PHYSICAL REVIEW B **68**, 081204(R) (2003)

Charge transport in doped organic semiconductors

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(Received 19 May 2003; published 20 August 2003)

We report an unusual transition in the conductivity of an organic semiconductor upon doping: For low doping levels, the conductivity of N,N,N',N'-tetra-*p*-tolyl-4-4′-biphenyldiamine dispersed polycarbonate increases with doping in a nearly linear fashion, and shows an activation energy of 0.2 eV. At high doping levels, a superlinear increase of conductivity with doping is observed, and the activation energy decreases, reaching a low of 0.12 eV. This behavior is understood in terms of broadening of the transport manifold due to enhanced disorder coming from the dopants.

DOI: 10.1103/PhysRevB.68.081204 PACS number(s): 72.80.Le, 85.60.Jb

Doped organic semiconductors were originally studied in the 1960s.[1] Recently, renewed interest has been spurred by their utilization as injection and transport layers in organic light emitting diodes.[2–8] Despite over 25 years of development, some rather ubiquitous features of charge transport in these materials are not understood. One primary example is the fact that the conductivity of conjugated polymers and small molecules is often found to increase in a superlinear fashion with doping.[4–5,9–12] There is little understanding as to the microscopic origins of this behavior, and a physical description of the doping process remains challenging.[4] This is mainly due to the fact that the morphology of organics is complex and often changes upon doping.

Molecularly dispersed polymers (MDP's),[13] which are solid solutions of aromatic molecules in an inert polymer matrix, can serve as model systems for studies of doping. One characteristic example is tri-*p*-tolylamine (TTA) dispersed in polycarbonate (PC). Mort *et al.* described *p*-type doping in this material using the electron acceptor $\mathrm{SbCl_5}$.[14,15] MDP's offer several distinct advantages that make them model systems for doping studies: The hopping sites in MDP's are well defined, which has motivated numerous studies of transport in these materials and enabled a reasonable understanding of their transport properties.[16] They are available at high purity, and often exhibit trap free transport.[16] Doping can be performed in such a way that the average distance between the hopping sites is kept constant, avoiding dilution effects that take place in other organic semiconductors. Finally, up to 100% of the transport sites can be doped without causing any changes in the morphology of the film.

In this paper we report a transition that takes place in the conductivity of an organic semiconductor upon doping. It is manifested by a change in the slope of the conductivity vs doping and the activation vs doping curves. We interpret this behavior in terms of broadening of the transport manifold due to enhanced disorder coming from the dopants.

The prototypical organic semiconductor PC:TMTPD was used for the doping studies, where TMTPD is N,N,N',N'-tetra-*p*-tolyl-4-4′-biphenyldiamine. This is a hole transport MDP similar to PC:TTA, but exhibiting a higher mobility and a more stable conductivity upon doping.[17] Doping was performed by replacing a fraction x of the TMTPD molecules with their salt $\mathrm{TMTPD^+{:}SbF_6^-}$,[17] in such a way as to maintain the number density of TMTPD molecules, therefore keeping the *number density of hopping sites* p_0 constant and equal to $6.7\times10^{20}\ \mathrm{cm^{-3}}$ (see Fig. 1). To the first approximation, the degree of positional disorder should be the same in all samples. Films were cast from a dichloromethane solution on quartz plates with photolithographically defined interdigitated Pt electrodes. The current was found to be proportional to the voltage, and the conductivity was determined from the slope of the I-V curves.

The conductivity was found to exhibit Arrhenius behavior for $T\geqslant200$ K (Ref. 18) throughout the doping range (see Fig. 2). Two regimes were found as a function of doping: For low doping ($x<0.01$) the conductivity was found to increase in a nearly linear fashion (logarithmic slope 0.9). This is shown in the inset of Figs. 2 and 3. At the same time, the activation energy E_A, shown in Fig. 4, remains approximately constant around 0.2 eV. In the high doping regime ($x>0.01$), the conductivity increases in a superlinear fashion (logarithmic slope 2.3) until x approaches 0.5, after which it levels off at 10^{-5} S/cm; E_A decreases dramatically to 0.12 eV.

The change in the slope of the conductivity and E_A above $x=0.01$ cannot be explained with a simple picture of doping, where holes are generated in a transport level by thermal excitation of electrons to a well-defined acceptor level. This suggests that a transition is taking place in the rate of generation or transport of carriers in the material. We propose a simple model that considers the influence of three mechanisms on conductivity and provides an explanation for the origin of this behavior.

