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Analysis of hole transport in a polyfluorene-based copolymer— evidence for the absence of correlated disorder

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The presence of spatial correlation between the disordered transport site energies in semiconducting polymers used in organic electronic devices is known to affect the mobility. However, it is not established whether such a correlation is present in relevant polymers. We study hole transport in a polyfluorene-based copolymer and provide evidence for the absence of spatially correlated disorder in this material, based on an analysis of the current-voltage characteristics of sandwich-type devices. Distinguishing correlated from uncorrelated disorder, which we achieve on the basis of the hopping site density, is shown to be highly relevant for the development of quantitative device models. © 2009 American Institute of Physics. [DOI: 10.1063/1.3119317]

It is widely agreed that the charge carrier mobility in the disordered organic semiconductors used in organic light-emitting diodes (OLEDs) is determined by hopping between localized states. However, the development of transport models with predictive value is hampered by a lack of consensus about the type of energetic disorder: completely random or with correlation between the energies on neighbor sites. Within their pioneering Monte Carlo studies of the effects of disorder on the mobility, Bässler[1] assumed an uncorrelated Gaussian distribution of hopping site energies. Pasveer et al.[2] showed that an extension of their model to include a carrier density (n) dependence of the mobility,[3,4] leading to the "extended Gaussian disorder model" (EGDM), can well describe the temperature (T) dependent current-voltage characteristics [$J(V,T)$] of hole transport in sandwich-type devices based on polyphenylene-vinylene (PPV) polymers. A similar conclusion was recently obtained by van Mensfoort et al.,[5] who analyzed the $J(V,T)$ characteristics of hole-only polyfluorene-based copolymer devices with various layer thicknesses L. The successful use of the EGDM mobility functions,[6] as obtained from a master-equation (ME) approach within which the nonequilibrium ("hot") carrier energy distribution is calculated assuming a *uniform* carrier density and field, indicates that for the systems studied energy relaxation after injection of carriers in actual devices with *nonuniform* densities and fields takes place on a time scale that is much shorter than the transit time. Recently, a three-dimensional ME modeling study of the $J(V)$ curves of complete devices has provided support for this point of view.[7]

The mobility (μ) in a system with spatially correlated energetic disorder was first analyzed by Gartstein and Conwell,[8] who showed that the effect can explain why time-of-flight measurements[9,10] often yield a Poole–Frenkel (PF) type electric field (E) dependence of the mobility, where $\ln(\mu)$ varies linearly with $\sqrt{E}$ in a rather wide E-range. Correlation can arise as a result of randomly oriented dipoles,[11,12] a variable morphology[13] or (for polymers) a variable strain of the backbone.[14] Dipolar disorder leads to a Gaussian density of states (DOS), with a pair correlation function of the site energies that decreases by a factor of ~2 within ~1.5 average intersite distances and which decreases at large distances (r) as $1/r$.[8] Recently, it was found from a ME approach that the mobility is then not only field and temperature dependent,[11] but also carrier density dependent (as for the EGDM), leading to the so-called "extended correlated disorder model" (ECDM).[15]

The question now arises whether a successful analysis of the $J(V,T,L)$-characteristics of a certain material using the EGDM or the ECDM would already convincingly proof that the disorder is completely random or correlated, respectively. This question was already addressed in Ref. 15 by reanalyzing the PPV-data given in Ref. 2 for a single device. It was concluded that also the ECDM can provide a good description, provided that a much smaller intersite distance is assumed within the ECDM (~0.3 nm) than within the EGDM (~1.6 nm). Unfortunately, the relatively large conjugation length in PPV-based polymers (typically 10 monomer units) implies that the basic starting point of both models (hopping between pointlike sites) is not well met. Therefore, it was not possible to derive from the observed intersite distances a conclusion about the presence of correlation.

