organic solar cells, the doping is induced by a photoinduced electron transfer from the lowest unoccupied molecular orbital (LUMO) of a donor to the lower lying LUMO of an electron – acceptor molecule.

Usually, conjugated polymers have a band gap around 2 eV, which is rather high in comparison to commonly used inorganic semiconductors used for photovoltaic applications. This leads to a limited absorption spectrum, which does not fit the maximum of the solar emission spectrum, located between 600 and 800 nm.

## 3 Organic solar cells

### 3.1 Working principles of organic solar cells

#### *Photoexcitation, excitons, charge transfer*

There is an important difference between solar cells based on inorganic or on organic semiconductors.

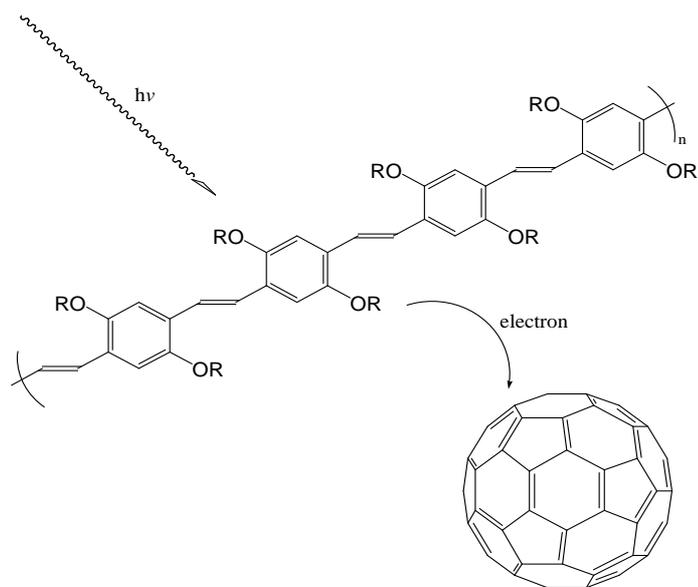
In solar cells made out of inorganic semiconductors, photons are directly converted into free charge carriers. These carriers then can be collected at their respective electrodes.

This is not the case in organic photovoltaic devices, where photoexcitation of a molecule leads to hole - electron - pairs, called 'excitons'. These excitons consist of coulombically bound charge carriers, with binding energies ranging from 0.05 to >1 eV.<sup>5</sup> They can diffuse over a length of approximately 5 - 15 nm and subsequently decay either radiatively or nonradiatively.

For photovoltaic applications, excitons have to be dissociated into free charges. One efficient way to trigger this separation is to use acceptor molecules: Upon absorption of a photon having an energy larger than the gap, an electron is promoted from the HOMO to the LUMO of the active material. If the created exciton can diffuse to another material where the LUMO is lying beneath the absorbing material's one, the electron is transferred to the accepting unit.<sup>6</sup>

In conjugated polymer based organic solar cells, the most efficient electron acceptors found so far are C<sub>60</sub> based fullerenes. C<sub>60</sub> can be described as carbon cage molecule that can accept up to 6 electrons.

Figure 5 shows the schematic picture of the photoinduced charge transfer in organic photovoltaics.



**Figure 5** Schematic illustration of a photoinduced charge transfer between polymer and C<sub>60</sub>.

### ***The 'bilayer' concept***

There are mainly two concepts of 'donor - acceptor' organic solar cells. One is the so called *bilayer heterojunction*, in which the superposition of a donor and an acceptor material on top leads to a sharp interface formation. Photogenerated excitons that are created in the donor or in the acceptor can diffuse to the interface and there, charge separation can occur.<sup>7 8</sup>

But, as mentioned above, excitons in organic solar cells have a short diffusion length, estimated to 5 – 15 nm.<sup>9</sup> This means that only excitons created within this distance from the interface between donor and acceptor can dissociate and contribute to the overall photocurrent of the cell. This leads to large losses of photons absorbed far away from the interface and thus limits the efficiency of the bilayer solar cell drastically.

Therefore, a new concept was introduced: the so called '*bulk heterojunction*'.

### ***The 'bulk heterojunction' concept***

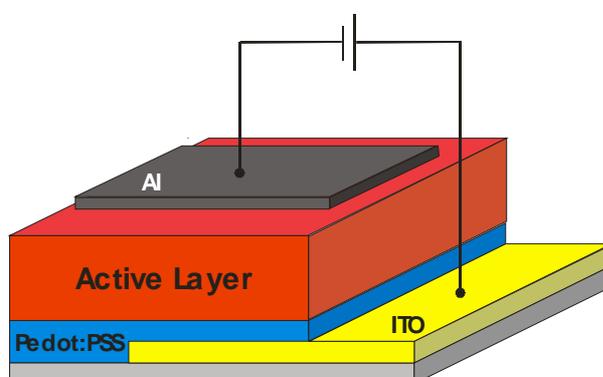
Here, the two dimensional interface of the bilayer approach was exchanged by a three dimensional interpenetration network. This can be achieved by mixing donor and acceptor materials together to form a blend and thus increasing the active surface area of the interface, so that excitons can dissociate wherever they are created within the bulk.<sup>10 11 12</sup>

### ***Charge separation***

When an exciton reaches the interface between donor and acceptor material, charge separation takes place in ultrafast timescale of about 45 femtoseconds.<sup>13</sup> Electrons are transferred to the acceptor, whereas the holes remain on the polymer. Because the separation is faster than any other competing process, its efficiency is about 100%. This can, for example, be observed in photoluminescence measurements, where excitonic photoluminescence signals of the polymer are drastically quenched by blending with an acceptor.

After the transfer reaction, the charges are transported to the electrodes. It is usually understood that this transport takes place because of the field, induced by the different work functions of the metals that are used for the electrodes.

The typical structure of a common bulk-heterojunction solar cell is shown in Figure 6.



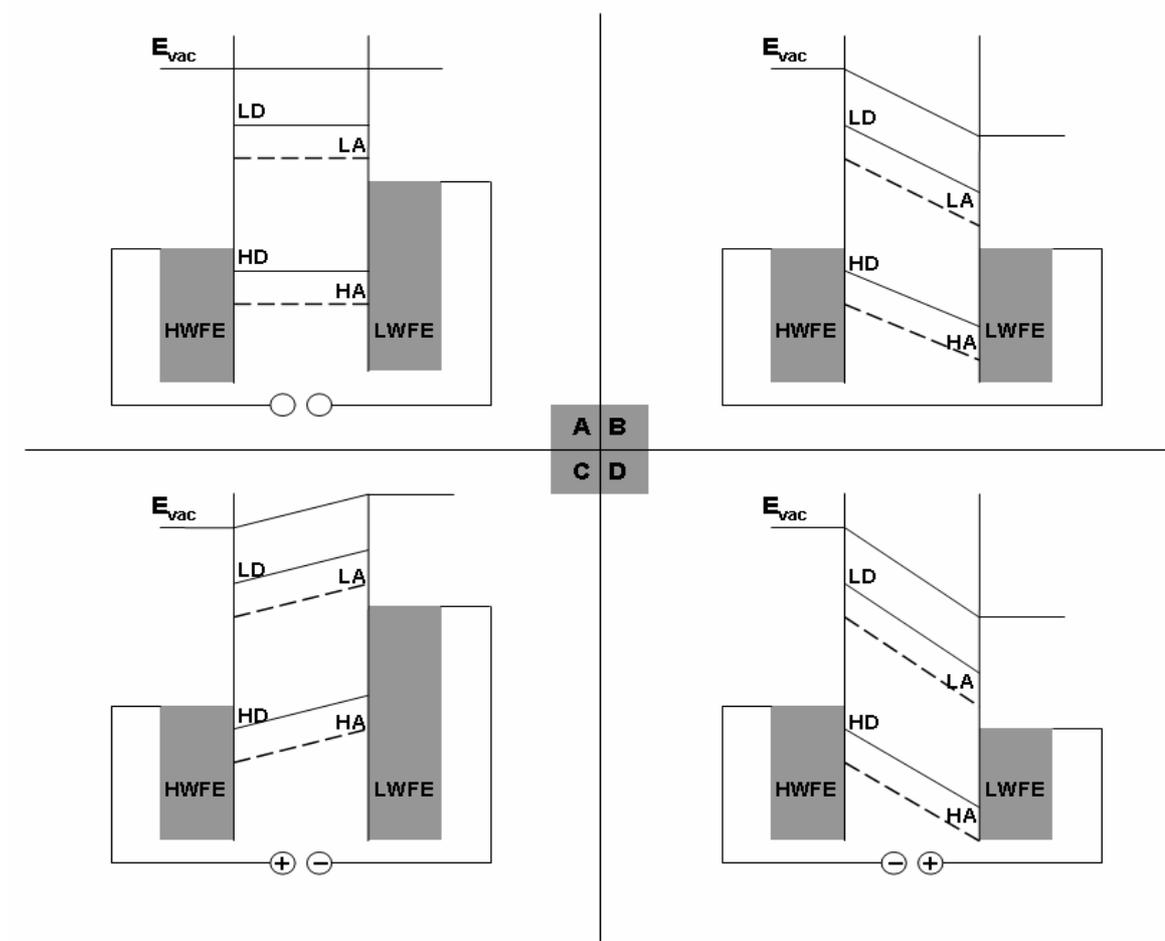
**Figure 6** Assembling of an organic solar cell (Active Layer consists of donor and acceptor molecules, either in bilayer or bulk assembling).

### 3.2 Characteristics of organic solar cells

A solar cell is described by several parameters which are described in the following sections.

#### *Operating modes*

The Metal - Insulator - Metal (MIM) picture is usually used to describe the operating modes of organic diodes.<sup>14</sup> Although this picture is a first approximation, it gives an impression of the energetic levels within the device.



**Figure 7** Metal - insulator - metal [MIM] picture of different operating modes of a donor – acceptor blend diode. [A] Open circuit condition. [B] Short circuit condition. [C] Forward bias. [D] Reverse bias.

HD / HA ...HOMO donor/ HOMO acceptor    HWFE ... high work function electrode  
 LD / LA ... LUMO donor/ LUMO acceptor    LWFE ... low work function electrode

Figure 7 shows the MIM picture of a donor – acceptor device under different working conditions:

[A] The energetic diagram of a bulk heterojunction solar cell in *open circuit condition* is represented: The vacuum levels of the different materials are aligned and no electrical field is present within the device. Since there is no driving force for charge carriers, the current within the device is zero.

[B] Sample under *short circuit condition*: The Fermi levels of the two electrodes align themselves and a built-in field appears in the bulk, resulting in a constant slope for the HOMO and LUMO levels of the donor and acceptor and for the vacuum levels. Under illumination, photo generated charges can be transported by drift to their respective electrodes - holes to the HWFE (high work function electrode) and electrons to the LWFE (low work function electrode).

[C] When the diode is polarized in the *forward direction* (HWFE is connected to the positive and the LWFE is connected to the negative contact), electrons can be injected from the LWFE to the LUMO of the acceptor and holes from the HWFE to the HOMO of the donor. The effective field in the device will ensure the drift of electrons from LWFE to HWFE and holes from HWFE to LWFE. If these charges can recombine radiatively, the device works as a LED.

[D] When the device is polarized in the *reverse direction* (HWFE connected to the negative and LWFE connected to the positive contact) charge injection is hindered by the field present in the device. Under illumination, the generated charge carriers drift under a potentially strong electric field to their respective electrodes and the diode works as a photodetector.

## Current - Voltage characteristics

Solar cells are operated between open circuit and short circuit conditions. This is in the fourth quadrant of the current - voltage characteristics, which is shown in Figure 8.

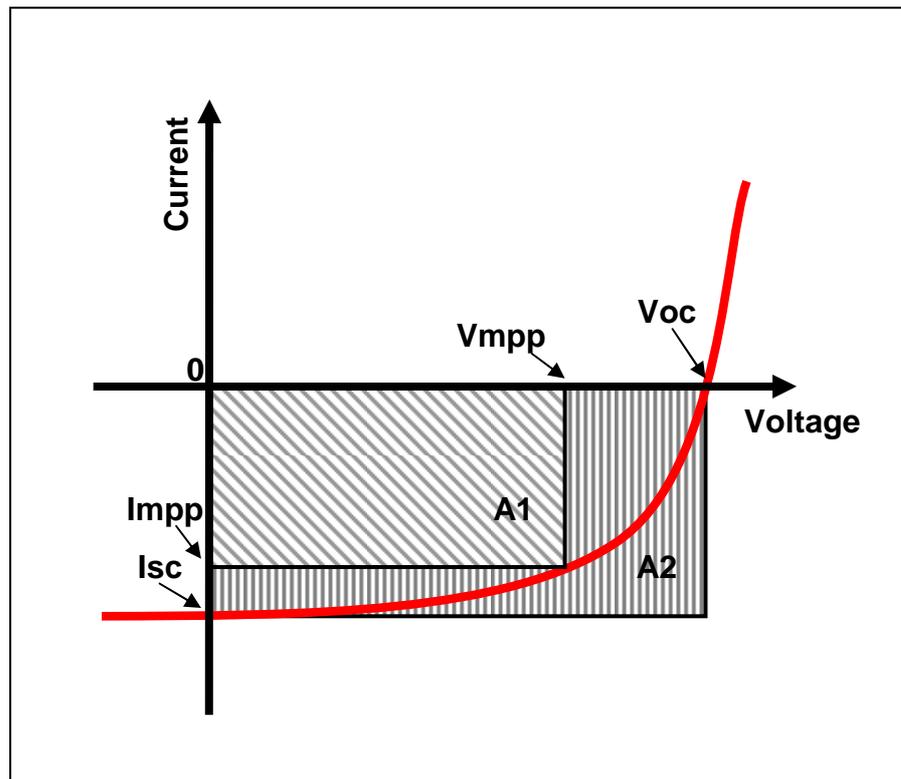


Figure 8 Important parameters for solar cells.

