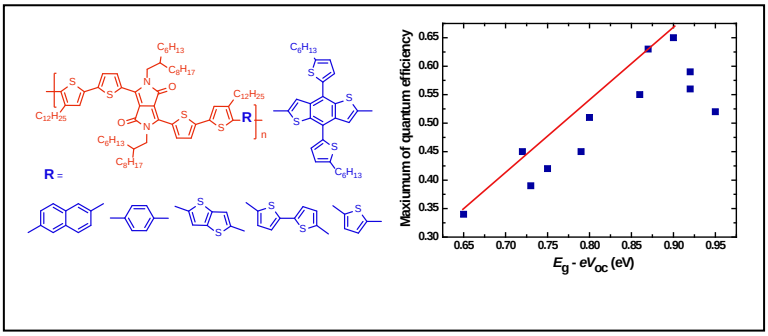
1. WP1: Synthesis and characterization of novel materials and scale-up of materials

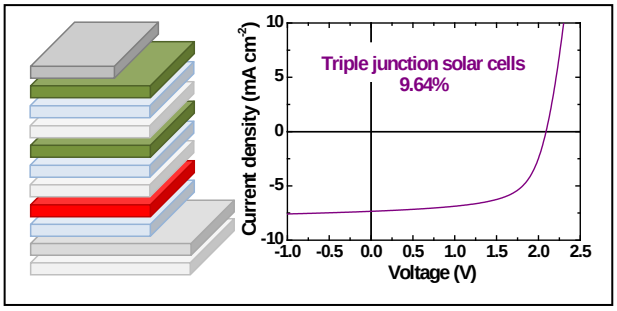
1.1. Enhancing the photocurrent in diketopyrrolopyrrole based polymer solar cells via energy level control

A series of diketopyrrolopyrrole (DPP) based small band gap polymers has been designed and synthesized by Suzuki or Stille polymerization for use in polymer solar cells. The new polymers contain extended aromatic conjugated segments alternating with the DPP units and are designed to increase the free energy for charge generation to overcome current limitations in photocurrent generation of DPP-based polymers. In optimized solar cells with [6,6]phenyl-C_{71}-butyric acid methyl ester ([70]PCBM) as acceptor, the new DPP-polymers provide significantly enhanced external and internal quantum efficiencies for conversion of photons into collected electrons.. This provides short-circuit current densities in excess of 16 mA cm^{-2}, higher than obtained so far, with power conversion efficiencies of 5.8% in simulated solar light. We analyze external and internal photon to collected electron quantum efficiency for the new polymers as function of the photon energy loss, defined as the offset between optical band gap and open circuit voltage and compare the results to those of some of the best DPP-based polymers solar cells reported in the literature. We find that for the best solar cells there is an empirical relation between quantum efficiency and photon energy loss that presently limits the power conversion efficiency in these devices.



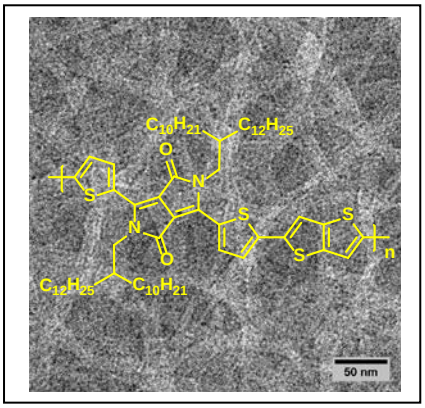
1.2. Efficient Tandem and triple junction polymer solar cells

We demonstrated tandem and triple junction polymer-fullerene solar cells with PCEs of 8.9% and 9.6%. The multi-junction cells use a new small band gap semiconducting polymer, PMDPP3T, with absorption in the near infrared region up to 960 nm. Compared to the single junction cells with the same layer thickness, the efficiency of the optimized tandem and triple junctions has increased by as much as 50-60% by using highly complementary absorber layers. The 1+2 triple junction architecture further enhances the performance of the tandem by exploiting the excess current generation of the non-limiting sub cell. The 1+2 configuration seems a valuable strategy to enhance the efficiency of tandem polymer solar cells with unbalanced sub cells.



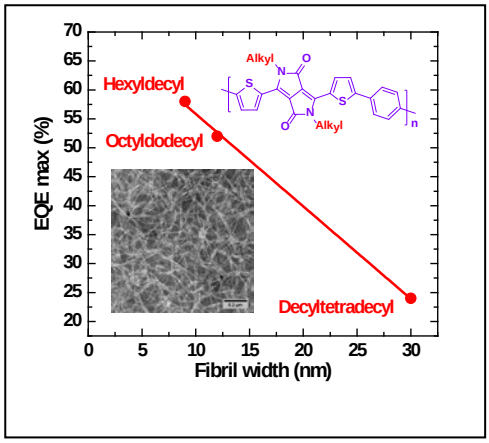
1.3. Efficient small band gap polymer solar cells with high fill factors for 300 nm thick films

We have developed a high molecular weight polymer, DT-PDPP2T-TT that has high hole carrier mobility (0.8 $cm^2 V^{-1} s^{-1}$) and allows making efficient solar cells for thick (> 200 nm) active layers. Blends of DT-PDPP2T-TT with [60]PCBM and [70]PCBM give maximum power conversion efficiencies of 6.0% and 6.9% for films of 210-220 nm thickness. Bimolecular recombination is small as a result of the high charge mobility and a nanomorphology in the film that consists of frequently interconnecting and crossing crystalline fibrous structures with lengths of hundreds and widths of a few tens of nanometers. Achieving high fill factors and efficiencies in organic solar cells with thick films, not only requires donor and acceptor materials with high hole and electron mobilities, but also a morphology that provides efficient percolating pathways for charges together with an essentially field-independent charge separation. The high efficiency for thick layers and its small sensitivity to variations in thickness make DT-PDPP2T-TT:PCBM films a promising candidate for large-scale industry printing applications of polymer solar cells.



1.4. Effect of the fibrillar microstructure on the efficiency of high molecular weight diketopyrrolopyrrole based polymer solar cells

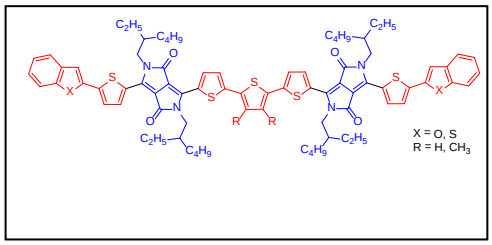
For high molecular weight PDPPTPT the PCE can be increased from ~3.2% to 7.4% in blends with [70]PCBM by decreasing the length of the solubilizing side chains from decyltetradecyl, via octyldodecyl, to hexyldecyl. The polymers form an extended semicrystalline fibrillar network in blends with [70]PCBM and the width of the fibrils correlates with the external quantum efficiency of photon-to-electron conversion. Blends with narrow (≤ 12 nm) fibrils, in which excitons are more likely to diffuse to the [70]PCBM interface afford much higher external quantum efficiencies and provide improved PCEs than blends with wider fibrils. Photoluminescence quenching studies provide qualitative support for this mechanism in which the performance is limited by exciton



dissociation. The results demonstrate that tuning the length of the side chains of conjugated polymers is critical for achieving high photovoltaic response. The main reason for this is that the side chains significantly affect the morphology that is formed when casting the blend films.

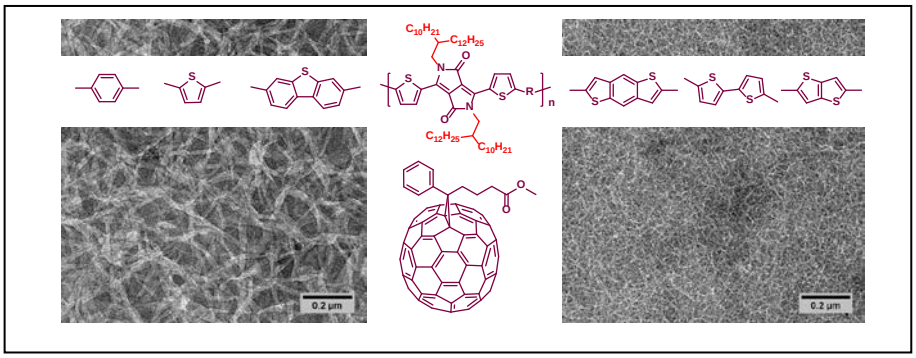
1.5. Effect of structure on the solubility and photovoltaic properties of bis-diketopyrrolopyrroles molecules

Four structurally related molecules consisting of two diketopyrrolopyrrole (DPP) units linked via a terthiophene aromatic π-bridge were synthesized and blended with [70]PCBM in solution-processed small-molecule organic solar cells. The four bis-DPP molecules possess nearly identical optical band gaps and energy levels, but their solubility differs significantly. The processing conditions, such as solvent, processing additive, and total concentration have a significant effect on the device performance. The bis-DPP derivative with the lowest solubility gives the highest power conversion efficiency (PCE) of 4.6% when blended with [70]PCBM, compared to 3.6–4.0% for the other three. The results illustrate that subtle changes and tailoring of the molecular structure can strongly affect solubility and, in turn, the processing conditions leading to the optimized device performance and its ultimate PCE.



1.6. Universal correlation between fibril width and quantum efficiency in diketopyrrolopyrrole-based polymer solar cells

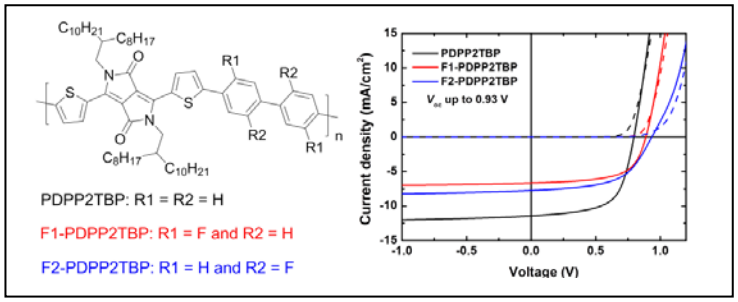
For a series of six diketopyrrolopyrrole (DPP) based conjugated polymers we establish a direct correlation between their external quantum efficiencies (EQE) in organic solar cells and the fibrillar microstructure in the blend. The polymers consist of electron-deficient DPP units, carrying long branched 2'-decyltetradecyl (DT) side chains for solubility, that alternate along the main chain with electron-rich aromatic segments comprising benzene, thiophene, or fused aromatic rings. The high molecular weight DT-DPP polymers were incorporated in bulk heterojunction solar cells with [6,6]-phenyl-C71-butyric acid methyl ester ([70]PCBM) as acceptor. The morphology of the DT-DPP:[70]PCBM blends is characterized by a semi-crystalline fibrillar microstructure with fibril widths between 4.5 and 30 nm as evidenced from transmission electron microscopy. A clear correlation is found between the widths of the fibrils and the EQE for photon to electron conversion. The highest EQEs (60%) and power conversion efficiencies (7.1%) are obtained for polymers with fibril widths less than 12 nm. For blends with fibrils wider than 12 nm, the EQE is low



because exciton diffusion becomes limiting for charge generation. Interestingly, the correlation found here matches with previous data on related DPP-based polymers. This suggests that for this class of materials the relation between fiber width and EQE is universal. The fiber width is largely correlated with the solubility of the polymers, with less soluble DPP-polymers giving narrower fibrils.

