JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 19, No. 5 - 6, May – June 2017, p. 406 - 411

Hole transport and electrical properties in polyspirobifluorene with copolymerized hole transport units

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

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

The hole transport and electrical properties in blue light-emitting polyspirobifluorene (PSF) with copolymerized $N, N, N^{'}, N^{'}$ tetraaryldiamino biphenyl (TAD) hole transport units are investigated. It is shown that the temperature dependent and TAD concentration dependent current density versus voltage characteristics of PSF hole-only devices can be accurately described by using our recently introduced improved mobility model based on both the Arrhenius temperature dependence and non-Arrhenius temperature dependence. For the light-emitting diodes based on PSF with 0% and 5% TAD units, it is found that the boundary carrier density has an important effect on the current density versus voltage characteristics. Too large or too small values of the boundary carrier density lead to incorrect current density versus voltage characteristics. In order to reach the same current density at the same boundary carrier density, the stronger electric field and corresponding larger voltage are needed at 5% TAD concentration than that of 0% TAD concentration. In addition, it is found that the numerically calculated carrier density is a decreasing function of the distance from the interface, and the numerically calculated electric field is an increasing function of the distance from the interface. Both the maximum of carrier density and the minimum of electric field appear near the interface.

(Received January 6, 2017; accepted June 7, 2017)

Keywords: Conjugated polymers, Hole transport, Electrical properties

1. Introduction

In recent decades, conjugated polymers have been investigated intensively due to their potential in display and lighting applications [1, 2]. A prerequisite for full-color applications is efficient blue emitters. Polyfluorenes (PFs) are attractive blue emitters due to their wide band gap and high photoluminescence efficiency [3, 4]. The first polyfluorene polymer light-emitting diode (PLED) was reported by Yoshino et al. [5, 6], and the material suffered from a low molecular weight and a poor device performance. Since then, considerable progress has been made in the synthesis of polyfluorene derivatives and the improvement of device performance. Polyspirobifluorene (PSF) is a polymer from the PFs family in which the spiro-center links two PF units to each other, making the polymer more stable and more efficient for light emission [7]. As is well known, charge balance is a critical issue for the efficiency of PLEDs. However, Polyfluorene derivatives mostly have a high ionization potential resulting in a large injection barrier for holes, which is detrimental for the PLED performance [8]. To improve the injection and conduction of holes, PFs are often copolymerized with hole-transport units (HTU) (called guests) like arylamines, and hole mobilities up to $3\times10^{-7} m^2V^{-1}s^{-1}$ have been reported in these copolymers [9]. Furthermore, the hole transport can be tuned by varying the arylamine content, under the condition that their highest occupied molecular orbital (HOMO) energy is higher than that of the host polymer [10]. At low concentrations the amine units act as trapping sites for holes and reduce the hole current, whereas above a critical concentration (typically 3-10%), the hole transport from guest to guest becomes possible, leading to an increase of the mobility with increasing amine concentration [11-13].

Understanding the charge transport and availability of physical models in conjugated polymers is very important to further improve device performances. In particular, it is crucial to understand how the charge-carrier mobility depends on various parameters of the system. In several literatures, the dependence of the carrier mobility on the temperature and electric field in conjugated polymers has been investigated [14-18]. Recently, it was recognized that the importance of another parameter had been overlooked: the charge-carrier density [19, 20]. It has been demonstrated that at room temperature it is sufficient to take only the carrier density dependence of the mobility into account, but that at low temperatures the field dependence of the mobility becomes increasingly more important [21]. Therefore, the mobility in conjugated polymers is dependent on the temperature, electric field, and carrier density. Based on these results, Pasveer et al. developed a charge transport model for the mobility that takes into account both the electric field and carrier density dependence [22], also termed as the “extended Gaussian disorder model” (EGDM). However, it should be noted that their model, only having a non-Arrhenius temperature dependence $\ln(\mu) \propto 1/T^2$, can well describe the charge transport at low carrier densities, whereas at high carrier densities, it becomes unsatisfactory. To better describe the charge transport, we proposed an improved unified description of the temperature, electric field, and carrier density dependence of the mobility based on both the Arrhenius temperature dependence $\ln(\mu) \propto 1/T$ and non-Arrhenius temperature dependence $\ln(\mu) \propto 1/T^2$ [23]. It has been demonstrated that the improved mobility model can well describe the charge transport at both low and high carrier densities.

