

Analysis of hole transport in a high-mobility conjugated polymer: evidence for the absence of correlated disorder

M. L. LIU, L. G. WANG*

School of Electrical Engineering and Automation, Henan Polytechnic University, Jiaozuo, 454000, People's Republic of China

The presence of spatial correlation between the site energies in organic semiconductors is known to affect the carrier mobility. However, it is not established whether such a correlation is present in relevant materials. In this paper, an analysis of the layer thickness and temperature dependence of the current density in hole-only devices based on a novel high-mobility n-type copolymer poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-dithiophene)} [P(NDI2OD-T2),PolyeraActivnk™ N2200] is presented. Consistent descriptions with equal quality are obtained by using the extended Gaussian disorder model (EGDM) and the extended correlated disorder model (ECDM), within which the mobility depends on the electric field and carrier density and within which spatial correlations between the site energies are absent or are included. Based on a comparison of the model parameters as obtained from both models, we view the more realistic intersite distance found using the EGDM (0.8 nm) compared to the value found using the ECDM (0.1 nm) as an indication that in N2200 correlations between the site energies are absent or play a minor role.

(Received October 13, 2017; accepted April 5, 2018)

Keywords: Organic semiconductors, Hole transport, Correlated disorder

1. Introduction

The interest in electronic devices based on disordered organic semiconductors is rapidly increasing. Important applications are organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs) [1-4]. It is of crucial importance to understand the charge transport and availability of physical models in these materials in order to synthesize appropriate materials and to improve the efficiency and lifetime of devices. The most important parameter is the charge-carrier mobility μ , which quantifies how easily charge carriers move when an electric field is applied. In particular, it is crucial to understand how the μ depends on the various parameters of the system.

In past decades, the dependence of the mobility μ on the electric field E and temperature T in disordered organic semiconductors has been extensively investigated [5-12]. BäSSLER et al. introduced a model with a spatially uncorrelated Gaussian distribution of hopping site energies, which is now known as the "Gaussian disorder model" (GDM) [5, 6]. In a limited field range, the field dependence of the mobility is well described by the Poole-Frenkel (PF) behavior [7, 8]. Gartstein and Conwell argued that in order to obtain a Poole-Frenkel behavior in a broad range of field strengths, it is necessary to assume a spatial correlation between the site energies, leading to what is now known as the "correlated disorder model" (CDM) [9]. A PF-type field dependence is then already

found at smaller fields than in the GDM, which has been argued to be in better correspondence with experiments [9, 10]. Recently, it was recognized that the importance of another parameter had been overlooked: the charge-carrier density p [13, 14]. From a numerical solution of the master equation (ME) for hopping transport in a disordered energy system, 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) [15]. Alternatively, Bouhassoune et al. had extended the correlated disorder model (CDM) to include the dependence of the mobility on the carrier density by using the master equation and percolation approach, leading to the "extended correlated disorder model" (ECDM) [16].

For the EGDM and ECDM, key issues are the roles of the energetic disorder of the states in between which the charge carrier hopping takes place, assuming a Gaussian density of state (DOS) with random and spatially correlated energetic disorder, respectively. In several studies, it has been shown that both with the EGDM and ECDM excellent fits between the calculated and measured current density versus voltage ($J-V$) characteristics of the charge transport in several organic semiconductors can be obtained [16-19]. The question now arises whether a successful analysis of the $J-V$ characteristics of a certain material using the EGDM or ECDM would convincingly prove that the disorder is random or correlated, respectively.

In this paper, the possible presence of correlated disorder and the $J-V$ characteristics of hole transport are investigated for a high-mobility n-type copolymer poly{[N,N'-bis(2-octyldecyl)-naphthalene-1,4,5,8-bis(di carboximide)-2,6-diy1]-alt-5,5'-(2,2'-dithiophene)} [P(NDI2OD-T2),PolyeraActivInk™ N2200]. Apart from its high electron mobility, this polymer shows trap-free electron transport due to the fact that the lowest unoccupied molecular orbital (LUMO) is low enough (~ 4 eV), while the highest occupied molecular orbital (HOMO) is sufficiently shallow (~ 5.6 eV) for efficient hole injection [20]. As a result, N2200 is a particular semiconducting polymer for a detailed investigation of the hole transport and the possible presence of correlated disorder. We analyze the layer thickness and temperature dependence of the $J-V$ characteristics for N2200 hole-only devices by using the EGDM and ECDM, respectively. Good descriptions can be obtained within the EGDM as well as the ECDM. However, a much smaller intersite distance is obtained within the ECDM (0.1 nm) than within the EGDM (0.8 nm). This is an indication that in N2200 correlations between the site energies are absent or play a minor role.

