Fabrication of large area photovoltaic devices containing various blends of polymer and fullerene derivatives by using the doctor blade technique

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Abstract

Large area photovoltaic devices based on interpenetrating networks of donor and acceptor molecules have been fabricated by using the doctor blade technique. Devices containing blends of poly (*para* phenylenevinylene, PPV) derivatives as donor materials with various C_{60} derivatives as acceptors are compared. It is shown that among the various combinations of materials short circuit currents are maximal for blends of PPV and a highly soluble fullerene derivative (PCBM monoadduct), whereas the open circuit potentials stay almost the same for all devices. For the best combination of donor – acceptor materials it has been shown that upscaling to 10 cm x 15 cm is possible by using the doctor blade technique without loosing efficiency.

Keywords: Solar Cells, poly (*para* phenylenevinylene) and derivatives, fullerenes and derivatives, bulk heterojunction, doctor blade technique

Introduction

Polymer photovoltaics offer great technological potential as a renewable, alternative source for electrical energy. The demand for inexpensive renewable energy sources is the driving force to new approaches in the production of low cost polymer photovoltaic devices. In the last couple of years, enhanced efforts have been put into the development of solar cells based on organic molecules and conjugated polymers.[1-11]

The technological advantages for the fabrication of polymer based organic solar cells, like roll to roll production of large areas, lead to a possible reduction of the production costs for large area production. The mechanical flexibility as well as the tunability of the bandgap offer interesting perspectives of polymer based solar cells as compared to solar cells based on inorganic materials. Because of these advantages, the development of polymer solar cells would have a major impact, even if the efficiencies of these types of photovoltaic devices up to now are smaller than the efficiencies achieved in inorganic solar cells.

For the generation of electrical power by absorption of photons it is necessary to spatially separate the electron-hole (e-h) pair generated by photoexcitation before recombination processes can take place. In conjugated polymers, the stabilization of the photoexcited e-h pair can be achieved by blending the polymer with an acceptor molecule, which has an electron affinity that is larger than the electron affinity of the polymer but still smaller than its ionization potential. In addition, the highest occupied molecular orbital (HOMO) of the acceptor should be lower than the HOMO of the conjugated polymer. Under these conditions it is energetically favorable for the photoexcited conjugated polymer to transfer an electron to the acceptor molecule. The hole remains in the polymer valence band, which is the lowest available energy state for the hole.

In our work this alignment of the energy levels is realized by blending poly(*para*-phenylenevinylene) (PPV) derivatives (acting as electron donors) with derivatives of C_{60} (electron acceptor). It has been shown that in these systems the transfer of the photoexcited electrons onto the fullerenes occurs within aprox. 200 fs after the excitation [12-13]. Since all other known competing relaxation processes in conjugated polymers occur on time scales that are orders of magnitudes larger than 200 fs, this ultrafast charge transfer must have a quantum efficiency of approximately 1, *i.e.* nearly all photons absorbed by the conjugated polymer generate an electron on C_{60} and a positive charge on the polymer. In addition, the recombination of the charge separated excited state takes place on a μs-time scale [12], allowing the generation of high concentrations of non-equilibrium electrons and holes.

In the following we compare surface qualities of polymer layers containing different derivatives of C_{60}. Using doctor blade technique uniform films with a thickness between 100 and 150 nm are produced. This technique also shows that upscaling is possible for plastic solar cells using a polymer substrate (roll to roll process) and also large cells up to 10 cm x 15 cm are produced and compared to 6 cm x 6 cm solar cells in their current/voltage (IV) behavior.

