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Effect of molecular p-doping on hole density and mobility in poly(3-hexylthiophene)

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Employing impedance spectroscopy, we have studied the hole density, conductivity, and mobility of poly(3-hexylthiophene), P3HT, doped with the strong molecular acceptor tetrafluorotetracyanoquinodimethane, F_4TCNQ. We find that the hole density increases linearly with the F_4TCNQ concentration. Furthermore, the hole mobility is decreased upon doping at low-to-medium doping level, which is rationalized by an analytic model of carrier mobility in doped organic semiconductors [V. I. Arkhipov, E. V. Emelianova, P. Heremans, and H. Bässler, Phys. Rev. B **72**, 235202 (2005)]. We infer that the presence of ionized F_4TCNQ molecules in the P3HT layer increases energetic disorder, which diminishes the carrier mobility. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3701729]

Molecular doping, in particular p-doping with the strong acceptor tetrafluorotetracyanoquinodimethane, F_4TCNQ, has been widely applied to soluble and insoluble organic semiconductors in attempting to advance organic electronic devices. For instance, an improvement of the efficiency of small-molecule organic light emitting diodes has been achieved by incorporating doped layers in proximity to the electrical contacts.[1,2] Molecular doping has also been employed on polymer field-effect transistors, where an improvement of the charge carrier mobility was attributed to the filling of deep traps in the channel region by doping-induced charge carriers.[3–6]

F_4TCNQ-doping has been shown to be applicable to a variety of hole-transporting polymers.[7] Apart from the generally observed increase of conductivity, systematic studies of the doping mechanism and how it affects charge carrier density and transport in the bulk of doped polymer layers are, however, rare. The electrical properties of F_4TCNQ-doped poly(2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene), MEH-PPV, layers have been studied by Zhang *et al.* Based on the modelling of unipolar *I-V* characteristics, they found that only a small fraction of the applied F_4TCNQ dopants is active in creating free holes in the polymer layer.[8] Moreover, the ionization of the F_4TCNQ dopants was reported to depend on the electric field and temperature.[9] These findings are in accordance with reports on the nature of the charge transfer in F_4TCNQ-doped polythiophenes and small hole-transporting molecules:[10–13] It has been suggested that the donor-acceptor interaction leads to a bound charge transfer (CT) state between F_4TCNQ and the donor site. In these complexes, supramolecular orbitals are formed as a result of hybridization of the acceptor's lowest unoccupied molecular orbital (LUMO) and the donor's highest occupied molecular orbital (HOMO). The band gap of the CT complex is significantly reduced when compared to those of the isolated donor and acceptor components, and the generation of free charges probably involves excitation into the energetically deep-lying LUMO of the complexes.

As a point of criticism, the aforementioned electrical studies neglect the effect that ionized dopant molecules supposedly have on the charge transport in doped polymer layers. Arkhipov *et al.* modeled the motion of free charge carriers within doped disordered media.[14,15] They have pointed out that the ionized dopants act as long-range trapping centers owing to the Coulomb attraction of mobile charge carriers. Effectively, this leads to a broadening of the density-of-states (DOS) distribution, which might cause a reduction of mobility at low-to-moderate doping concentrations. This prediction is in contrast to the usual presumption that the mobility is increased upon doping due to the filling of traps by doping-induced charge carriers. Interestingly, a decrease of mobility upon molecular doping has never been experimentally observed.

In the present Letter, we independently determine the hole density and low-field bulk conductivity of F_4TCNQ-p-doped P3HT layers at low to moderate doping concentration. For that, we employ admittance spectroscopy to a metal–insulator–semiconductor (MIS) structure as depicted in the inset of Fig. 1(b). The samples were prepared on glass substrates with a patterned indium-tin-oxide (ITO) electrode. On top of that, we spin-cast a methyl-/phenyl-substituted polysilsesquioxane (PSQ) solution that was rendered insoluble after heat treatment. Continuing in N_2 atmosphere, the F_4TCNQ-doped or undoped P3HT was spin-cast from chloroform solution, yielding a layer thickness in the range of 0.35 to 1.2 μm. The devices were completed by evaporation of 5 nm MoO_3 and 100 nm Al, followed by encapsulation using a glass sheet and an epoxy resin. Device stability without noticeable change in the measurement results has been maintained for at least one week. Details of the sample preparation and experimental setup can be found in the supplementary information.[16]

From the complex admittance, $Y = G_p + i\omega C_p$, we extract the parallel capacitance C_p and the loss G_p/ω. Fig. 1 shows exemplary C_p–DC bias curves and the loss spectra of

