

# Electron transport and energetic disorder in polymer:bisadduct fullerene photovoltaic blends

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In this paper, the electron transport and energetic disorder in photovoltaic blends of P3HT and a series of bisadduct analogues of PCBM and their thienyl versions have been studied. It is shown that the current density versus voltage characteristics of electron-only devices of all P3HT:fullerene blends can be accurately described using our recently introduced improved mobility model. The occurrence of a multitude of different isomers results in a decrease in the electron transport for these blends, and the charge-carrier mobility is closely related to the energetic disorder. Furthermore, it is shown that the mobility in P3HT:fullerene blends is carrier concentration dependent, and the effective mobility in a P3HT:fullerene blend device with higher multitude of isomers fullerene phase is obviously lower than that in a P3HT:fullerene blend device with lower multitude of isomers fullerene phase. Both the maximum of carrier concentration and the minimum of electric field appear near the interface of P3HT:fullerene blend electron-only devices. These results suggest that the amount of energetic disorder appears to govern the charge carrier transport in polymer:fullerene blends.

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## 1. Introduction

Polymer:fullerene bulk heterojunction solar cells are considered to be a promising candidate for a large-area, flexible, and low-cost sustainable energy source [1–5]. Despite the fact that considerable progress has already been made in this field, the relatively low power conversion efficiencies and stability issues are a drawback for commercialization of these devices. A significant research effort made in this field has been the optimization of the fabrication of solar cells based on poly(3-hexylthiophene) (P3HT) as the donor and [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PCBM) as the acceptor due to the commercial availability of these materials [6–9]. Although this material system show relatively high external quantum efficiencies and fill factors, its performance is still limited by the large energy loss in the electron transfer from donor to acceptor [10]. It has been shown that the use of fullerene multiple adducts derivatives for organic solar cells can reduce the energy loss. However, the higher fullerene adducts as compared to the mono-adducts do have a different degree of crystallinity, order, morphology, and so on. The complex interplay between these parameters does not always lead to an improvement of photovoltaic performance of organic solar cells [11, 12]. The addition of functional side chains on the fullerene cage can perturb the structural packing and make achieving the favourable morphology difficult. Lenes et al. have shown that the bisadduct analogue of

PCBM, bis[60]PCBM, can be used in combination with P3HT without further separation of the individual isomers, resulting in a 20% increase in open-circuit voltage and hence power-conversion efficiency compared to that of PCBM [13]. Moreover, they have also shown that the additional functionalization of the fullerene cage in bis-PCBM have a negative impact on the charge transport properties of the P3HT:fullerene blends due to the occurrence of shallow trapping in the bis-fullerene phase. Surprisingly, the additional disorder introduced by this mixture of isomers does not seem to have any negative effects on the device performance of the solar cell due to the filling of shallow traps under illumination [14]. Recently, Azimi et al. have further demonstrated that adding fullerenes negatively impacts both the electron and hole mobility in polymer:fullerene blends, and the adverse influence of bis-PCBM on the charge transport is considerably stronger than for mono-PCBM [15]. In addition, since the second functionalization can be made in a number of different positions on the fullerene cage, the synthesized material is composed of a large number of different isomers. To date, the effect of the additional disorder introduced by this mixture of isomers on the charge transport in polymer:fullerene blends and the device performance of solar cell is not fully understood.

In this paper, the electron transport and energetic disorder in photovoltaic blends of P3HT and a series of bisadduct analogues of PCBM and their thienyl versions will be investigated by using our recently introduced

improved mobility model. It is shown that the occurrence of a multitude of different isomers results in a decrease in the electron transport for these blends, and the charge-carrier mobility is closely related to the energetic disorder. The mobility in P3HT:fullerene blends is carrier concentration dependent, and the effective mobility in a P3HT:fullerene blend device with higher multitude of isomers fullerene phase is obviously lower than that in a P3HT:fullerene blend device with lower multitude of isomers fullerene phase. Furthermore, in this work we focus on using energetic disorder as a method for modeling the charge transport in polymer:fullerene blends, indicating that the use of a Gaussian disorder reduces the effects of many processes to a single disorder parameter without describing them explicitly. These results provide valuable information about the amount of energetic disorder appears to govern the charge transport in organic semiconductors.