In this paper, the hole transport and electrical properties in the blue light-emitting diodes based on polyspirobifluorene with a varying number of N,N,N',N' tetraaryldiamino biphenyl (TAD) hole-transport units (HTUs) are studied. Firstly, a detailed analysis of the temperature dependent and TAD concentration dependent current density versus voltage ($J-V$) characteristics of PSF hole-only devices is performed by using the improved mobility model. Subsequently, some important electrical properties for the PSF-TAD copolymer are analyzed, including the variation of $J-V$ characteristics with the boundary carrier density and the distribution of the carrier density and electric field with the distance from the interface. In Section 2 the improved mobility model and an uneven discretization numerical method are presented. In Section 3 the systematic study of the hole transport and electrical properties for the PSF-TAD copolymer is given. Section 4 contains a summary and conclusions.

2. Model and methods

The improved unified description of the temperature T, electric field E, and carrier density p dependence of the mobility μ based on both the Arrhenius temperature dependence and non-Arrhenius temperature dependence can be described as follows [23]:

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

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

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

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 charge-carrier density and electric field, $\hat{\sigma} \equiv \sigma/k_BT$ and σ the width of the Gaussian density of states (DOS), a the lattice constant, e the charge of the carriers, and ν_0 the attempt frequency.

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

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

where $g(T,E)$ is a weak density dependent function, c_4 and c_5 are weak density dependent parameters, given by

$$c_4 = d_1 + d_2\ln(pa^3) \tag{4a}$$

$$c_5 = 1.16 + 0.09\ln(pa^3) \tag{4b}$$

$$d_1 = 28.7 - 36.3\hat{\sigma}^{-1} + 42.5\hat{\sigma}^{-2} \tag{5a}$$

$$d_2 = -0.38 + 0.19\hat{\sigma} + 0.03\hat{\sigma}^2 \tag{5b}$$

By using the above model, the J-V characteristics and other electrical properties of conjugated polymers can be obtained by numerically solving the coupled equations.

$$J = p(x)e\mu(T,p(x),E(x))E(x), \tag{6a}$$

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

$$V = \int_0^L E(x)dx, \tag{6c}$$

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

It is obvious that Eq. (6) is nonlinear integrodifferential equation. In order to exactly solve the equation, a particular discretization method is presented. First, Eq. (6) is discretized by dividing the thickness L into n segments as follows:

$$\Delta x = L/n^m,\ x_i = i^m\Delta x,\ i = 0,\cdots,n. \tag{7}$$

The values of $p(x)$ and $E(x)$ are represented as

$$p_i = p(x_i),\ E_i = E(x_i). \tag{8}$$

Then Eq. (6) can be transformed to the following form

$$J = ep_i \mu(T, p_i, E_i) E_i , \tag{9a}$$

$$\frac{(E_{i+1} - E_i)}{[(i+1)^m - i^m]\Delta x} = \frac{e}{\varepsilon_r \varepsilon_0} p_i , \tag{9b}$$

$$V = \frac{1}{2} \Delta x \sum_{i=1}^{n} (E_i + E_{i-1})[i^m - (i-1)^m] , \tag{9c}$$

where Eq. (9b) is from Eq. (6b) by adopting the numerical differentiation and Eq. (9c) is from Eq. (6c) by adopting the trapezoid integral approach.

It can be seen from Eq. (9) that, for the given T and J, the corresponding value of V can be easily obtained by using the following procedure: Firstly, the value of p_0 for the given T and J is assumed. Subsequently, E_0 can be obtained from Eq. (9a) by using Newton Iterative Method. Then the following two steps are repeated n times ($i = 0 \sim (n-1)$): evaluating E_{i+1} from Eq. (9b) and solving p_{i+1} from Eq. (9a) by Newton Iterative Method again. Finally, once all values of E_i ($i = 0 \sim n$) are evaluated, the voltage V can be easily obtained from Eq. (9c).

