

COMBINED EFFECT OF ACTIVE LAYER THICKNESS AND LiF LAYER ON PHOTOVOLTAIC PERFORMANCE OF AN ANTHRACENE - CONTAINING PPE-PPV COPOLYMER

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The influence of the film thickness of anthracene-containing poly (*p*-phenylene-ethynylene)-*alt*-poly (*p*-phenylene-vinylene) (PPE-PPV) copolymers (**AnE-PVstat**) with phenyl C₆₁ acid butyric-methyl ester (**PC₆₁BM**) blends has been investigated. By varying the film thickness a good impact on all photovoltaics parameters have been obtained by increasing the short circuit current, J_{SC}, and the fill factor, FF (*i.e.* improved charge transport properties). The use of a thin layer of LiF enhanced the solar cell performance. The results obtained through the study are comparable to the best ones obtained so far for photovoltaics PPV- based materials.

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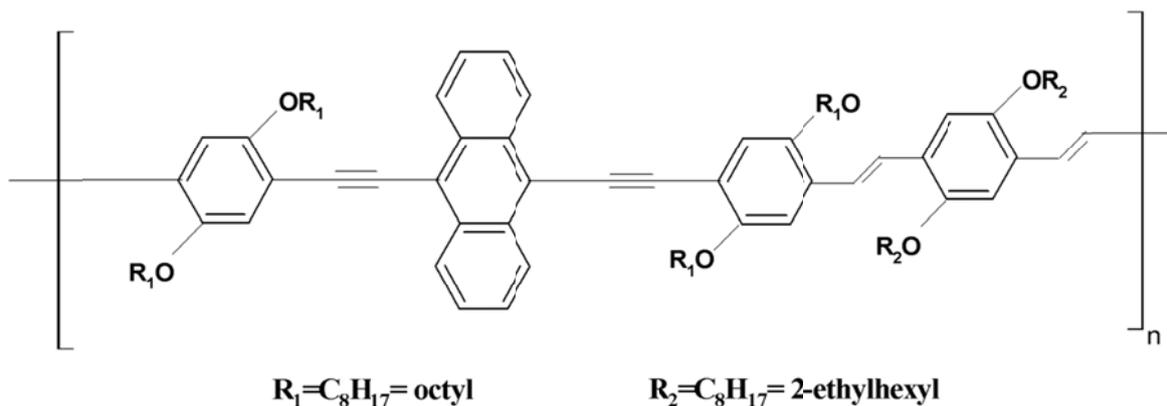
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1. Introduction

In the last decade, the research environment and the society increased their interests towards the organic photovoltaics due to their structure, ease of use and low prices. The organic solar cells have consistently improved their efficiency to around 8% due to continuing research and studies in the device structures based on planar¹ or bulk² heterojunction. The continued improvement has been driven by a deeper understanding of the physics governing the operation of organic photovoltaic's (**OPVs**), development of new molecular architectures for more efficient solar energy conversion and optimization of nanostructure and processing. The most effective organic solar cells with high performances in light conversion were reported on bulk heterojunction basis, a mixture of a donor and acceptor in the active layer³. Several studies were reported so far on the impact of bulk heterojunction on the performance of photovoltaics. The morphology of bulk heterojunctions based on polymer donor and fullerene derivative acceptor material is influenced by the characteristic of each component^{4, 5}. The type of the polymer donor, the solvent used for spin casting the film of the active layer, the use of PCBM ester¹³ and the applied thermal annealing^{6,7} treatments improved the performances of the solar cells³.

The OPV device of the present study is the poly (*p*-phenylene-ethynylene)-*alt*-poly (*p*-phenylene-vinylene) (**AnE-PVstat**):[6,6]-phenyl C₆₁-acid butyric-methyl ester (**PC₆₁BM**) bulk-heterojunction cell based on a donor-acceptor blend film. The structure of the **AnE-PVstat**⁸ copolymer is illustrated in Scheme 1.

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Scheme 1: Chemical structure of the copolymer AnE-PVstat.

