Trap-free electron transport in poly(*p*-phenylene vinylene) by deactivation of traps with *n*-type doping

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We demonstrate that the electron transport in conjugated polymers as poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) is limited by deep traps that mask the intrinsic transport properties of free electrons in these materials. These traps can be deactivated by addition of the *n*-type dopant decamethylcobaltocene (DMC). By filling the traps with electrons from the DMC donor a trap-free space-charge limited electron current can be obtained in MEH-PPV, enabling a direct measurement of the free-electron mobility. We demonstrate that the electron mobility is equal to the hole mobility with an identical temperature dependence, showing that the charge transport in conjugated polymers is intrinsically balanced.

Conjugated polymers have been widely studied for their potential usage in organic semiconducting devices such as light-emitting diodes (LEDs), field-effect transistors (FETs), or solar cells. The hole transport in poly(phenylene vinylene) (PPV)-based diodes has been explained by a space-charge limited (SCL) current (SCLC),[1] with a mobility μ_p originating from a hopping process between localized sites in a Gaussian density of states (DOS),[2] which is broadened due to disorder. At room temperature the dependence of the mobility on carrier density governs the hole conduction,[3,4] whereas at low temperatures the field dependence dominates.[5] Hence the hole transport in conjugated polymers has been well established. In contrast to holes, the transport of electrons in conjugated polymers as PPV is still under strong debate. The poor electron transport together with its strong dependence on applied voltage and sample thickness, as observed in poly(2-methoxy-5–3,7-dimethyloctyloxy-*p*-phenylene vinylene) (OC$_1$C$_{10}$-PPV), was explained by the presence of traps with an exponential distribution of trapping sites in energy.[1] These traps have been attributed to impurities related to molecular oxygen.[6] The weak temperature of the trap-limited electron current could be explained by incorporating the presence of a Gaussian DOS for free electrons.[7] A fundamental question is whether the concept of free and trapped carriers is applicable to conjugated polymers; in such a disordered system of localized states, there are no real free carriers since all carriers are localized. The distinction made here is between mobile carriers that hop between localized states in the Gaussian DOS and are referred to as "free" and immobile ones, which are trapped in *deep* states. However, when the exponential trap states strongly overlap in energy with the Gaussian DOS the differentiation between free and trapped charges cannot be made; in that case the electrons are hopping in a DOS that is a superposition of an exponential DOS with a Gaussian DOS, and all electrons are free. This model has recently been suggested by van Mensfoort *et al.*[8] to explain the electron transport in a polyfluorene based copolymer. However, in order to explain the weak temperature dependence of the electron currents they had to assume

that the Gaussian DOS had a width of only 70 meV. Such a low value has been observed in transport studies on small molecules,[2] but it is unrealistically small for disordered conjugated polymers as polyfluorene. The major problem so far is that modeling of the electron currents alone is not sufficient to disentangle the transport properties of free electrons from the total amount of trap states as well as their position inside the band gap. In order to clarify the nature of the electron transport in conjugated polymers as PPV *n*-type doping is employed. We demonstrate that the electron transport is consistently described by the concept of free electrons in combination with *deep* traps. By gradually filling the traps with electrons from the *n*-type dopant the free-electron mobility and the energetic position of the traps are disentangled.

The strong reduction in the electron transport in many conjugated polymers has been attributed to the presence of additional localized states in between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) gap. In Fig. 1 a number of possible configurations are sketched; in Fig. 1(a) the Gaussian DOS of the LUMO for the free electrons is shown together with an exponential DOS that is deep in the band gap. For an exponential DOS given by

$$D_t(E) = \frac{N_t}{kT_t} e^{|E-(E_C-E_{tc})|/kT_t},\tag{1}$$

starting at a sufficiently large energy E_{tc} below the center of the Gaussian DOS, the electron transport is expected to be trap limited. As mentioned above the mobile or free electrons hop between localized states in the Gaussian DOS, and the immobile ones are trapped in the exponential DOS. For that case the electron current is given by[7]

