Charge transport and electrical properties in a low bandgap semiconducting polymer

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In this paper, the charge transport and electrical properties in a low bandgap semiconducting polymer poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothia-diazole)] (PCPDTBT) are investigated. It is shown that the temperature dependent current density versus voltage characteristics of PCPDTBT hole-only and electron-only devices can be accurately described by using an improved mobility model in which the mobility depends on the temperature, carrier density, and electric field. For the semiconducting polymer studied, we find the width of the Gaussian density of states 0.092 eV for the hole transport and 0.132 eV for the electron transport. Apparently, the electron transport exhibits a significantly stronger energy disorder than the hole transport. This is also reflected in the lower electron mobility (2.43×10^{-9} m^2/Vs), as compared to the hole mobility (1.13×10^{-7} m^2/Vs). Furthermore, it is shown that the effective mobility in PCPDTBT electron-only device is obviously lower than that in PCPDTBT hole-only device. Both the maximum of carrier concentration and the minimum of electric field appear near the interface of PCPDTBT hole-only and electron-only devices.

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1. Introduction

Conjugated polymers blended with soluble fullerene derivatives show a great potential for low cost, flexible, and large area solar cells [1–6]. In contrast with inorganic solar cells, their chemical structure can be tuned in order to optimize photovoltaics performance. However, one of the main shortcomings in these polymer:fullerene bulk heterojunction (BHJ) solar cells is the poor overlap between the solar spectrum and the absorption of the materials used. Engineering of the optical bandgap is of particular interest, as low bandgap organic materials enable harvesting of lower energy photons that are not absorbed by wide bandgap organic materials. One of the most promising low bandgap organic semiconductors to date is poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2, 1-b;3,4-b']dithiophene)-alt-4,7-(2,1,3-benzothia-diazole)] (PCPDTBT), which has been widely used as an electron donor to the methanofullerene [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) in bulk heterojunction solar cells [7, 8]. In spite of the increased absorption the power conversion efficiency of PCPDTBT:PCBM solar cells is still low. In earlier investigations it has been shown that the main reason for the low performance is due to the poor charge transport in low bandgap polymers, resulting in low fill factors and quantum efficiencies [9-12]. However, measurements performed on field effect transistors (FET) based on PCPDTBT resulted in hole mobilities in the polymer as high as 2×10^{-6} m^2/Vs [7], indicating that the quality of the hole transport in PCPDTBT should be very good. Until now, the origin of the reduced fill factors and quantum efficiencies in PCPDTBT:PCBM solar cells is not clear. Consequently, knowledge about the charge carrier transport in PCPDTBT is indispensable to further improvement of the performance of PCPDTBT:PCBM photovoltaic devices.

Charge carrier transport in disordered organic semiconductors is commonly understood to occur via thermally activated tunneling (hopping) of charge carriers between localized sites. Due to the typically Gaussian distribution of site energies, the mobility becomes strongly dependent on temperature T, charge carrier density p, and electrostatic field E. During the past two decades, various approaches were proposed to calculate the mobility functional for hopping transport in disordered organic semiconductors [13-20]. Seminal work by Bässler et al. used Monte Carlo simulations, the random energies were described by a Gaussian density of states (DOS), leading to the Gaussian disorder model (GDM) [13], which only considers the low density Boltzmann limit and shows discrepancies in the field dependence that are attributed to spatial correlations of the site energies [15, 17]. The charge carrier density dependence of the mobility beyond the Boltzmann limit is included in the so-called

extended Gaussian disorder model (EGDM) introduced by Pasveer et al. [16]. However, it should be noted that the EGDM, only having a non-Arrhenius temperature dependence, cannot well describe the charge transport at high carrier densities. In order to better describe the charge transport, we proposed an improved model within which the temperature dependence of the mobility based on both the non-Arrhenius temperature dependence and Arrhenius temperature dependence, leading to the improved extended Gaussian disorder model (IEGDM) [21].

