

An improved expression of charge-carrier mobilities for disordered organic semiconductors

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Many studies conducted in recent years on the mobility of disordered organic semiconductors have demonstrated that the mobility functional based on the Gaussian disorder model given by Pasveer et al. still has several shortcomings. In this paper, we present an improved expression of charge-carrier mobility, and make a comparison between some results obtained from our model and the results reported by Pasveer et al. It is shown that our improved expression can extend the results of the description of the mobility to high densities and high electric fields. The improved model can accurately reproduce the experimental current-voltage characteristics of organic electronic device based on PDPP5T:PC₆₁BM blend. Furthermore, it is demonstrated that the effective mobility in PDPP5T:PC₆₁BM blend gradually increases with increasing temperature, and the maximum value of the carrier density and the minimum value of the electric field appear at the interface of PDPP5T:PC₆₁BM hole-only device.

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1. Introduction

Disordered organic semiconductors are currently in the focus of intensive experimental and theoretical research because of the successful applications of such materials in various organic devices such as organic light emitting diodes, organic field effect transistors, organic solar cells, and organic photodetectors [1-8]. Physical insight of charge carrier transport in disordered organic semiconductors is vital for understanding the operating mechanisms of these devices [9, 10]. Therefore, the study of charge carrier transport has dominated research on organic materials in recent years.

Most researchers agree that charge carrier transport in disordered organic semiconductors is due to incoherent hopping of charge carriers between randomly distributed localized states with a Gaussian energy spectrum [11-23]. The most important parameter characterizing charge carrier transport is the mobility μ . Understanding the effect of disorder on the dependence of the mobility on temperature T , electric field E and carrier concentration p is crucial for modeling the electronic processes in disordered organic semiconductors. Various approaches have been proposed to calculate the mobility functional, $\mu(T, p, E)$, for hopping transport in these materials. Seminal work by Bässler et al. used Monte Carlo simulations, the random energies were described by a Gaussian density of states (DOS) [11], leading to the Gaussian disorder model (GDM). This model provides a

description of the temperature dependence of the mobility for vanishing carrier density, and shows discrepancies in the field dependence that are attributed to spatial correlations of the site energies [14, 15]. Later, it was realized that, apart from the dependence of μ on temperature T and electric field E , there is a strong dependence on the carrier density p [16-20]. Based on a numerically exact approach, a parametrization scheme for the corresponding mobility functional $\mu(T, p, E)$ was constructed by Pasveer et al., which is known as the extended Gaussian disorder model (EGDM) [18]. Although this mobility model is conveniently implemented in drift-diffusion solvers and is widely used, it is also heavily criticized [21-23]. The model deviates significantly from the simulated results based on the master equation, particularly in the regions of high carrier densities and high electric fields. Therefore, the state of research related to the theoretical description of charge transport in disordered organic semiconductors can hardly be considered as satisfactory.

The purpose of this paper is to present an improved expression of charge-carrier mobility, and to make a comparison between some results obtained from our description and the EGDM results reported by Pasveer et al. It is shown that our improved expression can extend the results of the description of the mobility to the region of high densities and high electric fields. Furthermore, the improved mobility model can accurately reproduce the experimental current-voltage characteristics of organic

electronic devices. The rest of the paper is organized as follows. In Section 2, we explain some relevant theories and methods, and determine an improved description of the dependence of charge carrier mobility on the temperature, carrier density, and electric field. In Section 3, we compare the theoretical results of current-voltage characteristics obtained from our model with experiments, and analyze some electrical properties obtained by using our method. Finally, a summary and conclusions are given in Section 4.

2. Models and methods

The most popular theoretical model to describe charge carrier transport in disordered organic semiconductors is the so-called Gaussian disorder model (GDM), according to which localized states have a Gaussian energy distribution [10-23]

$$g(\varepsilon) = \frac{N}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\varepsilon^2}{2\sigma^2}\right) \quad (1)$$

where σ is the energetic disorder of the density of states (DOS), usually estimated in disordered organic semiconductors to the order of $\sigma \approx 0.1$ eV, and N is the concentration of localized states that is related to the mean intersite distance (lattice constant) by $a = N^{-1/3}$.

