

Electron transport in a high-mobility conjugated polymer: the role of uncorrelated disorder and correlated disorder

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In this paper, the electron transport and spatial correlation between the site energies in a high-mobility n-type conjugated polymer poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-dithiophene)} (N2200) are investigated. It is found that consistent descriptions for the thickness dependent and temperature dependent current density versus voltage ($J - V$) characteristics of N2200 electron-only devices can be 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 with the typical value of organic semiconductors, we find that the width of the Gaussian density of states from two models is considerably smaller than usually obtained for conjugated polymers and the intersite distance found using the ECDM (0.4 nm) is unrealistically small, which indicate a high electron mobility and a spatially uncorrelated Gaussian disorder in N2200, respectively.

(Received January 29, 2020; accepted August 18, 2020)

Keywords: Electron transport, Uncorrelated disorder, Correlated disorder, Intersite distance

1. Introduction

Organic semiconductors are promising candidates for replacing conventional inorganic semiconductors in electronic devices such as light-emitting diodes, solar cells, and field-effect transistors [1-4]. A common feature of most organic semiconductors is that hole and electron transport is highly unbalanced [5, 6]. In electronic devices fabricated from organic semiconductors, hole currents show trap-free, space-charge-limited behavior, whereas electron transport is reduced by the presence of charge trapping [6-8]. De Leeuw et al. pointed out that organic materials with an electron affinity lower than ~ 3 eV have a strong tendency to create electron-accepting units [9]. Therefore, for the development of stable electron transporting organic materials, high electron affinities are required. Recently, a novel high-mobility n-type polymer, poly{[N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-dithiophene)} (N2200) was developed [10]. Apart from its high electron mobility, this polymer is particularly interesting because of its energy levels. The lowest unoccupied molecular orbital (LUMO) is situated at an energy of ~ -4 eV, while the highest occupied molecular orbital (HOMO) is located at ~ -5.6 eV [11]. This implies that the LUMO is low enough

for stable trap-free electron transport, while the HOMO is sufficiently shallow for efficient hole injection. As a result, N2200 is an ideal organic semiconductor for a detailed investigation of the electron transport and possible presence of correlated disorder.

Understanding the charge transport and availability of physical models in organic semiconductors is of fundamental importance for further advancement of electronic and optoelectronic devices. In particular, it is crucial to understand how the charge-carrier mobility depends on the temperature, electric field, and charge carrier density. In past decades, the dependence of the mobility on the temperature and electric field has been extensively investigated. Bäessler 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) [12, 13]. Alternatively, 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 spatially correlation between the site energies. This leads to what we have called the "correlated disorder model" (CDM) [14]. Recently, a complete description of the charge transport has been developed by Pasveer et al. that determines the dependence of the mobility on the temperature, electric

field, and carrier density, which is known as the "extended Gaussian disorder model" (EGDM) [15]. On the other hand, Bouhassoune et al. have extended the CDM to include the dependence of the mobility on the carrier density, which leads to the so-called "extended correlated disorder model" (ECDM) [16]. This recent development was used to compare the applicability of the ECDM with that of the EGDM to the space-charge limited current hole transport in a polyfluorene-triaryamine (PF-TAA) based copolymer and in the archetypical small molecule material NPB [17-19]. Both studies revealed that equally good descriptions of the current density versus voltage curves could be obtained from both models, but that a distinction could be made on the basis of the effective hopping site densities obtained.

The question now arises whether it would also be possible to describe the current density versus voltage (J - V) characteristics of single-carrier devices based on electron transporting materials using the EGDM or ECDM, and whether it would be possible to make a distinction between both models to proof that the disorder is completely random or correlated. In this paper, we will investigate whether such an extensive analysis can be given for the electron transport in sandwich-type devices based on a high-mobility electron-transporting polymer N2200. From an analysis of the layer thickness and temperature dependence of the J - V characteristics for N2200 electron-only devices, it is found that good descriptions can be obtained within the EGDM as well as ECDM. However, a more realistic value of the intersite distance is obtained within the EGDM than within the ECDM. This is a first indication that in N2200 correlations between the site energies are absent or play a minor role.

2. Models 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 full description of the charge transport that determines the dependence of the mobility μ on the temperature T , electric field E , and carrier density p was obtained by Pasveer et al. in the form of the "extended Gaussian disorder model" (EGDM) [15], as described by

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

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

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

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

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

with $c_1 = 1.8 \times 10^{-9}$, $c_2 = 0.42$, where $\mu_{0,EGDM}(T)$ is the temperature dependent mobility in the limit of zero electric field and 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.

Using the master equation and percolation approach, Bouhassoune et al. have extended the CDM to include the dependence of the mobility on the carrier density, in addition to the dependence of the mobility on temperature and electric field. This leads to the so-called "extended correlated disorder model" (ECDM) [16], which can be described as follows

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

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

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

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

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

Using the above models and the 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 [20, 21].

