

Transient Measurements of Small Molecule Organic Solar Cells

**Abstract**

*As an advanced characterisation method of organic solar cells a setup for measuring photocurrent transients as response to a step function excitation of light has recently been developed at the University of Cambridge. It has successfully been applied to characterize several types of polymer cells. McNeill et al [1] and Hwang et al [2] have investigated the influence of trapping and detrapping effects and field dependent charge separation on the photocurrent response in P3HT based solar cells. Beside these solution processed polymer based devices, solar cells prepared by thermal evaporation in high vacuum are the second important representative in organic photovoltaics. Such solar cells consisting of small molecules (e.g. ZnPc and C<sub>60</sub>) are prepared in Dresden at the IAPP. Compared to polymer cells these devices usually consist of several organic layers. In the p-i-n architecture the absorber materials are sandwiched as an electron donor/acceptor combination between electrically doped transport layers [3]. This concept allows for a good distinction between contact and bulk effects. Additionally, the donor/acceptor heterojunction can be easily formed in a flat configuration with two adjacent layers or as a bulk heterojunction in a blend layer. These cells are characterized by the photocurrent transient method in Cambridge. The goal is to get an insight into the electrical transport mechanisms upon illumination that are dominating in these cells comparing them to polymer cells and comparing between different architectures like flat and bulk heterojunction with different mixing ratios. The results are used as inputs for drift-diffusion simulations, including space charge effects, charge dissociation, and trapping mechanisms.*

*In this report we focus on the comparison between a simple flat and bulk heterojunction ZnPc:C60 solar cell with and without doped transport layers. The measurement data with and without background illumination indicate that the doped layers introduce traps, which can be filled by an additional illumination.*

**Introduction**

In recent years much research has been done on organic solar cells, which are expected to be a promising low-cost alternative to conventional solar cells and capable for up-scaling to contribute significantly to satisfy the world's energy demand [4]. There exist two approaches for producing organic solid state solar cells, on the one hand solution processing (e.g. spin-coating) and on the

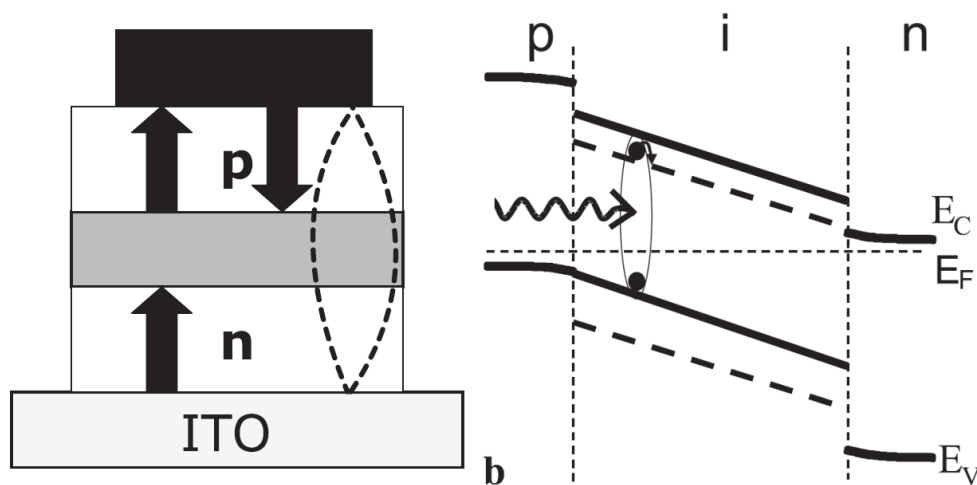


Fig. 1: pin concept: stack and schematic band diagram

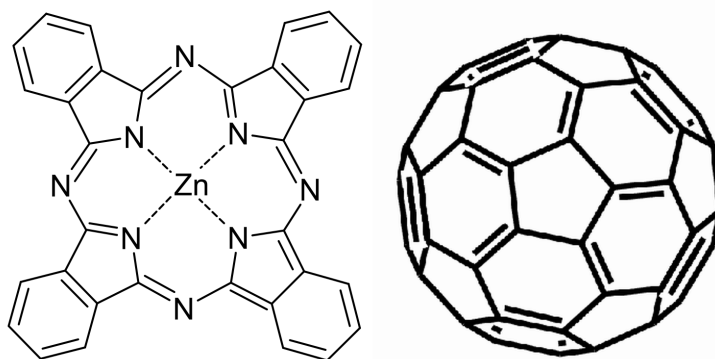


Fig. 2: ZnPc and C<sub>60</sub> as common absorber materials for small molecule organic solar cells

