

From evaporation to solution processed organic tandem solar cells

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ABSTRACT

In this study, we have investigated the possibility to realize different types of stacked, serially connected organic solar cells. First of all, we combined solution processed MDMO-PPV:PCBM or P3HT:PCBM and evaporated ZnPc-C60 bulk-heterojunction solar cells to achieved tandem cells exploiting the complementary absorption spectra of each single cells. Such devices exhibit open circuit voltages of 1V with a short-circuit current of approximately 5mA/cm² and a fill factor of 0.35 under simulated AM1.5 illumination. In the case of stacked, series connected cells with all active layers processed from solution, we observed a significant increase of the open circuit voltage in comparison with the single junction cells: Device fabricated from two bilayers comprising MDMO-PPV and PCBM as photoactive materials exhibit 1.28V open circuit voltage, 1.1mA/cm² short circuit current and a fill factor of 0.45 under simulated AM1.5 illumination.

Keywords: organic solar cells, conjugated polymers, fullerenes, small molecules, stacked cells, tandem cells.

1. INTRODUCTION

Thin films of organic semiconductors can have very high absorption coefficients in their visible absorption bands. This is interesting for generation of potentially thin, flexible, lightweight and cost-effective photovoltaic devices. The ease of fabrication via low temperature evaporation and/or solution processing opens up a potentially wide market for devices made of these organic materials since they can be integrated onto or into other products such as textiles, packages, toys, portable electronic equipments etc.¹⁻³ In the last years, large efforts have been employed to increase the efficiency and stability of organic solar cells. Recently, solar energy conversion efficiencies about 5 % were reported in a single device based on soluble polythiophene and fullerene derivatives.⁴ In the solution processed materials, most optimization efforts have been focused on the chemical structure and purity of the used compounds as well as the nanomorphology of the organic composite film.⁵ The usual structure of these devices is based on the “bulk heterojunction” concept.⁶

In solar cells made from evaporated small molecules, a promising material combination has been proposed, based on a layered stack of phthalocyanines, C₆₀-fullerenes and a homogenous blend of the two sandwiched in between: Solar energy conversion efficiencies of over 3 % have been reported.⁷⁻⁹ Recently, an increase of this efficiency up to 5.7 % was announced, when two small molecule solar cells were stacked with a serial connection to enhance the absorptive thickness of the solar cell without suffering losses due to the low conductivities of the absorbing materials.¹⁰⁻¹² This technique seems to be a novel way of increasing the maximum efficiency of organic solar cells and a first step towards true organic tandem solar cells. The tandem concept utilizing high-quality inorganic semiconducting materials with different bandgaps allows already solar energy conversion efficiencies over 30 %¹³, significantly more than single layer solar cell.¹⁴

The fabrication of stacked organic solar cells based on a series connection of two small molecules donor - acceptor heterojunction solar cells has been achieved using an ultrathin metal layer as recombination center between the individual cells.¹⁰⁻¹² The structure of such a stacked cell is shown in Fig. 1.

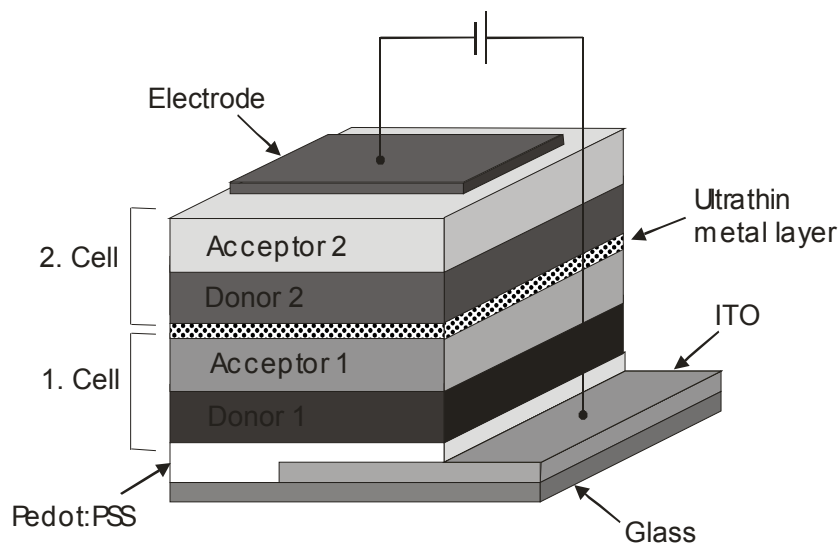


Figure 1: Schematic cross section of a tandem organic solar cell comprising two individual cells connected in series via a thin metallic layer.