In this paper, we address this question by reanalyzing the $J(V,T,L)$-characteristics of the hole transport in sandwich-type polyfluorene-based copolymer devices as studied in Ref. 5, now using the ECDM. The polymer (from the Lumation™ Blue Series, supplied by Sumation Co., Ltd.) consists of randomly copolymerized fluorene and triarylamine monomer units (7.5 mol %). From cyclic voltammetry (CV), the amine-related highest occupied molecular orbital (HOMO) energy is found to be at ~5.2 eV, well displaced from the HOMO energy of the polyfluorene-derived states (~5.8 eV) and very close to the Fermi level energy in the hole conducting poly(3,4-ethylene-dioxythiophene): poly-(styrenesulphonic acid) (PEDOT:PSS) anode layer (~5.1 eV).[5] These energy levels are close to those found

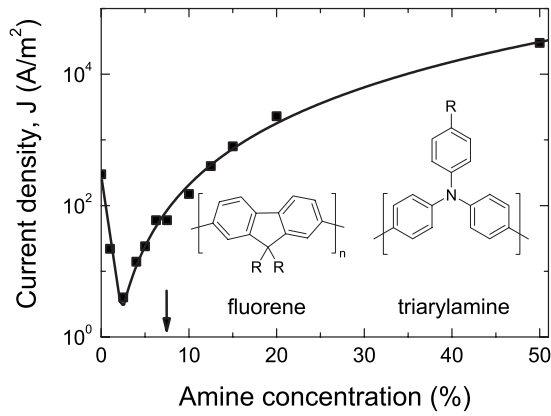a)Electronic mail: rein.de.vries@philips.com.

FIG. 1. Current density at 6 V, as a function of the amine concentration (the curve is a guide to the eyes), measured (symbols) in 80 nm hole-only devices (structure: see text). Inset: structure of the fluorene and amine monomer units used. The arrow indicates the amine concentration on which this study focuses.

from CV for similar materials.[16,17] Figure 1 shows the current density as measured at 6 V in 80 nm hole-only devices, for a series of copolymers within which the concentration of amines is varied. The device structure is as discussed below but with a gold cathode. Whereas the amines act as traps for small concentrations, the effective mobility increases strongly when the concentration is above the percolation threshold for guest-guest hopping. The copolymer studied in this paper is in the second regime. The figure thus suggests that in the copolymer studied the hole transport takes place via states localized predominantly on the amines. The rather small effective wave function decay length (well below 1 nm), as estimated in Ref. 5 within the EGDM from the temperature dependence of the mobility is consistent with this picture. From quantum-chemical calculations evidence for a fair degree of localization of the holes on the amines in similar copolymers was obtained.[16] This makes these polymers more suited for our purpose than the PPV-type polymers studied in Ref. 15. We note that Khan *et al.*[17] already analyzed similar systems (but with a 50 mol % amine concentration), with a single layer thickness and using the standard CDM and GDM. They also viewed the site density as a possible distinguishing factor. However, no final conclusion was obtained on the presence of correlated disorder. The availability of $J(V,T)$-characteristics for various device thicknesses and of the recently developed ECDM enable us to present a comparison with Ref. 5 employing the EGDM.

The devices studied have the structure

|Glass|ITO|100 nm PEDOT:PSS|LEP|100 nm Pd|,

with an indium tin oxide (ITO)/PEDOT:PSS anode layer, a light-emitting polymer (LEP) layer, and a palladium cathode. The PEDOT:PSS and LEP layers are deposited by spin coating; Pd is deposited by evaporation. The built-in voltage V_{bi} is approximately 2 V and the electron injection barrier at the cathode is approximately 1 eV. No evidence of electron injection or light emission was obtained.

