

Flexible organic P3HT:PCBM bulk-heterojunction modules with more than 1 year outdoor lifetime

Jens A. Hauch^{a,*}, Pavel Schilinsky^a, Stelios A. Choulis^a, Richard Childers^b,
Markus Biele^a, Christoph J. Brabec^a

^aKonarka Technologies GmbH, Landgrabenstr. 94, D-90443 Nuremberg, Germany

^bKonarka Technologies Inc., 116 John Street, Suite 12, Lowell, MA 01852, USA

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Abstract

Flexible organic solar cells and modules based on P3ht:PCBM bulk-heterojunctions were fabricated and their lifetime was investigated under laboratory and outdoor conditions. In the laboratory cells were exposed to 1 sun illumination at 65 °C in order to accelerate the degradation. The outdoor behavior of modules was investigated at the Konarka rooftop testing setup in Lowell, MA (USA). We show that these flexible polymer solar cells have a good light stability, passing 1000 h under accelerated light soaking conditions in the laboratory, and that flexible modules survived over 1 year of outdoor exposure without performance losses.

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1. Introduction

As the world energy demand continues rising, and the cost for natural resources like oil and coal is rising, new solutions for the cheap production of energy from renewable resources are needed. Solar cells are expected to be a major contributor to fill the future energy needs; however, new approaches are required that make the conversion of light to power less costly. Due to their processability via printing techniques organic solar cells based on polymer semiconductors are widely viewed as a potential solution to provide low cost solar power [1,2].

The reported efficiencies for organic solar cells have risen sharply, from the rather modest 1% in the first bulk-heterojunction device in 1995 [3]. By 2003, P3HT:PCBM cells with 3.5% [4] were reported, and in 2007 multiple groups are reporting efficiencies of 4–4.5% with this material combination [5–7] which appears to have reached its limit at this efficiency. However, new material systems have enabled the development of polymer cells with

certified efficiencies above 5% [8,9], and more complex architectures where multiple cells are stacked on top of each other have even been able to demonstrate non-certified white light conversion efficiencies of 6.5% [10].

While efficiencies are steadily improving, limited data are available on the stability of organic solar cells. Only a small amount of publications have investigated the lifetime performance and degradation of polymer solar cells. Schuller et al. [11] investigated the degradation of glass encapsulated cells stressed by light and temperature and showed that the degradation of the short circuit current (I_{sc}) could be modelled by an activated process with an Arrhenius behavior and a linear degradation over time. Similar degradation behavior for the overall efficiency was observed recently for P3HT:PCBM solar cells, exposed to AM1.5 illumination at 60 °C in a vacuum by De Bettigny et al. [12], where they noted a significant difference in the degradation behavior of cells with Ca/Ag electrodes vs. LiF/Al electrodes. The group studied not only the I_{sc} degradation, but also monitored the degradation of open circuit voltage (V_{oc}) and fill factor (FF), giving an improved insight into the degradation mechanisms. Krebs et al. [13] reported on degradation in MEH-PPV:PCBM

*Corresponding author. Tel.: +49 911 2178011; fax: +49 911 2178010.
E-mail address: jhauch@konarka.com (J.A. Hauch).

cells and found an exponential decay for I_{sc} when the degradation was monitored down to ca. 10% initial performance.

All the above studies made use of atmospherically unstable electrodes like Ca/Ag, LiF/Al, requiring oxygen and moisture dense packaging. In some recent studies shelf lifetime of flexible cells encapsulated with ultra-barrier films was reported. Dennler et al. [14–16] showed lifetimes up to 6000 h (for 80% degradation) for (MDMO:PPV):PCBM and P3HT:PCBM encapsulated with a flexible gas barrier material. Moro et al. [17] did a similar study on glass-based P3HT:PCBM devices encapsulated with a flexible barrier film where shelf lifetimes of 3500 h were reached with a barrier film water vapor transmission rate (WVTR) of 1.2×10^{-3} g/(m² day). They could show a good correlation between WVTR and lifetime for these devices with Ca/Ag electrodes, and presented a model that could explain the observed degradation through oxidation of Ca. Using Ca-oxidation testing allowed them to determine acceleration factors for damp-heat tests vs. shelf life. Only few studies of outdoor degradation of polymer solar cells have been published to date. Katz et al. [18] investigated the effect of temperature on the performance of glass encapsulated MDMO-PPV cells outdoors and observed an increase in efficiency up to 10% upon heating of the cells from 30 °C to 50 °C. Krebs et al. [19] studied large area printed MEH-PPV:PCBM cells during outdoor exposure and observed a loss of over 90% of efficiency was observed in the course of 12 days. While Krebs had done laboratory degradation studies on similar cells before [13], no attempt was made to correlate the outdoor data with the laboratory results. Only recently, Katz et al. published a new study of outdoor degradation based on cells, encapsulated by a combination of glass and aluminum, with different semiconductors in the active layer [20]. While a device encapsulated in a similar fashion by Krebs [21] showed a shelf life of ca. 1 year, with a loss of 35% in efficiency, the best cells in the report by Katz, based on P3CT-C60 active layers, showed a loss of ca. 50% after outdoor solar exposure of ca. 100 h, with overnight storage in a glovebox. P3HT:PCBM cells in the same study showed slightly worse performance, but a similar degradation pattern, with the main losses occurring in the short circuit

