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Improved Field-Effect Mobility in Short Oligothiophenes: Quaterthiophene and Quinquethiophene

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Organic field-effect transistors (OFETs) made of conjugated oligomers (oligothiophenes, pentacene), which were first fabricated in this laboratory eight years ago,[1] have now been reproduced by several groups,[2–5] and proved to be promising devices with a field-effect mobility μ_{FE} well into the 10^{-2} cm^{2}V^{-1}s^{-1} range and an on/off current ratio of up to 10^5. Enhanced performance of the sexithiophene (6T) OFET has been achieved by improving the ordering of the evaporated film, from a disordered three-dimensional (3D) structure to a well-ordered two-dimensional organization, where all the molecules align along a direction nearly perpendicular to the film and form layers parallel to it, with a preferential charge transport along the direction of the layers.[6] 6T belongs to the family of the oligothiophenes (nT, where n stands for the number of α-linked thiophene rings). Early results on shorter (3T to 5T)[2,7] and longer (8T)[7] oligomers than 6T revealed a very steep increase of μ_{FE}—by up to two order of magnitude for each additional ring—from 3T to 6T, followed by a slight decrease from 6T to 8T. The latter feature was attributed to the poor structural organization of evaporated films of longer oligomers, due to the lower purity of the raw material and a partial decomposition during the evaporation. The former behavior, namely the huge increase of μ_{FE} with n, is still unexplained. It is at variance with what has been observed for a long time on another intensively studied family of molecular crystals, the polyacenes, where the time-of-flight (TOF) mobility at room temperature is found to lie in the range 0.1–1 cm^{2}V^{-1}s^{-1}, whatever the length of the molecule, from naphthacene to tetracene.[8] (We note that, to the best of our knowledge, field-effect devices with these well-known molecular crystals have only been realized with polycrystalline pentacene.[7,9])

Charge injection in organic semiconductors has long been shown to be a crucial problem in organic-based devices, especially for large-bandgap compounds. This could explain the large scattering of results in the literature on the characteristics of these devices. In organic semiconductors, the Fermi level may be located far enough away from that of the metal electrode to impede efficient charge injection. One elegant way to overcome this obstacle would involve a modification of the Fermi level of the organic semiconductor through a local doping. It is well known that partial doping of an organic material, for instance by using an electron acceptor in the case of a p-type compound, lowers its Fermi level and increases its conductivity significantly. It has thus already been shown that doping oligothiophenes with iodine or FeCl$_3$ increases the conductivity up to some 10^{-1} S/cm.[10] However, these dopants must be regarded as mobile, owing to their small size and great hardness. Hence, it can be expected that such dopants would result in poor device characteristics, due to the large electric field developed in operation. Molecular dopants, involving large conjugated systems such as tetracyanoquinodimethane (TCNQ), appear much more promising.

In the present paper, we report on OFETs made with high purity quaterthiophene (4T) and quinquethiophene (5T). The field-effect mobility is much higher than that found in previous reports, and approaches that of 6T. The lower mobility of earlier devices is attributed to less efficient carrier injection from the electrodes. In the case of 4T, the use of a thin layer of TCNQ between the source and drain and the semiconducting layer results in an improved mobility, which we ascribe to a better carrier injection.

The source–drain current–voltage characteristics of a 4T OFET with undoped and TCNQ-doped contacts are shown in Figure 1. They present very well defined linear and saturation regimes. The effect of TCNQ is to increase the drain current by a factor of two. The fact that current amplification appears at negative drain and gate voltages is typical of a p-type material. The field-effect mobility was estimated from both the linear and saturation currents by using Equations 1 and 2, respectively.[11]

$$g_m = \left(\frac{\partial I_d}{\partial V_g}\right)_{V_d \to 0} = \frac{W}{L}C_i\mu_{FE}V_d \tag{1}$$

$$I_{d,sat} = \frac{W}{2L}\mu_{FE}C_i(V_g - V_t)^2 \tag{2}$$

Here, g_m is the transconductance, I_d the drain current, V_d and V_g the source–drain and source–gate voltages, respectively, W and L the channel width and length, C_i the insulator capacitance (per unit area), and V_t the threshold voltage. Values of μ_{FE} and V_t are summarized in Table 1 for 4T (with and without electrode doping) and 5T. "Ear-

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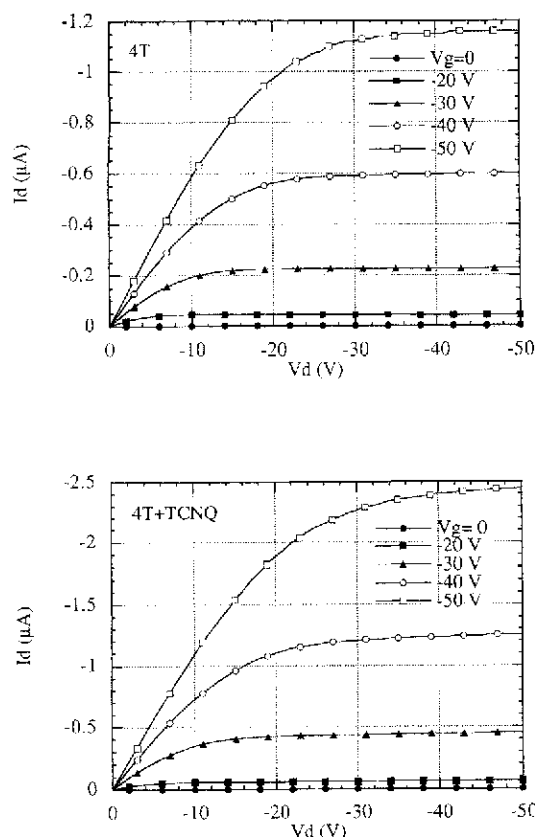   2 rue Henry-Dunant, F-94320 Thiais (France)

