

N-INNER Final Scientific Report

Project: Evaluation platform for polymer solar cells – Morphoso

March, 2012

Dr. Uli Würfel

Participants:

Prof. Olle Inganäs
Biomolecular and organic electronics,
N-309, Department of Physics
Linköping University
S-581 83 Linköping
Sweden



Prof. Ronald Österbacka
Åbo Akademi University
Department of Physics and Centre for Functional Materials
Porthansgatan 3
FI-20500 Åbo
Finland



Dr. Uli Würfel
Dye and Organic Solar Cells
Division Solar Cells – Development and Characterisation
Fraunhofer Institute for Solar Energy Systems
Heidenhofstr. 2
79110 Freiburg
Germany



N-INNER final scientific report for the project: Evaluation platform for polymer solar cells – Morphoso

Authors and organisations:

Prof. Olle Inganäs
Biomolecular and Organic Electronics,
N-309, Dept. of Physics
Linköping University
S-581 83 Linköping, Sweden
Email: ois@ifm.liu.se
phone: +46-13-28 12 31
fax: +46-13-28 89 69
<https://www.ifm.liu.se/applphys/biorgel/>



Prof. Ronald Österbacka
Organic Electronics
Åbo Akademi University
Department of Physics and Centre for Functional Materials
Porthansgatan 3, FI-20500 Åbo, Finland
Email: ronald.osterbacka@abo.fi
phone: +358 (0)2 215 4246
fax: +358 (0)2 215 4776
<http://www.abo.fi/~rosterba>



Dr. Uli Würfel
Dye and Organic Solar Cells
Fraunhofer Institute for Solar Energy Systems
Heidenhofstr. 2, 79110 Freiburg, Germany
Email: uli.wuerfel@ise.fraunhofer.de
phone: +49 761 203 4796
fax: +49 761 4588 9000
<http://www.ise.fraunhofer.de>



Keywords:

Organic solar cells, morphology, flexible solar cells, organic semiconductors, structured substrates, charge carrier transport, recombination

Abstract:

The objective of the project entitled "Morphoso" was to establish an evaluation platform for polymer solar cells in order to combine different approaches such as modeling, processing and characterization of devices with the aim to find both theoretical and experimental correlations between the thin film processes, the nanomorphology of the photoactive blend layer and the resulting generation, transport and recombination of charge carriers in organic solar cells. Synergies between the three project partners were used to achieve a better understanding of the fundamental processes taking place when operating an organic solar cell. Solar cells were built with different materials in all three labs and standard configurations were defined. To enhance absorption light trapping structures on the mm- and the μm -scale were employed and their potential was determined. 3D-tomography was applied to visualize the morphology of the donor/acceptor network. Electrical modeling was performed with a continuum approach and a 2D heterojunction model was developed during the three years project time. Different experimental techniques like photoinduced absorption and CELIV (current extraction through linear increasing voltage) were used extensively to probe the generation and recombination of charge carriers as well as their transport through the photoactive layer. Last but not least the long term stability of different cell geometries was investigated and proper encapsulation materials and techniques were identified. In addition to these ageing experiments unsealed cells were exposed to oxygen or water vapor when illuminated in order to learn more about the specific degradation mechanisms.

Executive Summary

Organic solar cells or organic photovoltaics (OPV) are a comparably young technology which attracted a lot of interest both from the scientific community and industry in the last years. This is on the one side due to the fact that it is relatively easy and cheap to start with research on organic solar cells as compared to their inorganic counterparts. On the other side, it is known since many years that this technology has one of the greatest potential for low costs among the next generation PV technologies. The reason is that organic solar cells can be processed at room temperature from solution with different printing techniques. High temperatures are not required which enables the use of flexible substrates (foils) and thus continuous processing with roll-to-roll technology becomes possible. Continuous roll-to-roll processing allows reaching very large throughput rates which translates directly into very low production costs.

By intensive research the photovoltaic power conversion efficiency of organic bulk-heterojunction solar cells could be increased up to values of more than 9% using a nanoscale interpenetrating network of two materials, a donor and an acceptor. Although this new solar cell technology promises very low production costs there are still major tasks to be worked upon for providing solar electricity on a larger scale.

For a technology breakthrough, the basic understanding of the fundamental processes in organic PV is necessary. This is anything but trivial to obtain due to the fact that the elementary processes take place on 1-20 nm scales within time frames from picoseconds to milliseconds. In addition, all this happens in disordered materials which are more difficult to describe on a quantitative manner than well-ordered, crystalline materials. The project "Morphoso" intended to make a contribution to the improvement in understanding the underlying processes which eventually determine the power output of solution-processed organic solar cells.

