Photovoltaic Effect in Blend Systems and Heterostructures of Poly(p-phenylenevinylene) and C_{60}

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Abstract
The photovoltaic effect in Poly(p-phenylenevinylene) (PPV) can be increased by an effective charge separation. In order to suppress the recombination of photogenerated charge carriers, it is useful to support the electron transfer from the semiconducting polymer (PPV) to an electron acceptor (C_{60}). We have built heterostructures of PPV and sublimed C_{60} on the one hand and blend systems of PPV with a methanole soluble C_{60} on the other hand. For this purpose a dendrimer with a C_{60} core has been synthesized to make the fullerene soluble in the precursor PPV. The photovoltaic properties are investigated in these blends and heterojunction devices sandwiched between ITO and Al.

Keywords: Heterojunctions, Poly(para-phenylenevinylene), Fullerenes, Solar Cells

1. Introduction

Energy conversion efficiencies of photovoltaic cells using a single layer of a conjugated polymer are usually very low (10^{-3}–10^{-2} %) [1,2,3]. Major cause is the recombination of excitons created by the incident light. G. Yu showed that the efficiency in blends of the conjugated polymer Poly(para-phenylene-vinylene) (PPV) and the buckminsterfullerene C_{60} increases dramatically [4]. The quantum yields were raised up to 29 %, because exciton separation was achieved by an ultrafast electron transfer from the polymer to the C_{60}. This transfer is about 1000 times faster than the competing radiative and non-radiative processes [5]. Halls et al. also achieved an increase of the quantum yield up to 9 % by using heterostructures of PPV and C_{60} [6]

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2. Experimental

PPV is synthesized via the sulfonium salt precursor route [7]. By thermal treatment at 160-180 °C the soluble precursor polymer is converted to the non-soluble PPV. The films of the precursor polymer were prepared by a doctorblade-technique from methanole solution onto ITO-coated glass. The C_{60} was thermally evaporated onto the converted PPV-film in the case of heterojunctions.

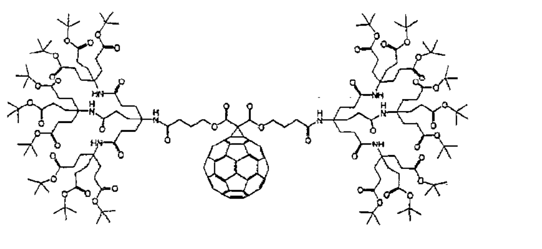

Fig. 1: Structure of the methanole soluble C_{60}-dendrimer

The blend systems were prepared from a mixture of the methanole-soluble C_{60}-derivative in several concentrations with the PPV precursor solution. Hence the C_{60}-derivative is thermally treated together with the PPV. As top electrode aluminium was used. Fig. 1 shows the functionalized C_{60} dendrimer. The molecular weight is 3837.7 g/mol. The devices were prepared in a nitrogen filled glove box. After preparation the samples were brought to ambient conditions before mounting them in a vaccuum chamber.

The devices were electrically characterized under vacuum (10^{-3} mbar). A 150 W-Xenon lamp and a monochromator were used to illuminate the samples through the ITO-electrode. Short circuit photocurrent spectra were measured with an electrometer, the I-V-curves were investigated by a Source-Measure-Unit. Futhermore, a Scanning Electron Microscope could give details of the surface structure of the samples.

3. Results and Discussion

3.1. Photoluminescence

Because of the ultrafast electron transfer from the PPV to the C_{60} the photoluminescence of PPV is expected to be quenched [5]. In the blends the molar concentrations of PPV-monomer to C_{60} reach from 18:1 to 2:1. The latter means that two monomer-units of PPV come together with one C_{60}-ball. The obtained quantum yields of the photoluminescence of PPV η_{PL} are given in table 1.

C_{60}:PPV	0	1:18	1:9	1:2
η_{PL} in %	6.6	2.7	1.5	0.7

Table 1: Quantum yield of the photoluminescence of PPV for different molar concentrations of C_{60} in PPV.

3.2. Photocurrent spectra

Fig. 2 compares short circuit photocurrent spectra of a single-layer, a two-layer and a blend system. In a single-layer device the excitons are separated within the depletion layer of the Schottky-contact at the PPV/Al interface [1]. Thus the major amount of light absorbed close to the ITO interface does not contribute to the photocurrent. In a blend system, however, the charge carriers should be separated in the whole bulk of the polymer. With

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increasing C_{60} content the photocurrent in the spectral range of 350-480nm grows. This indicates that the excitons generated in the bulk are separated and contribute to the photocurrent. The wavelength range above 480nm is dominated by the charge separation at the Schottky contact. The two-layer-system has an additional peak at 620nm. This peak can be explained by the absorption of C_{60}. The current in the two layer system is one magnitude larger than in the blend system. This indicates that in spite of the charge separation occuring in the whole PPV/C_{60} layer, the transport of carriers in the blend systems is worse than in the individual layers.

