



Temperature dependence of the electrical properties of single-crystals of dithiophene-tetrathiafulvalene (DT-TTF)

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Abstract

Organic single-crystal field-effect transistors based on dithiophene-tetrathiafulvalene (DT-TTF) showing a charge-carrier mobility of $1.4 \text{ cm}^2/\text{V s}$ were recently reported. These crystals were prepared from solution, making this material interesting for potential applications in low-cost electronics. Here, we studied the temperature dependence of a DT-TTF field-effect transistor as well as the transport properties of single DT-TTF crystals. We found that the field-effect mobility follows a thermally activated hopping model with activation energy values (E_a) of around 85 meV, which is in agreement with the standard four-contact conductivity measurements performed on the single-crystals. In addition, the dependence of the E_a with temperature and of the threshold voltage with gate-induced charge suggest that the crystals do not contain deep impurity traps.

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1. Introduction

An increasing interest in organic field-effect transistors (OFETs) has emerged over the last few years due to the device performance levels achieved, which are often comparable to those of conventional amorphous silicon FETs [1]. Organic semiconductors offer an appealing alternative for applications where low-cost, large-area coverage and flexibility are required. The highest OFETs mobilities have been reported for vacuum-deposited crystalline films or single-crystals of low-molecular weight species and, in particular, pentacene-based transistors have received special attention [2–7]. The main drawback of pentacene is that it has a very low solubility in organic solvents and, thus, is not suitable for low-cost integrated circuit technology. Some attempts have focused on directly functionalizing pentacene to impart solubility [8,9] and on preparing thin-films of a soluble pentacene precursor which is converted to pentacene upon heating [10]. However, another feasible approach is to search for

promising new organic materials. Following this line of investigation, we recently reported a high field-effect hole mobility of $1.4 \text{ cm}^2/\text{V s}$ for crystals of the organic semiconductor dithiophene-tetrathiafulvalene (DT-TTF, Fig. 1) [11,12]. Remarkably, these crystals were formed by a simple drop casting method, making this material viable for possible applications in low-cost electronics. In order to gain a better insight into the transport mechanisms that govern the mobility of these crystals, we report here on a study of the temperature dependence of the conductivity and field-effect mobility of DT-TTF crystals.

In contrast to covalently bonded inorganic semiconductors which exhibit band-type transport, organic crystals are formed by relatively weak Van der Waals interactions between molecules.

It is generally agreed that charge transport in organic semiconductors occurs via charge hopping between localized states, namely polaron hopping [13,14]. The polaron formation results from electron–phonon interactions and can be defined as the charge present in a crystal together with the induced lattice distortion caused by the ionic polarisation. Whereas in delocalised systems the transport is limited

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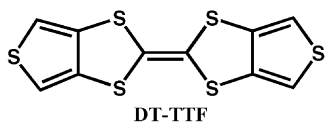


Fig. 1. Molecular structure of dithiophene-tetrathiafulvalene (DT-TTF).

by phonon scattering, hopping transport is phonon assisted. Several models have been developed to describe the hopping transport. Holstein's model [15] assumes successive uncorrelated carrier hops to neighbouring sites resulting in a simply activated-type dependence of the carrier mobility on temperature down to some critical temperature, below which band transport dominates. Mott's variable-range hopping model [16,17] is usually used to explain the charge transport in highly doped organic semiconductors, in which there is a high density of states at the Fermi level.

The study of the temperature dependence of mobility in OFETs is of great importance to understand the transport mechanisms that take place and to assist progress in the development of new materials for molecular electronics.

2. Experimental

2.1. Materials and device preparation

DT-TTF was synthesised as previously reported [18] and single crystals were obtained by recrystallization in carbon disulfide.

Silicon substrates with a 200 nm thermally grown oxide layer were purchased from Wacker Siltronic AG. Electrode fabrication was carried out in an electron beam pattern generator (EBPG5 HR 100 kV FEG) using a double layer of poly(methylmethacrylate) (PMMA) resist. Four nanometers of Ti and 20 nm of Au were evaporated at liquid nitrogen temperature to ensure a smooth surface and lift off was done in acetone.