The current - voltage curve provides a basis for the characterization of the properties of a solar cell. Such a cell is described by several parameters:

### *Open circuit Voltage (Voc)*

Voc is the maximum possible voltage delivered by a solar cell. At this voltage the current is zero – this is similar to flat band conditions in the MIM picture. For heterojunction devices, the energy distance between HOMO of the donor and LUMO of the acceptor is believed to be the limiting factor for the Voc.<sup>15</sup>

### *Short circuit Current (Isc)*

Isc is the current that flows when there is no external field applied, and charges are just drifting because of the internal field, which is believed to be determined by the different work functions of the two electrode materials. The cell is in short circuit conditions and the Fermi-Level of the two electrodes align.

Isc yields information about transport properties of the materials and charge separation.

### *Maximum power point (mpp)*

mpp is defined as the point where the product of the current and the voltage reaches a maximum: the device has to be operated at this point.  $V_{mpp}$  and  $I_{mpp}$  are the characteristic voltage and current in this point.

Out of these parameters, the *Fill Factor (FF)* can be calculated.

The FF describes the quality of the diode behavior of the solar cell. It is the ratio between two areas, namely A1 and A2 in Figure 8.

The size of these two areas should be similar; this means the fill factor should be nearest to 1.

The fill factor is described by the following equation:

$$FF = \frac{V_{mpp} * I_{mpp}}{V_{oc} * I_{sc}}$$

The photovoltaic power conversion efficiency for a solar cell is defined as follows:

$$\eta_{AM1.5} = \frac{P_{out}}{P_{in}} = \frac{I_{sc} * V_{oc} * FF}{P_{in}}$$

Where  $P_{in}$  is the incident light and  $P_{out}$  is the electric power generated by the cell at the maximum power point (mpp). The incident light power is usually standardized to AM 1.5 spectrum.<sup>16</sup>

## Equivalent Circuit

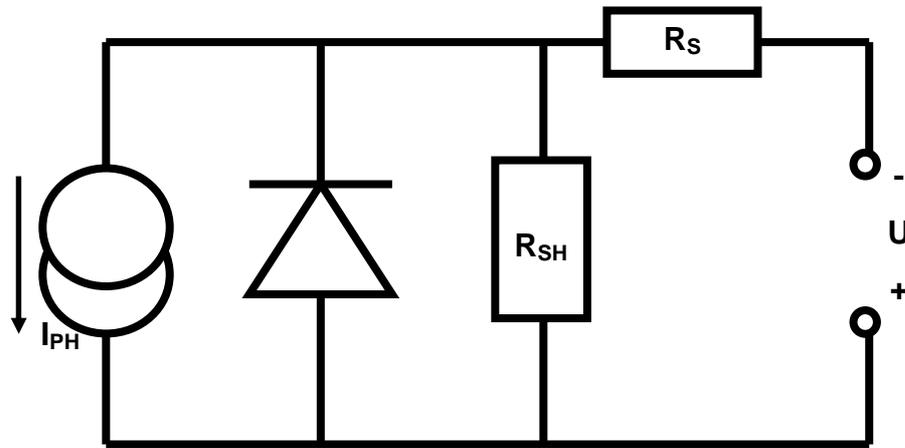


Figure 9 Equivalent circuit of a solar cell.

The equivalent circuit can be seen in Figure 9 and consists of the following:

- A current source that represents the photocurrent generated within the illuminated cell. This current flows in inverse direction compared to the forward one of the diode and depends on the voltage across the device.<sup>17</sup>
- A voltage source.
- A series resistance that include the ohmic contributions of the electrodes, the contact between the organic semiconductor and the metal, and the resistivity of the active materials. This resistance has to be minimized for maximum solar cell efficiency. Typically it decreases with decreasing thickness, increasing temperature and increasing light intensity.<sup>18</sup>
- A shunt resistance that illustrates the potential leakage current through the device. It has to be maximized to reach high efficiency cells. The shunt resistance increases with decreasing thickness, decreases drastically with increasing light intensity.

## 4 The Tandem concept

### 4.1 'Stacked cells' and 'Tandem solar cells'

Although power conversion efficiency of organic solar cells has steadily been increasing for the last couple of years, the device performance is still far from requirements.<sup>12 19 20</sup> Therefore new materials and device structures are under investigation.<sup>21</sup>

One promising attempt to improve the efficiency of organic photovoltaic devices would be to stack single heterojunction cells on top of each other to form a multilayer structure.

Using the same material for the different cells, the device is termed 'stacked cell' in contrast to a so called 'tandem solar cell'. Here, the cells are processed with different materials and therefore have different absorption spectra.

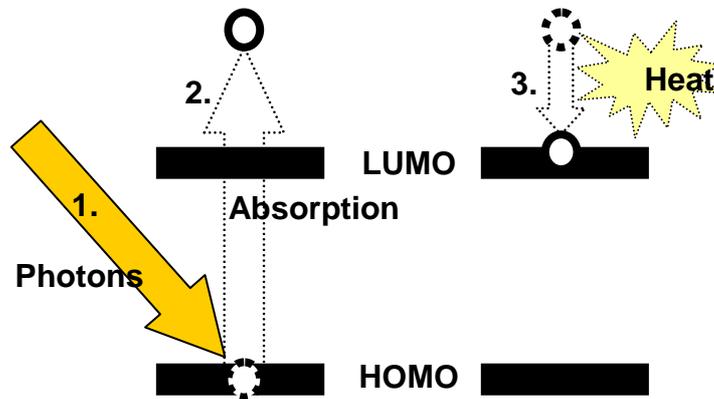
By balancing the optical absorption of each cell, it would be possible to enhance the efficiency of a 'tandem cell'.

Stacked cells have already reached the 5% efficiency benchmark when fabricated from small molecules by evaporation.<sup>22 23 24 25 26 27</sup> However, nothing was published yet about solvent processed organic semiconductor based stacked cells. One reason for that may be that most polymers have similar dissolving properties and therefore the processability is very problematic.

### 4.2 Limitation of solar cells efficiency

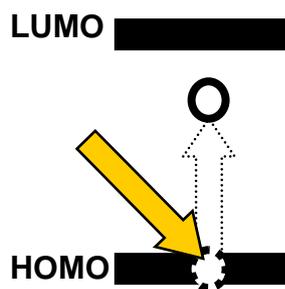
Two main reasons for the limitation of solar cell efficiency are losses by thermalisation and non-absorption of low-energy-photons.<sup>15</sup>

In the case of thermalisation, the excess energy of absorbed photons is transferred to the active material via phonons. This energy is then a pure loss for the photovoltaic conversion. Figure 10 illustrates this statement.



**Figure 10** Absorption process. Thermal energy is lost.

However, photons with energy smaller than the band gap cannot be absorbed (see Figure 11). Therefore, in single cell devices, a trade-off has to be found between thermalisation losses, and the usage of a too large band gap.

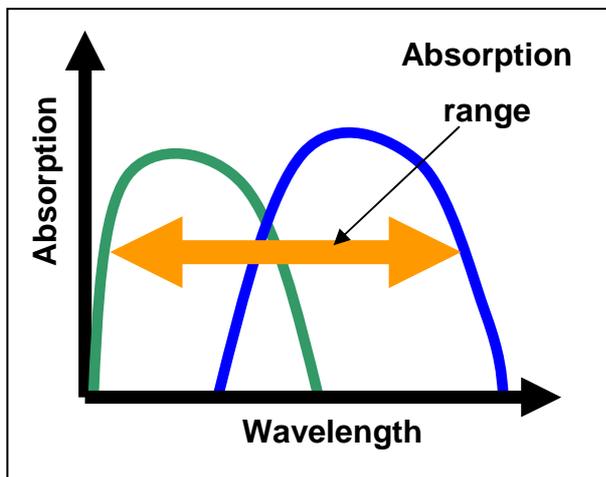


**Figure 11** Energy barrier between HOMO and LUMO is too high for photon absorption and exciton creation.

The idea of a tandem cell is to achieve better absorption efficiency by using materials having different band gap. One material should then collect the higher

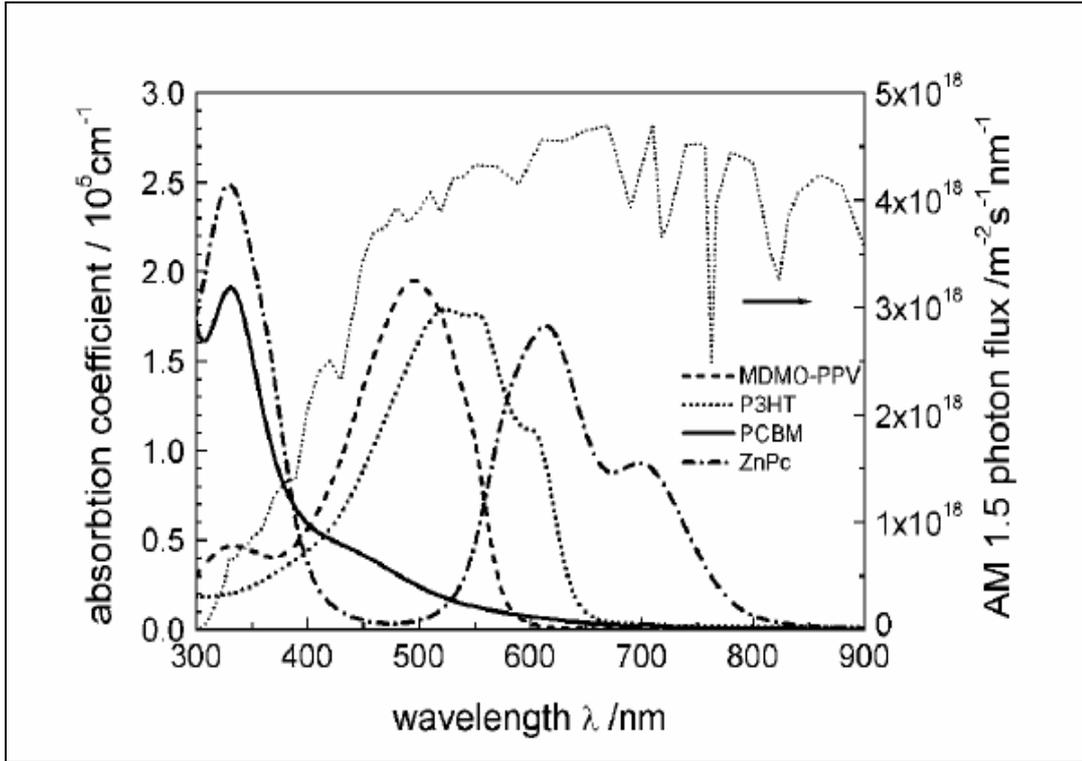
energetic photons and the other, with a lower band gap than the first one, should absorb photons with lower energy.

Figure 12 shows the ideal picture of the relation between the absorption spectra of the two materials used in an organic tandem solar cell.



**Figure 12** Absorption spectra of materials used for the tandem solar cell.

Another point is that the absorption spectrum should match the terrestrial solar spectrum as good as possible. To give an idea of the absorption properties of semiconducting polymers, the photon flux of the terrestrial solar spectrum (AM 1.5), in comparison with the absorption coefficients of several commonly used materials are shown on Figure 13.<sup>28</sup> One can directly see that MDMO-PPV, P3HT and ZnPC show complementary spectra, that could be combined to increase the photon harvesting.



**Figure 13** Absorption coefficients of MDMO-PPV, P3HT, PCBM and ZnPc and AM 1.5 photon flux.

### 4.3 State of the art

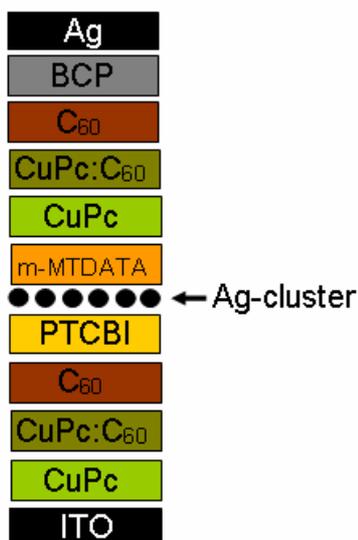
The maximum efficiency of single junction solar cells based on silicon is located in the range of 25 %. The tandem concept utilising high-quality inorganic semiconductor materials with different bandgaps already allows solar energy conversion efficiencies of far above 35 %, significantly more than theoretically possible in an ideal single layer solar cell.

Therefore, tandem solar cells are developed since over a decade and with inorganic active materials, this structure is already advanced and technologically implemented (e.g. satellite power supply).

Recently, connected stacked cells made of evaporated small molecules reached remarkable results. All of them are based on serial connections with thin metal layers as recombination centers. In 1990, Hiramoto, Suezaki and

Yokoyama published a paper in which they claimed the doubling of the voltage of a normal cell by evaporating two small molecule cells on top of each other, connected in series by a 10 nm gold layer. The currents of these cells were very low, but doubled voltages were reached.<sup>22</sup> In 2002, Yakimov and Forrest described a drastically enhanced efficiency of evaporated cells stacked in series by using copper- phtalocyanine (CuPc) and 3,4,9,10- perylenetetracarboxylic-bis- benzimidazole (PTCBI) connected by a 0.5 nm silver layer as recombination center. The efficiency was 2.5 %.<sup>23</sup>

In 2004, Rand, Uchida, Xue and Forrest reached maximum power conversion efficiency above 5 % with asymmetric multilayer cells made of copper-phthalocyanine and C<sub>60</sub> - a milestone in organic photovoltaics.<sup>24</sup> The structure of the cell is described in Figure 14.



**Figure 14** Structure of serial connected stacked cell based on small molecules.

Leo, Pfeiffer, Kozlowski, Männig, Drechsel and Hoppe used wide-gap transport layers for improving the charge recombination and claimed 3.8 % efficiency.<sup>27</sup>

No solution processed tandem solar cells can be found in literature yet – this may be due to severe technological difficulties.

