High Mobility of Dithiophene-Tetrathiafulvalene Single-Crystal Organic Field Effect Transistors

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The processing characteristics of organic semiconductors make them potentially useful for electronic applications where low-cost, large area coverage, and structural flexibility are required.[1] Charge carrier mobility is a measure of the quality of organic semiconductors and is a primary factor that determines the performance of organic field effect transistors (OFETs). The highest mobilities are found in single crystals due to molecular ordering that permits good overlapping of the $\pi-\pi$ orbitals. A mobility of 1.5 cm²/Vs was reported for pentacene,[2] and recently a mobility of 8 cm²/Vs was reported for rubrene.[3] These organic crystals were grown from the vapor phase in long and complex experiments. To progress in this field toward device applications, it is very important to search for new molecules that are able to act as organic semiconductors[4] and also to develop easy methods to grow single crystals or films. In this communication, we report on the clear observation of field effect hole mobility in single crystals of the organic semiconductor dithiophene-tetrathiafulvalene (DT-TTF, Figure 1a) grown by drop casting, a very simple method. The maximum mobility observed in these crystals was 1.4 cm²/Vs.

Tetrathiafulvalene (TTF) and its derivatives are successfully used as building blocks for charge-transfer salts, giving rise to a multitude of organic conductors and superconductors. These conducting salts are prepared mainly as single crystals but also as thin films of nanocrystals supported on dielectric polymers.[5-7] The driving force in the crystallization of the salts is the $\pi-\pi$ stacking, which permits, together with the S···S interactions, an intermolecular electronic transfer responsible for their transport properties. The transport properties of a few single crystals of neutral TTF derivatives have been measured, showing semiconductor character with a room-temperature conductivity on the order of 10^{-5} S/cm.[8-10] Additionally, organic thin films of TTF derivatives have been grown by vacuum deposition techniques, but only their morphology and nanomechanical properties have been studied.[11] However, TTF derivatives have never been used for the preparation of OFETs despite the fact that they are soluble in various solvents, easily chemically modified, and good electron donors.

DT-TTF is a particularly promising molecule because it is rigid and completely conjugated, having a low conformational freedom that favors stronger intermolecular interactions and, thus, higher carrier mobilities. Cyclic voltammetry measurements of DT-TTF show two separate reversible one-electron oxidations with $E_{1/2}^1$ and $E_{1/2}^2$ of 0.78 and 0.96 V, respectively (in DMF/0.1 M TBAPF₆ vs SCE). X-ray studies reveal that the DT-TTF molecules stack uniformly along the b axis in a herringbone pattern (Figure 1a).[12] Moreover, it is seen that the sulfur atoms also promote interactions between the different DT-TTF stacks within the layer which can lead to electronic dimensionality enhancing[5] (d(S···S) = 3.55 and
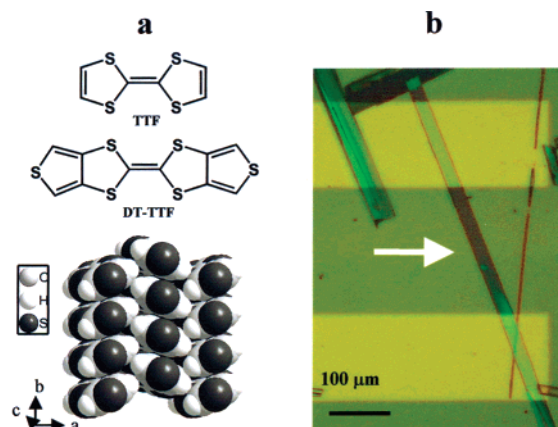

Figure 1. (a) Molecular structure of TTF and DT-TTF and crystal packing of DT-TTF. (b) The arrow points at the studied single crystal of DT-TTF formed on the microfabricated electrodes. The thin crystal to the right of the main bridging crystal was broken to avoid its contribution to the measurements.

3.61 Å). This crystal packing is reminiscent to the one reported for pentacene.[4,13] Similar to pentacene, the tilt angle between two molecular planes is 54° (53° for pentacene). However, the inter-planar distance between the molecules along one stack is only 3.56 Å for DT-TTF (4.20 Å for pentacene), and there exists an effective intrastack molecular overlap that is absent in pentacene.

DT-TTF was synthesized as previously reported[12] and purified by recrystallization in methylene chloride. A photograph of a DT-TTF crystal lying across two gold electrodes is shown in Figure 1b. The long axis of the crystals was determined to be the crystallographic b axis; that is, the stacking direction. The electrodes were fabricated by electron beam lithography on a 200-nm thick oxidized silicon wafer. The electrodes consist of 4 nm of titanium, acting as a sticking layer, covered by 26 nm of gold. A very simple and fast method was used to form the crystals: a warm saturated solution of DT-TTF in chlorobenzene was poured over the electrodes, and the solvent evaporated at room temperature. This process, known as drop casting, resulted in the formation of long, thin crystals, some of which connected two of the microfabricated gold electrodes. The formation of large regular crystals implies that the molecules are well-ordered within the crystals.