In this paper, the charge transport and electrical properties in a low bandgap semiconducting polymer PCPDTBT will be investigated. Firstly, we perform a detailed analysis of the current density versus voltage (*J* - *V*) characteristics for PCPDTBT hole-only and electron-only devices by using the IEGDM. Subsequently, we calculate and analyze the variation of *J* - *V* characteristics with the boundary carrier density and the distribution of carrier density and electric field with the distance from the interface of PCPDTBT hole-only and electron-only devices. The electron transport exhibits a significantly stronger energy disorder than the hole transport in PCPDTBT, which is also reflected in the lower electron mobility as compared to the hole mobility. The effective mobility in PCPDTBT electron-only device is obviously lower than that in PCPDTBT hole-only device. These results provide valuable information about the influence of the charge transport in PCPDTBT on the performance of PCPDTBT:PCBM photovoltaic devices.

2. Model and methods

Pasveer et al. used a master equation method to generate a parametrized mobility functional for hopping transport in a disordered energy system with a Gaussian density of states (DOS) distribution, leading to the "extended Gaussian disorder model" (EGDM) [16]. Based on the EGDM, we recently proposed an improved mobility model (IEGDM) in which the mobility μ depends on the temperature T, carrier density p, and electric field E [21]. In particular, the dependence of the zero-field mobility on the carrier density p and temperature T is given by

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

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

$$\delta\equiv 2\frac{\ln(\hat{\sigma}^2-\hat{\sigma})-\ln(\ln 4)}{\hat{\sigma}^2},\ \mu_0\equiv\frac{a^2\nu_0 e}{\sigma}, \quad (1c)$$

with $c_1=0.48\times10^{-9}$, $c_2=0.80$, and $c_3=0.52$. Where $\mu_0(T)$ is the mobility in the limit of zero carrier density and zero electric field, $\hat{\sigma}\equiv\sigma/k_BT$ is the dimensionless disorder parameter, σ 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 ν_0 is the attempt-to-hop frequency. The field dependence of the mobility is included via

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

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

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 [22, 23].

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

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

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

where x is the distance from the injecting electrode, ε_0 is the vacuum permeability, ε_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

As mentioned in Sec. 1, even though field effect mobilities give a valuable insight into the quality of the charge transport in PCPDTBT, ideally one would like to gain the mobility in a similar device geometry as the actual solar cell. In this work, the charge transport is investigated in a vertical device geometry similar to solar cells. By choosing suitable top and bottom contacts, one can choose

to block one carrier and measure either the hole or electron current [24]. The charge transport through these single carrier devices can be studied by using the space charge limited current (SCLC) approach. The solution of the coupled equations describing the SCLC with the improved mobility model as described in Sec. 2 and the experimental $J-V$ measurements from Ref. [24] for PCPDTBT hole-only and electron-only devices with various temperatures are displayed in Figs. 1 and 2, respectively. It can be seen from the figures that the temperature dependent $J-V$ characteristics of PCPDTBT hole-only and electron-only devices can be excellently described by using a single set of parameters, $a = 4.2$ nm, $\sigma = 0.092$ eV, $\mu_0 = 1400$ m^2/Vs and $a = 3.45$ nm, $\sigma = 0.132$ eV, $\mu_0 = 3200$ m^2/Vs, respectively. The parameters of σ, a, and μ_0 are determined in such a way that an optimal overall fit is obtained. Apparently, our numerical simulations based on the IEGDM are in good agreement with the experimental measurements, which suggests that the IEGDM is applicable to studying both the hole and electron transport in PCPDTBT. It is worth noting that the value of the disorder parameter σ in PCPDTBT hole-only device is significantly smaller than that in PCPDTBT electron-only device, indicating a lower degree of energetic disorder for the hole transport as compared to the electron transport. The well-known expression for the SCLC in electronic devices has been obtained by Mott and Gurney [25], given by