2. Model and methods

The extended Gaussian disorder model (EGDM) can be described as follows [15]:

$$\mu(T, p, E) \approx \mu(T, p)f(T, E), \quad (1)$$

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

$$\mu_0(T) = \mu_0 c_1 \exp(-c_2 \hat{\sigma}^2), \quad (3)$$

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

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

with $c_1 = 1.8 \times 10^{-9}$, $c_2 = 0.42$, where $\mu_0(T)$ is the temperature dependent mobility in the limit of zero electric field and zero charge-carrier density, $\hat{\sigma} \equiv \sigma/k_B T$ is the dimensionless disorder parameter, σ is the width of the Gaussian density of states (DOS), a is the lattice constant, e is the charge of the carriers, and v_0 is the attempt frequency.

The extended correlated disorder model (ECDM) can be described as follows [16]:

$$\mu(T, p, E) = [(\mu_{low}(T, p, E))^{q(\hat{\sigma})} + (\mu_{high}(p, E))^{q(\hat{\sigma})}]^{1/q(\hat{\sigma})}, \quad (6)$$

$$q(\hat{\sigma}) = 2.4/(1 - \hat{\sigma}), \quad (7)$$

with $\mu_{low}(T, p, E)$ the mobility in the low-field limit (the average reduced field $E_{red} = eaE/\sigma \leq 1$), and with $\mu_{high}(p, E)$ the mobility in the high-field limit (the average reduced field $E_{red} = eaE/\sigma \geq 1$).

$$\mu_{low}(T, p, E) = \mu_0(T)g(T, p)f(T, E, p), \quad (8)$$

with $\mu_0(T)$ the mobility in the zero carrier-density limit and zero field limit, and with $g(T, p)$ and $f(T, E, p)$ the dimensionless mobility enhancement functions. The function $g(T, p)$ gives the carrier-density induced enhancement of the zero field mobility with respect to the value in the zero carrier-density limit. The function $f(T, E, p)$ gives the field-induced enhancement of the mobility with respect to the mobility at zero field. These functions can be given by

$$\mu_0(T) = 1.0 \times 10^{-9} \mu_0 \exp(-0.29 \hat{\sigma}^2), \quad (9)$$

$$g(T, p) = \begin{cases} \exp[(0.25 \hat{\sigma}^2 + 0.7 \hat{\sigma})(2pa^3)^\delta], & pa^3 < 0.025 \\ g(T, 0.025 a^{-3}), & pa^3 \geq 0.025 \end{cases}, \quad (10)$$

$$\delta \equiv 2.3 \frac{\ln(0.5 \hat{\sigma}^2 + 1.4 \hat{\sigma}) - 0.327}{\hat{\sigma}^2}, \quad (11)$$

$$f(T, E_{red}, p) = \exp[h(E_{red})(1.05 - 1.2(pa^3)^{r(\hat{\sigma})}) (\hat{\sigma}^{3/2} - 2)(\sqrt{1 + 2E_{red}} - 1)] \quad (12)$$

$$h(E_{red}) = 1, \quad r(\hat{\sigma}) = 0.7 \hat{\sigma}^{-0.7}, \quad (13)$$

within the very low-field, $0 \leq E_{red} < 0.16 \equiv E_{red}^*$,

$h(E_{red})$ can be written as

$$h(E_{red}) = \begin{cases} \frac{4}{3} \frac{E_{red}}{E_{red}^*}, (E_{red} \leq E_{red}^*/2) \\ \left[1 - \frac{4}{3} \left(\frac{E_{red}}{E_{red}^*} - 1 \right)^2 \right], (E_{red}^*/2 \leq E_{red} \leq E_{red}^*) \end{cases}, \quad (14)$$

$$\mu_{high}(p, E) = \frac{2.06 \times 10^{-9}}{E_{red}} \mu_0 (1 - pa^3). \quad (15)$$

