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Organic Electronics 2 (2001) 165–169

Organic Electronics

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Charge transport in anthradithiophene single crystals

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Received 14 July 2001; received in revised form 4 September 2001; accepted 4 September 2001

Abstract

The intrinsic charge transport mechanism in anthradithiophene single crystals is investigated by temperature dependent space charge limited current spectroscopy. The mobility for in-plane transport in this layered p-type semiconductor exhibits an inverse power law temperature dependence, typical for coherent band-like charge transport. In contrast to that a thermally activated charge transport perpendicular to the molecular planes can be described by incoherent hopping motion. Consequently, the charge carriers (holes) can be characterized as partly delocalized between molecules of a given molecular layer, but localized within individual molecular layers. The results are compared to the related compounds, pentacene and α-sexithiophene, in order to investigate the influence of the sulfur orbitals on hole transport in these and other thiophene-based molecular materials. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Charge transport; Anisotropy; Thiophene; Mobility; Transistor

Organic thin film transistors based on oligothiophenes or pentacene have reached device performance with mobilities within the range of 0.1–1 cm^2/V s and on/off current ratios larger than 10^6 [1–8]. In addition, 'monolithical' integration of 'plastic' transistors and organic light emitting devices [9,10] promises potential applications, not only in low-end data storage, such as smart cards or identification tags, but also as switching devices in active matrix displays. However, the fundamental understanding of the intrinsic charge transport mechanisms and the relations to the molecular and crystal structure is still incomplete in this emerging class of materials. Most studies have used thin film geometries, where disorder, traps, and grain boundaries can significantly influence the charge transport behavior [11,12]. Consequently, the true intrinsic material properties are often masked by such extrinsic effects. Recent studies focused on the electrical properties of single crystalline oligothiophenes, mainly α-sexithiophene [13–18], and pentacene [8,19–21]. Here, we investigate charge transport in high-quality anthradithiophene (ADT) single crystals to study the influence of the molecular structure on charge transport. ADT is a promising organic thin film transistor material [22]; from its molecular structure it can be seen as an intermediate between pentacene and oligothiophenes (see Fig. 1). The importance of its sulfur orbitals on the electronic transport properties is especially interesting. The properties of ADT,

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PII: S1566-1199(01)00022-2

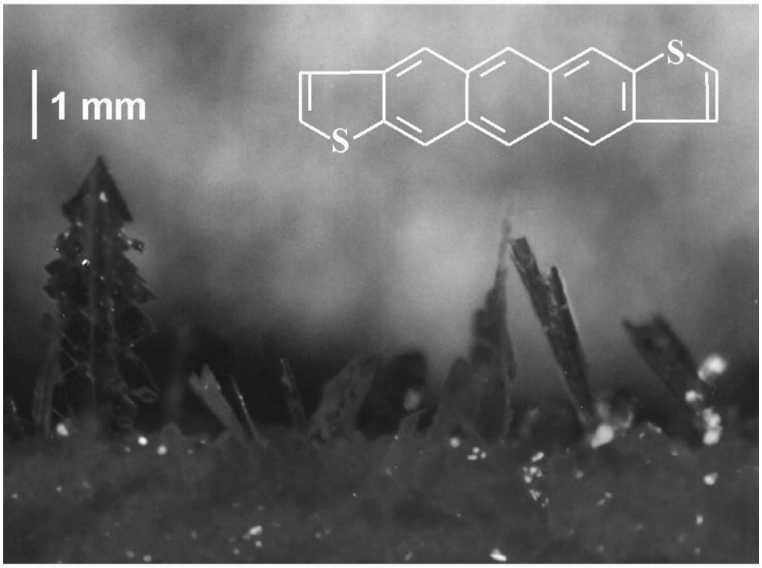

Fig. 1. Molecular structure of ADT and photograph of typical single crystals.

pentacene, and α-sexithiophene are compared. Temperature-dependent space charge limited current (SCLC) spectroscopy was used to determine charge carrier mobility as a function of temperature, electric field, and crystallographic direction.