The single crystal transistor was prepared by heating a saturated solution of DT-TTF in chlorobenzene to about 60 °C and pouring it over the substrates containing the microfabricated electrodes at room temperature. The solvent was allowed to evaporate very slowly for about 2 h in a sealed container giving rise to good quality long plate crystals, some of which bridged the electrodes. An optical microscope Olympus DP10 was also used to inspect the samples.

2.2. Transport measurements

The transport measurements of the DT-TTF transistor were carried out in a Microscope Probe Station coupled to an ADwin Gold external data acquisition system. The measurements of the conductivity with temperature were carried out by inserting a dipstick, containing the sample mounted on a chip holder, into a He vessel.

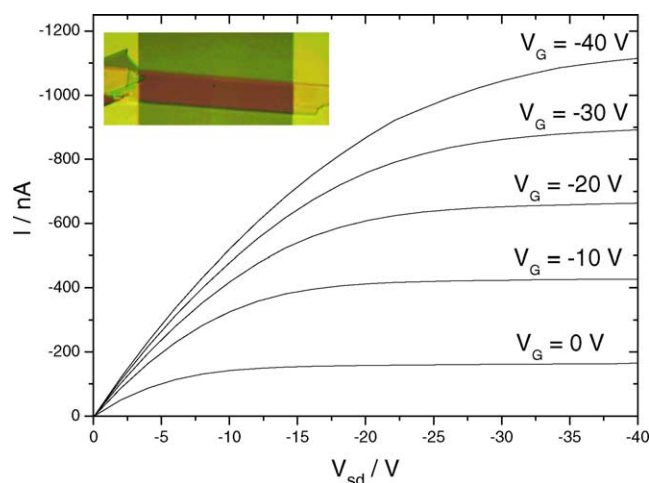


Fig. 2. I_{SD} vs. V_{SD} at different constant V_G for the single-crystal OFET of DT-TTF shown in the inset of this figure. This device has a channel length (L) and width (W) of 300 and 60 μm , respectively.

For the four floating contacts measurements of the single DT-TTF crystals, the crystals obtained from the recrystallisation in carbon disulfide were mounted with four platinum probes on PC boards using silver paste mixed with 2-butoxyethyl acetate as a thinner. These PC boards were then attached onto a sample holder, which was placed inside of a quasi-isothermal copper can in a constant liquid nitrogen flow cryostat. The temperature was controlled by a LakeShore Cryotronics Model 331 Temperature Controller.

3. Results and discussion

The inset of Fig. 2 shows a microscope photograph of a DT-TTF crystal lying across two gold electrodes (source and drain). This device has a channel length of 300 μm and channel width of 60 μm . In Fig. 2, the source-drain current (I_{SD}) versus the source-drain voltage (V_{SD}) at different gate voltages (V_G), applied to the silicon substrate, are plotted. The resulting graphs are typical of a p-type semiconductor: as a more negative V_G is applied, more holes are induced in the accumulation layer of the organic semiconductor and the conductivity increases. The device mobility was determined in the linear regime by first calculating the slope dI_{SD}/dV_{SD} of the curves for each V_G and then using the formula,

$$\mu = \frac{\partial^2 I_{SD}}{\partial V_{SD} \partial V_G} \frac{L}{CW}$$

where μ is the mobility, C is the capacitance per unit area of the gate, and W and L are the width and length of the crystal between the source and drain electrodes, respectively. The resulting mobility was 0.55 $\text{cm}^2/\text{V s}$. We should note here that this formula does not take into account the contact resistances and, thus, gives a lower limit of the intrinsic crystal mobility.

