

Balanced charge carrier mobilities in bulk heterojunction organic solar cells

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All solution processed ambipolar bulk heterojunction organic field effect transistors were fabricated using Au and Al as hole and electron injection contacts to study both types of charge carrier mobilities in a single device. Poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) were mixed with different ratios. Well balanced electron and hole mobilities were obtained at 1:0.3 ratio. Organic solar cells with the same ratio yielded draft enhancement in device performance parameters, indicating optimized carrier transport in the bulk of solar cell devices. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4745602>]

Bulk heterojunction of donor and acceptor provides the most promising device structure for solution processed organic solar cells by increasing the donor/acceptor interface which is crucial in exciton dissociation.¹ Separated charges should have high carrier mobilities in order to be efficiently collected at respective electrodes. Moreover, charge carrier mobilities should be balanced in the bulk to avoid building up of space charges which is detrimental for device efficiency.² One of the most extensively studied model system in organic solar cells is based on poly(3-hexylthiophene) (P3HT) as donor and [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as acceptor due to their high hole and electron mobilities.³ Majority of the studies has been focused on optimization of the device performance by annealing, mixing in different ratios, thickness and interface engineering etc, without proper attention given for balancing the charge carrier mobilities. Investigating both types of carrier mobilities in bulk-heterojunction system has been proven to be not trivial. Among most commonly used suitable techniques, time of flight (TOF) measurement can be applied, requiring films in micrometer thickness, which means using a different deposition method than the real device film deposition, resulting in rather different nano-morphology.⁴ Besides, in TOF, diffusion current plays significant role, whereas in organic photovoltaics (OPVs), charge transport is dominated by drift current. On the other hand, space charge limited current (SCLC) method requires two separate devices (hole only or electron only) using electrodes with different workfunctions to suppress the injection of either type of charge carriers.⁵ Moreover, due to high concentration of the charges close to the electrodes, diffusion current can not be neglected. In charge extraction with linearly increased voltage (CELIV) method, excess intrinsic carrier mobility is measured.⁶ Photo-CELIV is again limited by the diffusion current, although two types of charge carriers can be extrinsically generated in controllable densities.⁷ Even in that case, only the mobility of slower carrier is obtained.⁸ Despite having

different device configuration, organic field effect transistor (OFET) is a powerful technique in determining mobilities of both type of charge carriers in a single device. Charge carrier distribution can be very uniform within the channel in linear regime and charges can be selectively injected. Charge density can be precisely controlled by applied gate voltage. As an extra interface is involved (semiconductor/dielectric) in OFETs, careful optimization of the device structure is needed. First of all, suitable dielectric layer with similar trap densities for holes and electrons is essential. Second, electrodes should be designed in a way that both holes and electrons can be efficiently injected into the active layer. OFETs were used to investigate the bipolar transport relevant to OPVs in bulk heterojunction structure, where decrease in mobility imbalance using different solvents did evidence OPV device parameter improvement.⁹ Sill, the reported electron mobility was more than ten times higher than the hole mobility. Moreover, some device related factors, which severely distort the derived mobility values, were not considered, such as the transport variation in using Au/PCBM instead of Al/PCBM; difference in interface trap densities on the hexamethyldisilazane (HMDS) surface for electrons and holes; unreliability of deriving mobility at high gate voltage where very different contact resistance effect exist for Au/PCBM and Au/P3HT interfaces. In this paper, we present our work on balancing charge carrier mobilities in this system. Here, we applied water soluble poly(1-vinyl-1,2,4-triazole) (PVT) as the dielectric layer, as it was reported in our previous studies to have very low trap densities for both type of charge carriers.¹⁰ Moreover, its solubility in water allowed us to prepare the whole device by simple spin coating steps. Asymmetric source/drain contacts were applied to efficiently inject both holes and electrons. Fine mixing of donor/acceptor was carried out. Balanced mobilities were achieved in the OFET devices. Bulk heterojunction solar cells were fabricated under same experimental conditions, and drastic enhancement in device parameters were obtained.