## 2. Model and methods

From a numerical solution of the master equation for hopping transport in a disordered energy system with a Gaussian density of states (DOS) distribution, a commonly employed mobility functional has been developed by Pasveer et al., which is known as the "extended Gaussian disorder model" (EGDM) [16]. Based on the EGDM, we recently proposed an improved mobility model (IEGDM) in which the mobility  $\mu$  depends on the temperature  $T$ , carrier concentration  $p$ , and electric field  $E$  [17]. In particular, the dependence of the zero-field mobility on the carrier concentration  $p$  and temperature  $T$  is given by

$$\mu(T, p) = \mu_0(T) \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^\delta\right], \quad (1a)$$

$$\mu_0(T) = \mu_0 c_1 \exp(c_2 \hat{\sigma} - c_3 \hat{\sigma}^2), \quad (1b)$$

$$\delta \equiv 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}, \quad \mu_0 \equiv \frac{a^2 v_0 e}{\sigma}, \quad (1c)$$

with  $c_1 = 0.48 \times 10^{-9}$ ,  $c_2 = 0.80$ , and  $c_3 = 0.52$ . Where  $\mu_0(T)$  is the mobility in the limit of zero carrier density and zero electric field,  $\hat{\sigma} \equiv \sigma / k_B T$  is the dimensionless disorder parameter,  $\sigma$  is the width of the Gaussian density of states (DOS),  $a$  is the lattice constant (intersite distance),  $e$  is the charge of the carriers, and  $v_0$  is the attempt-to-hop frequency. The field dependence of the mobility is included via

$$\mu(T, p, E) = \mu(T, p)^{g(T, E)} \exp[c_4 (g(T, E) - 1)], \quad (2)$$

$$g(T, E) = [1 + c_5 (Eea / \sigma)^2]^{-1/2}, \quad (3)$$

where  $g(T, E)$  is a weak density dependent function,

$c_4$  and  $c_5$  are weak density dependent parameters, given by

$$c_4 = d_1 + d_2 \ln(pa^3) \quad (4a)$$

$$c_5 = 1.16 + 0.09 \ln(pa^3) \quad (4b)$$

$$d_1 = 28.7 - 36.3 \hat{\sigma}^{-1} + 42.5 \hat{\sigma}^{-2} \quad (5a)$$

$$d_2 = -0.38 + 0.19 \hat{\sigma} + 0.03 \hat{\sigma}^2 \quad (5b)$$

Using the above model and the following coupled equations, the  $J-V$  characteristics of organic electron devices can be exactly calculated by employing a particular uneven discretization method introduced in our previous papers [18, 19].

$$J = p(x) e \mu(T, p(x), E(x)) E(x), \quad (6a)$$

$$\frac{dE}{dx} = \frac{e}{\varepsilon_0 \varepsilon_r} p(x), \quad (6b)$$

$$V = \int_0^L E(x) dx, \quad (6c)$$

where  $x$  is the distance from the injecting electrode,  $\varepsilon_0$  is the vacuum permeability,  $\varepsilon_r$  is the relative dielectric constant of the organic semiconductors, and  $L$  is the organic semiconductor layer thickness sandwiched between two electrodes.