The project consortium consisted of three partners from the three countries Sweden, Finland and Germany. The partners were

- a) The group "Biomolecular and Organic Electronics" led by Prof. Olle Inganäs at the Department of Physics at Linköping University in Sweden
- b) The group "Organic Electronics" from Prof. Ronald Österbacka at the Department of Physics and Centre for Functional Materials of the Åbo Akademi University (University of Turku) in Finland
- c) The group "Dye and organic Solar Cells" headed by Dr. Uli Würfel at the Fraunhofer Institute for Solar Energy Systems ISE in Freiburg, Germany

The overall aim of the project consortium was to enhance the understanding of the physical processes taking place in solution-processed organic solar cells and contribute to the process of setting the basis for future improvements and thus pushing organic photovoltaics closer to real applications. We are all convinced that an enduring progress in this field can only be achieved when practical efforts and academic insights are combined in a proper way.

Therefore we put the expertises of the three partners together and exchanged our – sometimes differing – point of views in intensive scientific discussions. This was done either at one of the project meetings which took place regularly at one of the partners' institutions or at international conferences where we met each other. The exchange of ideas among the researchers of our three-national project consortium was regarded as something extremely valuable by all people contributing to the project. Another aspect was that this way people got to know each other and set the basis for some shorter and longer stays in the group of one of the other consortium members. These visits allowed for more and prolonged discussions about the interpretation of experimental data and the most appropriate theoretical description of the underlying processes.

In inorganic crystalline materials used as photoactive material for solar cells the absorption of a photon leads directly to the generation of free charge carriers, an electron and a hole. Although an electron and a hole are also created upon absorption of a photon in the photoactive layer of an organic solar cell they experience a strong binding energy in the range of ca. 0.5eV. This quasi-particle is called an exciton and as it is electrically neutral its transport is governed by diffusion. The thermal energy at temperatures around room temperature (or even at higher temperatures a solar cell would reach on a roof top, i.e. $\leq 85^{\circ}\text{C}$) is not enough to overcome this binding energy. Therefore a second component is present in the photoactive layer which offers a lower lying energy level for the electron which is called the acceptor. The exciton has to reach the interface between donor and acceptor within its lifetime. If this happens the electron is transferred from the donor to the acceptor on a picosecond-timescale with an efficiency approaching unity. This way free charge carriers are created and

subsequently both charge carriers have to be transported to their respective contact, i.e. the holes in the donor phase and the electrons in the acceptor phase.

In an organic solar cell the morphology of the photoactive layer is crucial for the performance of the device: if the two phases are very finely intermixed all excitons will reach an interface of donor and acceptor within their lifetime and the creation of free charge carriers is very efficient. On the other hand, the high interface area means that a charge carrier is always located very near to the other phase during its path toward the electrode. This leads to high(er) recombination which reduces especially the fill factor and thus the power output. On the other hand a coarse morphology will certainly improve the transport properties and thus reduce the recombination rate but will at the same time reduce the generation of free charge carriers because a certain fraction of the excitons will not be able to reach the donor/acceptor interface before they recombine. Of course the situation is far more complex and the morphology depends on layer thickness and process parameters like annealing, concentration and solvent.

The aim of our efforts was to achieve a deeper understanding of the correlation between the morphological characteristics of the photoactive layer and its electro-optical properties which finally determine the device performance of an organic solar cell or module to a large extent. Our approach was to establish an evaluation platform that integrates device-modelling, -processing and characterisation to find the theoretical and experimental correlation between the thin film process, its nanomorphology and the generation and transport of charge carriers in the finished devices.

In the beginning an inter-laboratory round robin study was performed and it confirmed that the measurements of the three project partners are well comparable.

Objectives

In the following a short and concise summary of the main objectives of the project is given together with a discussion if and how they were met. A more detailed description can be found in the subsequent main section of this report.

1) Modelling

The theoretical description of physical processes has been carried out with different approaches. Optical modelling was done using FEMLAB and a RCWA (rigorous coupled wave analysis) approach and it was applied to specific geometries for organic solar cells that allow for enhanced absorption through light trapping effects. Electrical modelling was done with the commercial semiconductor simulation tool Sentaurus Device from Synopsys. First, a 1D electrical model with one effective semiconductor was developed by adapting the description to organic semiconductors and it was used to evaluate quantitatively the influence of important physical properties on the characteristic output parameters of the device. In a later stage this model was extended to explicitly represent the donor/acceptor network of the photoactive layer. The objectives have been met.

2) New cell architectures

Two approaches were followed to enhance the absorption in the photoactive layer by efficient light trapping. First, substrates structured in the mm- to cm-range were used to reflect non-absorbed light in a V-shaped geometry to be harvested by a second cell. Another method was to employ substrates structured in the μm -range in prism geometry. Promising results could be obtained with the first approach. However, the second one faced difficulties in achieving a homogeneous coating of the thin layers from solution on the rough surface of the substrates. The objectives have been met.

3) Investigation of process parameters

Thin film coating with roll-to-roll methods or such that are compatible with roll-to-roll process technology was investigated. A homogeneous deposition on larger area ($>>10\text{cm}^2$) plastic substrates was achieved by slot-die coating. Real roll-to-roll processing of complete devices was however not possible due to a reduced funding of the Finnish partner. The objectives have been met.