The rates for carrier transitions between localized states are usually described by the Miller-Abrahams expression [24]:

$$V_{ij} = \nu_0 \exp\left(-\frac{2R_{ij}}{\alpha} - \frac{|\varepsilon_i - \varepsilon_j| + |\varepsilon_i - \varepsilon_F| + |\varepsilon_j - \varepsilon_F|}{2k_B T}\right) \quad (2)$$

where α is the localization length of charge carriers in the localized states, ε_i and ε_j are the carrier energies on the starting site i and the target site j , respectively, k_B is the Boltzmann constant, ε_F is the Fermi energy, T is the temperature and R_{ij} is the distance between sites i and j . The prefactor ν_0 is typically identified as the attempt-to-escape frequency, depends on the interaction mechanism that causes transitions.

Numerical solutions for the current density and carrier mobility in finite systems, with rates given by Eq. (2) and site energies randomly drawn from Eq. (1), have been reported by various researchers. Specifically, for hopping on a simple cubic lattice with uncorrelated Gaussian disorder, a full description of the mobility taking into account both the field and carrier density dependence was obtained by Pasveer et al. in the form of the extended Gaussian disorder model (EGDM) [18]. In the EGDM the mobility can be expressed as

$$\mu(T, p, E) = \mu(T, p)f(T, E) \quad (3)$$

with $\mu(T, p)$ and $f(T, E)$ in the form:

$$\mu(T, p) = \mu_0(T) \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(2pa^3)^\delta\right] \quad (4a)$$

$$\mu_0(T) = \mu_0 b_1 \exp(-b_2 \hat{\sigma}^2), \quad (4b)$$

$$\delta \equiv 2[\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)]/\hat{\sigma}^2, \quad \mu_0 \equiv a^2 \nu_0 e / \sigma, \quad (4c)$$

$$f(T, E) = \exp\left\{0.44(\hat{\sigma}^{3/2} - 2.2) \left[\sqrt{1 + 0.8 \left(\frac{eaE}{\sigma}\right)^2} - 1 \right]\right\} \quad (5)$$

where $\mu(T, p)$ and $f(T, E)$ are density dependent and field dependent factor, respectively. The EGDM is sometimes considered universal, and is the basis for commercially available organic devices simulation software [9, 25]. However, the methodology followed to derive the above EGDM parametrization has been heavily criticized for giving an inadequate description of especially the field dependence of the mobility [21-23]. As depicted in the inset of Fig. 2 from Ref. [18], the model deviates significantly from the simulated results based on the master equation, particularly in the regions of high densities and high electric fields. Pasveer et al. mentioned that Eq. (5) "should merely be considered as a description of the numerical data in a limited parameter range" and promised to rationalize this parametrization in future work. However, as has been recently proven, Eq. (5) cannot be rationalized because these equations do not contain the fundamental material parameter responsible for the field-dependent mobility in a system with spatial disorder. To solve above mentioned problems, we propose an improved theoretical description of the temperature T , carrier density p , and electric field E dependence of the mobility μ in disordered organic semiconductors. It can be described as follows:

$$\mu(T, p) = \mu_0(T) \exp\left[\frac{1}{2}(\hat{\sigma}^2 - \hat{\sigma})(c_1 p a^3)^\delta\right], \quad (6a)$$

$$\mu_0(T) = \mu_0 c_2 \exp(-c_3 \hat{\sigma}^2), \quad (6b)$$

In Ref. [26], Coehoorn et al. argued that the parameter δ depends only on $\hat{\sigma}$ and can be chosen to optimize the accuracy within a certain range of $\hat{\sigma}$. In this study, we provide a more accurate description of c_1 and δ using the following simplified temperature polynomial containing only $\hat{\sigma}$.

$$c_1 = (-3.326 + 3.666\hat{\sigma}) / (1 - 0.313\hat{\sigma} + 0.295\hat{\sigma}^2), \quad (6c)$$

$$\delta = 1 / (-1.022 + 1.828\hat{\sigma} - 0.081\hat{\sigma}^2), \quad (6d)$$

with $c_2 = 1.25 \times 10^{-9}$ and $c_3 = 0.445$.