other hand thermal deposition in high vacuum. The first is the method of choice for polymer, the second for small molecule solar cells. Consecutive evaporation of different materials allows for building stacks easily with layers of well defined thickness and purity. An in Dresden developed and well working concept is the pin structure [3], which has several advantages. A good contact to the metal independent of its choice is achieved by doped transport layers. The active materials can be placed in the optical interference maximum by adjusting the layer thicknesses of these transparent transport layers. This is schematically shown in Fig. 1. On the left hand side the spacer effect of the p-layer is demonstrated. On the right hand side a simple picture of the working principle of organic solar cells is depicted, showing a further advantage of the pin concept. Defining by the doping a high potential drop over the intrinsic layer, the p and n layer form a favourable situation for charge carrier extraction, which is supported by the selectivity of these contact layers by the energetic barrier for holes at the n-side and electrons at the p-side. This concept is coming very close to the ideal solar cell structure [5]. The intrinsic layer itself consists of two materials; either stacked forming a flat heterojunction (FHJ) or mixed in a blend layer forming a bulk heterojunction (BHJ). The heterojunction is needed to separate excited states, which are created upon light absorption, but which are still coulombically bound due to the low dielectric screening in organic materials. The excitons can diffuse to the interface with diffusion lengths of several nm. After dissociation the hole is located on the one material, called the donor, which should be hole conductive, and the electron on the acceptor. For efficient charge transport the morphology of the blend should allow for well ordered percolation paths. However, a strong mixing is required due to the low exciton diffusion lengths. In figures 2 and 3 typical small molecule materials are shown. As donor/acceptor ZnPc and the fullerene C<sub>60</sub> are used, MeO-TPD is a commonly employed transparent hole transport layer (HTL), which can be doped by F4-TCNQ, which has a LUMO value in the region of the HOMO of ZnPc to allow for charge transfer. As a further step the pin architecture allows stacking of cells, making tandem devices with optimized distance and good recombination currents, which lead to a certified efficiency of more than 8% [6].

Despite the progress in efficiencies details of the working principle of organic solar cells are still

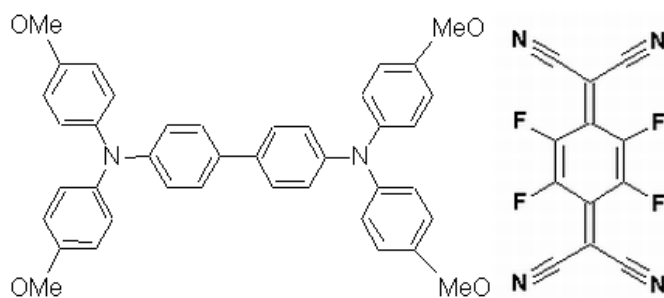


Fig. 3: Hole transport material MeO-TPD and F4-TCNQ as p-dopant

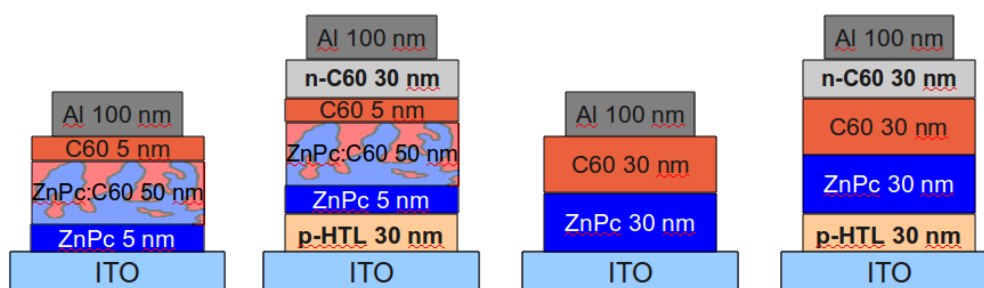
unclear and under discussion. In comparison to crystalline materials, thin films of the organic solar cell materials are usually amorphous. This leads to low charge carrier mobilities and probably the presence of several trap states. Furthermore HOMO and LUMO levels are broadened by spatial and energetic disorder in the material. Understanding the processes of charge transfer at the heterojunction and the formation of free charge carriers is still a challenge. These separation processes are expected on sub-microsecond time scale [e.g. 7, 8] and hence investigated by short-time spectroscopy. However, the mechanisms of charge transport and the role of traps are not well understood. Here transient photocurrent measurements could give insight into the process of trapping and detrapping [1], which is a loss mechanism in a solar cell, because it increases recombination probability and hence decreases current and open circuit voltage of the solar cell. Other transient techniques like carrier extraction by linear voltage (CELIV) [9] or time-of-flight measurements [10] are applied to solar cell material and show the benefits of such measurements. However, these methods are not performed under the working conditions of a complete organic solar cell.