$$J = N_c q \mu_n \left(\frac{\varepsilon_0 \varepsilon_r}{q N_t e^{(E_{tc}-E_a)/kT_t}}\right)^r \left[\left(\frac{2r+1}{r+1}\right)^{r+1}\left(\frac{r}{r+1}\right)^r\right]\frac{V^{r+1}}{L^{2r+1}},\tag{2}$$

with N_t as the total concentration of traps, T_t as the width of the exponential energy distribution of the traps, E_a as a char-
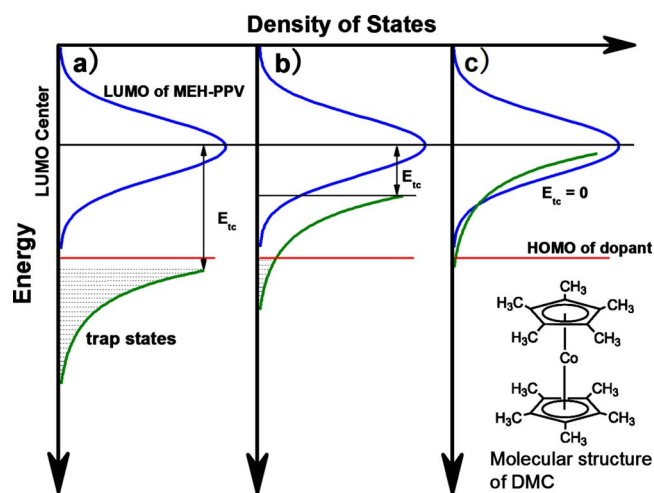
FIG. 1. (Color online) Schematic representation of the energy-level alignment of a Gaussian DOS (LUMO) for the transport of free electrons and an exponential DOS for electron traps that are separated by an energy E_{tc}. (a) For sufficiently large E_{tc} the exponential trap distribution does not overlap with the Gaussian DOS (deep traps) and the transport is trap limited, whereas for $E_{tc}=0$ (c) the Gaussian and exponential DOS superimpose to a new DOS in which electrons are transported, (b) represents the intermediate case.

acteristic energy given by $\sigma^2/2kT$ with σ as the width of the Gaussian DOS, N_c as the number of states in the Gaussian DOS, T as the temperature, $r=T_t/T$, q as the elementary charge, $\varepsilon_0\varepsilon_r$ as the dielectric constant, V as the applied voltage, L as the sample thickness, and μ_n as the free-electron mobility. This equation has successfully explained the voltage, thickness, and temperature dependence of the electron currents in various PPV derivatives.[7] However, the prefactor contains the three parameters μ_n, E_{tc}, and N_t that cannot be independently determined. It has been assumed before that the mobility of the free electrons is equal to the mobility of the free holes, which is supported by observations of Chua *et al.*, who demonstrated that in FETs the free electrons are as mobile as holes for OC_1C_{10}-PPV and a number of other conjugated polymers.[9] Furthermore, also in transistors based on the low band-gap material (diphenylethylenedithiolato)(1,3-dithiol-2-thione-4,5-dithiolato)nickel ambipolar transport with equivalent field-effect carrier mobilities for electrons and holes was observed.[10,11] However, it should be noted that in FETs the carrier densities are orders of magnitude higher as compared to diodes, such that transport measurements in FETs might only be performed in the trap-filled limit. In diodes, however, to our best knowledge, only for carefully purified regioregular poly(3-hexylthiophene) nearly equal electron and hole mobilities were obtained.[12] Moreover, also in a diode made from a crystalline blend of P3HT and high-density polyethylene ambipolar transport has been observed recently.[13] All other reported experiments on electron-only (EO) diodes of conjugated polymers exhibit strongly reduced current that mask the transport of free electrons. For the case that $E_{tc}=0$, as show in Fig. 1(c), the exponential DOS is superimposed on the Gaussian DOS. In that case the presence of the additional exponential DOS gives rise to an effective mobility of electrons hopping in this combined DOS.[8] Finally, for the intermediate case of Fig. 1(b) a distinction between the concepts of traps [Fig. 1(a)] and effective mobility [Fig. 1(c)] might be very difficult to make. A way to differentiate between these transport models is by making use of *n*-type doping. Typically, *p*- and *n*-type doping is applied to improve the charge injection and transport in small molecule-based organic electronic devices as light-emitting diodes.[14,15] For *n*-type doping molecules are required with a sufficiently low ionization energy (IE) to enable charge transfer to the unoccupied states of the host semiconductor. In this study we apply decamethylcobaltocene (DMC) that is an efficient *n*-type dopant for copper phthalocyanine (CuPC) as shown by Kahn and co-workers.[16] DMC has a remarkably low solid-state IE of only 3.3 eV, as measured by ultraviolet photoemission spectroscopy.[16] As indicated in Fig. 1 in combination with the LUMO of MEH-PPV at around 2.9 eV various scenarios can occur when MEH-PPV is *n*-type doped with the DMC donor; for $E_{tc}>0.4$ eV all traps will be filled by electrons from the dopant upon a sufficient level of doping, resulting in trap-free electron transport. For a combined DOS [Fig. 1(c)] only a very small part of the tail of the DOS will be filled, and there will be hardly an effect of doping on the *J*-*V* characteristics. The electrons injected from the contacts will directly overwhelm the few electrons added by the doping. For the intermediate case [Fig. 1(b)] part of the states will be filled, only leading to a partial improvement of the electron transport.

