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Quantitative analysis of the guest-concentration dependence of the mobility in a disordered fluorene-arylamine host-guest system in the guest-to-guest regime

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The charge transport in a polyspirobifluorene derivative with copolymerized N,N,N',N' -tetraaryldiamino biphenyl (TAD) hole transport units is investigated as a function of the TAD content. For TAD concentrations larger than 5%, guest-to-guest transport is observed. It is demonstrated that in this regime the charge carrier density dependent mobility can be described consistently with the extended Gaussian disorder model, with a density of hopping sites which is proportional to the TAD concentration and comparable to the molecular density. © 2011 American Institute of Physics. [doi:10.1063/1.3663563]

Since their discovery, organic semiconductors have been investigated intensively and they are today finding their way into applications such as displays and lighting. A prerequisite for full-color applications is an efficient blue emitter. Polyfluorenes (PF) form an attractive class of blue emitters due to their wide band gap and high photoluminescence efficiency.^{1,2} They are commonly used as blue emissive material in organic light-emitting diodes³ (OLEDs) or as host component for white emitting copolymers.^{4,5} The wide band gap, however, also complicates the charge injection; it is difficult to achieve efficient injection for both electrons and holes. Especially hole injection can be problematic in polyfluorenes due to the typical deep highest occupied molecular orbital (HOMO) level, which leads to an injection barrier when combined with a common anode material such as poly(3,4-ethylenedioxythiophene)/poly(styrenesulphonic acid) (PEDOT:PSS).⁶ By using the high work function electrode MoO₃, it has recently been possible to study the hole transport in the PF derivative poly(9,9-dioctylfluorene) in the space-charge limited current (SCLC) regime⁷ and to demonstrate that the hole transport is described by a mobility that depends on the electric field and the charge carrier density, as is well known for disordered organic materials.⁸ The electric field dependence of the mobility has, already in earlier work, been explained in the framework of hopping in a Gaussian density of states (DOS).^{9,10} More recently, it was recognized that the dependence of the mobility on the charge carrier density had been overlooked.^{8,11} A numerically exact description of the mobility in a Gaussian DOS, extended to include the dependence on the charge carrier density (“extended Gaussian disorder model,” EGDM), has been obtained from a master equation (ME) approach.¹² In this model, the mobility is characterized by three parameters, *viz.*

the width (standard deviation) of the Gaussian DOS σ , the density of hopping sites N_t , and the mobility in the limit of zero field, zero carrier density, and infinite temperature, μ_0^* .

Within the ME approach employed to derive the EGDM mobility functions, the hopping is assumed to take place between point-like sites on a cubic lattice. The question arises what the relationship is between the site density parameter N_t and the physical density of localized molecular states between which the hopping takes place. In this letter, we address this question by studying the hole transport in a series of polyalkoxyspirobifluorene- N,N,N',N' -tetraaryldiamino biphenyl (PSF-TAD) copolymers. These materials belong to a larger class of PF derivatives within which the injection and transport of holes is modified by the incorporation of arylamines, either blended in the active layer or incorporated into the polymer chain.¹³ Triarylamines are known to be good hole conductors¹⁴ and are commonly used as hole transport layers.^{2,15} Hole mobilities up to 3×10^{-7} m²/Vs have been measured in fluorene-triarylamine copolymers.¹⁶ Furthermore, the hole transport can be tuned by varying the arylamine content, under the condition that their HOMO energy is higher than that of the host polymer.¹⁷ At low concentrations the amine units act then as hole traps and reduce the hole current, whereas above a critical concentration, typically $\sim 3\%$,¹⁸ percolation can take place between the amine units and the hole transport will become governed by guest-to-guest hopping, leading to an increase of the mobility with increasing amine concentration.¹⁹ The EGDM transport parameters are then expected to be related to the guest DOS. For sufficiently dilute systems, one might envisage that σ is independent of the amine concentration and that N_t is equal to, or at least proportional to, the guest density. However, such relationships have so far not been established experimentally. We have studied the guest density dependence of σ and N_t for systems containing TAD as the hole transporting unit.