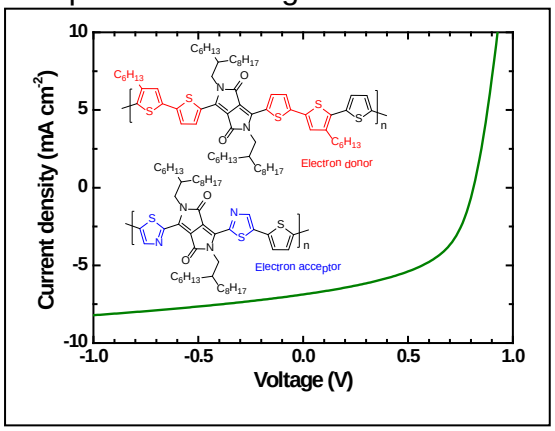
1.7. Wide band gap diketopyrrolopyrrole-based conjugated polymers incorporating biphenyl units applied in polymer solar cells

Wide band gap conjugated polymers based on electron deficient diketopyrrolpyrrole units incorporating biphenyl units were successfully designed and synthesized. Organic photovoltaic devices based on these polymers achieve power conversion efficiencies of 5.7% with spectral response to 760 nm. Further structure engineering by adding fluorine atoms on the biphenyl units increases the V_{OC} up to 0.93 V, but results in a somewhat lower efficiency of 4.1%. These results represent a successful example of incorporating biphenyl units in wide band gap conjugated polymers for polymer solar cells. Additionally, the results show that non-planar biphenyl units in conjugated polymers are not detrimental and in fact provide higher performance compared to planar and fused biphenyl systems such as fluorene and carbazole.

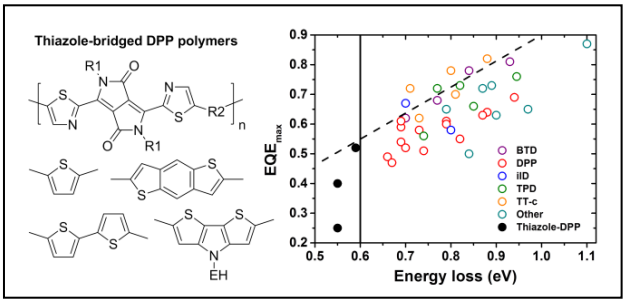


1.8. Polymer solar cells with diketopyrrolopyrrole conjugated polymers as electron donor and electron acceptor.

A new n-type acceptor polymer PDPP2TzT based on diketopyrrolopyrrole has been designed and synthesized. The polymer features low lying HOMO and LUMO energy levels, high electron mobility, and broad absorption up to 850 nm. When the new acceptor was blended with PDPP5T as electron donor polymer, a PCE of 2.9% was obtained after optimizing the solvent composition with a processing additive to adjust the phase separation. A higher PCE was found in inverted devices than in regular devices, which is due to enhanced photon absorption and charge collection in the inverted device. From a molecular design perspective we note that the donor and acceptor polymer are very much alike. The donor and acceptor DPP polymers merely differ by the simple interchange of electron rich bithiophene units by electron deficient thiazole units along the chain. The results show that DPP polymers form a interesting new class of acceptor n-type polymers, which approach the performance of perylenediimide or naphthalenediimide acceptor copolymers.

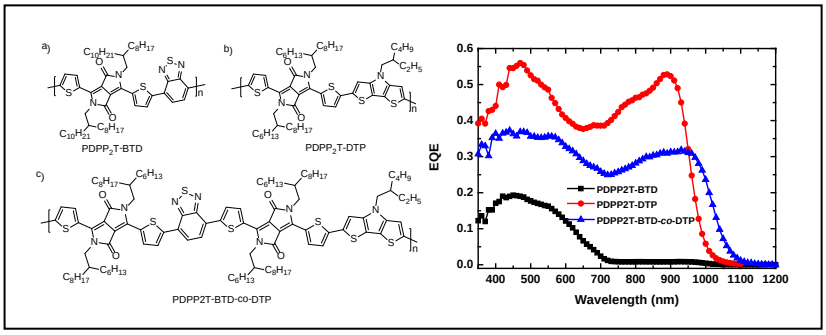


1.9. High quantum efficiencies in polymer solar cells at energy losses below 0.6 eV



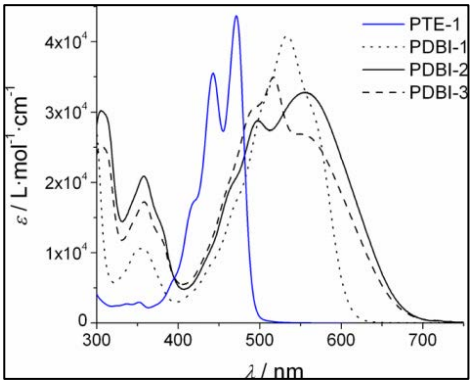
One of the main reasons that the performance of PSCs is low compared to the best inorganic solution processed thin film solar cells, such as e.g. perovskite solar cells, is the significant loss in energy of the open-circuit voltage (Voc) relative to the optical band gap (Eg). We successfully designed and synthesized several DPP-polymers bridged with thiazole for polymer solar cells. The photovoltaic devices based on these polymers gave high EQE sup to 0.52 and PCE up to 5.6% with low energy loss < 0.6 eV. The results indicate the possibility to further enhance the efficiencies limit by reducing the energy loss for polymer solar cells.

1.10. Small bandgap conjugated polymers with binary electron-deficient units for polymer solar cells



Efficiencies of organic solar cells can be further increased via tandem or triple junction structures, in which two or three photo-active layers with compensated absorption spectra were stacked in one cell with series connection. It has predicted that by applying different conjugated polymers with broad absorption from visible light to near-infrared region above 1000 nm, the conversion efficiencies of triple junction solar cells can achieve 17% due. For this, it will be important to explore the conjugated polymers with absorption extending to 1000 nm that can serve as the smallest band gap component is such triple cells. For this goal a new conjugated polymer with binary electron deficient units of diketopyrrolopyrrole and benzothiadiazole was designed. The energy level and absorption spectra of the polymer were finely tuned. The new polymer showed relatively high open-circuit (0.52 V) and a PCE of 3.7% with a photo-response up to 1050 nm.

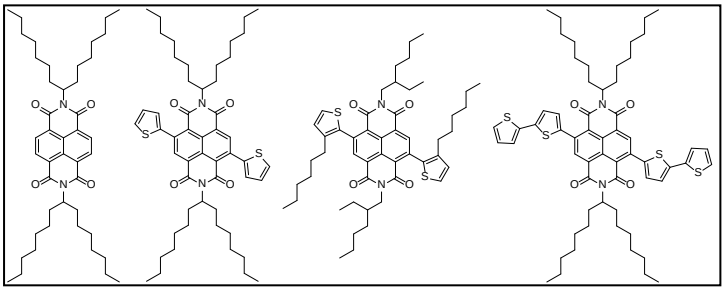
1.11. Perylene diester benzimidazoles and their polymers as acceptors



The fundamental interest was to extend the absorption of perylenebisimides (PBIs) to longer wavelength region. We developed a new soluble asymmetric molecules based on a perylene diester benzimidazole (PDBI) structure in which liquid crystalline organization along with an extended absorption in the red region of visible spectrum was realized. The electron affinity could also be maintained close to that of PBI. A

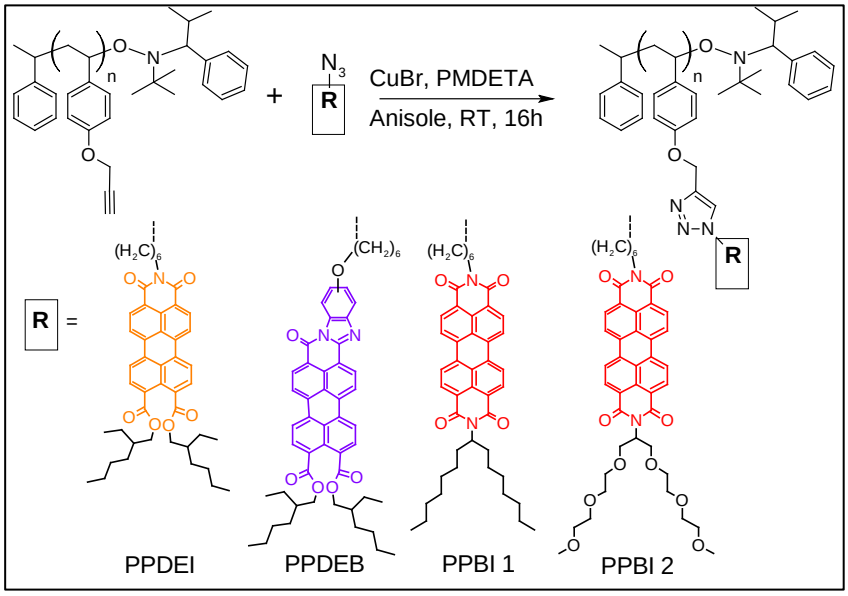
substitution at the bay positions of the perylene core was avoided in all cases in order to maintain planarity and to promote strong π-π interactions. The development of polymeric n-type semiconductors for organic photovoltaics is still challenging and less extensively investigated, compared to the remarkable work done on p-type polymers. Poor processability, insufficient electron mobilities or lack of air stability are present obstacles that have to be overcome in designing novel n-type polymer materials. Within this project, we synthesized novel perylene side chain homopolymers, based on LC perylene diester benzimidazole and perylene diester imide mesogens. Nitroxide mediated radical polymerization (NMRP) was found to be a suitable method for the controlled synthesis of homopolymers and block copolymers based on acrylate monomers with pendant perylene moieties. All the materials were characterized with rtespect to their structure formation, electron transport mobility and^suitability in devices. One of the compounds was synthesized in large scales to be tested in printing of fullerene-free devices.

