

HIGHLY EFFICIENT MOLECULAR ORGANIC SOLAR CELLS

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ABSTRACT: The photovoltaic behavior of perylene/phthalocyanine hetero-p/n-junction solar cell was investigated using intensity dependent I/V-characteristics, short circuit photocurrent spectroscopy, luminescence quenching and electroreflectance measurements. It is concluded that the charge carrier generation occurs only in a very thin active region at the contact for which light trapping needs to be optimized. However, here a very high quantum efficiency (close to 1) is achieved. Based on our experimental data a maximum solar AM 1.5 efficiency of about 2% can be calculated for this type of cell. A further increase can be achieved using a new cell structure. As used in polymer organic solar cells an interconnected network of C₆₀ particles was used to increase the interface area of the p- and n-type materials. Thereby an incident photon to current efficiency of more than 45% was achieved, resulting in more than double the efficiency obtained for classical cell structures.

Keywords: Organic Solar Cell-1: Fundamentals-2: Heterojunction-3

1. INTRODUCTION

Organic thin films are finding an increased application in xerography [1]. Here the photoconductivity based on the production of majority carriers upon illumination is the key process. However, when using organic materials for the production of organic solar cells [2-4] the majority as well as the minority carriers need to be produced and transported in the active charge generation layer. Therefore besides the charge separation mainly the mobility of minority carriers will determine the width of the active zone. Although the theory of electrical and optoelectrical phenomena is well understood in the case of organic crystals [5,6] there is a lack of adequate theories concerning organic thin film systems. A transfer of the theories developed for inorganic semiconductor thin films is seldom possible.

In our investigations photocurrent spectroscopy has proven to be the best tool to determine the width and effectiveness of the charge generation layer formed at Schottky or p/n-type junctions. However, the understanding of the spectra obtained, critically depends on the exact determination of light absorption profiles in our devices.

Although the width of the charge generation layer in an organic solar cell is much smaller than in an inorganic cell [7,8] a high power conversion efficiency may be reached because of the high absorption coefficients of the organic dyes. The sensitization solar cell, which is on the verge of industrial utilisation uses only one monolayer of an organic dye to absorb the light [9].

In the following we report on investigations of organic solar cells based on zinc phthalocyanine (ZnPc) and the methyl substituted perylene pigment (MPP) N,N-bis-methyl-perylene-3,4,9,10-tetracarboxylic acid diimide. These organic dyes have a good thermal stability, high absorption coefficients ($>10^5 \text{ cm}^{-1}$), and a sufficiently high electrical conductivity as p-conducting (ZnPc) and n-conducting (MPP) materials.

2. EXPERIMENTAL

The p/n-junction solar cells were produced by successive evaporation of the organic dyes on ITO coated substrates in a high vacuum evaporation system ($p < 3 \cdot 10^{-6}$ mbar). As a back electrode gold was evaporated on to the

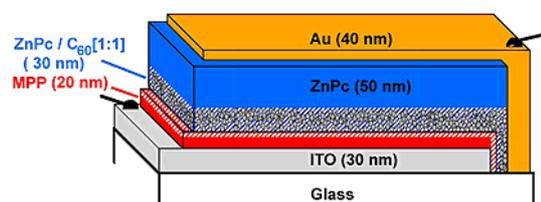


Figure 1: Structure of a sandwich organic solar cell consisting of substrate / ITO / MPP / ZnPc / Au containing an ZnPc/C₆₀-composite interlayer

top organic dye layer. Figure 1 shows a typical structure of our sandwich solar cells.

Most of the results presented in the following sections are obtained from a cell with the structure, substrate / ITO (30 nm) / MPP (20 nm) / ZnPc (220 nm) / Au (40 nm).

Interconnected network solar cells were prepared by coevaporating a ZnPc/C₆₀-composite layer between the MPP and ZnPc. Here the thickness of the composite layer was varied while keeping the total thickness of the ZnPc layer constant.

The best results presented in the following sections are obtained from a cell with the structure: substrate / ITO (30 nm)/MPP (20 nm)/ZnPc-C₆₀ [1:1](30 nm)/ZnPc (50 nm) / Au (40 nm). The short circuit photocurrent spectra were measured using a xenon arc lamp and a monochromator. For the I/V- characteristics under illumination an AM 1.5 solar simulator (K. H. Steuernagel Lichttechnik GmbH) was used. The photocurrent spectra as well as the I/V-characteristics were monitored using a Keithley SMU 236.

