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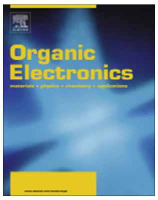

Role of electron blocking and trapping layers in transport characterization of a photovoltaic polymer poly(3-hexylthiophene)

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ABSTRACT

Hole injection and transport in films (300–350 nm) of poly(3-hexylthiophene) (P3HT) were investigated by dark-injection space-charge-limited current (DI-SCLC) technique. For samples with a nominally hole-only configuration of anode/P3HT/Au, the DI current transients depart significantly from the theory, and the signals cannot be used for reliable carrier mobility extraction. The origin of the departure can be attributed to electron leakage from the Au cathode. We outline a means of suppressing electron leakage by inserting an interlayer between the P3HT and the cathode. This interlayer has dual functions of blocking and trapping electrons. Using this interlayer, we obtain well-defined DI-SCLC signals for reliable carrier mobility determination. With a suitable interlayer to suppress undesirable carrier injection and transport, DI-SCLC technique should find broad applications in the transport characterization of narrow gap photovoltaic polymers.

1. Introduction

Carrier mobility (μ) is one of the key parameters that can be used to quantify the transport properties of an organic semiconductor (OS) [1]. Using μ, one can estimate the current that can go through an OS, and make some predictions about device characteristics. For example, μ can be used to estimate the carrier drift length in an organic photovoltaic (OPV) cell, and to optimize the thickness of an OPV cell [2]. Several techniques can be used for extracting μ. For semiconducting PV polymers, current–voltage (*J*–*V*) fitting is, perhaps, the most popular [3]. However, the method can be error-prone if the charge injection contact is non-Ohmic [4]. Another popular technique is photo-charge-extraction by linearly-increasing voltage (photo-CELIV). Photo-CELIV has enjoyed considerable success, especially for samples in an OPV configuration [5].

This contribution looks into a classic technique: dark-injection space-charge-limited current (DI-SCLC), and explores its applicability to PV polymers. DI-SCLC probes the transient current response (by electrons or holes) of a thin film after the application of a step voltage. The principles of this technique are well-known [6–8]. Indeed, there exist some studies on light-emitting polymers [9,10]. However, the application of DI-SCLC to PV polymers is rather scarce. Of the limited studies available so far for PV polymers, the DI-SCLC signals are often ill-defined, making the extraction of μ problematic [11]. Below, we demonstrate that the simultaneous presence of both electrons and holes is responsible for the ill-defined DI-SCLC signals. We outline a means of excluding electron injection in a PV polymer by inserting an interlayer between the polymer and the cathode. Through this interlayer, we obtained well-defined DI-SCLC signals for reliable carrier mobility determination.

2. Experimental

Two hole-conducting semiconducting polymers, namely, PFB and P3HT, are under investigation [12]. They were obtained from American Dye Source and Rieke (P200), respectively. Their energy levels and chemical structures are shown in Fig. 1, and the inset of Fig. 2,

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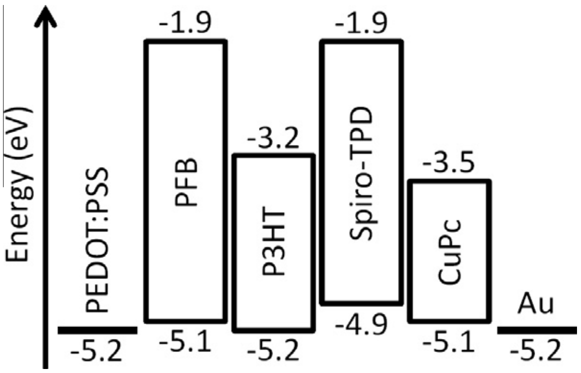

Fig. 1. Energy levels of different polymers and interlayers.

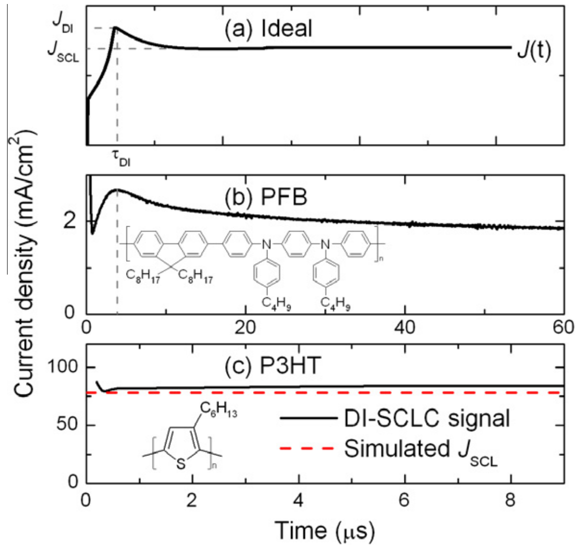

Fig. 2. (a) Ideal DI-SCLC transient, (b) DI-SCLC transient of PFB (418 nm) at 4.9 V, (c) DI-SCLC transient of P3HT (292 nm) at 3.9 V (solid line). In (c), the horizontal dashed line is the simulated steady state J_{SCL}.