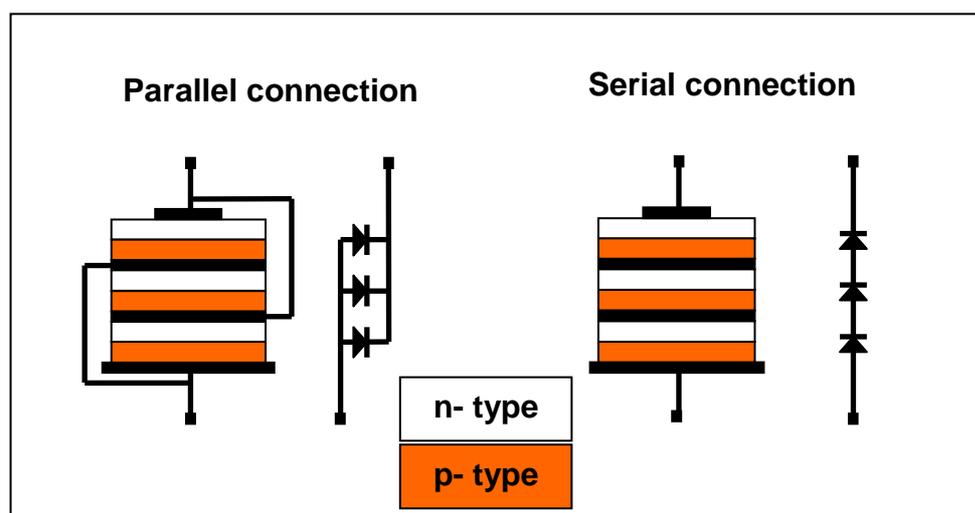
For this reason, it was decided to make investigations on the problems of solvent processed organic tandem solar cells.

## 5 The building of an organic tandem solar cell

In tandem cells, two (or more) heterojunction solar cells are deposited on top of each other. Two methods are available to stack these cells: parallel or serial connections.

For parallel connections [see Figure 15, left side], intermediate electrodes ensure the charge collection for each cell. These electrodes have to be transparent to minimize photon losses and highly conducting to maximize charge carriers collection. An obvious material for such electrode would be indium tin oxide [ITO]. However, ITO is usually deposited via reactive sputtering which might severely damage the conjugated polymer. Therefore, such parallel connections are not easily achievable in the case of organic semiconductor solar cells.

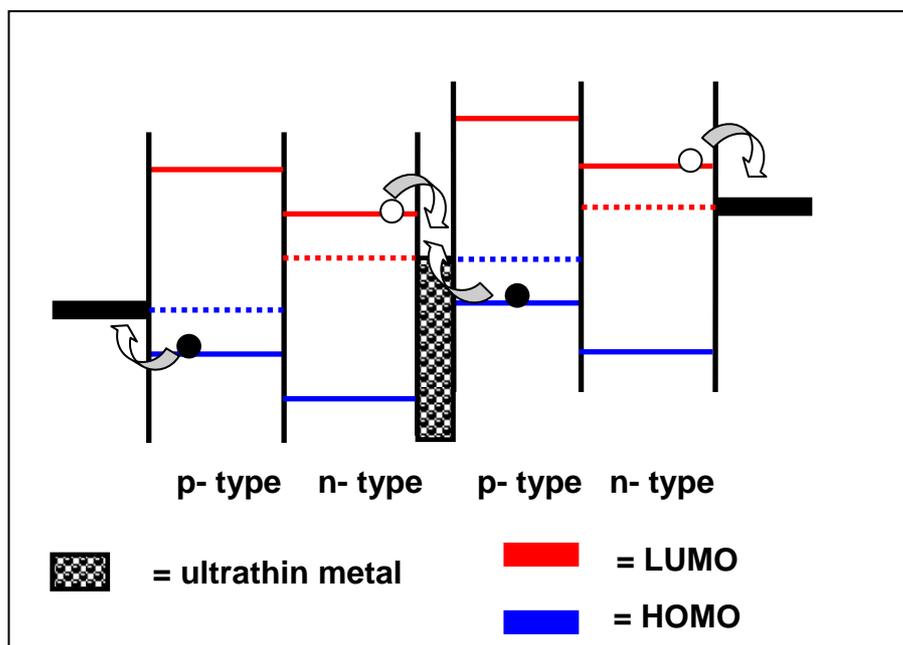
Serial connection is much likely to be realizable [see Figure 15, right side], since it does just require thin, non-continuous, non-absorbing metallic layers to separate the different cells and act as recombination layer.<sup>23</sup>



**Figure 15** Stacked solar cells with different connection types.

The electrical contact layers, formed by ultrathin metallic nanoclusters, simply act as recombination centers, allowing holes from the HOMO of the back cell to recombine with electrons from the LUMO of the front cell.

Upon light absorption, excitons are formed in both photovoltaic cells. After their dissociation at the donor - acceptor interface of each single bilayer cell, charges are transported to the electrodes. Holes from the first cell and electrons from the second cell are collected at the adjacent electrodes, as the opposite charges drift to the intermediate layer. This intermediate layer prevents the formation of an inverse heterojunction, as electrons that approach from the front- , and holes from the back cell recombine there (see Figure 16). This Recombination takes place at the same Fermi energy level and prevents cell charging.<sup>23</sup>



**Figure 16** Band diagram of serial connected bilayer cells. The intermediate non - continuous metal layer aligns the Fermi energy levels of the n- type material of the front cell and the p- type material of the back cell. This structure is used for small molecule stacked cells.

When two cells are serial - connected, the same current has to flow through the entire device. This current is dictated by the lowest current of the two cells. When the same material is used for the two cells it is normally the back cell which defines this current since most of the photons are collected in the front cell. To avoid such situations, optimization of the respective cell thickness has to be performed.<sup>24</sup>

In the case of serial connection, the voltage of a tandem cell is determined by the addition of the voltages of the individual cells. On the other hand, in the case of parallel connection, the currents are summed up. Figure 17 illustrates these statements.

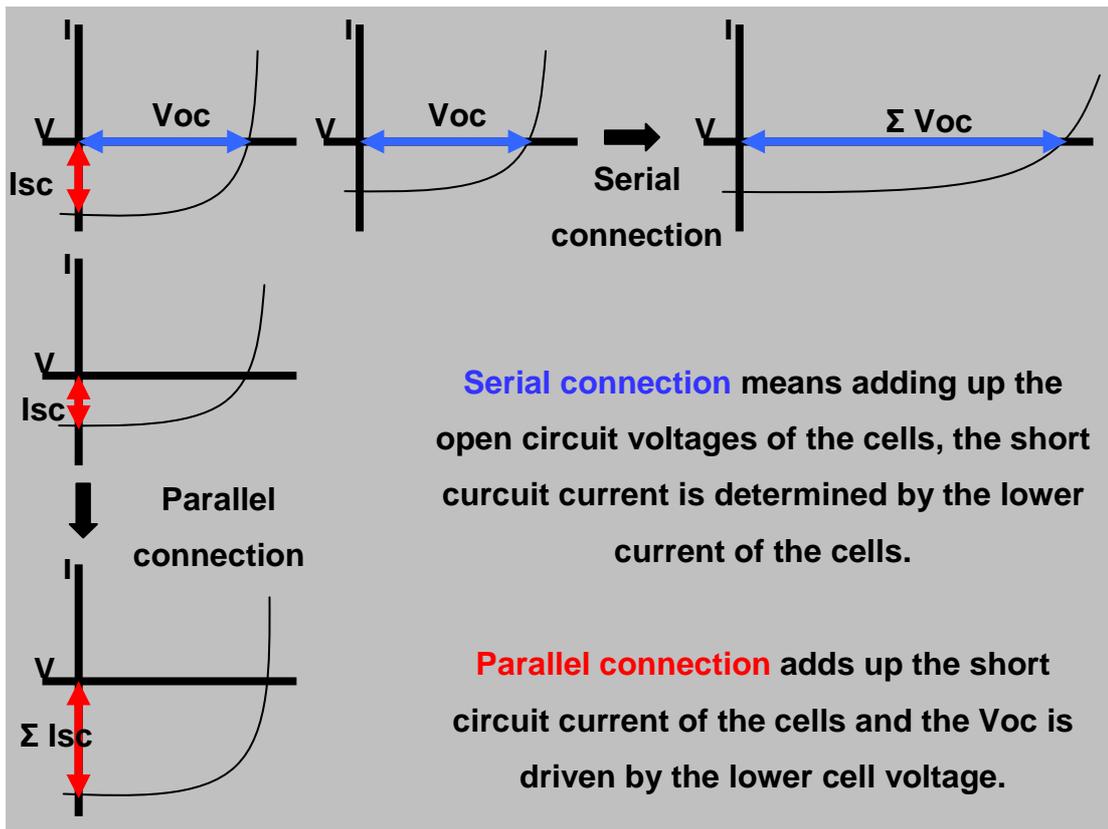


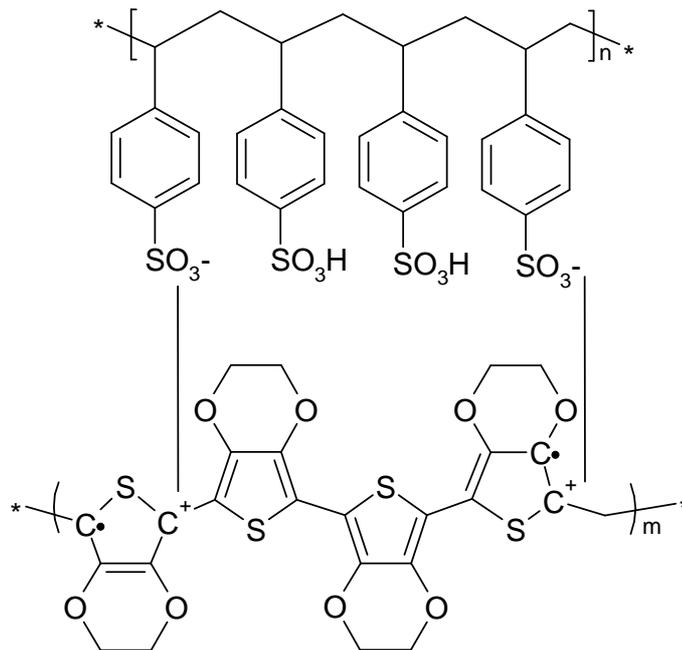
Figure 17 Current - voltage characteristics of single cells adding up for a tandem cell with serial (blue) and with parallel connection (red).

## 6 Used materials

### **PEDOT:PSS**

PEDOT:PSS, Poly(ethylene-dioxythiophene) doped with Poly(styrenesulfonate), is a stable, water soluble conjugated polymer.

It can easily be processed on substrates and films out of this material have transparencies of about 80 % and an electrical conductivity of ~10 S/cm when the spincoated layer has an average thickness of 80 nm. It is highly p- doped and is used as hole conducting and electron blocking layer. It also improves the surface and the work function of the ITO-layer. The chemical structures of PEDOT and PSS are shown in Figure 18.

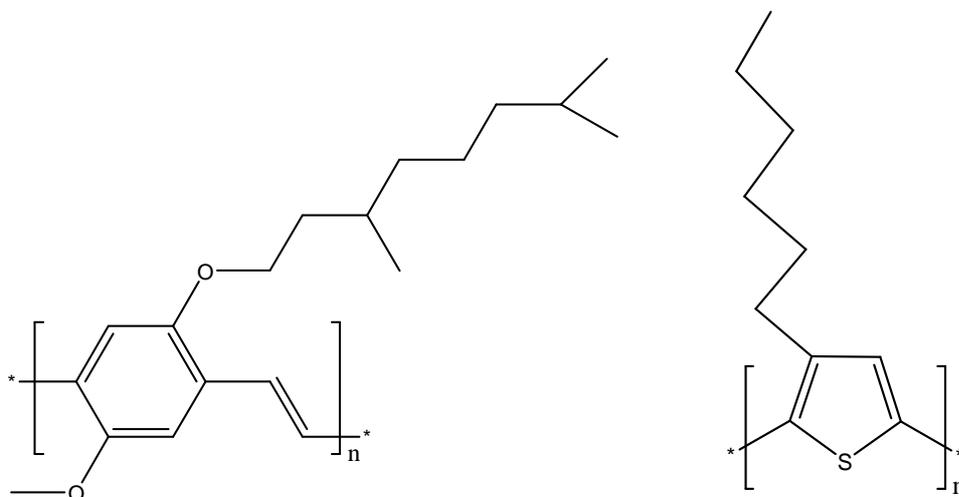


**Figure 18** Chemical structure of PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) and Poly(styrene-sulfonate)).

The material used for solar cells was an aqueous dispersion, 0.5 weigh percent, PEDOT:PSS ratio 2:3, purchased from Bayer AG Leverkusen, Germany.

### **MDMO-PPV**

MDMO-PPV, (Poly-(2-methoxy, 5-(3,7-dimethyloctyloxy)) para-phenylene-vinylene) is one of the most widely investigated polymers for solar cell purposes. It does usually act as electron - donating (p- type) material. HOMO and LUMO are located at 5.3 and 3.0 eV from the vacuum level, respectively. The material was purchased from Covion.



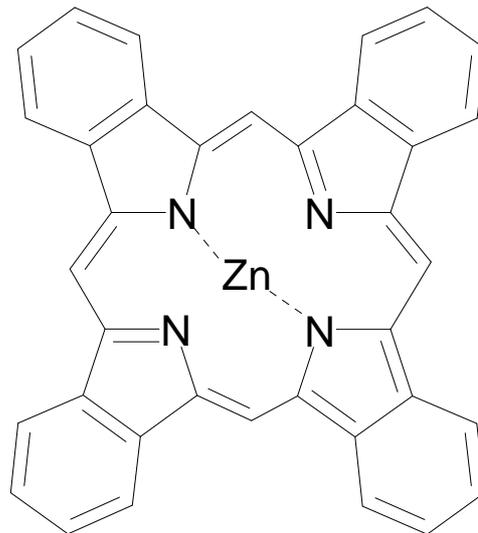
**Figure 19** Chemical structures of MDMO-PPV (left) and P3HT (right).