To investigate the electron transport as a function of *n*-type doping electron-only devices are fabricated with the (doped) MEH-PPV layers sandwiched between an environmentally oxidized Al anode (30 nm) and a 5 nm Ba cathode capped with 100 nm Al. MEH-PPV was dissolved in toluene under a concentration of 6 mg/ml with sufficient stirring at 70 °C on a hotplate for ~10 h. The active layer was then spin coated from solution with a spin speed of 1200 rpm, resulting in a typical film thickness of ~150 nm. Since the DMC molecule does not dissolve in common organic solvents as toluene or chlorobenzene a polar solvent dimethylformamide (DMF) has been used to dissolve DMC in a concentration of 10 mg/ml, which is subsequently blended with the MEH-PPV solution using a volumetric pipette. A similar procedure has also been reported for the realization of *p*-type doping of MEH-PPV with F4-TCNQ.[17] The spin-coated DMC-doped MEH-PPV films were characterized by a Dektak 6M Stylus Profiler and the thickness and roughness were found to be unaffected by doping. Furthermore, under an optical microscope no change in the morphology (aggregates) could be observed. The thermal evaporation of the Ba top contact was carried out under a chamber pressure of ~10^{-7} mBa, with the vapor pressure of water and oxygen lower than 2×10^{-8} mBa, as monitored by a mass spectrometer. Electrical measurements were performed in a nitrogen-purged glove box using a 2400 Keithley SourceMeter. A cryosystem with liquid nitrogen was utilized for the low-temperature characterization.

The *J*-*V* characteristics of MEH-PPV electron-only devices with various concentrations of DMC are shown in Fig. 2. With increasing doping concentration we observe a strong increase in the electron current over several orders of mag-
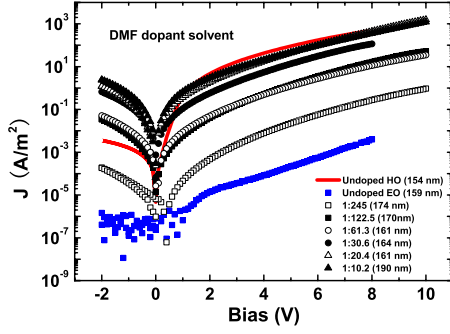
FIG. 2. (Color online) Current density–voltage characteristics of EO diodes with various amounts of *n*-type doping. Also shown is the (undoped) HO diode for reference.

nitude. For doping concentrations of about 1:20% (wt) the electron current is nearly equal to the hole current. This hole current has been measured as a reference using a ITO/PEDOT:PSS/MEH-PPV/Au hole-only (HO) device from the same (undoped) MEH-PPV solution. A further increase in the doping concentration to 1:10% (wt) does not lead to a further enhancement of the electron current, the electron current saturates on top of the hole current.