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

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

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

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

3. Results and discussion

The solution of the coupled equations (Eq. (16)) with the EGDM and the experimental J - V measurements from Ref. [22] for N2200 electron-only devices with various layer thicknesses and various temperatures are displayed in Figs. 1 and 2, respectively. Apparently, the experimental measurements can be well described by using the EGDM of the temperature, electric field, and carrier density dependence of the mobility. This suggests that taking the carrier density dependence of the mobility into account is essential for describing the electron transport in organic semiconductors. Also, the thickness dependent and temperature dependent J - V characteristics of N2200 electron-only devices can be excellently described only using a single set of parameters, the lattice constant $a = 2.0$ nm, the width of the Gaussian density of states $\sigma = 0.08$ eV, and $\mu_0 = 2050$ m²/Vs. The parameters of σ , a , and μ_0 are determined in such a way that an optimal overall fit is obtained.

As a next step, we reanalyze these experimental data

from Ref. [22] for N2200 electron-only devices by using the EGDM of the temperature, electric field, and carrier density dependence of the mobility. The numerically calculated results based on the EGDM and experimental measurements of the thickness dependent and temperature dependent J - V characteristics for N2200 electron-only devices are displayed in Figs. 3 and 4, respectively. It can be seen from the figures that the thickness dependent and temperature dependent J - V characteristics of N2200 electron-only devices can also be well described by the EGDM only using a single set of parameters, $a = 0.4$ nm, $\sigma = 0.09$ eV, and $\mu_0 = 4000$ m²/Vs. It is clear that the EGDM is also able to provide a good description of the experimental data.

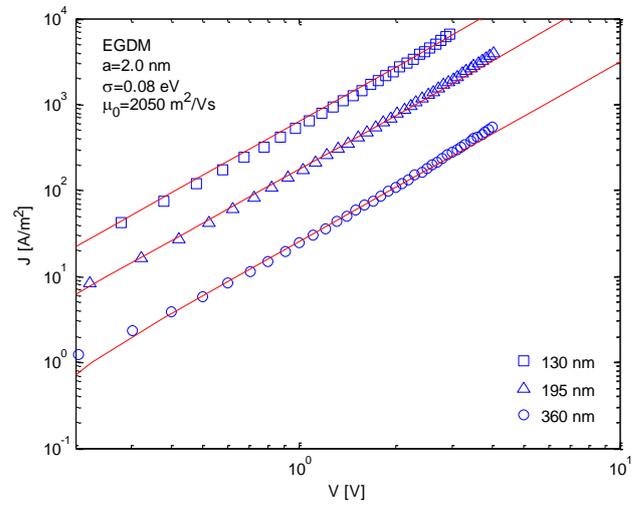


Fig. 1. Thickness dependent J - V characteristics of N2200 electron-only devices at room temperature. Symbols are the experimental data from Ref. [22]. Lines are the numerically calculated results based on the EGDM (color online)

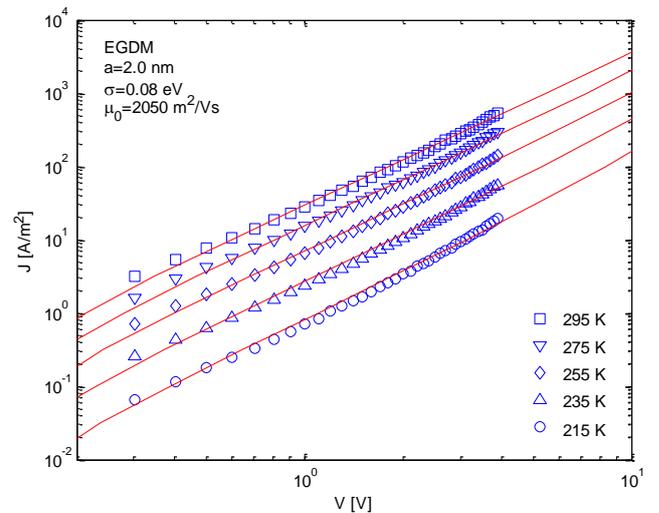


Fig. 2. Temperature dependent J - V characteristics of N2200 electron-only device with a layer thickness of 360 nm. Symbols are the experimental data from Ref. [22]. Lines are the numerically calculated results based on the EGDM (color online)

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 can be seen from Figs. 1-4 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 using only three parameters, a , σ , μ_0 , each with a clear physical meaning. For both models, the shape of the $J(V)$ curves depends on only two temperature and thickness independent parameters, a and σ . By optimizing the position of the $J(V)$ curves, using a shift along the vertical axes, the temperature dependent optimal values of μ_0 are determined. 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 EGDM as well as for the ECDM [15, 16, 23]. The values that yield the best fits in the present study ($C=0.46$ for the EGDM and $C=0.36$ for the ECDM) are both close to the values predicted within each model ($C=0.42$ for the EGDM and $C=0.29$ for the ECDM).