The transient photocurrent and photovoltage techniques developed in Cambridge examine the response of the device to a pulse of light, either with or without a constant background illumination. This technique was applied to several small-molecule solar cells, to show its capability of characterizing these devices regarding to mechanisms like trapping. This report focuses on the influence of the doped transport layers of pin solar cells comparing them to devices without these transport layers. Besides the samples shown in this report, other devices were measured, including hybrid FHJ and BHJ and devices with barriers at the contacts. These data will be published soon.

## Project description

Selected samples for the time resolved measurements have been prepared at the Institut für Angewandte Photophysik in Dresden by thermal evaporation in a high vacuum system. Fig. 4 shows the investigated device stacks. Directly after preparation the samples were encapsulated by a glass encapsulation, allowing the cells to survive several months without any degradation. The samples and a specific sample holder were taken to Cambridge, where the transient measurements have been carried out by Mr. Tress with the assistance of scientists in Dr. McNeill's group.

The experimental setup is shown schematically in Fig. 5. A function generator connected to a high intensity LED is used to pulse the organic solar cell. The solar cell is connected to an oscilloscope and the transient photocurrent (using the low impedance input of the oscilloscope) or transient photovoltage (using the high impedance input of the oscilloscope) recorded. For transient photocurrent measurements, the pulse width can be varied (typically between 500 ns and 200 microseconds or longer) to ensure that the time taken for the device to reach equilibrium is



*Fig. 4: Device stacks of the investigated samples. Bulk heterojunction (BHJ) and flat heterojunction (FHJ) ZnPc C60 devices with and without doped transport layers. Doping is done employing dopants from Novaled AG, Dresden*

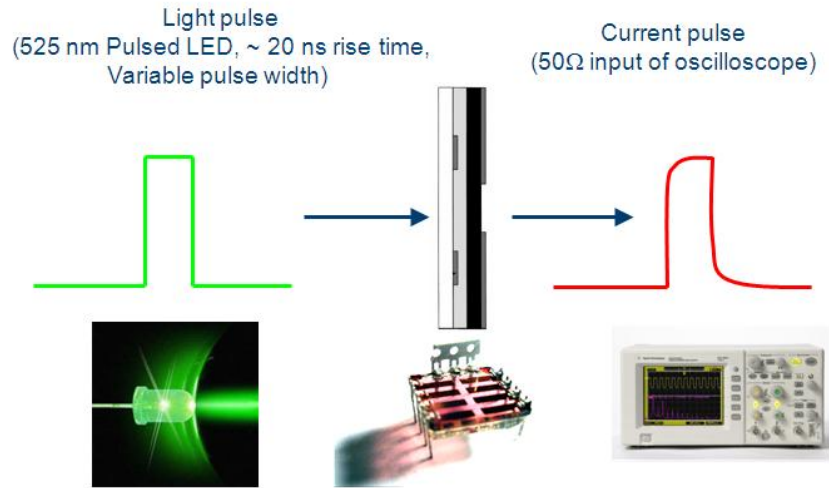


Fig. 5: Sketch of photocurrent method

ascertained. Furthermore, by varying the pulse intensity and comparing the normalised shape of the photocurrent curves information regarding charge-density dependent transport mechanisms and charge trapping can be obtained. In another configuration, a second LED is used to provide a constant background illumination and the response of the device to a light pulse recorded. In this configuration the intensity of the constant background illumination can be varied and the transient behaviour of the device under working (steady state) conditions investigated. It is in this configuration that the transient photovoltage works, with the photovoltage response of the device to a small perturbation recorded. In particular the photovoltage transient method records the decay of the photovoltage as a function of background illumination which provides information regarding the recombination rate of free charges under open-circuit conditions.