ADT was synthesized as reported earlier [22]. Thin (~10 μm), mm^2-sized platelets of ADT single crystals (Fig. 1) were grown from the vapor phase in a stream of gas (argon/hydrogen). Details of the experimental technique have been reported earlier [23]. The material crystallizes in a layered structure similar to rigid rod-like oligomers of thiophene. Consequently, the electrical and optical properties are expected to be highly anisotropic. Due to unintentional doping during the growth ADT behaves like a p-type semiconductor. For electrical measurements ohmic contacts were prepared by thermal evaporation of gold through a shadow mask. An annealing step in a flow of hydrogen at 150 °C was applied after contact preparation to reduce trapping states within the samples [24] and to improve the quality of the ohmic contacts. Current–voltage characteristics were measured in helium atmosphere in the temperature range from 30 to 350 K using a highly sensitive electrometer (Keithley 6517A).

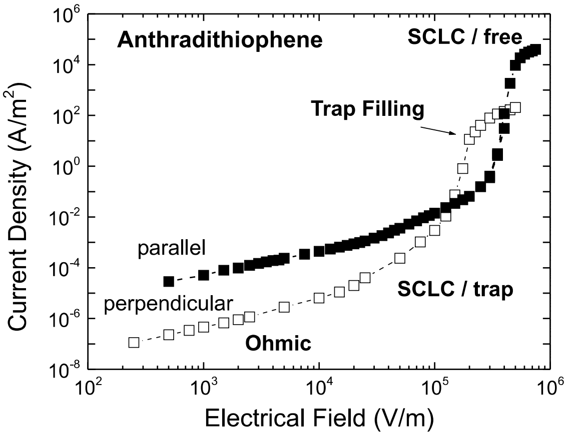

Fig. 2. Current density as a function of the applied electric field oriented parallel and perpendicular to the growth surface of the used ADT single crystal (room temperature). The ohmic, trap-limited space charge limited, trap filling, and trap-free SCLC regime are clearly observable. The multiple shallow trapping limited mobility is estimated from the deep trap-free SCLC regime according to Child's law.

The charge carrier mobility in ADT can be extracted from SCLC measurements, if the trap-free regime is reached [24] and unipolar (hole) transport can be assumed. Fig. 2 shows a typical current–voltage characteristics obtained for an ADT single crystal at room temperature. For high-purity samples four different regimes can clearly be distinguished [24]: (i) the ohmic regime, (ii) the trap-limited SCLC regime, (iii) the filling of the traps, and, finally, (iv) the trap-free SCLC regime. For unipolar conduction the mobility of the involved charge carrier sign can be determined from the trap-free SCLC regime according to Child's law [25]:

$$j_{\mathrm{SCLC}} = \frac{9}{8}\frac{\varepsilon_{\mathrm{r}}\varepsilon_0}{L^3}\mu V^2, \tag{1}$$

where ε_0 is the permittivity of free space, ε_{r} the relative dielectric constant, and L the distance between the two contact electrodes. For the samples used typical deep (~450 meV) trap concentrations were in the range of 10^{14} cm^{-3}, which is estimated from the trap-limited SCLC regime and the filling of the traps. At sufficiently high-electric fields, where these traps are filled and their influence on transport is negligible, the distance dependence ($\propto L^{-3}$) of the current density j has been checked to ensure the observation of trap-free SCLC, which is a pre-requisite for the estimation of the intrinsic mobility of the semiconductor. We like to mention, that due to the different electric field distribution for sandwich and surface geometry the comparison of the mobility parallel and perpendicular to the molecular layer bears at least a quantitative (factor) uncertainty.