The TAD hole transport unit studied here is functionalized with two tert-butyl groups. Its structure is depicted in the

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inset of Fig. 1(a). The structure of the complete copolymer is published elsewhere.²⁰ The HOMO levels of PSF and the TAD unit have been estimated at -5.6 eV and -5.4 eV , respectively.^{21,22} The TAD concentration was varied from 5 to 12.5 mol. %, enabling a systematic study of the influence of the TAD concentration on the guest-to-guest hole transport. Hole-only devices were fabricated by first spin-coating a layer of PEDOT:PSS on a glass substrate with a patterned indium tin oxide layer. The PSF-TAD copolymer layers were subsequently spin-coated from a toluene solution in a nitrogen environment. Hole-only devices with a PSF-TAD layer thickness equal to (approximately) 80, 120, 200, and 280 nm were studied. The top contacts were evaporated through a shadow mask at a base pressure of approximately 10^{-6} mbar and consisted of a 20 nm layer of palladium capped with an 80 nm gold layer. The high work function of palladium ensures that there is no electron injection into the LUMO level of the polymer and that the device current is determined by the hole transport. No electroluminescence was observed, which confirms the absence of electron injection.

Fig. 1(a) shows the room temperature current-density–voltage (J – V) characteristics of devices with an active layer thickness of $\sim 200\text{ nm}$ and a TAD concentration of 5% and 7.5%, and Fig. 1(b) shows the current density as a function of the TAD concentration measured at 10 V. As a reference,

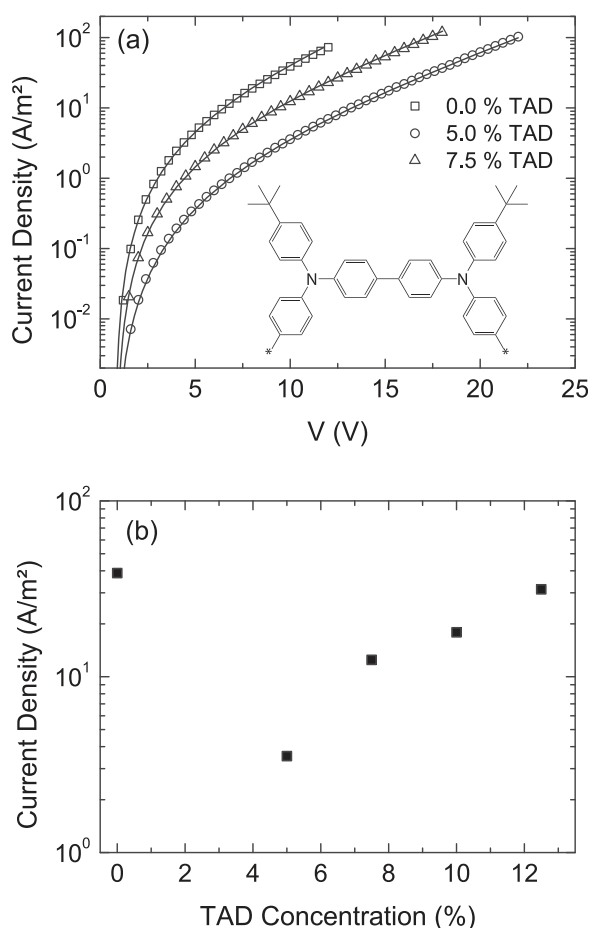


FIG. 1. (a) Current-density–voltage characteristics at TAD concentrations of 0%, 5%, and 7.5% and with a layer thickness of 207 nm, 215 nm, and 198 nm, respectively. The curves are best fits from the device model. The inset shows the structure of the TAD hole transporting unit. The asterisks indicate the attachment points. (b) Current density at 10 V as a function of the TAD concentration for the $\sim 200\text{ nm}$ systems studied.

