Effect of diffusion on charge transport in polymer:non-fullerene blends

Y. F. LI, Y. J. WANG*, L. G. WANG*, Y. GUO, L. ZHANG
School of Electrical Engineering and Automation, Henan Key Laboratory of Intelligent Detection and Control of Coal Mine Equipment, Henan Polytechnic University, Jiaozuo, 454000, People's Republic of China

Recently, non-fullerene organic semiconductors have attracted significant attention as acceptors in organic photovoltaics due to their great potential to realize high power conversion efficiencies. In this paper, the effect of diffusion on charge transport in the blend of polymer PBDB-T derivative PM6 and non-fullerene acceptor Y6 is investigated. It is shown that the current density-voltage characteristics from the drift-diffusion simulations incorporating the extended Gaussian disorder model (EGDM) are more consistent with experimental data in comparison with those obtained from the only drift model in both PM6:Y6 hole-only and electron-only devices. Moreover, it is found that the effect of diffusion on charge transport is more pronounced at low voltages and seems to be negligible when the applied voltage exceeds 1 V. For the analysis of charge transport in polymer:non-fullerene blends, it is essential that both drift and diffusion of charge carriers are taken into account.

(Received October 8, 2021; accepted April 8, 2022)

Keywords: Charge transport, Organic photovoltaics, Diffusion, Polymer:non-fullerene blends, Energy disorder

1. Introduction

Organic solar cells (OSCs) have several advantages, such as potential low cost, absorption tunability, ease of fabrication, and mechanical flexibility [1-5]. Despite the fact that considerable progress has been made in this field, improving the power conversion efficiency (PCE) of OSCs is an ongoing challenge. One of the prerequisites to achieve this goal is to enable efficient charge separation and small voltage losses at the same time. To date, the PCE of organic solar cells is still inferior to their inorganic counterparts. In order to improve the performance of such devices, further understanding of the underlying physics of charge transport becomes important, as the mobility μ of the generated charge carriers is one of the key factors that decides how efficiently the charges can escape recombination and be extracted [6-9]. In recent years, many research efforts have focused on charge transport in OSCs, theoretical models for describing charge transport and recombination have been derived [10-13]. When organic semiconductors are sandwiched between two electrodes, a metal-insulator-metal (MIM) diode stack is formed. The current that flows through such an organic semiconductor diode, results from drift and diffusion of charge carriers. Drift and diffusion are related through mobility and diffusion coefficient. The mobility is used to describe the ability of carrier movement under the action of electric field, while diffusion coefficient is used to describe the ability of carrier movement in the presence of non-uniform concentration. The transport properties in the drift-dominated regime of such diodes have been extensively investigated, whereas the diffusion-dominated regime has rarely been taken into account so far. An important question is now whether the omission of diffusion effect is relevant in the analysis of charge transport in these organic semiconductors.

In past decades, progress in bulk-heterojunction OSCs was dominated by the development of donor materials, since fullerene derivatives were believed to be the only option as acceptor materials in high efficiency OSCs. Recent rapid development of nonfullerene OSCs has changed the situation. Zhan et al. pioneered the development of a novel acceptor material named ITIC (Fig.1). ITIC and its derivatives have now become the superstar materials in state-of-the-art OSCs [14-16]. Recently, the new acceptor material developed by Zou et al. is named Y6 (Fig.1), which includes ladder-type electron-deficient-core-based central fused ring and is different from the electron-rich core in ITIC [17]. In addition, the absorption of Y6 extends to ~900 nm, which is optimal for balanced photocurrent and open-circuit voltage. For the selection of donor materials, they followed the rules to minimize the energetic offset between donor and acceptor, with the motivation to enhance open-circuit voltage [18]. By coupling Y6 with a PBDB-T derivative named PM6 (Fig.1), the authors were able to make a breakthrough and demonstrate a high PCE up to 15.7% [17]. It seems that this combination of PM6 and Y6 results in efficient optimization of all the parameters. It would be very interesting to have further investigations of the processes related with charge transport in this material combination [19].