As a next step we evaluate the free-electron mobility from the *J-V* characteristic. For the highest doping concentrations a quadratic dependence of the electron current density on voltage is observed, which is indicative for a trap-free SCLC. Together with the saturation upon doping this implies that at these doping levels all the electron traps are filled. Modeling of the electron current yields a room-temperature mobility of $\mu_n = 1.7 \times 10^{-10}$ m²/V s, as shown in Fig. 3. Also shown is the SCL hole current from the same batch of MEH-PPV, from which a hole mobility of $\mu_p = 1.4 \times 10^{-10}$ m²/V s is extracted. The complete filling of the electron traps, combined with a saturation upon doping of the electron current on the level of the hole current, and the equivalence of the free electron and hole transport are all consistent with a trap-limited current for which $E_{tc} > 0.4$ eV, as shown in Fig. 1(a). The electrons from the DMC gradually fill up the traps until for a given doping concentration all traps are filled. A further
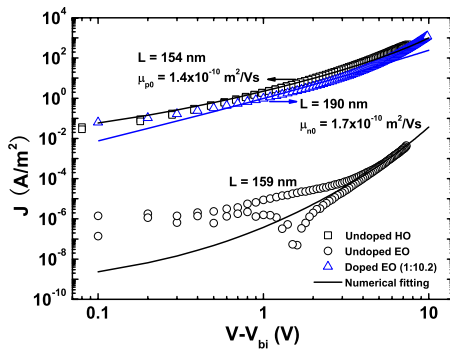

FIG. 3. (Color online) Comparison of the undoped and strongest doped electron-only (DEO) device (1:10% (wt), together with the hole current (symbols). Also shown are the numerically calculated space-charge limited currents from which electron and hole mobilities of $\mu_n = 1.7 \times 10^{-10}$ m²/V s and $\mu_p = 1.4 \times 10^{-10}$ m²/V s are extracted, respectively.
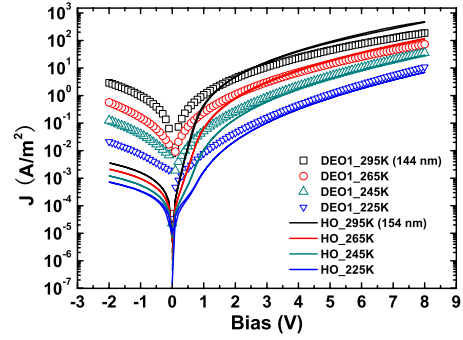

FIG. 4. (Color online) Current density–voltage characteristics of the (undoped) HO and DEO diodes with the highest doping concentration (1:10% in wt) as a function of temperature.

increase in the dopant concentration does not further enhance the electron current, because the ionization energy of 3.3 eV of DMC is not sufficient to add a large amount of free electrons to the LUMO of MEH-PPV, which is centered at around 2.9 eV. In case of a superimposed DOS, as shown in Fig. 1(c), the effect of the doping would be much smaller.

Subsequently we study the development of the electron currents as a function of *n*-type doping. For the case of an exponential DOS deep in the gap a relation exists between the amount of free and trapped electrons as given by[7]

$$\frac{n}{N_c} = \left(\frac{n_t}{N_t e^{(E_{tc}-E_a)/kT_t}}\right)^r = \left(\frac{n_t}{N_{t(eff)}}\right)^r. \quad (3)$$