3. EXPERIMENTAL RESULTS

The current/voltage-characteristics of a hetero-p/n-junction solar cell under AM 1.5 illumination are shown in Fig. 2 for different light intensities. The I/V-characteristics of these cells show a rectifying behavior for all light intensities used.

The characteristic quantities of the power plot, the fill factor, the short circuit current and the power conversion efficiency have a strong dependence on the light intensity (Fig. 3). The fill factor (Fig. 3 left) decreases with increas-

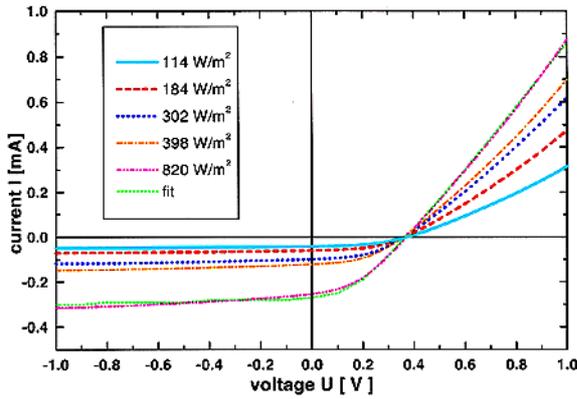


Figure 2: Structure of a sandwich organic solar cell consisting of substrate / ITO / MPP / ZnPc / Au containing an ZnPc/C₆₀-composite interlayer

ing light intensity because the increasing influence of the series resistance. The open circuit voltage (U_{OC}) does not depend on the light intensity. Therefore the power conversion efficiency is decreasing with the light intensity.

The short circuit current I_{SC} is directly proportional to the light intensity which indicates that an influence of the photoconductivity on the I_{SC} can be neglected. The photoconductivity was found to be proportional to the square root of the light intensity for all cases investigated.

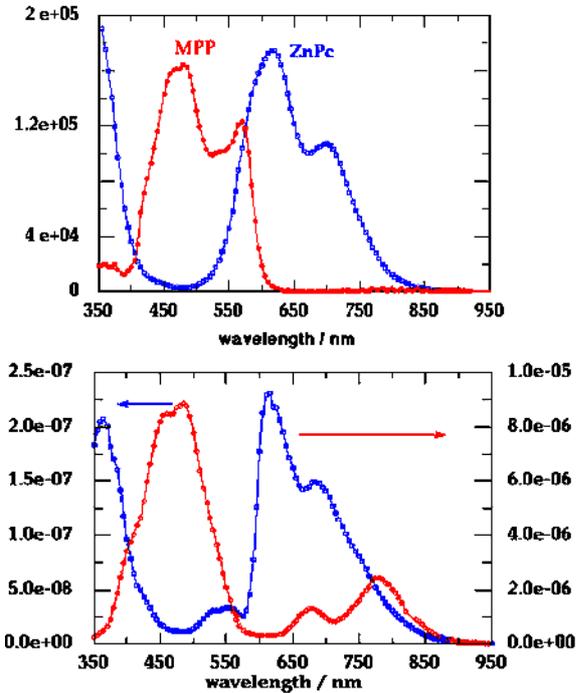


Figure 3:
Top: Experimental absorption spectra of the two materials
Bottom: Short current spectra for ZnPc-side (left) and MPP-side illumination (right) of the cell.
 The photocurrent of this cell consisting of two 200 nm thick films reflects the absorption of the back side film for both illumination directions, respectively.

The short circuit photocurrent spectra for the illumination through the ITO as well as through the semitransparent gold back contact are shown in Fig. 3, respectively. The $I_{SC}(\lambda)$ follows mainly the absorption coefficient of the backward, not primarily illuminated dye layer.

From this it is obvious that the short circuit photocurrent is generated in the interface region of the two organic dyes. In the case that also photons absorbed far away from the interface region would contribute to the I_{SC} , we would expect a short circuit photocurrent following the absorption spectra of both dyes. Also, in this case the shape of the I_{SC} would be identical for both directions of illumination.