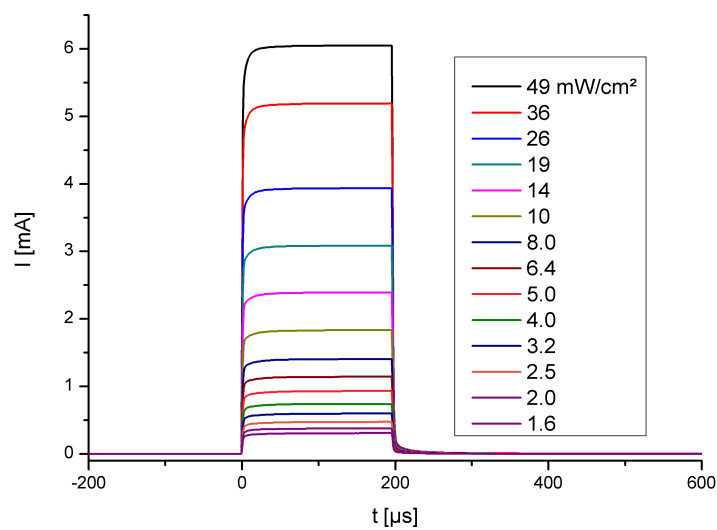


Fig. 6: Intensity dependent current transients for the BHJ without transport layers. The applied light pulse width is 200 $\mu$ s

## Results

Fig. 6 shows transient current data of a BHJ without transport layers illuminated by a 200  $\mu\text{s}$  pulse and varied light intensity. For better comparability this data is normalized to the plateau value, which is the steady state current, as shown in Fig. 7 for all four samples. Comparing flat and bulk heterojunction (Fig. 7a+c) without transport layers shows a significant difference. For the BHJ the transient is smooth and its intensity dependence can only be seen after the current reaches 90 % of the steady state value. With higher intensities charge carrier densities get higher in the device and the response gets faster. The FHJ shows a kind of kink at around 50 % of steady state current, which can be attributed to the high imbalance in charge carrier mobilities. In contrast to the BHJ, in the FHJ also the slower holes have to travel the same distance as the electrons from the heterojunction through the donor to the anode. This can explain the observed difference.

When comparing the BHJ with and without transport (Fig. 7a+b) layers a qualitative difference can be seen. The curves show an overshoot for the devices with transport layers. Such overshoots are commonly attributed to traps, as has been shown by McNeill et al [1] comparing simulation and experimental data for polymer solar cells. This leads to the conclusion that the doped layers and probably the dopant leads to traps at or close to the interface with the blend. In the FHJ these traps seem to be irrelevant. Reason is, that the heterointerface is spatially separated from the blend and the donor and acceptor are unipolar in contrast to the bipolar blend. A p-dopant is supposed to easily catch an electron, which means that contact to the blend, where photogenerated electrons are