Here $N_t e^{(E_{tc}-E_a)/kT_t}$ is defined as an effective trap concentration, $N_{t(eff)}$. The trap-free electron currents presented in Fig. 4 can now be modeled in a similar way as has been employed to the SCL hole currents in MEH-PPV.[5] Here we apply this model for the trap-free electron current, taking the dependence of the electron mobility on carrier density, electric field, and temperature into account. In Fig. 4 the trap-free *J-V* characteristics of the MEH-PPV electron-only device with all traps filled by the doping with DMC are shown as a function of temperature, together with the hole currents. We find that a mobility prefactor of $\mu_{0n} = 3.0 \times 10^3$ m²/V s, an intersite distance $a_n = 1.6$ nm and a width of the LUMO of $\sigma_n = 0.143$ eV consistently describe the free-electron transport. These parameters are similar to the ones reported for hole transport in OC₁C₁₀-PPV.[5] With the free-electron transport known there are only two parameters left to numerically fit the trap-limited current of the undoped MEH-PPV, namely, T_t and $N_{t(eff)}$. As shown in Fig. 5 a reasonable fit is obtained for $T_t = 1500$ K and $N_{t(eff)} = 1.6 \times 10^{24}$ m⁻³. It should be noted that $N_{t(eff)}$ still contains N_t and E_{tc}, however, from the saturation of the electron current upon doping we know that $E_{tc} > 0.4$ eV. For example, in case that $E_{tc} = 0.5$ eV this leads to $N_t = 3.3 \times 10^{23}$ m⁻³ and for an E_{tc} of 0.6 eV N_t amounts to 1.5×10^{23} m⁻³. From the calculation on the undoped sample we now proceed to the doped samples; these *J-V* characteristics only contain one fit parameter, namely, the amount of electrons that is supplied by the dopant at zero bias, given by $n_{t0} + n_0$. Here, n_{t0} is the amount of electrons in the traps at zero bias that is related to the
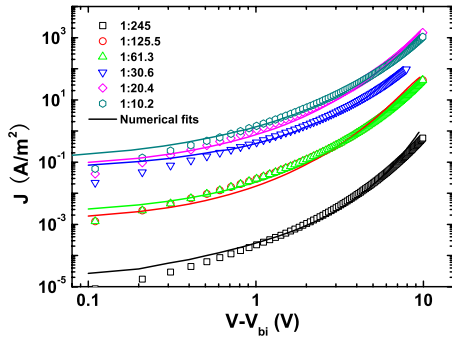
FIG. 5. (Color online) Current density–voltage characteristics of electron-only diodes with various amounts of n-type doping (symbols) together with numerical simulations (lines).

amount of free electrons n_0 by Eq. (3). The fact that some of the experimental J-V characteristics are very close as, for example, for the 1:125.5 and 1:61.5 doping ratios, is due to the fact that the thickness of the various electron-only devices is not exactly equal. In the numerical simulations this small variation in thickness has been taken into account In Fig. 6 $n_{t0}+n_0$ is shown as a function of the doping concentration. A linear dependence on doping concentration is obtained until a concentration of 1:20% (wt), after which saturation sets in at $n_{t0}+n_0 \sim 4 \times 10^{23}$ m^{-3}. As a comparison also the amount of free carriers n_0 as a function of doping concentration is shown in the inset. Due to the relatively large number of $N_{t(eff)}$ the amount of free electrons from the doping is only in the $\sim 10^{21}$ m^{-3} regime. Upon application of a voltage these free carriers are almost directly overwhelmed by electrons that are injected from the contacts, except at very low bias voltage, as is also visible in Fig. 4. Comparing the amount of ionized doping $n_{t0}+n_0$ with the doping concentration we find that only 0.23% of the DMC molecules are ionized. Possibly phase separation takes place, in which case only dopant molecule at the interface between the two phases will ionize. The exact reason for this relatively low doping efficiency is currently under study.

By filling the traps with electrons from the DMC donor we can eliminate trapping effects and demonstrate that for a conjugated polymer as MEH-PPV the mobilities of the free electrons and holes are very well balanced. This is in agree-
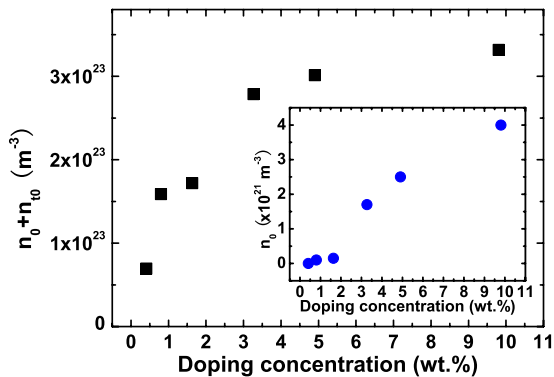