current and FF, which is likely to be an effect of degradation of the Al back electrode.

Recent improvements in polymer solar cells have enabled the production of air stable solar cells, through the use of air stable metals, like e.g. Ag or Au instead of electrode materials like LiF/Al or Ca/Ag [22]. In this paper we present degradation studies of organic solar cells and modules based on P3HT:PCBM bulk-heterojunctions. We investigate the performance evolution of modules exposed to outdoor conditions over a period of 14 months and show that a slight increase of efficiency has occurred after the rooftop exposure. In parallel we study the degradation of cells stored at 65 °C while being illuminated by 1 sun and compare the degradation patterns with the outdoor modules. We show that P3HT:PCBM cells and modules have very good light stability allowing them to survive multiple years in an outdoor environment.

2. Outdoor testing procedure

To investigate stability only P3HT:PCBM cells and modules with active areas > 1 cm² per cell and efficiencies > 1% under AM1.5 illumination were accepted to enter testing. Devices were prepared according to the procedure outlined elsewhere [23–26]. Following production the cells were packaged with transparent barrier films with a WVTR rate of 0.03 g/(m² day) at 38 °C/100%rh (evaluated by Mocon testing). A cross-section of the finished modules for rooftop testing is shown in Fig. 1. After determining the maximum power point (mpp) by jV -analysis, the modules were placed on the Konarka outdoor solar cell characterization setup in Lowell, MA (USA). The setup is shown in Fig. 2. The setup is facing directly to the solar south, with the modules placed at an angle of 42° from the horizontal (Lowell is at 42.6°N latitude). For the determination of the output power the modules are placed under load condition, by connecting a resistor between the terminals. The resistor is chosen such that the cells are operating at their maximum power point. On the rooftop, the voltage across the load resistor is then logged every 60 s, along with the air temperature in the shade (monitored by thermocouples) and the solar luminous intensity (monitored by an Eppley Precision Spectral Pyranometer).

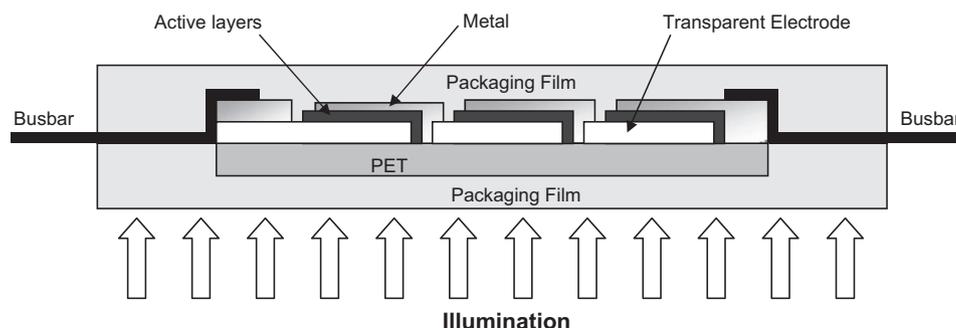


Fig. 1. Schematic cross-section of an encapsulated flexible solar cell.

