

# A reduced electron-extraction barrier at an interface between a polymer poly(3-hexylthiophene) layer and an indium tin oxide layer



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## ABSTRACT

Roles of the buried interface between polymer poly(3-hexylthiophene) (P3HT) layer and indium tin oxide (ITO) on the glass substrate have been characterized by transient photovoltage (TPV). Since P3HT is the hole-transporting material, from intuitiveness, ITO/P3HT contact (IPcontact) tends to be hole extracting. However, in this letter, the negative TPV of ITO/P3HT/Al demonstrates that IPcontact dominates the reversed built in electric field, namely pointing from ITO to Al, and is confirmed to be electron extracting. Meanwhile, an interesting biphasic feature of TPV is demonstrated in a device of ITO/P3HT:[6,6]-phenyl-C61-butyric acid methyl ester/Al. The negative component in biphasic TPV shows that IPcontact is one reason resulting in the leakage current for P3HT based solar cells in normal structures. The theoretical study is conducted, and reveals that the interaction between P3HT and ITO reduces electron barrier by 0.5 eV for IPcontact. Band bending and dipole formation are two possible reasons to reduce the electron barrier. By taking advantage of the electron extraction, IPcontact is employed as a composite cathode in an inverted solar cell by pre-coating a pristine P3HT buffer layer between a blended layer and ITO. The study paves a way to characterize the buried interface in solution processable optoelectronics by observing polarity change of TPV, and to fabricate the simplified inverted organic solar cell employing IPcontact to extract electrons.

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## 1. Introduction

Polymer semiconductors offer many advantages, namely, variety of materials, simple fabrication processes, cost-effectiveness and transparency, which make organic optoelectronic devices attractive for many applications [1–6]. Interfacial modifications on the buried interface are widely employed to improve the performance among all organic devices [7–10]. In comparison with the small molecule devices, characterization of the buried interface for the solution processable polymer devices is a challeng-

ing topic. For small molecule devices, simple control of the ultrathin layer by thermal evaporation in conjunction with the localized carrier transport feature make ultraviolet photoelectron spectroscopy (UPS) an ideal tool to detect the energy level alignment in both organic/organic and organic/metal interfaces [10–12]. While for polymer devices, due to the long polymer chains, carrier transporting appears to be delocalized and presents various inter-chain interactions. Furthermore, it is difficult to deposit the ultra thin layer and control the morphology because of the one-step-forming method, such as spin coating. Thus, UPS no longer provides the means to easily characterize the buried interface for polymer devices [13]. In the past 10-odd years, polymer P3HT has been largely used in polymer

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optoelectronics, such as organic light emitting devices [14], organic solar cells (OSCs) [15] and organic transistors [16]. Although the buried interface has proven crucial to the performance improvement of P3HT based optoelectronics [16–19], its feature is scarcely studied due to the difficulties stated above. Yang Yang's group determined the content ratio of blended layer near the buried interface by using X-ray photoemission spectroscopy (XPS) through lifting the polymer layer of P3HT:[6,6]-phenyl-C61butyric acid methyl ester (PCBM) from substrate in water [20]. However, peeling off the active layer from substrate destroyed the buried interface. Therefore, it is highly desirable to develop a simple non-destructive method to characterize the physical or chemical properties of the buried interface in the P3HT device.

Transient photovoltage (TPV) has been recently developed to study the minority mobility through measuring decaying rates in the long term of TPV [21,22]. In addition, decaying rate and establishing time of TPV are further explored to detect the trapping states in the bulk [23–25]. In this work, we report that polarity of TPV can be a potential tool to monitor the direction of build in electrical field of  $E_{\text{built-in}}$  which is sensitive to the interfacial interaction. Consequently, we characterize the roles of the buried interface between ITO and P3HT. Other widely used materials in OSCs, namely PCBM and  $C_{60}$ , will also be investigated for further confirmation.