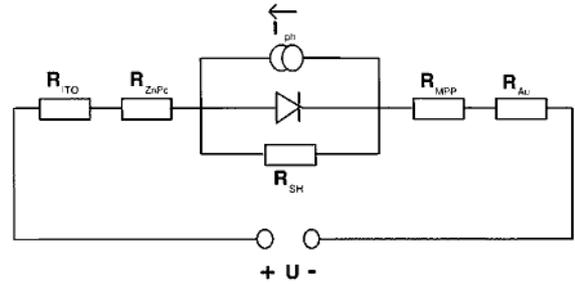


Figure 4: Equivalent circuit describing our solar cell

4. MODELLING

4.1 I/V-characteristics

The I/V-characteristics (Fig. 2) can be understood on the basis of an equivalent circuit as given in Fig. 4.

The equivalent circuit consists of a series resistance R_S which is the sum of all single layer resistances ($R_S = R_{Au} + R_{ZnPc} + R_{MPP} + R_{ITO}$), a shunt resistance R_{SH} , a photogenerator I_{PH} and the diode itself. The diode behavior is described by the well-known Shockley equation. The shunt resistance accounts mainly for shorts within the p/n-junction.

Using this equivalent circuit an equation for the total current I as a function of applied voltage can easily be derived (eq. 1).

$$I \left(1 + \frac{R_S}{R_{SH}} \right) - \frac{U}{R_{SH}} + I_{PH} = I_0 \left(\exp \left(\frac{e}{nkT} (U - I R_S) \right) - 1 \right) \quad (1)$$

I_0 represents the saturation current density, n the ideality factor, k the Boltzmann constant and T the temperature. This transcendental equation can be solved numerically.

The I/V-characteristics under AM 1.5 illumination with a light intensity of 820 W/cm^2 was simulated using the described equivalent circuit and is also plotted in Fig. 2 (dotted line). The current I was calculated for a given voltage U . The parameters of the equivalent circuit were varied until the deviations between experimental and simulated data were minimized. This was the case for $R_S = 78 \text{ } \Omega\text{cm}^2$, $R_{SH} = 4.6 \text{ k } \Omega\text{cm}^2$, $I_0 = 86 \text{ nA/cm}^2$ and $I_{PH} = 2.4 \text{ mA/cm}^2$.

The open circuit voltages of the experimental I/V-characteristics seem to be constant for the investigated light intensity regime. Therefore it is not possible to fit the curves for the other light intensities by simply changing the value of the short circuit photocurrent in the equivalent circuit. The equivalent circuit must be extended in a way such that it is capable of explaining a constant open circuit volt-

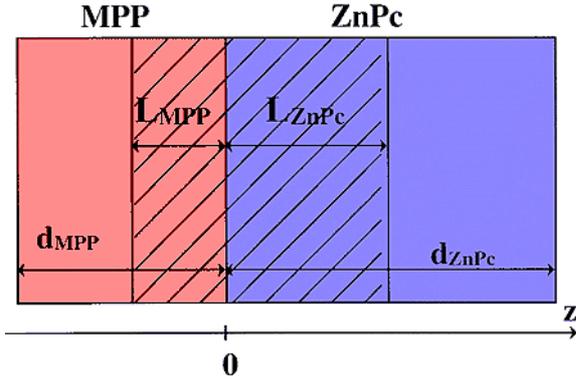


Figure 5: Box model used to calculate photocurrent spectra

age for varying short circuit currents. This extension is still under investigation.

4.2 Short circuit photocurrent spectra

In the experimental section we have already pointed out that a comparison of the absorption coefficients and the spectral shape of the I_{SC} has lead us to the assumption of small active regions at the organic / organic interface.

For a simulation of the short circuit photocurrent we use a box model as illustrated in Fig. 5.

The widths of the active regions at the contact (around $z = 0$) are L_{MPP} and L_{ZnPc} , with d_{MPP} and d_{ZnPc} being the total layer thicknesses of the organic dye layers. This model corresponds to a classical p/n-junction of semiconductors with a comparatively low diffusion length, with the $d_s = L_{MPP} + L_{ZnPc}$ being the thickness of the depletion layer.

In our model all photons absorbed within the active region contribute to the short circuit photocurrent with a probability of unity. The photons absorbed in the non-active regions will not contribute to I_{SC} . As a first approximation the effect of these absorbed photons on the photoconductivity will be neglected in the following considerations.