Several studies using the poly (*p*-phenylene-ethynylene)-*alt*-poly (*p*-phenylene-vinylene)s (**PPE - PPVs**) as active layer have been reported so far ^{9,12,13}. The studies were carried out by varying the linear and branched alkoxy side groups of the anthracene containing PPE – PPVs and different ratio of the blend film.

The bulk AnE-PVstat:PC₆₁BM had a significant improvement in the general photovoltaics performances reporting an increased efficiency up to ~3%, for an AnE-PVstat:PC₆₁BM blend with 75 wt.% PCBM⁹, and for an AnE-PVstat:PC₆₁BM layer thickness in the range of 190 nm – 245 nm¹⁰. Currently, the AnE-PVstat polymer stands as one of the best materials among anthracene-containing PPE-PPV copolymers¹¹. The performances of AnE-PVstat polymer proved to be comparable with those of the similar PPV-based materials (as poly(3-hexylthiophene) (P3HT)). It absorbs the radiation with around 500 nm wavelength and showing fluorescence with maxima at wavelength (λ_f) around 580 nm and being, among its class, the most stabilized and coplanarized conjugated system reflected by the red-shift of absorption¹².

Based on these findings, our focus was directed on the effect of the thickness of the active layer on the photovoltaic response of AnE-PVstat solar cell.

2. Experimental

All reagents and solvents were purchased from Aldrich and used without further purification. Aluminum and poly (3,4-ethylenedioxythiophene): polystyrene sulfonate (**PEDOT:PSS**) (Baytron/Clevios PH 500) were also purchased from Aldrich. Indium tin oxide (ITO) – covered glass plates were supplied by Kintec (China).

The characterization of the fabricated devices was carried out under inert nitrogen environment inside a glove box system. The current-voltage (*J-V*) curves were recorded with a Keithley 2400 source measure unit. A Solar Cell Test 575 unit irradiated the solar cell device with a class A AM1.5 – type solar spectrum simulator used as the excitation source, with an input power of 100 mWcm⁻² white-light illumination. The solar cells were illuminated through the ITO side.

The external quantum efficiency (EQE) measurements were conducted also under inert nitrogen atmosphere inside the glove box and recorded with a home-built set up photovoltaic spectral response characterization system having the following components: Müller Elektronik-Optik [LXH100] lamp, [Spectrapro 150] monochromator unit, Scitech LTD [300C] optical chopper and EG&G [7260 DSP] lock-in amplifier. The thicknesses of the films were determined by a Dektak XT mechanical profile. The evaluation of the solar cells was carried out by using the power conversion efficiency according to equation (1):

$$\eta_{AM\ 1.5(\%)} = \frac{P_{out}}{P_{in}} \times 100 = \frac{FF \times V_{OC} \times J_{SC}}{P_{in}} \times 100 \quad (1)$$