By using the above two models and following coupled equations, the $J-V$ characteristics of organic semiconductors can be exactly calculated by employing a particular uneven discretization method introduced in our previous papers [21, 22].

$$J = p(x)e\mu(T, p(x), E(x))E(x), \quad (16a)$$

$$\frac{dE}{dx} = \frac{e}{\epsilon_0 \epsilon_r} p(x), \quad (16b)$$

$$V = \int_0^L E(x) dx, \quad (16c)$$

where x is the distance from the injecting electrode, $\epsilon_0 \epsilon_r$ is the permeability of the organic semiconductor, and L is the organic semiconductor layer thickness sandwiched between two electrodes.

3. Results and discussion

It is difficult for hole injection into N2200 from common anodes due to a high hole injection barrier [23, 24]. Fortunately, it has been demonstrated that good hole injection can be obtained by using an molybdenum trioxide (MoO_3) hole-injection layer even for conjugated polymers with a deep HOMO [25, 26]. Recently, single carrier hole-only devices based on N2200 have been fabricated by Wetzelaer et al. with the evaporated MoO_3 as hole-injection layer and PEDOT:PSS as bottom contact to block the injection of electrons [27]. As a result, the occurrence of hole-only devices makes it possible to further investigate the hole transport and possible presence of correlated disorder in N2200.

Fig. 1 shows the thickness dependent $J-V$ characteristics of hole-only devices with N2200 layer thickness of 78 nm, 140 nm and 280 nm at room temperature. Apparently, the experimental data from Ref. [27] can be well described by using the EGDM of the temperature T , electric field E , and carrier density p dependence of the mobility μ . The parameters of the width of the Gaussian density of states σ , lattice constant a , and μ_0 are determined in such a way that an optimal overall fit is obtained.

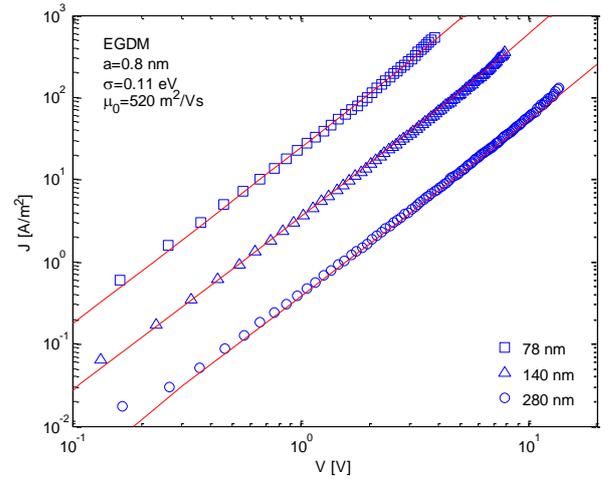


Fig. 1. Thickness dependent current density versus voltage characteristics of N2200 hole-only devices at 295K. Symbols are the experimental data from Ref. [27]. Lines are the numerically calculated results based on the EGDM.

Fig. 2 depicts the temperature dependent $J-V$ characteristics of a hole-only device based on N2200 with a layer thickness of 140 nm. For the entire range of electric field, the temperature dependent hole current can also be accurately described within the EGDM using the same parameters as the thickness dependent $J(V)$ curves. It can be seen from Fig. 1 and Fig. 2 that the thickness dependent and temperature dependent $J-V$ characteristics of N2200 hole-only devices can be excellently described within the EGDM only using a single set of parameters, $a = 0.8$ nm, $\sigma = 0.11$ eV, and $\mu_0 = 520$ m^2/Vs . The good agreement of the numerical simulations based on the EGDM with the experimental $J-V$ characteristics shows that the temperature, electric field, and carrier density dependence of the mobility needs to be taken into account for describing the hole transport in N2200.