Experimental

For a better smoothness of the substrate (ITO covered PET with a resistance of 55 ohm/square) a film of poly-(3,4-ethylenedioxythiophene)-poly-styrenesulfonate (PEDOT) from Bayer AG

was casted on the ITO by doctor blading. After drying of the PEDOT film, the solar active layer has been casted by doctor blading from a solution of poly [2-methoxy, 5-(3',7'-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV) mixed with C_{60} as well as mono- and multiadduct of the solubilized C_{60} derivative [6,6]-Phenyl C_{61}-butyric acid methyl ester (PCBM) in toluene. Devices were produced on 6 cm x 6 cm large transparent ITO coated PET substrates by doctor blading technique. With this technique the polymer-fullerene solution is deposited in a narrow slit between the surface of the substrate and the blade of the doctor blade. Then the blade is dragged by a motor at a constant velocity over the substrate and the substrate is covered uniformly by the polymer-fullerene solution. All doctor blading activities have been performed under room conditions. The mixing ratio of polymer to fullerene is 1:3 (weight/weight) for the mono- and multiadduct PCBM and 1:2 (weight/weight) for C_{60} due to its lower solubility in organic solvents compared to PCBM. The enhanced solubility of PCBM compared to C_{60} allows a high fullerene-conjugated polymer ratio and, therefore, strongly supports the formation of an interpenetrating network of donor and acceptor molecules (donor-acceptor bulk heterojunction). Although the mixing ratio between polymer and C_{60} is lower than the mixing ratio between the polymer and PCBM, the fullerene concentration is in all cases higher than 17 vol% of fullerene, which has been found to be the percolation threshold for a MDMO-PPV / PCBM solar cell [12,14,15]. The thickness of the polymer / fullerene layers is in a range of 100-150 nm.[12] In this blend the polymer acts as electron donor while C_{60} and its derivatives act as electron acceptors. The chemical structure of the compounds is shown in Fig 1.

The uniform donor acceptor layer of the solar cell is sandwiched between two electrodes with different work functions, in our case aluminum (Φ_m = 4.3 eV) and ITO (indium tin oxide, Φ_m= 4.7 eV) are used.

As a top electrode aluminum was deposited by vacuum evaporation. For the 6 cm x 6 cm substrates 4 Al-electrodes with a size of 4 cm² each were chosen, on the 10 cm x 15 cm substrates 2 Al-electrodes with an active area of 50 cm² each were vacuum evaporated. For all deposition steps the vacuum was below 10^{-5} mbar.

The IV characteristics were recorded under a illumination intensity of 6 mW/cm² white light (luminescence tube) by a Keithley SMU 2400 Source Meter (illumination through the transparent ITO side), whereas the surface properties were monitored by atomic force microscopy (AFM).

Results and discussion

The quality and the homogeneity of the polymer – fullerene strongly influences the efficiency of the solar cell. The doctor blading technique allows to cast thin layers of a solution containing the polymer and the fullerene uniformly on the surface of the substrate. A thin, wet layer with a constant thickness, still containing a certain amount of the solvent, is left on the substrate then. This residual solvent is removed by heating or under active vacuum pumping. During this drying process a separation of the two components within the otherwise homogeneous mixture may take place depending on the different solubility of polymer and fullerene. For different derivatives of fullerenes the solubility in organic solvents is different, therefore influencing the quality of the polymer-fullerene film. Inhomogeneous films with pin holes and/or large serial resistivities lead to small filling Factors (FF), lower rectification and decreased open circuit voltages (V_{oc}).

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Figure 2 shows AFM pictures of solar cells made from solutions of MDMO-PPV with PCBM monoadduct (Fig. 2a), PCBM multiadduct (Fig. 2b) and C_{60} (Fig. 2c) respectively. The most homogeneous film is found for the MDMO-PPV / PCBM multiadduct device. PCBM multiadduct has the same chemical structure than PCBM monoadduct, but contrary to PCBM monoadduct (one functionalized side group) two or three functionalized side groups are on the fullerene. These functionalized side groups give a better solubility in organic solvents compared to C_{60} or PCBM monoadduct. Also with PCBM monoadduct homogeneous films can be produced, but it is clearly seen that the surface is not as smooth as with PCBM multiadduct. This increasing roughness for MDMO-PPV / PCBM monoadduct might be due to the slightly lower solubility of PCBM monoadduct in organic solvents compared to PCBM multiadduct. For the MDMO-PPV film containing C_{60} phase separation on a µm scale can be observed. As all solutions were filtered by 0.2 µm syringe filters before casting, these large particles must have formed during the drying process of the doctor bladed films and are consequently assigned to C_{60} crystals. These crystals of C_{60} are up to several micrometers long. However, in spite of the enhanced surface roughness and phase separation no pin holes were detected on the surface of the doctor bladed films by AFM.