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

According to the Mott-Gurney law, we determine the room-temperature zero-field hole and electron mobilities from the $J-V$ measurements to be 1.13×10^{-7} m^2/Vs and 2.43×10^{-9} m^2/Vs, respectively. The hole mobility is about a factor of 50 higher than the electron mobility, which is consistent with that a lower degree of energetic disorder for the hole transport as compared to the electron transport. Furthermore, the hole mobility is about a factor of 20 lower than the earlier reported field-effect mobility [7], similar differences between FET and diode mobilities have been observed in P3HT due to the density dependence of the mobility [26]. This suggests once again that taking the carrier density dependence of the mobility into account is essential for describing the charge transport in disordered organic semiconductors.

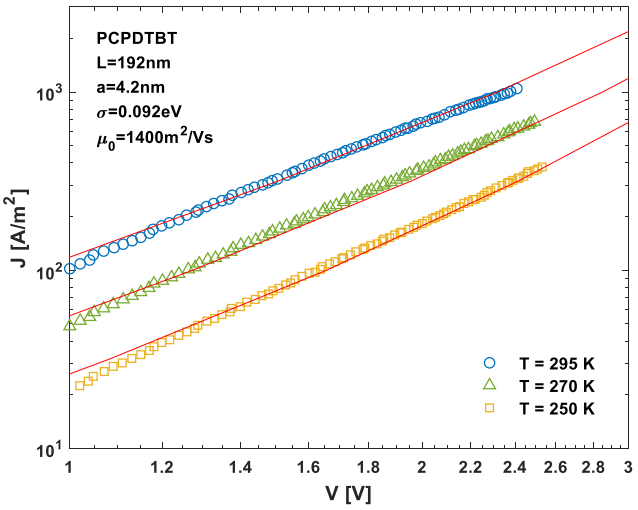

Fig. 1. Temperature dependent $J-V$ characteristics of PCPDTBT hole-only device with a layer thickness of 192 nm. Symbols are the experimental data from Ref. [24]. Lines are the numerically calculated results based on the IEGDM (color online)

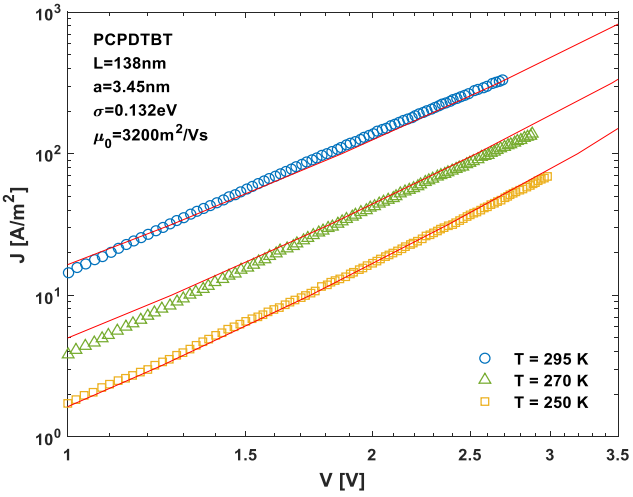

Fig. 2. Temperature dependent $J-V$ characteristics of PCPDTBT electron-only device with a layer thickness of 138 nm. Symbols are the experimental data from Ref. [24]. Lines are the numerically calculated results based on the IEGDM (color online)

The numerically calculated variations of $J-V$ characteristics with the boundary carrier density $p(0)$ for PCPDTBT hole-only and electron-only devices at room temperature are plotted in Fig. 3. 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} 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 is physically realistic in this region. 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 PCPDTBT electron-only device than those in PCPDTBT hole-only device, even if the thickness of the electron-only device is significantly lower than the hole-only device. This can be explained by the fact that the effective mobility as determined in hole-only device is higher than that in electron-only device, due to the presence of a lower degree of energetic disorder for the hole transport as compared to the electron transport. These results further suggest that the dependence of the mobility on the carrier density should be taken into account when describing the charge transport in disordered organic semiconductors.