4) Characterisation of morphology

The morphology of the photoactive layer has a high impact on the efficiency of organic photovoltaic devices. To visualize the morphology in the volume of the photoactive layer 3-D electron tomography was carried out. It is

rather complex to achieve a resolution high enough to recognize the details as the magnitude of the features lies in the range of 10-20nm. Another issue is the fact that both phases, donor and acceptor, are carbon-based organic materials and a contrast is quite hard to achieve. Nevertheless, "pictures" were taken that give a valuable insight in how the two materials are aligned to each other. Therefore, the objectives have been met.

5) Optical and electrical characterisation

This work package was executed in all the three groups intensively. Apart from recording the current-voltage characteristics of the solar cells a characterisation technique applied by all the partners in the consortium was CELIV, short for carrier extraction by linearly increasing voltage. This technique allows insight into the transport of the charge carriers and delivers a fingerprint of their mobility. Furthermore, optical methods such as photoinduced absorption were applied to investigate the energetics of generated charge carriers and to learn more about their recombination. The objectives have been met.

6) Tests of long time stability and determination of the degradation mechanisms

The aim was to identify reliable encapsulation materials and processes in order to achieve promising stability and lifetime data. We tested a number of different encapsulants, glues and barrier foils. We exposed sealed solar cells to different stress factors such as continuous illumination, UV-radiation and heat. In addition we performed ageing experiments with unsealed devices in order to identify the main degradation mechanisms. The objectives have been met.

Main section of the report

Table of Content

Introduction	VIII
Overview over the different work packages in the project	IX
Work package 1: Modelling	IX
Work package 2: New cell architectures	X
Work package 3: Investigation of process parameters	X
Work package 4: Characterisation of morphology	XI
Work package 5: Optical and electrical characterisation	XI
Work Package 6: Tests of long term stability and determination of the degradation mechanisms	XIII
Conclusions	XIV
Recommendations	XIV
Acknowledgement	XV

Introduction

Organic solar cells or organic photovoltaics (OPV) are a comparably young technology which attracted a lot of interest both from the scientific community and industry in the last years. This is on the one side due to the fact that it is relatively easy and cheap to start with research on organic solar cells as compared to their inorganic counterparts. On the other side, it is known since many years that this technology has one of the greatest potential for low costs among the next generation PV technologies. The reason is that organic solar cells can be processed at room temperature from solution with different printing techniques. High temperatures are not required which enables the use of flexible substrates (foils) and thus continuous processing with roll-to-roll technology becomes possible. Continuous roll-to-roll processing allows reaching very large throughput rates which translates directly into very low production costs.

By intensive research the photovoltaic power conversion efficiency of organic bulk-heterojunction solar cells could be increased up to values of more than 9% using a nanoscale interpenetrating network of two materials, a donor and an acceptor. Although this new solar cell technology promises very low production costs there are still major tasks to be worked upon for providing solar electricity on a larger scale.

For a technology breakthrough, the basic understanding of the fundamental processes in organic PV is necessary. This is anything but trivial to obtain due to the fact that the elementary processes take place on 1-20 nm scales within time frames from picoseconds to milliseconds. In addition, all this happens in disordered materials which are more difficult to describe on a quantitative manner than well-ordered, crystalline materials. The project "Morphoso" intended to make a contribution to the improvement in understanding the underlying processes which eventually determine the power output of solution-processed organic solar cells.

The project consortium consisted of three partners from the three countries Sweden, Finland and Germany. The partners were

- a) The group "Biomolecular and Organic Electronics" led by Prof. Olle Inganäs at the Department of Physics at Linköping University in Sweden
- b) The group "Organic Electronics" from Prof. Ronald Österbacka at the Department of Physics and Centre for Functional Materials of the Åbo Akademi University (University of Turku) in Finland
- c) The group "Dye and organic Solar Cells" headed by Dr. Uli Würfel at the Fraunhofer Institute for Solar Energy Systems ISE in Freiburg, Germany

The overall aim of the project consortium was to enhance the understanding of the physical processes taking place in solution-processed organic solar cells and contribute to the process of setting the basis for future improvements and thus pushing organic photovoltaics closer to real applications. We are all convinced that an enduring progress in this field can only be achieved when practical efforts and academic insights are combined in a proper way.

Therefore we combined the expertise of the three partners and exchanged our – sometimes differing – point of views in intensive scientific discussions. This was done either at one of the project meetings which took place regularly at one of the partners' institutions or at international conferences where we met each other. The exchange of ideas among the researchers of our three-national project consortium was regarded as something extremely valuable by all people contributing to the project. Another aspect was that this way people got to know each other and set the basis for some shorter and longer stays in the group of one of the other consortium members. These visits allowed for more and prolonged discussions about the interpretation of experimental data that needs to be understood.