In Fig. 3, the I-V characteristics of photovoltaic devices made from blends of PPV with the three different fullerenes are monitored under illumination with 6 mW/cm² white light from a luminescence tube. It is clearly shown that the highest short-circuit current is observed when PCBM monoadduct is used as electron acceptor ($|I_{sc}| = 280$ µA/cm²), whereas PCBM multiadduct devices show the lowest short circuit current ($|I_{sc}| = 50$ µA/cm²). Devices produced from blends containing C_{60} give a short circuit current, which is in between the two PCBM derivatives ($|I_{sc}| = 145$ µA/cm²).

The open circuit potentials V_{oc} of the three devices shown in Fig. 3 are around $V_{oc} = 0.72$ V, independent of the molecule used as acceptor. It is worth noting that the measured open circuit voltage is significantly higher than one would expect from a simple model describing the device as a metal-insulator-metal (MIM) diode. In such a model, the difference of the work functions of the electrode materials defines the upper limit of the open circuit voltage. Although the work function of ITO is a poorly defined quantity (values ranging from 5.5 eV [16] to 4.1 eV [17] are reported in literature), recent estimates seem to converge into the range between 4.4 [18] – 4.7 [19] eV. Using these values for the ITO work functions, one would expect the open circuit voltage of an ITO / polymer: C_{60} / Al device to be not larger than 0.4 V. Experimentally, however, an open circuit voltage of 0.72 V is observed. Up to now, the origin of the high open circuit voltage is not fully understood, it might be due to a formation of a dipol layer at the electrode / polymer interface [20].

To demonstrate the upscaling potential of the plastic solar cells by using the doctor blade technique, solar cells with a substrate area of 10 cm x 15 cm were fabricated. Again PEDOT / ITO covered PET foil was used. As solar active layer a thin film of MDMO-PPV / PCBM monoadduct was deposited by doctor blading. As top electrode aluminum was evaporated. The active area of the solar cell is 2 x 50 cm². Figure 4 shows the I-V behavior of such a large area solar cell under illumination with 6 mW/cm² white light from a fluorescence tube and under dark conditions. The large area solar cells show an open circuit voltage of 700 mV, what is only slightly lower than the open circuit voltage of the 6 cm x 6 cm solar cells. The short circuit current for the 10 cm x 15 cm solar cell is $|I_{sc}| = 276$ µA/cm²,

which is almost the same as for the smaller solar cell containing MDMO-PPV and PCBM monoadduct ($|I_{sc}|$ = 280 µA/cm²). The filling factor FF for the large area solar cell, calculated after equation (1):

$$FF = (V_{max} * I_{max}) / (V_{oc} * I_{sc}),$$

is 0.48. The rectification of the large area solar cell in the dark is around 10² (for −1.5 V to 1.5 V), whereas under illumination it is still around 10. At higher forward bias, the dark- and the photocurrent are quite similar, indicating that photoconductivity does not play an important role in these devices.

Conclusions

For photovoltaic devices fabricated from several blends of MDMO-PPV as donor material and different fullerene derivatives (C_{60}, PCBM mono and multiadducts) as acceptor materials, the highest open circuit voltage and short circuit currents were obtained with a 1:3 (weight/weight) blend of MDMO-PPV and PCBM monoadduct. Although it is shown that the PCBM multiadduct, which achieved the best film quality, shows the lowest short circuit current.

It has also been demonstrated that upscaling of plastic solar cells is possible without decreasing the short circuit current or the open circuit voltage. Using the doctor blade technique solar cells of 10 cm x 15 cm with an active area of 2 x 50 cm² were fabricated with efficiencies directly comparable to 6 cm x 6 cm cells with an active area of 4 x 4 cm².