For a quantitative simulation of the photocurrent spectrum the total amount of photons absorbed within the active regions has to be determined for every single wavelength. The light propagation in the system substrate / ITO / MPP / ZnPc / Au is calculated using the Transfer-Matrix method [10] to get the complex electrical field strengths, E_k and the time averaged Poynting vector $\langle S_k \rangle(z)$. The negative derivative of the time averaged Poynting vector gives us the amount of absorbed light $A(z)$, at every position inside the dye layers (eq. 2).

$$\begin{aligned}
 A(z) dz &= -\frac{\partial \langle S_k \rangle(z)}{\partial z} dz \\
 &= \frac{2\pi k n}{c \mu_0 \lambda} \left[\left(\vec{E}_k + \vec{E}_k' \right) \exp\left(-\frac{4\pi k}{\lambda} z\right) + \left(\vec{E}_k + \vec{E}_k' \right) \exp\left(-\frac{4\pi k}{\lambda} z\right) \right] dz \quad (2) \\
 &= \frac{4\pi k n}{c \mu_0 \lambda} \left[\left(\vec{E}_k \vec{E}_k' - \vec{E}_k' \vec{E}_k \right) \sin\left(-\frac{4\pi n}{\lambda} z\right) + \left(\vec{E}_k \vec{E}_k' + \vec{E}_k' \vec{E}_k \right) \cos\left(-\frac{4\pi n}{\lambda} z\right) \right] dz
 \end{aligned}$$

For an accurate calculation of equation (2) we have to determine the actual optical constants (n , k) of the dyes first. The optical constants show a strong dependence on the substrate type and the growth conditions. Therefore the optical constants and also the layer thicknesses were determined by fitting the experimentally determined optical

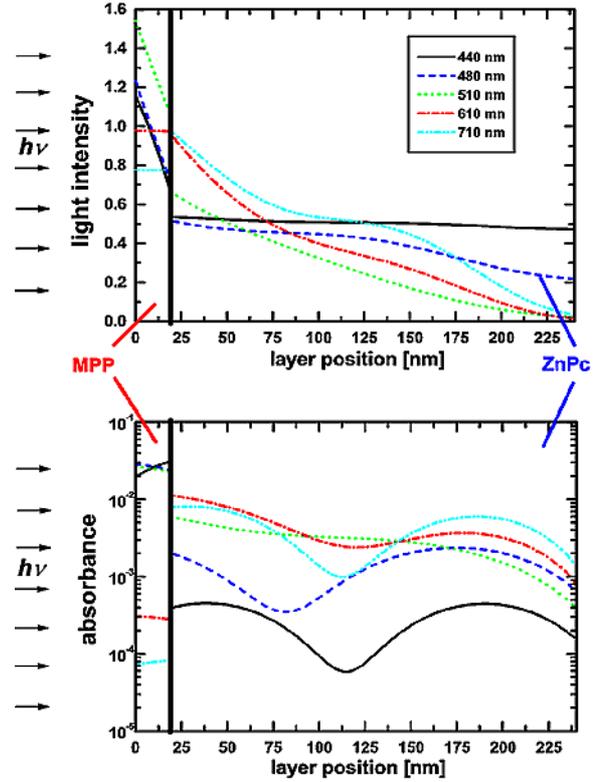


Figure 6: Light intensity (top) and absorbance profiles (bottom) in our solar cells. Illumination here through the ITO side.

reflectivity and transmission spectra of the whole multi layer system.

By using eq.(2) we get the intensity and absorption profiles. In Fig. 6 these profiles are shown for four selected wavelengths for illumination from the ITO side. The profiles were also calculated for light illumination through the gold back contact, but are not shown here.

A summation over all photons absorbed within the striped region in Fig. 6 results in the I_{SC} for every wavelength. In our box model the widths of the active regions remain as the only free parameter to fit the experimentally determined absolute current values. This rather simple model is capable of explaining the experimental data (Fig. 3) quantitatively whereas assuming more extended diffusion profiles fails to result in reasonable spectral fits.

The best correspondence between the experiment and the simulation is obtained for the case shown with $L_{MPP} = 1$ nm and $L_{ZnPc} = 5$ nm (Fig. 7). The rather small widths of the active regions and the total layer thickness, and therefore a rather thick film of unused but light absorbing and low conductive material exists and leads to unwanted efficiency losses.