respectively. P3HT is one of the most popular materials for OPV cell while PFB is widely used as a hole-injection and transporting layer in polymer light-emitting diodes [13]. Samples with the general structure of anode/polymer/Au cathode were prepared for DI-SCLC experiments. Poly(3,4-ethylenedioxythiophene) doped with polystrene-sulphonic acid (PEDOT:PSS) film (25 nm) on indium-tin-oxide (ITO) was used as the anode. P3HT and PFB (40 mg/ml) was dissolved in 1,2-dichlorobenzene (DCB) and toluene, respectively. Then, the solution was spin-coated on the top of the PEDOT:PSS layer and dried naturally in an N_2 atmosphere to form the polymer films. The film thicknesses were between 300 and 420 nm. Subsequently, 100 nm of gold was coated on the polymer by thermal evaporation. For P3HT samples, a 10 nm of hole-transporting, but electron blocking and/or trapping, interlayer was sometimes inserted in between P3HT and the Au cathode. Three kinds of interlayer were used: (i) spiro-TPD, (ii) CuPc, (iii) spiro-TPD doped with 2% of CuPc [14]. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of these materials are shown alongside with P3HT and PFB in Fig. 1. These layers were prepared by thermal evaporation of the respective materials on P3HT before the coating of the Au cathode.

3. Results and discussion

Fig. 2 shows the ideal DI-SCLC current, and the experimentally determined DI-SCLC signals for samples with the structure ITO/PEDOT:PSS/polymer/Au at room temperature. The HOMOs of P3HT and PFB are −5.2 and −5.1 eV, respectively. These values are very similar to the work function of PEDOT:PSS. Therefore, the anode contact is Ohmic for hole conduction. On the other hand, Au has a work function of about −5.2 eV, and is well below the LUMOs of P3HT (−3.2 eV) and PFB (−1.9 eV). Therefore, the Au cathode is expected to be electron-blocking. Under the conditions of Ohmic contact and unipolar transport, the standard theory of DI-SCLC predicts, after the application of a voltage step V, at $t = 0$, a transient current $J(t)$ that bears a characteristic temporal profile as indicated in Fig. 2(a) [6]. At $t = \tau_{DI}$, $J(t)$ reaches a maximum value of J_{DI}. For $t > \tau_{DI}$, the transient current decays to a steady state value of the space-charge-limited current J_{SCL}, where $J_{SCL} = (9/8)\varepsilon_0\varepsilon_r\mu_0 \exp(0.89\beta F^{1/2})F^2/d$. Here, ε_0 is the permittivity of free space, ε_r is the dielectric constant, μ_0 is the zero-field mobility, β is the Poole–Frenkel slope, d is the thickness of the sample and F is the electric field, V/d. τ_{DI} is related to the space-charge free carrier transit time τ by [6]:

$$\tau_{DI} = 2(1 - e^{-0.5})\tau = 0.787\tau \quad (1)$$

The carrier mobility can be determined by $\mu = d^2/(\tau V)$ [7,8]. Fig. 2(b) shows that for PFB, the DI signal follows the expected $J(t)$ quite well, with a well-defined J_{DI}, τ_{DI}, and a clear steady state J_{SCL}. Using Eq. (1), the hole mobility is found to be 7.3×10^{-5} cm^2 V^{-1} s^{-1}, in general agreement to those in the literature [15]. On the other hand, the DI signal in Fig. 2(c) for P3HT deviates significantly from Fig. 2(a). In fact, J_{DI} is barely resolvable. Thus, for P3HT, the determination of the carrier transit time and mobility are problematic.

The severe departure of DI-SCLC signal for P3HT can be understood as follows. For P3HT, only hole current should be expected, and ideally, electron current should be absent. In reality, despite the LUMO level of P3HT is −3.2 eV, it is conceivable that the intrinsic density-of-states (DOSs) distribution can be quite broad [16]. Besides the intrinsic DOS, defect states can be produced in the energy gap during hot Au atoms deposition. These defect states may effectively broaden the intrinsic electron DOS. Under a high enough electric field, the effective tailed states of the electron DOS can be accessible for electron injection from the Au cathode. The injected electrons transport under the applied field, and they result in an electron current. The superposition of the hole and electron currents results in a $J(t)$ that is larger than the expected SCLC as indicated in Fig. 2(c). In contrast, for PFB, the LUMO level is located at about

−1.9 eV, and presents a significantly higher barrier for electron injection. Thus, the DI current transient for PFB in Fig. 2(b) mimics the ideal signal as indicated in Fig. 2(a).