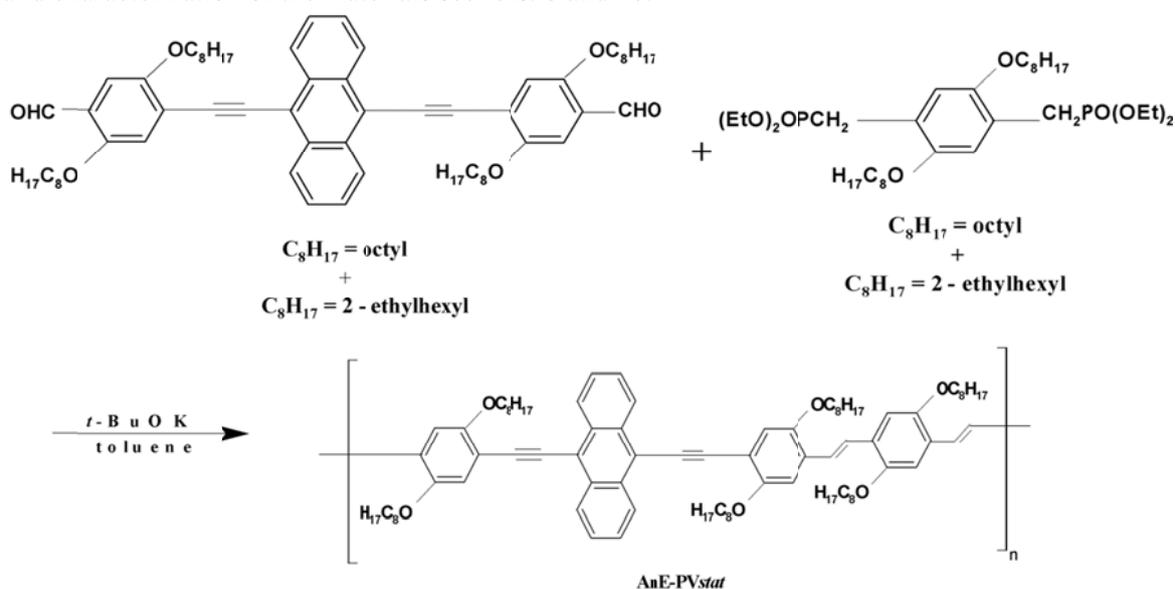
The percentage efficiency, $\eta_{AM1.5}$ is given by the ratio of the power output (P_{out}) to the power input from the solar simulator (P_{in} value of 100 mWcm^{-2}). The output power of a solar cell under illumination is the product of the fill factor (FF), open-circuit voltage (V_{OC} in volts) and the current density under short-circuit conditions J_{SC} (mAcm^{-2}). The fill factor is obtained using the following equation:

$$FF = \frac{V_{mpp} \times J_{mpp}}{V_{OC} \times J_{SC}} \quad (2)$$

Where V_{mpp} and J_{mpp} represent the voltage and current density corresponding to the maximum power delivered.

2.1 Materials

The synthesis of the polymer poly (*p*-phenylene-ethynylene)-*alt*-poly (*p*-phenylene-vinylene) (**AnE-PVstat**) was conducted following a well established procedure to polycondensate dialdehydes and bisphosphonate esters; the polymer **AnE-PVstat** is a statistical distributed¹³ polymer with octyloxy and 2-ethylhexyloxy side chains (Scheme 2). For details on the synthesis and characterization of the materials see refs. 8 and 10.



Scheme 2: Synthesis of anthracene based PPE-PPVs with a statistical distribution of side chains

Solutions of polymer and PC₆₁BM ester (with 0.7%, 1% and 1.5% polymer, for a 1:2 blend ratio) in chlorobenzene as solvent were used for the purpose of this study.

2.2 Substrate preparation

The indium tin oxide covered glass (glass-ITO) was cut into slices of 1.5 cm width and cleaned using an acid mixture of HCl:HNO₃:H₂O (4.6:0.4:5 vol.). The cleaning was performed by etching an area of approximately 0.5 (0.5 cm by immersing the slides into the solution for ~20 minutes. The remaining part of the glass-ITO was covered with an adhesive tape. After the

etching, the substrates were rinsed with deionised water, were air-dried and were cut into small squares of 1.5 cm. Each square was labelled on the non-conductive side and afterwards the squares were ultrasonically cleaned further using “Hellmanex” solution for 30 minutes, and then rinsed with acetone for 10 minutes, isopropanol for 20 minutes and pure water for 10 minutes. The squares are then dried by blowing nitrogen.

2.3. Device assembling

The first step on device assembling was to spin coat on each glass square a solution of filtered (using a 0.45 μm PTFE filter) PEDOT:PSS mixture using various combinations of spinning rates and times (2000 rpm for 1 second, 3000 rpm for 5 seconds and 4000 rpm for 25 seconds); this first PEDOT:PSS layer was dried under a dynamic vacuum and was typically ~ 40 nm thick. After partly wiping out the PEDOT:PSS from the edges with deionised water, the samples were annealed, in open air, at 150°C for 10 minutes. Over the PEDOT:PSS layer, the chlorobenzene solution of AnE-PVstat was supplementary spin coated at various spinning rates (between 700 and 1600 rpm) for 30 seconds to get the various active layer thickness; also, this second layer was partly wiped away from the edges with a cotton swab soaked in toluene or chlorobenzene. The samples were then transferred to a nitrogen-filled glove box to dry overnight (or at least for 6 hours). Then an ultrathin (~ 0.5 nm) LiF layer was deposited by evaporation at 2×10^{-6} mbar and an Al cathode layer (~ 100 nm) was also obtained by evaporation under high vacuum at 4×10^{-6} mbar by using a shadow mask for metal contact.