If both solar cells comprise the same active material combination, then a doubling of the open-circuit voltage (V_{oc}) is expected. The short circuit current (I_{sc}) corresponds to the lower I_{sc} of the components in the stack. The first cell has to be semitransparent and the film thicknesses have to be adjusted so that both cells will deliver optimally the same I_{sc} .¹⁰⁻¹¹ In a real tandem cell, the active materials have different band gaps with accordingly different V_{oc} for the two cells. The first cell absorbs the higher energy photons and converts them to electrons of higher potential while the second cell absorbs the remaining photons and converts them to electrons of lower potential. This leads to a more efficient conversion of photon energy to electron voltage and thus a tandem cell can exceed the maximum theoretical efficiency of a single layer solar cell.¹⁵ In the case of inorganic semiconductors, the enhancement of the cells' capabilities relies basically in the reduction of energy losses by thermalization. However, for organic semiconductors, which show usually limited absorption range, such approach would allow also a better harvesting of light.

Donor-acceptor bulk-heterojunctions made of either poly(2-methoxy-5-(3',7'-dimethyloctyloxy))-p-phenylene vinylene (MDMO-PPV) or poly-3-hexyl-thiophene (P3HT) and a soluble fullerene derivative [6,6]-phenyl C_{61} -butyric acid methyl ester (PCBM) absorb photons in the blue and the green spectral regions, while evaporated small molecule solar cell comprising zinc-phthalocyanine (ZnPc) and fullerene C_{60} as photoactive materials, absorb strongly in the red and near infrared part of the spectrum. Therefore, we have extended the stacked small molecule solar cell concept¹⁰ to a real tandem solar cell with organic active layers by stacking an evaporated small molecule solar cell onto a solution processed polymer:fullerene solar cell. Moreover, we have elaborated stacked cells of the very same active materials in the case of solution processed cells.

2. EXPERIMENTALS

Indium tin oxide [ITO] coated glass having a sheet resistance smaller than 20 ohm/square, was used as substrate. The ITO was removed from one half of the substrate using an acidic mixture and then the etched substrates were cleaned with acetone and iso - propanole in an ultrasonic bath. After drying, a PEDOT:PSS layer was spin-cast on the ITO in order to reduce the roughness and increase the wettability of the substrate surface. Before application, the aqueous PEDOT:PSS dispersion was stirred for 20 minutes and then filtered with a 0.45 μm filter.

The problem of processing a bilayer from solution lies in the dissolving properties of polymers and the fullerene PCBM. Both are soluble in organic solvents. Therefore, a new spin coating technique was introduced: One drop of PCBM solution was deposited onto the polymer layer while the sample was spinning at high speed. Several experiments showed

that the speed should be more than 6 000 rounds per minute to get a homogenous film of PCBM on the polymer layer. This operation may not result in a perfect bilayer structure, since the solution of PCBM in organic solvent might dissolve and diffuse in part of the polymer layer. But this phenomenon can be largely prevented by using high spin coating speeds and changing the solvent of the fullerene as already suggested before.¹⁷ Dichloromethane was found ideal in our case, because of its low vaporization temperature and good solubility of PCBM. The existence of a pure PCBM layer on the top of the polymer was revealed by photoluminescence (PL) measurements. In the case of PCBM spin-cast from solvent like chlorobenzene, the PL of PCBM was observed to be entirely quenched, indicating the existence of a mixture PCBM/MDMO-PPV. However, for PCBM spin-cast from dichloromethane, strong PL of PCBM could be detected. Though this observation cannot rule out the existence of a mixture PCBM/MDMO-PPV, it does ensure that a pure layer of PCBM is still present at the outmost surface of the structure.

In order to increase the wettability of PEDOT:PSS on the PCBM surface, a surface treatment of the latter was performed by using highly dissolved PEDOT:PSS in iso-propanol (1:20 in volume). This solution is prepared by dropping the aqueous PEDOT:PSS solution slowly into the alcohol while heavily stirring. This solution can be spincoated and gives an extremely thin conducting layer. The conductivity of this diluted PEDOT:PSS : iso-propanol layer is of primary importance to ensure good interconnection of the stacked cells.