Below, we outline a general scheme of suppressing electron leakage for P3HT in DI-SCLC experiments. Samples with the structure of ITO/PEDOT:PSS/P3HT/interlayer (10 nm)/Au were fabricated. The additional interlayer should have a high hole mobility, and be thin enough so that the hole transit time should not be affected. In addition, its HOMO levels should be comparable to P3HT. More importantly, the interlayer should prevent electron leakage from the Au cathode. There are three choices for the interlayer: (1) a hole-transporting, but electron-blocking (EB) layer that possesses a higher lying LUMO than P3HT. We chose spiro-TPD which has a hole mobility of $\sim 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ [17], and a LUMO value of −1.9 eV; (2) a hole-transporting, but electron-trapping (ET) layer. We picked CuPc as the ET layer. Pristine CuPc is known to be ambipolar with comparable electron and hole mobilities of $\sim 10^{-3}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ [18]. After air exposure, CuPc films can preserve its hole transport, but its electron transport is severely hindered due to electron traps induced by moisture or oxygen [18]; (3) a hole-transporting, but combined EB and ET layer. In this case, we doped spiro-TPD with 2% of CuPc by thermal co-evaporation onto P3HT. For the ease of discussion, we label this layer as spiro-TPD:CuPc below.

Fig. 3 shows the resulting DI-SCLC signals. The signal without the interlayer is also shown in Fig. 3(a). After the insertion of nominally EB spiro-TPD layer, the transient current spike in $J(t)$ does not really improve, suggesting that spiro-TPD is not effective in EB. Fig. 3(c) shows the effect of an electron-trapping CuPc interlayer. A distinct peak can now be observed at $t = 0.65\ \mu\mathrm{s}$. In addition, the background current is suppressed right after the spike at τ_{DI}. So, CuPc is useful in suppressing electron leakage. However, the signal is still not desirable. Fig. 3(d) shows the result with spiro-TPD:CuPc. In contrast to Fig. 3(a–c), Fig. 3(d) captures all the salient features of the classic DI-SCLC signal. A distinct current peak occurs at $\tau_{\mathrm{DI}} = 0.61\ \mu\mathrm{s}$, corresponding to a hole mobility value of $4.3 \times 10^{-4}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$. Furthermore, the ratio of $J_{\mathrm{DI}}/J_{\mathrm{SCL}}$ is 1.2, the same as the ideal value of 1.21 in DI-SCLC theory [6]. Thus, spiro-TPD:CuPc is the most effective interlayer in suppressing electron leakage.

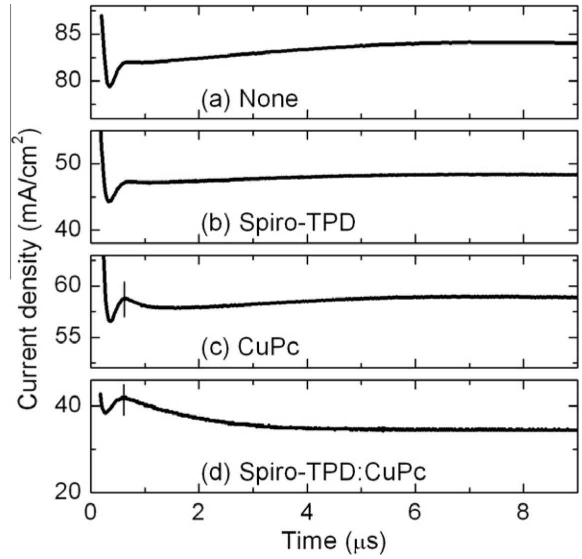

Fig. 3. DI-SCLC transients of P3HT with an electron blocking layer and/or electron trapping layer ($V = 3.9$ V) (a) no interlayer, (b) spiro-TPD, (c) CuPc, (d) spiro-TPD:CuPc (2%).

Although the Fig. 3 carries primarily information about the hole transit times, the current levels indicate the degrees of electron leakage in P3HT. In the absence of an interlayer as shown in Fig. 3(a), electron leakage is the most severe, and the current is clearly not space-charge-limited. Therefore the background current level is the highest. In the presence of the nominally EB spiro-TPD or ET CuPc, Fig. 3(b or c) respectively, the electron leakage currents are reduced, resulting in lower background steady-state current levels of about 48 and 59 mA/cm^2, respectively. Finally, with the spiro-TPD:CuPc interlayer, the background current level (35 mA/cm^2) is the smallest as this interlayer is the most effective in blocking and trapping leakage electrons from the cathode, and this observation is consistent with the changes in the shape of the transient currents.