## 2. Experimental

ITO glass substrates with a sheet resistance of 15  $\Omega$  were cleaned and treated in the ultra-violet ozone cleaner for 15 min. Polymer solutions (P3HT 20 mg/ml, PCBM 20 mg/ml and P3HT:PCBM 1:1 40 mg/ml in chlorobenzene) were spin coated at 700 rpm for 40 s to form films in a nitrogen-filled glove box, followed by 110 °C annealing for 10 min on a hot plate. Device area was 5.8 mm<sup>2</sup>.  $C_{60}$ , Al and LiF were thermally evaporated at rates of 1, 1.5 and 0.2 Å/s. As for the inverted solar cell in Fig. 8, the buffer layer of P3HT is deposited through spin-coating the 70  $\mu$ l solution of 10 mg P3HT in 1 ml dichlorobenzene onto the surface of ITO followed by the 100 °C annealing for 10 min. All thicknesses of polymer layers were measured by profilometer with error band <10 nm.

The setup of TPV and the structure of the device are shown schematically in Fig. 1a. The 800 ps pulse laser with a wavelength of 355 nm transmits into the device through ITO to excite the sample; the energy for each pulse is 20  $\mu$ J. TPV is recorded by 300 MHz Tektronix oscilloscope. Fig. 1b schematically shows the principal of the TPV generation. After dissociation of excitons – excited by the laser pulse in the active layer – the generated electrons and holes transport toward different electrodes, driven by  $E_{\text{built-in}}$ . The collection of carriers by electrodes yields TPV.  $E_{\text{built-in}}$  hereby determines the polarity of TPV [14,15,22]. In principle,  $E_{\text{built-in}}$  starts from a low work function (WF) electrode, and ends in a high WF electrode.

## 3. Results

### 3.1. Observation of an unexpected negative TPV in ITO/P3HT/Al

Fig. 2 plots TPVs of ITO/PCBM/Al and ITO/P3HT/Al. For the PCBM device, ITO and Al are respectively used as the anode and the cathode.  $E_{\text{built-in}}$  points from Al to ITO in light of 4.6 eV [26]/4.3 eV [27] WFs for ITO/Al. Therefore, electrons and holes move respectively to Al and ITO. The collection of electrons by Al and holes by ITO results in an expected positive sign of TPV as schematically drawn in Fig. 1b and c, consistent with experimental observations for TPV of ITO/PCBM/Al in Fig. 2. However, TPV of ITO/P3HT/Al shown in Fig. 2 is negative. The unexpected negative sign denotes that ITO collects electrons rather than holes. It can be speculated that either the interfacial effect or the bulk effect in P3HT device reverses the direction of  $E_{\text{built-in}}$ , and then yields the negative TPV.

### 3.2. The feasibility of the unexpected negative TPV arising from the interfacial interaction between the active layer and the electrode

To examine whether the interfacial interaction can lead to the negative TPV, small molecule  $C_{60}$  is selected as the referent material because the interfacial interaction between  $C_{60}$  and Al has been studied clearly by UPS [27]. Fig. 3a plots TPV of ITO/ $C_{60}$ /Al. TPV shows unexpected negative TPV. Due to the strong ability of accepting electrons, acceptor  $C_{60}$  forms dipole at the interface of  $C_{60}$ /Al which increases WF of Al from 4.3 eV to 5.2 eV which is even higher than ITO [27,28].  $E_{\text{built-in}}$  is from ITO to Al, which opposites to the general case in Fig. 1b. Such  $E_{\text{built-in}}$  drives electrons to ITO, and holes to Al, which generates the negative TPV, which is schematically illustrated in Fig. 3b. To further verify the domination of  $C_{60}$ /Al in the negative signal, 4 nm LiF was inserted at  $C_{60}$ /Al. Fig. 3a shows that TPV becomes positive. The insulating LiF layer prevents the interfacial interaction between  $C_{60}$  and Al. Therefore, dipoles cannot form between them. Moreover, interaction between LiF and  $C_{60}$  followed by deposition of Al makes LiF clusters chemically dissociate. The generated Li atoms reduce WF of Al [29]. The LiF's dual roles of blocking dipole formation and providing lower WF for LiF make WF of Al lower than that of ITO. Therefore, TPV becomes positive again. From TPV results of the devices based on the referent material  $C_{60}$ , one can see that interfacial interaction gives rise to the negative TPV, which can be proved by the response of polarity to the insertion of buffer layer at the corresponding interface.