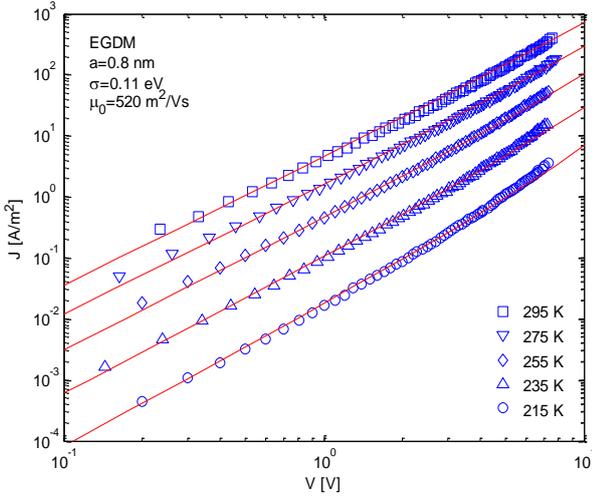


Fig. 2. Temperature dependent current density versus voltage characteristics of N2200 hole-only device with a layer thickness of 140 nm. Symbols are the experimental data from Ref. [27]. Lines are the numerically calculated results based on the EGDM.

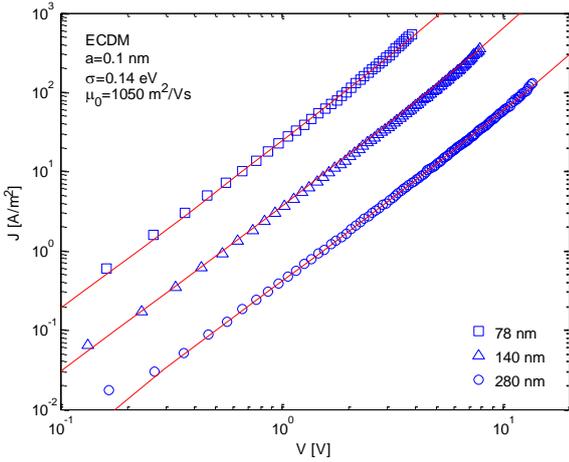


Fig. 3. Thickness dependent current density versus voltage characteristics of N2200 hole-only devices at 295K. Symbols are the experimental data from Ref. [27]. Lines are the numerically calculated results based on the ECDM.

As a next step, we re-analyse these experimental data for N2200 hole-only devices by using the ECDM of the temperature T , electric field E , and carrier density p dependence of the mobility μ . The thickness dependent and temperature dependent $J-V$ characteristics of N2200 hole-only devices are displayed in Fig. 3 and Fig. 4, respectively. It can be seen from the figures that the thickness dependent and temperature dependent $J-V$ characteristics of N2200 hole-only devices can also be well described within the ECDM only using a single set of parameters, $a=0.1$ nm, $\sigma=0.14$ eV, and $\mu_0=1050$ m²/Vs. This suggests that the ECDM is also able to provide a good description of the experimental data.

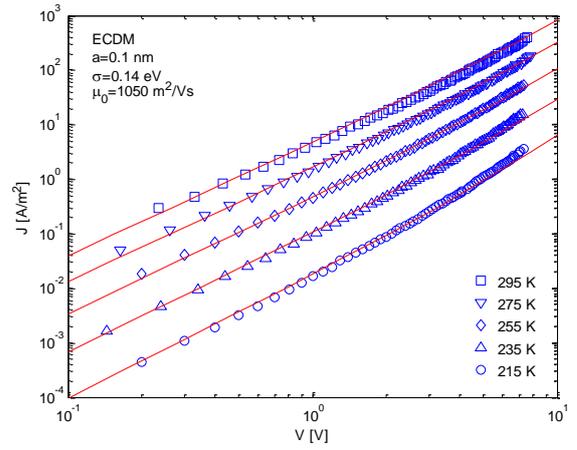


Fig. 4. Temperature dependent current density versus voltage characteristics of N2200 hole-only device with a layer thickness of 140 nm. Symbols are the experimental data from Ref. [27]. Lines are the numerically calculated results based on the ECDM.