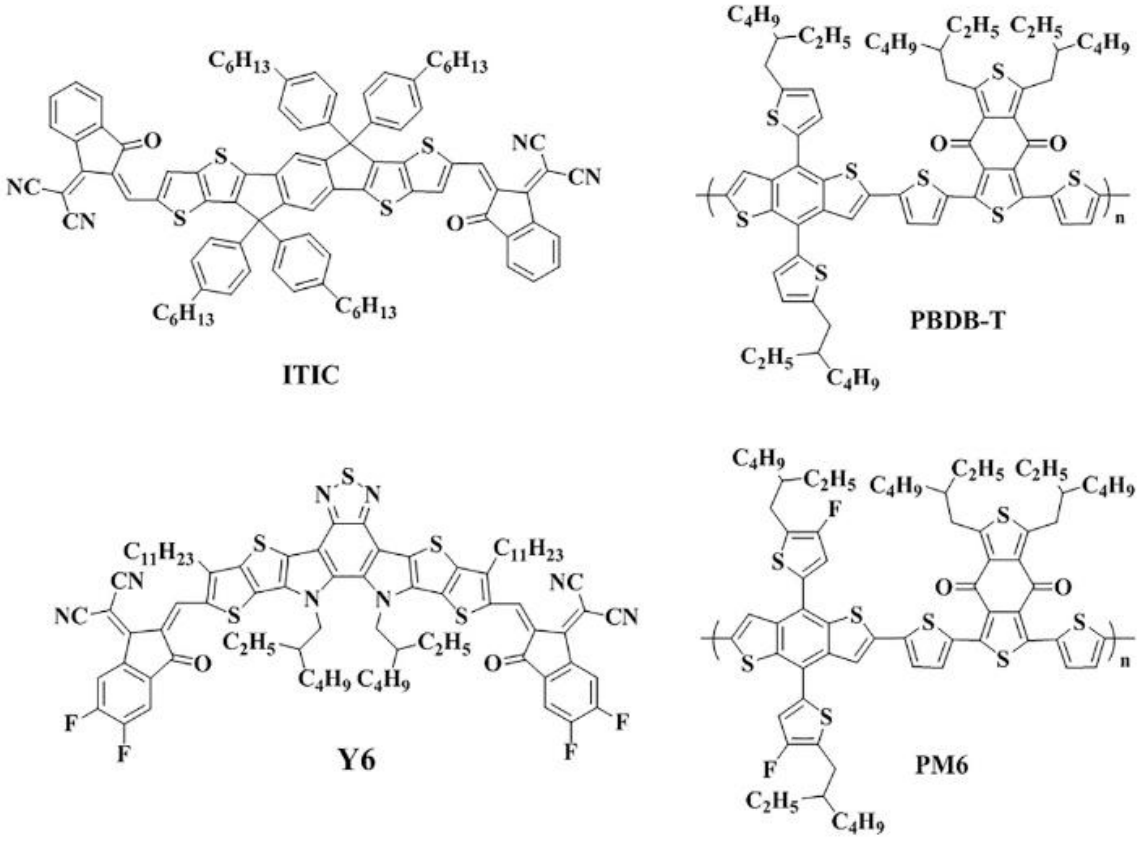

Fig. 1. Chemical structures of the materials studied in this paper

In this paper, we investigate the effect of diffusion on charge transport in polymer:non-fullerene blend (PM6:Y6), one of the currently best performing binary systems used in state-of-the-art OSCs. Firstly, a brief description of the model is given, followed by an overview of the relevant equations. Subsequently, we perform a detailed analysis of the temperature dependent current density-voltage ($J-V$) characteristics of hole-only and electron-only devices based on PM6:Y6 blend by using the drift-diffusion simulations incorporating the extended Gaussian disorder model (EGDM), and the only drift model incorporating the EGDM, respectively.

2. Models

For the description of charge transport in organic photovoltaic devices, the general semiconductor drift-diffusion equations for electrons and holes are valid. Drift-diffusion models rely typically on the simultaneous solution of the charge transport, continuity and Poisson equations, while contacts are accounted for as boundary conditions. Only one spatial dimension is considered in this study, since the organic photovoltaic devices have a planar structure with a very small thickness compared to the lateral dimensions. The basic equations used in this simulation are the Poisson equation, given by

$$\frac{\partial^2}{\partial x^2}\psi(x) = \frac{q}{\varepsilon_0 \varepsilon_r}\left[n(x) - p(x)\right] \tag{1}$$

where q is the elementary charge, ε_0 is the vacuum permittivity, ε_r is the material's relative dielectric constant, the electrical potential ψ is related to the electron and hole densities n and p, respectively. The carrier densities n and p consist of mobile charge carriers and trapped charges. The drift-diffusion equations for electrons and holes are

$$J_n = -qn\mu_n \frac{\partial}{\partial x}\psi + qD_n \frac{\partial}{\partial x} n \tag{2a}$$

$$J_p = -qp\mu_p \frac{\partial}{\partial x}\psi - qD_p \frac{\partial}{\partial x} p \tag{2b}$$