### 3.3. ITO/P3HT contact (IPcontact) at the buried interface dominates the negative TPV

Back to P3HT devices, the top interface of P3HT/Al and the buried interface of ITO/P3HT possibly contribute to the negative signal. To confirm which one the negative TPV origins from, buffer layers of 4 nm LiF and 40 nm poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)

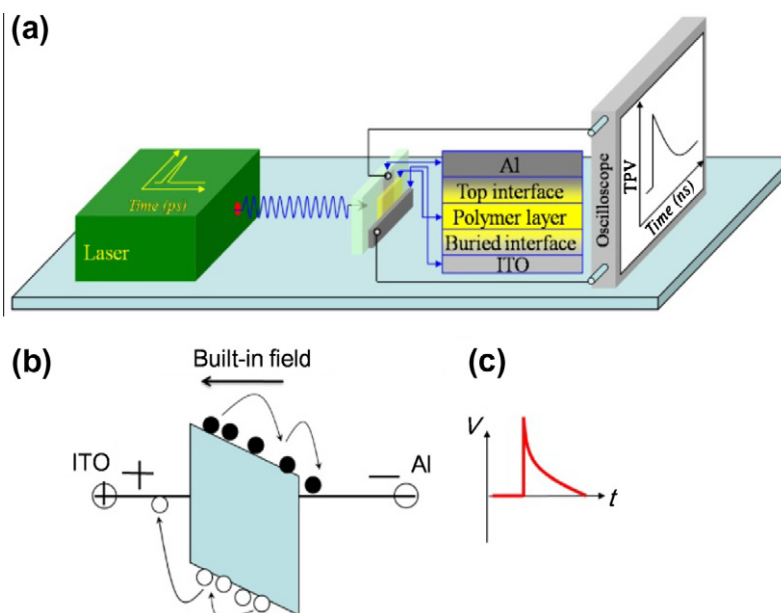


**Fig. 1.** Schematic diagram of (a) setup of TPV measurement and device structure, (b) directions of charge transport driven by the built-in field in conventional device and (c) the polarity of TPV determined by the direction of charge transport.

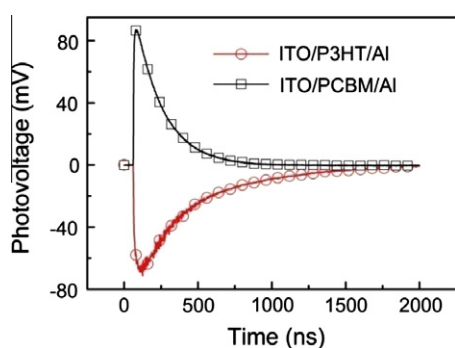


**Fig. 2.** TPVs for single polymer layered devices of ITO/PCBM/Al and ITO/P3HT/Al. Thicknesses for P3HT and PCBM are 210 nm and 140 nm. (TPV of ITO/P3HT/Al is amplified by three times.)

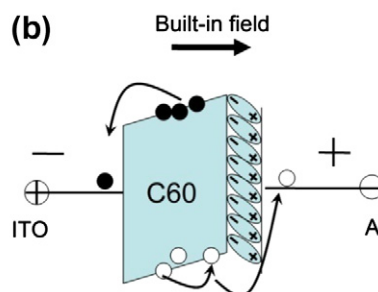
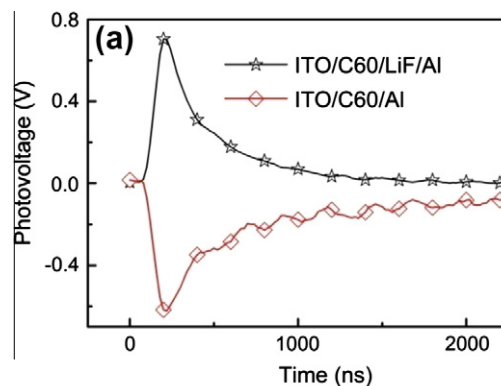