## 3. Results and discussion

In order to study the effect of the additional disorder introduced by the mixture of isomers on the charge transport in polymer:fullerene blends and gain more insight into the loss mechanisms in the polymer:fullerene solar cells, we investigate the  $J-V$  characteristics of electron-only devices based on the blends of P3HT and a series of bisadduct analogues of PCBM and their thienyl versions. The generalized chemical structures of [60]PCBM (PCBM), the bisadduct analogues of [60]PCBM (bis[60]PCBM), [70]PCBM (bis[70]PCBM), and [60]ThCBM (bis[60]ThCBM) are shown in Figure 1. Due to its less symmetric shape the [70]PCBM has a higher absorption coefficient compared to [60]PCBM, which has shown to be useful for complementing the absorption of small bandgap polymers [20]. The thienyl-based [6,6]-thienyl-C<sub>61</sub>-butyric acid methyl ester (ThCBM) has been developed to provide a better conformity between polymer and fullerene in P3HT-based photovoltaic devices [21].

The solution of the coupled equations (Eq. 6) with the IEGDM as described in Sec.2 and the experimental  $J-V$  characteristics of electron-only devices of all

P3HT:fullerene blends at room temperature are displayed in Figures 2 and 3. Apparently, our numerical simulations based on the IEGDM are in good agreement with the experimental measurements, which suggests that the IEGDM is suitable to study the electron transport in P3HT:fullerene blends and taking the carrier density dependence of the mobility into account is essential for describing the electron transport in organic semiconductors. The device currents of the bisadducts are all lower compared to P3HT:PCBM blends, where the biggest difference occurs for the blend based on bis[70]PCBM. At low voltages the current through these single carrier devices can be described with a space charge limited current (SCLC) using a field dependent mobility. The well-known expression for the SCLC in electronic devices has been obtained by Mott and Gurney [22], given by

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3} \quad (7)$$

According to the Mott-Gurney law, from the  $J - V$  measurements we determine the room-temperature zero-field mobilities to be  $1.4 \times 10^{-7} \text{ m}^2/\text{Vs}$ ,  $5 \times 10^{-8} \text{ m}^2/\text{Vs}$ ,  $1.2 \times 10^{-8} \text{ m}^2/\text{Vs}$ ,  $4 \times 10^{-9} \text{ m}^2/\text{Vs}$  for P3HT:[60]PCBM blends, P3HT:bis[60]ThCBM blends, P3HT:bis[60]PCBM blends, P3HT:bis[70]PCBM blends, respectively. Looking at the zero-field mobilities of all the P3HT:fullerene blends, as compared to PCBM, a decrease in mobility of up to two orders of magnitude for the bisadducts. A possible explanation for this drop in device current and zero-field mobility can be an increase in disorder in the fullerene phase, due to the presence of a higher multitude of isomers in the bisadducts. According to the IEGDM, the values of the width of the Gaussian DOS  $\sigma$  of the various fullerene-based derivatives can be determined in such a way that an optimal overall fit is obtained. The amount of disorder  $\sigma$  obtained in present work are 0.07 eV, 0.087 eV, 0.095 eV, 0.102 eV for P3HT:[60]PCBM blends, P3HT:bis[60]ThCBM blends, P3HT:bis[60]PCBM blends, P3HT:bis[70]PCBM blends, respectively. For P3HT:PCBM blends a  $\sigma$  of 0.07 eV is obtained, which is almost equal to the previously reported value [14, 23]. For all the P3HT:bisadduct fullerene blends the magnitude of the disorder is significantly larger than the P3HT:PCBM blends, due to

the presence of a higher multitude of isomers in the fullerene phase. Furthermore, it appears that the zero-field mobility of electrons in P3HT:fullerene blends is closely related to the width of the Gaussian DOS  $\sigma$ , and the electron mobility gradually decreases with increasing the energetic disorder. As a consequence, the molecular conformation and strongly ordered stacking of the molecules should be the origin of the excellent electrical properties in organic semiconductors, and the mobility is closely related to the energetic disorder. This indicates that the amount of energetic disorder in organic semiconductors appears to govern the charge transport properties. From these results, it can be found that the use of a Gaussian disorder in mobility model can reduce the effects of a number of unknown properties to a single disorder parameter without describing them explicitly. Generally, the IEGDM can provide a simple yet adequate method for describing the charge transport in a range of complex disordered systems and can be included in device models with the inclusion of a minimal set of model parameters.