The current density consists of a drift part caused by the electric field and a diffusion current. The mobility μ is dependent on the electric field F, temperature T and carrier concentration c. The diffusion coefficient D is assumed to be related to the mobility and given by the generalized Einstein relation as discussed further below.

In this paper, we focus on charge transport in devices containing an organic semiconductor with Gussian disorder. The energy levels at neighboring sites are

assumed to be uncorrelated. The Gaussian density of states (DOS) is described by

$$N(E)=\frac{N_0}{\sqrt{2\pi\sigma^2}}\exp\left[-\left(\frac{E-E_0}{\sqrt{2}\sigma}\right)^2\right] \quad (3)$$

where σ stands for the disorder parameter, i.e. the width of the Gaussian DOS. The parameter N_0 stands for the site density. In small-molecule organic semiconductors and in polymers, N_0 may be associated with the number of molecules and with the number of conjugated segments per volume unit, respectively. And the parameter E_0 denotes the reference energy level.

The disorder in organic semiconductors also affects the mobility function. A well-established mobility function that includes the effects of temperature T, carrier concentration c, and electric field F on the mobility μ is the extended Gaussian disorder model (EGDM) [20]. Previously, the EGDM has been successfully applied to describe charge transport in disordered organic semiconductors [10-13, 21]. In the EGDM the mobility can be expressed as a product of a density-dependent and field-dependent factor

$$\mu(T, c, F) = \mu_0(T)g_1(T, c)g_2(T, F) \quad (4)$$

where $\mu_0(T)$ is the temperature-dependent mobility in the limit of a zero carrier density and zero electric filed. And g_1 and g_2 are dimensionless carrier density and field-dependent mobility enhancement factors, which are nonlinear and strongly increase with larger values of the disorder parameter [22].

In the EGDM, the Gaussian DOS also influences charge diffusion. Tessler et al. pointed out that the use of the generalized Einstein relation instead of the classical Einstein relation is correct [23, 24]. In this case the generalized Einstein diffusion coefficient is determined by

$$D = \frac{k_B T}{q}\mu(T, c, F)g_3(T, c) \quad (5)$$

where k_B is the Boltzmann constant and g_3 is a dimensionless diffusion coefficient enhancement function that follows from the shape of the density of states

$$g_3(T, c) = \frac{1}{k_B T}\frac{c}{\frac{\partial c}{\partial E_f}} \quad (6)$$

where E_f is the Fermi energy.

3. Results and discussion

In order to study the effect of diffusion on charge transport in polymer:non-fullerene blends, we investigate the temperature dependent $J-V$ characteristics of hole-only and electron-only devices based on PM6:Y6 blend by using the drift-diffusion model incorporating the EGDM mobility function, and the only drift model incorporating the EGDM, respectively. As we have confirmed in previous studies that the site energy in PM6:Y6 blend is not correlated with the spatial location, we adopt the EGDM model with an uncorrelated Gaussian distribution of the random energies of hopping sites for simulation calculation. In amorphous silicon solar cells, traps play a dominant role in the description of the solar cell characteristics [25]. This behavior is characteristic for a space-charge limited current (SCLC). The occurrence of SCLC enables us to directly determine the mobility from the current density-voltage ($J-V$) characteristics. It should be noted that a material with shallow traps would also exhibit an identical voltage and thickness dependence, and the observed mobility would be an effective mobility in that case, including trapping effects.

