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# Control of carrier mobilities for performance enhancement of anthracene-based polymer solar cells

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**High performance organic solar cells were realized using an anthracene-based polymer. Charge carrier mobilities of both electrons and holes in solvent annealed polymer and fullerene derivative mixtures were studied using organic field effect transistors. Fine tuning of donor to acceptor ratios revealed optimum conditions for balanced mobilities, which led to high power conversion efficiency (PCE) of 4.02% in organic solar cells. Methanol wash approach further enhanced PCE to 4.65%. This work demonstrates the importance of carrier transport control in optimizing the performance of polymer solar cells.**

Although polymer solar cells have a number of advantages over silicon based solar cells in terms of low cost, light weight and flexibility etc., one of the bottlenecks in their application is their relatively low power conversion efficiencies (PCE). Recent advances in chemical and device engineering have pushed PCE of polymer solar cells over 10%.<sup>1</sup> However, for market application, PCE has to be further improved. Developing new materials and integrating them in efficient device configurations have to be explored. One of the approaches is to fabricate tandem solar cells. Indeed, until now, highest PCE in polymer solar cells was obtained using tandem structure.<sup>2</sup> In this configuration, two or more active layers are stacked in series, gaining the sum in the open circuit voltages (Voc) of sub-cells. Absorption profile of the sub-cells should be complementary in order to achieve maximum possible short circuit current densities (Jsc) from each sub-cells. Recently, identical active layers with low band gap polymer were proposed with quite thin films.<sup>3</sup> However, large scale process at industrial level prefers thicker films due to requirements of homogeneity and robustness for high production yield. Therefore, both low

and wider band gap polymers should be incorporated in tandem solar cells in each sub-cells, in which case, wider band gap polymers that yield high Voc is appreciated. One such promising polymer is anthracene-based PPV polymer. It has an optical band gap of about 2 eV, with high oxidation potential, resulting in generally high Voc in polymer solar cells when combined with [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PCBM, classical).<sup>4</sup> Several studies have been carried out to optimize device performance. Side chain variation showed rather strong impact on pi-pi stacking ability of the polymer backbone, consequently on device performance. PCE of 3.03 % was achieved for the polymer with optimum side chain distribution, named AnE-PVstat.<sup>5</sup> Fine tuning of macromolecular parameters such as molecular weight and polydispersity resulted in PCE of 3.26%.<sup>6</sup> Through the control of blend morphology by solution concentration and PCBM weight fraction, PCE as high as 4.33% was recently achieved.<sup>7</sup> Applying different fullerene derivatives as acceptors was proposed, and significant variation in PCE was observed.<sup>8</sup> High PCE of 4.3% was achieved when specific fullerene derivatives was applied, comparing to 2.9% from classical PCBM.<sup>9</sup> Until now, highest PCE based on this polymer is 4.8%, again reached with specific fullerene derivatives.<sup>10</sup> Here in this work, we demonstrate that comparable efficiency can be achieved using classical PCBM, when carrier mobilities are controlled. For that aim, we first looked at electron and hole charge transport behavior in the bulk-heterojunction films. We started with donor to acceptor ratio generally used in literature, then fine-tuned to the ratio towards where balanced mobilities could be observed. PCE of over 4% was obtained. Methanol washing of the films gave 4.65% PCE, highest reported so far for this promising polymer when classical PCBM is used as acceptor.