In Fig. 1, we display the carrier density p dependence of the mobility μ for different temperatures. It can be found that our description is fairly good agreement with the original numerical results. In particular, it is clear that Eqs. (6) give an improved description for numerical results in high carrier density region compared with Eqs. (4).

In Eq. (5), Pasveer et al. adopt a density-independent prefactor $f(T, E)$ to consider electric field dependence. However, it can be easily found that for $\hat{\sigma} > 1.69$, $f(T, E)$ gives incorrect limitation infinity as E tends infinity ($E \rightarrow \infty$); Whereas the correct limitation should be finite. To overcome the above shortcomings, we introduce a weakly density-dependent function $g(T, E)$ in Eq. (7) to consider electric field dependence.

$$\mu(T, p, E) = \mu(T, p)^{g(T, E)} \exp[c_4(g(T, E) - 1)], \quad (7)$$

$$g(T, E) = [1 + c_5(Eea/\sigma)^2]^{-1/2}. \quad (8)$$

where c_4 and c_5 are weakly density-dependent parameters.

$$c_4 = d_1 + d_2 \ln(pa^3) \quad (9a)$$

$$c_5 = 1.16 + 0.09 \ln(pa^3) \quad (9b)$$

$$d_1 = 20.724 + 0.091\hat{\sigma} + 0.075\hat{\sigma}^2 \quad (10a)$$

$$d_2 = -0.292 + 0.144\hat{\sigma} + 0.035\hat{\sigma}^2 \quad (10b)$$

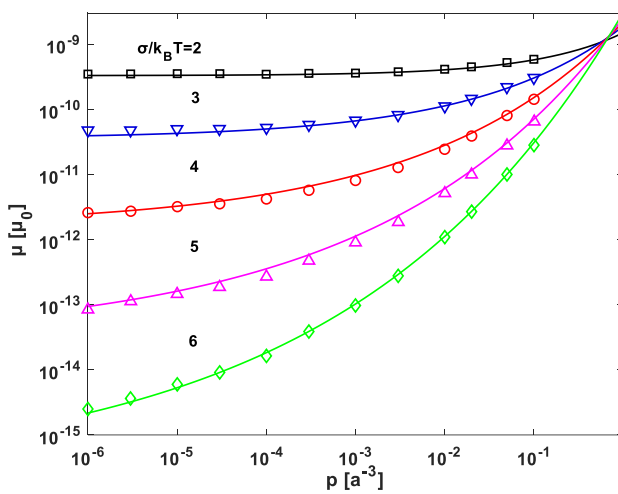


Fig. 1. Carrier density dependence of the mobility at various temperatures for a vanishing electric field. Symbols are numerical results from Ref. [18]. Lines are theoretical fits using the parametrization scheme given in Eq. (6) (color online)

In Fig. 2, the mobility μ as a function of the electric field E is plotted at a low carrier density, $p = 10^{-5}/a^3$, a typical value for the operation regime of organic light emitting diodes, and a high carrier density, $p = 0.05/a^3$, a typical value for the operation regime of organic field effect transistors. The figure illustrates that the improved parameterization scheme is optimized for both low and high carrier density. The improved model is superior to the original model, particularly at high carrier densities and high electric fields. It also demonstrates that our method can expand the conclusions of the standard hopping model's description of mobility with Gaussian density of states to the region of high carrier densities and high electric fields. In Fig. 3, we display the results of temperature dependence of the low-field mobilities $\mu_0(T)$ for PDPP5T:PC₆₁BM blend. It can be seen from the figure that the temperature dependence of $\mu_0(T)$ can be excellently described by Eq. (6b). These results show that the improved mobility model is more applicable for disordered organic semiconductors.