The temperature dependent current density-voltage characteristics of PM6:Y6 hole-only device are displayed in Fig. 2 and Fig. 3. The solid lines in Fig. 2 and Fig. 3 represent the numerically calculated results from the drift-diffusion model incorporating the EGDM mobility function and the only drift model incorporating the EGDM, respectively. The symbols in Fig. 2 and Fig. 3 are the experimental measurements from Ref. [5]. It can be seen from Fig. 2 and Fig. 3 that the temperature dependent $J-V$ characteristics of hole-only device based on PM6:Y6 blend can be well described by using a single set of parameters, σ = 0.1 eV, a = 1.9 nm and μ_0 = 5000 m^2/Vs. The parameters of σ, a, and μ_0 are determined in such a way that an optimal overall fit is obtained. What's more, it can be clearly found that the simulation curves calculated using the only drift model are not consistent with the experimental measurements at low voltages, the current density obtained is lower than the experimental measurements. The results present at various temperatures are very different, in which the deviation of calculated curves from experimental data gradually increases with increasing temperature. And it is not difficult to find that the calculated current density is always lower than the experimental measurements. However, as the voltage increases, this deviation becomes so small that it is almost negligible at high voltages. On the other hand, as shown in Fig. 2, the fit quality of the drift-diffusion model to the experimental data is nearly perfect. From the above results, it can be concluded that the influence of diffusion effect on charge transport in PM6:Y6 hole-only device is significant and cannot be ignored.

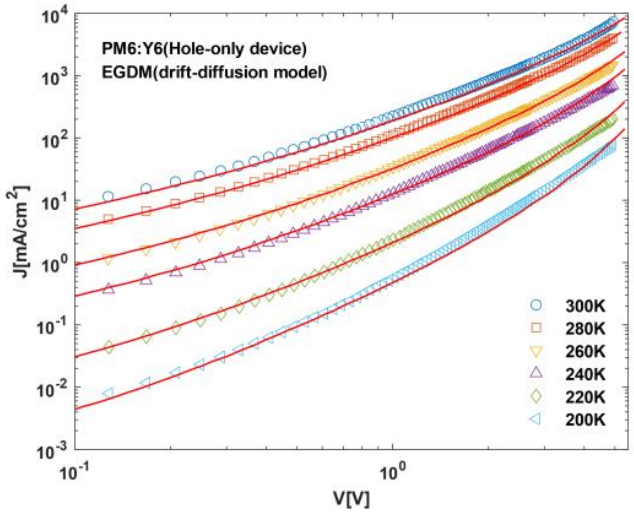

Fig. 2. Temperature dependent J-V characteristics of PM6:Y6 hole-only device. Symbols are experimental data from Ref. [5]. Lines are the numerically calculated results from the drift-diffusion model incorporating the EGDM (color online)

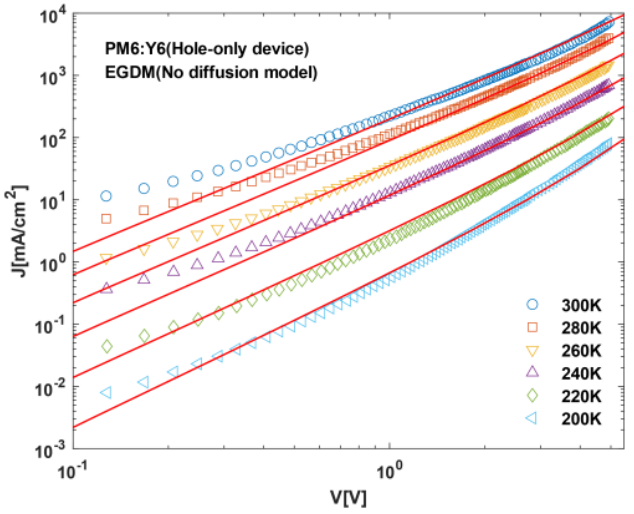

Fig. 3. Temperature dependent J-V characteristics of PM6:Y6 hole-only device. Symbols are experimental data from Ref. [5]. Lines are the numerically calculated results from the only drift model incorporating the EGDM (color online)

We now consider the question whether the diffusion also affects charge transport in PM6:Y6 electron-only device. When the above two models are also applied to electron-only device, it is not difficult to find in Fig. 4 and Fig. 5 that the influence of diffusion on the $J-V$ characteristics is also notable. It is clear from the figures that the temperature dependent $J-V$ characteristics of electron-only device based on PM6:Y6 blend can also be well described by using a single set of parameters, σ = 0.09 eV, a = 2.1 nm and μ_0 = 2500 m^2/Vs. By comparing the fit quality in Fig. 4 with Fig. 5, we can find that the numerically calculated results from the drift-diffusion model are more consistent with experimental data than the only drift model. The $J-V$ curves calculated by the only drift model at low voltage are obviously lower than the experimental measurements.