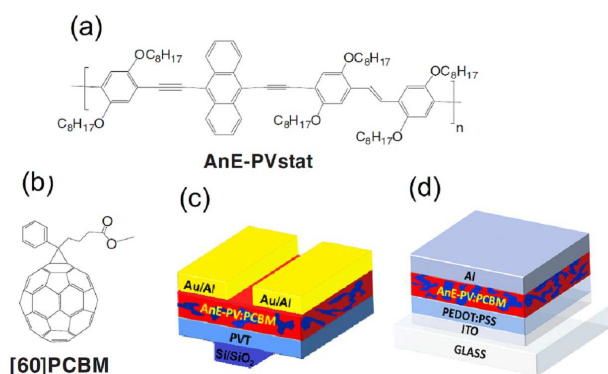
The synthesis of the polymer, AnE-PVstat was described elsewhere.<sup>11</sup> PCBM was purchased from Solaris (> 99.5%). Molecular structures are given in Fig.1 (a) and (b). To fabricate bottom gate, top-contact organic field-effect transistor (OFET) devices, heavily doped Si substrate with thermally grown SiO<sub>2</sub> (200nm) was used as the gate and dielectric. Water soluble poly(1-vinyl-1,2,4-triazole) (PVT) was used as the passivation layer.<sup>12-14</sup> PVT was dissolved in high resistivity

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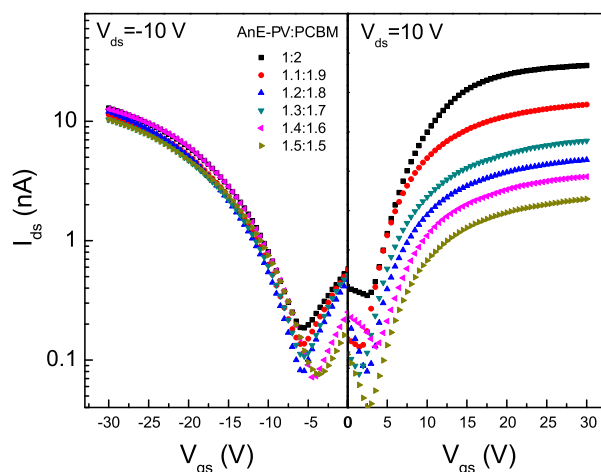


**Fig. 1** Molecular structure of AnE-PVstat (a), octyl and 2-ethylhexyl side chains are randomly distributed; Molecular structure of PCBM (b); device structure of OFETs (c); device structure of OPVs (d).

ultrapure water in a weight ratio of 3%. The solution was filtered and spin-coated (2000 rpm for 60s) on SiO<sub>2</sub>. The films were dried in a vacuum oven for two hours at 80 °C. AnE-PVstat and PCBM were mixed in different weight ratio and dissolved in 1,2-dichlorobenzene with polymer concentration of 10 mg/mL and spin-coated (1000 rpm for 20 s) directly on top of PVT in dry nitrogen glove box. Spin coated films were slowly dried in petri dish over two hours. As source/drain contacts, Au for p-channel operation and Al for n-channel operation were evaporated thermally through shadow mask to complete the OFET devices. The channel length was 0.05 mm and channel width was 1 mm. I–V characterizations were performed using Keithley 4200 semiconductor analyzer in dry nitrogen glove box. For solar cell device preparation, etched ITO glass substrates with a sheet resistance of 10 Ω/sq were used. After cleaning in an ultrasonic bath with acetone, ethanol, iso-propanol for 15 min and treated in a UV/O<sub>3</sub> cleaner for 20 min, PEDOT:PSS was spin coated at a spin speed of 4000 rpm for 40 s forming 20 nm thick layers and were annealed for 30 min at 110 °C. Same solutions and deposition method were used as applied for OFET devices. Thickness of the active layer is about 170 nm. Finally, Al cathode (100 nm) was thermally evaporated under high vacuum (10<sup>-6</sup> mbar) through a shadow mask determining the active surface area of 10 mm<sup>2</sup>. Current-voltage (I–V) curves were recorded using a Keithley 2400 semiconductor analyzer under illumination of an AM1.5 solar simulator set at 100 mWcm<sup>-2</sup>, which was calibrated using an IL1400BL radiometer. Samples were measured in dry nitrogen glove box.