The numerically calculated distribution of the carrier density and electric field as a function of the distance from the interface in PCPDTBT hole-only and electron-only devices are plotted in Fig. 4. 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 $p(0)$. The variation tendency of carrier density $p(x)$ and electric field $E(x)$ with the distance x in PCPDTBT electron-only device is more obvious than that in PCPDTBT hole-only device. Both the maximum of carrier density and the minimum of electric field appear near the interface of PCPDTBT hole-only and electron-only devices. As a result, the injection of carriers from the electrode into the PCPDTBT 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 $E(x)$.

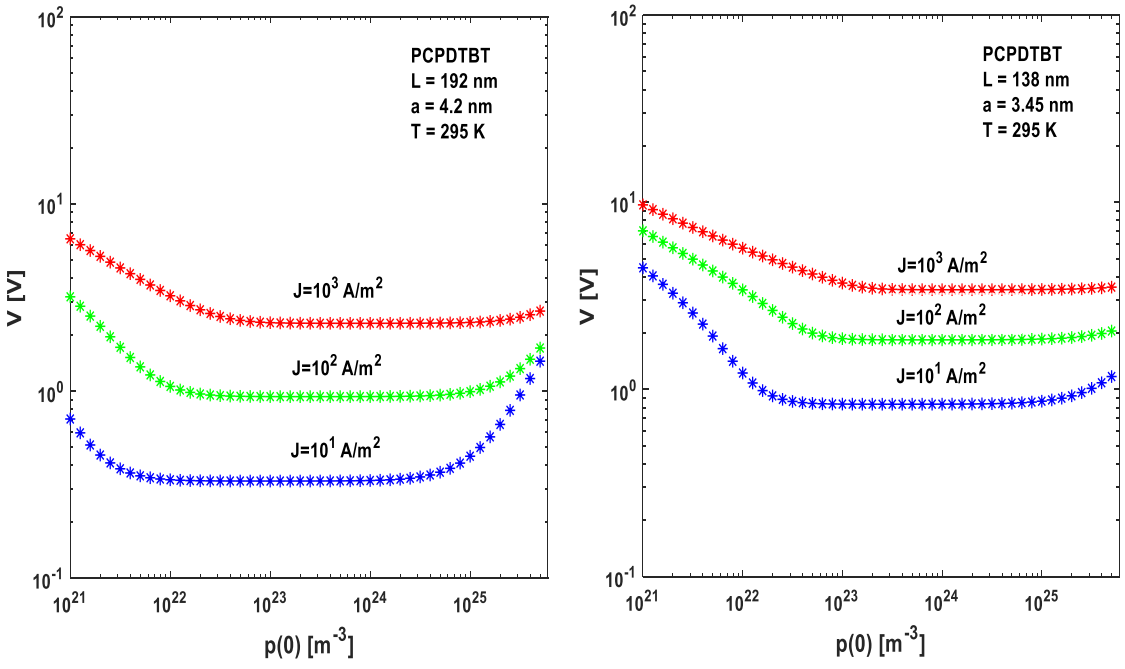

Fig. 3. Theoretical results of voltage versus the boundary carrier density of PCPDTBT hole-only (Left) and electron-only (Right) devices at room temperature. Different lines correspond to different current density values (color online)

