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Field-assisted ionization of molecular doping in conjugated polymers

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ABSTRACT

The field- and temperature dependence of the charge transport in solution-processed poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) doped with tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) is investigated. Conventional charge transport models based on a density- and field-dependent mobility in combination with a constant background hole density from the dopant do not explain the strongly enhanced hole current at high electric fields. Addition of field-assisted ionization of F4-TCNQ with a field-enhancement factor $\sim \exp(\gamma\sqrt{E})$, which increases with decreasing temperature and doping concentration, consistently describes the charge transport in F4-TCNQ doped MEH-PPV.

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After the discovery in 1977 that the conductivity of polyacetylene can be enhanced over many orders of magnitude, up to one percent of copper or silver through *p*-type doping by iodine [1], the field of organic electronic devices was tremendously boosted. In the last decade *p*-type doping of organic thin films was realized by co-sublimation of a matrix of organic molecules as vanadyl- or zinc-phthalocyanine and the acceptor tetrafluoro-tetracyanoquinodimethane (F4-TCNQ) [2–4]. Introduction of *p*-type doping not only strongly increased the conductivity of the matrix but also modified the electronic structure of the interfaces [5,6], leading to an enhanced hole injection into the matrix [7]. Application of *n*-type doping is more challenging due to the intrinsic instability of *n*-type dopants in air. As possible candidates for *n*-type doping in organic matrices alkali metals, cationic salts, or organic materials with a low ionization potential as cobaltocene have been investigated [8–14]. The application of doped hole and electron trans-

port layers in organic light-emitting diodes (OLEDs) based on evaporated small molecules strongly reduced their operation voltage [15,16].

Compared to organic small molecules doping of soluble conjugated polymers (CPs) is more challenging: already in solution charge transfer between the host polymer and the dopant leads to aggregation and precipitation of the active components. In a recent study by Kim and co-workers [17], *p*-type doping of a variety of conjugated polymers with F4-TCNQ was demonstrated via solution based co-blending from a common organic solvent. The addition of F4-TCNQ resulted in a conductivity increase of several orders of magnitude. Simultaneously we realized controllable doping of poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) by F4-TCNQ using a polar co-solvent [18]. From current density–voltage (*J*–*V*) and impedance measurements the fraction of dopant molecules that ionize as well as the resulting free hole density p_0 were obtained. For a doping ratio of 1:600 the resulting spin-coated layers demonstrated a doping-induced free carrier density p_0 of $4 \times 10^{22} \text{ m}^{-3}$. We demonstrated that in order to describe the *J*–*V* characteristics of the doped MEH-PPV devices at room temperature it is essential to take the charge–carrier

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density dependence of the hole mobility into account. Neglecting the charge-carrier density dependent effect would lead to an overestimation of p_0 by an order of magnitude for the 1:600 doping ratio. Further understanding of the charge transport in doped conjugated polymers is required to advance the performance of polymeric optoelectronic devices. In this study we investigate the field (E) and temperature (T) dependence of the charge transport of p -type doped MEH-PPV. We demonstrate that in order to describe the hole transport at low temperatures and high electric fields a field-assisted ionization of the F4-TCNQ dopants has to be taken into account.

Upon addition of p -type doping free holes are introduced into the organic semiconductor. At low voltages these free holes, or background density p_0 , will largely outnumber the charges that are injected from the contacts. As a result an Ohmic-like current will flow, given by