For the EGDM and ECDM, the temperature dependence of the mobility in the zero field and zero carrier-density limit has the form

$$\mu_0(T) = \mu_0 \exp[-C(\sigma/k_B T)^2], \quad (17)$$

as discussed already in Section 2 (Eq. (3) for the EGDM and Eq. (9) for the ECDM). It may be seen that both with the EGDM and ECDM excellent fits to the measured $J-V$ characteristics can be obtained. We note that within both models the mobility at any temperature is described by using only three parameters, viz. a , σ and μ_0 , each with a clear physical meaning. Also, we have treated C as a free parameter upon making the fits. The reason is that different values of C can be found in literature, both for the GDM [6, 15, 28, 29], as well as for the CDM [10, 16]. For both models, the shape of the $J(V)$ curves depends on only two temperature and thickness independent parameters, a and σ . For the EGDM, we find $a=0.8$ nm and $\sigma=0.11$ eV, and for the ECDM $a=0.1$ nm and $\sigma=0.14$ eV. By optimizing the position of the $J(V)$ curves, using a shift along the vertical axes, the temperature dependent optimal values of μ_0 is determined.

The optimal fit values of a as obtained from the EGDM and ECDM are very different, viz. 0.8 nm and 0.1 nm, respectively. The value of a found for the EGDM is very close to the typical value of organic semiconductor [16], in agreement with the result reported for N2200 in previous work [29, 30]. On the other hand, the value of a found for the ECDM may be considered as unrealistically small (10 times lower than the typical value). We view this as an indication that for N2200 the energies of the sites in between which hopping takes place are uncorrelated. The comparison between the values obtained for σ and C does not change this point of view. As for disordered

organic semiconductors, the σ is typically observed to fall in the range 0.06-0.15 eV, the optimal values of σ which are obtained within both models (0.11 eV for the EGDM and 0.14 eV for the ECDM) are physically realistic. Lacking independent experimental results on the width of the DOS, the values of σ can presently not be used to make a distinction between both models. Within the GDM the C-value is expected in the range 0.38-0.46 [6, 15, 28, 29], and for the CDM Monte Carlo calculations [10] and 3D-ME calculations [16] have then yielded $C \sim 0.36$ and $C \sim 0.29$, respectively. The values obtained from the best fits in the present work, $C = 0.44$ for the EGDM and $C = 0.27$ for the ECDM, are both consistent with the typical values mentioned above and very close to the values predicted within each model ($C = 0.42$ for the EGDM and $C = 0.29$ for the ECDM). Therefore, we regard the C-values for both models as also physically realistic. In addition, the C-values depend weakly on the decay length α^{-1} of the wavefunctions in between which the hopping takes place (for which we have assumed $\alpha = 10/a$), and increase slightly with a decreasing decay length [28, 31].

4. Summary and conclusions

In summary, the thickness dependent and temperature dependent $J - V$ characteristics of the N2200 hole-only devices can be accurately described by using the EGDM and ECDM, within which the mobility depends on the temperature, electric field, and carrier density. This suggests that a successful analysis of the $J(V)$ curves using either model does not yet convincingly prove that the disorder is completely random or correlated. In particular, for the material studied, we argue that the most remarkable distinction between the two sets of optimal fit parameters is an observed large difference between the effective lattice parameter a . The intersite distance found using the EGDM ($a = 0.8$ nm) is very close to the typical value of organic semiconductor, whereas the value of a found for the ECDM ($a = 0.1$ nm) may be considered as unrealistically small. We view this as an indication that for the N2200 studied correlations between the site energies are absent or insignificant. Consequently, we expect that the present work is useful to build up the quantitative device models.

Acknowledgements

This work is supported by the National Natural Science Foundation of China Grant No. 61501175 and Doctoral Scientific Research Foundation of Henan Polytechnic University Grant No. B2014-022.