**Fig. 3.** (a) Polarity change of TPV for reference material of C<sub>60</sub>: ITO/C<sub>60</sub>(200 nm)/Al and ITO/C<sub>60</sub>(200 nm)/LiF(5 nm)/Al, (b) schematic diagram of charge transport in the case of dipole formation at top interface for ITO/C<sub>60</sub>/Al.

(PEDOT:PSS) were inserted at the top interface and buried interface respectively. Unlike C<sub>60</sub> devices, the insertion of LiF does not change the sign of TPV as shown in Fig. 4a, but only weakens the amplitude due to the decreased  $E_{\text{built-in}}$  strength by the insulating LiF. However, the negative signal is switched back to the positive one in the case of inserting PEDOT:PSS at IPcontact as illustrated in Fig. 4b. Results shown in Fig. 4a and b imply that it is IPcontact, rather than P3HT/Al, to result in the negative polarity. Additionally, on account of the zero signal in ITO/PEDOT:PSS/Al in Fig. 4b, there is no generation of TPV by the bulk of PEDOT:PSS. Therefore, the positive signal is achieved because (1) the insertion of buffer layer PEDOT:PSS blocks the interaction between P3HT and ITO and (2) PEDOT:PSS has a WF of 5.2 eV [18] higher than ITO.

The resulting  $E_{\text{built-in}}$  thus points from Al to ITO/PEDOT:PSS, and gives rise to the positive TPV again.

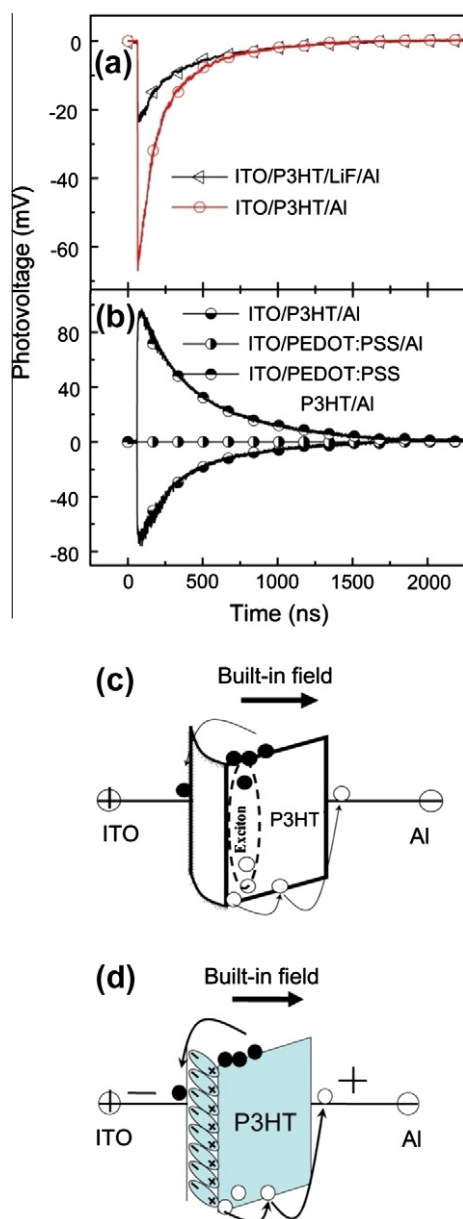


**Fig. 4.** Polarity change of TPV for P3HT based devices. Interfacial modification at (a) the top interface and (b) the buried interface. Schematic diagram of charge transport in the case of dipole formation, (c) or band bending, (d) at the buried interface for ITO/P3HT. (All TPVs are amplified by three times.)