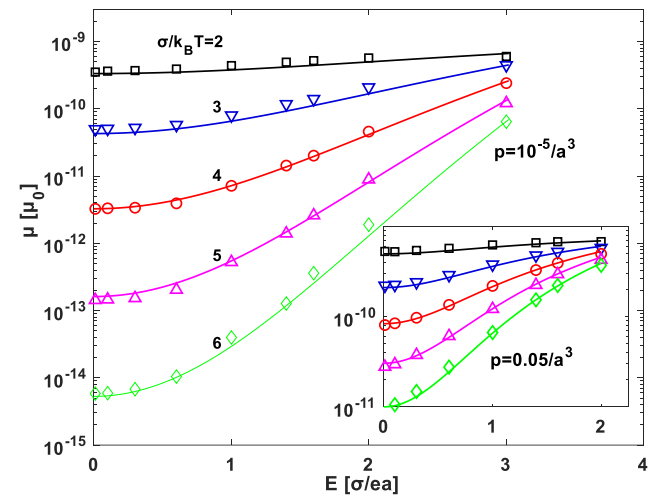


Fig. 2. Electric field dependence of the mobility at various temperatures for low densities in LEDs (main panel) and high densities in FETs (inset). Symbols are numerical results from Ref. [18]. Lines are theoretical fits using the parametrization scheme given in Eqs. (6)-(10) (color online)

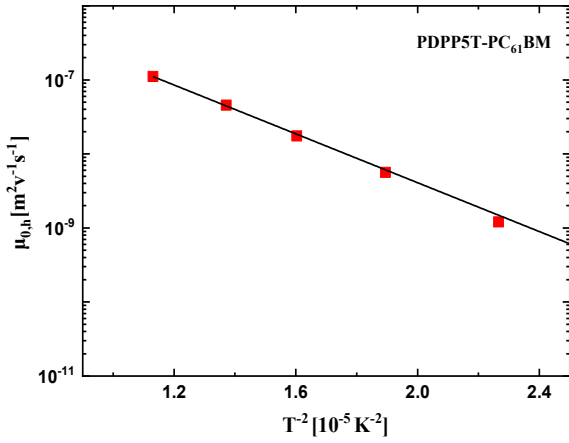


Fig. 3. Temperature dependence of the low-field mobilities for PDPP5T:PC₆₁BM blend. The symbols are the experimental data from Ref. [27]. The solid lines are theoretical fits using Eq. (6b) (color online)

3. Results and discussion

Using the improved mobility model, we now proceed to calculate the current-voltage ($J - V$) characteristics of hole-only device based on PDPP5T:PC₆₁BM blend. The relation between the space-charge limited current (SCLC) density J and voltage V then follows from the solution of the equations

$$J = p(x)e\mu(T, p(x), E(x))E(x), \quad (11a)$$

$$\frac{dE}{dx} = \frac{e}{\epsilon_0\epsilon_r} p(x), \quad (11b)$$

$$V = \int_0^L E(x)dx, \quad (11c)$$

where L is the active layer thickness sandwiched between two electrodes. x is the distance from the injecting electrode, ϵ_0 is the vacuum permeability, and ϵ_r is the relative dielectric constant of organic materials.