3. Laboratory testing procedure

For laboratory testing individual cells, rather than modules were used. The cells were manufactured and packaged in the same fashion; however, instead of attaching leads to the terminals, the top packaging film was simply recessed, in order to gain direct access to the metal contacts. Following production the cells were placed in a custom measurement holder, which was designed to withstand the environmental test, and remained in this holder throughout the testing period. The holders had $30 \times 30 \text{ mm}^2$ openings above and below the cell to allow for illumination and atmospheric exposure in the Suntester Atlas XLS⁺. The cells were characterized by measuring their jV -characteristics under AM1.5 illumination at 100 mW/cm^2 with a Steuernagel Solartest 1200 solar simulator. Prior to measurements the cells were always

allowed to cool back down to room temperature, in order to eliminate temperature effects from the measurements. A total 8 cells each were placed at $65^\circ\text{C}/1 \text{ sun}$ (sun soak) at ambient humidity ($\sim 30\%–60\% \text{ rh}$) and J_{sc} condition (terminals shorted together). From the jV -characteristics V_{oc} , J_{sc} , FF, and efficiency were extracted.

4. Results

We will focus the discussions on the modules, which showed the overall best performance. Fig. 3 shows the evolution of the measured power density, normalized with the power density at $t = 0$. Shown are only the values that were measured on sunny days, where the illumination reached a power density of 100 mW/cm^2 , at the time immediately after this illumination was reached. Along with the normalized efficiency the air temperature at the same time is plotted. There are several interesting trends observable in the data. Immediately following the placement of the modules on the rooftop, the performance increases by up to 40%. Following this, there is a period where the efficiency of the module strongly correlates with the outdoor temperature as measured by the thermocouples. Finally, in May '07 an almost linear degradation begins, at a rate of ca. 10% per month, resulting in measured power output of 80% of its starting efficiency in November '07. At this point the module was taken off the roof in order to investigate the degradation processes more closely.

After removal from the rooftop the jV -characteristic of the module was re-measured. The relative change of the performance parameters, as evaluated by the laboratory measurement, is shown in Fig. 4. Surprisingly the total efficiency of the module has not decreased, but increased by 3.3%. This increase is due to a relative increase in FF of 10.8%, with a drop in V_{oc} by 6.8%. There is no apparent change in J_{sc} before and after, which shows that there is no

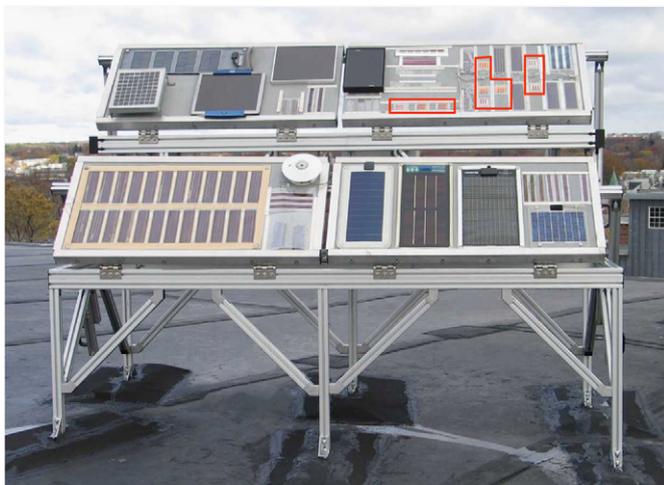


Fig. 2. Konarka outdoor testing setup in Lowell, MA (42.6°N latitude) on the east coast of USA. The setup is facing the solar South at an angle of 42° from the horizontal. Modules that were part of this study are outlined.

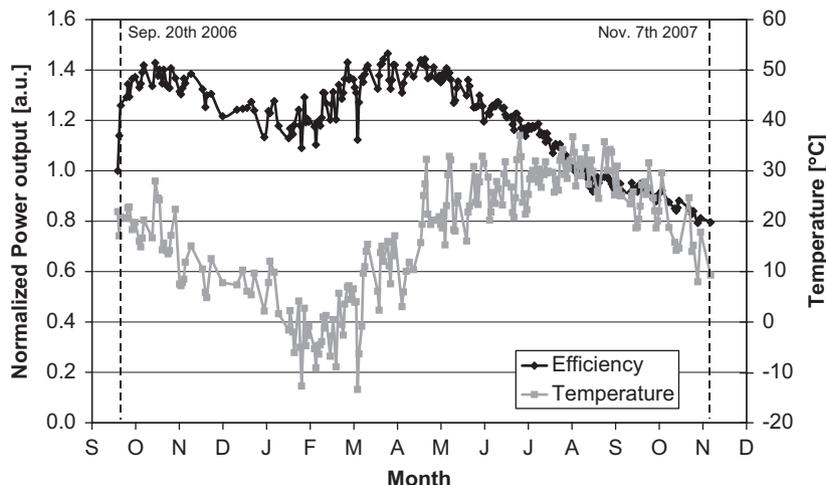


Fig. 3. Evolution of the normalized power density of the rooftop module as a function of time (in months). The air temperature at the time of measurement is shown as well.