(i) *Filling of the transport manifold*. Hole transport in MDP's takes place via hopping in the manifold of highest occupied molecular orbitals (HOMO).[19–21] The HOMO density of states (DOS) approximates a Gaussian due to numerous independent contributions to the site energies coming from long-range electrostatic interactions with the surrounding disordered matrix.[22,23] Excess holes thermalize in the tail at an average energy σ^2/kT above the mean, where σ^2 is the variance of the Gaussian. Consequently, the (zero-field) hole mobility should be independent of hole concentration as long as the number of holes is lower than the *critical hole density*

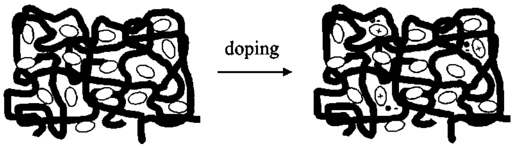

FIG. 1. Doping in PC:TMTPD. Left: The pristine state, where TMTPD molecules (ovals) are dispersed in the polycarbonate matrix. Right: A fraction ($x=0.2$) of the TMTPD molecules is replaced with their salt. The filled circle represents SbF_6.

p_C required to fill all states above σ^2/kT. Deviations are expected when the concentration exceeds p_C, so that the average hole energy dips further into the DOS. Time-of-flight measurements in TMTPD estimate σ to be between 0.102 eV (TMTPD dispersed in polystyrene)[24] and 0.078 eV (TMTPD glass).[25] For a 1 to 1 correspondence between holes and dopants, this would imply p_C between 8.0×10^{16} and 2.6×10^{18} cm^{-3}, respectively. However, the superlinear increase in the conductivity (inset of Fig. 2) is not observed until $x>0.01$, which corresponds to $p_C>6.7\times10^{18}$ cm^{-3}. This is on the high side of the expected range, indicating that manifold filling alone is not responsible for the observed transition.

(ii) *Coulombic trapping of carriers*. Holes introduced in the HOMO of the TMTPD molecules upon doping are trapped due to the Coulombic attraction with the SbF_6^- ion. The $TMTPD^+:SbF_6^-$ complex resembles a charge transfer exciton with a binding energy Δ that depends on the electron-hole distance. In order to model the influence of the Coulombic traps in a simple manner, we will assume that a hole becomes free when it hops to an uncomplexed TMTPD molecule, i.e., the spatial extent of a trap is equal to the intermolecular distance. The overall DOS is a superposition of the Gaussian energy densities for the TMTPD and $TMTPD^+:SbF_6^-$ sites, respectively,

$$\mathrm{DOS}(E)=\frac{(1-x)}{\sqrt{2\pi}\sigma}e^{-(E/\sqrt{2}\sigma)^2}+\frac{x}{\sqrt{2\pi}\sigma}e^{-[(E+\Delta)/\sqrt{2}\sigma]^2}. \tag{1}$$

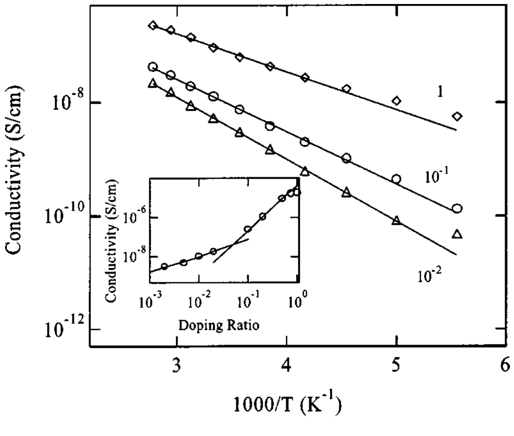

FIG. 2. Temperature dependence of conductivity for films with different doping ratios. The lines are fits to the Arrhenius equation. Inset: Conductivity (at room temperature) as a function of the doping ratio. The lines are fits with slopes 0.9 and 2.3.