Fig. 3 shows the in-plane mobility μ_{par} and the mobility perpendicular to the molecular planes μ_{perp} for an ADT single crystal as a function of temperature. The decrease of μ_{par} at low temperatures is ascribed to the presence of more than 10^{16} cm^{-3} shallow traps (~20 meV), which are not filled up, not even at the highest applied electrical field (applied voltage limited to 1000 V). Nevertheless, due to the small thermal activation energy of these shallow trapping states their influence on the transport properties is rather small above 200 K. All the measured mobility curves of different crystals of different purity tend asymptotically with rising temperature to the trap-free, intrinsic mobility μ_{tf}, which follows a power law ($\mu_{\mathrm{tf}} \propto T^{-n}$, $n \sim 1.8$), typical for coherent band-like charge transport determined by phonon scattering. The measured mobility of the sample with the lowest trap density increases from 1.1 cm^2/V s at room temperature up to 4 cm^2/V s at 120 K. With decreasing temperature the measured high-field mobility μ is gradually more decreased by shallow trapping ($\mu \propto \exp(-E_{\mathrm{t}}/k_{\mathrm{b}}T)T^{-n}$) [26] and, therefore, thermal activation becomes apparent (inset Fig. 3). Nevertheless, the same μ_{tf} can be extracted assuming a constant trap energy for all samples (~20 meV), but different trap concentrations N_{t} for the different samples.

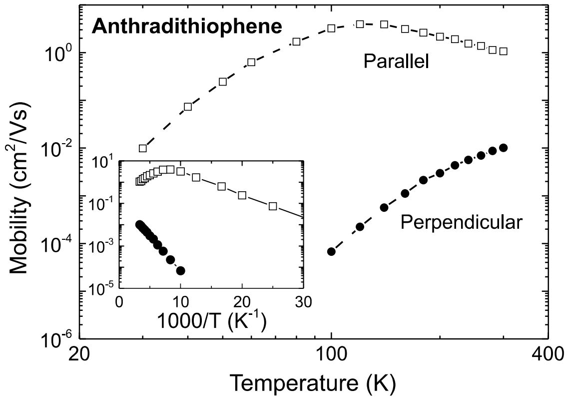

Fig. 3. Hole mobility parallel and perpendicular to the molecular planes in an ADT single crystal as a function of temperature. The inset shows the mobility as a function of inverse temperature, revealing unique, but different thermal activation energies at low temperatures for in-plane motion, and, throughout the whole experimentally accessible range, for transport perpendicular to the molecular planes.

Moreover, the in-plane mobility is found to exhibit a strong electric field dependence, which is shown in Fig. 4. A similar dependence of the charge carrier velocity v as function of applied electric field E has been observed in polyacene single crystals, such as naphtalene [27], anthracene [28,29], or pentacene [21]. This behavior can be explained by scattering at acoustic phonons. Using the deformation potential approximation the hole velocity v is given by [30]

$$v = \mu E = \mu_0 E\sqrt{2}\left\{1 + \left[1 + \frac{3\pi}{8}\left(\frac{\mu_0 E}{c_{\mathrm{l}}}\right)^2\right]^{1/2}\right\}^{-1/2}, \tag{2}$$

where μ_0 is the low-field mobility and c_{l} the longitudinal sound velocity. Fig. 4 shows a good

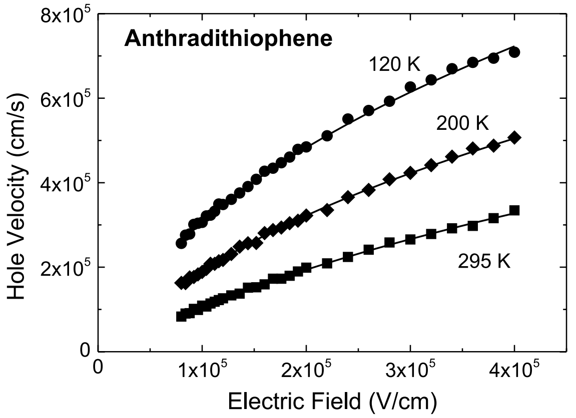

Fig. 4. Hole velocity for in-plane transport in an ADT single crystal as a function of the applied electric field at three different temperatures. The solid lines represent fits according to acoustic deformation potential scattering, using only the experimental parameters c_l and μ_0.

agreement between the experimental data for holes with Eq. (2). A longitudinal sound velocity of $c_l \approx 2 \times 10^5$ cm/s has been used for calculating the solid lines with taking μ_0 obtained at low field. Hence, the in-plane transport shows strong evidence for phonon scattering-limited band transport in extended states.