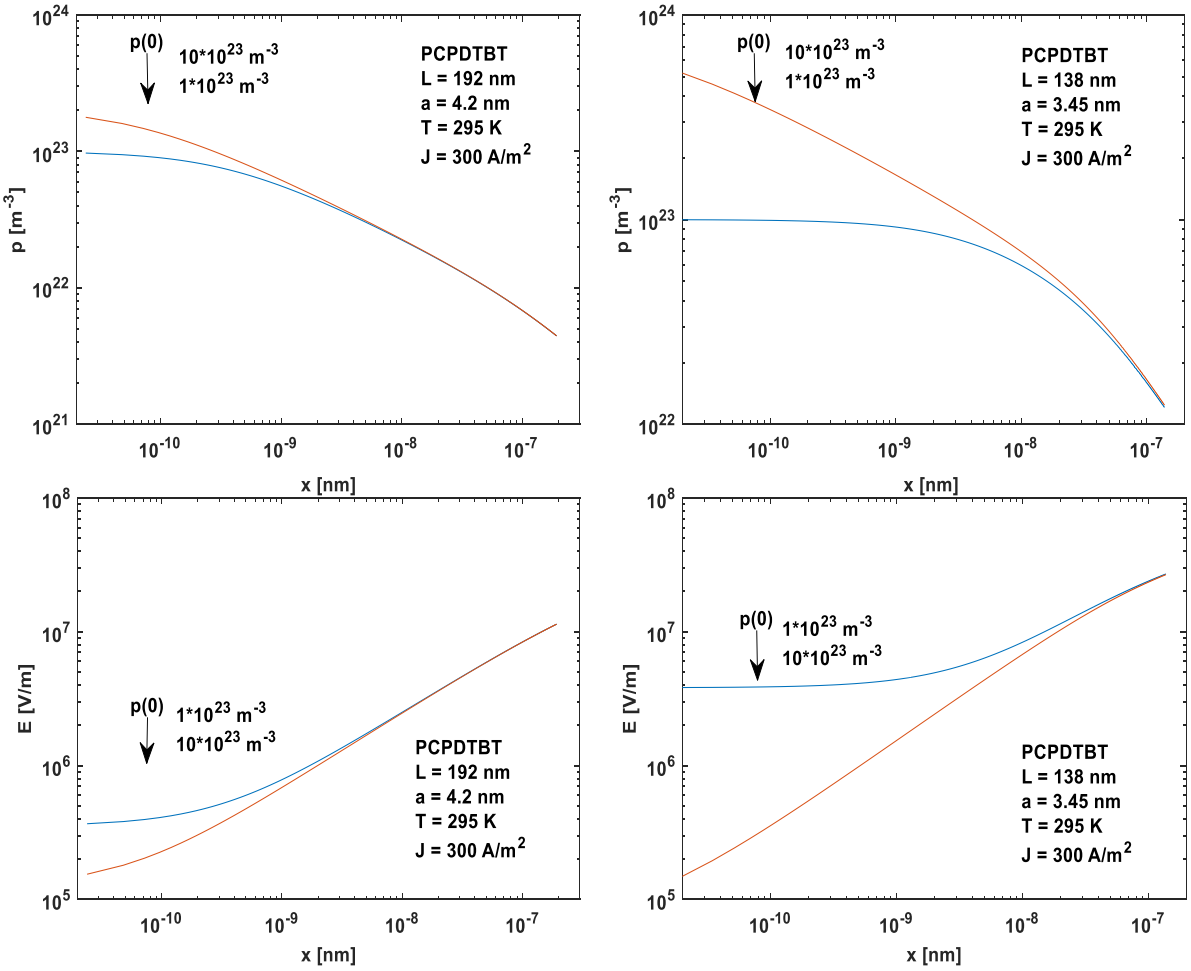

Fig. 4. Numerically calculated distribution of the charge carrier density p and electric field E as a function of the distance x in PCPDTBT hole-only (Left) and electron-only (Right) devices at room temperature (color online)

4. Summary and conclusions

In conclusion, the charge transport and electrical properties in a low bandgap semiconducting polymer PCPDTBT have been investigated by using an improved mobility model in which the mobility depends on the temperature, carrier density, and electric field. It is shown that the improved model is applicable to studying both the hole and electron transport in PCPDTBT, leading to simplified modeling of the charge transport in disordered organic semiconductors. For PCPDTBT, we find that the electron transport exhibits a significantly stronger energy disorder than the hole transport in PCPDTBT, which is also reflected in the lower electron mobility as compared to the hole mobility. The effective mobility in PCPDTBT electron-only device is obviously lower than that in PCPDTBT hole-only device. Our findings strongly suggest that taking the carrier density dependence of the mobility into account is essential for describing the charge transport in disordered organic semiconductors.