In inorganic crystalline materials used as photoactive material for solar cells the absorption of a photon leads directly to the generation of free charge carriers, an electron and a hole. Although an electron and a hole are also created upon absorption of a photon in the photoactive layer of an organic solar cell they experience a strong binding energy in the range of ca. 0.5eV. This quasi-particle is called an exciton and as it is electrically neutral its transport is governed by diffusion. The thermal energy at temperatures around room temperature (or even at higher temperatures a solar cell would reach on a roof top, i.e. $\leq 85^\circ\text{C}$) is not enough to overcome this binding energy. Therefore a second component is present in the photoactive layer which offers a lower lying energy level for the electron which is called the acceptor. The exciton has to reach the interface between donor and acceptor within its lifetime. If this happens the electron is transferred from the donor to the acceptor on a picosecond-timescale with an efficiency approaching unity. This way free charge carriers are created and

subsequently both charge carriers have to be transported to their respective contact, i.e. the holes in the donor phase and the electrons in the acceptor phase.

In an organic solar cell the morphology of the photoactive layer is crucial for the performance of the device: if the two phases are very finely intermixed all excitons will reach an interface of donor and acceptor within their lifetime and the creation of free charge carriers is very efficient. On the other hand, the high interface area means that a charge carrier is always located very near to the other phase during its path toward the electrode. This leads to high(er) recombination which reduces especially the fill factor and thus the power output. On the other hand a coarse morphology will certainly improve the transport properties and thus reduce the recombination rate but will at the same time reduce the generation of free charge carriers because a certain fraction of the excitons will not be able to reach the donor/acceptor interface before they recombine. Of course the situation is far more complex and the morphology depends on layer thickness and process parameters like annealing, concentration and solvent.

The aim of our efforts was to achieve a deeper understanding of the correlation between the morphological characteristics of the photoactive layer and its electro-optical properties which finally determine the device performance of an organic solar cell or module to a large extent. Our approach was to establish an evaluation platform that integrates device-modelling, -processing and characterisation to find the theoretical and experimental correlation between the thin film process, its nanomorphology and the generation and transport of charge carriers in the finished devices.

In the beginning an inter-laboratory round robin study was performed and it confirmed that the measurements of the three project partners are well comparable.

Overview over the different work packages in the project

Work package 1: Modelling

This work package was divided into two parts, namely

- a) Modelling of the optical absorption under various angles of incidence
- b) Electrical modelling: Development of continuum models, extension from 1D to 2D

a) Optical modelling has been carried out using FEMLAB and a RCWA (rigorous coupled wave analysis) approach. In organic solar cells the thickness of each layer is typically below but in the same order of magnitude of the wavelength of the incoming radiation. For this reason interferences between waves being reflected at the various interfaces of the different layers have to be taken into account explicitly in order to determine the spatial generation profile correctly. The objectives for the optical modelling have been met and a journal paper has been published on the impact of changes of the angle of incidence and in the spectral composition on the maximum attainable current of an organic solar cell with a V-shaped geometry: B. Viktor Andersson, Uli Würfel and Olle Inganäs: "Full day modelling of V-shaped organic solar cell", *Solar Energy*, **2011**, 85, 1257.

b) First, a 1D electrical model was developed with the commercial semiconductor simulation tool Sentaurus Device from Synopsys. The tool uses a finite volume approach to solve the differential equations for drift and diffusion self-consistently with the Poisson equation. Fermi statistics were used for electrons and holes. The bulk-heterojunction was modelled as a single effective semiconductor (blend layer) with an electron transport level (ETL) corresponding to the LUMO of the acceptor and a hole transport level (HTL) corresponding to the HOMO of the donor phase. This approach has been employed by various theoretical studies on bulk-heterojunction organic solar cells. Further parameters are: the densities of states, the mobilities of electrons and holes, and the dielectric permittivity. For sake of simplicity, no trapping effects or impurities were considered, i.e., states for electrons and holes were restricted to the bands (transport levels) only. The effective semiconductor was sandwiched between two (metal) contacts, which were characterized by their work functions and the surface recombination velocities of electrons and holes.

Numerical simulations of the electrical processes are contained in a joint publication on morphology and transport: L. M. Andersson, C. Müller, B. H. Badada, F. Zhang, U. Würfel, O. Inganäs: "Mobility and fill factor correlation in geminate recombination limited solar cells", *Journal of Applied Physics*, **2011**, 110, 024509.

In the course of the project the model has been extended to represent explicitly the donor/acceptor network of the photoactive layer. This extended model is a real 2D description of the organic solar cell. In contrast to the 1D model with an effective semiconductor it contains a quantitative description of the excitons. This includes their generation, their transport towards the donor/acceptor interface (as only there they can be dissociated) and their recombination, i.e. decay.

In another publication which will be submitted soon (by Felix Stelz and Uli Würfel) a detailed comparison is drawn between the modelling of the electrical processes in 1D and 2D. In addition an investigation of the influence of doping on the photovoltaic performance is presented. In the 1D approach with an effective semiconductor only one type of doping can be considered. In contrast, the 2D model allows for doping both the acceptor and the donor.