In contrast to the in-plane mobility μ_{par}, the temperature dependence of the perpendicular mobility, μ_{perp}, exhibits a thermally activated behavior with a larger activation energy over the entire temperature range from 100 to 350 K, as shown in Fig. 3. This activated transport can not be explained by trapping, because one would expect that detrapping activation energies should not strongly depend on the transport direction. Assuming a phonon-assisted hopping process of a polaronic charge carrier, the temperature dependence of the mobility is essentially given by [1,25]

$$\mu = \mu_0 \exp\left(-\frac{E_{\mathrm{b}}}{2k_{\mathrm{B}}T}\right), \tag{3}$$

where E_{b} is the binding energy of the polaron. From the plot of Fig. 3 a value of 65 meV can be estimated for ADT. Hence, the charge transport behavior suggests a charge carrier, which is delocalized across the molecules of a molecular sheet but localized within the plane. We like to mention that the in-plane anisotropy has been checked and found to be less than 50% (similar to acenes or oligothiophenes [17,18,21]); it has, therefore, been neglected in the discussion.

Table 1
Parameters of hole transport in pentacene, ADT, and α-sexithiophene (high-temperature modification/α-6T (HT)): μ_{RT} room temperature mobility for in-plane transport, μ_{TF} thin film transistor mobility at room temperature, $\mu_{\mathrm{par}}/\mu_{\mathrm{perp}}$ ratio of the anisotropy at room temperature, and E_{b} polaronic binding energy for charge transport perpendicular to the molecular planes

Material	μ_{RT} (cm^2/V s)	μ_{TF} (cm^2/V s)	$\mu_{\mathrm{par}}/\mu_{\mathrm{perp}}$	E_{b} (meV)
Pentacene	3.2	2	3	–
ADT	1.1	0.9	100	65
α-6T (HT)	1.1	0.2	70	75

The two-dimensional charge transport behavior is very much similar to that observed in oligothiophene single crystals [17]. In contrast, for hole transport in pentacene [21] and related materials (see Table 1) only a small anisotropy (~3 at room temperature) has been observed. Moreover, band-like hole transport is observed in pentacene in all crystallograhic directions. Since the molecular structure of pentacene and ADT is very similar (linear chain of five fused rings with delocalized π-electrons) we assume that the differences arise from the presence of the thiophene units, especially, due to the presence of sulfur. Further evidence is found by the similarity of the properties of ADT and α-sexithiophene single crystals. There, theoretical band-structure calculations revealed that the hole transport properties are related to the molecular overlap of the sulphur orbitals [2]. The charge transport properties are governed by shorter carbon–sulphur contacts [31]. The importance of the d–π wave function overlap between sulfur and carbon has been pointed out for substituted oligothiophenes as well [32].

In conclusion, the hole transport in high-quality ADT single crystals has been investigated by means of temperature-dependent SCLC spectroscopy. The in-plane transport properties can be described as two-dimensional multiple shallow trapping limited band-like motion of delocalized charge carriers, whereas the transport perpendicular to the molecular sheets is thermally activated by a larger activation energy and ascribed to polaron hopping motion. Different charge carrier transport behavior parallel and perpendicular to molecular sheets has also been observed for electron transport in anthracene and naphthalene [29,33]. A comparison with pentacene and α-sexithiophene suggests that the pronounced two-dimensionality is related to the importance of the molecular orbitals of the sulfur atoms impeding charge transport.

Acknowledgements

We like to thank Z. Bao, B. Batlogg, E. Bucher, A. Dodabalapur, and J. Rogers for many valuable discussions.

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