For the evaporated small molecule cells, 10 nm of ZnPc were evaporated with a rate of 0.03 nm/sec. After that, a mixture of ZnPc and C₆₀ 1:1 (40 nm), and finally a pure 15 nm C₆₀ layer was deposited (rate 0.03 nm/sec) onto top. The vacuum in the evaporation chamber was about 5×10^{-6} mbar. For the top electrode, 5 nm Chromium and 95 nm Aluminum were evaporated.

Finally, the solar cells were characterized under 100 mW/cm² (AM 1.5, calibrated with a silicon diode) white light illumination from a Steuernagel solar simulator. The measurements were carried out under argon atmosphere in a glove box. A Keithley 2400 unit was used for the measurement of the current – voltage characteristics.

3. RESULTS AND DISCUSSION

3.1 Solution and evaporation processed tandem cells

As explained above, our intention was to fabricate a tandem cell made of an evaporated cell stacked on, and connected in series with a solution processed cell. In such a case, the middle recombination junction has to be contacted with a hole blocking layer from the first cell and with an electron blocking layer from the second. For the second cell, this is easily achieved by depositing a layer of pure ZnPc that shows very good electron blocking behavior.¹⁶ However, for the first, solution processed cell, this requirement is much more difficult to fulfill, since using the standard bulk-heterojunction concept would leave a mixture of polymer and fullerene at the recombination junction. Therefore we developed a spincoating technique (see experimental part), inspired by previous works¹⁷, which allows to deposit a PCBM layer on the pristine polymer surface. Using this diffusion-bilayer technique we have achieved MDMO-PPV:PCBM single cells showing an I_{sc} of 3.2 mA/cm², a V_{oc} of 800 mV and a fill factor of 0.46. In the case of P3HT:PCBM diffusion-bilayer, we measured an I_{sc} of 8.5 mA/cm², a V_{oc} of 550 mV and a fill factor of 0.55 without any subsequent annealing steps.

To further increase the charge carrier selectivity of the interface, we evaporated a thin layer of C₆₀ onto this bilayer polymer:fullerene device before continuing with an ultrathin (0.5 nm) silver recombination contact and the ZnPc:C₆₀ upper cell. The performances of these devices are shown in Fig. 2.

It can be observed that the V_{oc} increases as compared to the respective single layer devices, as is expected for a tandem solar cell based on a series connection. The measured V_{oc} of the tandem device is close to the sum of the individual V_{ocs} of the single cells (1160 mV for MDMO-PPV and 1020 mV for P3HT based tandem cells). If the first cell is fabricated without the hole blocking layers the voltage stays significantly below the optimal value, indicating the importance of the charge carrier selectivity at the recombination contact.

One can note that the I_{sc} of the tandem cells is lower than in either single cell so that the overall solar power conversion efficiency is not increased. This is due to the fact that the thickness of the cells was not yet optimized to provide matched currents under simulated AM1.5 irradiation. Power conversion efficiency at 100 mW/cm² simulated AM1.5 illumination reaches values of above 1.5 % for the P3HT:PCBM / ZnPc:C₆₀ – tandem solar cell.