Work package 2: New cell architectures

Nano-, micro- and millistructured solar cells for better light trapping were to be developed.

In order to harvest as much of the useful part of the solar spectrum as possible we worked on innovative cell architectures which make use of light trapping structures. On the macroscopic scale in the mm-cm range this was developed as a folded V-shape geometry. The experimental efforts were accompanied by the development of a 2D optical modelling of organic photovoltaic devices (OPV) to predict the absorptance of planar and folded OPVs, at normal incidence and all along a solar day. Predictions for tandem OPVs in folded geometry essentially establish the folded geometry as a viable competitor to the planar multilayer stack OPVs. We have built multifolded cells, with four devices in series connection.

The organic solar cells on substrates structured in the millimetre range showed a clear light trapping effect as had been reported earlier already:

Kristofer Tvingstedt, Viktor Andersson, Fengling Zhang, and Olle Inganäs: "Folded reflective tandem polymer solar cell doubles efficiency", *Applied Physics Letters*, **2007**, *91*, 123514.

This topic was therefore tracked intensively and two more papers were published. The first one was:

Yinhua Zhou, Fengling Zhang, Kristofer Tvingstedt, Wenjing Tian, and Olle Inganäs: "Multifolded polymer solar cells on flexible substrates", *Applied Physics Letters*, **2008**, *93*, 033302.

The second one was:

B. Viktor Andersson, Nils-Krister Persson, and Olle Inganäs: "Comparative study of organic thin film tandem solar cells in alternative geometries", *Journal of Applied Physics*, **2008**, *104*, 124508.

Another approach was to use substrates structured in the μm -range. This implied the use of innovative evaporation techniques and we were able to demonstrate fully operating cells on these kind of pre-structured plastic substrates. Again, these experimental studies have been complemented by 2D optical modelling.

The objectives have been met but it has to be stated that the concepts nano- and microstructured substrates for light trapping failed to deliver higher short circuit currents compared to the normal planar setup. Although the light trapping effect could be demonstrated by numerical simulations we were not able to reproduce it experimentally. One of the reasons was the rather poor coating quality on the substrates structured in the nano- and micrometre range. This led to very nonuniform layer thicknesses which are known to be detrimental for the photovoltaic performance.

Work package 3: Investigation of process parameters

Åbo Akademi University was able to demonstrate a roll-to-roll printed device processed by a reverse gravure coating technique. P3HT:PCBM bulkheterojunction solar cell devices were made using the reverse gravure (RG) coating technique for the hole-injecting layer (PEDOT:PSS) and the active layer (P3HT:PCBM). The device performance was compared to a spin coated device, both devices showed similar characteristics. The reported efficiency under AM 1.5 solar spectrum was 0.74 %.

The devices were made on ITO covered plastic substrates onto which the PEDOT:PSS layer was RG coated. The device was then heated to remove water from the film. After this the P3HT:PCBM layer was coated, also by the RG technique. The devices were then heat treated at 120°C for 15 minutes after which LiF and Al contacts were thermally evaporated.

Reverse gravure coating is a roll-to-roll technique and the coating of the PEDOT:PSS and P3HT:PCBM layers is a significant step towards all printed roll-to-roll manufactured solar cells. The initial results were published in the following article, but due to reduced funding for the Åbo Akademi group, the work had to be dropped.

D. Tobjörk, H. Aarnio, T. Mäkelä, and R. Österbacka: "Roll-to-Roll Fabrication of Bulk Heterojunction Plastic Solar Cells using the Reverse Gravure Coating Technique", *Materials Research Society Symposium Proceedings*, **2008**, *1091*, 1091-AA05-45.

At Fraunhofer ISE experiments were carried out with a newly purchased lab coating unit. Slot die coating proved to be an appropriate method to deposit the photoactive P3HT:PCBM layer from solution as well as the conductive PEDOT:PSS layer for hole transport. Although no fully functional modules were fabricated in the

framework of this project at Fraunhofer ISE the coating quality was good. The method used was sheet to sheet based, i.e. the slot die coating head had to be moved over the substrate. Nevertheless, this coating technique is roll-to-roll compatible which underlines the significance of the results.

Work package 4: Characterisation of morphology

To visualize the morphology in the volume of the photoactive layer 3-D electron tomography was carried out. These pictures give a valuable insight in how the two materials are aligned to each other. As already discussed above, this is of outermost importance for the efficiency of bulk heterojunction solar cells. Also here, the results were published in a peer reviewed journal:

Sophie Barrau, Viktor Andersson, Fengling Zhang, Sergej Masich, Johan Bijleveld, Mats R. Andersson and Olle Inganäs: "Nanomorphology of Bulk Heterojunction Organic Solar Cells in 2D and 3D Correlated to Photovoltaic Performance", *Macromolecules*, **2009**, 42, 4646.