1.12. Naphthalenediimides as acceptors



A series of low molecular weight naphthalenediimides carrying different thiophene donor units were synthesized from 2,6-dibromonaphthalene dianhydride by imidization and a subsequent Suzuki coupling reaction. The structure-property relationship for these donor-acceptor model compounds was elucidated by a systematic study of the optical and electrochemical properties. The thiophene substituents in the core positions enhance the absorption and influence the HOMO levels towards low band gap energy materials. Thus, the HOMO/LUMO energy gap could be selectively lowered to 1.81 eV by keeping the LUMO energy level constant at -3.7 eV. Owing to the strong absorption in the visible range and suitable HOMO/LUMO levels, this class of donor-acceptor system is highly suited as electron acceptor materials.

1.13. Pendant perylene polymers as acceptors

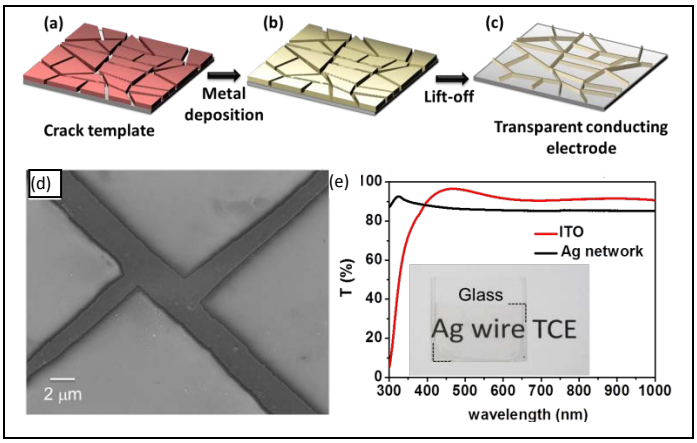


These are side chain polymers carrying perylene diester benzimidazoles (PDBIs), and perylene bisimides (PBIs) as substituents. Four different perylene side chain semiconductor polymers, synthesized by a combination of “click” chemistry and nitroxide mediated radical polymerization (NMRP), are compared in terms of their optical,

electrochemical and charge transport properties. The nature of the solubilizing side chains and the chromophoric π-conjugation system of the pendant perylene moieties are systematically changed. Two poly(perylene bisimide)s with hydrophobic (PPBI 1) and hydrophilic substituents (PPBI 2) are compared with poly(perylene diester benzimidazole) (PPDEB) and poly(perylene diester imide) (PPDEI). Optical properties are investigated by UV/vis and Photoluminescence spectroscopy and charge transport is studied by organic field effect transistor (OFET) and space-charge-limited current (SCLC) measurements. Cyclic Voltammetry is used to estimate HOMO and LUMO levels. The extended π-conjugation system of PPDEB leads to a broader absorption in the visible region compared to PPDEI and the PPBIs. While absorption properties of PPDEB could be considerably improved by varying the perylene core, the charge carrier mobility could be drastically improved by tuning the substituents. Very high electron mobilities of 1×10-2 cm2V-1s-1 were achieved for PPBI 2 carrying oligoethyleneglycol substituents.

1.14. ITO-free Ag-Grid transparent conducting electrodes (TCE)

A big highlight is the realization of a highly transparent, low resistant Ag metal network electrode templated from a cracked polymer thin film and its incorporation in an organic solar cell. This was a joint research work between Bayreuth and Bangalore. The performance of this scalable metallic network is comparable to that of conventional ITO electrode. This is a general approach to replace ITO in diverse thin film devices.



Using the cracked template, Ag metal is deposited by vacuum evaporation and subsequently, the template is washed away in chloroform. Using this method bottom-illuminated inverted photovoltaic cells consisting of poly-3-hexylthiophene (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) were fabricated on a glass substrate with Ag network derived TCE. With optimized ZnO thickness (135 nm) all devices were found to be functioning. Significantly, here all the devices showed uniform performance with average efficiency of 2.26 ± 0.05%. The method developed in this study for TCE and associated OSC fabrication has several merits. Its scope of application can be easily extended to other thin layer devices by varying the template thickness and other parameters in the initial stages of crack template formation. Thus, it is possible to obtain TCEs with different network thicknesses and connectivity and importantly with different metals. Here, Ag was used as a typical example, since the work function is favourable for inverted geometry P3HT-PCBM solar cell. This is a general approach to replace ITO in diverse thin film devices.

2. WP2: Large area device fabrication using printing techniques and characterization

2.1. Large scale processing towards R2R printing – Device design and printing techniques

The main objective of work package 2 was large scale processing of newly developed active layer materials for organic solar cells and fabrication of test devices for lifetime and stability tests. The experiences gained in the laboratory were used for industrialized processes at the project partner Mekoprint.

In the early beginning of the project several ITO-based inverted solar cell and module designs were planned to use for device manufacturing with active areas ranging from 5 to 360 cm^2 that follow the proved Process One procedure with ZnO as electron transport layer, active layer, PEDOT:PSS back electrode and silver as current collector. For laboratory development we designed a new transparent electrode layer stack with huge upscaling potential, which is free from ITO and based on silver grid, PEDOT:PSS, and ZnO (Flextrode substrate).[1] All processes are additive and can be fully printed and coated directly on barrier foil at high speed on our R2R equipment. Our main fabrication methods are flexo printing, slot-die coating and rotary screen printing. The Flextrode substrate can be cut and used for single coating experiments on a mini rollcoater. Hereby only very small amounts of active layer polymers are required, which makes it optimal for testing materials within the Largecells project.

Furthermore we standardized our development platform with an organic solar cell module based on Flextrode and 8 serially connected cells with an active area of ca. 57 cm^2. The complete module as illustrated in Figure 1 and 2 has the size of a typical postcard and is named freeOPV.[2] The processes are very robust and reliable. We achieved competitive efficiency results of > 1.8% for P3HT:PCBM based modules. The fill factors can surpass 60%. The design allows easy testing of new materials on a standardized platform. In the final stage we also produced similar modules entirely free from ITO and silver (Figure 2). [3]

[1] M. Hösel, R.R. Søndergaard, M. Jørgensen, F.C. Krebs, Fast Inline Roll-to-Roll Printing for Indium-Tin-Oxide-Free Polymer Solar Cells Using Automatic Registration, Energy Technology. 1 (2013) 102–107. doi:10.1002/ente.201200029.

[2] Krebs, F. C., Hösel, M., Corazza, M., Roth, B., Madsen, M. V., Gevorgyan, S. A., et al. (2013). Freely available OPV - The fast way to progress. *Energy Technology*, *1*(7), 378–381. doi:10.1002/ente.201300057

[3] G.A. dos Reis Benatto, B. Roth, M.V. Madsen, M. Hösel, R.R. Søndergaard, M. Jørgensen, et al., Carbon: The Ultimate Electrode Choice for Widely Distributed Polymer Solar Cells, Adv. Energy Mater. (2014). doi:10.1002/aenm.201400732.

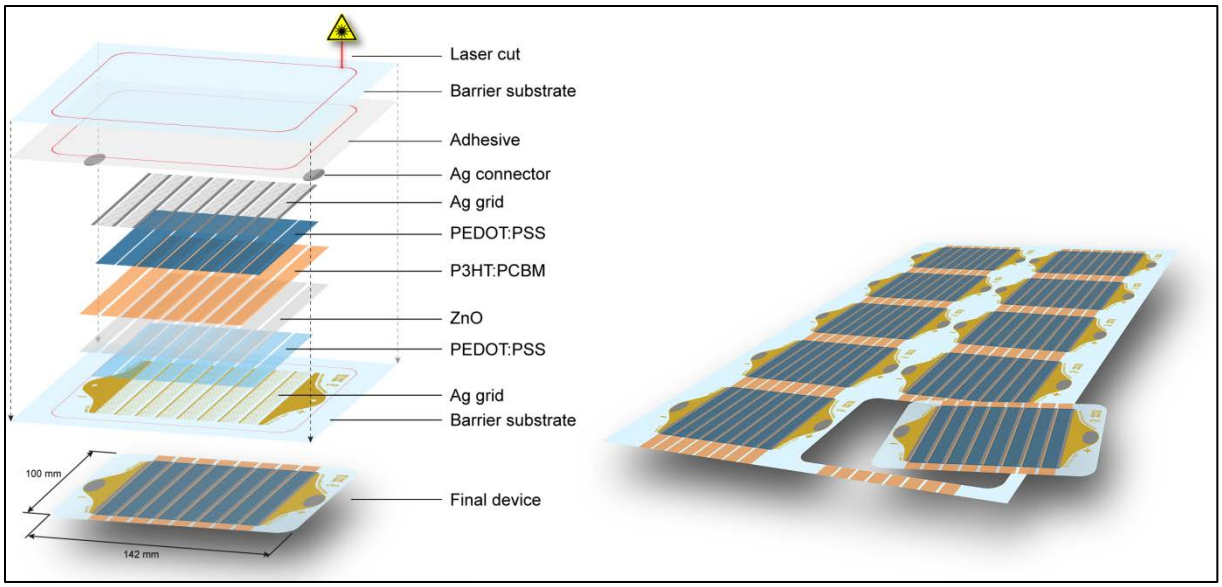


Figure 1. Schematic illustration of the freeOPV layer stack (left) and the laser cut form the R2R processed foil (right).

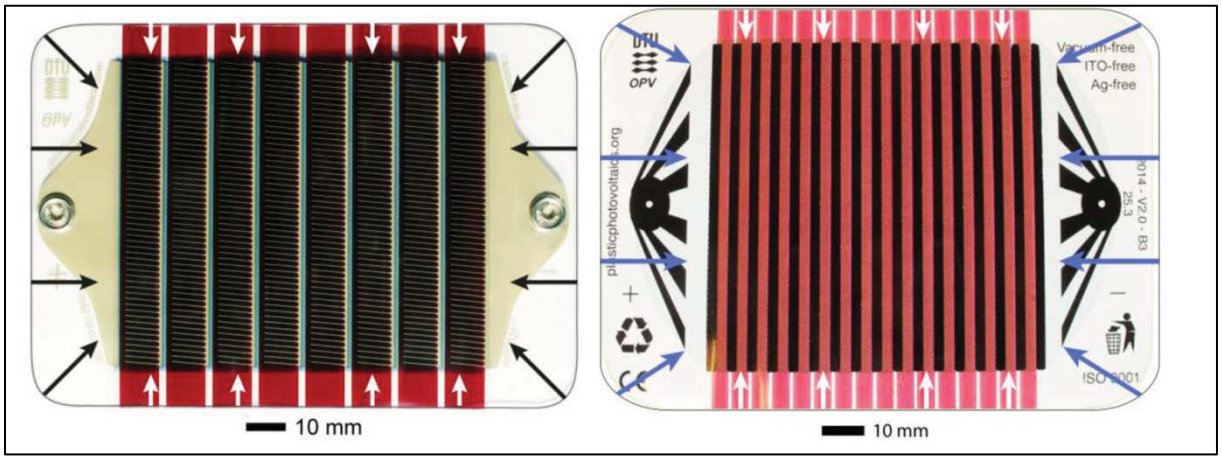


Figure 2 Silver based freeOPV vs. silver-free freeOPV module.