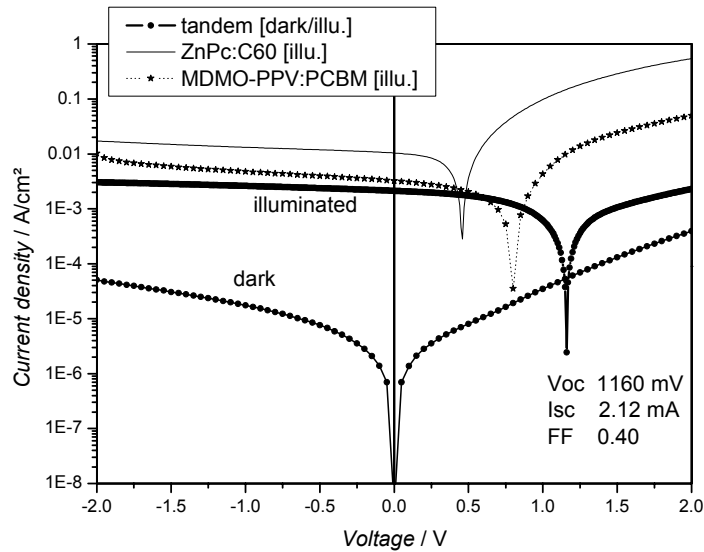
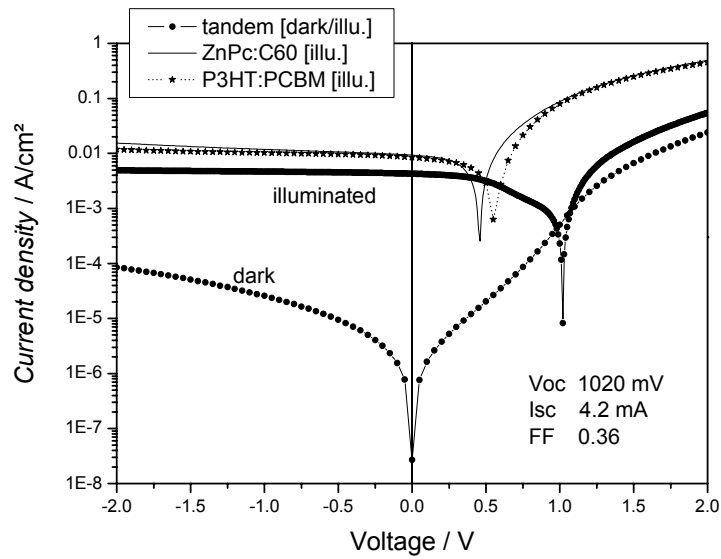


Figure 2: Dark/Light I-V-characteristics of single and tandem solar cells.

Wavelength dependent short circuit current was measured for the P3HT:PCBM and ZnPc:C₆₀ single cells and the corresponding tandem cell and is shown in Fig. 3. The single cell spectra show a very clear spectral distinction between the two material systems: The Zn-PC/C60 cell covers the range from 550 to 800 nm while the solution processed (P3HT-PCBM) device absorbs photons below 650 nm. The tandem solar cell shows a very weak signal in the regions where only one cell is active, since the photocurrent is blocked by the inactive device. Only in the regions where the

photocurrent efficiencies of both cell types overlap (below 450 nm and between 550 and 650 nm), a significant current from the tandem cell is measured. Above 720 nm the tandem cell shows no photocurrent response indicating leakage loss mechanism being negligible.

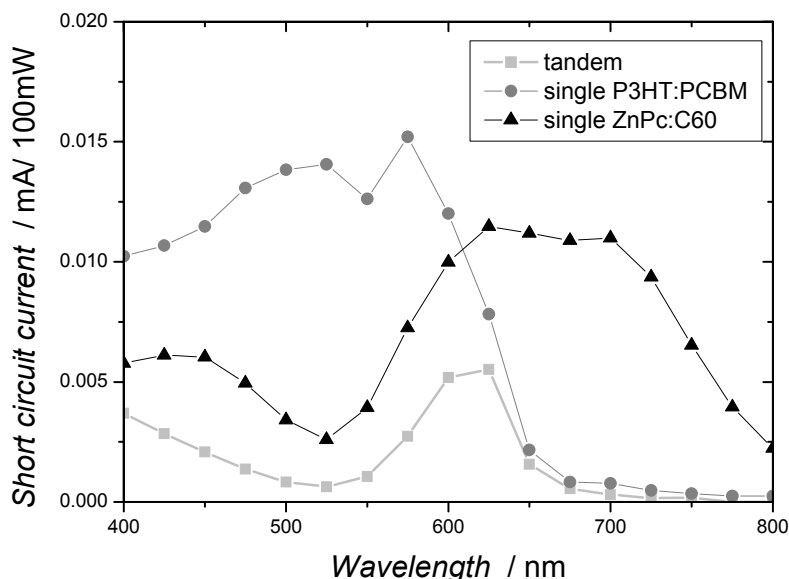


Figure 3: Short circuit current measurement at different wavelengths, for a P3HT:PCBM single cell, a ZnPc:C60 single cell, and a P3HT:PCBM/ZnPc:C60 tandem cell.