In earlier study we used OFETs to deduce charge carrier behavior in OPVs in P3HT/PCBM system, where balanced mobilities in OFETs correlated well with the drastic enhancement in device performance parameters in polymer solar cells.<sup>15</sup> For that, suitable dielectric with low trap density for both elec-

trons and holes should be employed. Proper source/drain contacts should be used for efficient injection of both charges. Furthermore, all the device related parameters have to be taken into account for deriving reliable mobility values. Thus, we first fabricated OFET devices with bulk heterojunction as active layer. Fig. 2 shows the transfer characteristics of the OFET devices for n-channel and p-channel operations. We have chosen 1:2 as the starting ratio, for it has been generally used in the previous studies as the optimum ratio for AnE-PVstat polymer.<sup>5,9</sup> We observed much higher electron current comparing to hole current in OFET devices for this ratio. Thus, we finely tuned the polymer to PCBM ratio, in order to reach similar current for electrons and holes. The ratio of polymer to PCBM was varied between 1:2 to 1:1, decreasing the relative amount of PCBM in the mixture of bulk heterojunction film. A notable observation was when polymer fraction increased from 33% (1:2) to 50% (1:1), hole current did not change much, while electron current decreased more than one order of magnitude, which indicated percolation of polymer phase was not much affected due to its bulky nature.



**Fig. 2** transfer characteristics of the OFET devices at a drain voltage of -10V for p-channel devices and 10V for n-channel devices. Donor to acceptor ratios were varied between 1:2 to 1:1. Au source/drain contacts were used for p-channel devices and Al source/drain contacts were used for n-channel devices.

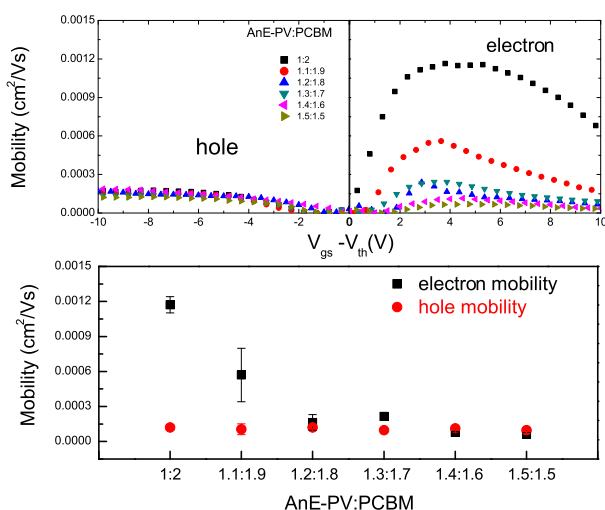
We derived respective mobilities of electrons and holes in this system using gradual channel approximation. In disordered system, charge carrier mobility is strongly dependent on carrier concentration, i.e. the mobility is gate voltage dependent in an OFET device.<sup>16</sup> Gate voltage dependent carrier mobility in saturation regime is given as the formula below:

$$\mu(V_{gs}) = \frac{2L}{C_i W} \left( \frac{\partial(\sqrt{I_{ds}})}{\partial(V_{gs})} \right)^2 \quad (1)$$

Where  $\mu(V_{gs})$  is the gate voltage dependent mobility;  $W$  is

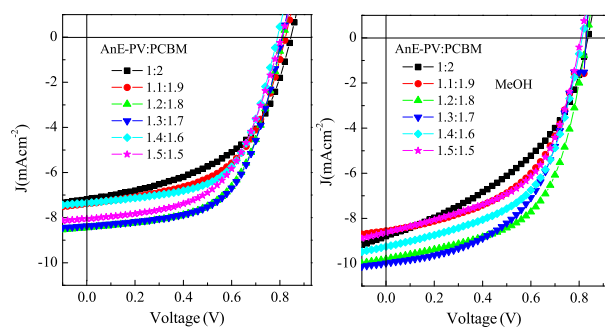
the channel width (1 mm);  $L$  is the channel length (0.05 mm);  $C_i$  is the dielectric capacitance in unit area ( $14.7nFcm^{-2}$ );  $I_{ds}$  is the drain current and  $V_{gs}$  is the gate voltage.