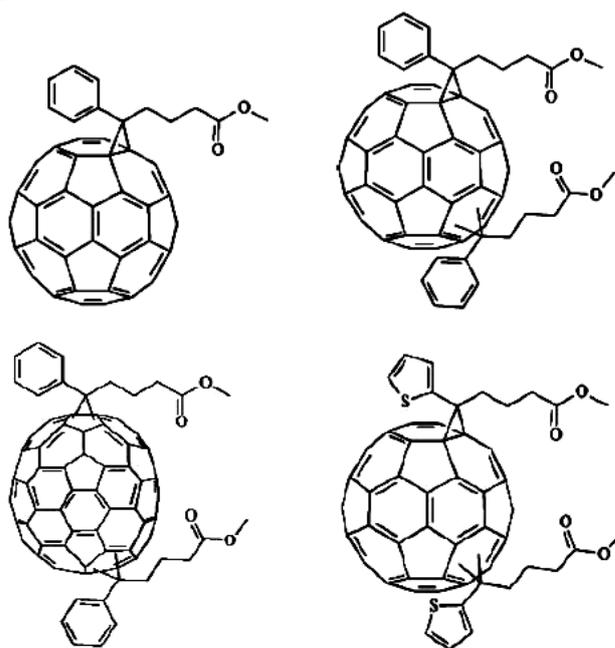


Fig. 1. Chemical structures of materials used in this study. From top left to bottom right, [60]PCBM, and highly generalized structures for the isomeric mixtures of the bis[60]PCBM, bis[70]PCBM and bis[60]ThCBM

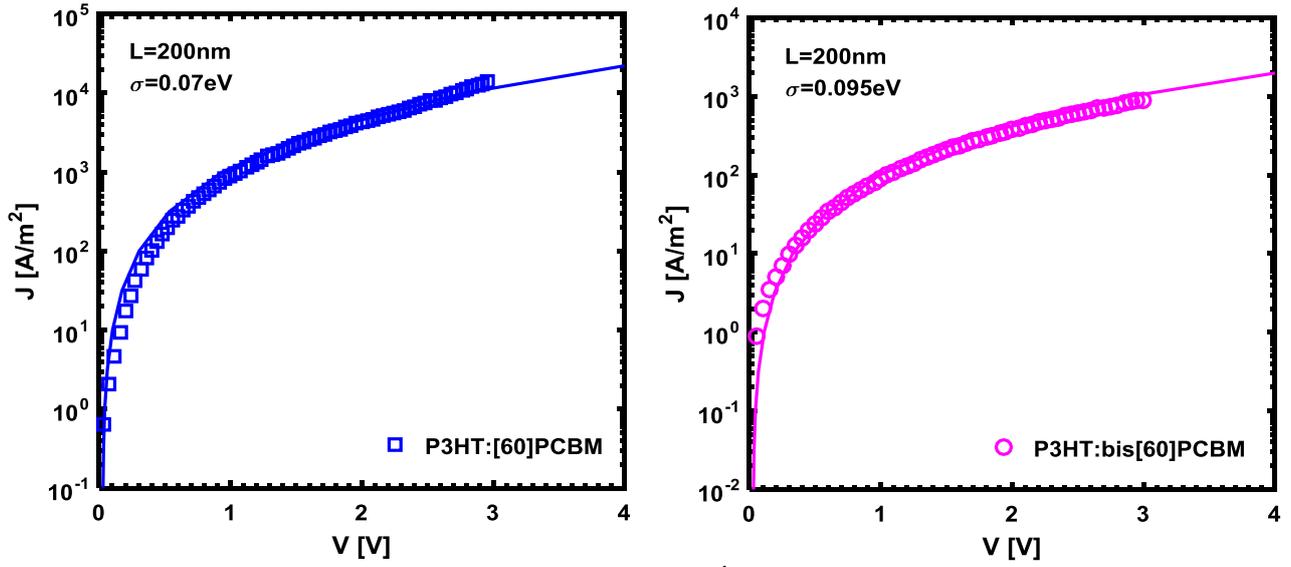


Fig. 2.  $J$ - $V$  characteristics of electron-only devices for P3HT:[60]PCBM and P3HT:bis[60]PCBM. Symbols are experimental data from Ref. [14], lines are the numerically calculated results from Eqs. (1)~(6)