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Figure captions

Fig.1: Molecular structures of MDMO-PPV, C_{60} and PCBM monoadduct. PCBM multiadduct has the same functionalized side groups as PCBM monoadduct, but contrary to PCBM monoadduct it has between two and three side groups.

Fig.2: AFM picture of MDMO-PPV blended with PCBM monoadduct (Fig.2a, weight ratio 1:3), PCBM multiadduct (Fig.2b, weight ratio 1:3) and C_{60} (Fig.2c, weight ratio 1:2).

Fig.3: IV-behavior of MDMO-PPV solar cells containing different fullerene derivatives: PCBM monoadduct (open squares), PCBM multiadduct (small open circles) and C_{60} (solid line).

Fig.4: IV-behavior of a 10 cm x 15 cm MDMO-PPV / (PCBM monoadduct) solar cell with an active area of 50 cm² under light (solid squares) and in the dark (open squares). Illumination is provided by white light from a fluorescence tube with an intensity of 6 mW/cm².
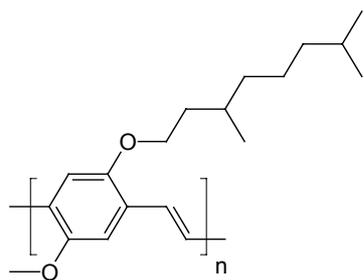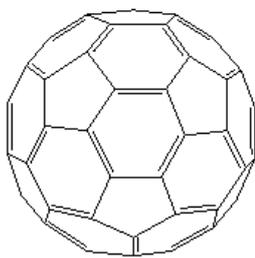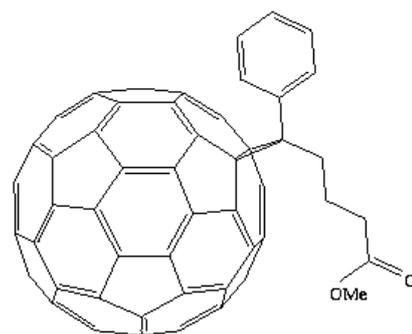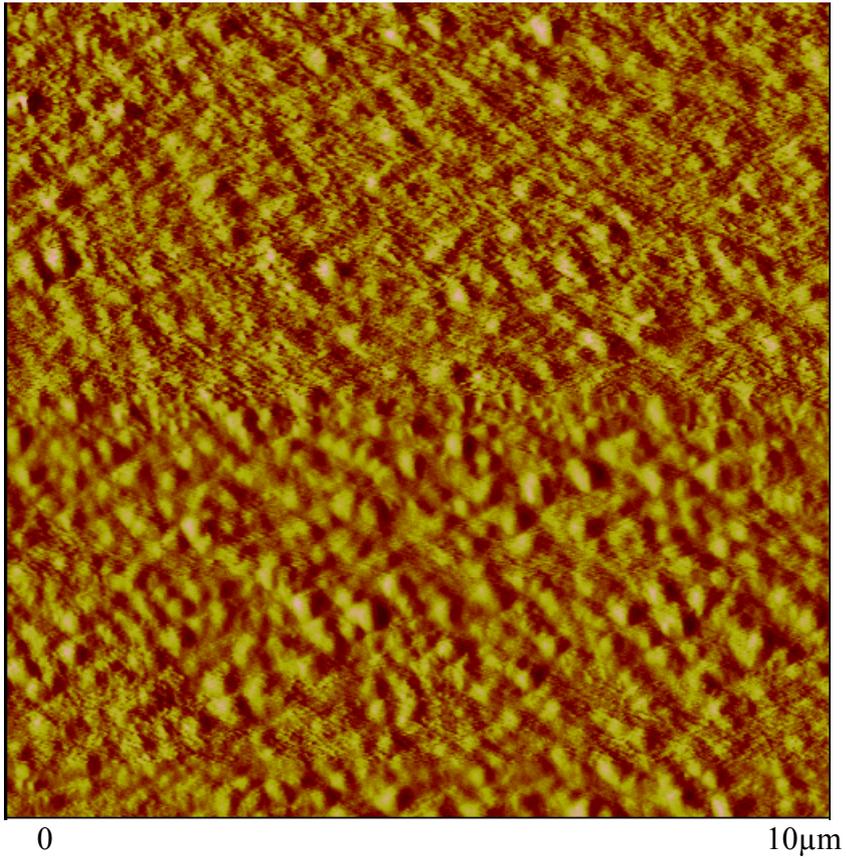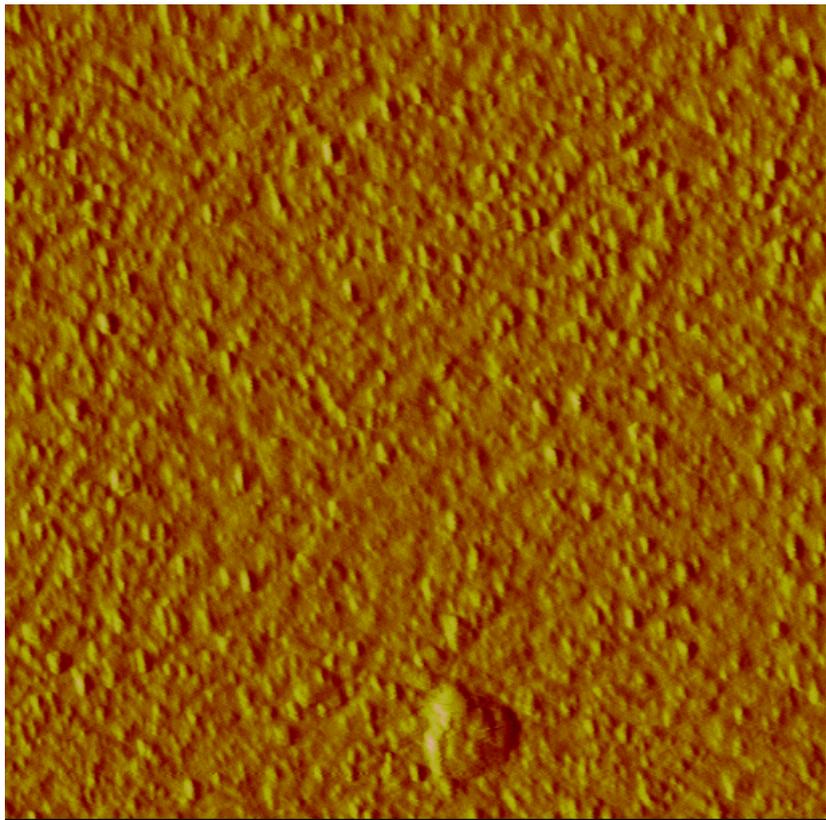
MDMO-PPV   C$_{60}$ PCBM monoadduct