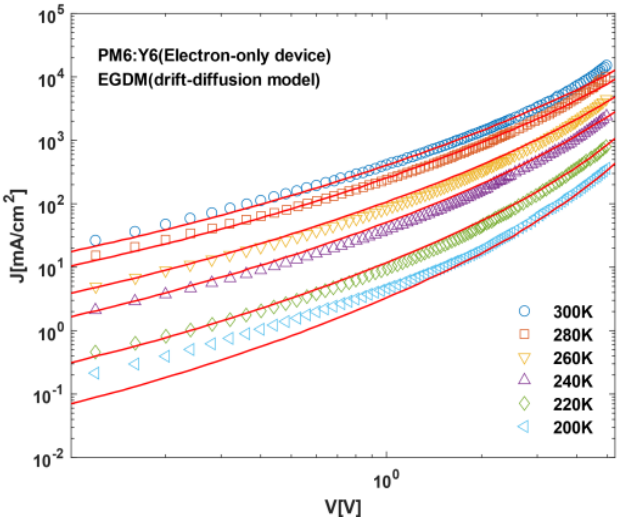

Fig. 4. Temperature dependent J-V characteristics of PM6:Y6 electron-only device. Symbols are experimental data from Ref. [5]. Lines are the numerically calculated results from the drift-diffusion model incorporating the EGDM (color online)

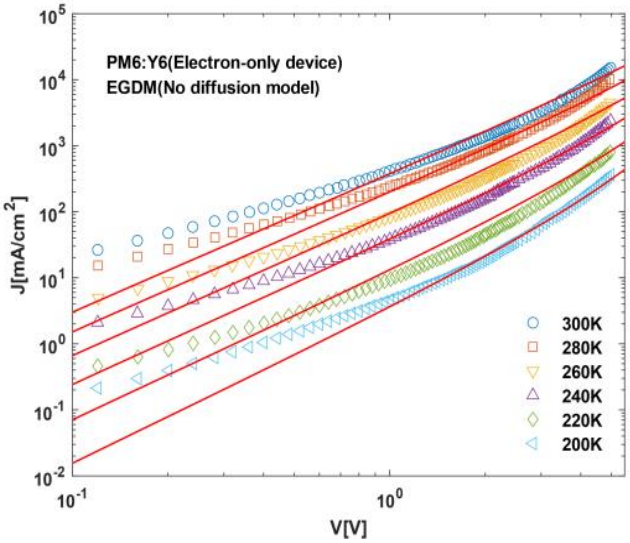

Fig. 5. Temperature dependent J-V characteristics of PM6:Y6 electron-only device. Symbols are experimental data from Ref. [5]. Lines are the numerically calculated results from the only drift model incorporating the EGDM (color online)

It can be seen from Figs. 2-5 that the EGDM excellent fits to the temperature dependent $J-V$ characteristics of PM6:Y6 hole-only and electron-only devices can be obtained. There is no significant difference in the fit quality, and in the extracted disorder and hopping parameters for hole-only and electron-only

devices. Intuitively, on the basis of the low energy loss in this OSC system, one might expect a relatively small energetic disorder [17, 19]. However, we find $\sigma = 0.1$ eV for hole-only device and $\sigma = 0.09$ eV for electron-only device, which would correspond to a disorder-induced voltage loss in excess of 0.2 V [26]. Although this is beyond the scope of the present work, we note that the high PCE values observed for this system are unlikely to be related to a suppressed energetic disorder. Furthermore, it is worth noting that regardless of the PM6:Y6 hole-only device or electron-only device, ignoring the diffusion effect will have a significant impact on charge transport, which is reflected in the current density-voltage characteristics. At very low bias, the current density is significantly lower than the experimental measurements. At higher voltages ($>$1V), the effect of diffusion on charge transport can be disregarded.