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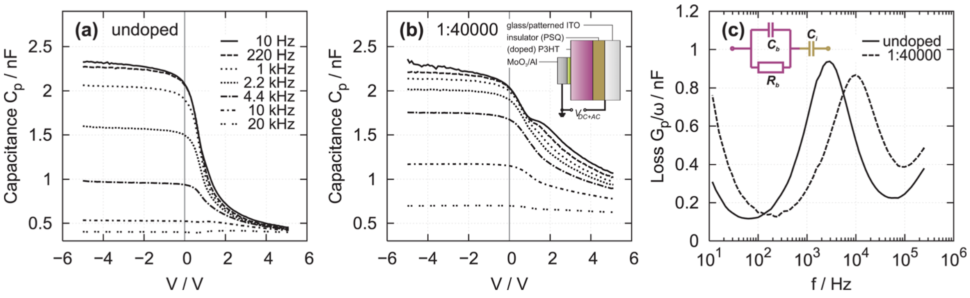

FIG. 1. Capacitance vs. DC bias of (a) undoped and (b) 1:40 000-doped MEH-PPV MIS samples. The inset depicts the MIS sample structure. (c) shows the corresponding loss spectra and the equivalent circuit in accumulation (at −5 V DC bias).

undoped and 1:40 000 F_4TCNQ-doped P3HT MIS samples. Note that a doping ratio χ of 1:40 000, or equivalently 2.5×10^{-5}, refers to the addition of 1 F_4TCNQ molecule per 40 000 thiophene repeat units of P3HT. At low frequency and negative bias, the devices exhibit the capacitance of the insulator layer C_i due to the accumulation of holes. Sweeping to positive bias, C_p drops as the semiconductor is depleted. From that region, we determine the hole density p following standard MIS theory.[17] Hence,

$$p = \frac{2}{e\varepsilon_0\varepsilon_r A^2 \frac{\partial C_p^{-2}}{\partial V}}, \tag{1}$$

where A is the active area of the device and $\varepsilon_r = 3.5$ is the dielectric constant of P3HT. The capacitance drop of the 1:40 000-doped sample shows a shoulder at low frequencies ($f = 10$ Hz). This is typical of an inversion layer at the insulator interface, whose charging/decharging dynamics are slower than the cycles of the applied AC voltage, and whose capacitance contribution is therefore less than C_i.[17] The coincidence of depletion and inversion features renders the evaluation of the hole density difficult. In order to determine p most reliably in these layers, we evaluate the C_p–V curve at a frequency at which the inversion feature is minimized and C_i is still retained at accumulation bias. This was possible up to dopant concentrations of 10^{-4}.

At higher frequencies, C_p is reduced towards the geometrical capacitance even at negative DC bias, because charging and discharging inside the device cannot keep track with the applied AC voltage. Concomitantly, this leads to a peak in the loss spectrum, which is related to the conductivity of the bulk semiconductor layer. Applying the equivalent circuit shown in Fig. 1(c), the characteristic frequency is given by $f_p = [2\pi R_b(C_i + C_b)]^{-1}$ in accumulation, i.e., at highly negative bias, with C_b being the bulk layer capacitance. Knowing the geometric dimensions of the semiconductor layer, the bulk conductivity can be calculated according to

$$\sigma = 2\pi f_p (C_i + C_b)\frac{d}{A}, \tag{2}$$

where d is the semiconductor layer thickness. Note that σ is the conductivity at very low field where bulk transport is governed by intrinsic charges. Applying an AC signal of $V_{rms} = 20$ mV, the rms electric field in the bulk layer typically amounts to $F \sim 2 \times 10^4$ V/m.

The hole density and bulk conductivity determined in this manner are shown in Fig. 2. A significant increase of the hole density is seen at doping ratios χ exceeding 10^{-6}. The data can be well described by a linear function of the form $p = D\chi + p_0$, considering a background density of $p_0 = 1.2 \times 10^{21}$ m^{-3} and a slope parameter of $D = 2.0 \times 10^{26}$ m^{-3}.

From that we conclude first that the amount of doping-induced holes is increasing linearly with the concentration of dopants. This is in accordance with our previous finding that CT complexes between F_4TCNQ and P3HT are highly localized and, thus, do not interact even if they are located on the same P3HT chain at very high doping densities.[10] Note that linear dependencies between hole density and doping ratio have been reported in F_4TCNQ-doped MEH-PPV (Ref. 8) and P3HT (Ref. 18) at higher doping concentrations than we used here.