2.2. R2R printing of materials from within the consortium

Material testing has been carried out with PCBM substitute HW655 provided by project partner UBT and polymer P17 provided from TUE. All tests have been performed either R2R or roll-based using miniaturized slot-die heads with very low dead volume. Hundreds of 5.2 cm^2 large cells with P3HT:HW655 on ITO substrate were fabricated and showed very good coating performance but efficiency was low. The performance was 10x lower than the spin coated reference cells but at the same time the area was 10x larger. Nevertheless, we showed that this material could be easily coated under industrial conditions.

The research focus for the material supplied by the project partners was primary on rollcoated cells on Flextrode substrate. The slot-die coating on the lab-scale rollcoater enables a minimized usage of material and opens up a large set of different

testing parameters such as layer thickness, processing temperature, and drying/annealing time. All processing steps were carried out under ambient conditions without evaporation of electrodes. We chose the Flextrode material over ITO-PET for most of the experiments because of its lower embodied energy and its full additive manufacturing workflow.

The low bandgap polymer P17 (PDPPTPT) has been studied under optimized conditions in the TUE laboratories and achieved efficiencies of more than 6% in their labs (spincoating and evaporated electrodes). The rollcoating at DTU was carried in an inverted layer structure on Flextrode substrate whereby hundreds of cells could be fabricated out of just 50 mg polymer. The P17:PCBM active layer was coated from chloroform solution and o-DCB at room temperature in different layer thicknesses. We were able to significantly improve the efficiency to 1.02% by implementing a additional interlayer. The spin-coated cells at TUE were fabricated with evaporated electrodes whereby all cells at DTU were fully printed/coated on larger area under ambient conditions, which is a reason for lower performance.

Nevertheless, DTU achievements and improvements have lead to single cell efficiencies of 3.5 % with PDTSTTz-4 as donor polymer and high fill factors of up to 59%.[4] The cells were fabricated in ambient using the rollcoater and Flextrode substrate that allows an easy upscaling. The advantage of the PDTSTTz-4:PCBM active layer is the good solar cell performance even at large layer thicknesses with an optimum found to be at 420 nm. The same polymer has also been tested on ITO-PET substrate that has been patterned by the project partner Mekoprint in a fully industrial process. It was found that efficiencies close to 3.3% could be achieved. Small modules as shown in Figure 3 with 4 connected stripes and a total area of 8 cm^2 have been produced as well.

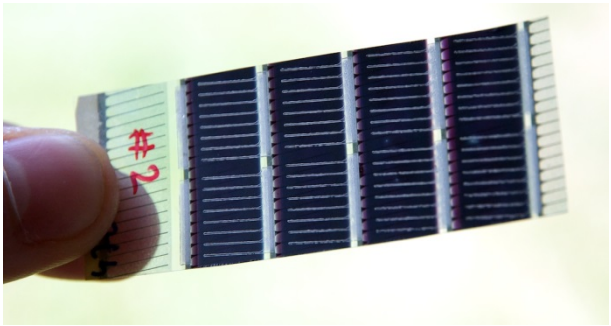


Figure 3. Solar cell module with 4 serial connected stripes and an active area of 8 cm^2.

The best performing module (Figure 9) had an efficiency of 3.3% and can be manufactured with a good reproducibility and efficiencies. The record efficiency of 3.82% on a 2-cell module was achieved using proprietary polymers and $PC_{70}BM$ as acceptor.

It should be noted that *all* processes were solution-processed under ambient atmosphere with long drying cycles, elevated temperatures and ITO-free printed electrodes. In principle all high efficient record cells presented so far in the literature are

[4] Helgesen, M., Carlé, J. E., & Krebs, F. C. (2013). Slot-Die Coating of a High Performance Copolymer in a Readily Scalable Roll Process for Polymer Solar Cells. *Advanced Energy Materials*. doi:10.1002/aenm.201300324

manufactured on ITO glass substrates using spincoating and evaporated electrodes under optimized atmospheres. Their active area is in the range of square millimeters and a direct transfer to large scale processing is not easy or not possible at all.

The fabrication experience and knowledge gathered in the Largecells project also helped to fabricate tandem solar cells with up to 12 layers.[5] in a rollcoating process under ambient conditions. All devices are fabricated on ITO-free Flextrode substrate. The efficiency was up to 1.33% under double side illumination in a mirror setup. Dark storage lifetime tests and bending tests show no significant difference to single junction cells.

For patterning ITO substrates Mekoprint has optimized their industrial screen printing process in several ways. A completely new machine layout ensures a minimum of scratches and cracks on each side of the film - both the visual front PET side and the functionally important ITO side with the transparent electrode. A new type of etch resist has been implemented to significantly lower the amount of UV light power used to cure the resist when patterning. This result in a low development of heat during the curing process and thereby a more stable substrate and overall process. A photograph of the patterned ITO-PET is shown in Figure 4 and consists of a modified version of the freeOPV electrode layout.

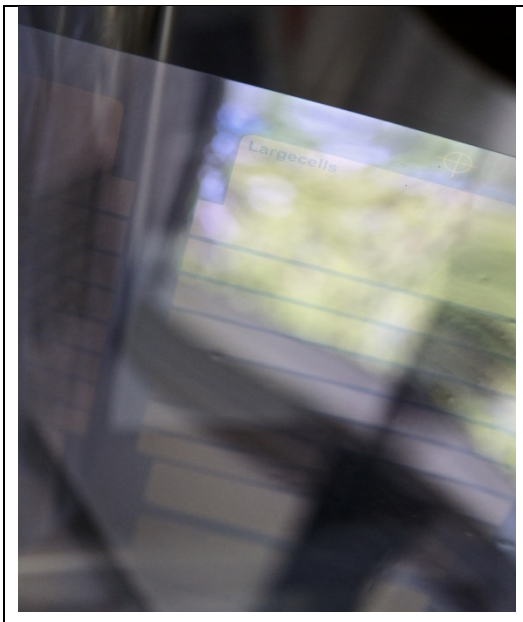


Figure 4. Photograph of the etched ITO-PET including Largecells logo in the top left corner.

R2R upscaling is not only about the active layer but also critical for the silver backside electrode. Screen printing, rotary screen printing, flexo printing and inkjet have been compared for its applicability and reliability.[6] Photographs of the layer qualities are shown in Figure 5. Finally, both screen printing methods performed best, but flexo printing and rotary screen printing have the largest upscaling potential regarding speed. Currently, the back electrodes in large-scale produced organic solar cells and modules are entirely rotary screen printed on R2R machinery.

[5] T.R. Andersen, H.F. Dam, B. Andreasen, M. Hösel, M.V. Madsen, S.A. Gevorgyan, et al., A rational method for developing and testing stable flexible indium- and vacuum-free multilayer tandem polymer solar cells comprising up to twelve roll processed layers, Sol. Energy Mater. Sol. Cells. 120 (2014) 735–743. doi:10.1016/j.solmat.2013.07.006.

[6] Hösel, M., Søndergaard, R. R., Angmo, D., & Krebs, F. C. (2013). Comparison of fast roll-to-roll flexographic, inkjet, flatbed and rotary screen printing of metal back electrodes for polymer solar cells. *Advanced Engineering Materials*, *15*(10), 995–1001. doi:10.1002/adem.201300011

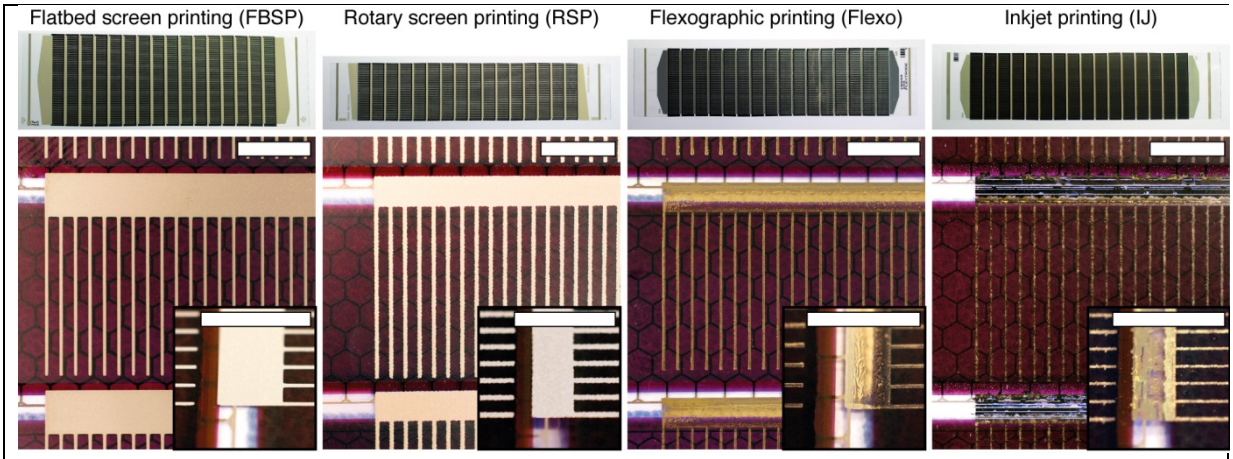


Figure 5. Printed back silver electrode.

2.3. Encapsulation of R2R printed devices for stability tests

Organic solar cells are sensitive towards oxygen and water and therefore encapsulation is required to ensure long lifetime. A scientific overview on the stability of organic solar was recently published in a review paper partly supported by the Largecells projects.[7] The overall aim is to use as thin as possible barrier foils with appropriate barrier characteristics and thin adhesives to decrease the amount of material and lowering the embodied energy. By doing this the energy payback time of the solar cell module can be decreased.

Cold foil lamination with pressure sensitive adhesives with a thickness of around 50 µm is a proved process both at Mekoprint and DTU. Despite that, other R2R lamination technologies such as hot-melt and UV-lamination are available[8] and have been studied throughout the project. Different barrier materials and adhesives suitable for R2R processing have been tested as well[9] and our typical lamination procedures are currently carried out with optimized food barrier packaging material. The seal around the edges of the devices has also been explored in detail and it was found that it significantly increase the stability.[10] We compared UV-curable adhesive, hotmelt, and pressure sensitive adhesive PSA in a full R2R process either with a single backside lamination or double encapsulation with improved edge sealing.[11] It was found that single side encapsulation with UV-curable adhesive is sufficient for

[7] Mikkel Jørgensen et al., "Stability of Polymer Solar Cells," *Advanced Materials* 24, no. 5 (2012): 580–612.