## 4. Discussion

### 4.1. Two possible interfacial interactions in IPcontact – dipole formation and band bending

There are two viewpoints about the features of ITO: semiconductor and metal.

#### 4.1.1. ITO as a metal

In the case that ITO functions as a metal, namely, Fermi energy is higher than conductive band of ITO, Hwang et al.

reported that if the hole barrier, namely energy difference between highest occupied molecule orbit (HOMO) of polymer and Fermi energy is larger than 0.6 eV, the band will keep flat. However, if the barrier is less than 0.4 eV, energy band near the organic/metal interface will bend at least 0.3 eV [13]. This is because, when Fermi surface approaches the frontier orbital of the polymer at the interface, the tail of the density of states extending into the gap starts to fill up, and an excess density of charges accumulates in the organic material (holes in the present case). These interface charges induce an electric field that displaces the frontier orbital, namely HOMO level, away from Fermi energy, limiting further penetration of charges into the bulk of the film, via a kind of self-regulating mechanism. The density of excess interface holes depends on the barrier. Considering the hole barriers in buried interface and top interface are around 0.3 eV and 0.6 eV respectively, the band bending only occurs at IPcontact, in conjunction with more than 0.3 eV bending,  $E_{\text{built-in}}$  is reversed. The energy diagram is schematically shown in Fig. 4c.

#### 4.1.2. ITO as a semiconductor

If the ITO functions as a semiconductor, Yi et al. investigate the interface of P3HT/ITO by performing low intensity XPS assisted by UPS on the sample fabricated through an eight-step P3HT deposition on an *ex situ* cleaned ITO substrate [30]. Finally, they found that a 0.76 eV dipole formed at IPcontact. Such strong dipole is sufficient to shift WF of ITO to be lower than Al, which is described in Fig. 4d. The origin of dipole formation is still unclear, but can be enlightened from  $C_{60}$ . As a kind of acceptor,  $C_{60}$  forms a covalent bond with metals by charge transfer. The properties of metal are consequently modified by the bonding formation [27]. The covalent bond formation between  $C_{60}$  and Al arises from the electron transfer from metal to acceptor  $C_{60}$ . The transferred charges in conjunction with the 3 nm region yield a strong electric field pointing from Al to  $C_{60}$ , which prevents further electron transfer from Al to ITO, but promote the hole injection from Al. Therefore, the formed dipoles increase WF of Al. Back to P3HT, different from the acceptor role of  $C_{60}$ , P3HT is employed as a donor in OSCs, which easily donates electrons especially for high WF electrodes. Therefore, P3HT can possibly form bonds with electrodes by charge transfer and thus modify the electrical properties of the P3HT and electrodes at the contact region. For example, for ITO and P3HT, electron can be transferred from P3HT to ITO. If the left vacant states in P3HT accumulate in the several nanometers region, the strong electric field is produced with direction from P3HT to ITO, which prevents hole injection from ITO but is good for electron injection. Therefore, the dipole formation decreases the work function of ITO. The negative signal is possible as schematically shown in Fig. 4d.

However, it is hard to confirm which one of the band bending and the dipole formation dominates in such system. Because whether ITO should be regarded as a metal or semiconductor is still in hot debate now. Importantly, no matter what role of ITO plays, both of the dipole formation and the band bending are interfacial effects and reduce the electron barrier to reverse  $E_{\text{built-in}}$ , which fully

coincides with the negative TPV of ITO/P3HT/Al. Expectably, high performance OSCs in the normal structure requires that electrons are collected by Al rather than ITO. Therefore, the reduced electron barrier for IPcontact gives the detrimental influence on the hole extraction in the ITO side, which is disadvantageous to the performance of P3HT based OSC with normal structure and will be demonstrated in Fig. 8.