$$J_{\Omega}(V, T) = qp_0(T)\mu_p(T, p_0(T), E) \frac{V}{d} \quad (1)$$

with q the magnitude of electron charge, p_0 the free hole density, μ_p the hole mobility, d the thickness of the polymer layer, and $E = V/d$. At higher voltages space-charge due to holes injected from the contacts will start building up and a transition to the space-charge limited current (SCLC) will occur. From Eq. (1) it is already obvious that the analysis of the temperature dependence of the J - V characteristics is not straightforward: the amount of free holes p_0 might be temperature-dependent due to a thermally activated ionization process of the dopant. Furthermore, the mobility will not only depend on temperature due to the hopping of holes in a disorder broadened Gaussian DOS, but also on the free hole density p_0 (that in itself also might be temperature-dependent) due to the filling of states in the tail of the Gaussian DOS [19,20]. All these possible temperature-dependent contributions from the density and mobility have to be disentangled in order to understand the charge transport. To measure the T -dependence of the transport in conducting polymers upon doping, MEH-PPV hole-only devices were made by sandwiching the matrix in between two metal contacts. As a bottom electrode indium-tin-oxide (ITO) covered with PEDOT:PSS was used, and a Pd top electrode of 20 nm was thermally evaporated on top of the MEH-PPV layer under a chamber pressure of 8×10^{-7} mbar and then capped with 100 nm of Au. The MEH-PPV was dissolved in toluene, whereas for F4-TCNQ tetrahydrofuran (THF) was used as the solvent. Further details of the processing are given in Ref. [18]. A Keithley 2400 SourceMeter and a Solartron SI 1260 Impedance/Gain-Phase analyzer were used for the I - V and C - V measurements, respectively. All electrical measurements were performed in a nitrogen-purged glove box and the temperature was controlled by a cryosystem with liquid nitrogen.

As a first step we investigate the temperature- and density dependence of the hole mobility in MEH-PPV by measuring the SCLC in undoped MEH-PPV. Fig. 1(a) shows the current density versus voltage (J - V) characteristics of a PEDOT:PSS/undoped MEH-PPV/Pd/Au hole-only device at various temperatures. The J - V characteristics are numerically modeled by using a recently developed trans-

port model, that takes into account both the field E and density p dependence of the hole mobility μ_p [19]. The mobility is given by

$$\mu_p(T, p, E) \approx \mu_p(T, p)f(T, E), \quad (2)$$

with

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

$$\mu_0(T) = \mu_0 c_1 \exp(-c_2 \hat{\sigma}^2), \quad (4)$$

$$\delta = 2 \frac{\ln(\hat{\sigma}^2 - \hat{\sigma}) - \ln(\ln 4)}{\hat{\sigma}^2}, \quad (5)$$

$$\mu_0 = \frac{a^2 v_0 e}{\sigma}, \quad (6)$$

and

$$f(T, E) = \exp \left\{ 0.44(\hat{\sigma}^{3/2} - 0.22) \left[\sqrt{1 + 0.8 \left(\frac{Eea}{\sigma} \right)^2} - 1 \right] \right\} \quad (7)$$

where, $\hat{\sigma} \equiv \sigma/K_b T$ with σ the width of the Gaussian DOS, and a is the lattice constant. The lines in Fig. 1(a) are the numerically calculated J - V characteristics using a μ_{p0} of $6.4 \times 10^3 \text{ m}^2/\text{Vs}$, an a_{p0} of 1.55 nm, and a σ_{p0} of 0.143 eV. These parameters are similar to the ones reported for another PPV derivative with a similar mobility [19], and the temperature dependence of the J - V characteristics is well described, both at low and high voltages. The activation energy of the mobility Δ_{mobility} at low fields and densities, defined as $\mu_p(T, 0) = \mu_0 \exp(-\Delta_{\text{mobility}}/kT)$, typically amounts to 0.42 eV.

With $\mu_p(T, p, E)$ known we can analyze the J - V characteristics of the p -type doped MEH-PPV. Fig. 1(b) shows the J - V characteristics of p -type doped MEH-PPV with a molar doping ratio of 1:150. The linear part of the J - V characteristic (Eq. (1)) is governed by the product of the hole density p_0 and the hole mobility μ_p . With $\mu_p(T, p, E)$ known (Eqs. (2)–(7)) we can determine them individually, leading to $p_0 = 2.2 \times 10^{23} \text{ m}^{-3}$ and $\mu_p = 1.2 \times 10^{-9} \text{ m}^2/\text{Vs}$ at room temperature. The enhanced mobility upon doping is a direct result from the filling of the tail states of the Gaussian DOS by holes. The resulting rise of the Fermi-level decreases the energy step required for hopping towards the transport states, which enhances the mobility.

