Hole and electron transport in a fluorene-based copolymer

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Hole and electron transport in a fluorene-based poly[(9,9-di-n-octylfluorenyl-2,7-diyl)-alt-(benzo[2,1,3]thiadiazol-4,8-diyl)] (F8BT) are investigated. It is shown that the current density versus voltage characteristics of F8BT hole- and electron-only devices can be well described using our recently introduced improved mobility model. For the material studied, we find the width of the Gaussian density of states 0.11 eV for F8BT hole-only devices, and 0.19 eV for F8BT electron-only devices. Apparently, the electron transport exhibits a significantly stronger energy disorder than hole transport. Furthermore, we investigate the current density versus voltage characteristics of F8BT electron-only devices doped with 4% and 10% concentrations of n-type dopant decamethylcobaltocene (DMC). It is demonstrated that our improved model can also be applied to *n*-type doping conjugated polymers and the electron transport in doped conjugated polymers can be calculated without needing to add an additional free electron background density. The width of the Gaussian density of states obtained for doped electron-only devices exhibits the same disorder as undoped hole-only devices and a smaller disorder than undoped electron-only devices, indicating that the electron mobility can be enhanced by doping up to the hole mobility.

(Received April 2, 2018; accepted October 10, 2018)

Keywords: Hole Transport, Electron Transport, Fluorene-based copolymer

1. Introduction

Fluorene-based conjugated polymers are attractive as active material in organic electronic devices such as organic light-emitting diodes (OLEDs), organic photovoltaic (OPV) devices, and organic field-effect transistors (OFETs). They combine high quantum efficiencies with thermal stability, insensitivity to photo-oxidation, and cheap processing methods for fabrication of electronic devices. With an alternation of poly(fluorene-2,7-diyl) (F8) and benzothiadiazole (BT) units, poly(9,9-dioctylfluorene-alt-BT) (F8BT) has been intensively used for polymer light-emitting diodes (PLEDs) exhibiting high quantum and power efficiencies [1-3]. Next to PLEDs, F8BT is also utilized as active electron donor or acceptor material in all-polymer bulk heterojunction solar cells, where it is blended with other fluorene based copolymers [4-8]. Furthermore, F8BT is also a good candidate for light-emitting field effect transistors because of its good luminescent properties and relatively high electron field-effect mobility of $\sim 10^{-3}$ cm^2/Vs [9, 10]. However, in diode structures, relevant for PLEDs and OPV blends, the charge transport of F8BT has not been extensively studied so far.

It is of crucial importance to understand the charge transport of F8BT in order to improve the efficiency and lifetime of devices. However, the investigations of hole transport properties in the past are hindered by the large hole injection barrier from common electrodes as Au or poly(3,4-ethylenedioxythiophene):poly(styrenesulfonicacid) (FEDOT:PSS), due to the deep highest occupied molecular orbital (HOMO). Fortunately, it is demonstrated that the hole injection problem can be solved by using the high work function molybdenum trioxide (MoO_3) as an anode in organic electronic devices based on poly(9,9-dioctylfluorene) (PFO), which has a similar HOMO level as F8BT [11]. In a recent study, an Ohmic hole contact on F8BT has been achieved by Zhang *et al.* using the anode MoO_3 as hole injection contact, enabling the occurrence of space-charge limited currents (SCLC) [12]. On the other hand, regarding electron transport the intrinsic electron mobility in conjugated polymers is often masked by the presence of traps [13-15]. However, it has recently been shown that the electron traps in poly(2-methoxy-5–2-ethylhexyloxy-1,4-phenylenevinylene) (MEH-PPV) can be deactivated by addition of the *n*-type dopant decamethylcobaltocene (DMC) [16]. Furthermore, Zhang *et al.* have demonstrated that a trap-free SCL electron current can be obtained in F8BT by filling the traps with electrons from the DMC donor [12], enabling a direct measurement of the free electron mobility. As a result, the occurrence of SCL hole and electron current makes it possible to further investigate the hole and electron transport in F8BT.

In order to better describe the charge transport, we recently proposed a device model in which the mobility depends on the electric field, charge-carrier density, and temperature [17]. It has been demonstrated that the mobility model can rather well describe the charge transport in various organic materials [18-21]. Herein, we will apply the model to study hole and electron transport in F8BT. Firstly, we analyze the temperature dependent current density versus voltage ($J-V$) characteristics of a F8BT hole-only device. Subsequently, we perform a detailed analysis of thickness dependent $J-V$ characteristics of electron-only devices based on pure F8BT and the $J-V$ characteristics of electron-only devices based on F8BT doped with different concentrations of DMC. These results are very important for the design of new organic materials and further improvement of the performance of organic electron devices.