### **P3HT**

Poly(3-hexylthiophene) (P3HT) is also widely used as donor in organic solar cells. This material has higher hole mobility than any other known conjugated polymer until now, including Poly(phenylvinylene)s. This high mobility is related to side-chain induced self-organization. Figure 19 shows the chemical structure of this polymer. HOMO lies at 5.1 eV, LUMO at 2.9 eV. The material was purchased from Rieke.

## **ZnPc**

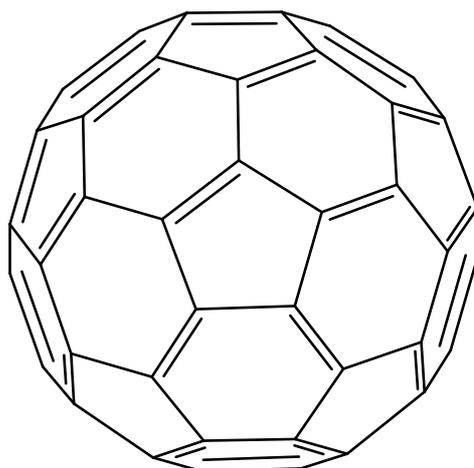
ZnPc, Zinc- Phthalocyanine, is a so called small molecule and acts as a hole conducting p- type material. For usage in organic solar cells, this dye has to be evaporated under high vacuum in an evaporation chamber.



**Figure 20** Chemical structure of Zinc- Phthalocyanine.

## **Fullerene C<sub>60</sub>**

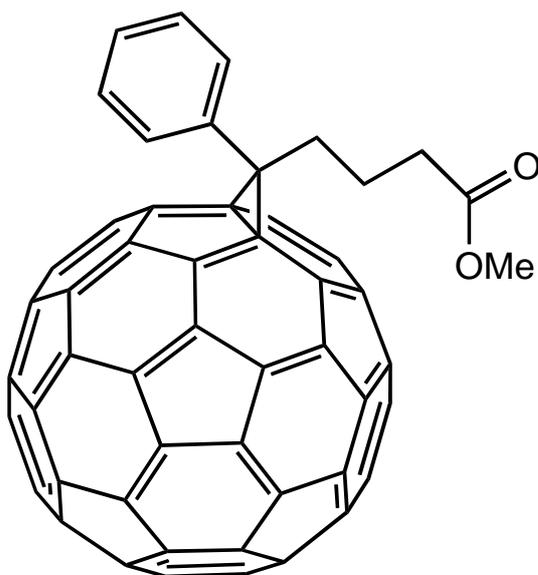
This Fullerene consists of 60 sp<sup>2</sup> - hybridized carbon atoms. Each atom is bonded to three others. 20 Hexagonal and 12 pentagonal rings form a spherical shape. C<sub>60</sub>, also called 'buckminsterfullerene' after the architect Buckminster Fuller, was first identified in 1985. Kroto, Curl, and Smalley were awarded the Nobel Prize in Chemistry in 1996 for the discovery of this class of compounds.<sup>29</sup> C<sub>60</sub> acts as electron accepting polymer, and can accept up to 6 electrons. The material was purchased from MER Corporation.



**Figure 21** Chemical structure of C<sub>60</sub>.

### ***PCBM***

PCBM is a high soluble derivate of C<sub>60</sub>, that also acts as an electron acceptor. Solubility is achieved by side chain attachment of a (1- (3- methoxycarbonyl) propyl-1 -phenyl - group.<sup>30</sup> It is soluble in chlorobenzene, toluene and similar organic solvents. The material was purchased from Nano-C.



**Figure 22** Chemical structure of PCBM.

## 7 Experimental work

### 7.1 Substrate preparation

For normal structured solar cells, indium tin oxide [ITO] coated glass was cut into pieces of 15 x 15 mm. The thickness of the ITO - layer was around 120 nm, having a sheet resistance smaller than 20 Ohm square.

One half of each substrate was covered with adhesive tape, and on the other half, a acidic mixture, consisting of 9 parts concentrated HCl, 1 part HNO<sub>3</sub> and 10 parts of water, was deposited for more than 30 minutes to remove the metallic layer. Then the tape was removed and the etched substrates were cleaned two times with acetone and two times with iso - propanole in an ultrasonic bath.

After drying, a PEDOT:PSS layer was spin-cast on the ITO in order to reduce the roughness and increase the wettability of the substrate surface. Before application, the aqueous PEDOT:PSS dispersion was stirred for 20 minutes and then filtered with a 0.45 µm filter.

### 7.2 Device characterization: Current - Voltage measurement

The solar cells were characterized under 100 mW/cm<sup>2</sup> (calibrated with a silicon diode) white light illumination from a Steuernagel solar simulator. This simulates AM 1.5 conditions with a Xenon lamp as light source. The measurements took place under argon atmosphere in a glove box.

A Keithley 2400 unit was used for the measurement of the current – voltage characteristics.

ITO and Aluminum were connected to the positive and negative terminal, respectively. The curves were acquired by continuously sweeping from -2 Volts to +2 Volts and data points in 10 or 50 mV steps were recorded.

## 8 Tandem cell preparation

### 8.1 Stacked cell out of MDMO-PPV : PCBM blend

For simplification it was decided to take the same photoactive materials for both cells, otherwise the number of parameters would be too large, making the experimental work more complex. Attention was mainly focused on the adding of the voltages of the two cells, indicating that the serial connection is working properly.

#### *Bulk heterojunction attempt*

The most obvious way to start with organic tandem solar cells is to take the well known bulk heterojunction structure<sup>10 12</sup>, evaporate a very thin metallic recombination layer, as it is known from small molecule tandem cells<sup>23 24 25 26</sup><sup>27</sup>, and spin-cast a second bulk heterojunction cell on this layer.

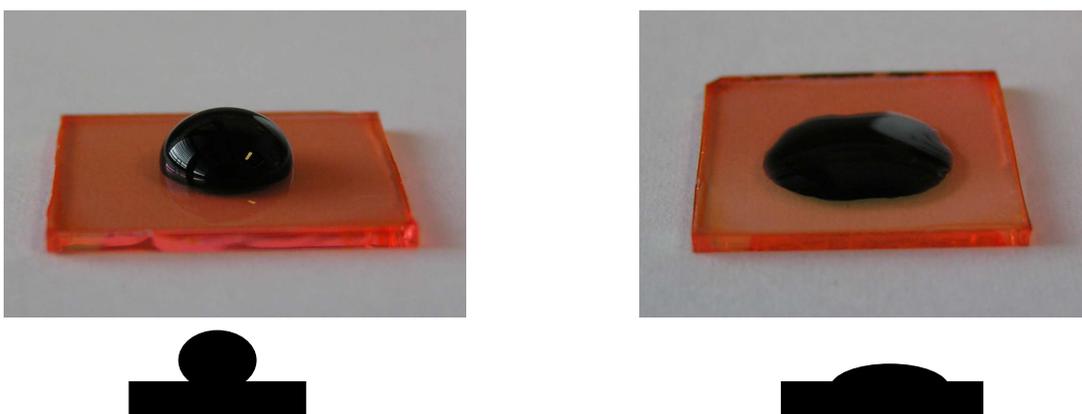
This procedure sounds quite simple, yet couples of issues have to be addressed here.

After the evaporation of the ultra-thin metal layer (1 nm), which has to be done with a very fast evaporation rate to prevent diffusion of the metal into the polymer layer, the second cell of the tandem device has to be processed. An obvious next step would be spincoating an organic layer on top of the sample. However, the metal-layer is not likely to be continuous (1 nm) and the underlayer is strongly soluble in organic solvents. Therefore spin-coating a MDMO-PPV : PCBM solution on a slightly metalized MDMO-PPV : PCBM layer has been observed to induce a dissolution of the first layer and a total removal of the metallic clusters.

It appears clearly that the deposition of a second cell requires that the first one is protected towards dissolution: This can be achieved by the usage of a thin buffer layer soluble in another solvent.

Pedot:PSS was used for this purpose. However, spin-coating Pedot:PSS on highly hydrophobic MDMO-PPV : PCBM surface requires a preliminary treatment the surface to ensure wettability and adhesion. Such a treatment was achieved by using, a highly diluted solution of Pedot:PSS in iso - propanol (1:~20). This one is prepared by dropping the Pedot:PSS solution slowly into the alcohol while heavily stirring (otherwise it agglomerates and would not be useful for processing). This solution can be spincoated and gives an extremely thin conducting layer. The spinning speed for this operation should not be too high, on order to avoid the removal of the metallic clusters by mechanical striction.

Figure 23 shows a sample before and after the surface treatment with the Pedot:PSS : iso - propanol solution. The surface tension of the sample without the treatment does not allow producing a Pedot:PSS layer whereas with this treatment, the wettability of the surface toward Pedot:PSS is increased and a layer can be deposited.

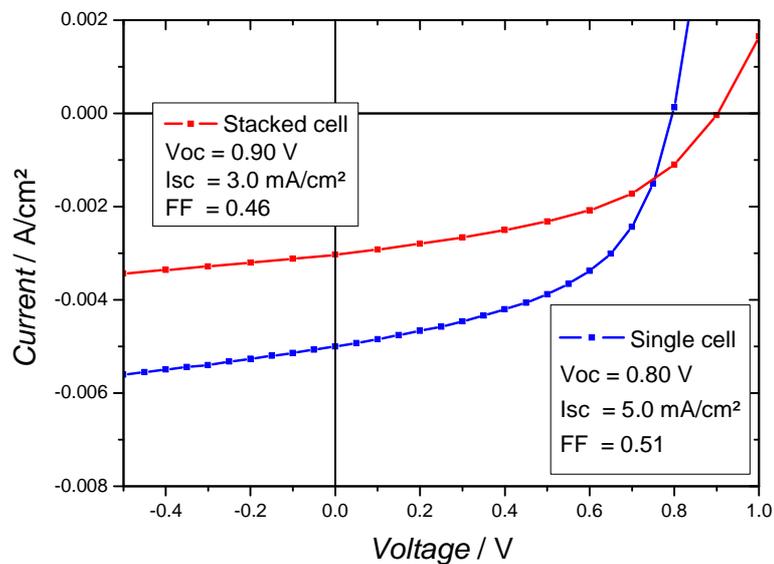


**Figure 23** Aqueous Pedot:PSS solution on a MDMO-PPV layer before (left) and after (right) the surface treatment.

The conductivity of this diluted Pedot:PSS : iso-propanol layer is of primary importance to ensure good interconnection of the stacked cells. In order to determine its conductivity, a glass sample with MDMO-PPV layer is treated with the alcoholic diluted Pedot:PSS layer and the resistivity is measured. Conductivity is considered sufficient when the measured value is located between 5 and 15 M $\Omega$  (measured in a distance of 5 mm).

After drying the Pedot:PSS - layer overnight, the second bulk heterojunction cell can be processed on top and the electrodes can be evaporated.

The measured results of these cells are shown on Figure 24. It shows clearly that the voltage of the tandem cell (900 mV) is higher than those of normal single cells (800 mV). However, this improvement is very small and correlated with a reduction in FF and Isc.



**Figure 24** Current – voltage characteristics of single and stacked cells of MDMO-PPV.

Previous studies performed on small molecule stacked cells showed that it may be very important to have well pronounced p- and n- type characters for generating the full open circuit voltage of each cell of the device. Therefore the

bulk heterojunction concept was substituted by a rather unconventional type of cell: a solution processed bilayer.

### ***Bilayer attempt - the first cell***

As already mentioned, it is believed that for tandem cells it is important to have distinctive n- and p- characters at the interconnection between the two cells.

The problem of processing a bilayer from solution lies in the dissolving properties of polymers and the fullerene PCBM. Both are solvable in organic solvents like chlorobenzene and toluene. This makes it hard to process layers onto each other, not dissolving the layer underneath. Several experiments were carried out by just changing the solvents for donor and acceptor and spincoating the different layers on top of each other<sup>31</sup>, but it was not possible to process and develop a well working bilayer.

Therefore, a new spin coating technique was introduced: One drop of PCBM solution was deposited onto the polymer layer while the sample was spinning at high speed. Several experiments showed that the speed should be more than 6 000 rounds per minute to get a homogenous film of PCBM on the polymer layer.

It might not be entirely correct to talk about real bilayer, because the solution of PCBM in organic solvent dissolves and diffuses in part of the polymer layer. But this phenomenon can be largely prevented by using high spin coating speeds and changing the solvent of the fullerene.

A solvent that has high solubility for PCBM and does not dissolve the polymer would be ideal. Furthermore, the vaporization temperature should be low, in order to prevent dissolving too much of the lower polymer film.

Taking into account all of these points, some dissolubility experiments were carried out, with PCBM solutions based on xylene, chlorobenzene and dichloromethane.

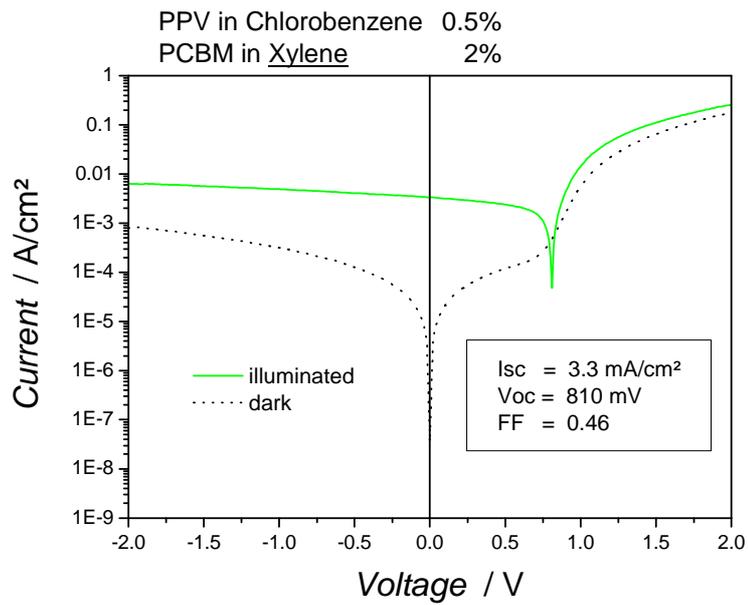
Xylene, chlorobenzene and dichloromethane have vaporization points of 140 °C, 132 °C and 40 °C, respectively. The first two were used because of the good solubility of PCBM; the dichloromethane was chosen for its low vaporization point, yet it does not dissolve PCBM very well. To get a solution of about 1 percent, it has to be stirred and heated at 40 °C for more than 12 hours, and even then it has to be filtered with a 0.45 µm Teflon filter (dichloromethane dissolves the usual types of filters).

