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Electron transport in polyfluorene-based sandwich-type devices: Quantitative analysis of the effects of disorder and electron traps

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Results of a combined experimental and modeling study of electron transport in a blue-emitting polyfluorene-based copolymer in sandwich-type devices are presented. We show how, for wide temperature and layer thickness ranges, an accurate and internally consistent drift-diffusion model description of the voltage-dependent current density can be obtained. We employ an adapted form of the "extended Gaussian disorder model," within which the density of states (DOS) is described as a superposition of a Gaussian DOS and an exponential DOS ("trap states"), characterized by only a small set of physically meaningful parameters. A comparison is made with the hole mobility reported for related polymers.

In recent years, many research efforts have focused on charge transport in organic light-emitting diodes (OLEDs).[1–4] For hole transport, it is now well established that a proper model should include the effects of the disordered nature of the organic semiconductors used on the mobility.[5–7] For electrons, however, it is not yet understood in detail how the transport is affected by the disorder. Furthermore, there are strong indications that electron transport is affected by the presence of traps. This is evident from the experimental observation that for commonly used undoped conjugated polymers, the electron current density (J) is at low voltages (V) often much lower than the hole current density and that it increases more steeply with voltage.[8,9] As an example, Fig. 1 shows measured $J(V)$ curves for a polyfluorene (PF)-based copolymer. This material is studied in this Brief Report; the detailed material and device structure are given below. As demonstrated in Ref. 10, an excellent description of the hole current density in devices based on this material is obtained using the extended Gaussian disorder model (EGDM, dotted curve in Fig. 1). The EGDM takes the dependence of the mobility on the local carrier concentration and on the electric field into account.[7,11] The model has also been shown to be very successful in describing the hole transport in several other polymers, including derivatives of the commonly used polymer poly(*p*-phenylene vinylene) (PPV).[7,10]

To explain the much steeper $J(V)$ curve for electrons, such as shown in Fig. 1 and such as observed as well for many other polymers, transport models have been used that assume that the conductivity is reduced by the presence of "trap states," in which most of the electrons reside. The conductivity is then due to the hopping of the small remaining fraction of electrons in "transport states."[12–14] Conventionally, the mobility of these electrons is assumed either to be constant or to be field dependent as described by a Poole-Frenkel factor.[8,9,15] Recently, Mandoc *et al.* investigated the effect of the detailed shape of the density of transport states on the temperature dependence of electron transport in devices based on PPV-derivatives and showed that a more proper description of the experimental data is obtained when

assuming an exponential density of trap states and a Gaussian density of transport states.[16] However, the authors did not use the EGDM. Instead, the carrier concentration and the field dependence of the mobility of the electrons were taken from a phenomenological model and the diffusion contribution to the current density was neglected.

In this Brief Report, we present a comprehensive analysis of the electron current density in a set of devices containing the PF-based copolymer for which a selected result has already been shown in Fig. 1. We assume an electron density of states (DOS) which is a superposition of a Gaussian DOS (with a site density $N_{t,G}$ and width σ) and an exponential DOS of the form $g(E) = N_{t,e}/(k_B T_0)\exp[E/(k_B T_0)]$ for $E \leq E_c = 0$, which are each shown schematically in Fig. 2. $E = 0$ at the top of the Gaussian DOS, $N_{t,e}$ is the trap site density, and $k_B T_0$ is the width of the exponential DOS, with k_B as the Boltzmann constant. We thus avoid the use of an additional free parameter which would describe the cutoff