2. Model and methods

For a complete description of the SCLC, both the electric field dependence- and carrier density dependence of the mobility need to be taken into account [22, 23]. Based on the extended Gaussian disorder model (EGDM) [24], we recently proposed an improved device model in which the dependence of the mobility μ on the electric field E, carrier density p, and temperature T can be described as follows [17]:

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

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

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

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

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

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 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 intersite distance, and ν_0 is the attempt frequency, c_4 and c_5 are weak density dependent parameters, given by

$$c_4=d_1+d_2\ln(pa^3) \quad (4a)$$

$$c_5=1.16+0.09\ln(pa^3) \quad (4b)$$

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

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

To better describe the hole and electron transport in F8BT, the SCLC model is combined with the above improved field- and carrier density dependent mobility of Eqs.(1)-(5). The $J-V$ characteristics of the electron devices based on F8BT can be obtained by solving the following equations adopting a particular numerical method introduced in our previous papers [25, 26].

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

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

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

where x is the depth in the organic film, $\varepsilon_0\varepsilon_r$ is the permeability of the organic materials, and L is the organic film layer thickness.

3. Results and discussion

In Fig. 1 the $J-V$ characteristics of a F8BT hole-only device using an Ohmic MoO_3 top contact are shown for various temperatures. The experimental data from Ref. [12] are fitted with the improved mobility model of the temperature, carrier density and electric field dependence of the mobility and the numerical method as described in Section 2. At room temperature a hole mobility of 4×10^{-10} m^2/Vs is obtained. As shown in Fig. 1, the temperature dependent $J-V$ characteristics are described by using a of 1.3 nm, σ of 0.11 eV, and μ_0 of 150 m^2/Vs. Similar values for parameters of a and σ were recently found for other polyfluorene derivatives [18, 26, 27]. It is clear that our calculated results are in good agreement with the experimental data. This suggests that the improved mobility model is suitable to study the $J-V$ characteristics of F8BT hole-only devices.

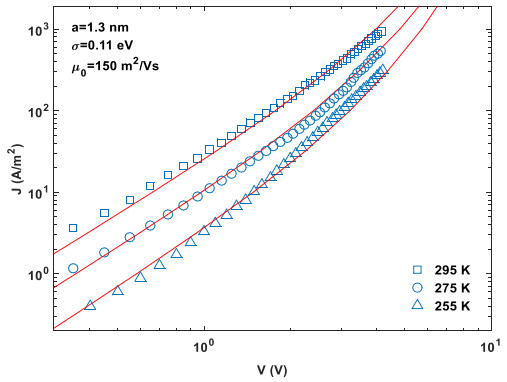

Fig. 1. Temperature dependent current density versus voltage characteristics of a F8BT hole-only device with a layer thickness of 74 nm. Symbols are the experimental results from Ref. [12]. Lines are the numerically calculated results from Eqs. (1) – (6)

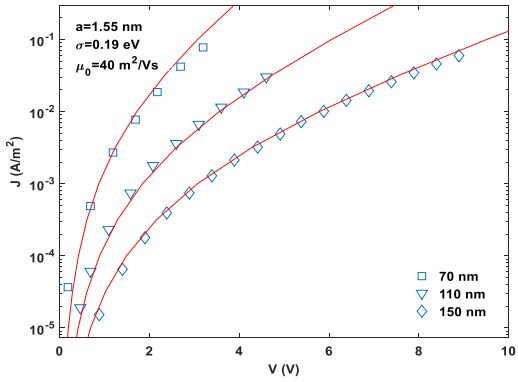

Fig. 2. Thickness dependent current density versus voltage characteristics of F8BT electron-only devices at 295 K. Symbols are experimental results from Ref. [28]. Lines are the numerically calculated results from Eqs. (1) – (6)

The $J-V$ characteristic of F8BT electron-only devices for various thicknesses at room temperature is shown in Fig. 2. Apparently, the experimental results of different thicknesses devices from Ref. [28] can be accurately described by our improved mobility model only with a set of parameters, $a=1.55$ nm, $\sigma=0.19$ eV, $\mu_0=40\,\mathrm{m^2/Vs}$. However, interpreting the similar results using the standard analytical model was found to be apparently dependent on the thickness of the polymer film, which needs to vary the values of fitting parameters to obtain the best-fit curves for different thicknesses [27, 28]. Therefore, to completely understand the charge transport, it is necessary that a proper model include the effects of the carrier concentration and energetic disorder to mobility. As for the parameters, the width of the DOS distribution (0.19 eV) is considerably larger than obtained for hole-only device (0.11 eV), indicating a high degree of energetic disorder. The observation of strong disorder is in agreement with the low value obtained for F8BT electron mobility, which is $4\times10^{-13}\,\mathrm{m^2/Vs}$ at room temperature. It is clear that electron transport exhibits a significantly stronger disorder than hole transport for F8BT, which is also reflected in the lower electron mobility as compared to the hole mobility of $4\times10^{-10}\,\mathrm{m^2/Vs}$. The larger value of the width of the DOS for electron-only devices and poor electron transport in F8BT can be explained by the presence of traps. Previous studies of electron transport in conjugated polymers have included specific modeling of shallow traps or traps combined with energetic disorder in order to account for apparent temperature and thickness dependence of mobility [13, 14]. The latter of these studies reconciles the difference in electron and hole mobilities by assuming that electron transport is limited by charge trapping. However, the above results in the present work suggest that models based solely on energetic disorder can also account for such effects, indicating that organic materials can be described simply by a single value of energetic disorder, without needing to refer to an explicit distribution of trap states.