Then, bilayer devices from these solutions were made.

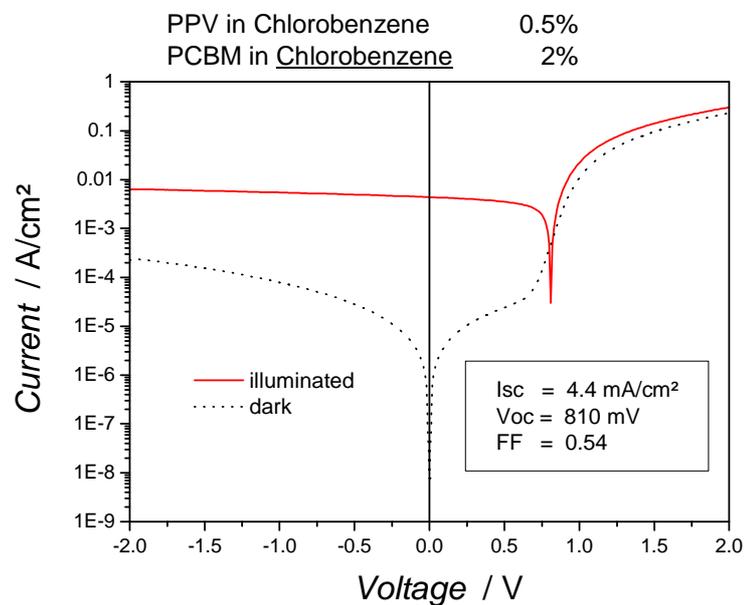
A film of MDMO - PPV 0.5 % in chlorobenzene (this solvent was not changed because it gives the best surface properties) was deposited on a glass / ITO / Pedot:PSS substrate and dried for more than 1 hour in vacuum. After that, one to two drops of the fullerene solutions were deposited onto the rotating sample spinning with 8 000 rounds per minute.

To have an idea if this process works for organic solar cells, Aluminum was evaporated on top of the fullerene layer and the current - voltage curves of these devices were characterized. These are shown in the next figures.

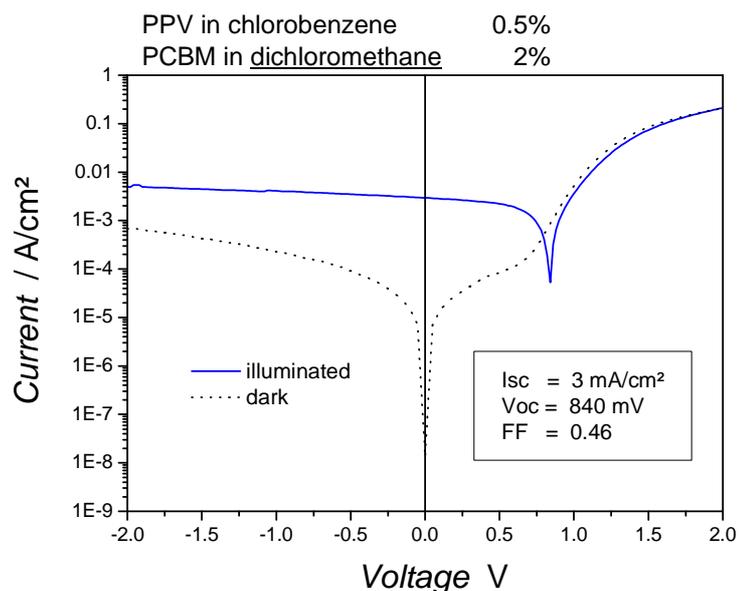
It should be mentioned that no LiF - layer was used, yet this material is known to improve the work function of the electrode when deposited before the Aluminum<sup>19 32</sup>. This choice was made to allow maximum reproducibility and avoid source of uncertainty.



**Figure 25** Current – voltage characteristics of solution processed bilayer devices. PCBM dissolved in xylene.



**Figure 26** Current – voltage characteristics of solution processed bilayer devices. PCBM dissolved in chlorobenzene.



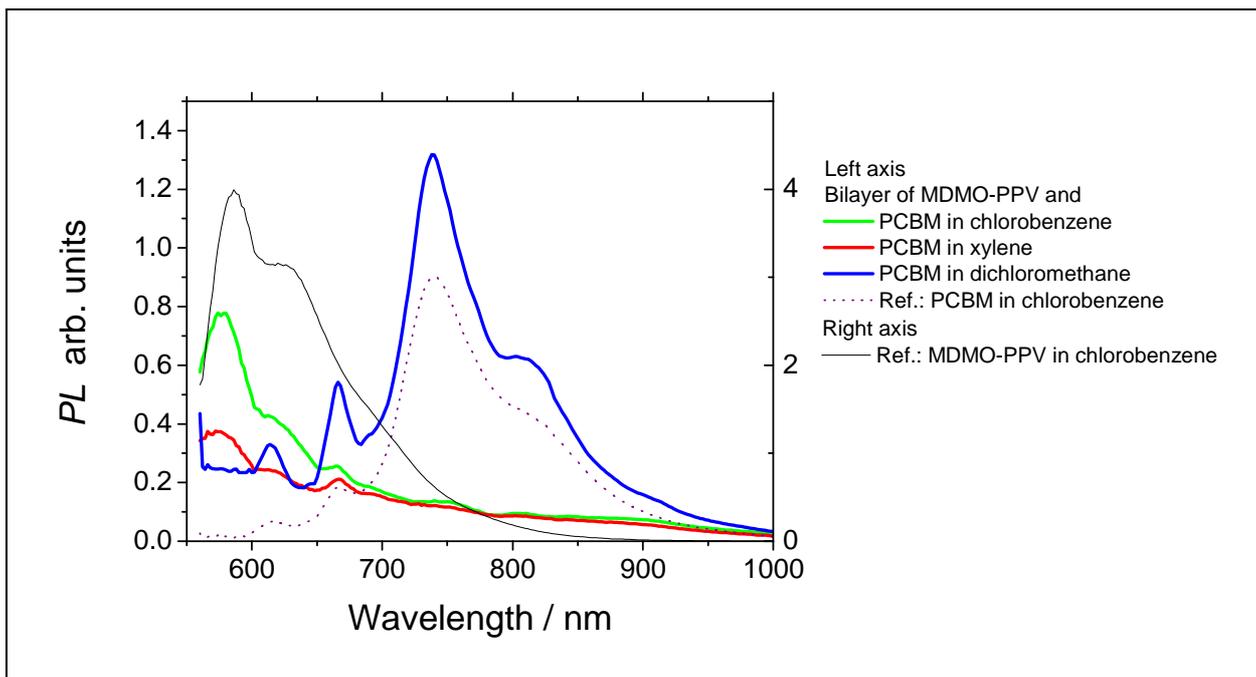
**Figure 27** Current – voltage characteristics of solution processed bilayer devices. PCBM dissolved in dichloromethane.

As already mentioned, the bulk heterojunction concept increased efficiencies, since bilayer organic solar cells show lower current, due to the limited charge generation. Accordingly, lower efficiencies than those produced from blends of polymer and fullerene could be estimated.

It appears that the current of the bilayer cells is just slightly smaller than that for the bulk heterojunction devices. This observation might indicate that the expected bilayer does not present a sharp interface, but a gradient of PCBM in the polymer layer – high concentration on top and low at the bottom.

To verify this statement, photoluminescence (PL) measurements were performed.

Samples with bilayer structures were fabricated from MDMO-PPV and PCBM in all three solvents and measured at the photoluminescence – set-up. As a reference, the luminescence of pristine MDMO-PPV and PCBM was determined. The results of the measurements are shown in Figure 28.



**Figure 28** PL measurements.

In all three combinations, the photoluminescence of the MDMO-PPV is not completely quenched, but the intensity is at least 5 times less than the luminescence of the pristine poly(vinylene). This indicates that some acceptor-molecules (PCBM) diffuse into the polymer film and form an intermixed layer, similar to the interpenetrating donor- acceptor network of a bulk heterojunction blend. Because of this intermixing, electrons from the polymer can be transferred to the fullerene and a quenching of the luminescence can be observed.

In contrast to the other curves, the sample with dichloromethane based PCBM solution shows some photoluminescence of PCBM molecules. This observation tends to prove the presence of a pure PCBM layer on the top of the device, probably caused by the high volatility of dichloromethane.

### ***Ultrathin metallic recombination layer***

The next step of optimization to build up a stacked solar cell was the intermediate metallic layer.

This should act as a recombination centre, allowing holes from the HOMO of the back cell to recombine with electrons from the LUMO of the front cell.

The thickness of this layer should not be too high, because this would cause high absorption and losses of photons in the back-cell. 0.5 - 1 nm turned out to be the optimum, accordingly to previous works.<sup>23 25</sup>

Several metals were used in stacked cells, all of them evaporated with high rates (0.5 nm per second), to prevent diffusion into the photovoltaic layers.

The characteristics of voltage and current of tandem cells with different metal cluster layer thicknesses (0.5, 1.0, 1.5, 2.0 nm) will be shown later.

### ***The second cell***

The other sub cell was processed like the first cell: pure MDMO-PPV spincoated from chlorobenzene and one drop of a PCBM – dichloromethane solution.

### ***The electrode***

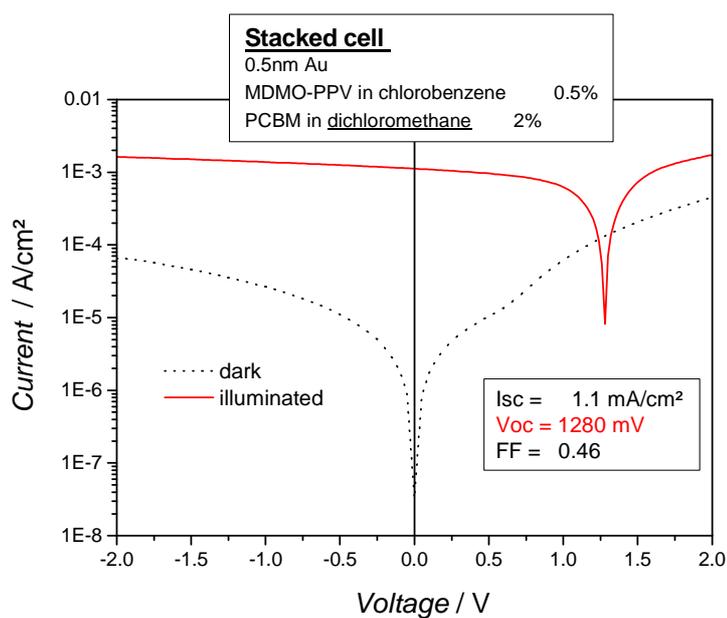
The Aluminum - electrode with a thickness of 100 nm was deposited under high vacuum with a rate of around 0.1 nm per second.

### ***The results***

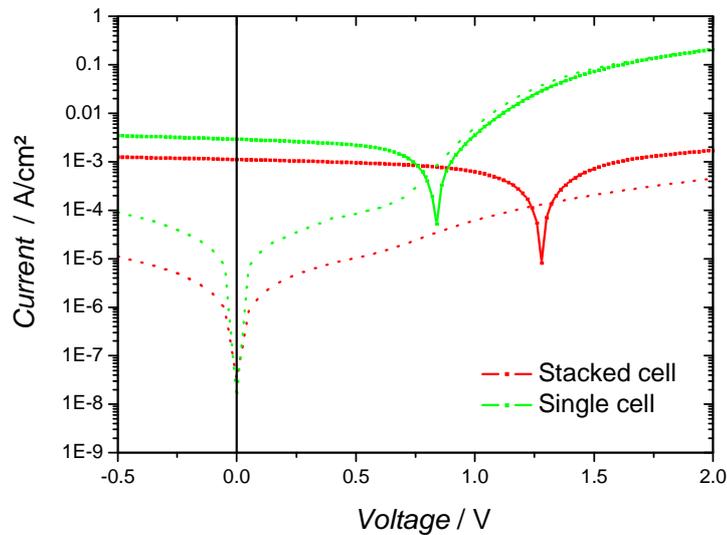
As already expected, distinctive p- and n- characters in the cell are mandatory to develop high voltages in the device.

In the case of tandem cells with PCBM layer out of chlorobenzene and xylene, no explicit n- type border layer could be observed out of photoluminescence measurements. As a consequence, the results obtained from these stacked cells are quite similar to those obtained with bulk heterojunction cells: the Vocs in both are around 900 mV, and the short circuit currents are slightly smaller, around 2 mA/cm<sup>2</sup>.

However, in the case of stacked bilayer cells made from dichloromethane PCBM-solution, a more or less distinctive n- type / metal / p- type character and a significant increase of  $V_{oc}$  is observable, as it is shown in Figure 29 and a comparison of single bilayer and stacked bilayer from dichloromethane is shown in Figure 30.