Under the assumption that the temperature dependence $p_0(T)$ is very small and can be neglected the full temperature- and voltage dependence of the transport in the doped MEH-PPV can be numerically calculated. The calculations using $\mu_p(T, p, E)$ in combination with a constant p_0 of $2.2 \times 10^{23} \text{ m}^{-3}$ are shown in Fig. 1b by the solid lines. However, we observe that the model calculations become inconsistent with the experiments at high electric fields (E) and low T (<270 K). At low voltages the experimental hole currents exhibit a weaker temperature dependence as expected from the model. Furthermore, at high voltages the experimental J - V curves show a stronger dependence

Fig. 1. Current density versus voltage characteristics of (a) an undoped and (b) a doped MEH-PPV hole-only device with a molar doping ratio of 1:150. Shown by the solid lines are the numerically calculated currents using a constant free hole density (p_0).

on voltage. As a result the inclusion of only a constant background density p_0 in the existing charge transport model characterized by $\mu_p(T, p, E)$ is not sufficient to explain the J - V characteristics of p -type doped MEH-PPV.

One could argue that the mobility as measured in the undoped sample is not only changed by the density p_0 , but also by the presence of the F4-TCNQ⁻ counter ions. The hole transport in undoped conjugated polymers is dominated by energetic and positional disorder [21,22]. Upon doping the energetic disorder and corresponding width of the Gaussian density of states (DOS) is expected to increase due to potential fluctuations caused by the Coulomb field of randomly distributed dopant ions [23,24]. Such a modification of the DOS upon doping would lead to a reduction of the mobility as well as to an increased temperature dependence of the mobility. This enhanced temperature dependence would even further increase the discrepancy between calculations and experiments at low fields. Furthermore, in a previous study [18] we verified

by C - V measurements that the p_0 as extracted from the J - V measurements, thereby making use of the intrinsic density dependence of the mobility as obtained in the undoped sample, is indeed correct. If the mobility would have been strongly modified upon doping other than due to the increase of the carrier density our extracted densities from the J - V measurements would deviate from the densities as obtained from the C - V measurements. Theoretically, the modification of the Gaussian DOS upon doping is also expected to set in at higher densities, typically when $N_A^- > 10^{23} \text{ m}^{-3}$ [24,25]. As a result in our experimental regime with the amount of ionized acceptors N_A^- low in the $\sim 10^{23} \text{ m}^{-3}$ no significant change of the mobility is expected other than due to the increased free carrier concentration.

By comparing the amount of doping with the free hole density we find that only $\sim 1\%$ of the F4-TCNQ molecules in the MEH-PPV are ionized. A possible explanation for this low doping efficiency may be phase separation between the

host and the dopant, in which case only dopant molecule at the interface between the two phases will ionize. Our modeling results shown in Fig. 1(b) demonstrate that the field- and temperature dependence of the doped sample can not be described assuming a constant p_0 . We postulate that the strong increase of the J - V characteristics at high voltages and the reduced temperature dependence is a result of a field-assisted release of holes from the dopants. We therefore introduce a field-dependent p_0 with a Poole-Frenkel like dependence on the applied electric field,

$$p_0(E) = p_0 \exp(\gamma\sqrt{E}) \quad (8)$$

where, p_0 is now the zero-field free hole density, and γ the field-enhancement factor. In Fig. 2 the J - V characteristics are shown at various temperatures for doped MEH-PPV hole-only devices with varying molar doping ratios of 1:600, 1:350, 1:250 and 1:150. The corresponding free hole density p_0 is ranging from 5×10^{22} to $2.0 \times 10^{23} \text{ m}^{-3}$, respectively. Since for every molar doping ratio a new solution is made the thickness after spin coating is slightly varying. The lines are the numerical simulations by combining the mobility from Eqs. (2)–(7) and the field-enhanced free carrier density given by Eq. (8). We assume that p_0 is temperature independent. Taking the field-as-

sisted ionization of the dopants into account a good description of the J - V characteristics can be made, as shown by the solid lines in Fig. 2. The variation of γ with temperature and doping concentration is shown in Fig. 3a. We find that similar to the prefactor that is responsible for the field-dependent mobility in disordered materials [26], γ follows the empirical relation