significant bleaching of the active layer. The drop in the power output as measured on the rooftop may be explained by a shift in the maximum power point of the module from

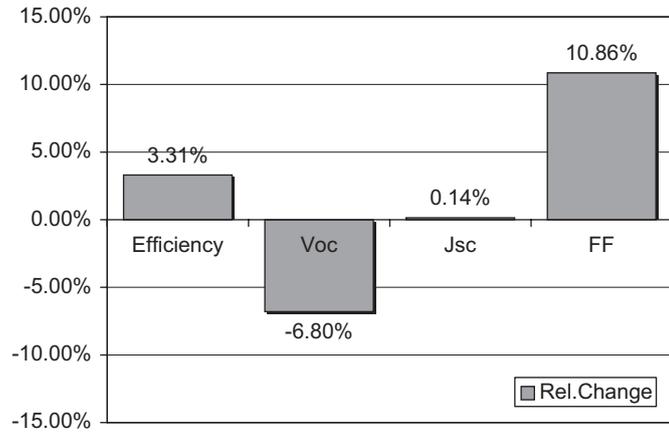


Fig. 4. Relative change of the performance parameters extracted from the jV -characteristics of the module, before and after 14 months outdoor degradation.

initially 0.87–0.8 V, which resulted in a non-optimal loading of the module during the outdoor measurement.

For product development it is of interest to try to correlate the outdoor measurements with accelerated lifetime testing. In the laboratory it is possible to track all performance parameters, and the evolution of the normalized performance parameters, averaged over all the laboratory reference cells, is shown in Fig. 5. Similar to the outdoor modules the laboratory cells show a drop in V_{oc} that rapidly sets in during the first ~250 h of the experiment. Unlike the outdoor modules the light soaked cells also show a corresponding initial decrease in j_{sc} , which also sets in during the first ~250 h of the experiment and then stabilizes, following the same trend as V_{oc} . This stabilization, in agreement with the outdoor results, suggests that no bleaching of the semiconductor layer over time occurs. An interesting behavior is displayed by FF, which increases by up to 10% for the first ~600 h, followed by a continual decrease. The cumulative effect of these degradation processes results in the evolution of the efficiency, which initially drops for the first ~250 h,