#### 4.2. Ensuring coexistence of P3HT and PCBM near the buried interface by observing the biphasic TPV

The coexistence of P3HT and PCBM was reported before [20]. However, the effect of the coexistence on the performance of OSCs is still unclear. To further reveal the influence of the buried interface on charge dynamics of OSCs, the device with the blended layer of P3HT:PCBM was fabricated. Interestingly, the TPV has a biphasic feature as shown in Fig. 5, namely a negative component before 240 ns and a followed positive component. As demonstrated in Fig. 2, P3HT and PCBM at the buried interface can generate negative and positive TPV respectively, the biphasic feature can occur only when P3HT and PCBM coexist at the buried interface. In the process of forming blended film, P3HT and PCBM in the bulk are separated into many micro-phases. The micro-phases of P3HT with IPcontact function as the channels of leakage current in OSC. It should be noted that two counteract properties of charge transport in the P3HT and PCBM shown by our TPV study cannot be verified by steady-state measurement, which can only provide the equilibrium state or superposition of many fast processes.

#### 4.3. Excluding the influence of ITO absorption on the polarity change of TPV

It should be noted that the wavelength of laser light employed in above sections was 355 nm, which is very close to the absorption edge of ITO, and indium oxide could be somehow excited. To confirm whether the absorption of ITO can influence the polarity of TPV, laser with a longer wavelength of 532 nm, which is far beyond the absorption range of ITO, is employed to excite the photovoltage. The experimental results demonstrate that the polarity of TPV is only dependent on the device structure rather than the

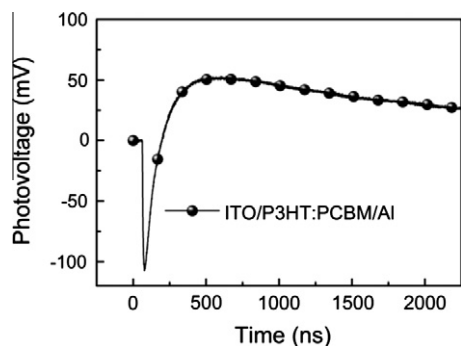


Fig. 5. Biphasic TPV for blended-layered device: ITO/P3HT:PCBM (1:1 240 nm)/Al.

photon wavelength. For instance, Fig. 6 plots TPVs of three devices excited by 532 nm laser. The only difference between 355 nm excited TPVs and 532 nm excited TPVs for the same device structure is the amplitude of TPV. Due to the different absorbing capabilities of the polymer in different wavelengths, the number of generated free carriers is different, consequently resulting in the tiny change in amplitude. However, TPV polarities of three devices excited by 532 nm photons keep the same as those excited by 355 nm photons as shown in Figs. 2 and 4b, namely TPV polarities of ITO/PCBM/Al, ITO/P3HT/Al and ITO/PEDOT:PSS/P3HT/Al are positive, negative and positive, respectively.

Therefore, it can be confirmed that there is no influence of ITO absorption on the polarity change of TPV.

#### 4.4. Theoretical confirmation

Time-dependent device model is adopted to further confirm the reduced electron barrier [22]. Two issues including dynamics of excitons generation and the dynamics of charge carriers are as follows:

$$\frac{\partial}{\partial t} \rho_{ex}(x, t) = D \frac{\partial^2}{\partial x^2} \rho_{ex}(x, t) + G(x, t) \frac{\rho_{ex}(x, t)}{\tau} \quad (1)$$

where  $\rho_{ex}$  is the density of excitons,  $D$  the diffusion coefficient,  $\tau$  the lifetime of excitons,  $x = 0$  is at buried interface (ITO/polymer) and  $x = L$  at top interface with  $L$  the thickness of polymer layer. The generation function  $G(x, t)$  follows the form of the input laser pulse, i.e.  $G(x, t) = g_0 \exp(-x/L_a)$  when  $t \geq t_{off}$  or  $t \leq t_{on}$  and  $G(x, t) = 0$  where  $g_0$  is the generation rate of excitons depending on the light intensity.  $L_a$  is the absorption length, and  $t_{on}(=0)$  and  $t_{off}$  are the time when the laser is on and off, respectively. All these parameters are determined by experiments and listed in the Supporting information S11. The second issue based on current continuity equations is given as

$$\frac{\partial \rho_{n(p)}}{\partial t} = -J_{n(p)} + G_{ca} - R \quad (2)$$

where  $\rho_{n(p)}$  is the electron(hole) density,  $J_{n(p)}$  the current density,  $G_{ca}$  the carrier generation rate, and  $R$  the