3.2 Solution processed stacked cells

As the fabrication of solution processed solar cells shows obvious technological advantages¹⁸, a tandem cell using only solution processed materials in its active layers is desirable. As a first step, we fabricated stacked solar cells made from MDMO-PPV:PCBM. The most problematic issue is the deposition of the second solar cell on top of the first one without destroying the underlying cell, since all the organic semiconductors used are soluble in the very same solvent as it is the case for MDMO-PPV and PCBM. In addition, the ultrathin metallic recombination contact in between would also be washed away by the spin-coating of the second cell. Therefore we used the water-soluble conducting polymer PEDOT:PSS as a recombination buffer layer in order to protect the first cell. This involves a surface treatment of the first solar cell to ensure a better wetting of the aqueous solution of PEDOT:PSS required for spincoating (see experimental part).

To ensure the selective contact to the recombination junction, we utilized the spincoating technique to deposit the MDMO-PPV:PCBM solar cells in a diffusion-bilayer configuration (see experimental part). The performance of these organic stacked solar cells can be seen in Fig. 4.

A significant increase in the Voc of the stacked device in comparison to the single cells is achieved, with Voc up to 1.280 mV. The Isc is rather low, due to mismatch of the thickness of the individual cells. A power conversion efficiency of about 0.6 % under 100 mW of simulated AM1.5 illumination was calculated.

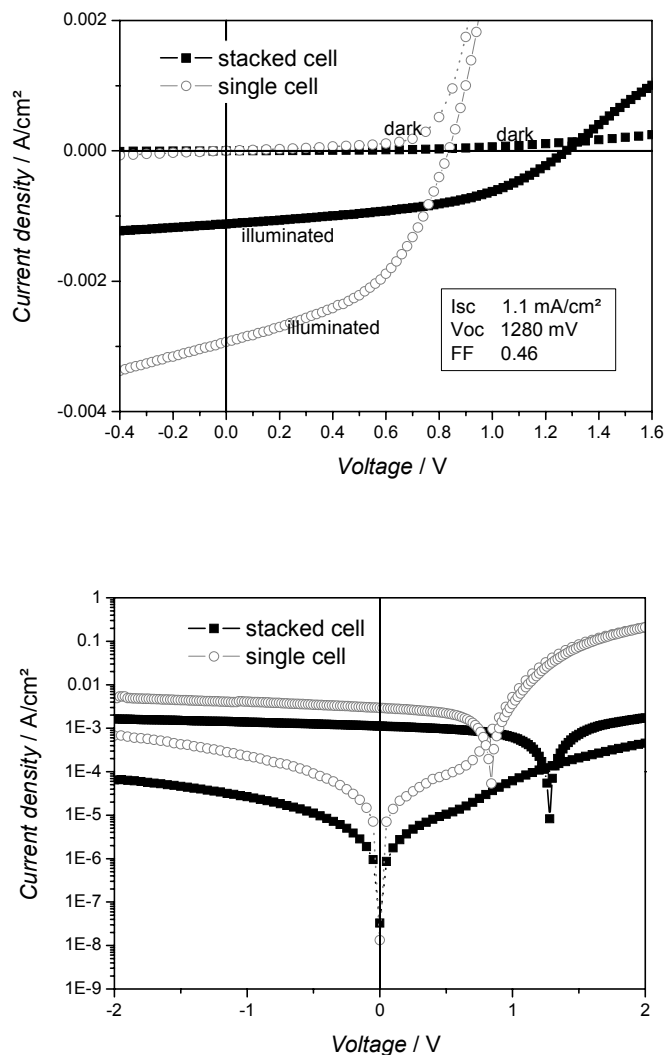


Figure 4: Dark/Light I-V-characteristics of stacked MDMO-PPV:PCBM cells.

4. CONCLUSIONS

In conclusion, we have produced organic tandem solar cells comprising both a solution processed polymer:fullerene as well as an evaporated small molecule photovoltaic device. An increase of the photovoltage of the single cell devices has been achieved near the limit of superposition of values. Further optimization, especially concerning the thickness of the active layers may lead to high efficiencies in these very promising devices. Moreover, fully solution processed organic stacked solar cells based on MDMO-PPV:PCBM blends were fabricated and characterized. A Voc of 1 280 mV is

demonstrated. Various technological challenges were overcome to reach these first steps that will certainly fuel the interest in further scientific investigations concerning organic tandem or stacked solar cells.

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