3. Results and discussion

To study the hole transport in blue light-emitting PSF with TAD hole transport units in a systematic way, the investigation of the host PSF polymer itself (0% TAD) is performed first. Figure 1 shows the hole transport for a PSF hole-only device with 300 nm thickness at different temperatures. The hole transport is modeled using the improved mobility model and numerical calculation method as described in Sec. 2. For the PSF polymers with 0% TAD, a single set of parameters $\sigma = 0.125$ eV, $a = 1.3$ nm, and $\mu_0 = 250$ m^2/Vs can consistently describe the hole transport. In an earlier study for the PSF-TAD copolymers, Nicolai et al. demonstrated that the hole transport in the copolymers with TAD concentrations ranging from 5~12.5 molar percent is trap-free space-charge-limited transport, and can be described by the extended Gaussian disorder model (EGDM) [25]. In order to further study the hole transport in PSF polymers with different concentrations of TAD, the improved mobility model is used to describe the hole transport in the PSF polymers with 0%, 5%, and 10% TAD concentration. Figure 2 shows the $J-V$ characteristics of all hole-only devices for 0%, 5%, and 10% TAD copolymers with thickness around 200 nm. As is clear from the figure for the 5% TAD copolymer, the mobility drops an order of magnitude as compared to the 0% TAD. The disorder parameter σ is 0.125 eV and the site spacing value is 1.3 nm for all copolymers, same as the parameters obtained in Figure 1. In addition, it is worth noting that the value of the disorder parameter σ and the site spacing a are significantly smaller than what were obtained by using the EGDM [25]. As for the parameter μ_0, it ranges from 250, 35, and 80 m^2/Vs for 0%, 5%, and 10% TAD concentration, respectively. It is clear from Fig. 1 and Fig. 2 that our calculated results are in good agreement with experimental data. This suggests that the improved mobility model is suitable to study the $J-V$ characteristics of PSF-TAD copolymer.

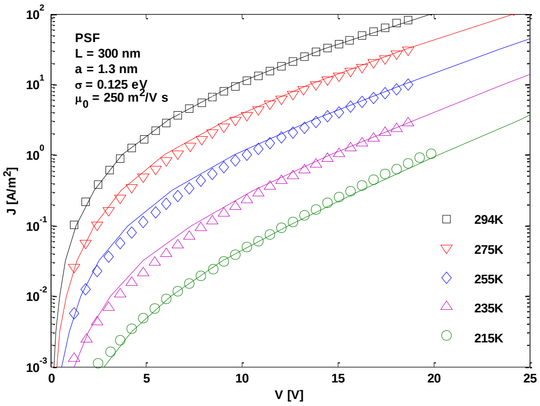

Fig. 1. Temperature dependent J-V characteristics of a PSF hole-only device with a layer thickness of 300 nm. Symbols are experimental data from Ref. [24]. Lines are the numerically calculated results from Eqs. (1) – (6)

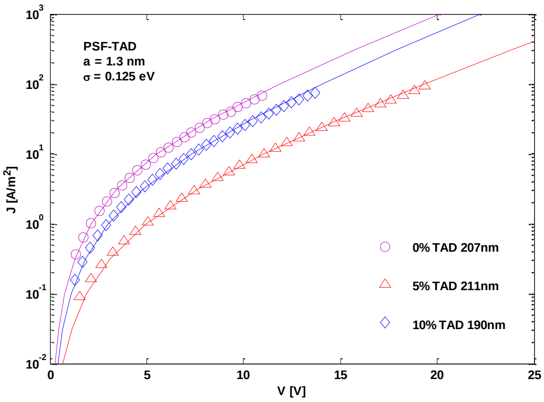

Fig. 2. J-V characteristics of hole-only devices based on PSF with 0%, 5% and 10% TAD concentration. Symbols are experimental data from Ref. [24]. Lines are the numerically calculated results from Eqs. (1) – (6)