FIG. 6. (Color online) Amount of ionized dopants at zero bias $n_{to}+n_o$ as well as the amount of free electrons n_0 (inset) as a function of doping concentration.
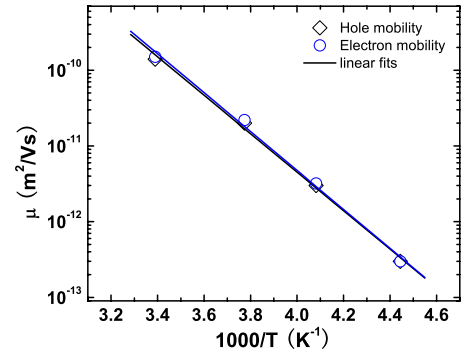

FIG. 7. (Color online) Free-carrier zero-field mobilities for electrons and holes extracted from numerical modeling of the SCL transport as a function of reciprocal temperature.

ment with quantum-chemical calculations which demonstrate that the packing between the molecular units is mainly dominating the magnitude of the transfer integrals, leading to equivalent charge transport properties for electrons and holes.[18] However, a fundamental question that remains is whether the free-electron mobility that we observe is representative for the intrinsic transport of electrons in MEH-PPV. It is generally accepted that the hole mobility in conjugated polymers is dominated by the effects of the disordered nature of organic semiconductors, leading to energetic and positional disorder.[2] The energetic disorder and corresponding width of the Gaussian DOS is expected to increase upon doping due to potential fluctuations caused by the Coulomb field of randomly distributed dopant ions.[19,20] Such a modification of the DOS upon doping would mask the intrinsic transport properties of the free electrons in undoped MEH-PPV. In an earlier study on p-type doping of MEH-PPV we demonstrated that until ionized doping levels of $\sim 10^{17}$ cm^{-3} the mobility is unaffected by the presence of doping.[17] The intrinsic dependence of the hole mobility on carrier density can be measured by combining space-charge limited and field-effect measurements on undoped PPV.[3,4] By using this intrinsic mobility dependence on hole density we extracted from the J-V characteristics of the doped devices both the mobility and amount of ionized dopants. If, however, the mobility would change upon doping other than due to the increase in the carrier density our extracted densities of ionized dopants would not be correct. By carrying out capacitance-voltage measurements on Schottky diodes, we verified that the concentration of ionized dopants was exactly as predicted from the intrinsic mobility. Also from theory the modification of the Gaussian DOS is expected to set in at higher densities, typically when $N_d > 10^{23}$ m^{-3} at least.[19] Since in the present study the amount ionized donors is also in the $\sim 10^{23}$ m^{-3} regime no significant change in the mobility is expected other than due to the increased free-carrier concentration.

The amount of energetic disorder is specifically reflected in the temperature dependence of the charge-carrier mobility.[2] When the Gaussian DOS of the free electrons would be broadened upon doping this would be reflected in a lowering of the electron mobility as compared to the hole mobility as well as a stronger temperature dependence. In

Fig. 4 the *J-V* characteristics of the MEH-PPV electron-only device with all traps filled by the doping with DMC are shown as a function of temperature, together with the hole currents. It is evident that next to an equivalent mobility at room temperatures, the electron and hole transport exhibit an equal temperature dependence. The temperature dependence of the zero-field mobilities extracted from numerical modeling of the SCL transport are plotted in Fig. 7 for electrons and holes. The equivalent temperature dependence shows that the disorder induced broadening of the HOMO—and LUMO levels are equal. As a result the electron and hole transport in MEH-PPV have an identical microscopic origin.

In conclusion, we have demonstrated that the electron transport in MEH-PPV is limited by *deep* traps that are exponentially distributed in energy. By applying *n*-type doping these traps can be filled with electrons and therefore they are electrically made inactive, enabling the measurement of trap-free electron transport in MEH-PPV diodes. It is demonstrated that the mobility and microscopic origin of the electron and hole transport in conjugated polymers as MEH-PPV are identical, showing that the charge transport is intrinsically balanced.

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