This device was cooled down to study the dependence of the mobility with the temperature. Figs. 3a and b show the

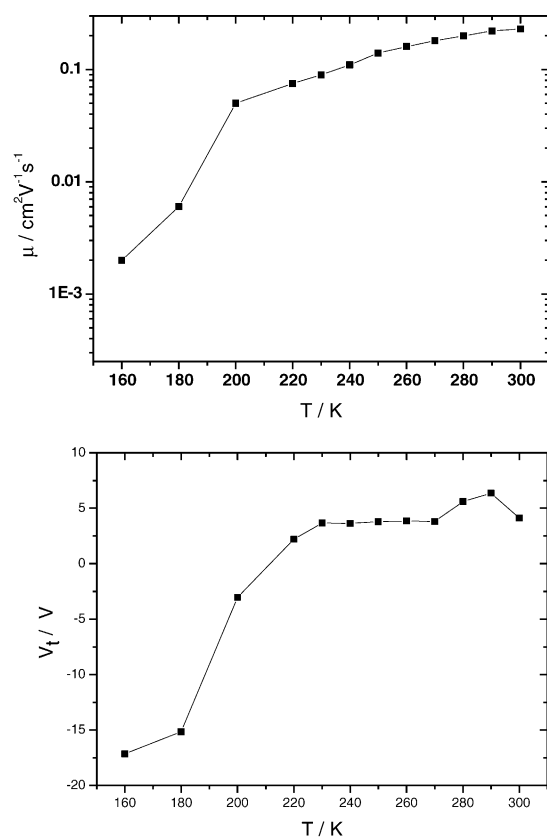


Fig. 3. (a) Dependence of the mobility (μ) of the DT-TTF crystal OFET with temperature when increasing the temperature after having cooled down. (b) Threshold voltage (V_t) vs. temperature for the same DT-TTF device.

temperature dependence of the DT-TTF crystal mobility, calculated as shown above, and threshold voltage V_t (i.e. the gate voltage necessary to suppress the conductivity in the crystal in the limit $V_{SD} \rightarrow 0$) in the range between 140 and 300 K. Below 140 K no detectable current could be measured. The sudden decrease of both mobility and V_t below 200 K was initially attributed to a crystallographic phase transition. However, X-ray studies indicate that there are no changes in the mosaicity and lattice constants of DT-TTF crystals down to 125 K. For this reason, we believe that this dramatic jump in the measured current results from different expansion coefficients of the crystal and the substrate or changes in the contacts. Accordingly, when the sample reached room temperature again, the mobility had decreased to $0.23 \text{ cm}^2/\text{V s}$. The temperature dependence of the mobility above 200 K resembles the prediction of Holstein's model for thermally activated hopping transport. Additionally, we observe that V_t remains approximately constant in a wide temperature range, and only decreases significantly below 230 K, implying that it becomes harder to turn on the device. This can be explained in terms of trapping: as the temperature is reduced, more gate-induced charge must be induced in the film to fill trap states before conduction begins [19,20].

Fig. 4 shows an Arrhenius plot of conductance versus inverse temperature for fixed $(V_G - V_t)$ values. The conduc-

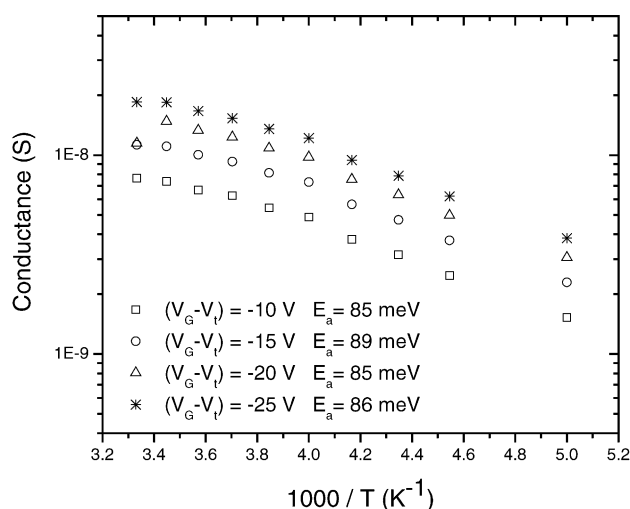


Fig. 4. Conductance vs. inverse temperature for fixed values of $(V_G - V_t)$ of -10 , -15 , -20 , and -25 V. The inset of the figure also shows the activation energies (E_a) calculated from the slopes of the curves.