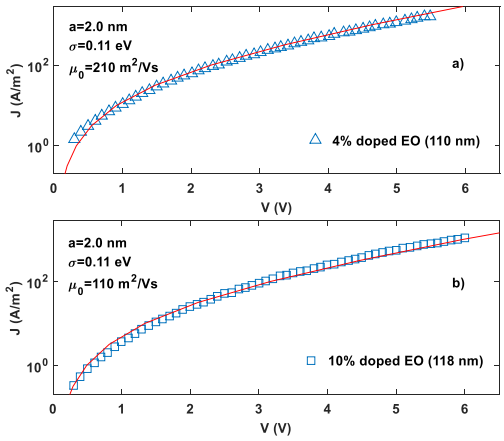

Fig. 3. The current density versus voltage characteristics of F8BT electron-only devices doped with 4% and 10% concentrations of DMC. Symbols are experimental results from Ref. [12]. Lines are the numerically calculated results from Eqs. (1) – (6)

The poor electron transport in many conjugated polymers has been explained by the presence of traps. It was proposed that modeling of the electron currents alone is not sufficient to determine the intrinsic electron mobility as well as the total amount of trap states and their position inside the band gap. However, it has been demonstrated that the electron traps in MEH-PPV can be deactivated by addition of the *n*-type dopant decamethylcobaltocene (DMC) [16]. Recently, a trap-free space-charge limited electron current has been obtained in F8BT by employing the same method [12], enabling a direct measurement of the free electron mobility. It is shown that the electrons of DMC not only fill the traps, but also donate electrons to the LUMO of F8BT such that the electron transport can be

enhanced even beyond the hole transport. As can be observed in Fig. 3, the $J-V$ characteristics of electron-only devices based on F8BT doped with various concentrations of *n*-type dopant DMC can be excellently described by using the improved mobility model. The parameters, $a = 2.0$ nm, $\sigma = 0.11$ eV, $\mu_0 = 210$ m^2/Vs for 4% doping concentration and $\mu_0 = 110$ m^2/Vs for 10% doping concentration are determined in such a way that an optimal fit is obtained. Apparently, our improved mobility model can also be applied to fluorene-based copolymer doped with *n*-type dopant DMC. Furthermore, it is clear that the electron transport in DMC-doped electron-only devices can be calculated without needing to add an additional free electron background density, leading to a simplified model as compared to the EGDM adopting by Zhang *et al*. [12]. As for the parameter σ, the doped electron-only devices of F8BT exhibits a significantly smaller disorder than undoped electron-only devices of F8BT. This is also in agreement with the fact that the traps can be deactivated by *n*-type dopant DMC, resulting in a higher electron mobility in doped F8BT. In addition, it should be noted that the values of obtained parameter σ for doped F8BT electron-only devices is the same as the undoped F8BT hole-only devices, indicating that the electron mobility can be enhanced by doping up to the hole mobility or even more.

4. Summary and conclusions

In conclusion, the hole and electron transport in F8BT have been characterized. We have implemented an improved mobility model that can successfully describe the temperature and thickness dependence of SCL charge transport in F8BT without needing to include specific trapping sites. This is especially significant in the case of electron transport as most previous attempts to model electron transport in conjugated polymers have described electron currents as being a trap-limited process. For F8BT, we found that hole transport can be modeled using a Gaussian disorder of 0.11 eV and electron transport with 0.19 eV, suggesting that electron transport exhibits a significantly stronger energy disorder than hole transport. This is also reflected in the lower electron mobility of 4×10^{-13} m^2/Vs as compared to hole mobility of 4×10^{-10} m^2/Vs. Furthermore, it was found that electron transport can be enhanced using *n*-type doping by DMC, leading to the same disorder as hole transport. These results suggest that the improved model can be used for both positive and negative charge carriers in conjugated polymers, leading to simplified modeling of charge transport.

Acknowledgements

This work is supported by the National Natural Science Foundation of China Grant Nos. 61501175 and 61703145, and the Doctoral Scientific Research Foundation of Henan Polytechnic University Grant No. B2014-022.

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