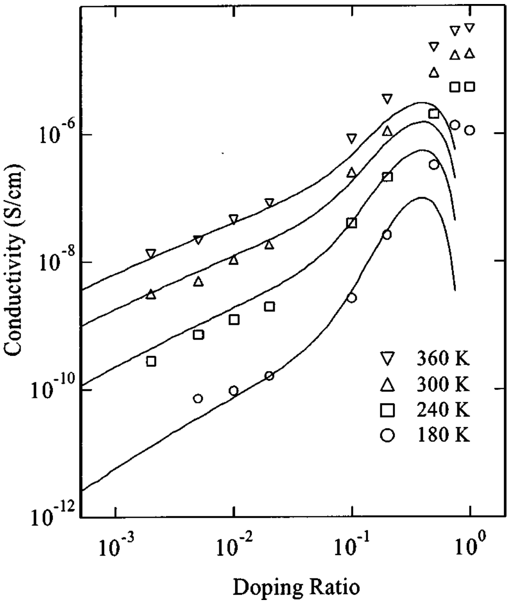

FIG. 3. Conductivity (at various temperatures) as a function of the doping ratio. The lines are fits to Eq. (3).

Assuming that these have the same width σ, which should be the case for long range electrostatic interactions, what distinguishes one from the other is the Coulomb trap energy Δ. The doping fraction determines their relative contribution to the overall DOS.

(iii) *Broadening of the transport manifold*. Introduction of dipoles in an MDP is known to broaden the HOMO manifold.[26] Approximating this additional contribution as Gaussian, the width of the DOS should then increase with x as[27]

$$\sigma=\sqrt{\sigma_0^2+x\left(7.04\frac{P}{a^2\varepsilon}\right)^2}, \tag{2}$$

where σ_0 is the intrinsic width (sample with $x=0$), P is the dipole moment of the $TMTPD^+:SbF_6^-$ complex, a is the av-

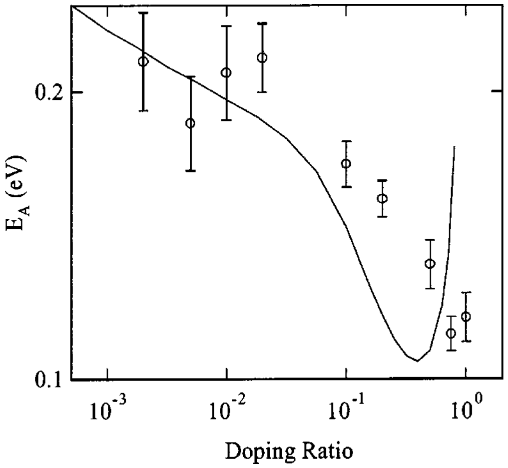

FIG. 4. Activation energy extracted from Arrhenius fits of the experimental data (circles) and the calculated values of conductivity (line) as a function of the doping ratio.

erage distance between TMTPD sites (in Å), and ε the dielectric constant.

In order to quantify the effects described above, we have applied the theory of Ambegaokar, Halperin, and Langer[28] for conductivity in the presence of strong spatial and energetic disorder. In MDP systems having a high concentration of transport sites, energetic disorder is large enough to make the conductances exponentially disparate at temperatures of interest, but not so large as to induce significant preferential hopping beyond the immediate nearest neighbors.[29] In such a case, the conductivity g is to be estimated by the critical conductance[28]

$$g = ep_0\mu_0 e^{-(E_C-E_F)/kT}, \tag{3}$$

where μ_0 is a prefactor mobility and E_F is the Fermi energy. The critical energy E_C determines the half width $\delta_C = E_C - E_F$ of an energetic window in the DOS, centered about the Fermi energy, which provides the minimum fraction η of nearest neighbor connections required for a percolating network of the highest conductances:

$$\eta = \int_{-\delta_C}^{\delta_C} \mathrm{DOS}(E-E_F)\,dE. \tag{4}$$

Equations (3) and (4) have been obtained assuming a Miller-Abrahams form for the underlying hopping rate, ignoring charge-charge interactions except by imposing a maximum of one charge per hopping site, ignoring complications which arise due to spatial correlations in the energetic disorder and, as noted above, the extended nature of the Coulomb traps. For large x, however, we must keep in mind that a number of other effects are expected to become important, such as overlap of the Coulomb traps, screening of electrostatic disorder, and possible alignment of the $\mathrm{TMTPD}^+ : \mathrm{SbF}_6^-$ dipoles. For this reason we have limited the application of the model to the regime of low x.