tance was calculated as the slope dI_{SD}/dV_{SD} . The data were fit to the expression $\mu \alpha \exp(-E_a/k_B T)$ to determine the activation energies, E_a . We calculated E_a of 86, 85, 89, and 85 meV for $(V_G - V_t)$ of -10 , -15 , -20 , and -25 V, respectively. Previous work [16] has shown that the activation energy of OFETs decreases with gate voltages until it saturates at a value, which is limited by the polaron-binding energy. This is because some molecules have polaronic states deep in the gap due to spatial disorder. As the gate-induced charge is increased, these deeper states are filled leaving only the shallow traps to dominate the transport. Very recent experiments have shown that by employing a series of intensive purification processes of pentacene by vacuum sublimation, much higher single-crystal mobilities can be obtained, which exhibit a temperature dependence consistent with the band model [4]. The fact that our DT-TTF crystals have been prepared from solution might induce some small unintentional doping and incorporation of some impurities. However, the high mobilities found for these devices, together with the fact that V_t is relatively constant with temperature and the E_a is also constant at different $(V_G - V_t)$ values, suggest exclusion of deep trapping impurities in the samples. However, we should also keep in mind that the contacts resistances could also depend on temperature; this effect cannot be evaluated from the above measurements.

Four floating-contacts conductivity measurements were performed on five different DT-TTF crystals prepared in two different crystallizations in carbon disulfide. The crystals were plate-needle shaped with dimensions of $0.80\text{--}3.5 \text{ mm} \times 0.08\text{--}0.30 \text{ mm} \times 0.02\text{--}0.30 \text{ mm}$. The measurements were performed along the longest axis of the crystals, which corresponds to the molecular stacking axis b . All the crystals exhibited similar room temperature conductivities in the range between $5 \times 10^{-5} \text{ S/cm}$ and 10^{-4} S/cm . Three crystals from the first batch showed E_a of 90, 85, and 88 meV , while two crys-

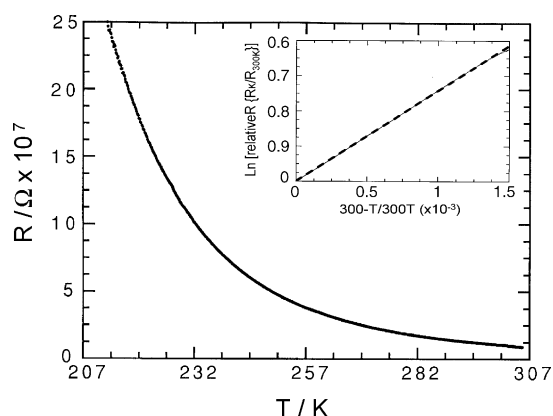


Fig. 5. Dependence of the resistance vs. temperature for a representative DT-TTF crystal measured using four floating-contacts. The inset shows the plot for calculating the activation energy with a linear square fit ($y = -0.0072215 + 2312.4x$; $r = 0.99987$; dashed line), resulting in a final E_a value of 0.199 eV.

tals from the second batch exhibited E_a of 199 and 197 meV. Fig. 5 shows the resistance dependence with the temperature of a representative crystal. The differences in activation energies are probably due to different crystal purities. That is, if more crystal defects are present, the charges will be more localised and, therefore, the energies required to induce conductivity will be higher. It is interesting to note that the E_a values obtained for the crystals from the first batch are in agreement with the E_a of the single-crystal OFET measured.

4. Conclusions

In conclusion, in order to study the transport mechanisms present in DT-TTF single-crystal OFETs, we studied the dependence of the field-effect mobility on temperature. We found that the temperature dependence of the mobility above 200 K follows the prediction of Holstein's model for thermally activated hopping transport. Additionally, the approximately constant values obtained for V_t at different temperatures, and of E_a at different fixed ($V_G - V_t$) voltages, suggest the exclusion of deep trapping impurities in the samples. This E_a value was also in agreement with the four-contact conductivity measurements performed in single crystals. The high mobility of this material together with its processability makes it very interesting for potential applications.

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