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References

[1] C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, Adv. Funct. Mater. **11**, 15 (2001).
[2] M. Lenes, M. Morana, C. J. Brabec, P. W. M. Blom, Adv. Funct. Mater. **19**, 1106 (2009).
[3] H. Azimi, A. Senes, M. C. Scharber, K. Hingerl, C. J. Brabec, Adv. Energy Mater. **1**, 1162 (2011).
[4] Y. Ie, K. Morikawa, W. Zajaczkowski, W. Pisula, N. B. Kotadiya, G. A. H. Wetzelaer, P. W. M. Blom, Y. Aso, Adv. Energy Mater. **8**, 1702506 (2018).
[5] N. B. Kotadiya, P. W. M. Blom, G. A. H. Wetzelaer,

Phys. Rev. Applied **11**, 024069 (2019).
[6] T. Upreti, Y. Wang, H. Zhang, D. Scheunemann, F. Gao, M. Kemerink, Phys. Rev. Applied **12**, 064039 (2019).
[7] D. Muhlbacher, M. Scharber, M. Morana, Z. Zhu, D. Waller, R. Gaudiana, C. Brabec, Adv. Mater. **18**, 2884 (2006).
[8] D. J. D. Moet, M. Lenes, M. Morana, H. Azimi, C. J. Brabec, P. W. M. Blom, Appl. Phys. Lett. **96**, 213506 (2010).
[9] S. E. Shaheen, D. Vangeneugden, R. Kiebooms, D. Vanderzande, T. Fromherz, F. Padinger, C. J. Brabec, N. S. Sariciftci, Synth. Met. **121**, 1583 (2001).
[10] A. P. Smith, R. R. Smith, B. E. Taylor, M. F. Durstock, Chem.Mater. **16**, 4687 (2004).
[11] X. Wang, E. Perzon, F. Oswald, F. Langa, S. Admassie, M. R. Andersson, O. Inganas, Adv. Funct. Mater. **15**, 1665 (2005).
[12] L. M. Campos, A. Tontcheva, S. Gunes, G. Sonmez, H. Neugebauer, N. S. Sariciftci, F. Wudl, Chem. Mater. **17**, 4031 (2005).
[13] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[14] Y. N. Gartstein, E. M. Conwell, Chem. Phys. Lett. **245**, 351 (1995).
[15] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).
[16] 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).
[17] M. Bouhassoune, S. L. M. van Mensfoort, P. A. Bobbert, R. Coehoorn, Org. Electron. **10**, 437 (2009).
[18] J. O. Oelerich, A. V. Nenashev, A. V. Dvurechenskii, F. Gebhard, S. D. Baranovskii, Phys. Rev. B **96**, 195208 (2017).
[19] S. D. Baranovskii, Phys. Status Solidi A **215**, 1700676 (2018).
[20] N. Felekidis, A. Melianas, M. Kemerink, Org. Electron. **61**, 318 (2018).
[21] L. G. Wang, H. W. Zhang, X. L. Tang, C. H. Mu, Eur. Phys. J. B **74**, 1 (2010).
[22] L. G. Wang, H. W. Zhang, X. L. Tang, Y. Q. Song, Optoelectron. Adv. Mat. **5**, 263 (2011).
[23] M. L. Liu, L. G. Wang, J. Optoelectron. Adv. M. **19**, 406 (2017).
[24] O. V. Mikhnenko, M. Kuik, J. Lin, N. van der Kaap, T. Nguyen, P. W. M. Blom, Adv. Mater. **26**, 1912 (2014).
[25] N. F. Mott, R. W. Gurney, Electronic Processes in Ionic Crystals, Oxford University Press, London 1940.
[26] C. Tanase, E. J. Meijer, P. W. M. Blom, D. M. de Leeuw, Phys. Rev. Lett. **91**, 216601 (2003).

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