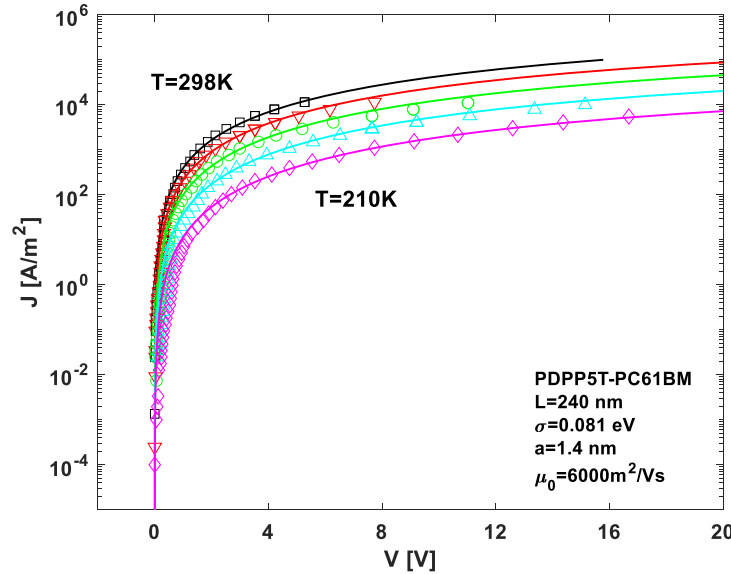


Fig. 4. Temperature dependent $J - V$ characteristics of PDPP5T:PC₆₁BM hole-only device. Symbols are experimental data from Ref. [27]. Lines are the numerically calculated results from the improved mobility model (color online)

In Fig. 4, we display the solution of Eq. (11) with the T , p , and E dependence on μ from the parametrization scheme given in Eqs. (6)-(10) and the experimental $J - V$ measurements of hole-only device based on PDPP5T:PC₆₁BM blend from Ref. [27]. The parameters $\sigma = 0.081$ eV, $a = 1.4$ nm, and $\mu_0 = 6000$ m²/Vs are determined in such a way that an optimal overall fit is obtained. A clear observation is that the

agreement between the calculation results from the improved model and experiment measurements is excellent. This also further shows that our improved description is a useful approach to study the $J - V$ relationship of disordered organic semiconductors. The three best-fitting values of σ , a and μ_0 derived from the improved model are close to those reported by Simone et al. in Ref. [27]. For the values of model

parameters, Pasveer et al. pointed out that the lower value of σ can be mainly attributed to the omission of the p dependence and the lower value of a can be mainly attributed to the overestimation of the E

dependence [18]. These results also indicate that more precise mobility expression has an important impact on model parameters.

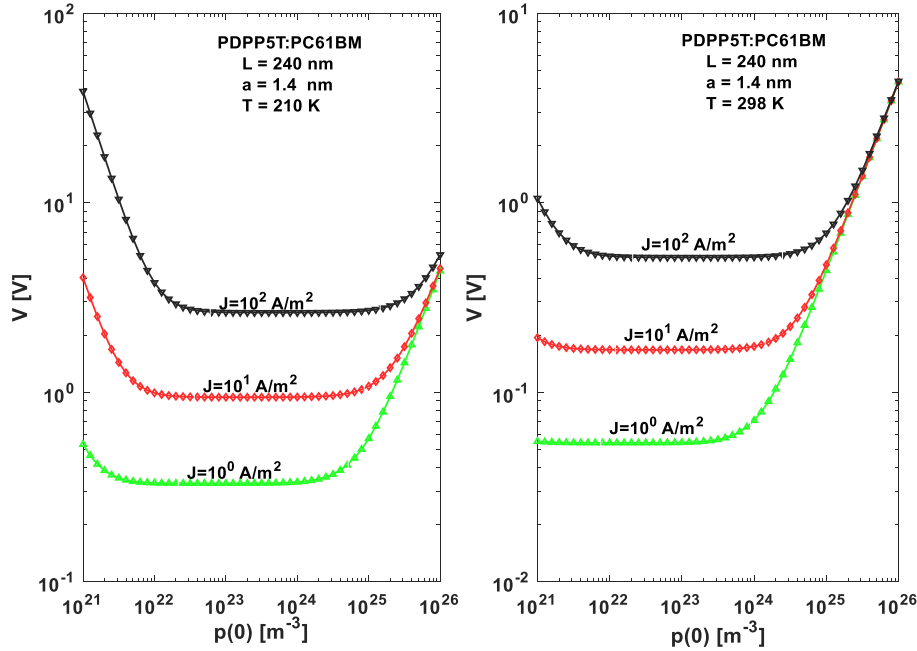


Fig. 5. Theoretical results of voltage versus the boundary carrier density of a hole-only device based on PDPP5T:PC₆₁BM blend at 210 K and 298 K (color online)