Poly(3-hexylthiophene) (P3HT) (Rieke Metals, average molecular weight: 50 000, Fig. 1(a) for chemical structure) and PCBM (Solenne BV, Fig. 1(b) for chemical structure)

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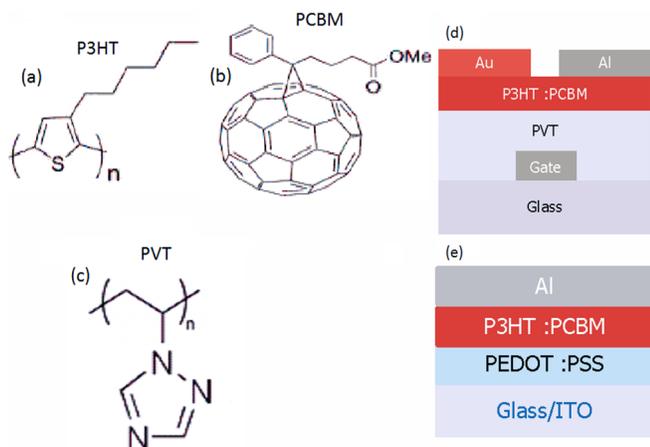


FIG. 1. Chemical structures of (a) P3HT, (b) PCBM, and (c) PVT; (d) Ambipolar bulk-heterojunction bottom-gate top-contact OFET device structure; (e) Bulk heterojunction OPV device structure.

were dissolved in chlorobenzene (10 mg/ml) separately. Bottom gate, top contact OFET device structure is shown in Fig. 1(d). Al gate contact (100 nm thick) was vacuum evaporated on pre-cleaned glass substrate. PVT dielectric layer (see Fig. 1(c) for chemical structure) was spin coated from a solution of ultra-pure water (70 mg/ml), dried in low vacuum at 50 °C overnight. Finely mixed ratios of P3HT:PCBM were then spin coated directly on PVT layer (700 rpm/60 s). Films were kept in nitrogen glove box overnight, and annealed at 150 °C for 5 min. Au (50 nm) and Al(50 nm) as sources/drain contacts were angle-evaporated thermally through shadow mask to complete the device. Channel length is 0.05 mm and channel width is 3 mm. Whole devices were annealed at 100 °C for 10 min before measurement. The completed devices were subject to such post annealing treatment in order to improve the contact between the metal electrode and the active layer. I - V characterizations were performed using Agilent E5273A system. Solar cell devices were fabricated on cleaned indium tin oxide (ITO) coated glass substrates. The conducting hole transport buffer layer (50 nm) of PEDOT:PSS was spin coated from a water solution on ITO/glass substrates (4000 rpm/40 s), and subsequently dried in air for 30 min at 150 °C. The active layers (blend of P3HT and PCBM) of the same solution mixtures for OFET devices were used for solar cells at the same spin coating rate. Films were kept in nitrogen glove box overnight, and annealed at 150 °C for 5 min. 100 nm thick aluminum electrode was thermally deposited using a shadow mask to define an active device area of 10 mm² (device structure is shown in Fig. 1(e)). Whole devices were annealed at 100 °C for 10 min before measurement. A Steuernagel solar simulator for AM1.5 conditions was used as the irradiation source with an input power of 100 mW/cm² white-light illumination which was calibrated using a standard silicon diode.

In Fig. 2 is displayed the transfer characteristics of pristine P3HT, pristine PCBM and bulk heterojunction of P3HT:PCBM OFETs with Au and Al source/drain contacts. Au contact was grounded for p-type operation and Al was grounded for n-type operation. Operations in both coordinates are shown. Both n-channel and p-channel operations do not show observable hysteresis. An important observation was the significant increase in on/off ratio of p-channel

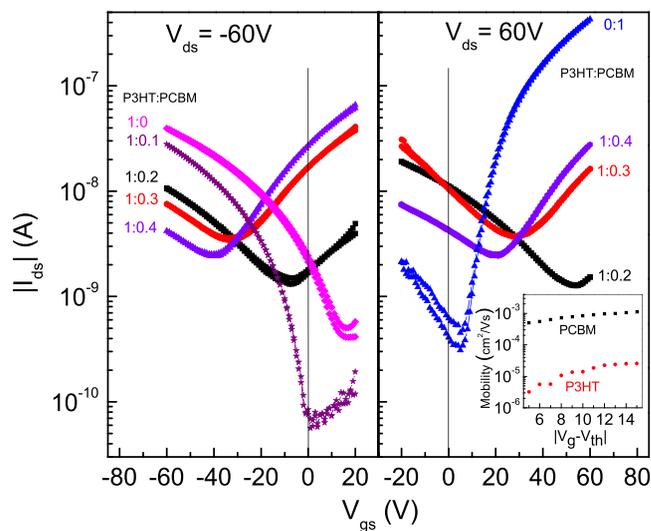


FIG. 2. Transfer characteristics in saturation regime in both coordinates of the bulk-heterojunction OFETs with different donor/acceptor ratios. PCBM and P3HT pristine devices are also presented. For n-type operation, Al contact was grounded, while for p-type operation Au contact was grounded. Inset in the right panel shows the gate voltage dependent mobilities of pristine PCBM electron mobility and P3HT hole mobility in low effective gate voltage range.