[8] Roar Søndergaard et al., "Roll-to-Roll Fabrication of Polymer Solar Cells," *Materials Today* 15, no. 1 (February 22, 2012): 36–49.

[9] Frederik C Krebs et al., "The OE-a OPV Demonstrator Anno Domini 2011," *Energy & Environmental Science* 4, no. 10 (2011): 4116

[10] David M Tanenbaum et al., "Edge Sealing for Low Cost Stability Enhancement of Roll-to-Roll Processed Flexible Polymer Solar Cell Modules," *Solar Energy Materials and Solar Cells* 97 (February 1, 2012): 157–163.

[11] Hösel, M., Søndergaard, R. R., Jørgensen, M., & Krebs, F. C. (2013). Comparison of UV-curing, hotmelt and pressure sensitive adhesive as roll-to-roll encapsulation methods for polymer solar cells. *Advanced Engineering Materials*.

long lifetimes. Further details on outdoor stability will be presented under the lifetime and testing section

2.4. Manufacture of ITO-free transparent electrodes

In collaboration with the Indian project partner JNCASR, Bangalore, ITO-free electrodes were manufactured and prototyped under simple lab conditions using lift-off processes and ordinary office laser printers. The fast prototyping of silver structures was performed by printing the negative layer on a toner laser printer and by overcoating the structures with silver. In a second step the toner is removed. All types of silver structures including semitransparent layers as shown in Figure 6 can be easily produced using simple lab equipment.[12]

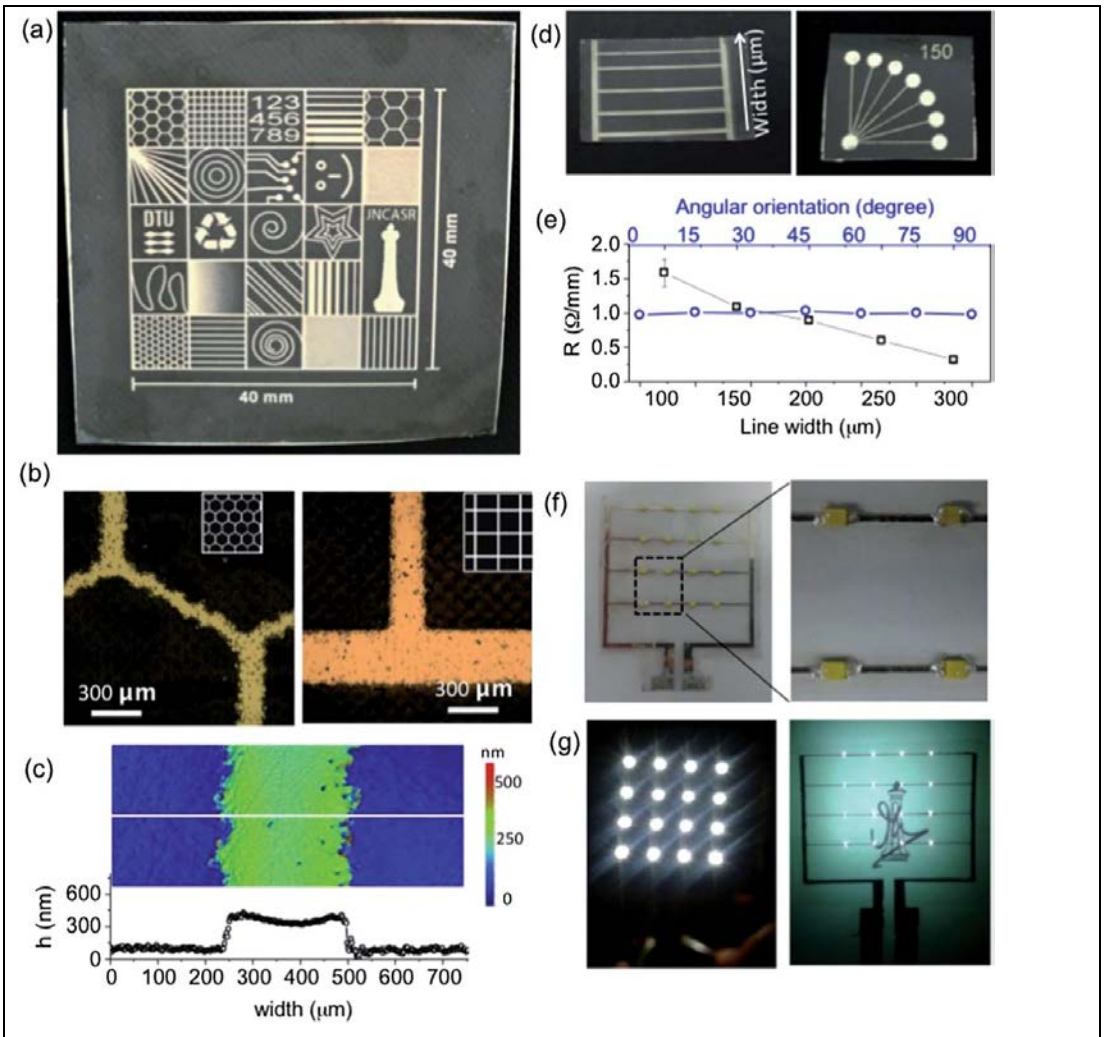


Figure 6 Electrode samples fabricated through toner laser printing, silver coating, and lift-off.

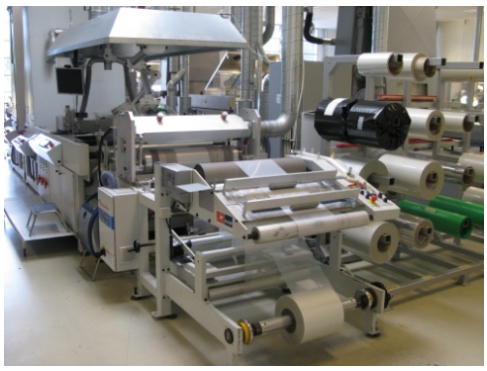
[12] R. Gupta, M. Hösel, J. Jensen, F.C. Krebs, G.U. Kulkarni, Digital grayscale printing for patterned transparent conducting Ag electrodes and their applications in flexible electronics, J. Mater. Chem. C. 2 (2014) 2112–2117. and R. Gupta, S. Walia, M. Hösel, J. Jensen, D. Angmo, F.C. Krebs, et al., Solution processed large area fabrication of Ag patterns as electrodes for flexible heaters, electrochromics and organic solar cells, J. Mater. Chem. A. 2 (2014) 10930–10937.

The electrodes were used to fabricate all kinds of devices including organic solar cells. Slot-die coating on the mini-rollcoater was successfully implemented as well.

2.5. Industrialization of R2R printed cells and modules

Mekoprint has successfully fulfilled the industrialization steps during the Largecells project. From the start of this project Mekoprint converted an existing machine park into an advanced coating pilot line for production of polymer solar cells in an industrial environment as shown in Figures 7a and b. During the project this pilot line has been equipped with necessary improvements, such as more precise coating tools with higher yield, better curing for a faster process, high degree of traceability through the entire production, and highly adapted inline vision inspection of the coated films. These improvements were necessary in order to create a stable production of advanced polymer solar cells. The requirements for precise control of production parameters and the complex interaction of the involved materials are unprecedented in the printed electronics production already present at Mekoprint. During the LARGECELLS project Mekoprint has optimized their industrial production with commercial material suppliers to move the technology close to commercialisation.

a)



b)

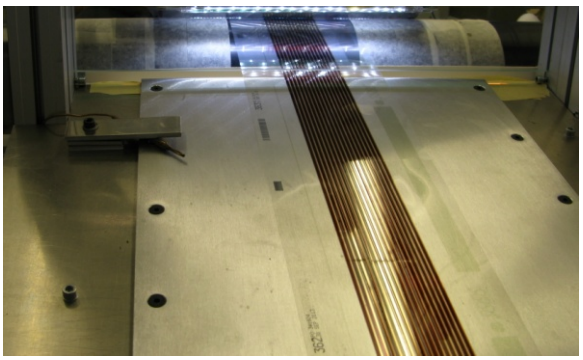


Figure 7. a) The entire coating pilot line at the Mekoprint production, b) Image from the production of one layer in a polymer solar cell.

3. WP3: Stability and degradation - accelerated aging tests and outdoor testing

Organic solar cells are known to be of shorter lifetime than conventional solar cells and the stability and degradation challenges have been covered extensively.[13] Test cells with materials developed by the projects partners were manufactured under industrial relevant processes but the particular lifetime was limited. For further studies the proved P3HT:PCBM active layer has been chosen R2R produced test modules that were extensively test under real-world operational conditions in Israel, Denmark,

[13] [1]M. Jørgensen, K. Norrman, S.A. Gevorgyan, T. Tromholt, B. Andreasen, F.C. Krebs, Stability of Polymer Solar Cells, Adv. Mater. 24 (2012) 580–612. doi:10.1002/adma.201104187.

and India using indoor accelerated ageing conditions as well as real outdoor testing for more than 9000 hours.

Exemplary factors that influence the operational stability of an organic solar cell are

- Photo-degradation with or without oxygen
- Chemical structure (e.g. side chains)
- UV-irradiation
- Temperature
- Humidity (water)
- Atmosphere (oxygen)
- Hygroscopic nature of PEDOT:PSS hole transport layer
- Encapsulation (barrier transmission rate)
- Barrier lamination (adhesives, fabrication processes)

The Largecells project covered this particular field by developing tools for accelerated lifetime tests and long term outdoor studies under different climatic conditions. Furthermore, several encapsulation strategies were tested with the objective to prove lifetime of OPVs beyond 9000 hours under outdoor conditions. The toolset for studying the operational lifetime of organic solar cells is as followed:

- Concentrated sunlight (continuous and chopped light)
- Outdoor lifetime studies (Israel, India, Denmark)
- Solar simulators (different light sources)
- Thermal cycling chamber
- Weathering chamber
- Characterization tools such as LBIC and IPCE

3.1. Accelerated ageing tests of R2R printed cells and modules

Accelerated testing plays an important role in understanding degradation mechanisms. In our experiments described previously[14] the cell temperature and power density of the incoming sunlight can be varied separately but not independently. For the complete independent control of the light intensity and the cell temperature we use the chopped-irradiation solar concentrator system (Fig. 8) located at BGU in Israel. In this system sunlight is reflected by a heliostat into the lab,

[14] T. Tromholt, E. A. Katz, B. Hirsch, A. Vossier and F. C. Krebs. Effects of concentrated sunlight on organic photovoltaics, *Appl. Phys. Lett.*, v. 96, No.7, 073501 (2010).

where it is concentrated by the high – irradiance "solar furnace".[15] The intensity of sunlight delivered to the cell is moderated without modifying its angular distribution by a louvered shutter between the heliostat and the flat indoor mirror. “Solar furnace” can operate in continuous-irradiation or flash-like mode.