In order to obtain reliable mobility values from OFET devices, device related parameters have to be taken into account. One of them is threshold voltage. The square root of drain current versus gate voltage of the saturation curve can be linearly extended to zero current to determine the threshold voltage. Threshold voltage is dependent on several factors: such as carrier injection barrier between source contact and the semiconducting active layer, total trap densities (including dielectric and semiconductor bulk, dielectric /semiconductor interface trap densities), interface dipole and dielectric capacitance. Therefore, in an OFET device, most of the device related parameters are accounted by the threshold voltage. Contact resistance is another factor to be considered which gives underestimated mobilities in the higher gate voltages.<sup>5</sup> Taking into account these considerations, effective gate voltage  $V_{gs} - V_{th}$  dependent mobilities of electrons and holes are given in Fig. 3.



**Fig. 3** Upper panel: electron and hole mobilities in saturation regime for different AnE-PVstat to PCBM ratios derived from OFET devices. Lower panel: Mobility values obtained at  $V_{gs} - V_{th} = \pm 3V$ . Six devices were tested for each condition.

As manifested in hole and electron currents in transfer curves, the hole mobilities remained mainly constant for the donor to acceptor ratio change within the considered range, while the response of the electron mobilities were rather drastic. Both gate voltage dependent mobility curves reached a maximum and started to decrease when the gate voltage further increased, a clear effect of contact resistance. Therefore, avoiding this part of the data values, we have chosen mobility values at  $\pm 3V$  for quantitative comparison, and shown in lower panel of Fig. 3.



**Fig. 4** Left panel: J-V curves of solar cell devices tested under  $100 mWcm^{-2}$  AM 1.5 G illumination for different AnE-PVstat to PCBM ratios. Right panel: J-V curves of the devices of which active layers were treated with methanol.

When polymer to acceptor ratio was 1:2, electron mobility was almost ten times higher than hole mobility. Electron mobility started to drastically decrease until the ratio of 1.2:1.8. When acceptor content further reduced to 53% (polymer to acceptor ratio of 1.4:1.6), we observed that hole mobility became higher than electron mobility.

We fabricated polymer solar cells in the same active layer processing condition as that in OFETs. J-V curves of the devices tested under  $100 mWcm^{-2}$  AM 1.5 G illumination for different AnE-PVstat to PCBM ratios are shown in the left panel of Fig. 4, and device performance parameters are given in Table I.

General trend in device performances was quite clear. When polymer to PCBM ratio was 1:2, we obtained  $J_{SC}$  of  $7.19 mAcm^{-2}$  and fill factor of only 51% which consequently yielded lowest PCE of 3.06%. We attribute this to large difference (almost ten times) between the mobilities of holes and electrons as shown in OFET device mobilities. When charge carrier mobilities are highly unbalanced, built up space charges can be detrimental for charge carrier extraction, which results in low current density and fill factor. Both  $J_{SC}$  and fill factor were greatly enhanced to  $8.37 mAcm^{-2}$  and 60% respectively for devices at the polymer to PCBM ratio of 1.3:1.7, where electron mobility decreased to be only slightly higher than hole mobility. We have achieved PCE of 4.02% for this device. When PCBM content further dropped,  $J_{SC}$  and fill factor started to decrease again. In these cases, we had observed lower electron mobilities comparing to hole mobilities. One can argue, though, that the difference in electron and hole mobilities is comparable for polymer to PCBM ratios of 1.3:1.7 and 1.5:1.5, only in the former case electron mobility is slightly higher than hole mobility whereas in the latter case, it is vice versa. This can be explained by the difference in the distance of charge carrier collection in thick active layer devices. As has been reported, charge carrier generation in OPVs is mainly limited to region close to transpar

ent electrode.<sup>17</sup> Therefore, in conventional device architecture with thick active layer, electrons have to travel longer distance comparing to holes to be collected. In our case, the active layers were solvent annealed with a thickness of about 170 nm. Hence, slightly higher electron mobility than hole mobility is favorable for efficient collection of both charges at respective electrodes.