The variation of $J-V$ characteristics with the boundary carrier density $p(0)$ (the carrier density at the interface) for PSF with 0% and 5% TAD concentration at room temperature is plotted in Fig. 3. The figure shows that the voltage is an increasing function of the current density, and the variation of voltage with $p(0)$ is dependent on the current density. The voltage decreases with increasing $p(0)$ for relatively small $p(0)$, and also increases with increasing $p(0)$ for sufficiently large $p(0)$. However, in the middle region of $p(0)$, the $V - p(0)$ curves are fairly flat. This means that the voltage is almost independent on $p(0)$ in this region. As a result, too large or too small values of the boundary carrier density lead to incorrect $J-V$ characteristics, whereas the values of the boundary carrier density in the middle region can achieve reasonable results. The physical reason of variation in the figure can be explained as follows. At small $p(0)$ region, the carrier concentration in the bulk materials is small, and the impedance and voltage are relatively large. As $p(0)$ increasing into the middle region, the injection of carriers near the interface and the drain into the bulk materials reach equilibrium, the $J-V$ characteristics enters into the Ohmic region, and the $V-p(0)$ curves become flat. Moreover, it is clear from the figure that in order to reach the same current density J at the same $p(0)$, the stronger electric field and corresponding larger voltage are needed at 5% TAD concentration than that of 0% TAD concentration.

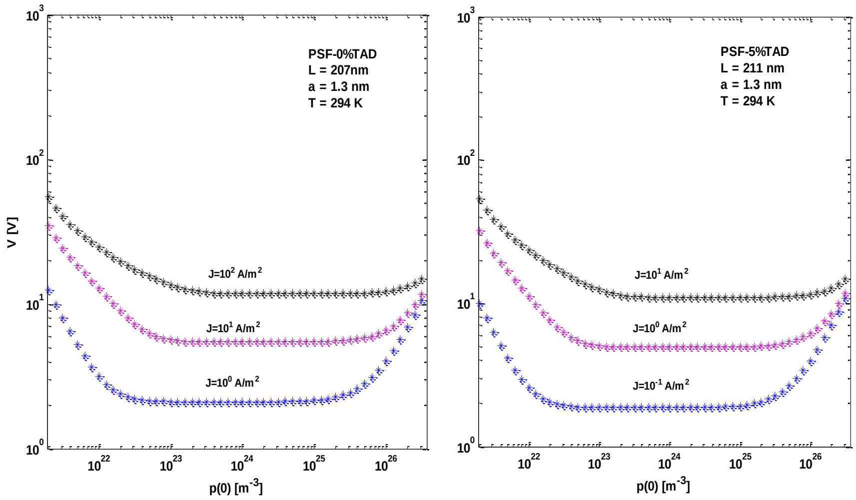

Fig. 3. Theoretical results of voltage versus the boundary carrier density for polymer layers of PSF with 0% and 5% TAD concentration at room temperature. Different Lines correspond to different current density values

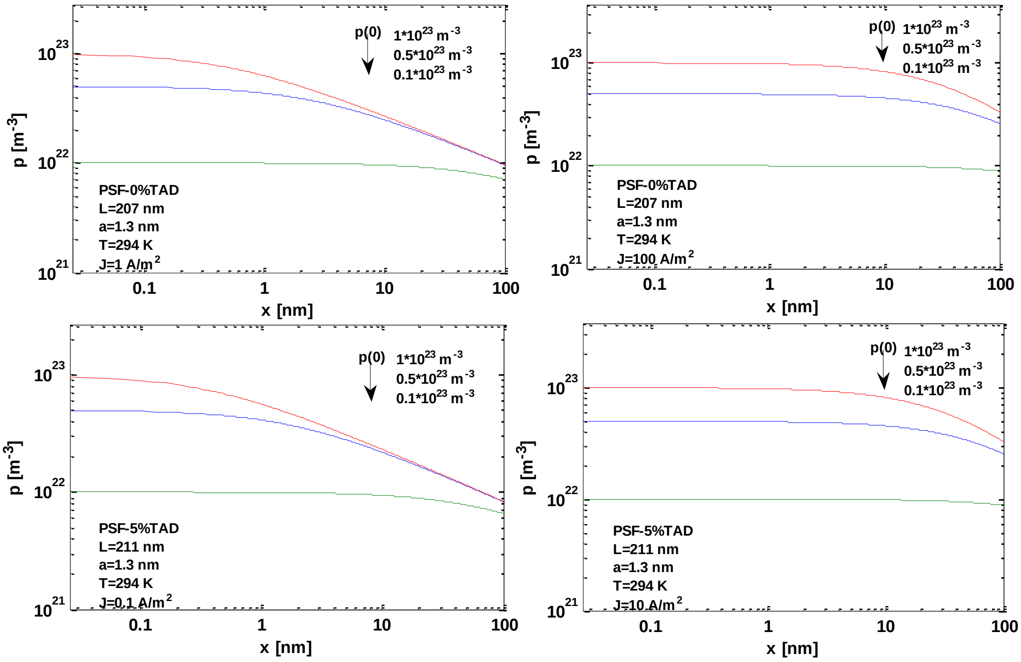

Fig. 4. Numerically calculated distribution of the charge-carrier density p as a function of position x in hole-only devices based on PSF with 0% and 5% TAD concentration at various current densities