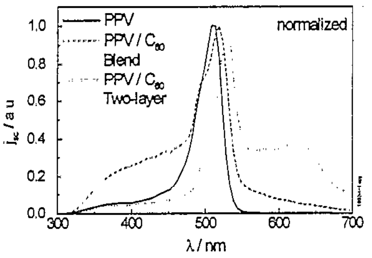

Fig. 2: Normalized short circuit photocurrent spectra of a PPV single-layer, a PPV/C_{60} two-layer and a blend system.

3.3. Current-voltage characteristics

Quantum yields and power efficiency can be determined from I-V-curves. Fig. 3 compares a single-layer PPV device, a two-layer system and a blend system in the dark and under monochromatic illumination at 520nm with an intensity of $100\mu W/cm^2$.

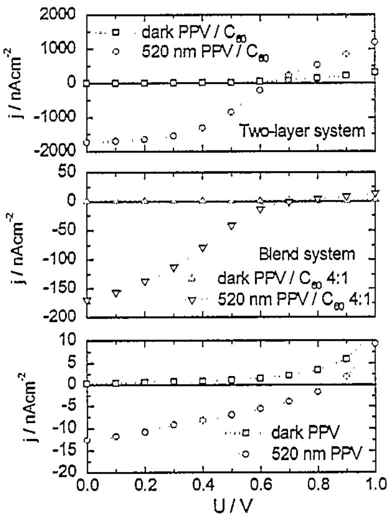

Fig. 3: I-V-curves of a PPV single-layer, a two-layer and a PPV/C_{60} blend system in the dark and under illumination at 520nm with $100\mu W/cm^2$.

Table 2 shows that the efficiencies of the two-layer system are almost one order of magnitude larger than of the blend systems and two orders of magnitude higher than in the PPV single-layer device. The transport in the two-layer systems is significantly better than in the blend systems as can be seen from the short circuit current. The open circuit voltage in the blend and the two-layer systems is smaller than in the single-layer systems. Probably the LUMO of C_{60} which is 0.7eV below the LUMO of PPV decreases U_{oc}.

	PPV	PPV/C_{60} blend system	PPV/C_{60} two-layer system
U_{oc}/V	0.85	0.7	0.65
j_{sc}/$nAcm^{-2}$	13	170	1800
η_C in %	0.03	0.4	4.4
η_e in %	0.003	0.03	0.5
FF	0.32	0.29	0.47

Table 2: Comparison of single-layer, blend and two-layer systems under monochromatic illumination at 520nm with $100\mu W/cm^2$. (U_{oc}: open circuit voltage, j_{sc}: short circuit current density, η_C: quantum yield, η_e: external power efficiency, FF: filling factor).

3.4. Scanning Electron Microscopy

The morphology of the films has been studied by a SEM. PPV films show no structures, the surface is smooth. The blend systems, however, have a structure like a cratered landscape (Fig.4). The density of the craters increases with the film thickness and the C_{60}-concentration. Reactions of the precursor leaving groups (thioether and HCl) with the C_{60} while the prepolymer is thermally converted to PPV, the occurence of phase separation and the escape of residual solvents are probable reasons for these craters. Obviously these structural changes are responsible for the bad electrical transport properties of the blend system.

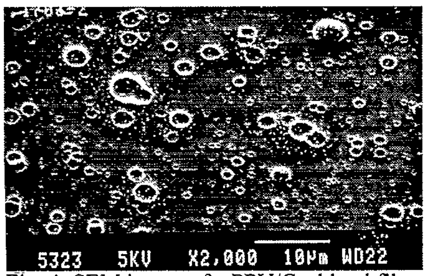

Fig. 4: SEM image of a PPV/C_{60} blend film.

4. Conclusion

Heterojunctions and blend systems of PPV and C_{60} have been compared. To realize the blend with precursor route PPV, a methanole soluble C_{60} has been synthesized. Although an electron transfer from PPV to C_{60} occurs in the whole PPV bulk, as indicated by photoluminescence quenching and photocurrent spectra, the efficiencies in the PPV/C_{60} blends are about one order of magnitude lower than in PPV/C_{60} heterostructures. This indicates that charge carrier transport in the blend systems is worse than in pure PPV and C_{60} layers. As possible reasons for this we could identify morphological inhomogenities of the PPV/C_{60} blends.

5. References

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