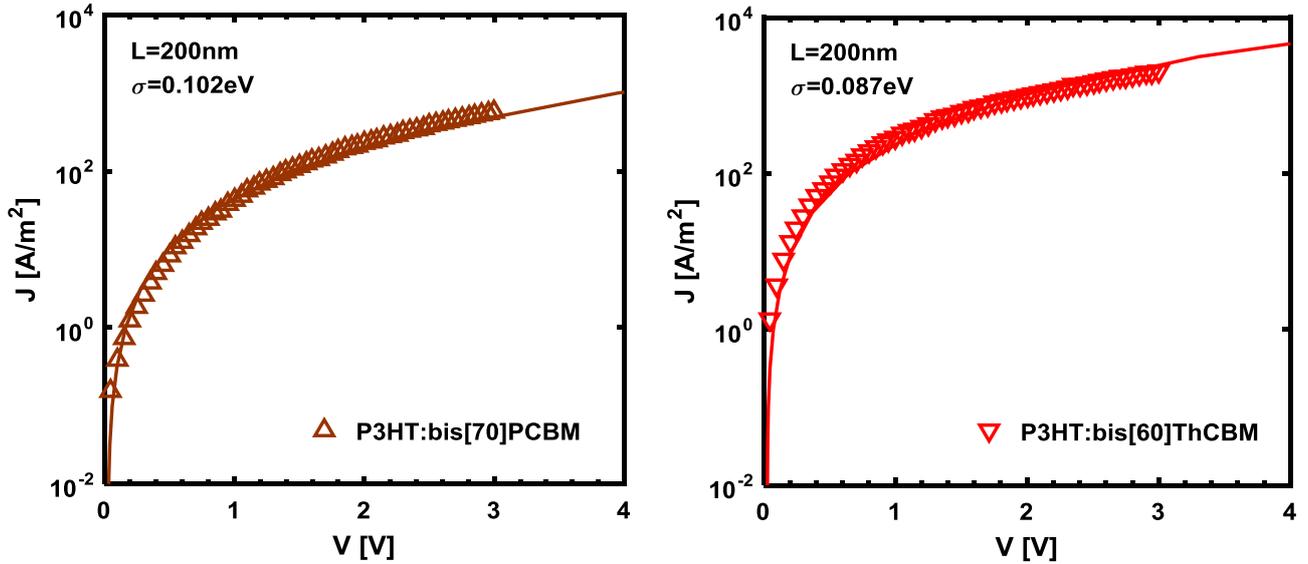


Fig. 3.  $J$ - $V$  characteristics of electron-only devices for P3HT:bis[70]PCBM and P3HT:bis[60]ThCBM. Symbols are experimental data from Ref. [14], lines are the numerically calculated results from Eqs. (1)~(6) (color online)

As a next step, we will perform a systematic study for electrical properties of P3HT:bisadducts fullerene blends by using the IEGDM and numerical calculation method as described in section 2. The numerically calculated variations of  $J$ - $V$  characteristics with the boundary carrier concentration  $p(0)$  for P3HT:bis[60]PCBM and P3HT:bis[70]PCBM electron-only devices at room temperature are plotted in Figure 4. The figure shows that the voltage increases with increasing the current density, and the variation of voltage with  $p(0)$  is dependent on the current density. In the density range of  $10^{22}$ - $10^{24}$   $m^{-3}$ , the  $V$ - $p(0)$  curves are fairly flat, indicating that the voltage is almost independent of  $p(0)$  and the  $J$ - $V$  characteristics are physically realistic in this region. This result is fully consistent with that of Zhang et al. on the