Finally, methanol wash treatment on the active layer was carried out to further enhance the device performances as reported in earlier studies for various donor/acceptor systems.<sup>18,19</sup> Here we observed that in all the devices, short circuit current density increased corroborating with the decrease in the series resistance. Although fill factors were compensated in accordance with decreasing trend in shunt resistance, overall PCE improved in all the devices. The maximum PCE achieved was 4.65% with a  $J_{SC}$  of  $9.81 \text{ mAcm}^{-2}$  and fill factor of 56%. Passivation of surface trap states was proposed to be the possible mechanism behind the effect of methanol wash on device performance in PTB7/PCBM system.<sup>19</sup> Decreased series resistance as well as enhancement in hole mobility towards more balanced electron/hole mobilities were also suggested to be the factors. In our study, we did not see observable difference in both electron and hole mobilities before and after methanol treatment, except at higher gate voltage where contact resistance effect is pronounced. This is in agreement with the decrease in series resistance in OPV devices after methanol wash, coming from enhanced surface charge densities due the passivation of surface trap states.

In summary, we proposed a rational approach to optimize the device performance of a promising anthracene based polymer. We realized solar cell device with highest power conversion efficiency for this polymer using classical PCBM as acceptor. Firstly, we investigated charge carrier mobilities of both electrons and holes in donor/acceptor bulk heterojunction layer using OFETs. We observed almost ten times higher electron mobility than hole mobility for polymer to PCBM ratio of 1:2 which was generally used in literature. Based on this result, we fine tuned the ratio by reducing the amount of PCBM in the mixture aiming to reach the range where holes and electrons have comparable mobilities. Indeed, we achieved highest PCE over 4% at a ratio of 1.3:1.7, where electron mobility was only slightly higher than hole mobility. Methanol wash approach further enhanced cell performances in all the devices leading to decreased series resistance and consequently to increased  $J_{SC}$ . Highest PCE of 4.65% was achieved. We consolidated that OFETs are useful in examining charge carrier mobilities in bulk heterojunction system, providing guideline towards optimum ratio of balanced mobilities. We conclude that depending on the device configurations (conventional or inverted) and film thickness, slightly unbalanced charge carrier mobilities may lead to best performing solar cell devices. Finally, surface treatment (such as methanol wash) can be ap-

plied to further push for higher performance.

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**Table 1** Best device performance parameters obtained from J-V curves of solar cells with different donor to acceptor ratios. Results for devices with methanol treated active layer are given in the brackets

AnE-PVstat:PCBM	$J_{SC}(mAcm^{-2})$	$V_{OC}(V)$	FF(%)	$\eta(\%)$	$R_s(\Omega)$	$R_{sh}(\Omega)$
1:2	7.19 (8.79)	0.84 (0.84)	51 (43)	3.06 (3.14)	25 (18)	680 (271)
1.1:1.9	7.38 (8.56)	0.82 (0.82)	55 (52)	3.35 (3.61)	26 (19)	740 (623)
1.2:1.8	8.45 (9.81)	0.82 (0.84)	57 (56)	3.98 (4.65)	23 (15)	1079 (515)
1.3:1.7	8.37 (9.98)	0.80 (0.82)	60 (52)	4.02 (4.27)	22 (21)	1323(674)
1.4:1.6	7.35 (9.25)	0.80 (0.82)	59 (53)	3.46 (4.05)	22 (19)	1072 (426)
1.5:1.5	8.05 (8.63)	0.80 (0.80)	55 (53)	3.56 (3.69)	29 (19)	1092 (373)