In order to decrease the negative influence of the dead bulk material, we must decrease the total layer thickness down to a value for which the whole organic material is active. Fig. 8 shows the simulated I_{SC} under AM 1.5 illumination for a cell system substrate / ITO (30 nm) / MPP (1 nm) / ZnPc (5 nm) / Au (40 nm).

Also shown in Fig. 8 is the case where we introduced a non-absorbing dielectric with high conductivity between the ZnPc and the gold in order to tune the coherent light

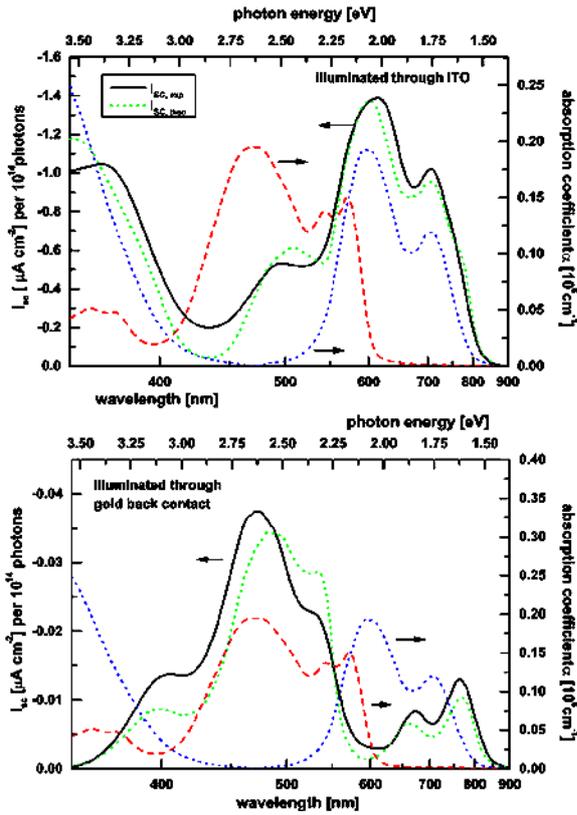


Figure 7: Comparison of the experimental and simulated ($L_{\text{MPP}} = 1 \text{ nm}$, $L_{\text{ZnPc}} = 5 \text{ nm}$) short circuit photocurrent spectra (left axis) and absorption coefficients (right axis) for both illumination directions

superposition in the layers to get maximum light absorption within the dye layers. The introduction of a 60 nm thick dielectric layer with an index of refraction of 2.0 results in an increase of the integrated I_{SC} by a factor of about 3 (Fig. 8).

If we assume an open circuit voltage between 0.4 V and 0.5 V, a fill factor of 50%, and neglect all resistivity effects, the maximum power conversion efficiency would be 1.9% for AM 1.5 illumination (820 W/m^2).

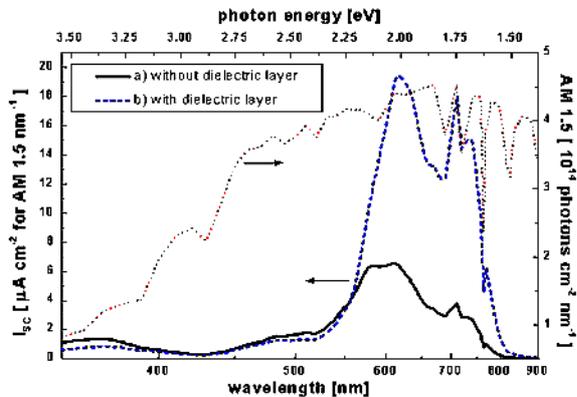


Figure 8: Calculated effect of an additional dielectric layer on the short circuit photocurrent

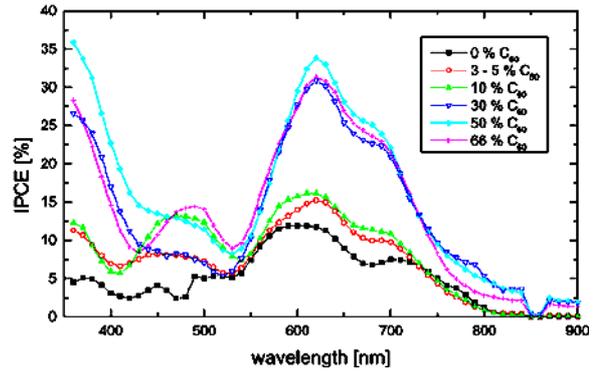


Figure 9: Incident photon to current efficiency spectra for solar cells made from 20 nm MPP and 165 nm ZnPc coevaporating different concentrations of C_{60} to the ZnPc layer.