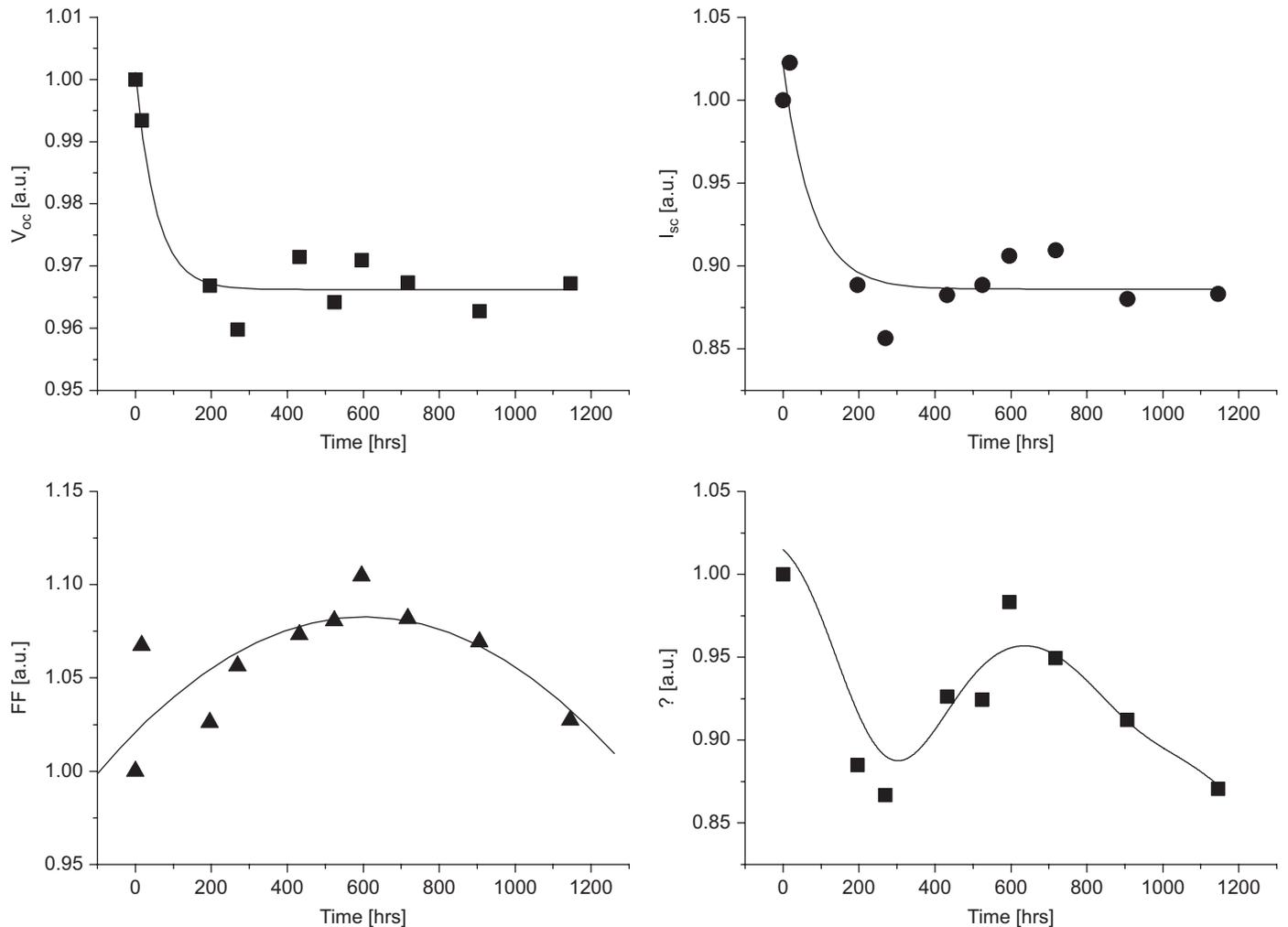


Fig. 5. Evolution of the averaged performance parameters of single cells exposed to 65°C and 1 sun illumination. The performance parameters are normalized with the performance at $t = 0$. Lines in the diagrams are shown to guide the eye.

followed by a rise up to ~ 600 h and then again leading into a continual loss throughout the rest of the experiment. Despite this, by the end of the experiment at 1200 h, the cells have only lost $\sim 15\%$ of their initial performance. Though an initial V_{oc} or j_{sc} loss during the early phase of a degradation cycle has been observed frequently, other trends, like e.g. a j_{sc} increase during the first 100 h can be observed as well. Despite the qualitative and quantitative differences in the early phases of a degradation run, the overall lifetime of cells, as defined by 20% loss of the time zero value, shows remarkably little variation.

5. Conclusion

In this paper we have demonstrated that P3HT:PCBM based bulk-heterojunction solar cells can show outstanding stability both in outdoor exposure, and exposure to accelerated lifetime testing at the light soak condition of $65^\circ\text{C}/1$ sun. Modules in our rooftop testing setup even showed a slight increase in their performance after 14 months of outdoor testing, mainly due to an increase in FF by 10%. A similar increase in FF is observed in laboratory cells within the first 600 h of the light soak experiment. This quite rough and preliminary correlation seems to indicate that some 600–800 h of accelerated light soaking under 1 sun, 65°C are roughly equivalent to 1 year of outdoor exposure at 42° lateral altitude, where the annual average daily total solar illumination is between 4 and $4.5 \text{ kWh}/(\text{m}^2 \text{ day})$ [27].

In our experiments the flex modules degraded outdoors show no losses in j_{sc} and the flex cells stressed by the light soak condition show only small initial losses in j_{sc} throughout the course of the experiments. This proves that P3HT:PCBM layers have an encouraging light stability, since no continuous bleaching was observed over time.