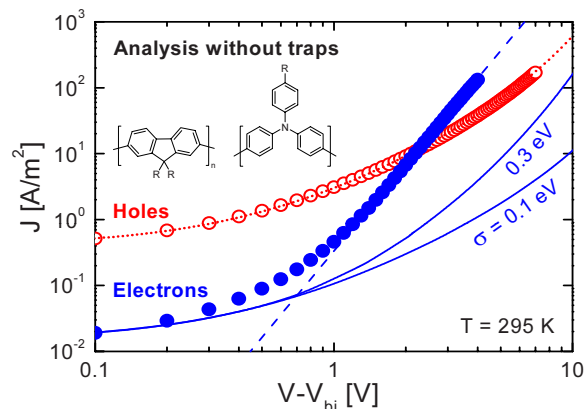FIG. 1. (Color online) Measured (symbols) and calculated (dotted and full lines) $J(V)$ curves for an electron-only (hole-only) device, with $L = 96(98)$ nm and with a built-in voltage $V_{bi} = 1.0(1.9)$ V. The calculations were performed using the EGDM (see text, σ is the width of the DOS). The dashed line is a guide for the eyes. Inset: chemical structure of the fluorene and triarylamine monomer units of the polymer used.
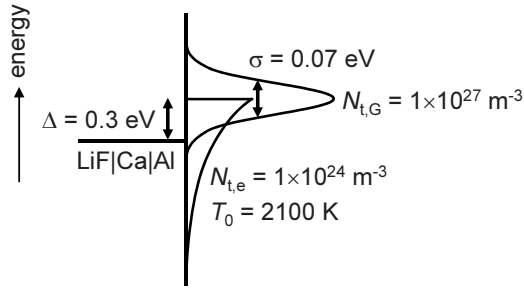
FIG. 2. Schematic of the energy-level alignment in the electron-only devices studied, indicating the Gaussian DOS and the exponential trap DOS for electron transport, and the injection barrier at the LiF|Ca|Al electrode.

energy E_c or, in the case of a bimodal Gaussian DOS or a symmetrized exponential DOS (as in the work of Mandoc *et al.*[16]), the characteristic trap depth. Our results are insensitive to the value of E_c, as long as it does not affect the position of the Fermi level. In contrast to the approach used in Ref. 16, the charge-density-dependent and field-dependent mobility is now obtained from an adapted form of the EGDM within which the effects of trapping are taken into account. We show that this yields an excellent description of the thickness-dependent and temperature-dependent electron transport.

The polymer studied is a blue-emitting polymer from the Lumation™ Blue Series supplied by Sumation Co., Ltd. and consists of fluorene units copolymerized with (7.5 mol %) triarylamine units (see the inset of Fig. 1). The hole transport in this polymer takes place via the amine units.[10] Their large average intersite distance leads to a strongly reduced hole mobility as compared to that in, e.g., poly(9,9-dioctylfluorene) (PFO). The hole transport in similar materials was studied by Khan *et al.*[17] The electron transport takes place via PF-derived lowest unoccupied molecular-orbital (LUMO) states.[18]

For analyzing the electron transport, "electron-only" sandwich-type devices with hole-blocking contacts were fabricated. For that purpose, an aluminum layer of 30 nm is evaporated through a shadow mask on precleaned glass substrates in a high-vacuum environment to form the patterned anode. Without exposing the substrates to air, the light-emitting polymer (LEP) layer is deposited by spincoating from a toluene solution in a nitrogen glovebox, resulting in LEP layer thicknesses L in the range 90–150 nm. The LEP layer thicknesses were determined from step-height measurements using a Veeco™ Dektak stylus profilometer. Subsequently, thin layers of LiF (3 nm), Ca (5 nm), and Al (100 nm) are evaporated in high vacuum through a mask to form the top electrodes. The total sample structure is thus (glass |Al|LEP|LiF|Ca|Al). The first Al layer is not fully opaque. This allows verifying that the Al anode does not inject holes, which would lead to light emission. No light was observed up to the highest voltages applied in this study. To protect the devices from water and oxygen contamination, the devices are encapsulated using a metal lid enclosing a desiccant getter. For each LEP layer thickness 27 nominally identical 3×3 mm^2 devices were prepared on a single substrate.

Around 10% of these devices showed relatively high currents under reverse bias and were not used in this study. The $J(V)$ curves of the remaining devices are nearly identical.

First, we investigate to what extent the EGDM, which appears so successful in describing the hole transport in the polymer considered, can also appropriately describe the electron transport, without the assumption of trapping. In Fig. 1, the effect on the $J(V)$ curve of varying the width of the Gaussian DOS is shown for two values of σ, viz., 0.1 and 0.3 eV, using $N_{t,G} = 1 \times 10^{27}$ m^{-3}, which is close to the density of the fluorene units.[18] The calculations were performed using the drift-diffusion device model presented in Ref. 19. Considering $\sigma = 0.3$ eV as a realistic upper limit, the figure shows that it is not possible to describe the electron current density (filled circles) without the inclusion of traps. We note that the introduction of a Schottky injection barrier, lowered by the local electric field due to the image charge potential,[20] or a variation in the transport site density did not lead to an improved description. At the highest voltages, the electron-only current reaches a slope on the double-log scale chosen of 4.3 at room temperature (dashed line in Fig. 1). It has been argued in the literature that the observation of a linear $\log(J)$-$\log(V)$ curve with such a high slope is an indication of trap-limited charge transport.[8,9,21]