OC<sub>1</sub>C<sub>10</sub>-PPV:PCBM blends [24]. Furthermore, it can be seen from the figure that in order to reach the same current density  $J$  at the same  $p(0)$ , the stronger electric field and the corresponding larger voltage are needed in P3HT:bis[70]PCBM device than those in P3HT:bis[60]PCBM device. This phenomenon can be explained by the fact that the effective mobility as determined in P3HT:bis[60]PCBM device is higher than that in P3HT:bis[70]PCBM device, due to the presence of a higher multitude of isomers in bis[70]PCBM fullerene phase than that in bis[60]PCBM. These results further suggest that the dependence of the mobility on the carrier concentration should be taken into account when describing the charge transport in organic semiconductors.

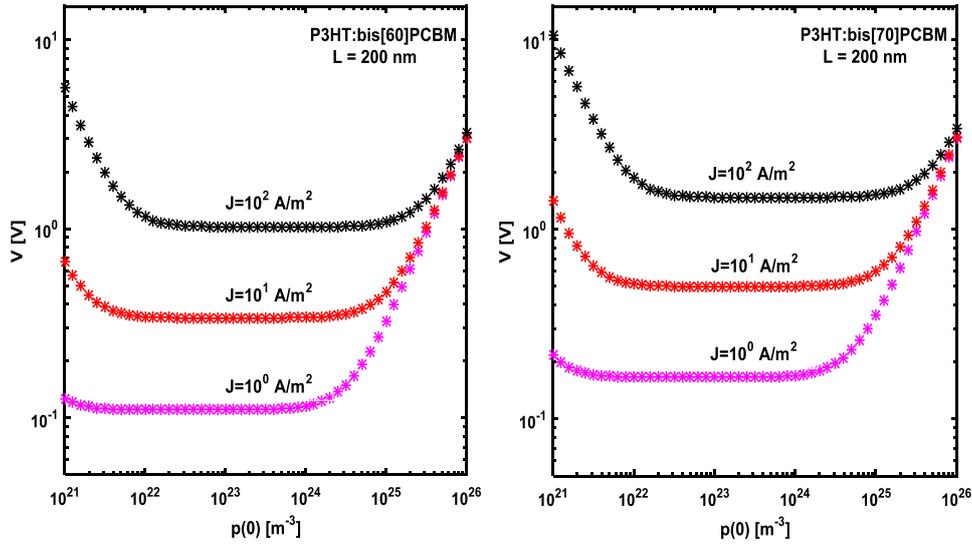


Fig. 4. Theoretical results of voltage versus the boundary carrier density of electron-only devices based on the P3HT:bis[60]PCBM and P3HT:bis[70]PCBM. Different Lines correspond to different current density (color online)

The numerically calculated distribution of the carrier concentration and electric field as a function of the distance from the interface in P3HT:bis[60]PCBM and P3HT:bis[70]PCBM electron-only devices are plotted in Figure 5. It is clear from the figure that the carrier density  $p(x)$  is a decreasing function of the distance  $x$ , whereas the electric field  $E(x)$  is an increasing function of the distance  $x$ . The decrease of the carrier density

$p(x)$  for relatively large  $p(0)$  is faster than that for relatively small  $p(0)$ . On the other hand, the increase of the electric field  $E(x)$  for relatively large  $p(0)$  is faster than that for relatively small  $p(0)$ . With the distance  $x$  increasing,  $p(x)$  rapidly reaches saturation. The thickness of accumulation layer decreases with increasing  $p(0)$ .