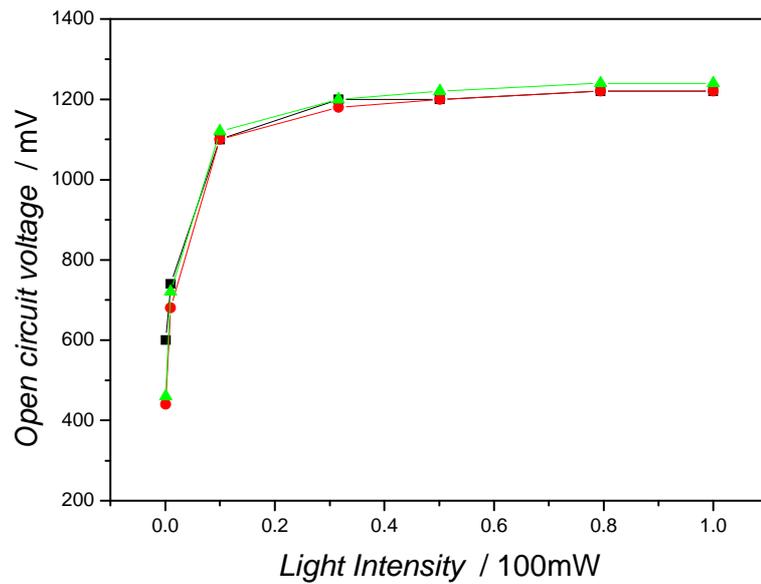
**Figure 29** Current – voltage characteristics of solution processed stacked cells. PCBM dissolved in dichloromethane.



**Figure 30** Comparison of single bilayer cell and stacked bilayer cell. PCBM dissolved in dichloromethane.

The measured 1 280 mV open circuit voltage means an increase of the Voc of around 60 %, which is the highest for this type of a cell, so far.

Surprisingly, the fill factor is constant in comparison to single bilayer cells. But the short circuit current is quite low. This might be due to the fact that only a small number of photons can go through the first cell and create charge carriers in the back cell. This phenomenon might hamper the building up of the Voc. In order to verify that the Voc is saturated, current – voltage curves were measured at different light intensities by positioning several grey filters between the light source and the samples. The results of these measurements are shown in Figure 31.

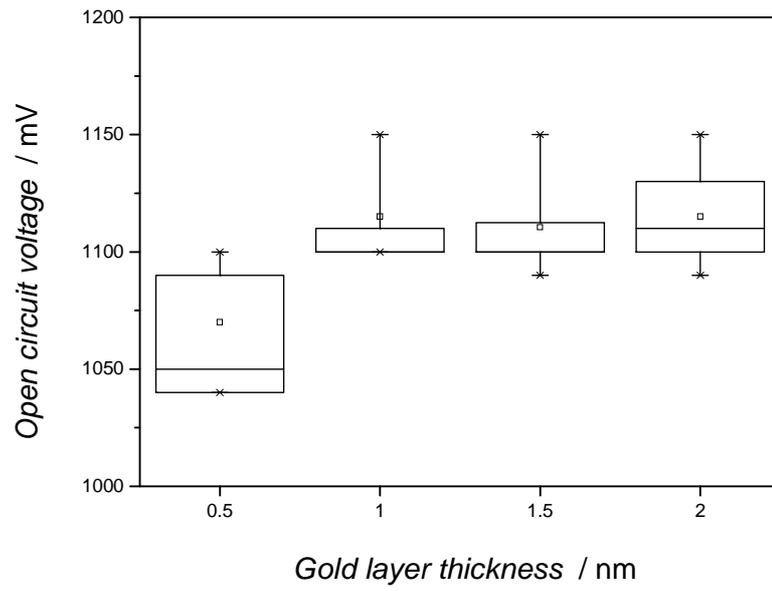


**Figure 31** Open circuit voltage vs. Light Intensity.

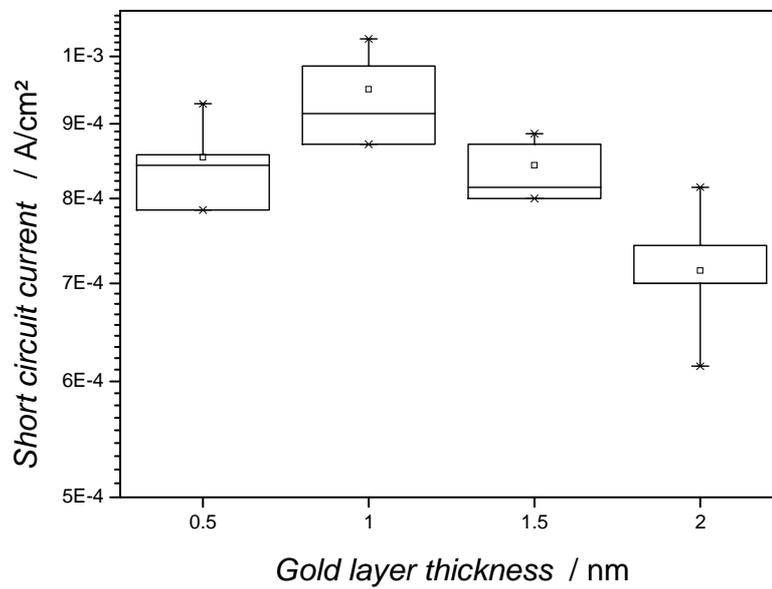
As the Voc is constant above about 30 mW, it can be assumed that both stacked cells do deliver their maximum Voc, and that the overall Voc of the device is saturated.

Using silver instead of the intermediate gold cluster layer, the results were not so good, increasing the Voc to just around 1 000 mV.

Figure 32 and Figure 33 show the dependence of the Voc and the Isc of the stacked solar cell from the thickness of the intermediate Gold layer.



**Figure 32** Dependence of open circuit voltage from the recombination layer thickness.



**Figure 33** Dependence of short circuit current from the recombination layer thickness.

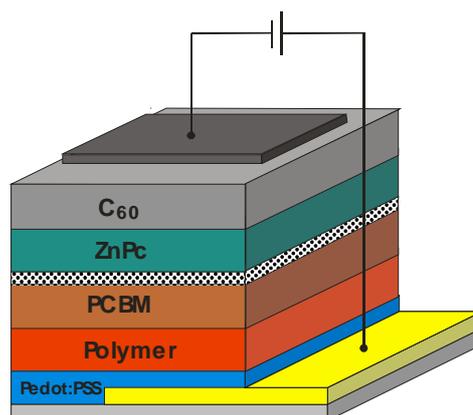
Consequently, the optimum intermediate layer thickness is found around 1 nm. The decrease of the  $I_{sc}$  observed for metal thicknesses above 1 nm may be due to the loss of photons in this layer. The  $V_{oc}$  appears quite constant for thickness above 1 nm.

As the voltage of around 1 300 mV could not be further improved, it has been decided to combine spin-coated cells and evaporated cells in order to understand where do the limitation comes from.

## 9 Polymer / small molecule based tandem cells

As tandem cells with polymer / polymer structure were not easily reproducible, it was decided to exchange the back cell of the tandem device by an evaporated small molecule Zinc-Phthalocyanine : C<sub>60</sub> cell. These ZnPc : C<sub>60</sub> cells have been investigated during the last 10 years and can reach good efficiencies with high reproducibility.<sup>33</sup>

The main advantage of this structure is that it allows one to avoid all solubility issues addressed above. Moreover, the intermediate Pedot:PSS layer of the second cell can be left out. The structure of that kind of solar cell is shown in Figure 34.



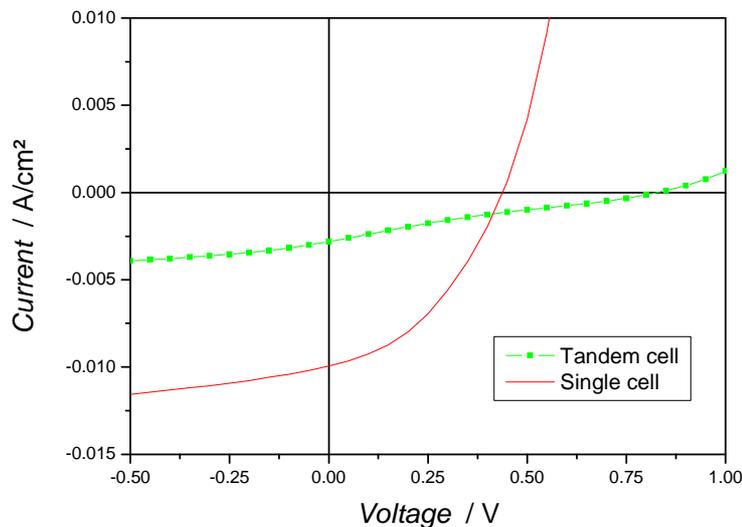
**Figure 34** Picture of a polymer / small molecule - tandem solar cell.

First, a single configuration evaporated solar cell was fabricated.

ITO - coated glass with Pedot:PSS layer on top was used as substrate and 10 nm of ZnPc were evaporated with a rate of 0.03 nm/sec. After that, a mixture of ZnPc and C<sub>60</sub> 1:1 (30 nm), and finally a pure 15 nm C<sub>60</sub> layer was deposited (rate 0.03 nm/sec) onto top. The vacuum in the evaporation chamber was better than  $5 * 10^{-6}$  mbar. For the top electrode, 5 nm Chromium and 95 nm Aluminum were evaporated.

This ZnPc : C<sub>60</sub> solar cells reached efficiencies of around 2.2 %, with open circuit voltages of 400 - 450 mV, short circuit currents of about 10 mA/cm<sup>2</sup> and fill factors of about 0.5. Tandem cells with MDMO-PPV should therefore reach 1 250 mV at open circuit conditions, since the expected Voc of a single MDMO-PPV : PCBM cell is at approximately 800 mV.

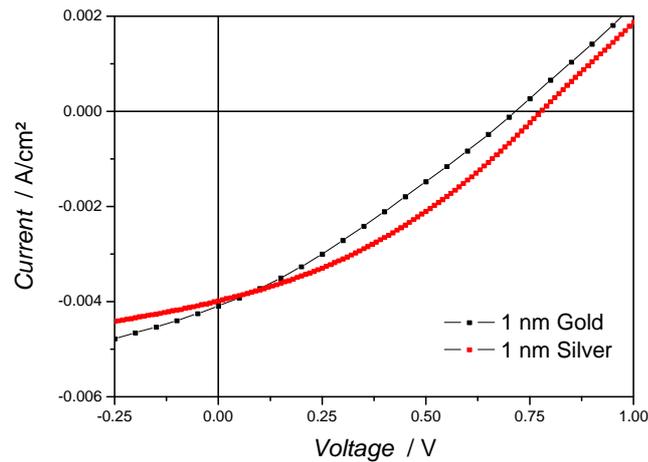
A fully evaporated ZnPc : C<sub>60</sub> - stacked cell was also built: two ZnPc : C<sub>60</sub> cells were connected by a 1 nm Silver recombination zone. The Voc reached 850 mV, which means a more or less doubling of the Voc of the single cells (see Figure 35). The current was not that good because of missing optimization of the layer thicknesses, and therefore the serial resistance and layer absorption may limit the current of the device under simulated AM1.5 irradiation.



**Figure 35** Current - voltage curves of evaporated ZnPc : C<sub>60</sub> single and tandem solar cells.

But the doubling of the Voc shows that the 1 nm Silver layer as recombination center between the two cells works properly and therefore the range of C<sub>60</sub> / metal - recombination layer / ZnPc layer was not changed for the polymer / small molecule devices.

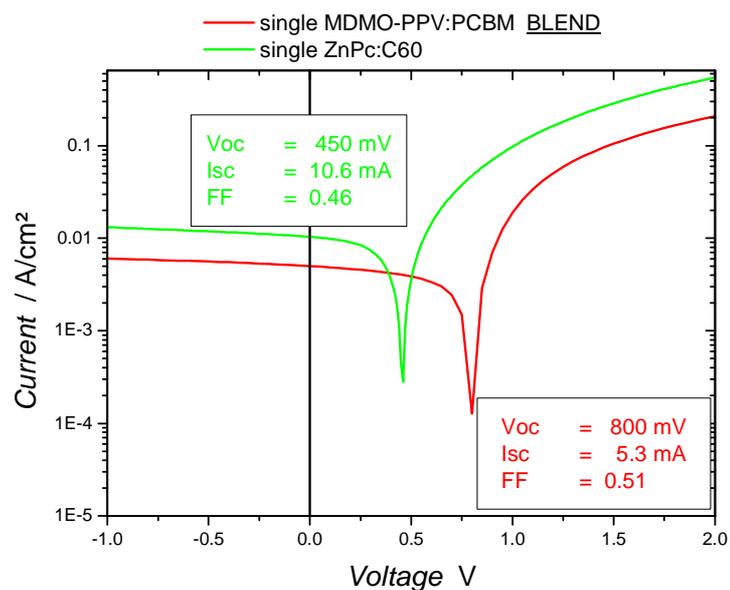
To verify which metal would be the optimum in the cell, two different metals, namely Silver and Gold, were used in fully evaporated ZnPc : C<sub>60</sub> / ZnPc : C<sub>60</sub> stacked cells. In contrast to solution processed stacked cells, Silver turned out to give slightly better results. Hence, Silver was used for the following experiments.



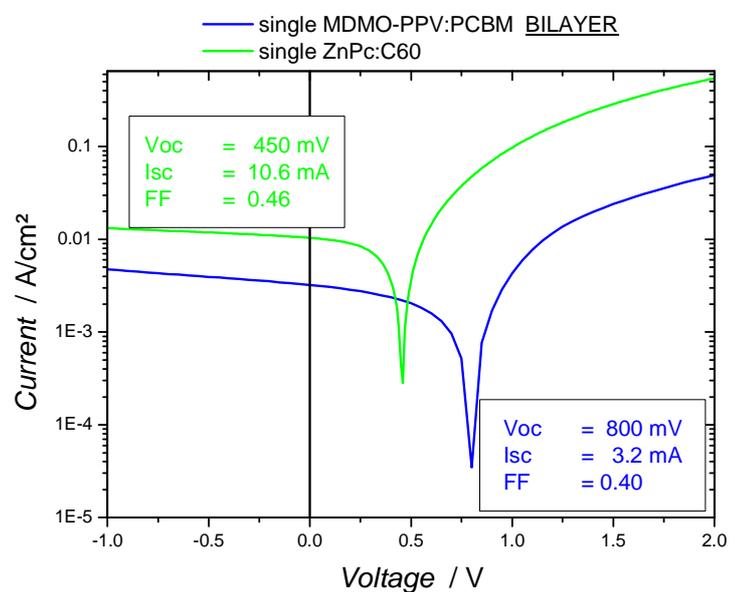
**Figure 36** Difference between Silver and Gold in tandem solar cell current - voltage characteristics.