We have established electron tomography as the premium method to image the nanostructure of OPV materials. Until very recently it was only possible to assess the surface of the photoactive blend layers in the bulk-heterojunction solar cells, mostly by atomic force microscopy (AFM). With the new method of electron tomography we are now able to observe the full 3D nanostructure by reconstruction methods. This enables to get important information about the underlying nanomorphology which has a great impact on the performance of the device. We have correlated processing conditions to the resulting nanostructure, and to the photocurrent generation within devices.

Work package 5: Optical and electrical characterisation

This work package was executed in all the three groups intensively. A characterisation technique applied by all the partners in the consortium was CELIV, short for carrier extraction by linearly increasing voltage. This technique allows insight into the transport of the charge carriers and delivers a fingerprint of their mobility.

Charge-carrier transport and recombination in thermally treated and untreated bulk-heterojunction blends of poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl) propyl-1-phenyl-[6,6]-methanofullerene (PCBM) have been measured using various electro-optical techniques. In untreated films, the recombination is close to Langevin-type with electric-field-dependent quantum efficiency, consistent with the typically observed Onsager-type generation. Heat treated P3HT/PCBM solar cells on the other hand, show greatly reduced carrier recombination compared to what is typically expected in low-mobility materials and electric-field-independent carrier generation. The reason for the improved performance of the heat treated solar cells can in part be explained by the formation and enhancement of lamellar structure in regioregular P3HT, which has a large effect on the efficiency, carrier transport, and recombination of photogenerated charge carriers. However, much of the physics leading to higher charge generation efficiency in the heat treated blends is still unclear.

In this work we present UV photoelectron spectroscopy measurements on both regiorandom- and regioregular P3HT, and interpret the results using the Integer Charge Transfer model. We show that spontaneous charge transfer from P3HT to PCBM occurs after heat treatment of P3HT:PCBM blends (see Figure 1). The resulting formation of an interfacial dipole is suggested as an explanation to why geminate recombination is reduced and charge generation is increased in regioregular-P3HT:PCBM blends after heat treatment. Extensive photoinduced absorption measurements using both above and below-bandgap excitation light were presented, in good agreement with the suggested dipole formation in the following journal paper:

Harri Aarnio, Parisa Sehati, Slawomir Braun, Mathias Nyman, Michel P. de Jong, Mats Fahlman, and Ronald Österbacka: "Spontaneous Charge Transfer and Dipole Formation at the Interface Between P3HT and PCBM", *Advanced Energy Materials*, **2011**, 1, 792–797.

To determine how bimolecular recombination is affected by the thermally induced interfacial dipoles, intensity dependent photoinduced absorption measurements were performed before and after heat treatment of the P3HT:PCBM films. In the regioregular films there was no significant difference in the bimolecular recombination coefficient before and after heat treatment. We thus conclude that the main effect of the interfacial dipoles is a reduction of the initial geminate recombination of separated electron-hole pairs at the P3HT:PCBM interfaces.

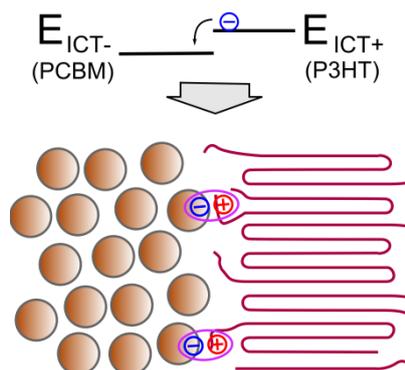


Figure 1: Schematic view of the spontaneous transfer of an electron from the positive integer charge transfer state E_{ICT+} of P3HT to the negative integer charge transfer state E_{ICT-} of PCBM. This happens as a result of heat treatment, and leads to dipole formation at the P3HT:PCBM interface.

The interface dipole, or charge-transfer state is also causing the formation of back-ground charges by the probe-light in the combined electro-optical set-up scheme that was being developed in the project. Care must be taken, when performing transient photo-induced absorption spectroscopy, since the probe-light is also generating charge carriers.

In order to study the dark extraction of charges CELIV measurements have been performed of P3HT:PCBM devices with various metal contacts. Measurements done on solar cell devices (ITO/PEDOT/P3HT:PCBM/LiF/AI) show that charges can be extracted without light excitation when approaching flat band conditions. In order to discern whether the charges are due to charge injection due to the applied offset voltage or due to some charge transfer at the P3HT:PCBM interface, devices using the same metal as both top and bottom contacts were studied. Both Al:Al (electron dominated transport) and Au:Au (hole dominated transport) show dark extraction of charges. By using a metal equally blocking for both electrons and holes (Sn:Sn) little or no charges were detected as can also be seen in Figure 2. In addition it is seen that charges extracted by the voltage pulse are regenerated by a current backflow into the device. It is concluded that the charges arise from charge injection at the contacts due to Fermi level pinning. The results have been presented in the following contribution:

Mathias Nyman, Fredrik Pettersson, Ronald Österbacka: "Origin of equilibrium charges in poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester solar cell devices", *Chemical Physics*, **2012**, <http://dx.doi.org/10.1016/j.chemphys.2012.02.023>.