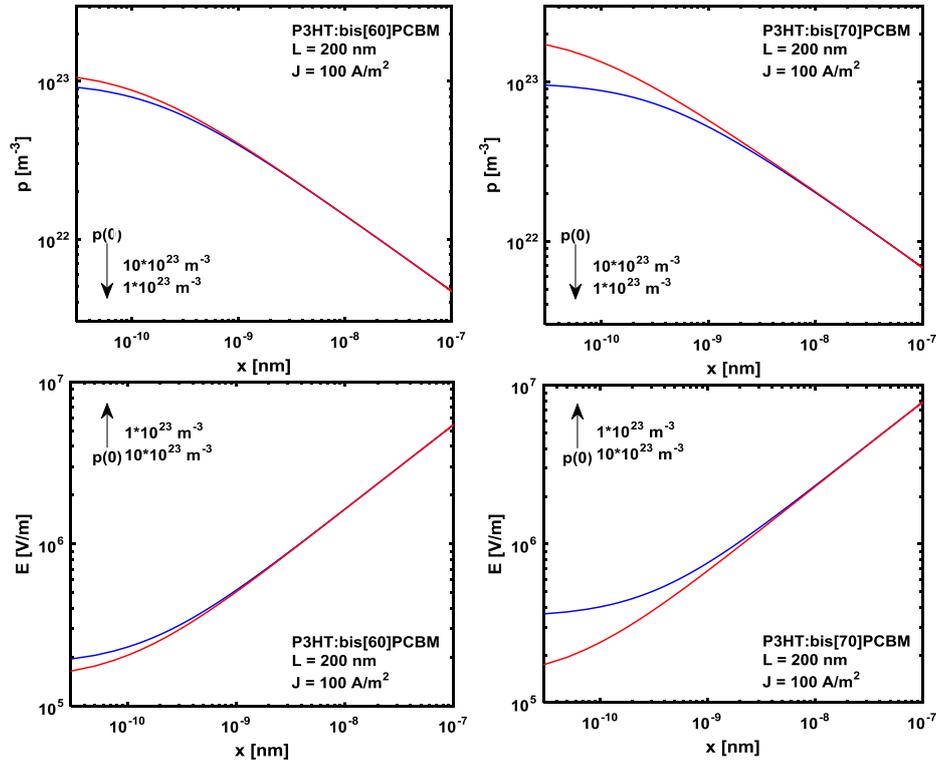


Fig. 5. Numerically calculated distribution of the charge carrier density  $p$  and electric field  $E$  as a function of the distance  $x$  in P3HT:bis[60]PCBM and P3HT:bis[70]PCBM electron-only devices (color online)

Both the maximum of carrier concentration and the minimum of electric field appear near the interface of electron-only devices based on the P3HT:bis[60]PCBM and P3HT:bis[70]PCBM. As a result, the injection of carriers from the electrode into the P3HT:fullerene layer leads to carriers accumulation near the interface and a decreasing function  $p(x)$ . The distribution of  $p(x)$  leads to the variation of  $E(x)$ , and the carriers accumulation near the interface results in increasing function  $E(x)$ .

#### 4. Summary and conclusions

In summary, the electron transport and energetic disorder in P3HT:PCBM blends and P3HT:bisadduct PCBM blends have been investigated. Compared to P3HT:PCBM blends, the drop in device current and zero-field mobilities of P3HT:bisadduct PCBM blends should be an increase in disorder in the fullerene phase, due to the presence of a higher multitude of isomers in the bisadducts. The zero-field mobility of electrons in P3HT:fullerene blends is closely related to the width of the Gaussian DOS  $\sigma$ , and the electron mobility gradually decreases with increasing the energetic disorder. The molecular conformation and strongly ordered stacking of the molecules should be the origin of the excellent electrical properties in organic semiconductors, and the mobility is closely related to the energetic disorder. Furthermore, the mobility in P3HT:fullerene blends is carrier concentration dependent, and the effective mobility in P3HT:bis[60]PCBM device is higher than that in P3HT:bis[70]PCBM device, due to the presence of a higher multitude of isomers in bis[70]PCBM fullerene phase than that in bis[60]PCBM. Both the maximum of carrier concentration and the minimum of electric field appear near the interface of P3HT:bis[60]PCBM and P3HT:bis[70]PCBM electron-only devices.

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