Fig. 1. Drain current as a function of the source–drain voltage at various source–gate voltages of a 4T field-effect transistor without (top) and with (bottom) a TCNQ layer inserted between the 4T layer and the source and drain gold electrodes.

Table 1. Field effect mobility and threshold voltage of 4T, 4T/TCNQ, and 5T. The earlier mobility is given for comparison.

Oligothiophene	Mobility [cm^{2}V^{-1}s^{-1}]		Threshold voltage [V]
	"Earlier" report	This work	
4T	2×10^{-7} [a]	2.5×10^{-3}	-15
4T/TCNQ		5.4×10^{-3}	-15
5T	2.5×10^{-5} [b]	1.5×10^{-3}	$+5$

[a] From Ref. [2]. [b] From Refs. [3] and [7].

lier" results are also shown for comparison. We note that a mobility ranging from 2×10^{-4} to 6×10^{-3} has recently been reported by a group from AT&T Labs for 4T OFETs with silicon oxide insulator.[12] It is worth noting that the mobilities of 4T and 5T are nearly equal, and that they are both only one order of magnitude lower than that of well-ordered 6T.

The transfer characteristic of the 4T OFET is shown in Figure 2. The on/off current ratio is mainly limited by a high off-current, which we attribute to leaks through the insulator. We have already noted that our PMMA insulator is of poorer quality than the more frequently used thermally grown silicon dioxide. Preliminary results from this laboratory[13] (with 6T as the semiconductor) have shown that, in the latter case, the off-current can be as low as

some picoamps. The attractive feature of Figure 2 is that, unlike what we usually observe with 5T and 6T, the off-current occurs at $V_g = 0$ and no depletion is detected at $V_g > 0$. This means that 4T displays a lower doping level. Practically all organic semiconductors exhibit a non-intentional doping. The lower doping level of 4T, compared to 5T or 6T, can be ascribed to its higher bandgap.
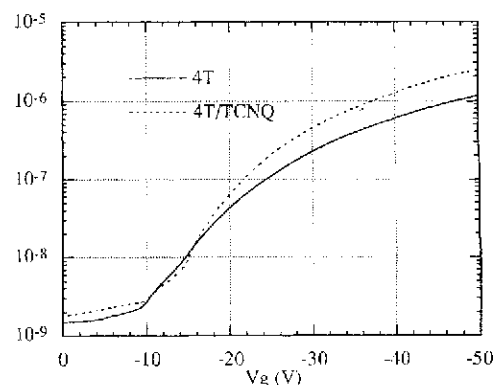

Fig. 2. Transfer characteristic at a source–drain voltage of 50 V for the same devices as in Figure 1.

The highest mobility of 6T has been achieved by realizing a two-dimensional structure in which the molecules align in a direction close to the normal to the film and form layers parallel to it. Such an orientation can be demonstrated by measuring the UV-vis absorption under polarized light. As shown in Figure 3, the measurement is performed at an angle of incidence of 60°. The s-polarized light has its polarization vector perpendicular to the plane of incidence, i.e., parallel to the film, whereas the p-polarized light has its polarization vector parallel to the plane of incidence, hence partly parallel and partly perpendicular to the film. The absorption spectra under s- and p-polarized light of 4T and 5T films are shown in Figure 4. They all show three peaks, two in the UV, which are virtually independent of the polarization, and one in the visible range, the intensity of which changes with the polarization. We explain the latter feature by recalling that the visible peak corresponds to a transition polarized along the long axis of the molecule,
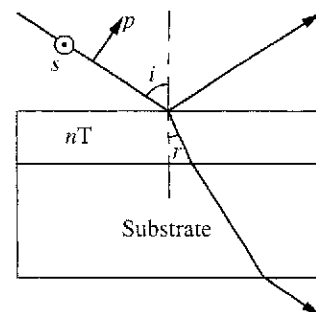