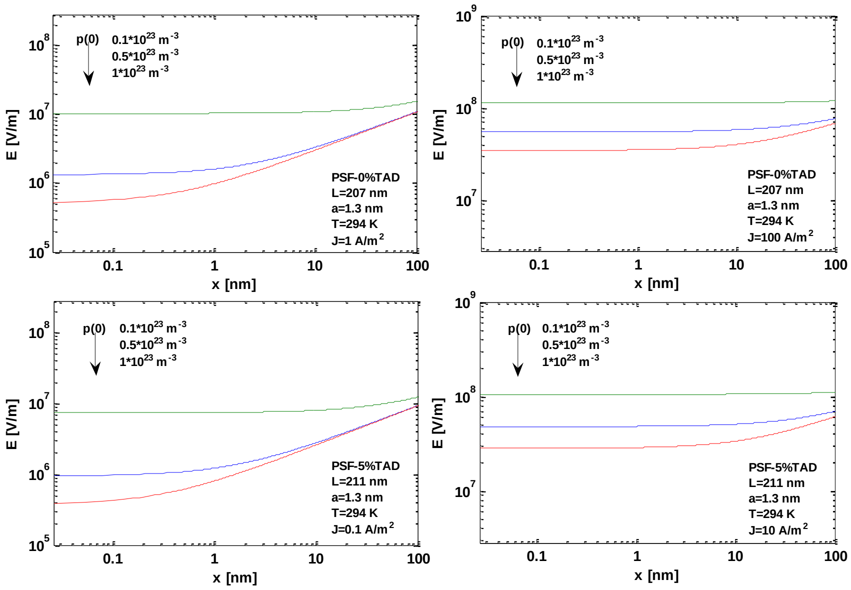

Fig. 5. Numerically calculated distribution of the electric field E *as a function of position* x *in hole-only devices based on PSF with 0% and 5% TAD concentration at various current densities*

Fig. 4 shows the calculated results of the carrier density as a function of the position (the distance from the interface) for hole-only devices based on PSF with 0% and 5% TAD concentration. As in an earlier study for a similar type of copolymer, R. J. de Vries et al. indicated that the density range of 10^{22}–10^{23} m^{-3} is the most sensitive region used for probing the mobility in the related organic electronic devices [26]. Thus we take three values of $p(0)$, (0.1, 0.5, 1) $\times 10^{23}$ m^{-3}, for PSF and PSF-TAD in the calculations. It is clear that the carrier density $p(x)$ is a decreasing function of the distance x, the speed of decrease is rapid for relatively large $p(0)$. With the distance x increasing, $p(x)$ rapidly reaches saturation in the bulk materials. Moreover, it can be seen from the figure that the thickness of accumulation layer (or decay distance) is a function of $p(0)$. The larger the value of $p(0)$ is, the smaller the thickness of accumulation layer is, vice versa. Figure 5 shows the calculated results of the electric field as a function of the position for hole-only devices based on PSF with 0% and 5% TAD concentration. It is clear that the electric field $E(x)$ is an increasing function of the distance x. The speed of increase is rapid for relatively large $p(0)$, and is slow for small $p(0)$. The thickness of accumulation layer deduced from the figure is consistent with Fig. 4. In the end, the results on $p(x)$ and $E(x)$ presented in Fig. 4 and Fig. 5 clearly exhibit the space-charge limited current density and voltage. The injection of carriers from electrode into polymer layers leads to carriers accumulation near the interface and a decrease in function $p(x)$. The distribution $p(x)$ leads to the variation in $E(x)$, and the carriers accumulation near the interface results in an increase in function $E(x)$.