operation of P3HT when 1/10 of PCBM was added, with the implication in improving device performance of easily doped polymer OFET devices with the addition of small amount of acceptor. Ambipolar characteristics started to appear with both electron and hole current enhancements when the ratio of PCBM was increased. When the P3HT:PCBM ratio was increased to 1:0.4, the channel was starting to be dominated by electron current.

Gate voltage dependant charge mobility can be determined by gradual channel approximation given as the formula below,

$$I_{ds} = \frac{W}{L} \mu(V_{gs}) C_i ((V_{gs} - V_{th}) V_{ds} - 1/2 V_{ds}^2),$$

where I_{ds} is the drain current; W is the channel width (3 mm); L is the channel length (0.05 mm); $\mu(V_{gs})$ is the gate voltage dependant mobility; C_i is the dielectric capacitance in unit area (5 nF/cm²); V_{gs} is the gate voltage and V_{th} is the threshold voltage.

The square root of drain current versus gate voltage of the saturation curve can be linearly extended to the “off” 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/semiconductor bulk, dielectric/semiconductor interface trap densities), interface dipole, and dielectric capacitance. It should be noted that in an OFET device, most of the device related parameters will be accounted by the threshold voltage. Extracted charge carrier mobility in the linear regime is considered to be more reliable as the distribution of the carriers in the channel is more uniform. Moreover, in a disordered system, charge carrier mobility is strongly dependent on the carrier concentration, i.e., the mobility is gate voltage dependent in an OFET device. Contact resistance is another factor to be considered which

gives underestimated mobilities in the higher gate voltages. Taking into account these considerations, effective gate voltage ($V_{gs} - V_{th}$) dependant electron mobility of pristine PCBM and hole mobility of pristine P3HT is shown in the inset of the right panel of Fig. 2. In pristine films, electron mobility of PCBM is more than an order of magnitude higher than the hole mobility of P3HT, which explains why seemingly balanced charge carrier mobilities in our bulk-heterojunction system was achieved at the donor/acceptor ratio of only 1:0.3.

To confirm the balancing of the hole-electron mobilities of the sample with P3HT:PCBM at 1:0.3 ratio, the linear regime transfer characteristics were measured with low drain voltage, where the injection of another type of carrier was suppressed so that separately enhanced currents could be measured in a wider region (see Fig. 3, left panel). The difference in the threshold voltages mainly comes from the difference in the injection barrier for holes from Au to P3HT and for electrons from Al to PCBM. Subthreshold swing for p-channel operation and n-channel operation is comparable, indicating similar interface trap densities for electrons and holes at the interface of PVT and active layer. The hole current seems to be higher than the electron current at higher gate voltages, which is evident also in the output characteristics where super-linearly increasing electron current in p-channel operation has higher current than the saturated hole current (see Fig. 3, right panel) and vice-versa in n-channel operation. Due to the difference in the injection barrier for holes from Au to P3HT and the electrons from Al to PCBM, it should be expected that the contact resistance at Al/PCBM varies from that of at Au/P3HT. Indeed, much earlier saturation is observed in the hole mobility comparing to the electron mobility when the gate voltage is increased as shown in the inset of the right panel of Fig. 3, indicating higher contact resistance at the Au/P3HT interface than that of Al/PCBM interface. Nevertheless, when threshold voltage and contact resistance are taken into account by looking at the mobility versus effective gate voltage in low gate voltage region, it is evident that the electron and hole mobility is well balanced at this donor/acceptor ratio.