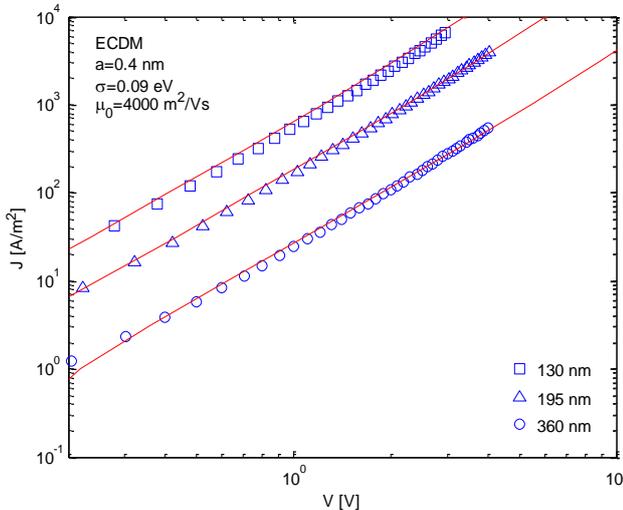


Fig. 3. Thickness dependent $J-V$ characteristics of N2200 electron-only devices at room temperature. Symbols are the experimental data from Ref. [22]. Lines are the numerically calculated results based on the ECDM (color online)

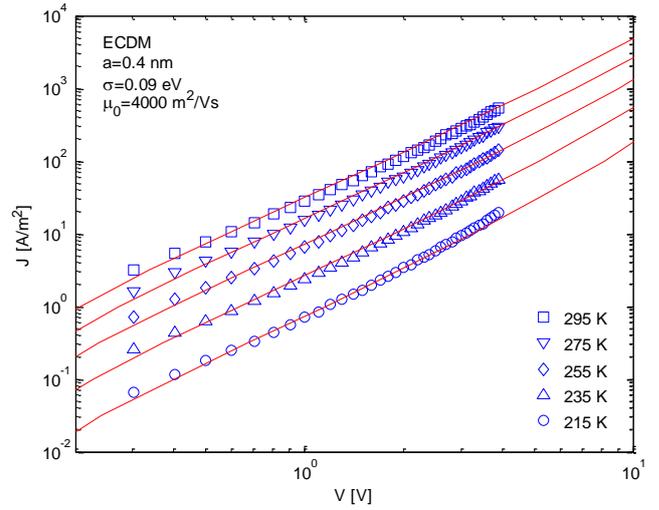


Fig. 4. Temperature dependent $J-V$ characteristics of N2200 electron-only device with a layer thickness of 360 nm. Symbols are the experimental data from Ref. [22]. Lines are the numerically calculated results based on the ECDM (color online)

The optimal fit values of a as obtained from the EGDM and ECDM are very different, 2.0 nm and 0.4 nm, respectively. The value of a found for the ECDM may be considered as unrealistically small (significantly lower than the typical value of organic semiconductors), in view of the fact that the conjugated polymer N2200 consisting of a naphthalene diimide core (NDI), connected with a bithiophene unit (T-T), which is expected to give rise to a larger typical distance between neighboring polymer chains [10]. This indicates that in N2200 studied correlations between the site energies are absent or insignificant. The comparison between the values obtained for σ and C does not change this point of view. As for disordered organic semiconductors the width of the DOS is typically observed to fall in the range 0.06-0.15 eV, the values of σ which are obtained within both models (0.08 eV for the EGDM and 0.09 eV for the ECDM) are physically realistic. Both the width of the DOS distribution from the two models are considerably smaller than usually obtained for conjugated polymers, indicating a low degree of energetic disorder of the LUMO in N2200. The observation of weak disorder is in agreement with the high values obtained for the bulk electron mobility. Lacking independent experimental information 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 [13, 15, 23], and for the CDM Monte Carlo calculations [24] and 3D-ME calculations [16] have then yielded $C \sim 0.36$ and $C \sim 0.29$, respectively. The values that yield the best fits in the present study ($C=0.46$ for the EGDM and $C=0.36$ 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.

4. Summary and conclusions

In conclusion, the electron transport of polymer N2200 has been investigated. It is found that the thickness dependent and temperature dependent J - V characteristics of N2200 electron-only devices can be accurately described by using the EGDM only with a single set of parameters, $a = 2.0$ nm, $\sigma = 0.08$ eV, and $\mu_0 = 2050$ m²/Vs. Alternatively, the thickness dependent and temperature dependent J - V characteristics of N2200 electron-only devices can also be well described using the ECDM only with a single set of parameters, $a = 0.4$ nm, $\sigma = 0.09$ eV, and $\mu_0 = 4000$ m²/Vs. This shows that a successful analysis of the $J(V)$ curves using either model does not yet convincingly prove that the disorder is uncorrelated or correlated. In particular, for the specific material studied, we argue that the energies of the sites in between which hopping takes place are uncorrelated, based on a comparison of the effective lattice parameter a found using both models with the typical value of organic semiconductors.

Acknowledgements

This work is supported by the Fundamental Research Funds for the Universities of Henan Province Grant No. NSFRF200304, the Training plan of young backbone teachers in Colleges and Universities of Henan Province Grant No. 2019GGJS060, 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 and No. B2017-20.

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