3. Results and discussion

The OPV device investigated in this study has the following structure: Glass/ITO/PEDOT:PSS (40 nm)/AnE-PVstat:PC₆₁BM (x nm)/LiF (0.8 nm)/Al (100 nm), where the active layer is a AnE-PVstat:PC₆₁BM blend at 1:2 mass ratio with thickness x varying from 83 nm to 140 nm. The terminal electrode LiF/Al represents the back contact and it was used as ohmic contact in OPV devices¹⁴ as the negative and positive electrodes match the LUMO (Lowest Unoccupied Molecular Orbital) of the acceptor (~ 3.7 eV) and the HOMO (Highest Occupied Molecular Orbital) of the donor¹⁵.

Table 1 depicts the photovoltaic parameters of thickness optimized devices obtained from AnE-PVstat:PC₆₁BM blends. Fig. shows these parameters as a function of AnE-PVstat concentration with respect to fullerene. Changing the blend ration between the polymer and fullerene in the bulk heterojunction resulted in a variation of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (η). Although the results obtained are comparable, a relatively large power conversion efficiency was found for the active layer containing the highest concentration of AnE-PVstat and with the smallest thickness, whereas the lower results were obtained for thicker layers. This in accordance with the previous studies conducted on the same polymer^{9,10}. The open circuit voltage is progressively increasing with the concentration of AnE-PVstat up to 1.5 wt% and is decreasing with thickness (at constant concentration); the same behaviour is noted for the field factor and the device efficiency.

Table 1. Performance parameters of OPV devices with varying active layer thicknesses

Thickness of the active layer (nm)	V_{oc} (mV)	J_{sc} (mA cm ⁻²)	FF (%)	η (%)
140	820	6.2	37	0.9
125	800	8.5	38	1.3
103	830	8.8	50	1.9

93	860	9.5	50	2.1
83	840	10.3	53	2.5

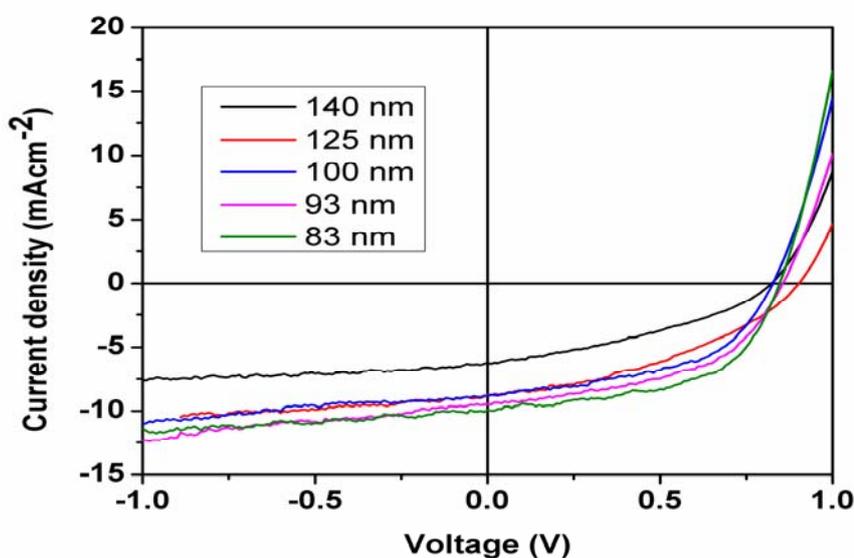


Fig. 1. Current-voltage (J - V) characteristics under 100 mWcm^{-2} white light illumination of OPV devices with varying the AnE-PVstat:PC₆₁BM layer thicknesses.