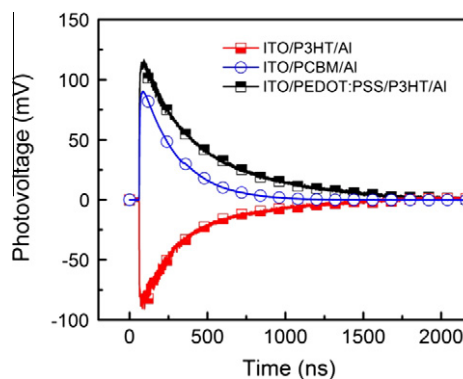


Fig. 6. TPVs for ITO/PCBM/Al, ITO/P3HT/Al and ITO/PEDOT:PSS/P3HT/Al excited by 532 nm laser. TPVs of ITO/P3HT/Al and ITO/PEDOT:PSS/P3HT/Al are amplified by three times).

recombination in the materials. The process and parameters in the theoretical calculation is introduced in details in [Supporting information S11](#).

**Fig. 7** summarizes both theoretical and experimental results. For ITO/PCBM/Al, the fast establishment of the theoretical TPV is from light absorption and photo-generated excitons in PCBM near the buried interface. Excitons are quickly dissociated to free carriers in PCBM due to the fast dissociation rate with the order of magnitude of tens fs. Therefore, the diffusion and drift of generated carriers to electrodes dominates initial stage of TPV. The gradual reduction of free carriers results in the slow decay after the pulse is off. For ITO/P3HT/Al, the theoretically negative signal originates from the reduced electron barrier at IPcontact. The electron barrier is reduced by 0.5 eV, which is large enough to reverse the direction of  $E_{\text{built-in}}$  and similar to the value reported by Yi et al. [30]. For P3HT:PCBM (1:1) based device, the consistence between theoretical and experimental results further confirm that the processes corresponding to the positive signal and negative signal coexist and compete in the device as depicted in the above.

#### 4.5. Fabrication of a simplified OSC with an inverted structure based on IPcontact

Although the reduced electron barrier for IPcontact is not conducive to the performance of OSC in the normal structure, it can be used to improve the electron extraction in an inverted structure by employing ITO/P3HT as the composite cathode. Two inverted structures of (1) ITO/P3HT:PCBM/MoO<sub>3</sub>/Ag and (2) ITO/P3HT/P3HT:PCBM/MoO<sub>3</sub>/Ag have been fabricated. The main difference for the two devices is the insertion of P3HT between ITO and the blended layer in Device No. 2. P3HT is pre-coated before depositing the blended layer of P3HT:PCBM. The coating condition for pure P3HT layer is introduced in the section of experimental method. **Fig. 8** illustrates  $J-V$  curve under 1 Sun, air mass 1.5 (AM 1.5) illumination. **Table 1** lists the device performance. For the Device No. 1, S-shape curve is observed, and leads to the low fill factor of 38%. Recently, both theory and experiment demonstrate that the S-shape can be achieved through bulk effect, namely, tuning the recombination occurring between free carriers and carriers trapped in an exponential tail of states [23–25,31].

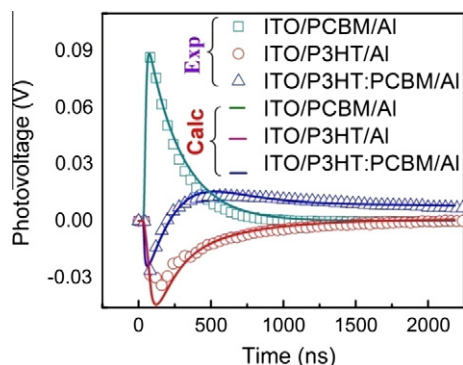


**Fig. 7.** Theoretical calculation and experimental results of ITO/PCBM/Al, ITO/P3HT/Al (both theoretical and experimental results are amplified by three times) and ITO/P3HT:PCBM(1:1)/Al.