The only way to further improve the solar efficiency would be an expansion of the widths of the active regions or a new cell structure closer to that used in recent sensitization solar cells [11]. Therefore a better control of the growth conditions and the doping is needed.

5. NANOPOROUS INTERFACES

As in sensitization solar cells [11], a major breakthrough became possible when instead of using a flat interface (compare fig. 5), a nanoporous interface was formed by introducing an interlayer in which ZnPc was mixed with C_{60} particles [12].

Used at first for polymers [13], C_{60} also proved to be a very efficient electron acceptor for ZnPc, leading to a dramatic increase of the short circuit photocurrent generation efficiency as shown in Fig. 9. Here the incident photon to current efficiency (IPCE) is shown, which is simply the number of electrons measured under short circuit conditions (zero applied bias), divided by the number of incident photons.

In order to normalize the measured photocurrent spectrum of the IPCE to the lamp spectrum one must verify that the short circuit current is really directly proportional to the light intensity. In the case of molecular organic solar cells,

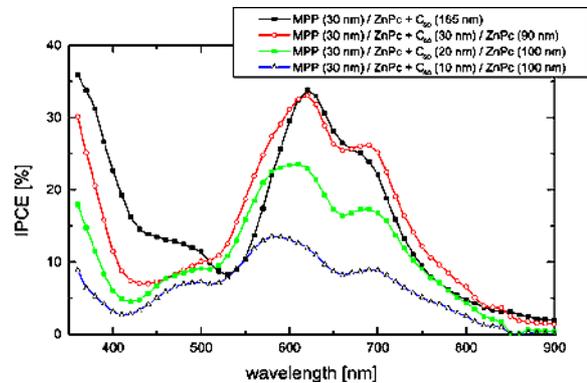


Figure 10: Incident photon to current efficiency spectra for solar cells made from 20 nm MPP and about 120 nm ZnPc of which an increasingly thick part contains C_{60} . The highest value is reached already with 30 nm of composite.

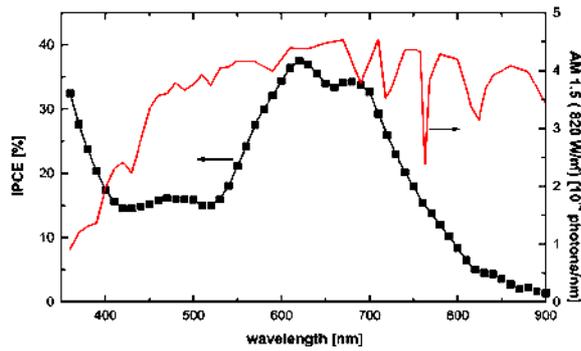


Figure 11: Incident photon to current efficiency spectra for solar cells made from 20 nm MPP and 165 nm ZnPc coevaporating different concentrations of C_{60} to the ZnPc layer.

this is the case only if the photoconductivity of the organic materials does not influence the measured photocurrent. The latter is found proportional to the square root of the photon flux [14]. A good test of an appropriate normalization of the photocurrent spectrum is provided by the relatively sharp emission maxima of a xenon lamp. They disappear completely in a normalized photocurrent spectrum only, if the correct intensity dependence is used.

In Fig. 9, we present the IPCE of organic solar cell structures as described above. The structure of the lowest curve is similar to the classical Tang [2] structure and consists of 20 nm MPP on ITO, followed by 165 nm of ZnPc and a gold back contact. The better curves are obtained from the same structures with different amounts (wt-%) of C_{60} . A maximum is found for 50 wt-% corresponding to a molar ratio close to 1, a value very similar to that found to be optimal also for conductive polymers [15-18].