Second, the slope of the linear increase allows an estimate of the doping efficiency. Taken a mass density of P3HT (Ref. 19) of 1.1 g/cm^3 and a molecular mass of one thiophene unit of 166.28 g/mol, the number density of thiophene units per volume is 4.0×10^{27} m^{-3}. In considering our previous findings that, at our low doping ratios, almost every F_4TCNQ acceptor forms a CT complex with P3HT,[10] the doping efficiency amounts to ca. 5%.

The trend of the conductivity vs. doping ratio resembles that of the hole density, i.e., a strong increase is seen at doping ratios higher than 10^{-6} (Fig. 2(b)). However, the log-log representation suggests a weaker, sublinear dependency according to a power law $\sigma \propto \chi^\gamma$ with $\gamma \sim 0.63$, indicating that the hole mobility is not constant upon doping. The hole mobility, calculated according to $\mu = \sigma/(pe)$, is depicted in

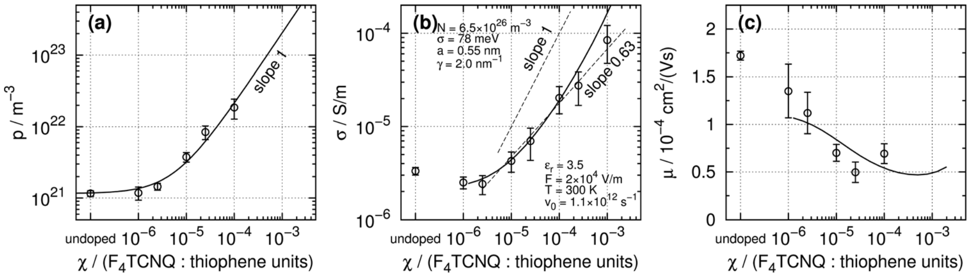

FIG. 2. (a) Hole density of undoped and doped P3HT layers. The line models a linear increase of hole density, starting from a background of 1.2×10^{21} m^{-3}. (b) Low-field bulk conductivity and (c) hole mobility. The solid lines are calculated according to the model of Arkhipov *et al.*[15] using the parameters given in the inset. Physical symbols are the same as in Ref. 15.

Fig. 2(c). Compared to the undoped sample, the mobility is steadily reduced up to doping ratios approaching 3×10^{-5}. Due to the increasing uncertainty in determining p, it was not possible to clarify if the mobility settles or eventually increases at higher doping ratios.

Most importantly, the trends of bulk conductivity and mobility from low to moderate dopant concentrations are in line with the above mentioned model by Arkhipov *et al.*[14,15] Simulated conductivity and mobility curves that reproduce our experimental data are shown in Figs. 2(b) and 2(c) (solid lines). We used a parameter set which contains the total site density $N = 6.5 \times 10^{26}\ \mathrm{m}^{-3}$, the Gaussian disorder parameter $\sigma = 78$ meV, the bound pair distance $a = 0.55$ nm, the inverse carrier localization length $\gamma = 2.0\ \mathrm{nm}^{-1}$, and the attempt-to-hop frequency $\nu_0 = 1.1 \times 10^{12}\ \mathrm{s}^{-1}$. These values compare well to those used by Arkhipov *et al.*[15] for electrochemically doped P3HT.

Following Arkhipov *et al.*, we infer that the reduction of hole mobility and, hence, the sublinear increase of conductivity with increasing doping ratio is most likely caused by a doping-induced broadening of the DOS distribution. The actual dependence of the mobility on the dopant density is governed by the counteracting occurrence of doping-induced tail broadening and the filling of the DOS distribution by doping-induced charges. Especially at low electric fields and low intrinsic electronic disorder, the combination of these effects can result in a reduced charge carrier mobility at low-to-moderate doping as seen in this work.

At higher dopant concentrations, it is expected that the individual Coulomb potentials of the countercharges overlap, such that the trap depth is essentially reduced.[15] Hence, the drop of the mobility should be reversed at sufficiently high doping levels. Indeed, the mobility of electrochemically or chemically doped P3HT was shown to increase for doping levels in the percent regime.[20] This may be as well the case for our F_4TCNQ-doped P3HT system, as indicated by our simulation. In the strong-doping regime, the mobility enhancement is due to the filling of the DOS distribution by doping-induced charges.

In summary, we have measured the hole density, bulk conductivity, and bulk mobility in F_4TCNQ-doped P3HT layers within a broad range of doping ratios, particularly including very low dopant concentrations. The free hole density increases linearly with doping ratio, suggesting that the charge transfer between F_4TCNQ and P3HT is electronically localized. We point out that the mobility is decreasing from low to moderate doping levels, which can be rationalized by the broadening of the DOS distribution owing to the Coulomb potential of the ionized acceptor molecules.

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