It can be seen from

Table 1 that the photocurrent delivered by the cell depends on the thickness of the AnE-PVstat:PC₆₁BM layer showing, as expected, a weak-dependence on the reverse bias voltage, and yielding a variable FF. The OPV cell with the thinnest active layer tends to have a better performance, with $\eta \sim 2.5\%$ and FF of ~ 0.53 . As the active layer thickness decreases from 140 nm to 83 nm, the J_{SC} also increases gradually from 6.2 to 10.3 mAcm^{-2} with only a small change in V_{oc} from 0.80 to 0.86 V.

Adding LiF/Al as back electrode improves all the relevant parameters of the photovoltaic devices, strongly suggesting that the charge injection is much more efficient, probably as a result of an improved interface and tunneling junction¹⁶. Therefore, the use of the LiF/Al improves the charge carrier injection process¹⁷ and as a result both FF and η increase, as can be seen from Table 2. The investigated photovoltaics devices showed values for open circuit voltage in the range 0.82– 0.87 V, which is characteristic to the HOMO of the polymer and of the LUMO of the acceptor and is independent of the blend ratio^{18–20} (Fig.).

Table 2. Photovoltaic parameters from solar cells with different blend solutions of AnE-PVstat:PC₆₁BM measured with (a) and without (b) LiF/Al electrode. The active layer thickness was of $\sim 90 \text{ nm}$ for 1:2 blend ratios.

Concentration in blend solution	V_{oc} (V)		J_{sc} (mA cm^{-2})		FF (%)		η (%)	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
0.7	0.86	0.82	8.4	8.6	65	60	2.4	1.9
	0.87	0.80	6.8	6.5	63	61	1.9	1.5
	0.85	0.81	8.7	6.9	68	64	2.5	1.8
1	0.86	0.80	9.5	9.8	55	45	2.1	1.9
	0.85	0.83	9.9	8.9	55	50	2.3	1.8
	0.84	0.82	8.5	8.9	62	46	2.2	1.8

1.5	0.84	0.81	8.7	9.8	52	50	2.8	2.0
	0.83	0.86	9.1	7.8	52	56	2.4	1.8
	0.82	0.83	9.8	8.5	50	66	2.8	2.3

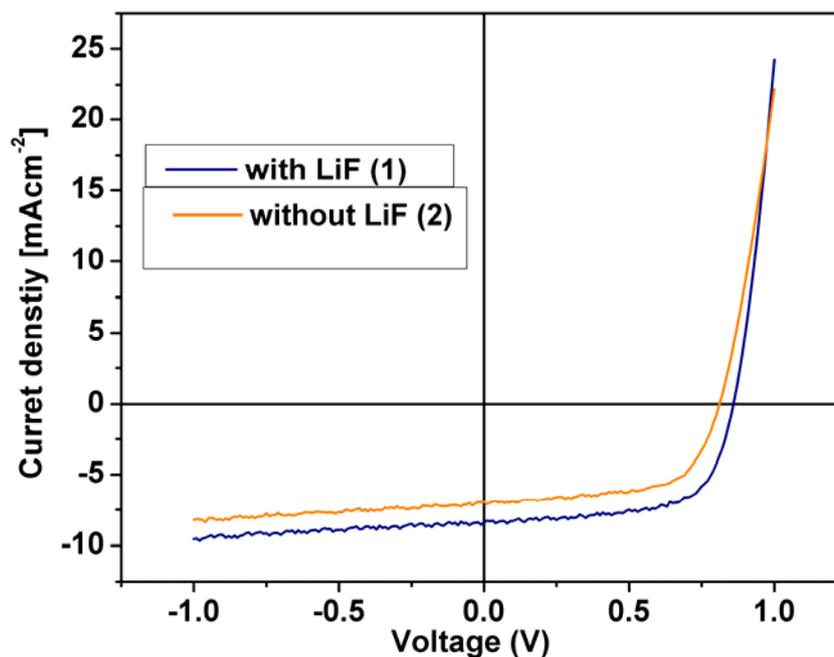


Fig. 2. Current-voltage characteristics of solar cells with the thickness of AnE-PVstat:PC₆₁BM layer of ~ 90 nm measured with (1) and without LiF/Al electrode (2).