also the results for the PSF host polymer are given (0% TAD concentration). As in an earlier study for a similar type of copolymer, the inclusion of 5% TAD lowers the hole current by approximately one order of magnitude compared to the hole current in the pure polyspirobifluorene polymer.¹⁸ No data are available for TAD concentrations below 5%. Therefore, it cannot firmly be established whether at 5% the TAD units act still as traps for the hole transport through the polyspirobifluorene. However for TAD concentrations of 7.5% and above, the hole transport increases with increasing TAD concentration, demonstrating the occurrence of guest-to-guest hopping for these concentrations. A simplified analysis of the $J(V)$ curves, using the well-known Mott-Gurney (MG) equation which neglects diffusion and which assumes a constant mobility,²³ gives rise to an effective mobility of approximately $8 \times 10^{-11} \text{ m}^2/\text{Vs}$ for the pure (0%) reference polymer, in reasonable agreement with the result of earlier time-of-flight measurements on a similar copolymer.²⁴ In that study the mobility could be increased beyond the host mobility by the inclusion of 50% TAD.

To take the effects of disorder on the carrier density dependence and field dependence of the mobility and the diffusion coefficient as described within the EGDM into account, the numerical drift-diffusion model developed in Ref. 25 has been used. We have analyzed the voltage, temperature, and layer thickness dependence of the current density to obtain the parameters describing the mobility function in the guest-to-guest hopping regime (TAD concentration $>5\%$). The polymer with 5% TAD is included, although it is not *a priori* clear whether the transport is then already well within this regime. The PEDOT:PSS contact is assumed to be Ohmic. In the following, V_{bi} is the built-in voltage, $\mu_0(T)$ is the mobility at temperature T in the limit of zero field and zero carrier density, and k_B is the Boltzmann constant. For each polymer, a least-squares method was first used to fit the dependence on voltage, thickness and temperature to the EGDM equations using a common set of parameters σ and N_t , but allowing $\mu_0(T)$ to be determined by the fitting. Different samples were allowed to have somewhat different temperature-independent values of V_{bi} . The resulting values of $\mu_0(T)$ were then fit to the expression $\mu_0(T) = \mu_0^* \exp[-C\hat{\sigma}^2]$, with $\hat{\sigma} \equiv \sigma/(k_B T)$, as expected within the EGDM. Using this expression for $\mu_0(T)$, Fig. 2 shows the measured and calculated temperature dependence of the $J(V)$ curves for a 198 nm device with a TAD concentration of 7.5%, with $V_{\text{bi}} = 1.6\text{ V}$. The inset shows the measured and calculated $1/T^2$ dependence of $\mu_0(T)$. For the systems studied, C ranged from ~ 0.42 to ~ 0.47 , with an error margin of approximately ± 0.04 . The values found are close to the value 0.42 given in Ref. 12 or 4/9 in Ref. 9. At room temperature, $\mu_0(T)$ was found to increase approximately 20-fold as the concentration increased from 5% to 12.5%. Assuming constant values of σ (see below) and of C , μ_0^* would then be expected to show a similar increase. However, in view of the error margin in the C -parameter, the required high-temperature extrapolation could not be made with sufficient accuracy. The values of V_{bi} ranged from 1.45 to 1.75 V for the various samples, perhaps because of variations of the dipole layer formed at the cathode interface. Well above V_{bi} , the shape of the $J(V)$ curves is almost independent of V_{bi} , greatly facilitating the accurate determination of the EGDM parameters.

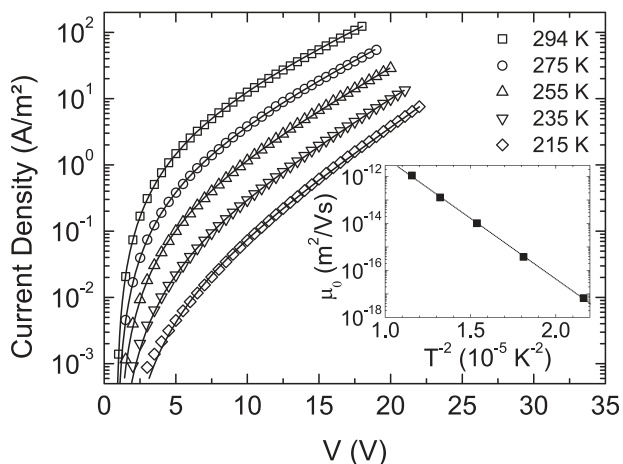


FIG. 2. Temperature dependent hole transport at 7.5% TAD and fits to the EGDM, for a 198 nm device. The inset shows the $1/T^2$ dependence of $\mu_0(T)$.