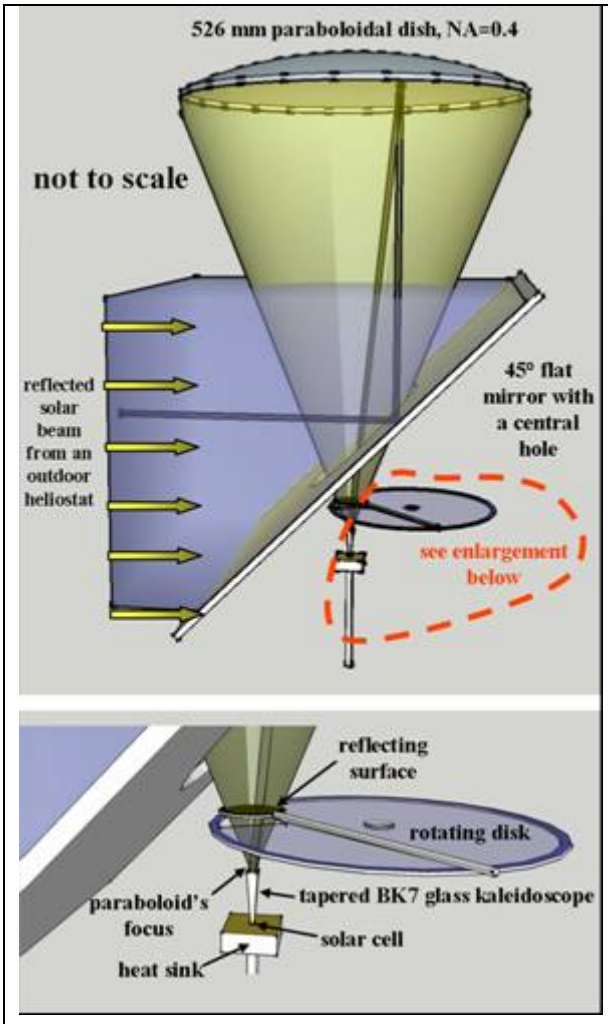


Figure 8. Schematic of the concentrator operation in the flash-like mode.

Experiments showed that inverted bulk hetero-junction OPV cell can be kept isothermally (completely avoiding cell overheating by sunlight) under various sunlight concentrations up to 100 suns.[16] Further tests could be performed using dual-axis tracking solar concentrators and fiber optics.

During tests under concentrated light it was found that degradation is repairable, and could even be prevented by simple electrical treatment (short pulses of the reverse bias). Moreover, the same process can improve even freshly prepared cells. The physical reasons for the degradation and its reversibility were analyzed in detail, especially in the context of the inverted solar cell geometry.[17] Generation and de-generation of shunts in the ZnO hole blocking layer as underlying physical mechanisms for the cell degradation and restoration, respectively, can explain all observed phenomena.

3.2. Outdoor tests of R2R printed cells and modules in India

For the lifetime studies in India an outdoor test stand as shown in Figure 9 was set up at JNCASR, Bangalore. The location was ideal due to all kinds of different weather

[15] A. Braun, B. Hirsch, A. Vossier, E. A. Katz, and J. M. Gordon, “Temperature dynamics of multijunction concentrator solar cells up to ultra-high irradiance,” *Prog. Photovolt: Res. Appl.*, 202-208 (2013).

[16] E. A. Katz, A. Manor, A. Mescheloff, T. Tromholt and F. C. Krebs. 2012. Accelerated Stability Testing of Organic Photovoltaics Using Concentrated Sunlight. In**:** *Proc. of the 38th IEEE Photovoltaic Specialists Conference*, Austin, TX, USA, June 3-8, 2012.

[17] A. Manor, E. A. Katz, T. Tromholt and F. C. Krebs. Electrical and photo-induced degradation of ZnO layers in organic photovoltaics. Advanced Energy Materials, v.1, No. 5, p. 836-843 (2011).

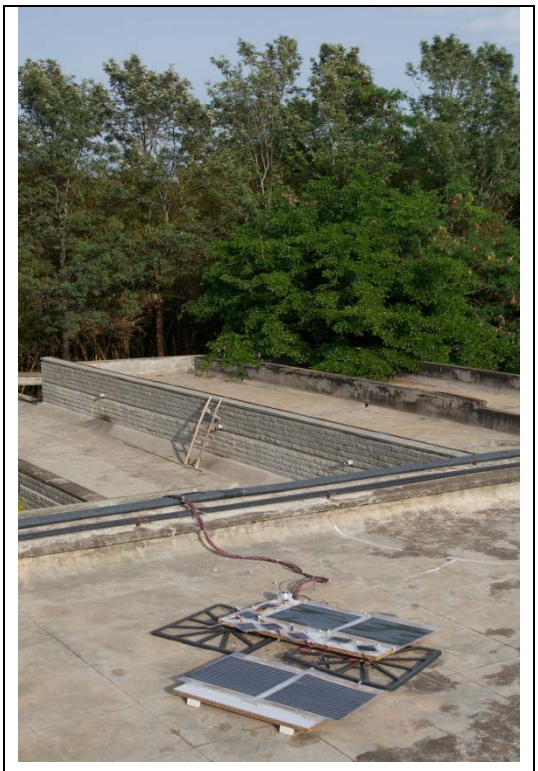


Figure 9. Rooftop test setup at JNCASR, Bangalore, India

conditions from high temperature to high humidity over to heavy rain in the monsoon period. The setup was built during a research exchange of a DTU PhD student together with the local researchers and PhD students. Parallel outdoor studies were also performed in Denmark and India on fixed and tracked solar testing platform. All outdoor tests have been intended to last at least 9000 hours and were successfully fulfilled. The functionality of the setup and guidance for the Indian researcher was carried out with ITO-based modules.

For the long term test in India, another set of large-scale R2R printed solar cells was set up at JNCASR. Five edge-sealed modules (rim < 1 cm) based on ITO-free Flextrode substrate and conventional P3HT:PCBM active layer were mounted on the test stand.

The last measurement has been carried out on August 3rd 2013 and marks 9696 hours (404 days). The common result is that all modules still worked! The efficiency dropped throughout the test but somehow stabilized to the end of the test period. The modules were shipped back to DTU for further studies. The main drop in efficiency is caused due to decreasing voltage and current. We observed some delamination in the cells that lead to a decreasing active area. Oxidation of the copper tapes to was also observed.

The same modules with a larger edge-sealing margin (>> 1cm) have also been studied in Denmark and Holland and were compared to the cells in India with a smaller edge sealing.[18] The importance of a wider edge sealing can be clearly seen in the operational lifetime of the modules as shown in Figure 10. The maximum power after 1 year decreased by 15-24 % for the cells in Holland and 91-95 % in India. Interestingly, a module placed in Denmark showed and maximum power increase by 11 % due to the large edge sealing.

[18] D. Angmo, P.M. Sommeling, R. Gupta, M. Hösel, S.A. Gevorgyan, J.M. Kroon, et al., Outdoor Operational Stability of Indium-Free Flexible Polymer Solar Modules Over 1 Year Studied in India, Holland, and Denmark, Adv. Eng. Mater. 16 (2014) 976–987. doi:10.1002/adem.201400002.

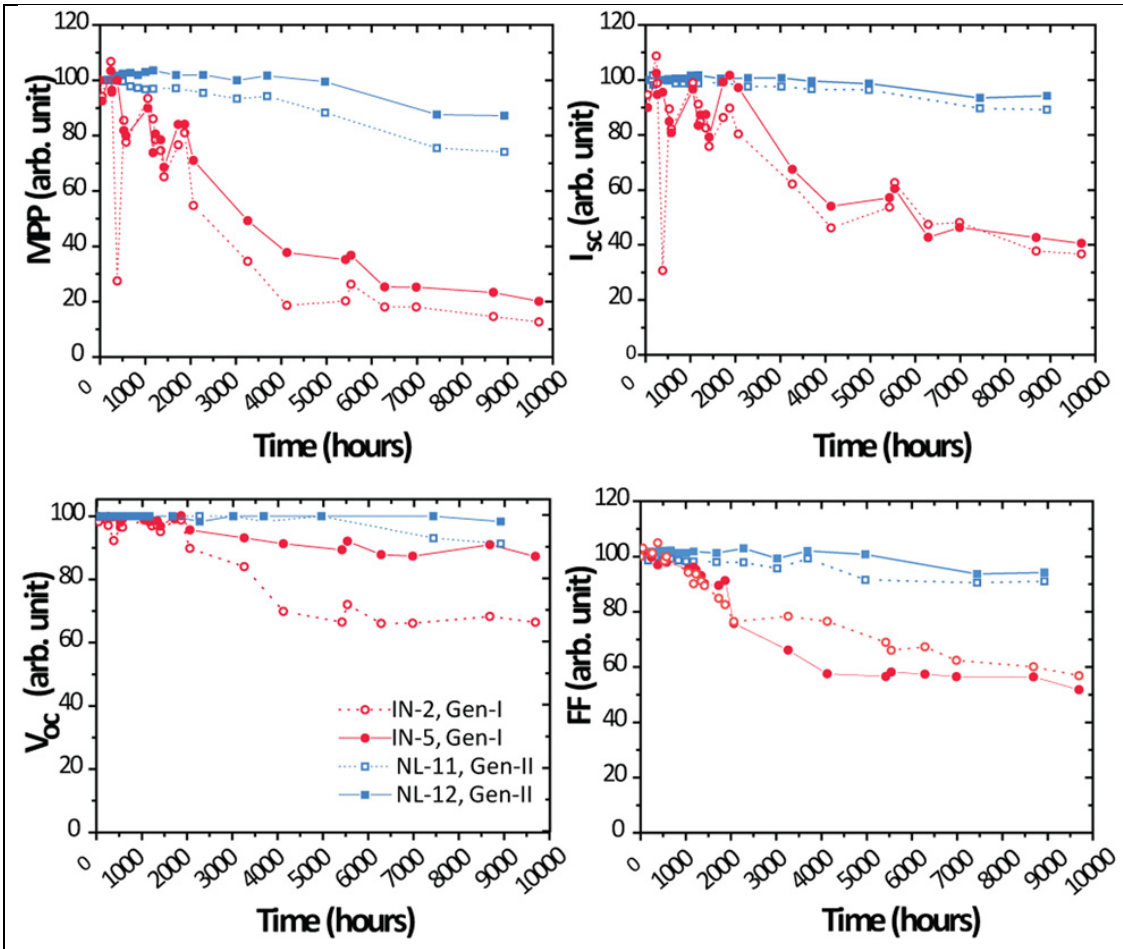


Figure 10 Outdoor operational stability of modules with edge sealing < 1cm measured in India (IN) and modules width edge sealing > 1 cm measured in Netherlands (NL). In India, modules were intermittently measured when the solar irradiance was above 800 W m^{-2}, AM 1.5G whereas the modules were intermittently measured under a solar simulator supplying 1000 W m^{-2} in Netherlands. The data of all modules are normalized to their respective initial measurement.