The EQE spectra of the AnE-PVstat:PC₆₁BM blend heterojunction was recorded under bias illumination with an intensity corresponding to one sun and the results are presented in Fig. . The EQE spectra corresponds to the observed short-circuit densities. It may be observed from this figure that for the photovoltaic devices with thin films of AnE-PVstat:PC₆₁BM the spectral response is quite close to the pristine AnE-PVstat polymer absorption spectrum in the range between 500 nm and 600 nm, with a small shoulder at ~700 nm; the shape of the spectrum changes little in the presence of LiF/Al as back electrode. The blend AnE-PVstat:PC₆₁BM exhibits a concentration-dependent EQE; it should be noted that that for a high concentration of the polymer in the blend solution results in an additional contribution between 420 nm and 480 nm. It may be observed that for the photovoltaic devices with thin films of AnE-PVstat:PC₆₁BM the spectral response is quite close to the pristine AnE-PVstat polymer absorption spectrum in the range between 500 nm and 600 nm, with a small shoulder at ~700 nm; the shape of the spectrum changes little in the presence of LiF/Al as back electrode. For AnE-PVstat:PC₆₁BM layers obtained from 1.5% blend solutions a maximum due to PC₆₁BM is clearly visible around 420 nm.

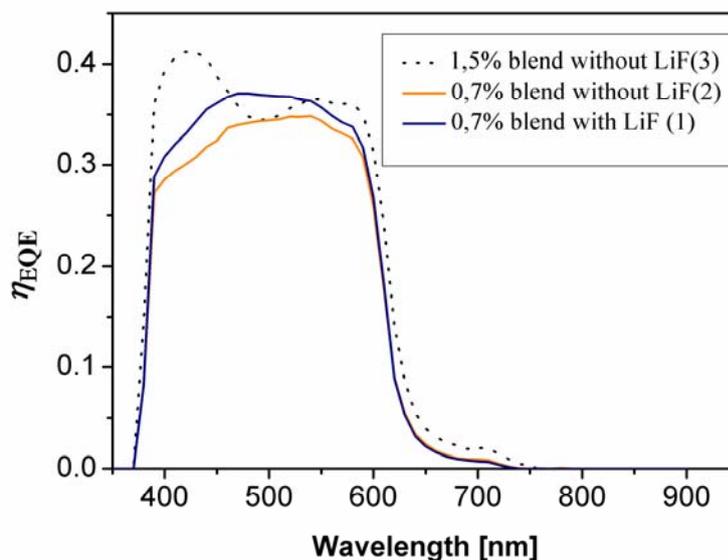


Fig. 3. Spectral response of solar cells with AnE-PVstat:PC₆₁BM layer obtained from blend solutions with various concentrations measured with (1) and without LiF/Al electrode (2 and 3). The dotted line (3) shows the same spectrum with AnE-PVstat:PC₆₁BM layer obtained from the same blend solution.

4. Conclusions

Bulk heterojunction AnE-PVstat:PC₆₁BM photovoltaic were characterized by recording their performances; it was evidenced that both the short-circuit current density and power conversion efficiency are inversely proportional to the active layer's thickness. AnE-PVstat:PC₆₁BM bulk heterojunction has very good efficiencies, of about 2.5%. The performance in efficiency is comparable to the results obtained for bulk heterojunction P3HT:PCBM photovoltaics.

The spectral response of the device follows closely the AnE-PVstat:PC₆₁BM absorption spectrum, with absorption due to PC₆₁BM clearly visible. LiF/Al back contact increases significantly the charge injection, and also the power efficiency and field-factor.

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