As a second step, we developed an adapted version of the EGDM which properly describes the effective mobility in a system with a DOS as shown in Fig. 2. No spatial correlation between the site energies is assumed. Although we do not make any distinction in our model between the physical nature of the states in the Gaussian and exponential contributions to the total DOS, one might view the former states as "intrinsic," derived from the LUMO of the PF-based copolymer, and the latter states as "extrinsic," due to impurities, imperfections in the chemical structure, or by the presence of residual water or oxygen.[22–24] In the remainder of the Brief Report we will refer to the latter states as trap states. We make use of the fact that for the small values of $N_{t,e}$ considered, direct hopping between these states may be neglected. The effective mobility is then fully determined by the density of electrons occupying the Gaussian DOS, n_G, which follows straightforwardly from the total electron density, n_{tot}, assuming local thermal equilibrium between all carriers in the combined Gaussian and exponential DOS. So n_G is at any position in the device a well-known function of n_{tot}. This approach is an extension of the "multiple-trap-and-release (MTR) model,"[15,25] and accounts for "thermal detrapping." It was used successfully for treating the mobility in a bimodal Gaussian DOS,[26] as confirmed by numerically exact master-equation calculations.[27] It is known that in the presence of a field the effective mobility in a system containing trap states can be larger than as obtained from the MTR model.[28] For materials with the shape of the DOS assumed in this Brief Report (Fig. 2) no theoretical model which describes this so-called "field-induced detrapping (FID)" effect is available. From an estimate of the effect based on an analysis given in Ref. 27 for the case of a bimodal Gaussian DOS, we have found that the effect is very small for the systems and experimental conditions considered in this Brief Report. In our analysis, FID was therefore neglected.
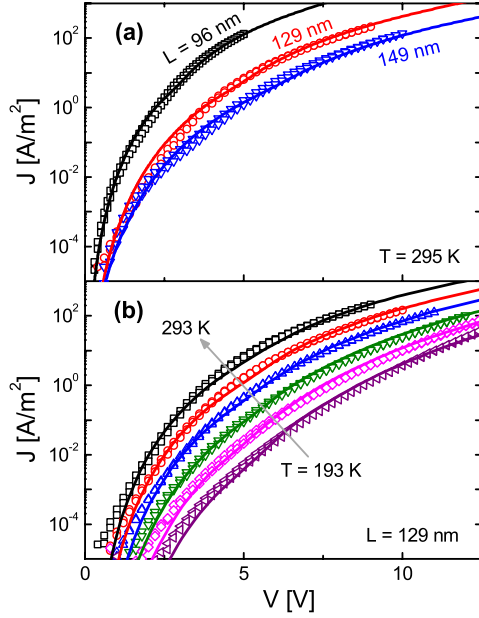
FIG. 3. (Color online) Measured (symbols) and calculated (curves) electron-only $J(V)$ curves for $L=96$, 129, and 149 nm at room temperature (a), and at $T=193-293$ K in steps of 20 K for $L=129$ nm (b). The calculations were performed including an exponential density of trap states (see text).

The current density is viewed as a result of drift and diffusion of the fraction of carriers which reside in the Gaussian DOS.

$$J = en_G(n_{tot})\mu F + eD\frac{dn_G(n_{tot})}{dx}, \qquad (1)$$

with e as the elementary charge, F as the electric field, and x as the position in the device. The mobility of the charge carriers in the Gaussian DOS, μ, is given by $\mu_{EGDM}\{n_G[n_{tot}(x)], F(x), T\}$, with μ_{EGDM} as the mobility as given by the EGDM and T as the temperature. The diffusion coefficient, D, follows from μ using the generalized Einstein equation.[29] At the injecting electrode interface, we allow for the presence of a Schottky injection barrier with a height Δ, and we include the effective image charge barrier lowering to an effective barrier, Δ_{eff}.[20] The carrier density at the interface is then obtained by assuming local thermal equilibrium. At the injecting and exit interfaces, n_G is thus equal to the carrier density in the Gaussian DOS for a Fermi energy $E_F = -\Delta_{eff}$ and $E_F = -\Delta - eV_{bi}$, respectively, with V_{bi} as the built-in voltage. We calculate $J(V)$ curves using an extended version of the drift-diffusion device model presented in Ref. 19 within which Eq. (1) is solved in conjunction with the Poisson equation for determining F from n_{tot}.