4. Summary and conclusions

The hole transport and electrical properties in a series of PSF-TAD copolymers are studied. It is shown that the current density versus voltage characteristics of PSF hole-only devices with various temperatures and TAD concentrations can be well described using our improved mobility model. The width of the DOS and the value of the lattice constant are found to be essentially independent of the TAD concentration. The mobility of the 5% TAD copolymer is one order of magnitude lower than the 0% TAD copolymer. Moreover, it is found that too large or too small values of the boundary carrier density lead to incorrect $J-V$ characteristics. The maximum of carrier density and the minimum of electric field appear near the interface. In conclusion, the coupled equations combining the improved mobility model can give an excellent description of the hole transport in PSF-TAD copolymers. The results open the prospect that our improved mobility model can provide the appropriate framework for describing the guest concentration dependence of the charge carrier transport.

Acknowledgements

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

References

[1] 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).
[2] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. D. Santos, J. L. Bredas, M. Logdlund, W. R. Salaneck, Nature **397**, 121 (1990).
[3] Q. Pei, Y. Yang, J. Am. Chem. Soc. **118**, 7416 (1996).
[4] W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, E. P. Woo, Appl. Phys. Lett. **73**, 629 (1998).
[5] M. Fukuda, K. Sawada, K. Yoshino, Jpn. J. Appl. Phys. **28**, L1433 (1989).
[6] Y. Ohmori, M. Uchida, K. Muro, K. Yoshino, Jpn. J. Appl. Phys. **30**, L1941 (1991).
[7] W. L. Yu, J. Pei, W. Huang, A. J. Heeger, Adv. Mater. **12**, 828 (2000).
[8] A. J. Campbell, D. D. C. Bradley, H. Antoniadis, J. Appl. Phys. **89**, 3343 (2001).
[9] M. Redecker, D. D. Bradley, M. Inbasekaran, W. W. Wu, E. P. Woo, Adv. Mater. **11**, 241 (1999).
[10] S. Harkema, R. A. H. J. Kicken, B. M. W. Langeveld-Voss, S. L. M. van Mensfoort, M. M. de Kok, R. Coehoorn, Org. Electron. **11**, 755 (2010).
[11] D. M. Pai, J. F. Yanus, M. Stolka, J. Phys. Chem. **88**, 4714 (1984).
[12] 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).
[13] I. Fishchuk, A. Kadashchuk, A. Vakhnin, Y. Korosko, H. Bässler, B. Souharce, U. Scherf, Phys. Rev. B **73**, 115210 (2006).
[14] H. Bässler, Phys. Status Solidi B **175**, 15 (1993).
[15] Y. N. Gartstein, E. M. Conwell, Chem. Phys. Lett. **245**, 351 (1995).
[16] D. H. Dunlap, P. E. Parris, V. M. Kenkre, Phys. Rev. Lett. **77**, 542 (1996).
[17] S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, A. V. Vannikov, Phys. Rev. Lett. **81**, 4472 (1998).
[18] Z. G. Yu, D. L. Smith, A. Saxena, R. L. Martin, A. R. Bishop, Phys. Rev. Lett. **84**, 721 (2000).
[19] Y. Roichman, N. Tessler, Synth. Met. **135**, 443 (2003).
[20] C. Tanase, E. J. Meijer, P. W. M. Blom, D. M. de Leeuw, Phys. Rev. Lett. **91**, 216601 (2003).
[21] C. Tanase, P. W. M. Blom, D. M. de Leeuw, Phys. Rev. B **70**, 193202 (2004).
[22] W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. deLeeuw, M. A. J. Michels, Phys. Rev. Lett. **94**, 206601 (2005).
[23] L. G. Wang, H. W. Zhang, X. L. Tang, C. H. Mu, Eur. Phys. J. B **74**, 1 (2010).
[24] D. Abbaszadeh, H. T. Nicolai, N. I. Crăcium, P. W. M. Blom, Phys. Rev. B 90, 205204 (2014).
[25] H. T. Nicolai, A. J. Hof, M. Lu, P. W. M. Blom, R. J. De Vries, R. Coehoorn, Appl. Phys. Lett. **99**, 203303 (2011).
[26] 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).

---

[*] Corresponding author: wangliguo@hpu.edu.cn