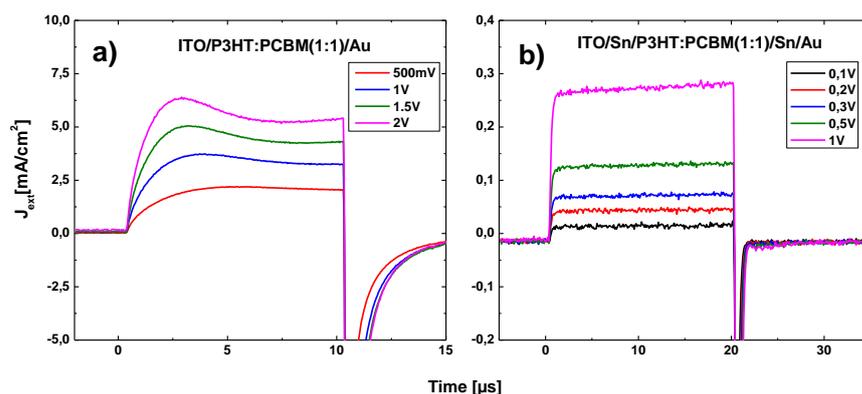


Figure 2: CELIV current transients with different extraction voltages for a) an ITO/P3HT:PCBM(1:1)/Au device and b) an ITO/Sn/P3HT:PCBM(1:1)/Sn/Au device.

Work Package 6: Tests of long term stability and determination of the degradation mechanisms

Even if the efficiency of organic photovoltaic devices can be brought up to a competitive level and cost reduction could be realized by means of efficient continuous manufacturing processes (roll-to-roll), there is still the issue long term stability which needs to be addressed. For most applications a lifetime of at least 2-5 years is indispensable. If one thinks of power generation such as roof top installations or building integrated photovoltaics lifetimes of less than 10 years are unrealistic and lifetimes of more than 20 years should be met. As it is known organic materials are subject to severe instability when exposed to oxygen or water vapour, especially in conjunction with UV- and/or visible irradiation and/or higher temperatures. Two main tasks were to be fulfilled here. First, appropriate encapsulation materials and methods have to be identified which can guarantee reproducibly a reasonable lifetime. Second, insight into the specific nature of the degradation processes has to be gathered. This includes investigating in which way the physical properties of the different parts of the device are altered and how this influences the output parameters of the solar cell.

The investigation of the long term stability of encapsulated organic solar cells was performed by exposing them to different aging conditions: continuous illumination, UV radiation and heat. In the standard architecture ITO/PEDOT:PSS/Blend/LiF/Al, the Al electron contact can oxidize quickly and cause a dramatic decrease of the cell performance due to the built-up of an insulating Aluminium-Oxide layer at the interface to the photoactive blend layer. As we were more interested in the stability of the photoactive layer itself we carried out all long term stability experiments with cells comprising the inverted architecture: Cr/Al/Cr/Blend/PEDOT:PSS/Au-grid. Cells encapsulated with an epoxy glue between two glass plates as well as cells on glass substrates with a flexible barrier foil on top were investigated. After testing a number of different encapsulants we found a good combination which provided reliable protection against oxygen at least at temperatures up to 60°C. The best results were achieved under continuous illumination. A sulphur plasma lamp was used and has to be stressed that it exhibits a lower UV content than the solar spectrum. The intensity was ca. 1000 W/m². Under this intensity, a duration of 1000 hours equals the amount of radiation impinging on middle Europe in one year. Of course this is restricted to the number of photons and does not consider any possible thermal or humidity stress or things alike. But it does account for the number of "photovoltaic cycles", i.e. the generation of an exciton by absorption of a photon, the diffusion of the exciton to the donor/acceptor interface, the dissociation of the exciton, i.e., the transfer of an electron into the acceptor, the subsequent transport of the charge carriers through their respective phase toward the contacts and, finally, their collection at the electrodes. The best data is represented in Figure 3.

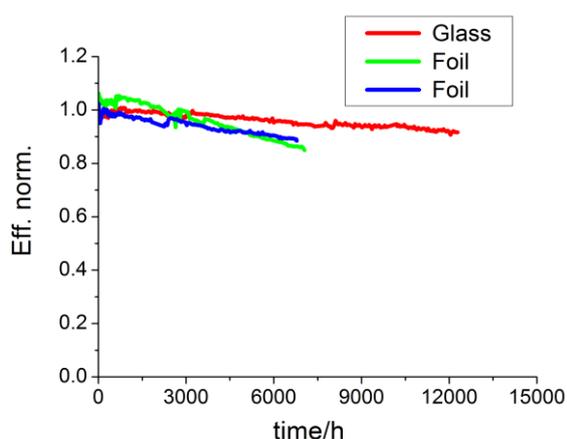


Figure 3: Normalized values of the efficiency of three devices under continuous illumination. One was encapsulated between two glass plates the other two were sealed with a flexible barrier foil. The intensity of the illumination was 1000 W/m². 1000 hours correspond roughly to the radiation dose impinging on middle Europe in one year.