Fig. 3 shows the optimal values of N_t and σ for each polymer. The error margins indicate the range of values of N_t and σ for which the fit error (defined as the sum of the squares of the logarithmic deviation) is within 3% of the minimum fit error. The width of the Gaussian DOS needed to fit the data is close to $\sigma = 0.15$ eV, essentially independent of the TAD concentration, and consistent with the value obtained earlier for the polymer with 10% TAD.²⁰ For a TAD concentration of 7.5% and above, the TAD concentration dependence of N_t is, taking the error margins into account, well described by the proportionality relation given by the dashed line in Figure 3. For the concentration of 5%, N_t is slightly higher than expected, which might be due to the possibility that at this concentration the charge transport is in an intermediate regime where both the TAD units and the fluorene units contribute to the transport. In this regime, a more complicated model is required.²⁶ We remark that for higher concentrations the quality of the fit was less sensitive to the value of N_t , leading to a large error margin in N_t .

The hopping site density, as roughly estimated by assuming a density of 1 g/cm^3 for the polyspirobifluorene copolymer and assuming two transport sites per TAD unit, is equal to $\sim 2 \times 10^{26} \text{ m}^{-3}$ for the 10% copolymer. The value of N_t obtained from the present transport study ($\sim 3.5 \times 10^{26} \text{ m}^{-3}$) is in reasonable agreement with this estimate. This supports the point of view that the parameters as obtained when

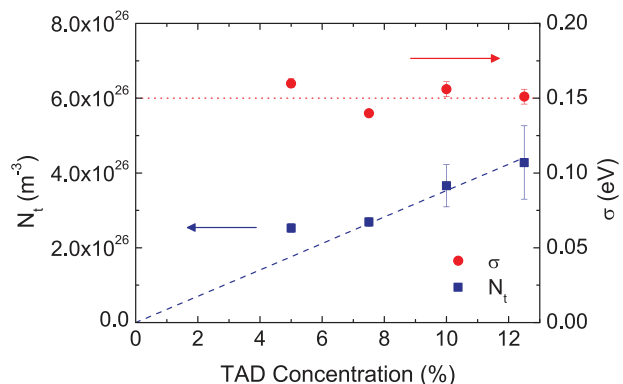


FIG. 3. (Color online) Optimal values of N_t and σ for each polymer. The experimental uncertainties are similar to the symbol sizes, or as indicated. The dashed and dotted lines are a guide to the eye.

describing the transport properties within the EGDM are physically meaningful.

In conclusion, we find that the hole transport in the poly-spirobifluorene copolymers as studied in the guest-to-guest regime is well-described using the EGDM. The analysis supports the point of view that the parameters obtained, describing the Gaussian DOS, is physically meaningful. First, the site density N_t is found to be proportional to the TAD concentration and reasonably close to the actual molecular site density. Second, the disorder parameter σ (~ 0.15 eV) is found to be essentially independent of the TAD concentration, as expected for sufficiently dilute systems. The results open the prospect that the EGDM can also provide the appropriate framework for describing the guest concentration dependence of the charge carrier transport in other host-guest systems operating in the guest-to-guest regime, including dye-doped fluorescent and phosphorescent emissive layers in small-molecule based OLEDs at high dye-concentrations.