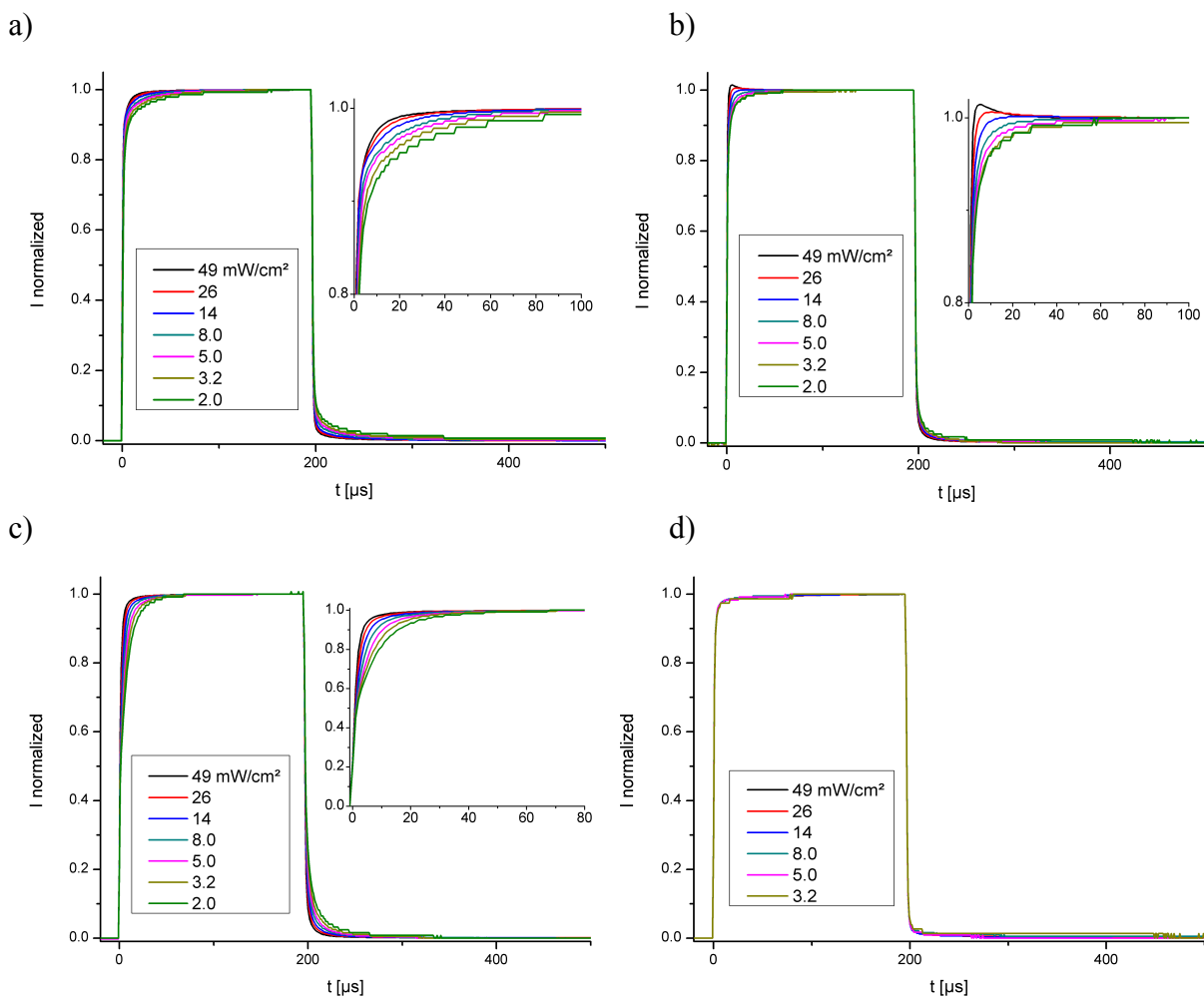
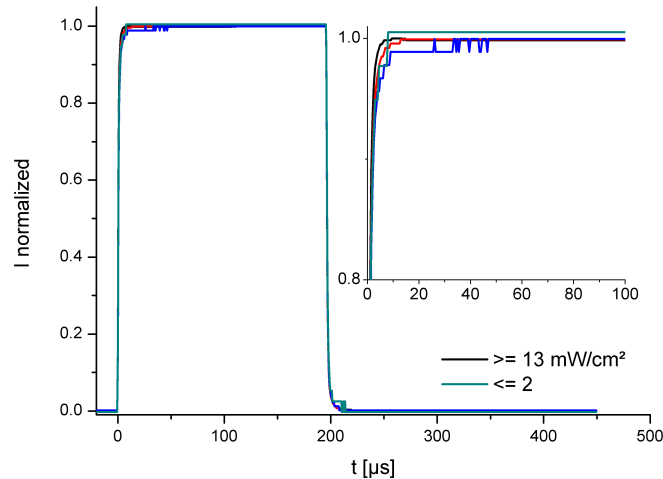


Fig. 7: normalized data for a) BHJ without transport layers (data of Fig. 6); b) BHJ with transport layers; c) FHJ without transport layers; d) FHJ with transport layers.



*Fig. 8: BHJ with transport layers under constant background bias illumination*

present, is harmful, whereas contact to the donor only lets the traps stay inactive. The introduction of traps by doped transport layers is also seen by other methods like impedance spectroscopy [11].

The measurements are repeated under an applied light bias. Significant changes in the photocurrent transients can only be seen in the BHJ with transport layers. The former overshoot is not observable (Fig. 8). Reason can be that the traps are already filled by the constant background illumination, which makes them inactive for charge carriers created by the additional light pulse. This has been shown for polymer cells in Ref. [1], too. Light intensities are, however, lower than in the previous experiment due to technical issues.

## Planned publications and further collaboration

A conference contribution at the EMRS 2011 is dealing with the interpretation of the measurement data obtained during this visit.

Furthermore, measurement data, which is not shown in this report, is planned to contribute to two publications concerning hybrid FHJ/BHJ solar cells and devices with barriers. These publications are planned to be submitted until mid of 2011.

No concrete collaboration is planned at the moment. The visit, however, has shown the applicability and power of the method for the characterisation of small molecule solar cells, so that further measurements will be done in the near future.

## References

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## Date of visit

March 15 2010 for 1 week

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