A typical failure mode in the package cells is the oxidation of the copper tapes inside the laminated cells as well as photo-bleaching of the active layer near the outer copper contacts. Figure 11 shows the comparison of two modules.

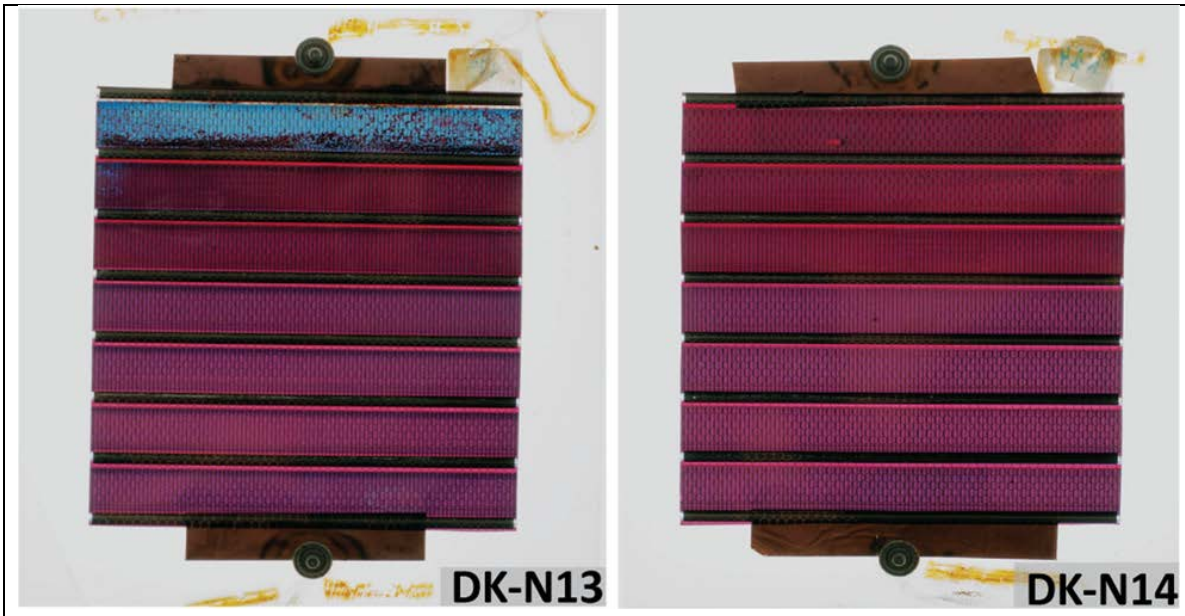


Figure 11 Images of the serially-intergrated modules width small edge sealing, each with several cells, after being tested under outdoor conditions (ISOS-O) in Denmark. The active area is 70 cm^2 .

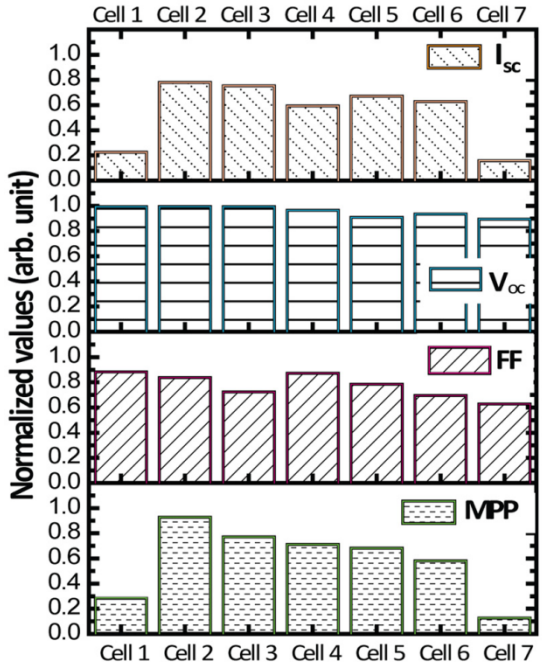


Figure 12 The bar graph shows the performance of each cell in the module DK-N14 after >1 year of outdoor operational stability (ISOS-O-3) testing conducted in Roskilde, Denmark. The module is comprised of seven interconnected cells, each of 1 cm x 7 cm (7 cm^2) active area.

Although not visual by eye the modules tend to degrade close to the outer electrodes. But measurements after 1 year of the single cells inside the modules show only slight degradation as shown in Figure 12. The outcome of this lifetime study is that large edge sealing with a 1-2 cm rims clearly improves lifetime and the best module operate above T80 at the end of 1 year (> 9000 hours). The problem with copper tapes as contact has been eliminated in current freeOPV modules, where a graphite pad is printed in the last step that acts as contacting area for the buttons after lamination.

3.3. Outdoor tests of R2R printed cells and modules in Israel and other locations

Another long-term outdoor study over a time frame of 10000 hours had been carried out with test cells situated in Israel (BGU) beside other locations all around the world.[19] The modules at BGU were tested for more than 3500 hours. The 16-stripe modules were ITO-based and edge-sealed using pressure sensitive adhesive and barrier foil.

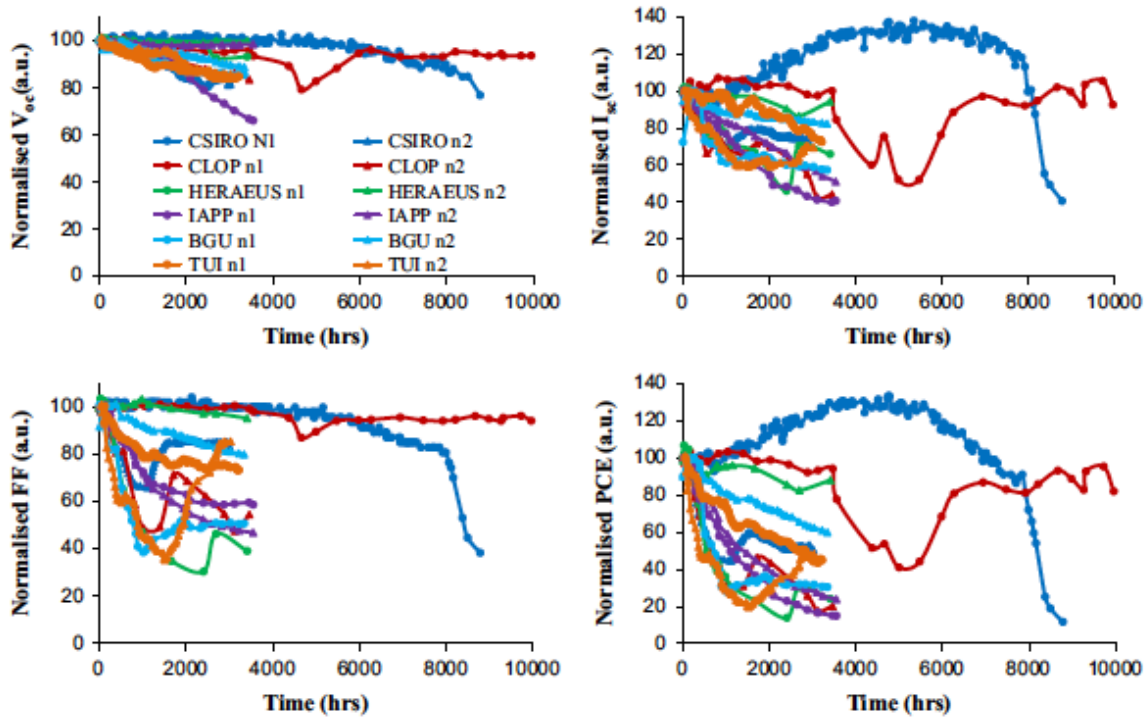


Figure 13 Stability curves of the short circuit current (Isc), open circuit voltage (Voc), fill factor (FF) and photo conversion efficiency (PCE) of the 12 modules measured in 6 locations. The photovoltaic parameters are normalized to the initial values at the respective locations.

The lifetime behavior was different for all modules around the world as shown in Figure 13. Although the efficiencies dropped fast for the modules we were able to achieve T80 lifetimes of more than 10000 hours. The sealing of the terminals with the copper tape and push buttons seem to have the most impact on the lifetime as shown before. Nevertheless, internal subcells could be measured with stable performances over 17 months as shown in Figure 14.

[19] Gevorgyan, S. A., Madsen, M. V., Dam, H. F., Jørgensen, M., Fell, C. J., Anderson, K. F., et al. (2013). Interlaboratory outdoor stability studies of flexible roll-to-roll coated organic photovoltaic modules: Stability over 10,000 h. *Solar Energy Materials and Solar Cells*, *116*, 187–196. doi:10.1016/j.solmat.2013.04.024

All studies and lifetimes tests within the Largecells project results in new insight into degradation mechanics and we proved that advanced packaging can result in organic solar cell devices with lifetimes easily exceeding 9000 hours.