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- ¹Q. Pei and Y. Yang, *J. Am. Chem. Soc.* **118**, 7416 (1996).
- ²A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Appl. Phys. Lett.* **73**, 629 (1998).
- ³K. T. Kamtekar, A. P. Monkman, and M. R. Bryce, *Adv. Mater.* **22**, 572 (2010).
- ⁴D. Buchhauser, M. Scheffel, W. Rogler, C. Tschamber, K. Heuser, A. Hunze, G. Gieres, D. Henseler, W. Jakobetz, K. Diekmann *et al.*, *Proc. SPIE* **5519**, 70 (2004).
- ⁵M. A. Parshin, J. Ollevier, M. Van der Auweraer, M. M. de Kok, H. T. Nicolai, A. J. Hof, and P. W. M. Blom, *J. Appl. Phys.* **103**, 113711 (2008).
- ⁶A. J. Campbell, D. D. C. Bradley, and H. Antoniadis, *J. Appl. Phys.* **89**, 3343 (2001).
- ⁷H. T. Nicolai, G. A. H. Wetzelaer, M. Kuik, A. J. Kronemeijer, B. de Boer, and P. W. M. Blom, *Appl. Phys. Lett.* **96**, 172107 (2010).
- ⁸C. Tanase, E. J. Meijer, P. W. M. Blom, and D. M. de Leeuw, *Phys. Rev. Lett.* **91**, 216601 (2003).
- ⁹H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).
- ¹⁰S. V. Novikov, D. H. Dunlap, V. M. Kenkre, P. E. Parris, and A. V. Vannikov, *Phys. Rev. Lett.* **81**, 4472 (1998).
- ¹¹R. Coehoorn, W. F. Pasveer, P. A. Bobbert, and M. A. J. Michels, *Phys. Rev. B* **72**, 155206 (2005).
- ¹²W. F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P. A. Bobbert, P. W. M. Blom, D. M. de Leeuw, and M. A. J. Michels, *Phys. Rev. Lett.* **94**, 206601 (2005).
- ¹³E. Bellmann, S. E. Shaheen, S. Thayumanavan, S. Barlow, R. H. Grubbs, S. R. Marder, B. Kippelen, and N. Peyghambarian, *Chem. Mater.* **10**, 1668 (1998).
- ¹⁴M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.* **88**, 4707 (1984).
- ¹⁵C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.* **51**, 913 (1987).
- ¹⁶M. Redecker, D. D. C. Bradley, M. Inbasekaran, W. W. Wu, and E. P. Woo, *Adv. Mater.* **11**, 241 (1999).
- ¹⁷S. Harkema, R. A. H. J. Kicken, B. M. W. Langeveld-Voss, S. L. M. van Mensfoort, M. M. de Kok, and R. Coehoorn, *Org. Electron.* **11**, 755 (2010).
- ¹⁸R. J. de Vries, S. L. M. van Mensfoort, V. Shabro, S. I. E. Vulto, R. A. J. Janssen, and R. Coehoorn, *Appl. Phys. Lett.* **94**, 163307 (2009).
- ¹⁹D. M. Pai, J. F. Yanus, and M. Stolka, *J. Phys. Chem.* **88**, 4714 (1984).
- ²⁰H. T. Nicolai, A. Hof, J. L. M. Oosthoek, and P. W. M. Blom, *Adv. Funct. Mater.* **21**, 1505 (2011).
- ²¹L. B. Lin, R. H. Young, M. G. Mason, S. A. Jenekhe, and P. M. Borsenberger, *Appl. Phys. Lett.* **72**, 864 (1998).
- ²²F. Laquai and D. Hertel, *Appl. Phys. Lett.* **90**, 142109 (2007).
- ²³N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940).
- ²⁴F. Laquai, G. Wegner, C. Im, H. Bässler, and S. Heun, *J. Appl. Phys.* **99**, 023712 (2006).
- ²⁵S. L. M. van Mensfoort and R. Coehoorn, *Phys. Rev. B* **78**, 085207 (2008).
- ²⁶Y. Y. Yimer, P. A. Bobbert, and R. Coehoorn, *J. Phys.: Condens. Matter* **20**, 335204 (2008).