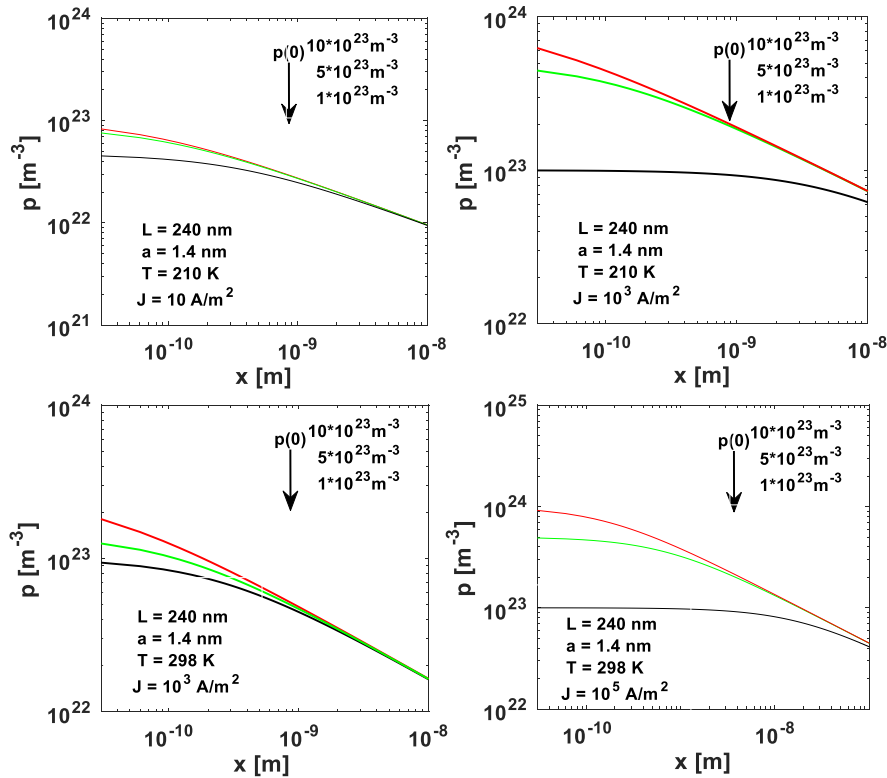


Fig. 6. Calculated distribution of charge carrier density p as a function of position x in a hole-only device based on PDPP5T:PC₆₁BM blend (color online)