As in full polymer / polymer cells, two different types of cells were built: on one hand, the polymer was blended (1:4 ratio) with PCBM; on the other hand a bilayer was made, out of pure MDMO-PPV solution and one drop of PCBM in dichloromethane on a high spinning sample.

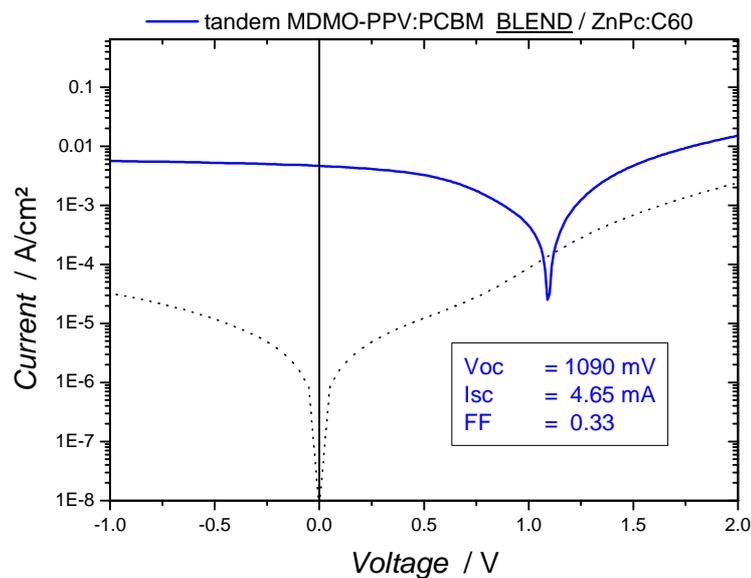
The recombination layer was a 1 nm thick Silver coating. The results of the single and tandem solar cells are shown below.



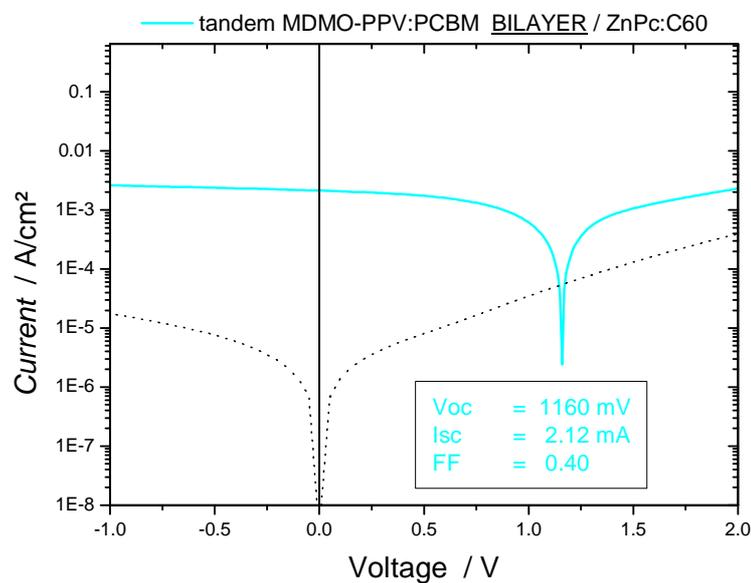
**Figure 37** Current - voltage characteristics of a single MDMO-PPV : PCBM blend device and a single ZnPc : C<sub>60</sub> device.



**Figure 38** Current - voltage characteristics of a single MDMO-PPV : PCBM bilayer device and a single ZnPc : C<sub>60</sub> device.



**Figure 39** Current - voltage characteristics of a tandem MDMO-PPV : PCBM blend / Ag / ZnPc : C<sub>60</sub> device.

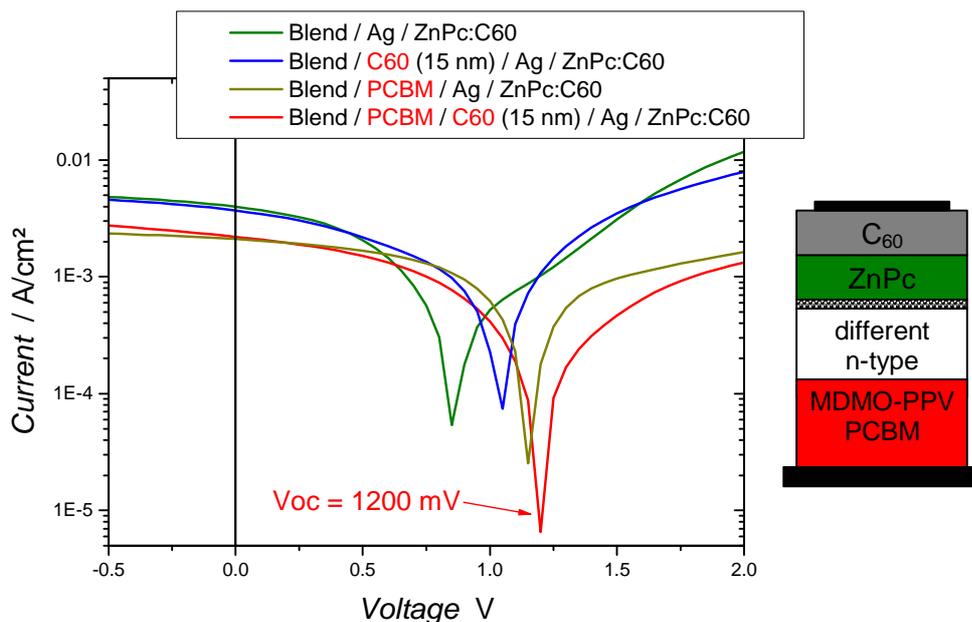


**Figure 40** Current - voltage characteristics of a tandem MDMO-PPV : PCBM bilayer / Ag / ZnPc : C<sub>60</sub> device.

These results show that the voltages of the single cells are nearly added in the tandem cell.

There is a small difference between stacked cells where the polymer cells are either bilayer or blend processed, that could also be observed in full polymer tandem cells. It shows that, since the p- and n- type character is more pronounced in the bilayer than in the blend, the Voc might be directly related to the quality of this grading.

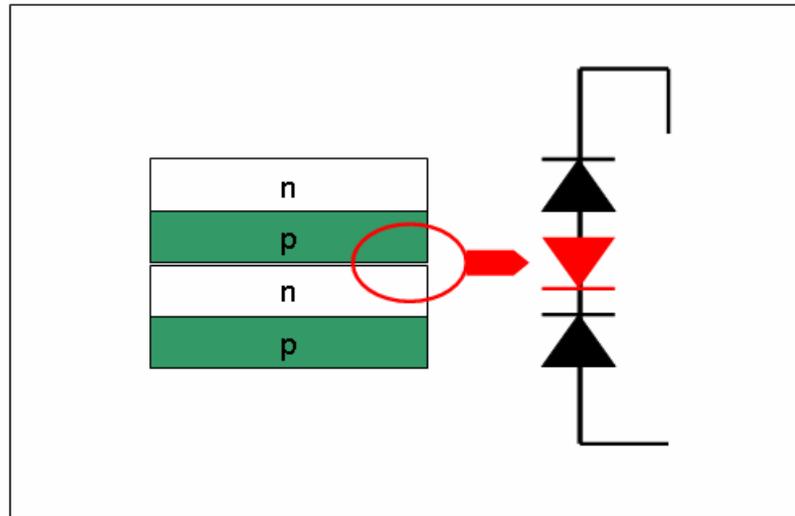
To improve this graduation, a new series of cells was built, using a MDMO-PPV:PCBM blend solution (because this gives better current) and additional layers with different n- type characters on top of the first cell. The second cell was evaporated as before. The results are shown in Figure 41.



**Figure 41** Polymer / small molecule cells with different n- type characters in front cell. Right: structure of the devices.

Comparing the different curves it is obvious that better n- type character of the first cell, and maybe also better p- character of the second cell (but in this case that was held constantly), are very important for the development of the Voc. Furthermore, a difference between C<sub>60</sub> and PCBM is obvious.

Without a blocking layer near the recombination center, a back diode is observable (see Figure 42). This means that holes from the upper cell reach the metal layer and can go through the first cell to the electrode. This can reduce the open circuit voltage of the stacked cell.



**Figure 42** Occurrence of a back diode because of missing recombination zone.

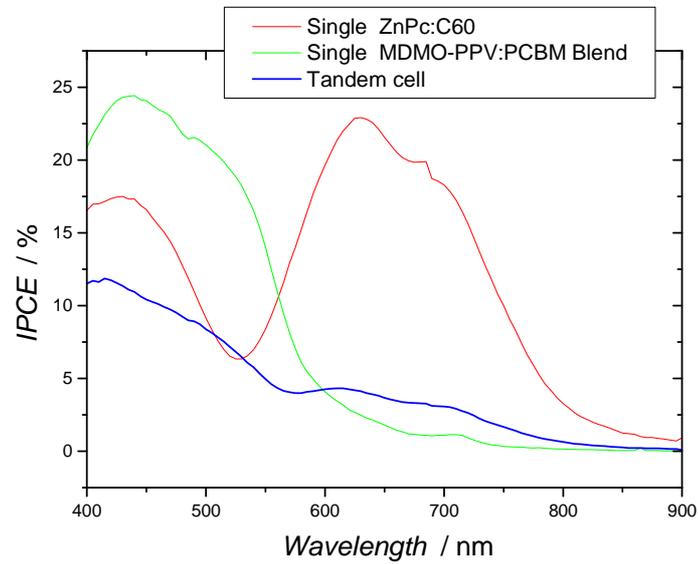
For more investigation, it was decided to perform some IPCE measurements of single (MDMO-PPV : PCBM blend and ZnPc / ZnPc : C<sub>60</sub> / C<sub>60</sub>) and tandem (MDMO-PPV : PCBM [blend] / C<sub>60</sub> / Ag / ZnPc / ZnPc : C<sub>60</sub> / C<sub>60</sub>) cells.

The incident-photon-to-current-efficiency (IPCE) measurement gives the spectral resolution of the photocurrent. Light coming from a monochromator is focused onto a solar cell and the current can be measured at certain wavelength.

From theory of tandem cells it can be expected that, when serial connected, the current of the tandem cell is determined by the current of the worst of the two cells. Therefore, no current should be measurable when the tandem cell is excited at wavelengths where just one cell is absorbing.

From these IPCE measurements, the existence of a small current in the region of 600 – 800 nm can be observed in the tandem cell (see Figure 43). This current is quite interesting since the overall current of the device should be

imposed by the worst cell, namely the MDMO-PPV : PCBM based one which is almost non absorbing in this region.



**Figure 43** IPCE measurements of single and tandem cells.

In order to verify the reproducibility of this effect, another conjugated polymer was chosen: *P3HT*.

### ***P3HT tandem cells***

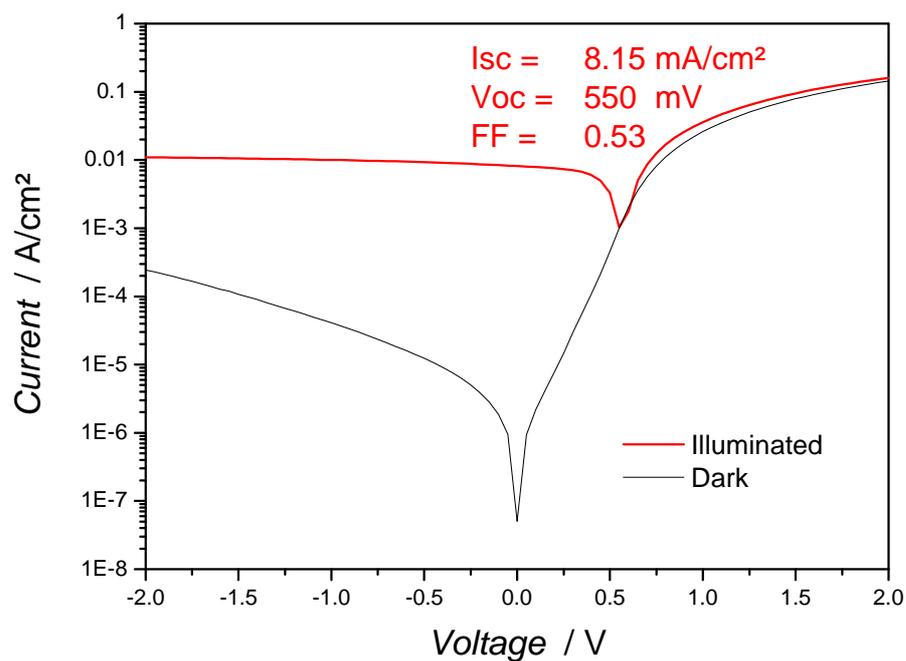
For tandem cells with P3HT : PCBM for the first cell, bilayer built-up was used because this leads to more pronounced p- and n- characters and, as already known from experiments, when using a bilayer structure for the polythiophene and fullerene, no heat treatment is necessary for getting efficient solar cells.

Normally, a post-production heating step is necessary for the P3HT:PCBM solar cell to gain high efficiencies. It is verified that for improving the short circuit current and the fill factor of the solar cell, the cell should be exposed to 110 - 150°C for around 5 - 30 minutes.<sup>34 35 36 37</sup>

With this treatment, the crystallinity of P3HT is improved and a demixing of the two components in the interpenetrating donor - acceptor network occurs. This leads to a better charge transport to the electrodes and a more efficient charge generation is observable.