F. Padinger et al. Fig 1

0 10μm

F. Padinger et al. Fig. 2a

0   10 µm
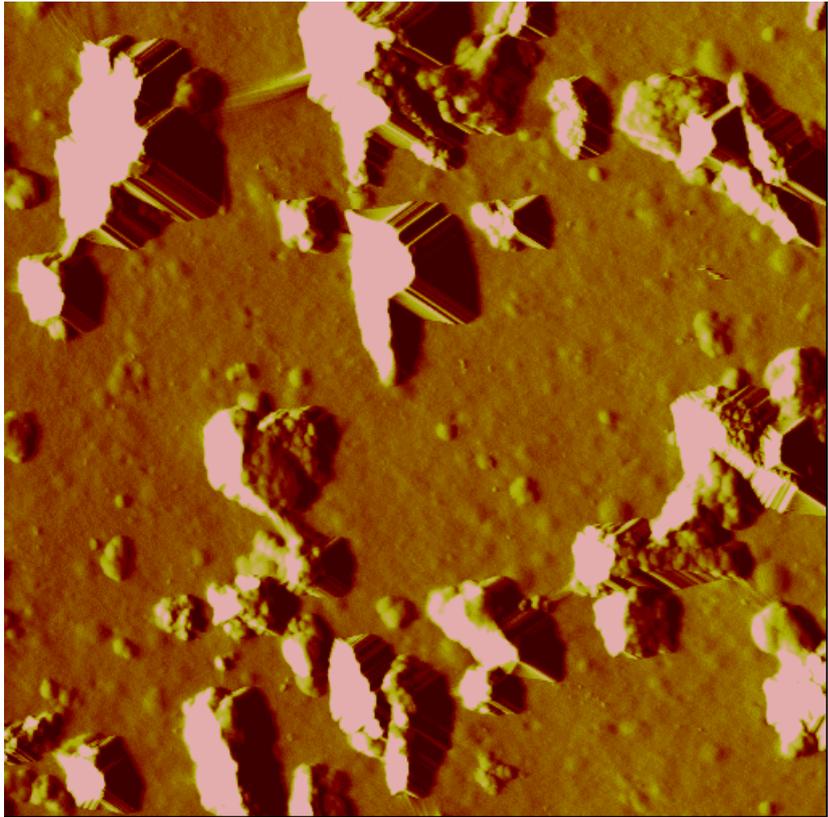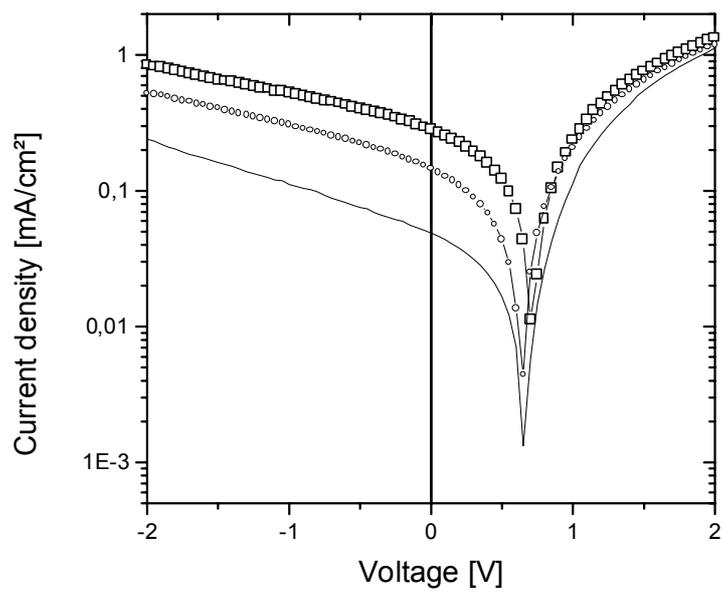
F. Padinger et al. Fig. 2b

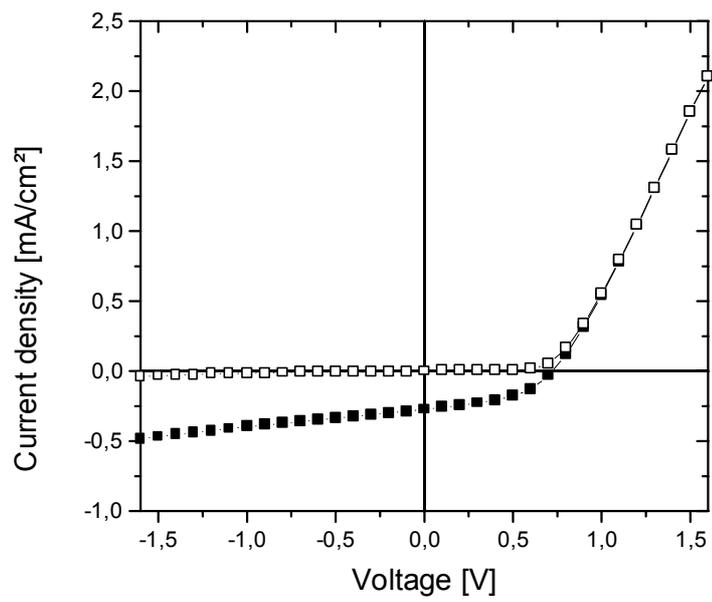0   50µm

F. Padinger et al. Fig. 2c

F. Padinger et al. Fig. 3

F. Padinger et al. Fig. 4