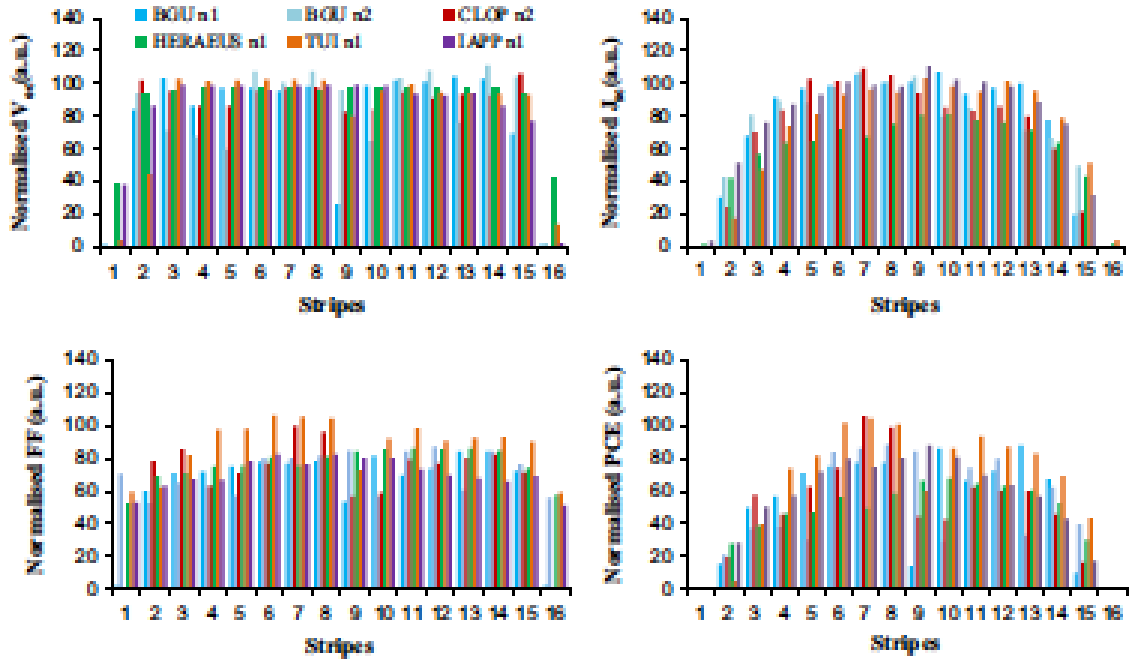


Figure 14 The column charts show the PV parameters of the individual solar cells in 6 modules. The values are normalized to the indoor measurements of the corresponding whole modules performed before the ageing tests. Each module comprised 16 serially connected solar cell stripes represented with a numerical value from 1 to 16, each with active area of approximately 2 cm^2. Before the individual solar cell characterization the THU n1 and HERAEUS n1 modules were stored in dark for about 8 months, aged in outdoor conditions for 5 months and stored in dark again for 12 months, while the other four samples were stored in dark for about 8 months and aged in outdoor conditions for 17 months.

4. WP4. Dissemination

To solve the problem of a stable and reliable energy supply even after the era of the crude oil ends is one of the most important and challenging tasks for our societies in the future. The project LARGECELLS paved the grounds for more efficient solar cells with a longer lifetime. As the project is financed by the European Commission, it is tax payer's money that is being invested. In order to inform the general public on the project, its aims and outcomes, the public outreach is of substantial importance.

A public website has been established at www.largecells.eu where up-to-date information is published while internal project communication and document sharing is handled through www.projectplace.com.

For the dissemination tasks, a huge effort has been put into the public media as well as scientific publishing. This is done in recognition of the fact that solar cells are

popular in mainstream media and the LARGECELLS project can provide some of the answers for our future energy supply. This is as much in the interest of the public as in the interest of the academia and therefore a large effort is put into distributing the dissemination in both areas. Here especially the press releases and the participation in exhibitions resulted in a very good effect. The project was mentioned on 56 other webpages, which were all open-source and accessible. What is also important is that in such a technical subject as in Largecells, it is necessary to “translate” the scientific content into some text which can be understood by the broader public. In the case of Largecells this was very successful. Especially in Germany the discussion about the so-called “Energiewende”, the turning point in the energy policy towards green energy, resulted in great public interest towards the topic. What was a niche topic some years ago became of interest for financially oriented investment magazines like Wallstreet, was covered by general newspapers and was mentioned in many forums around the topic of saving energy also for households.WP4 is in charge of the dissemination to the scientific community, but also to the broader public. In order to reach this goal, a large effort was taken also during the 4 years period. The project has generated 34 scientific articles and 47 articles in a broad range of public written media during the whole period. Furthermore, Mekoprint has made 4 application notes that will were published on their website. The application notes revolve around polymer solar cells and will help engineers and system integrators to work with commercially available modules in their own device development. To further disseminate polymer solar cells Mekoprint has entered in to a project where “grass root” geeks of the “maker” community will have the possibility to use Mekoprint’s polymer solar cells in a fully printed electronics platform called Printoo.

4.1. The official meetings of EU consortium and joint meetings between Indian and EU Consortia

Altogether the following meetings were organized and intensive exchanges of ideas, experiments and know-how was reached within the project period.

- EU-consortium Kick-off meeting in Munich (2010.10.14-15)
- EU-consortium Group meeting at Risø DTU and Mekoprint (2011.05.4-6)
- EU and Indian consortia collaboration meeting in India (2012.01.24-25)
- EU-consortium Group meeting at BGU in Israel (2012.08.15-16)
- EU and Indian consortia collaboration meeting in Bangalore (12-13 Feb 2013)
- EU-consortium Group meeting at Tue, Eindhoven (23-24 May 2013)
- EU-consortium Group meeting at UBT, Bayreuth1(6-17 Jan 2014)
- International workshop at Brussels (23-26 June 2014)

4.3. Management of intellectual property

There has not been any publishable information that was deemed patentable before publication. The cost of patents compared to the gain in the current OPV technology space has not been estimated to be in favor of patenting the work done in Largecells.

4.4. Exchange of results and joint publications with India

An important part of the LARGECELLS project is the staff exchange between the Indian consortium and the European consortium. On the project website www.largecells.eu there is a quick and easy-to-use application form for candidates for the staff exchange program within LARGECELLS.
There are two types of exchanges to be distinguished: senior scientists and young scientists. The young scientists (PhDs and Postdocs) have to apply for our exchange program after they have discussed the short-term project between the host and guest institutions and written down the planned experiments. In order to make the application from India to Europe as easy as possible, we implemented a web-based form that can be filled out online. The data will be stored and delivered to BayFor in an excel sheet format, so that the data can be easily processed for acquiring an overview. There is also the option to upload a CV and a brief project proposal.

The principal investigators don't have to undergo the application procedure for their visits. But they can take direct contact to the partners of the host institute. In order to activate the exchange programme, the EU-coordinator, Thelakkat conducted week-long tutorial lectures at two centers, JNCASR, Bangalore and NIIST, Trivandrum for the benefit of junior scientists from India involved in this joint project. The lectures were well-attended at both places with more than 25 PhD students from different groups participating in both. At the end of lectures, solar cell preparation and characterization was demonstrated involving the students to get a first-hand feeling for hybrid and polymer solar cells. This was very productive, since the PhD students from India learned a lot in these intensive and elaborate tutorial lectures on this topic. There were altogether 22 travels by Indian guests who joined the European partners for different periods of time ranging from days to months. A complete list of all the exchanges is given below.

Abdul Rahim	Moochikkadavath	Phd student	Photosciences and Photonics (NIIST)	Trivandrum	Bayreuth	21.10.2011-20.12.2011
Subila	K.B.	Phd student	School of Chemistry, IISER TVM	Trivandrum	Bayreuth	31.5.2012-31.7.2012
Ritu	Gupta	Phd Student	JNCASR	Bangalore	Bayreuth	25.9.2011-28.9.2011
Ritu	Gupta	Phd student	JNCASR	Bangalore	DTU, Roskilde	17.3.2013-14.6.2013
Ritu	Gupta	Phd student	JNCASR	Bangalore	Eindhoven	23.5.2013-25.5.2013
K.D. Mallikharjuna	Rao	Phd student	Jawaharlal Nehru Centre for Advanced Scientific Research, CPMU	Bangalore	Bayreuth	12.9.2013— 8.12.2013

Rajamani	Ashokkumar	Junior Research Fellow	National Centre for Ultrafast Processes, University of Madras	Chennai	Bayreuth	16.5.2013-13.7.2013
G.U.	Kulkarni	Professor	JNCASR	Bangalore	Eindhoven/Riso	June 2013, 1 week
G.U.	Kulkarni	Professor	JNCASR	Bangalore	DTU, Roskilde	May 2011, 3 days
Suresh	Das	Professor	NIIST		DTU, Roskilde	May 2011, 3 days
D. Prabhu	Deepak	Senior Research Fellow	Photosciences and Photonics, Chemical Sciences and Technology Division, NIIST	Trivandrum	Eindhoven	28.5.2013-31.7.2013
Rajamani	Ashokkumar	Junior Research Fellow,	National Centre for Ultrafast Processes, University of Madras	Chennai	Bayreuth	16.5.2013-13.7.2013
G.U.	Kulkarni	Professor	JNCASR	Bangalore	Eindhoven/Riso	June 2013, 1 week
G.U.	Kulkarni	Professor	JNCASR	Bangalore	DTU,Roskilde	May 2011, 3 days
Suresh	Das	Professor	NIIST		DTU,Roskilde	May 2011, 3 days
Vinayak	M.V.	phd student	NIIST	Trivandrum	Bayreuth	1.5.14-27.6.14
Vinayak	M.V.	phd student	NIIST	Trivandrum	Brussels	23.6.-25.6.14
Anju	V. Gopinath	phd student	IISc	Bangalore	Bayreuth	22.6.14-28.7.14
Anju	V. Gopinath	phd student	IISc	Bangalore	Brussels	23.6.-25.6.14
Subila	K.B:	phd student	School of Chemistry, IISER TVM	Trivandrum	Bayreuth	18.6.14-17.8.14
Subila	K.B:	phd student	School of Chemistry, IISER TVM	Trivandrum	Brussels	23.6.-25.6.14
Lakshmykanth		senior research scholar	NIIST	Trivandrum	Tue	1.6.14 -31.7.14
Lakshmykanth		senior research scholar	NIIST	Trivandrum	Brussels	23.6.-25.6.14
Rao	Mallikarjuna	phd student	JNCASR	Bangalore	Bayreuth	12.11.13-8.12.13
Kiruthika	Shanmugam	phd student	JNCASR	Chennai	Brussels	23.6.-25.6.14
Suresh	Das	Professor	NIIST		Brussels	23.6.-25.6.14
K.R.	Gopidas	Professor	NIIST	Trivandrum	Brussels	23.6.-25.6.14
George	Thomas	Professor	IISER	Trivandrum	Brussels	23.6.-25.6.14
S.	Sampath	Professor	IISc	Bangalore	Brussels	23.6.-25.6.14
P.	Ramamurthy	Professor	NCUP	Madras	Brussels	23.6.-25.6.14
G.U.	Kulkarni	Professor	JNCASR	Bangalore	Brussels	23.6.-25.6.14

As planned in the DoW, an international workshop was organized at Kowi, Brussels from 23rd to 25th June 2014. From EC official side, the PO Dr. Schilde and the reviewer Prof. Vikram Kumar participated. Additionally, all the project partners from EU and India together with the PhD students and Postdocs participated in the workshop. Three external tutorial talks by renowned scientists working on different aspects of organic and solar cells, Prof. Lukas Schmidt-Mende, Konstanz; Prof. Carsten Deibel, Chemnitz; and Prof. Christoph Brabec, Erlangen gave good overview regarding the present stage of third generation solar cell activities. Altogether there were 14 talks by PIs and invited guests and 10 posters were presented by the students and postdocs participating in the workshop. This workshop has given not only the current international status of organic and hybrid

solar cells research, but also a final impression of what has been achieved in this project.