The solid curves in Fig. 3 were generated from a four-parameter fit to Eq. (3), up to a maximum concentration $x \cong 0.2$ (hole density $1.3\times 10^{20}\ \mathrm{cm}^{-3}$). The percolation fraction was taken to be $\eta = 0.25$ (the fit was found not to be particularly sensitive in the value of η). The model gives a reasonably good accounting of conductivity versus x in this range, describing the transition between the low and the high doping regimes, while at the same time giving a dependence on T which is in agreement with the experiment. The predicted E_A, superimposed with the experimental data in Fig. 4, also shows a transition between the two doping regimes.

The values of the four fitted parameters are $\mu_0 = 0.87 \times 10^{-6}\ \mathrm{cm}^2/\mathrm{V\,sec}$, $\sigma_0 = 0.086\ \mathrm{eV}$, $P = 28\ \mathrm{D}$, and $\Delta = 0.36\ \mathrm{eV}$. With the exception of μ_0, these parameters are within the range expected for the PC:TMTPD system. The value of σ_0 is in the range of values measured with time of flight.[24–25] The values of P and Δ imply a distance between the TMTPD^+ and the SbF_6^- ions of 5.8 and 4.3 Å, respectively. Although not identical, these values are close to each other and reasonable for a salt. However, the mobility prefactor μ_0 is approximately 4 orders of magnitude lower than what was measured in TMTPD in polystyrene using time of flight.[24] A similar discrepancy of two orders of magnitude was found by Mort *et al.* in PC:TTA.[14] This is not entirely unexpected since one underestimates the propensity for trapping by ignoring the volume of the Coulomb traps, which extends not only to the complexed TMTPD molecule, but to the full extent of the Coulomb radius. Another source of discrepancy comes from the distinction between the true prefactor, and the zero-field "extrapolated" prefactor which is determined from Poole-Frenkel plots.[30]

Close examination of the fits shows that the increase in dipolar disorder with doping is the primary reason for the transition from the low to the high doping regime, which is manifested by the abrupt reduction of the E_A, as well as the superlinear increase of the conductivity. Namely, the width of the DOS [Eq. (2)] begins to increase markedly above $x = 0.01$. The resulting broadening of the manifolds of complexed and uncomplexed TMTPD molecules increases the density of states in the neighborhood of the Fermi energy, which decreases δ_C. This implies an increase in the number of isoenergetic sites which participate in conduction, increasing the critical conductance while simultaneously decreasing E_A. In such a case, it is not surprising that the exact shape of the conductivity vs doping curve is rather subtle, and depends on the detailed manner in which the DOS corresponding to the complexed and uncomplexed TMTPD molecules overlap in the neighborhood of the Fermi energy.

It should be noticed that the model proposed here predicts a maximum in the conductivity and a subsequent decrease at high doping ratios. This is a combined effect of dipolar broadening of the DOS and manifold filling. At $x \cong 0.5$, $\sigma = 0.36\ \mathrm{eV}$, the two manifolds are broadened so that they overlap into one, which is half filled. Any further increase of carrier concentration causes a decrease of the conductivity. Such behavior has been experimentally observed in PC:TTA,[14,15] where the conductivity abruptly decreases above $x = 0.5$. In contrast, the conductivity of PC:TMTPD does not show such a decrease. The reason for this likely resides in the fact that holes are able to access an additional lower lying manifold that corresponds to accommodating two holes per TMTPD molecule. Indeed, such a double oxidation of TMTPD has been experimentally observed in electrochemical studies.[31]

In conclusion, we observed a transition in the conductivity of an organic semiconductor upon doping. This was manifested by a change in the slope of the conductivity vs doping curve, which changed from nearly linear (slope of 0.9) for $x < 0.01$, to superlinear (slope of 2.3) for $x > 0.01$. At the same time, the activation energy changed from being independent of doping for $x < 0.01$, to decreasing with doping for $x > 0.01$. This behavior was understood in terms of broadening of the transport manifold due to enhanced disorder coming from the dopants.

Thanks are due to Martin Abkowitz, Jack Blakely, J. Campbell Scott, Steve Barlow, and Seth Marder for fruitful discussions. This work was supported by the National Science Foundation (Grant No. DMR-0094047 and No. DMR-0097204) and by the Cornell Center for Materials Research (CCMR), a Materials Research Science and Engineering Center of the National Science Foundation (Grant No. DMR-9632275).

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