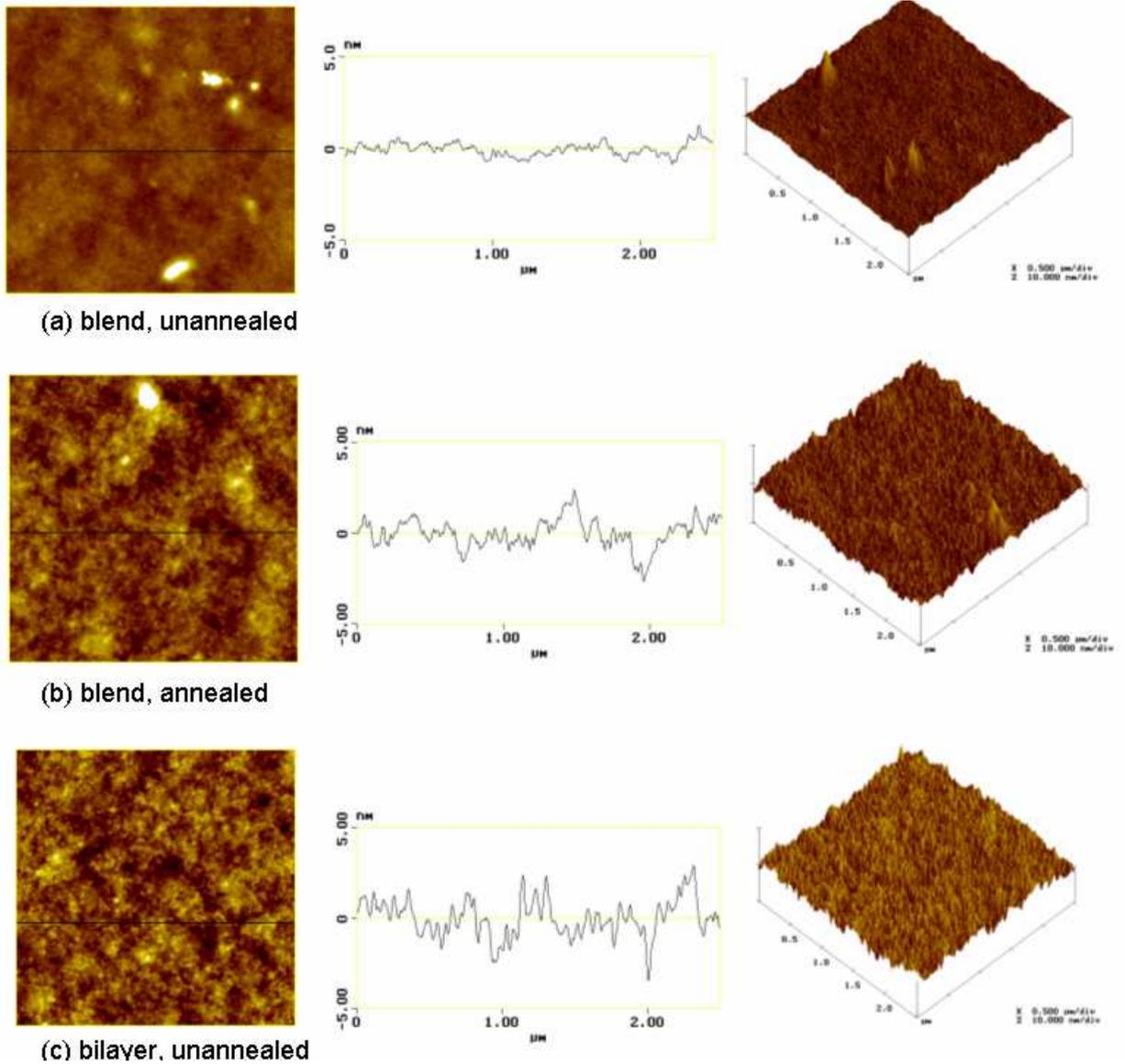
For the bilayer approach, Poly(3-hexylthiophene) was dissolved in chlorobenzene and spincoated. After drying, a drop of PCBM in dichloromethane was deposited on the very fast spinning substrate, as explained above.

This gives remarkable results even without the heat treatment, as it can be seen in Figure 44.



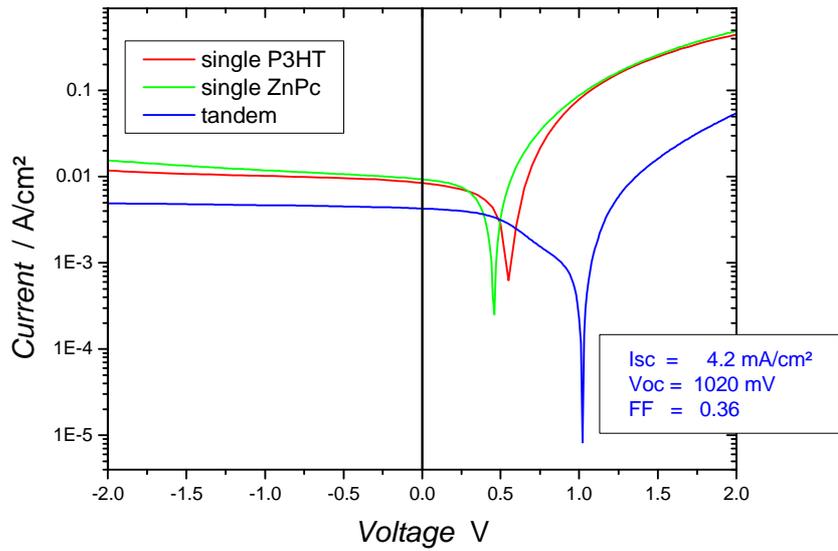
**Figure 44** Current - voltage characteristics of a P3HT : PCBM bilayer cell without heat treatment.

Figure 45 shows AFM pictures of a P3HT:PCBM blend unannealed (a), annealed (b) and a bilayer unannealed (c). The comparability of annealed blend and non-annealed bilayer is obvious.



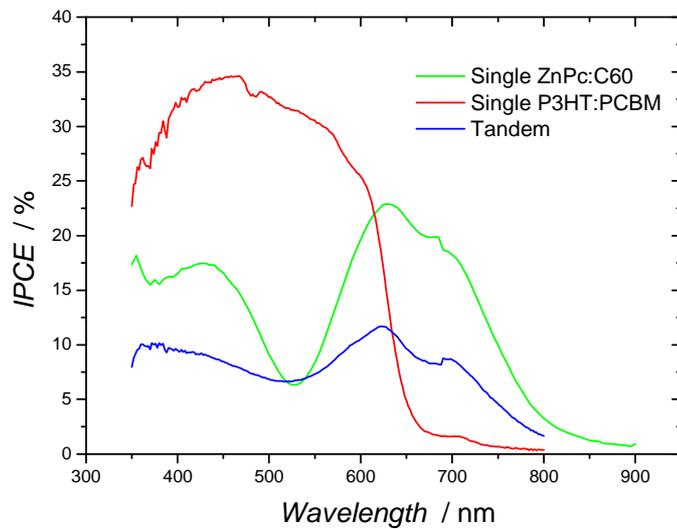
**Figure 45** AFM-measurements of P3HT:PCBM devices.

When we grow a ZnPc : C<sub>60</sub> cell by evaporation on this bilayer cell, a Voc of up to 1 020 can be observed. This means an adding of the voltages of the P3HT : PCBM (550 - 600 mV) and the ZnPc : C<sub>60</sub> (450 - 500 mV) cell. However, the fill factor degrades and the short circuit current undergoes a reduction of 50 %.



**Figure 46** Current - voltage characteristics of single cells and stacked cells.

Then IPCE was measured and the results show similar tendency for the P3HT and for the MDMO-PPV (Figure 47).

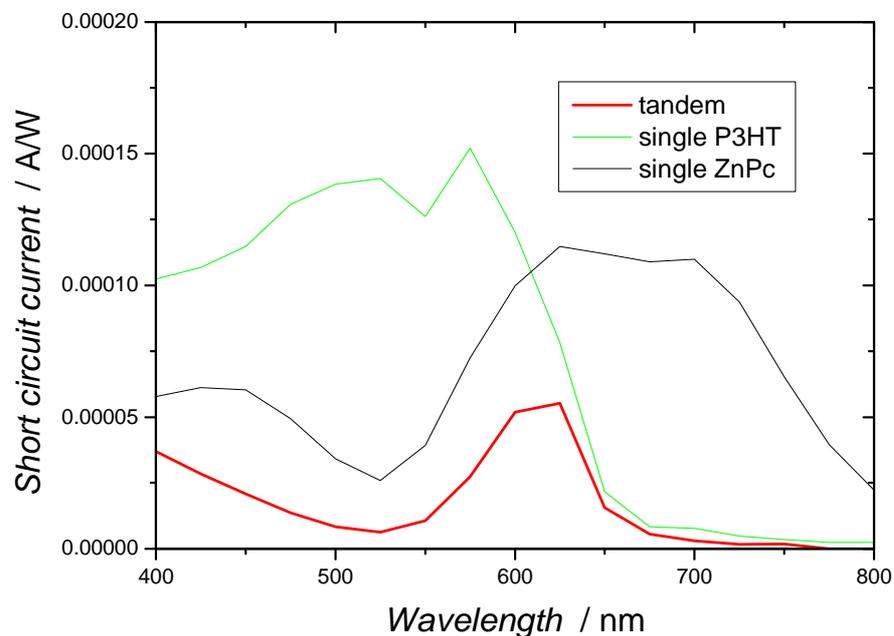


**Figure 47** IPCE measurements of single and tandem cells.

Indeed, in the region where no current would be expected from the P3HT based cell, the tandem device cell delivers a current, which is higher than in the single P3HT cell. It has to be noted that the IPCE set-up used in this experiment is based on a quite low intensity Xenon lamp. Therefore, the currents measured are typically in the nA range. In the special case of tandem cells, such low currents are comparable to the leakage current in the individual cell involved in the tandem device. This might explain why a non-zero IPCE can be detected in the spectral range where P3HT is not expected to provide any photocurrent.

This limitation can be overcome by using higher light intensity source. Thus the current - voltage characteristics of single and tandem cells were measured outside the glove box on a set-up inducing currents in the  $\mu\text{A}$  range.

The short circuit current versus the wavelength of the exciting light (from 375 nm until 800 nm in 25 nm steps) is shown in Figure 48.



**Figure 48** Short circuit current of single and tandem cells in dependence of the wavelength.

It can be observed that, contrarily to the low current IPCE results, the curve of the tandem cell always lies beneath the curves of the two individual single cells:

The total current of the cell is driven by the weaker cell, as expected from theory. In the region between 600 and 650 nm, where both cells have high absorption, a peak in the  $I_{sc}$  of the tandem cell is visible.

On the left hand side of the peak, the red curve is downshifted compared to the ZnPc spectrum. This might be due to a reduction of the current of the ZnPc : C<sub>60</sub> cell caused by a non negligible loss of the photons in the P3HT cell.

Finally, it should be mentioned that the fact that the overall current is downshifted compared to the individual cell can be as well induced by the large serial resistance of the tandem cell as visible in Figure 46.

## 10 Conclusion and Outlook

During this work, the possibility of producing solvent based organic tandem solar cell has been shown. Some experimental innovations have been established to overcome technological problems related to common solubility of successive layers. Most of the effort has been devoted to the realization of serial connected stacked cells, inducing the addition of the Voc of the individual cells. The balancing of the current through optimization of the respective sub-cell thickness has not been considered so far. For this critical steps, the use of evaporated small molecule tandem cells and optical modelling of the entire device sound mandatory.

In the case of solvent processed conjugated polymer tandem solar cells, an increase in the Voc was achieved, yet real doubling could not be observed. Voc up to 1280 mV was obtained, to be compared to the 800 mV measured with the individual sub-cells.

The loss of voltage might be explained by the p- and n- characters which are not as pronounced as in evaporated cells because of solvent processing and material features. The solar cells have to have a defined interface with the middle contact to avoid injection of charge carriers from one cell into the other, inducing a leakage current. Therefore, the recombination junction has to be contacted with a hole blocking layer from the first cell and with an electron blocking layer from the second. This is not easy processable in solvent based built up.

The low short circuit currents may occur first of all due to the high serial resistance of those devices which is obvious from the current – voltage measurements. Secondly, because of the absorption of photons in the first cell due to missing optimization of layer thicknesses, the back cell may have a lack of photons for efficient energy generation.

Further efforts to be invested into the investigation of organic tandem devices sound mandatory. The realization of this concept might not only have an important impact on the world of science but also for the establishment of

organic solar cells as competing substitutes for predominant fossil and nuclear energy sources.

For better understanding the mode of operation of tandem solar cells it may also be an idea to work with two different wavelengths and measure the current – voltage curves of the device (as it was done with one wavelength in this work). One wavelength should be constant at certain number where just one of the two cells is highly absorbing and the second wavelength should be varied. From this experiment it may be possible to detect from which cell the losses come from.

Lamination may also be one possible way to avoid the complicated solvent processing of too many layers. This was already tried in the course of this work, but it was difficult to spincoat a polymer from solution onto the evaporated electrode for an inverse solar cell.

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## Curriculum Vitae

**Name:** Hans-Jürgen Prall  
**Date of Birth:** October 20<sup>th</sup>, 1977  
**Birthplace:** Gmunden  
**Nationality:** Austrian  
**Marital Status:** Unmarried  
**Parents:** Johann Prall, died 1994  
Margarita Prall

### Education:

Sep. 2004 – Nov. 2005:

Diploma Thesis at the *Institute for Physical Chemistry*

Oct. 1997 – Sep. 2004:

Studies at the University of Linz:

Economical Engineering of Technical Chemistry

1996: School leaving exam passed with distinction

1988-1996: Grammar school in Altmünster

1984-1988: Primary school in Steyrermühl and Laakirchen

### Military Service:

Oct. 1996 - May 1997 Linz, Ebelsberg, Hillerkaserne

### Languages:

since 1988: French, spoken and written

since 1990: English, spoken and written

1992 - 1996: Latin

---

**Related Experience:**

**Jul. - Sep. 2003: Project collaborator at the *Linz Institute for Organic Solar cells***

**Further Employers:**

**Summer 2001: *Lenzing AG***

**Summer 2000: *Lenzing AG***

**Summer 1999: *Lenzing AG***

**Summer 1997: *Köblinger Stahl und Metallbau GesmbH***

**Additional Qualifications:**

**Driver's license since 1995**

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