Figure 2 shows the measured $J(V,T)$-characteristics for devices with LEP layer thicknesses of 67 and 122 nm for the temperature range as available from Ref. 5 (symbols). Using a least-squares method, a fit to the data for these layer thicknesses was made using functions of the form $\mu_{ECDM}(n,E,T) = \mu_{0,ECDM}(T) \times f(n,E,T)$. Here, $\mu_{0,ECDM}$ is
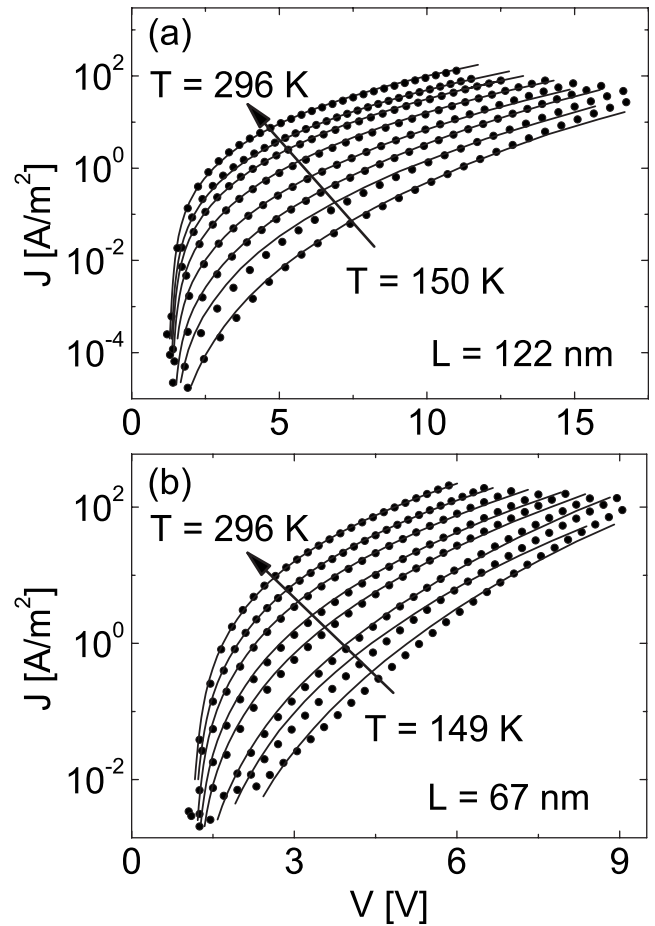

FIG. 2. Experimental current-voltage characteristics (symbols) at various temperatures and at a layer thickness of (a) 122 nm and (b) 67 nm, and best fits using the ECDM (curves) with the parameters given in Table I.

the temperature dependent mobility in the $n=0$ and $E=0$ limit and $f(n,E,T)$ is a dimensionless function which depends on the width of the Gaussian DOS σ, and on the density of hopping sites N_t in a manner described in Ref. 15. From this procedure, we find that the most likely solutions (fit error less than 3% larger than the minimum) reside in a narrow zone in $\{\sigma[eV], N_t[m^{-3}]\}$-space, ranging from $\{0.08; 2 \times 10^{27}\}$ to $\{0.11; 2 \times 10^{28}\}$. The optimal fit to the data was obtained using the set of in total five parameters given in Table I. The figure shows that the ECDM is able to provide a good description of the experimental data.

The internal consistency of the fitting procedure follows from the observation that for the optimal $\{\sigma, N_t\}$-set (i) V_{bi} is

TABLE I. Overview of the ECDM and EGDM model parameters that optimally describe the experimental current-voltage curves shown in Fig. 1. In both models an experimentally determined relative permittivity of 3.2 ± 0.1 was used (see Ref. 5).

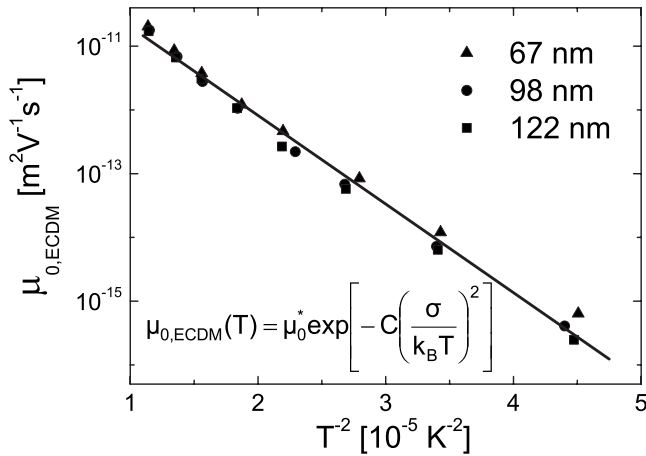| Parameter	ECDM[a]	EGDM[b]
σ (eV)	0.085 ± 0.005	0.13 ± 0.01
N_t (10^{27} m^{-3})	5 ± 2	0.6 ± 0.1
V_{bi} (V)	1.9 ± 0.1	1.95 ± 0.05
μ_0^* (10^{-8} m^2 V^{-1} s^{-1})	0.05 ± 0.02	14 ± 6
C	0.33 ± 0.02	0.39 ± 0.01

[a]This paper.
[b]Reference 5.