Figure 2 shows the source-drain current, I_{SD}, versus the applied source-drain voltage, V_{SD}, across the two electrodes for different gate voltages, V_G, applied to the silicon substrate, which acts as a gate. These electrical measurements were performed on the crystal shown in Figure 1b. The resulting graphs are typical of a p-type semiconductor biased in the linear regime[14] and are very similar to the previous reported ones for pentacene FETs.[2] As a more negative V_G is applied, more holes are induced in the semiconductor, and

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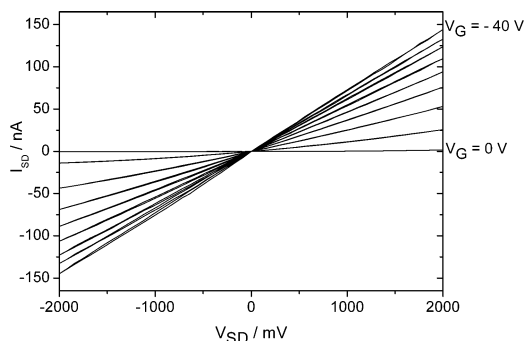‡ Institut de Ciència de Materials de Barcelona.

Figure 2. I_{SD} versus V_{SD} at V_G (from top to bottom on the right): -40, -35, -30, -25, 20, -15, -10, -5, and 0 V.
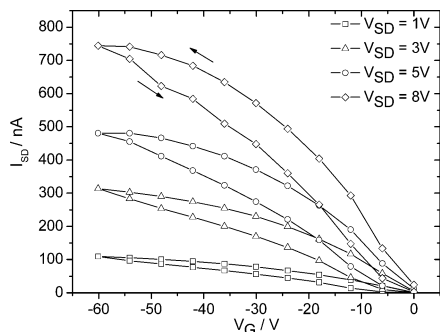

Figure 3. I_{SD} versus V_G at constant V_{SD}.

the conductivity increases. The conductance dI_{SD}/dV_{SD} was found to be a linear function of the gate voltage for 0 V $> V_G > -25$ V, as expected in the linear regime. The mobility was determined by first calculating the slope dI_{SD}/dV_{SD} of the curves for each V_G in this range and then using the formula

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

Here μ is the mobility, C the capacitance per unit area of the gate, and W and L the width and length of the crystal between the electrodes, respectively. For the crystal shown in Figure 1b, $W = 28\ \mu m$, $L = 310\ \mu m$, and $C = 1.7 \times 10^{-4}$ F/m^2, giving rise to a mobility of 1.4 cm^2/Vs, which was the maximum mobility achieved. For all the single crystals investigated, we found mobility values larger than 0.01 cm^2/Vs. In many cases, the mobility was larger than 0.1 cm^2/Vs. All the crystals were very stable for months in air.

Atomic force microscope measurements indicated that the crystal in Figure 1b was about 60 nm thick. The conductivity defined as $I_{SD}L/(WtV_{SD})$ was 10^{-3} S/cm for $V_G = 0$ V and 10^{-1} S/cm for $V_G = -60$ V. Here t is the thickness of the crystal. This is a surprisingly high value for a neutral organic crystal, indicating the presence of some unintentional doping or gating due to charge trapped at the interface.[15]

The linear and symmetric characteristics of the $I-V$ curves imply that there is good contact of the crystal to the Au electrodes. For crystals showing poor overlap with one of the metal contacts, asymmetric $I-V$ curves were obtained. Density functional (DF) calculations[16] show that the HOMO level of the molecule in the planar conformation is 4.9 eV (4.6 eV for pentacene), which is close to the work function of gold, at 5.1 eV.[17]

Figure 3 shows the I_{SD} as a function of V_G for different bias voltages. The gate was swept slowly from 0 to -60 V and back to 0 V in 90 s. The gate voltage sweeps are hysteretic probably due

to trapped charge. If positive charges are trapped on the organic semiconductor, the effective field effect arising from the negative gate voltage is diminished. The threshold voltage of this device (i.e., the gate voltage necessary to suppress the conductivity in the crystal) is 0.4 V. For positive gate voltages, the current is below the resolution of our instrumentation of 1 pA. This means that the ON/OFF ratio is at least 7×10^5 for this device, which is high for an organic transistor.

Thin polycrystalline film transistors of DT-TTF showing high mobilities in the range $0.01-0.1$ cm^2/Vs were also prepared. Currently, we are working on the study of the field effect mobility of other TTF derivatives to gain a better insight of the potential use of this family of molecules.

In conclusion, we prepared crystals of DT-TTF, which exhibited one of the highest hole mobilities observed in OFETs of 1.4 cm^2/Vs. These crystals were prepared using simple room-temperature drop casting. This is the highest mobility reported for an organic semiconductor which is not based on pentacene and is of the order of that of amorphous silicon that is widely used in solar cells and flat screen displays. The high mobility of DT-TTF combined with the simple processing required makes it a very good candidate material for electronic applications where low-cost, large-area coverage, and flexibility are required.

Supporting Information Available: Experimental procedures and additional data for other crystals (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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