Although the cells are not fully stable the glass/glass based has still more than 90% of the initial efficiency after more than 12000 hours. This shows that the intrinsic stability of the materials is given provided that contact with oxygen and water vapour is impeded.

Additionally, the degradation processes of APFO3:PCBM devices were studied using several measurement techniques. Devices fabricated at Fraunhofer ISE in Freiburg, Germany were subjected to accelerated aging in air under simulated sunlight. The devices were then sealed and sent to Turku, Finland for characterization. The results show significant bleaching of the active layer as well as reduced mobility and recombination caused by

the aging. The work was submitted for publication: Mathias Nyman, Harri Aarnio, Sebastian Mühlbach, Uli Würfel and Ronald Österbacka: "The Effect of Degradation on the Active Layer in APFO3:PCBM Solar Cells", submitted to *Elsevier Energy Procedia*.

In order to elucidate the nature of the degradation processes taking place and how they are influencing the important physical properties we carried out a number of experiments in which non-encapsulated cells were exposed to controlled ageing conditions. We constructed a flow cell with which we could expose the solar cell either to dry oxygen, to nitrogen saturated with water vapour or to pure nitrogen. At the same time, the cell was illuminated with a standard intensity of approx. 1000 W/m². We found that the simultaneous exposure to oxygen and light had the most severe effect on the lifetime of the organic solar cell. For cells in the so-called standard configuration, i.e. glass/ITO/PEDOT:PSS/Blend/LiF/Al, an oxidation of the Aluminium electron contact leads to a (comprehensible) breakdown of the device performance after 35-45 hours. But even before this happens we could detect a doping effect in the photoactive layer by means of impedance spectroscopy. This doping effect is detrimental for the device performance as it reduces the current. Employing an inverted layer sequence, i.e. Cr/Al/Cr/Blend/PEDOT:PSS/Au-grid, confirmed this observation. The effect of a reduced output current for a doped photoactive layer could also be reproduced by numerical simulations. But in contrast to the experimental data the simulation results showed an increase of the forward current when the doping concentration was raised. This led us to take into account the mobility of the charge carriers as well as there was also one publication out that reported a reduction of hole mobility in P3HT after exposure to oxygen. When the mobility was decreased we no longer saw an increased forward current in our simulated curves. For this reason we performed CELIV (current extraction by linearly increasing voltage) measurements with cells exposed to oxygen. We could see two things: first, with increasing time of exposure the extraction current increased strongly. This could easily be explained with the larger concentrations of charge carriers present in the dark when the semiconductor gets doped. Second, we saw a decrease in the charge carrier mobility. This way our experimental observations and our theoretical description were in good agreement.

This work was presented in two oral contributions, one at the MRS conference in San Francisco, USA, April 2010 and another one at the OPV Stability Summit in Golden, Colorado, December 2011.

Conclusions

Who has benefited from the results?

It is always difficult to define exactly the success of a scientific project and therefore also to answer the question above since much of the project outcome are developments and insights which very often cannot be quantified easily. It has to be stressed here once more that it is never a single project which revolutionizes the progress in a certain area of research but we all know that new technical products are a consequence of intensive effort in research and development over a longer period of time. Seen in this context the project "Morphoso" is an important contribution to the progress in the field of organic photovoltaics on its way to become a reliable source of renewable energy. It has enabled considerable skill enhancement for young researchers, has fostered exchange of people as well as ideas and views in intensive scientific discussions and has set a base for further cooperation between institutions from different countries. It was the members of the consortium who have benefited from these things. From the progress which was announced through publications in peer-reviewed journals the whole OPV research community has benefited.

Recommendations

Organic Photovoltaics has still to overcome severe obstacles before being able to contribute significantly to the production of renewable energy. A continuation of research funding through the authorities on a national and European level is therefore of outermost importance. Collaborations between scientists from different groups in different countries is one of the key aspects in funding on a European level as it can be seen in many examples that progress occurs in small steps which often do not all take place in the same group. Close ties between the research groups can therefore bring together different types of expertise and thus accelerate developments. On a technical level, 3-D electron tomography was proven to be an appropriate tool to visualize the morphology of the photoactive layer of bulk-heterojunction solar cells on the 10nm level. One possible next step is to parameterize those nanomorphologies in order to use them as input geometries for quantitative electrical modelling. This leads of course to a considerable increase in the required computational power but could help to foster our understanding of organic solar cells.

Another important point is that new materials are needed to further enhance the efficiency of organic photovoltaic devices. It is important to bring together synthetic chemists and device physicists in order to shorten the time for the innovation cycles.

The topics which were started in the N-INNER Morphoso project will of course not be abandoned after its end. New funding sources have to be identified and collaborations will be renewed.

Acknowledgement

The member of the consortium would like to express their gratitude to N-INNER for the funding of our joint project.