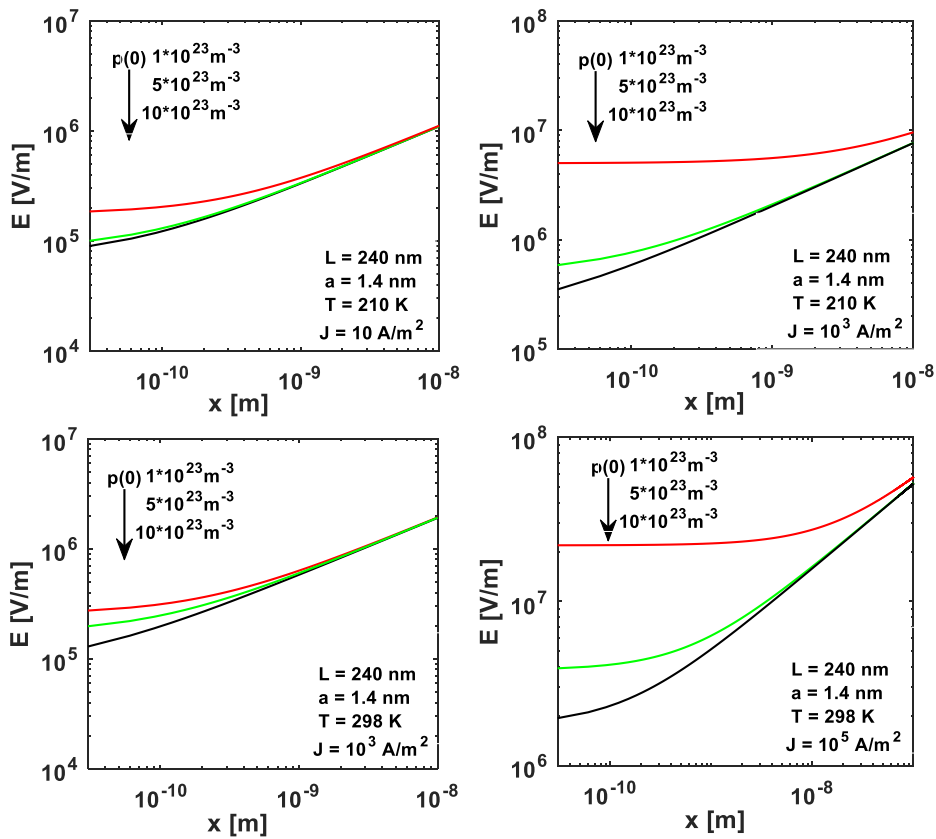


Fig. 7. Calculated distribution of electric field E as a function of position x in a hole-only device based on PDPP5T:PC₆₁BM blend (color online)

Using the improved mobility model, we further calculate and analyze the electrical properties of hole-only device based on PDPP5T:PC₆₁BM blend. Fig. 5 shows the variations of $J - V$ characteristics with the boundary carrier concentration $p(0)$ for hole-only device based on PDPP5T:PC₆₁BM blend at low temperature and at room temperature. 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 $10^{23} - 10^{24} \text{ m}^{-3}$, the $V - p(0)$ curves are fairly flat, indicating that the voltage is independent of $p(0)$ and the $J - V$ characteristics are physically realistic in this region. On the other hand, the voltage decreases with increasing $p(0)$ for $p(0)$ less than 10^{23} m^{-3} , and also increases with increasing $p(0)$ for $p(0)$ more than 10^{24} m^{-3} . 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 at low temperature than those at room temperature. This can be explained by the fact that the effective mobility as determined at room temperature is higher than that at low temperature.

In Fig. 6 and Fig. 7, we display the numerically calculated distribution of the carrier density and electric field as a function of the distance from the interface of hole-only device based on PDPP5T:PC₆₁BM blend. It can

be seen from the figure that the carrier density $p(x)$ is a decreasing function of the distance, and the electric field $E(x)$ is an increasing function of the distance x . The function of $p(x)$ with a relatively large $p(0)$ decreases faster than that with a relatively small $p(0)$. On the other hand, the function of $E(x)$ with a relatively small $p(0)$ increases faster than that with a relatively large $p(0)$. As the distance x increases, $p(x)$ in the active layer rapidly reaches saturation. The thickness of accumulation layer decreases with increasing $p(0)$. The variation of carrier density $p(x)$ and electric field $E(x)$ with the distance x at low temperature (210 K) is greater than that at room temperature (298 K), which further indicates that the effective mobility at room temperature is higher than that at low temperature. Both the maximum of carrier concentration and the minimum of electric field appear at the interface of hole-only device based on PDPP5T:PC₆₁BM blend. As a result, the injection of carriers from the electrode into the PDPP5T:PC₆₁BM organic 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, an improved mobility formula for disordered organic semiconductors is proposed. For high carrier densities and high electric fields, the improved mobility model fits the numerical results from the master equation much better than the original model introduced by Pasveer et al. This shows that our approach can expand the results of the mobility description to the regions of high densities and high electric fields. Using the improved description, we also obtain excellent fits with the experimental current–voltage characteristics of hole-only device based on PDPP5T:PC₆₁BM blend. This indicates that the improved mobility model is appropriate for investigating the related properties of disordered organic semiconductors. In addition, we show that too large or too small values of the boundary carrier density will yield incorrect $J - V$ characteristics. The effective mobility in PDPP5T:PC₆₁BM blend gradually increases with increasing temperature, and the maximum value of the carrier density and the minimum value of the electric field appear at the interface of PDPP5T:PC₆₁BM hole-only device.

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