4. Summary and conclusions

In conclusion, the effect of diffusion on charge transport in the blend of polymer PM6 and non-fullerene acceptor Y6 is investigated. It is shown that the temperature dependent $J-V$ characteristics of hole-only and electron-only devices based on PM6:Y6 blend can be well described using the EGDM, and the numerically calculated results from the drift-diffusion model are more consistent with experimental data in comparison with those obtained from the only drift model. The effect of diffusion on charge transport in PM6:Y6 blend is more pronounced at low voltages and seems to be negligible when the voltage exceeds 1 V. These results show that it is necessary to take the effect of diffusion on charge transport into account in both PM6:Y6 hole-only and electron-only devices, especially at low voltages.

Acknowledgements

This work is supported by the Fundamental Research Funds for the Universities of Henan Province Grant No. NSFRF200304 and No. NSFRF210424, the Science and Technology Project of Henan Province No. 202102210295, the Young Key Teacher Program of Henan Polytechnic University Grant No. 2019XQG-17, and the Doctoral Scientific Research Foundation of Henan Polytechnic University Grant No. B2014-022.

References

[1] G. Dennler, M. C. Scharber, C. J. Brabec, Adv. Mater. **21**, 1323 (2009).
[2] K. A. Mazzio, C. K. Luscombe, Chem. Soc. Rev. **44**, 78 (2015).
[3] G. J. Hedley, A. Ruseckas, I. D. W. Samuel, Chem. Rev. **117**, 796 (2017).
[4] N. B. Kotadiya, P. W. M. Blom, G. A. H. Wetzelaer, Phys. Rev. Applied **11**, 024069 (2019).
[5] T. Upreti, Y. Wang, H. Zhang, D. Scheunemann, F. Gao, M. Kemerink, Phys. Rev. Applied **12**, 064039 (2019).
[6] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[7] C. Deibel, A. Wagenpfahl, V. Dyakonov, Phys. Status Solidi Rapid Res. Lett. **2**, 175 (2008).
[8] I. A. Howard, F. Etzold, F. Laquai, M. Kemerink, Adv. Energy Mater. **4**, 1301743 (2014).
[9] A. Melianas, F. Etzold, T. J. Savenije, F. Laquai, O. Inganas, M. Kemerink, Nat. Commun. **6**, 8778 (2015).
[10] R. Coehoorn, P. A. Bobbert, Phys. Status Solidi A **209**, 2354 (2012).
[11] M. Kuik, G. J. A. H. Wetzelaer, H. T. Nicolai, N. I. Craciun, D. M. De Leeuw, P. W. M. Blom, Adv. Mater. **26**, 512 (2014).
[12] S. D. Baranovskii, Phys. Status Solidi A **215**, 1700676 (2018).
[13] N. Felekidis, A. Melianas, M. Kemerink, Org. Electron. **61**, 318 (2018).
[14] P. Cheng, G. Li, X. Zhan, Y. Yang, Nat. Photonics **12**, 131 (2018).
[15] J. Zhang, H. S. Tan, X. Guo, A. Facchetti, H. Yan, Nat. Energy **3**, 720 (2018).
[16] J. Hou, O. Inganas, R. H. Friend, F. Gao, Nat. Mater. **17**, 119 (2018).
[17] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H. L. Yip, T. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski,Y. Li, Y. Zou, Joule **3**, 1140 (2019).
[18] D. Qian, Z. Zheng, H. Yao, W. Tress, T. R. Hopper, S. Chen, S. Li, J. Liu, S. Chen, J. Zhang, Nat. Mater. **17**, 703 (2018).
[19] F. Gao, Joule **3**, 908 (2019).
[20] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005).
[21] X. L. Wang, L. Zhang, L. A. Kang, L. G. Wang, Optoelectron. Adv. Mat. **14**(7-8), 372 (2020).
[22] S. L. M. van Mensfoort, R. Coehoorn, Phys. Rev. B **78**, 085207 (2008).
[23] Y. Roichman, N. Tessler, Appl. Phys. Lett. **80**, 1948 (2002).
[24] Y. Preezant, N. Tessler, J. Appl. Phys. **93**, 2059 (2003).
[25] L. J. A. Koster, Phys. Rev. B **72**, 085205 (2005).
[26] J. C. Blakesley, D. Neher, Phys. Rev. B **84**, 075210 (2011).

*Corresponding authors: yunjian_wang@163.com; wangliguo@hpu.edu.cn