Fig. 3. Schematic view of the geometry for the measurement of the UV-vis absorption spectra of nT under polarized light. s and p polarizations correspond to light polarized perpendicular and parallel to the plane of incidence, respectively.
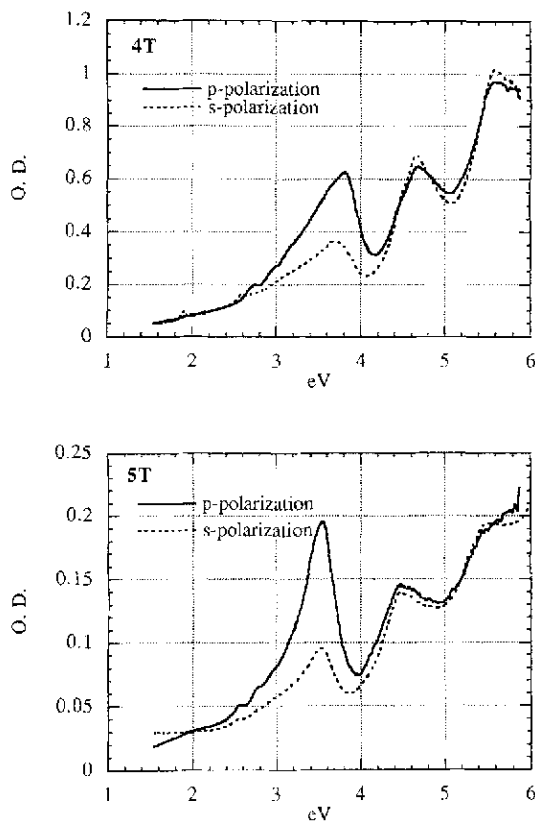
Fig. 4. UV-vis absorption spectra under polarized light at an angle of incidence of 60° for 4T and 5T evaporated films. The thickness of the film is 100 nm and 20 nm, respectively.

whereas the UV peaks are transitions polarized perpendicular to this axis. The fact that the absorption is greater under *p*-polarized light is consistent with the molecules being preferentially oriented perpendicular to the film.[14]

In summary, we have fabricated OFETs with 4T and 5T that present a mobility highly enhanced compared to that reported earlier. The mobility can be increased even further by doping the source and drain contacts with the electron acceptor TCNQ. This is interpreted in terms of the field-effect mobility in short oligothiophenes being limited more by charge injection than charge transport within the material. Moreover, the doping level in 4T films is much lower than in 6T, which favors a high on/off current ratio. UV-vis absorption under polarized light indicates that, as in the case of 6T, molecules in 4T and 5T films are preferentially oriented perpendicular to the film.

Experimental

Quaterthiophene (4T) was synthetized through the oxidative coupling of 2,2′-bithiophene. 20 mmol of bithiophene was lithiated at −70 °C in anhydrous tetrahydrofuran using *n*-buthyllithium (22 mmol of 2.5 M *n*-BuLi in hexane). After one hour at −70 °C, 2 molar equivalents of anhydrous copper(II) chloride were added. The solution was then slowly warmed up to room temperature while being stirred. After 18 h, water was added under acidic pH, leading to a yellow precipitate, which was filtered and thoroughly washed with a 4 N HCl solution, and then with acetone. The powder was

dried in vacuo in the presence of P_2O_5. Quaterthiophene was obtained as a yellow powder (yield 80 %). mp 212 °C. ^{1}H NMR (CDCl$_3$): H$_2$ (7.35 ppm, 2H, dd); H$_3$ (7.15 ppm, 2H, dd); H$_4$ (7.30 ppm, 2H, dd); H$_4$ (7.20 ppm, 4H, s).

The synthesis of quinquethiophene (5T) involved the Grignard coupling of 5-bromo-2,2′-bithiophene (B2) to 5-bromo-2,2′;5′2″-terthiophene (T2) in the presence of Ni(dppp) as catalyst. To 3 g of B2 was added 315 mg of magnesium in 15 cm^3 of anhydrous ether under argon atmosphere. The mixture was stirred slowly for two hours, then poured into a three-necked flask with 3.08 g of T2 and 270 mg of Ni(dppp) in 50 cm^3 of anhydrous ether. The solution was stirred for 15 h. Following hydrolysis and after the solution had been washed several times in water and dichloromethane, the organic phases were mixed and dried on MgSO$_4$. Upon subsequent washing in a Soxhlet with heptane and chloroform, 5T was obtained as a light brown powder (yield 30 %).

The geometry of our all-organic FETs has been described previously. It comprises a glass substrate, onto which the gate electrode (aluminum) is first evaporated. The insulating layer is made of spin-coated polymethylmethacrylate (PPMA). The semiconducting oligothiophene is then vacuum evaporated at a pressure in the 10^{-6} torr range and a rate of some nanometers per minute. The thickness and evaporation rate were controlled by a quartz thickness monitor Kronos. The gold source and drain electrodes, which consist of two 100 μm wide, 5 mm long stripes separated by 25 or 50 μm, are then evaporated through a nickel shadow mask. (The source and drain electrodes are more usually deposited between the insulating and the semiconducting layer. In the present case, it was found that devices made according to that configuration displayed poor characteristics. We think that depositing the gold electrode over the oligomer layer favors carrier injection.) In the case of "doped" contacts, TCNQ was evaporated through the same mask before the deposition of gold.

Device characteristics were recorded with a Hewlett-Packard 4140B picoammeter–DC voltage source. UV-visible absorption spectra of the 4T and 5T films were obtained with a Varian CARY 2410 spectrophotometer.

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