FIG. 3. Parameter $\mu_{0,\text{ECDM}}$ as found from a fit to curves obtained at various temperatures and layer thicknesses (symbols) and a best fit using the expression shown (line).
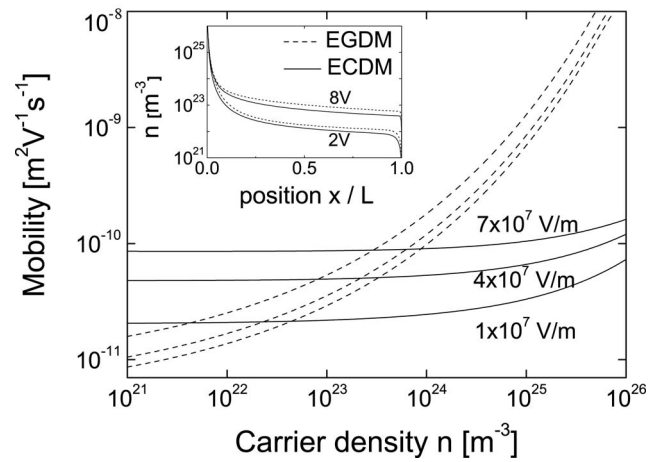

FIG. 4. Carrier density dependence of the mobility for the ECDM (full curves) and for the EGDM (dashed curves) at 296 K and at various fields. The model parameters are given in Table I. The inset shows for both models the carrier density in a 122 nm device; x is the distance to the anode.

independent of T for every thickness, and (ii) the values of $\mu_{0,\text{ECDM}}(T)$ are essentially thickness independent and well described by an exponential $1/T^2$ dependence consistent with the ECDM, as shown in Fig. 3. The line through the data points is described by the expression included in the figure, with a slope parameter $C = 0.33 \pm 0.02$. This value is close to the ECDM value $C = 0.29$ given in Ref. 15, calculated for a specific value of the wave function decay length. The actual value of C is expected to depend slightly on that length, as discussed in Ref. 18 for the EGDM. In order to more sensitively probe the shape of the DOS, it would be of interest to extend the temperature range to smaller values. However, we note that the numerical ECDM study in Ref. 15 yields mobility functions for cases up to $\sigma/(k_B T) = 5$. Accurately analyzing data well below $T = 150$ K $[\sigma/(k_B T) \sim 6.5]$ would therefore require an extension of the model.

We find that the smallest overall fitting errors using both models are almost equal. However, we regard the very high value of N_t (5×10^{27} m^{-3}) found using the ECDM as evidence that the model is not appropriate, as it is ~ 25 times larger than the amine density ($\sim 2 \times 10^{26}$ m^{-3} for the concentration used). Much better agreement was found using the EGDM, which yields $N_t \approx 6.0 \times 10^{26}$ m^{-3}.

The two sets of model parameters given in Table I lead to distinctly different predictions concerning the mobilities in devices within which much higher carrier densities occur, e.g., in OLEDs with internal interfaces at which blocking takes place and in organic field effect transistors in the accumulation regime. This may be seen in Fig. 4, which shows that within the ECDM the n and E dependences of the mobility are significantly smaller and larger, respectively, than within the EGDM. The experiments used in the present study probe the mobility most sensitively in the density range of 10^{22}–10^{23} m^{-3}, found in the bulk of the LEP layer of a device such as used for calculating the density profiles given in the inset (at 2 and 8 V). The two mobility functions cross in this carrier concentration range and both models lead to a comparable fitting quality.

In summary, for the copolymer studied, the ECDM yields over a wide temperature range and for three layer thicknesses an equally accurate description of the $J(V)$-curves of sandwich-type devices as the EGDM. This shows that a successful analysis of the curves using either

model does not yet convincingly prove that the disorder is completely random or correlated. So being able to describe $J(V)$ curves using a PF-type field-dependence of the mobility (as in the ECDM within a wide field range) does not yet prove that the site energies are correlated. In particular, for the specific material studied we argue that the site energies are uncorrelated, based on a comparison of the hopping site densities found using the two models with the amine density.

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