In spiro-TPD:CuPc, the LUMO of CuPc is located at about −3.5 eV, which is lower than those of both spiro-TPD (−1.9 eV) and P3HT (−3.2 eV). After the application of the voltage step, the high-lying LUMO of spiro-TPD presents a high barrier for electron injection. For those electrons that manage to cross this barrier, they are trapped by the CuPc dopants. Electron conduction within the CuPc dopants is not viable due to low dopant concentration. Alternatively, detrapping into the LUMO of the spiro-TPD host is also not feasible due to the 1.6 eV offset in the LUMO levels of the host and the dopant (Fig. 1). Fig. 4 is a schematic diagram, illustrating how electrons are trapped by the CuPc dopants in the spiro-TPD host within the interlayer. On the other hand, transport of holes is effectively barrier-free throughout the entire sample.

Fig. 5 summarizes the hole mobilities of P3HT at room temperature by DI-SCLC. For comparison, we also

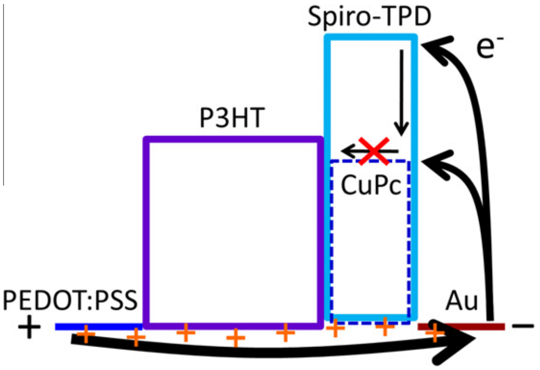

Fig. 4. Schematic diagram illustrating how leakage electrons from the Au electrode are trapped by the CuPc dopants in the spiro-TPD host within the interlayer.

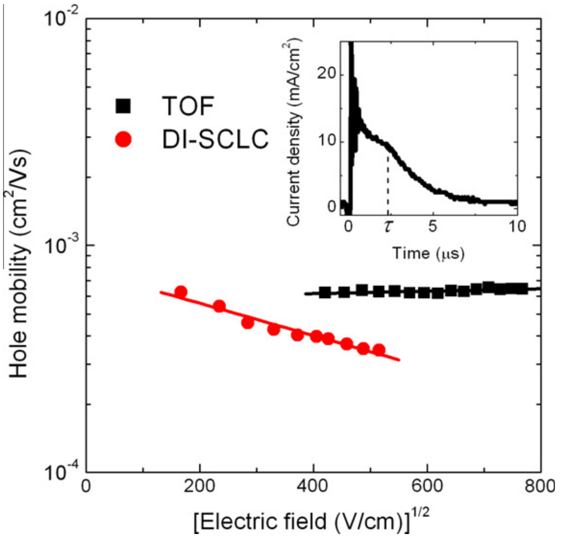

Fig. 5. Hole mobilities of P3HT at room temperature from TOF and DI-SCLC experiments. The film thicknesses for TOF and DI-SCLC experiments were 6.8 μm and 339 nm, respectively. The inset shows a typical TOF signal. The vertical dashed line indicates the position of the hole transit time τ.

measured hole mobilities of a thick film (6.8 μm) of P3HT using time-of-flight (TOF) technique. We can see there is a good agreement between the two techniques with μ in the range between 3 and 6×10^{-4} cm^2 V^{-1} s^{-1}. The experimental values also agree to those in the literatures [16,19]. In the case of P3HT, we only need ~300 nm for measurements. However, in TOF, a much thicker film is required for measurements.

4. Conclusions

DI-SCLC technique was used to study the injection and transport property of PFB and P3HT. By using nominally hole only device structure, PEDOT:PSS/polymer/Au, well-defined DI-SCLC signals for PFB but ill-defined DI-SCLC signals for P3HT were obtained. The ill-defined signals for P3HT arise from electron leakage from the cathode. Three kinds of layer, spiro-TPD (EB), CuPc (ET), and spiro-TPD:CuPc (EB and ET), were used to prevent the electron leakage. Among these three interlayers, only spiro-TPD:CuPc can effectively prevent the electron leakage resulted in a meaningful DI-SCLC transient measurement. With a suitable interlayer to suppress undesirable carrier injection and transport, DI-SCLC technique should find broad applications in the transport characterization of PV-based polymers.

Acknowledgments

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