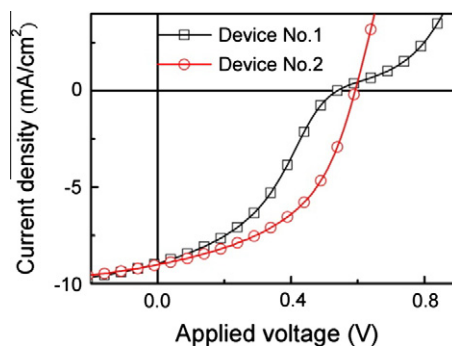


**Fig. 8.**  $J-V$  curves of Device No. 1: ITO/P3HT:PCBM/MoO<sub>3</sub>/Ag and Device No. 2: ITO/P3HT/P3HT:PCBM/MoO<sub>3</sub>/Ag. Total polymer layer thicknesses for Device No. 1 and Device No. 2 are 240 and 250 nm. MoO<sub>3</sub> is 4 nm in thickness.

**Table 1**

Summary of device performance.

| Device no. | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF (%) | $V_{oc}$ (V) | PCE (%) |
|------------|--------------------------------|--------|--------------|---------|
| 1          | 8.9                            | 38     | 0.54         | 1.8     |
| 2          | 9.0                            | 48     | 0.59         | 2.5     |

In this work, the only difference between two structures lies in the buried interfaces. For Device No. 1, both P3HT and PCBM contact with ITO, while for Device No. 2, there is only IPcontact in the buried interface. Therefore, besides the bulk effect, the interfacial effect can also give rise to the S-shape. As shown in **Fig. 5**, biphasic TPV illustrates that P3HT and PCBM touch ITO concurrently. Two channels of P3HT and PCBM provide different charge transporting directions, which could be the root of S-shape in  $J-V$  curve. The insertion of P3HT removes the contact between PCBM and ITO. Since PCBM/ITO contact results in the positive component in biphasic TPV, which goes against the electron extraction in the inverted structure. Therefore, removing such contact is good for the electron extraction. Consequently, the S-shape vanishes in the Device No. 2 as plotted in **Fig. 8**. Li Gang et al. has reported that when the electrons and holes in the active layer are unbalanced, the photocurrent is space-charge limited. The photocurrent is then governed by a square-root dependence on bias and an FF above 40% is unachievable [3]. MoO<sub>3</sub>/Ag has been proved to be an effective anode for hole extraction [32]. The insertion of thin P3HT buffer layer results in the more efficient electron extraction. So the balanced electrons and holes extraction also relieves the unbalanced charge accumulation in the bulk. The fill factor is thus improved to 48.2% and power conversion efficiency increases from 1.8% for the Device No. 1 to 2.6% for the Device No. 2. It is noteworthy that the further optimization of device performance based on such structure will be reported in the subsequent literature.

## 5. Conclusions

Without damaging the buried interface and with similar structure as practical optoelectronic devices, TPVs of polymer devices have been systematically studied. The

influence of the buried interface on the electron extraction for polymer P3HT based device has been unveiled by observing negative polarity of TPV. By studying TPV of ITO/P3HT:PCBM/Al, biphasic feature shows that the IPcontact is disadvantageous to the performance of P3HT based OSC in the normal structure, but a benefit to the performance of OSC in the inverted structure. Our finding contributes to better understanding the role of the buried interface and properly using surface modification to achieve high performance OSC in conjunction with the simplified structure. Meanwhile, the polarity of TPV can function as a sensor to track the direction of built in electric field across the active layer, thus revealing the role of the buried interfaces in all polymer electronics.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.orgel.2012.12.007>.

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