$$\gamma = B \left(\frac{1}{k_B T} - \frac{1}{k_B T_0} \right) \quad (9)$$

with $T_0 = 400 \text{ K}$ and the prefactor B ranging from 1.3×10^{-5} to $6.4 \times 10^{-6} \text{ eV(m/V)}^{1/2}$ for the range of $p_0 = 5 \times 10^{22} \text{ m}^{-3}$ to $p_0 = 2 \times 10^{23} \text{ m}^{-3}$, respectively. These values for B are considerably smaller than the values reported for the field-dependent mobilities [26]. The increase of p_0 as a function of the electric field is plotted in Fig. 3(b) to illustrate the impact of the electric field on the background hole density from doping. We find that a p_0 of $\sim 10^{22} \text{ m}^{-3}$ is enlarged by ~ 5 times at high E and 2–3 times for a p_0 of $\sim 10^{23} \text{ m}^{-3}$. In the field-enhanced charge transport the factor γ is usually related to a hopping distance [27]. For higher doping concentrations it is expected that the average distance that holes will have to hop from a dopant molecule to a site of the matrix will decrease. This would result

Fig. 2. Current density versus voltage characteristics of MEH-PPV hole-only devices with various doping concentrations. Also represented (solid lines) are the calculated current densities taking a field-dependent background hole density into account.

Fig. 3. (a) Field-enhancement factor γ versus temperature for different doping concentrations. (b) Free hole density calculated as a function of electric field at $T = 230 \text{ K}$.

in a weakening of the field-enhanced ionization factor, but at present a microscopic theory or explanation is still lacking.

As a last step we investigate the temperature dependence of the low-field background density p_0 using impedance spectroscopy. For this we fabricate Ag/MEH-PPV Schottky diodes with an Ohmic PEDOT:PSS back contact. The molar doping ratio amounts to 1:500. Fig. 4(a) shows the capacitance of the depletion region versus voltage at room temperature. The capacitance at zero-voltage slightly reduces upon cooling down, indicating that the density of free holes is slightly reduced at low temperatures. A reduced density will lead to an enlargement of the depletion region with a resulting smaller capacitance. The capacitance of the depletion region C is given by

$$\frac{1}{C^2} = \frac{2(V - V_{bi} - \frac{kT}{q})}{q\epsilon_s p_0}, \quad (10)$$

with V_{bi} the built-in voltage and ϵ_s the permittivity of the semiconductor. As a result, from the slopes of the lines in Fig. 4(a) p_0 can be determined at various temperatures.

The temperature dependence of p_0 is plotted in Fig. 4(b). At a doping level of $3.4 \times 10^{22} \text{ m}^{-3}$ we obtain that the activation energy for the ionization of free holes from the F4-TCNQ acceptor in MEH-PPV only amounts to 46 meV. This means that in the entire temperature interval of 230–300 K the p_0 only changes by a factor 1.5. For higher doping levels the change of p_0 with temperature is within experimental error. The observed activation energy of p_0 is so small that its weak temperature dependence does not affect the modeling results shown in Fig. 2b. Therefore, the C–V measurements confirm that a temperature independent p_0 is a valid assumption in the modeling.

It might seem counterintuitive that the strongest γ occurs at the lowest doping densities, whereas in a previous study [18] we showed that at low background densities the room temperature J – V characteristics could be reasonably well described by a constant background density p_0 . At low voltages the J – V characteristics of doped semiconductors exhibit an Ohmic behavior, as given by Eq. (1). At a certain voltage V_t the charges injected from the contact overwhelm the charges from the doping and the current becomes space-charge limited. This transition voltage V_t

Fig. 4. (a) Depletion capacitance as a function of negative bias for a MEH-PPV Schottky diode at various temperatures. (b) Extracted background hole density as a function of temperature. The activation energy amounts to $\Delta_{\text{doping}} = 46 \text{ meV}$ for $p_0 = 3.4 \times 10^{22} \text{ m}^{-3}$.

depends on the amount of doping; for low doping densities V_t is also low, meaning that the Ohmic regime is only observable in a small voltage range. The enhancement of p_0 at higher voltages ($>V_t$) and fields is then not really visible in the J - V characteristic. For high doping densities the resulting Ohmic behavior due to the large p_0 dominates the J - V characteristics over a much larger voltage range, and then the increase of p_0 with field, together with the enhancement of the mobility by the increased p_0 , make this effect strongly visible.

In conclusion, the transport in MEH-PPV doped with F4-TCNQ can be explained by taking into account a field-assisted ionization of the dopant, leading to a field-dependent background carrier density. The ionization of the dopants becomes more pronounced at low temperatures and high electric field.

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