References

- [1] C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- [2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. B. Holmes, *Nature* **347**, 539 (1990).
- [3] A. R. Brown, C. P. Jarrett, D. M. de Leeuw, M. Matters, *Synth. Met.* **88**, 37 (1997).
- [4] G. Yu, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **270**, 1789 (1995).
- [5] L. Pautmeier, R. Richert, H. Bässler, *Synth. Met.* **37**, 271 (1990).
- [6] H. Bässler, *Phys. Status Solidi (b)* **175**, 15 (1993).
- [7] P. M. Borsenberger, D. S. Wiess, *Organic Photoreceptors for Xerography* (Marcel Dekker, New York, 1998).
- [8] W. Brütting, S. Berleb, A. G. Mückel, *Org. Electron.* **2**, 1 (2001).
- [9] Y. N. Gartstein, E. M. Conwell, *Chem. Phys. Lett.* **245**, 351 (1995).
- [10] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, *Phys. Rev. Lett.* **81**, 4472 (1998).
- [11] S. D. Baranovskii, H. Cordes, F. Hensel, G. Leising, *Phys. Rev. B* **62**, 7934 (2000).
- [12] V. I. Arkhipov, P. Heremans, E. V. Emelianova, G. J. Adriaenssens, H. Bässler, *J. Phys.: Condens. Matter* **14**, 9899 (2002).
- [13] Y. Roichman, N. Tessler, *Synth. Met.* **135**, 443 (2003).
- [14] C. Tanase, E. J. Meijer, P. W. M. Blom, D. M. de Leeuw, *Phys. Rev. Lett.* **91**, 216601 (2003).
- [15] 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).
- [16] M. Bouhassoune, S. L. M. van Mensfoort, P. A. Bobbert, R. Coehoorn, *Org. Electron.* **10**, 437 (2009).
- [17] R. J. de Vries, S. L. M. van Mensfoort, V. Shabro, S. I. E. Vulto, R. A. J. Janssen, R. Coehoorn, *Appl. Phys. Lett.* **94**, 163307 (2009).
- [18] S. L. M. van Mensfoort, V. Shabro, R. J. de Vries, R. A. J. Janssen, R. Coehoorn, *J. Appl. Phys.* **107**, 113710 (2010).
- [19] S. L. M. van Mensfoort, R. J. de Vries, V. Shabro, H. P. Loebel, R. A. J. Janssen, R. Coehoorn, *Org. Electron.* **11**, 1408 (2010).
- [20] H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dtz, M. Kastler, A. Facchetti, *Nature* **457**, 679 (2009).

- [21] L. G. Wang, H. W. Zhang, X. L. Tang, Y. Q. Song, *Optoelectron. Adv. Mat.* **5**, 263 (2011).
- [22] M. L. Liu, L. G. Wang, *J. Optoelectron. Adv. M.* **19**, 406 (2017).
- [23] N. I. Craciun, J. J. Brondijk, P. W. M. Blom, *Phys. Rev. B* **77**, 035206 (2008).
- [24] K. Asadi, T. G. de Boer, P. W. M. Blom, D. M. de Leeuw, *Adv. Funct. Mater.* **19**, 3173 (2009).
- [25] H. T. Nicolai, G. A. H. Wetzelaer, M. Kuik, A. J. Kronemeijer, B. de Boer, P. W. M. Blom, *Appl. Phys. Lett.* **96**, 172107 (2010).
- [26] M. Kröger, S. Hamwi, J. Meyer, T. Riedl, W. Kowalsky, A. Kahn, *Org. Electron.* **10**, 932 (2009).
- [27] G. J. A. H. Wetzelaer, M. Kuik, Y. Olivier, V. Lemaire, J. Cornil, S. Fabiano, M. Antonietta Loi, P. W. M. Blom, *Phys. Rev. B* **86**, 165203 (2012).
- [28] R. Coehoorn, W. F. Pasveer, P. A. Bobbert, M. A. J. Michels, *Phys. Rev. B* **72**, 155206 (2005).
- [29] L. G. Wang, M. L. Liu, J. J. Zhu, L. F. Cheng, *Optoelectron. Adv. Mat.* **11**, 202 (2017).
- [30] J. C. Blakesley, M. Schubert, R. Steyrlleuthner, Z. Chen, A. Facchetti, D. Neher, *Appl. Phys. Lett.* **99**, 183310 (2011).
- [31] S. D. Baranovskii, I. P. Zvyagin, H. Cordes, S. Yamasaki, P. Thomas, *Phys. Status Solidi (b)* **230**, 281 (2002).

*Corresponding author: wangliguo@hpu.edu.cn