In order to determine the thickness of the active area in this type of cell the following experiment was performed (fig. 10). Keeping the total thickness of the MPP and ZnPc layers constant, an increasingly thicker part of the ZnPc was enriched with 50 wt-% C_{60} . As can be seen in Fig. 10, the maximum value of ICPE is reached already for a composite interlayer of 30 nm. Further extension of the com-

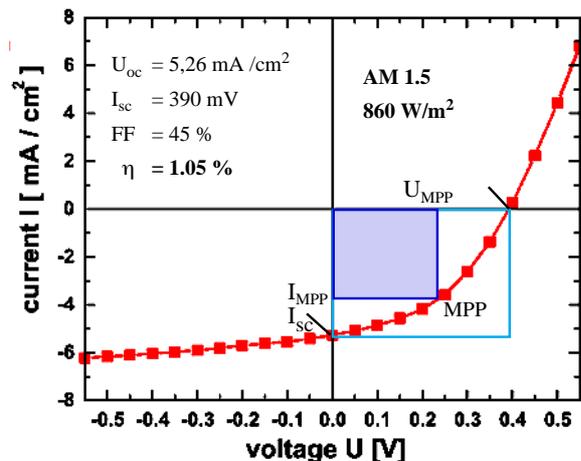


Figure 12: Current/voltage curve (including the power plot) of an optimized three layer cell measured under AM 1.5 solar simulator light with 860 W/m^2 light intensity.

posite film results in a decrease of the solar efficiency due to increased series resistance.

Fig. 11 gives an optimized three-layer cell in which the 50% C_{60} -containing ZnPc layer of 30 nm is followed by a 50 nm film of pure ZnPc to prevent pin hole shortcuts. With this cell a maximum IPCE of 37.5 % is obtained at 600 nm. Together with the solar spectrum (also shown) the measured photocurrent efficiencies correspond to a maximum solar current conversion efficiency of 17% in the spectral range of the ZnPc Q -band absorption (between 540 and 900 nm).

6. SOLAR EFFICIENCIES

In the case of polychromatic efficiencies, such as the power conversion efficiency and the current efficiency, it is necessary to use a well-defined light spectrum. The AM-solar spectra are certainly the standard light spectra to use for outdoor photovoltaic applications.

The AM 1.5 global sun light spectrum of a solar simulator must be used to estimate the solar power conversion efficiency, because it uses a well-defined spectrum. All other light sources make it impossible to compare efficiencies obtained by different groups. By e.g. using metal grids, one can decrease the light intensity without changing the spectral distribution significantly.

Fig. 12 shows a power plot of our organic solar cell. The power conversion efficiency as defined was determined to 1.05%.

The maximum value of 37% for the IPCE spectrum for the solar cells based on C_{60} -doped ZnPc is a very encouraging result. In contrast to the classical cells, which have an active film thickness of less than 10 nm, the composite film has an active film thickness of about 30 nm. This yields a photocurrent in the range of above 5.3 mA/cm^2 , corresponding to a solar current efficiency of 15.8%!

Using the IPCE spectrum and typical values for the open circuit voltage and the fill factor, a solar efficiency of 1.2% can be calculated. This is in satisfying agreement with the directly measured value of 1.05%. However, this is only because the series resistance at high light intensities is decreased to values below 100Ω .

These calculations show that in state-of-the-art molecular organic solar cells, sufficiently high currents can be produced to reach solar efficiencies of practical interest if the cell voltage and the fill factor can be improved accordingly.

5. SUMMARY

We presented experimental data for an organic solar cell made from the dyes ZnPc and MPP.

The I/V-characteristics of a classical Tang-type cell shows a clearly rectifying behavior with an efficiency of about 0.5% under AM 1.5 illumination (860 W/m^2). The experimental short circuit photocurrent spectrum was presented and simulated in terms of a p/n-junction model. The generation region of the photocurrent is only a small space charge region at the interface of the two organic materials.

Furthermore, we estimated that light trapping in this cell can be optimized by introduction of an additional dielectric layer, resulting in a solar power conversion efficiency of about 1.9%. These cells are limited by the small photocurrent obtainable from an active film thickness below 10 nm

A breakthrough in terms of photocurrent generation was obtained by coevaporation of C₆₀ and ZnPc. Thereby the active film reaches a thickness of about 30 nm leading to an overall solar current efficiency of nearly 18%. With this type of cell solar efficiencies above 5% should be achievable by only minor improvements.

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