In summary our experiments show that OPV modules manufactured on flexible substrates and packaged with flexible low performance barriers are sufficiently stable for first outdoor application.

References

- [1] C.J. Brabec, J.A. Hauch, P. Schilinsky, C. Waldauf, MRS Bull. 1 (2005).
- [2] C.J. Brabec, Sol. Energy Mater. Sol. Cells 83 (2004).
- [3] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Science 270 (1995) 1789.
- [4] F. Padinger, R.S. Ritterberger, N.S. Sariciftci, Adv. Funct. Mater. 13 (2003) 85.
- [5] Y. Kim, S. Cook, S.M. Tuladhar, S.A. Choulis, J. Nelson, J.R. Durrant, D.D.C. Bradley, M. Giles, I. McCulloch, C.S. Ha, M. Ree, Nat. Mater. 5 (2006).
- [6] J.Y. Kim, S.H. Kim, H.-H. Lee, K. Lee, W. Ma, X. Gong, A.J. Heeger, Adv. Mater. 18 (2006) 572.
- [7] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, Nat. Mater. 4 (2005) 864.
- [8] NREL Certificate Konarka, 5.24% (device area 1.024 cm^2) under AM1.5 spectrum, 2006.
- [9] NREL Certificate Plextronics, 5.4% (device area 0.096 cm^2) under AM1.5 spectrum, 2007.
- [10] J.Y. Kim, K. Lee, N.E. Coates, D. Moses, T.-Q. Nguyen, A.J. Heeger, Science 317 (2007).
- [11] S. Schuller, P. Schilinsky, J. Hauch, C.J. Brabec, Appl. Phys. A 79 (2004) 37.
- [12] R. De Bettignies, J. Leroy, M. Firon, C. Sentein, Synth. Met. 156 (2006).
- [13] F.C. Krebs, J.E. Carlé, N. Cruys-Bagger, M. Anderson, M.R. Lilliedal, M.A. Hammond, S. Hvidt, Sol. Energy Mater. Sol. Cells 86 (2005).
- [14] G. Dennler, C. Lungenschmied, H. Neugebauer, N.S. Sariciftci, M. Latrèche, G. Czeremuszkin, M.R. Wertheimer, Thin Solid Films 349 (2005).
- [15] G. Dennler, C. Lungenschmied, H. Neugebauer, N.S. Sariciftci, J. Mater. Res. 20 (2005) 12.
- [16] C. Lungenschmied, G. Dennler, H. Neugebauer, S.N. Sariciftci, M. Glatthaar, T. Meyer, A. Meyer, Sol. Energy Mater. Sol. Cells 91 (2007).
- [17] L. Moro, N.M. Rutherford, R.J. Visser, J.A. Hauch, C. Klepek, P. Denk, P. Schilinsky, C.J. Brabec, Proc. SPIE 6334 (2006).
- [18] E.A. Katz, D. Gaiman, S.M. Tuladhar, J.M. Kroon, M.M. Wienk, T. Fromherz, F. Padinger, C.J. Brabec, N.S. Sariciftci, J. Appl. Phys. 90 (2001) 10.
- [19] F.C. Krebs, H. Spanggard, T. Kjær, M. Biancardo, J. Alstrup, Mater. Sci. Eng. B 138 (2007).
- [20] E.A. Katz, S. Gevorgyan, M.S. Orynbayev, F.C. Krebs, Eur. J. Appl. Phys 35 (2007) 307.
- [21] F.C. Krebs, Sol. Energy Mater. Sol. Cells 90 (20) 3633–3643.
- [22] K. Lee, J.Y. Kim, S.H. Park, S.H. Kim, S. Cho, A.J. Heeger, Adv. Mater. 19 (2007).
- [23] P. Schilinsky, C. Waldauf, C.J. Brabec, Adv. Funct. Mater. 16 (2004).
- [24] M. Koppe, M. Scharber, C. Brabec, W. Duffy, M. Heeney, I. McCulloch, Adv. Funct. Mater. 17 (2007).
- [25] C. Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S.A. Choulis, C.J. Brabec, Appl. Phys. Lett. 89 (2006) 23.
- [26] D. Mühlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana, C. Brabec, Adv. Mater. 18 (2006).
- [27] PV Solar Radiation Map (flat plate, facing south, latitude tilt), 2004 <www.nrel.gov>.