In order to validate the balanced mobilities in our bulk-heterojunction system and its effect on the device efficiency

in OPV devices, we fabricated OPV devices in exact the same condition as that for the OFETs using same solution, deposition method/rate, pre and post annealing temperature/time in a single process. Here, one concern can be the orientation of polymer backbone with respect to the surface. In OFETs, higher mobility will be achieved if a polymer tends to have predominant edge-on configuration, which results in low efficiency for OPVs as charge transport along polymer backbone $\pi - \pi$ stacking direction is much faster than alkyl chain direction. Addition of PCBM should in principle affect such configuration if exists. However, systematic decrease in the hole mobility of P3HT with the addition of PCBM suggests anisotropic nature of the films. This is generally expected for solution processed polymer films without special treatment to enhance one particular type of edge-on or face-on configuration. It should be noted that PEDOT:PSS was the hole collecting electrode in OPVs while Au is the hole injection electrode in our ambipolar OFETs. This limitation is due to the difficulty in realizing asymmetric OFET contacts from solution processed PEDOT:PSS and vacuum evaporated Al. However, the work functions of Au and PEDOT:PSS are comparable, suggesting similar hole mobilities that can be achievable from P3HT/Au and P3HT/PEDOT:PSS interface for OFETs. $I-V$ curves of the OPVs with different donor/acceptor ratios after annealing at $100^\circ\text{C}/10\text{ min}$ are shown in the upper panel of Fig. 4. Drastic change was observed when P3HT:PCBM increased from 1:0.2 to 1:0.3, corroborating balanced hole-electron mobilities observed in our OFETs. Derived device performance parameters are given in the lower panel of Fig. 4, which evidences strong enhancement in open circuit voltage (V_{oc}) (from 450 mV to 580 mV), short circuit current density (J_{sc}) (from 2.56 mA/cm^2 to 4.25 mA/cm^2) as well as fill factor (FF) (from 36.6% to 50.2%). Obtaining V_{oc} higher than 550 mV and fill factor higher than 50% at such low annealing temperature indicates well optimized bulk of the OPV device. In OPVs, interface plays significant role in device performance. At P3HT:PCBM of 1:0.3 ratio (acceptor three times less than the donor), the contact area between PCBM and Al is relatively small, inhibiting efficient extraction of the charges. When the ratio increased to 1:0.4, despite slightly unbalanced mobilities of electrons and holes, increased contact area between PCBM/Al facilitated the electron extraction,

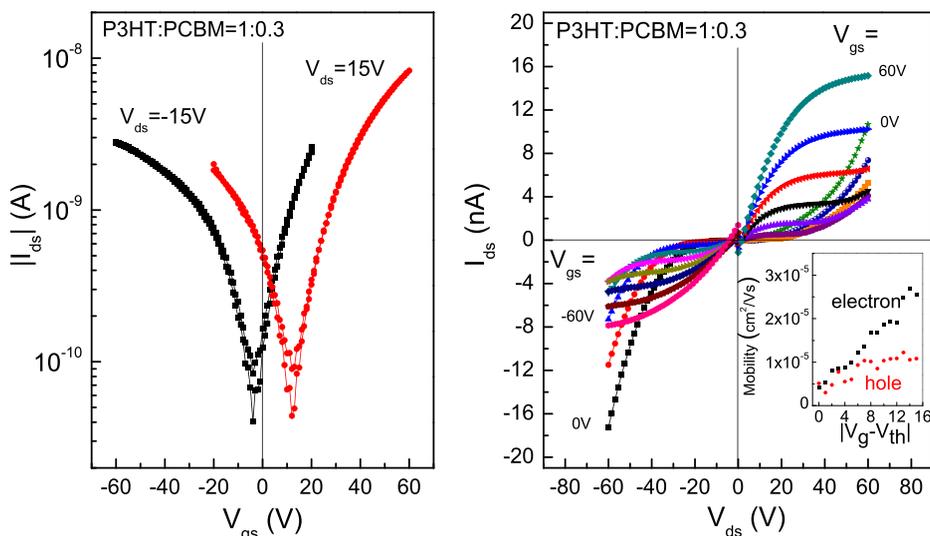


FIG. 3. Left panel: transfer characteristics in linear regime in both coordinates of the bulk-heterojunction OFETs with donor/acceptor ratio of 1:0.3. Right panel: output characteristics of the same device in both coordinates. Inset in the right panel shows the gate voltage dependent electron and hole mobility in low effective gate voltage range.