Figures 3(a) and 3(b) show the measured (symbols) and calculated (lines) $J(V)$ curves of the electron-only devices with $L=96$, 129, and 149 nm at room temperature, and for $L=129$ nm at temperatures in the range of 193–293 K, respectively. We find that an excellent description of the thickness- and temperature-dependent electron transport can be obtained using the set of parameter values given in Fig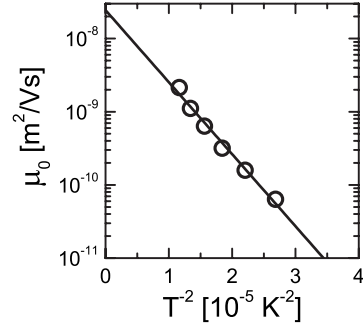. 2. The accuracy of the fit parameters, given below, was obtained from an analysis of the sensitivity of the fit quality to

FIG. 4. Temperature dependence of the electron mobility in the zero-field and zero carrier-concentration limit, μ_0 (symbols). The solid line is a fit (see text).

a variation in the parameters. The value of $N_{t,G}=(1.0\pm0.5) \times 10^{27}$ m^{-3} corresponds to an average intersite distance $a =0.9-1.2$ nm, which is slightly larger than the 0.84 nm distance between two successive fluorene monomer units, and consistent with the value $a\approx1.1$ nm as obtained from the volume density of fluorene monomer units in the PF-based copolymer studied.[18] The value of $\sigma=0.07\pm0.02$ eV coincides with the 0.07–0.10 eV range reported previously for *hole* transport in PFO.[17,30] This is consistent with the point of view that, in the absence of the traps, the electron transport is due to the hopping in a Gaussian DOS formed by the PF-derived LUMO states, with a similar width as the Gaussian DOS formed by the PF-derived highest occupied molecular-orbital (HOMO) states. For the *electron mobility* in the low electric field and low carrier-concentration limit, we find $\mu_0=2.2\times10^{-9}$ m^2/V s at room temperature. The full uncertainty interval, $1-10\times10^{-9}$ m^2/V s, overlaps with the range of typical low-field *hole mobilities* reported for PFO ($5-30 \times10^{-9}$ m^2/V s),[17,23] which most likely are not strongly affected by hole trapping.

The density of trap states and the characteristic trap temperature obtained from the fit, $N_{t,e}=(1.0\pm0.5)\times10^{24}$ m^{-3} and $T_0=2100\pm300$ K, respectively, are similar to the values given in previous reports on a variety of organic semiconductors.[1,9,31] We view the fact that the density of trap sites is ∼3 orders of magnitude lower than the density of transport sites and that, therefore, the intertrap distance is ∼10 nm as a justification of our assumption that trap-to-trap transport can be neglected. We find from our model that the electron injection barrier at the cathode, $\Delta=0.3\pm0.1$ eV, is sufficiently small, so that the current density is not injection limited.

The modeling yields $V_{bi}=0.7\pm0.2$ V, independent of the temperature. This indicates that the model is internally consistent. In order to further investigate the internal consistency, we analyze the temperature dependence of μ_0, obtained from the analysis. As shown in Fig. 4 we find an $\exp\{-C[\sigma/(k_BT)]^2\}$ dependence, consistent with the assumption of transport in a Gaussian DOS. The C parameter obtained from Fig. 4 is 0.34. From a variation in the material and device parameters within the error margins given, the estimated error margin is ±0.1. The result is consistent with

the range of values expected for the EGDM, $0.38 < C < 0.5$, depending on the wave-function decay length.[11]

In conclusion, we have presented an adapted form of the extended Gaussian disorder model within which the effects on the effective mobility of the presence of an exponential trap DOS are taken into account. The model can successfully describe the thickness and temperature dependence of the electron transport in an application-relevant blue-emitting PF copolymer. The parameters which describe the transport in the Gaussian electron DOS are found to be very close to those which describe the hole transport in the related poly-mer PFO, as could be expected on the basis of the similarity of the fluorene HOMO and LUMO wave functions.

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