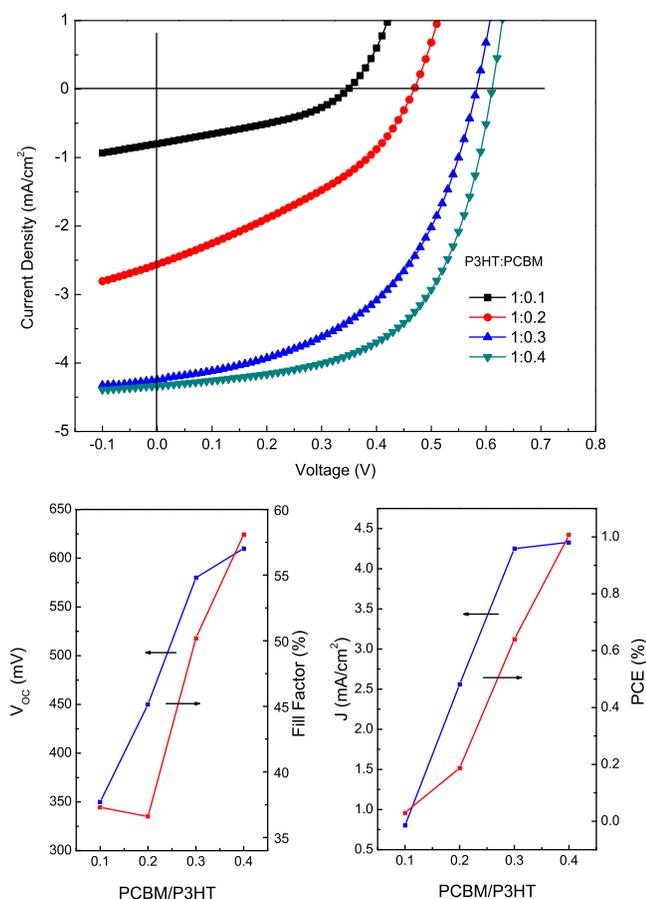


FIG. 4. Upper panel: I - V curves of the solar cell devices with different donor/acceptor ratios. Lower panel shows the device performance parameters as a function of PCBM/P3HT ratio.

compensating space-charge buildup effect. Enlarged donor/acceptor interface is also another factor for higher exciton dissociation rate. Therefore, we observed further increase of FF to 58.1%. However, both V_{oc} and J_{sc} tend to saturate after 1:0.3 ratio.

When vertical phase separation is disregarded, ideal case for optimum device efficiency for OPVs is equal contact areas of separate donor/acceptor at respective electrodes at the same time balanced charge carrier mobilities for electrons and holes. For that aim, comparable hole/electron mobilities of pristine donor/acceptor should be pursued. The thickness of the sample is not critical in OFETs, as the charge transport occurs within very thin layer at the interface between dielectric and active layer. On the contrary, in OPVs, the thickness should be optimized for maximum absorption of incident light and minimum charge recombination. Additionally, annealing process will eventually affect the mobilities of the donor and acceptor due to the enlarged crystal domain sizes.

Evolution of the respective mobilities of donor and acceptor following systematic temperature treatment will provide deeper understanding of the carrier transport in this bulk heterojunction system. Applying higher hole mobility pristine P3HT, thickness and annealing treatment optimization of OPV devices are expected to yield optimum device performance. Work is in progress in this direction.

In summary, we studied both electron and hole mobilities of bulk heterojunction system in a single device using ambipolar organic field effect transistors. Efficient injection of both carriers was realized using asymmetric source/drain contacts of Al and Au. Water soluble dielectric PVT provided optimum dielectric/active layer interface with the similar trap densities for both carriers. Fine tuning of donor/acceptor ratio revealed balanced charge carrier mobilities at a ratio of 1:0.3, which was due to much lower hole mobility of pristine P3HT comparing to electron mobility of pristine PCBM. Such a balancing effect was confirmed in the OPV devices, where drastic enhancement of device performance parameters were obtained. We propose an important criterium for OPV device optimization, where comparable mobilities should be pursued for pristine donor and acceptor, so that balanced mobilities will not be compensated by unbalanced interface area for charge collection in bulk heterojunction. We also convincingly showed that OFETs can be applied to infer balanced charge carrier mobilities in OPVs provided optimum charge injection from the contacts to the active layer and similar low trap densities at the dielectric/active layer interface for both carriers are guaranteed.

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