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## STRUCTURE EFFECTS ON TRANSPORT OF CHARGE CARRIERS IN CONJUGATED OLIGOMERS

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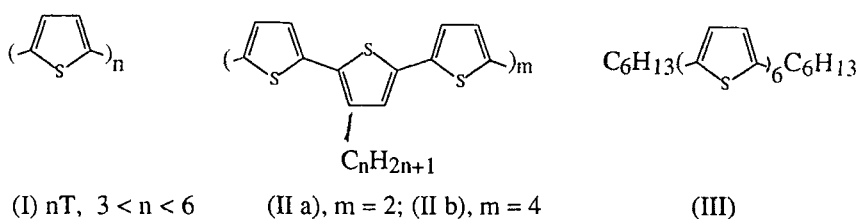
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**Abstract** Charge carrier mobility has been determined in field-effect transistors fabricated from conjugated thiophene oligomers and some of their  $\alpha$  or  $\beta$  alkylated derivatives. The results allow to analyze the contributions of conjugation length, interchain spacing and long range order in the charge transport in conjugated materials.

### INTRODUCTION

Field-effect transistors, FETs, based on organic conjugated materials have been reported during the past few years.<sup>1</sup> Polyacetylene, various polythiophenes and more recently short conjugated thiophene oligomers have been used as active semiconducting layer in these devices, and, whereas their electrical conductivity lies in the same range of  $10^{-7}$  to  $10^{-6}$  S  $\text{cm}^{-1}$ , their field-effect mobility has been shown to be very sensitive to the nature of the organic semiconducting material, varying from about  $10^{-5}$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  for polythiophene to about  $10^{-1}$  for the thiophene oligomer sexithienyl. This large variation observed in a same class of  $\pi$ -conjugated materials clearly indicates that structure effects control the transport efficiency of charge carriers. In this regard, and according to the well accepted variable hopping range mechanism, the most significant structural parameters which can be invoked for describing the charge transport process are i) the conjugation length of the conjugated segments, ii) the interchain spacing over which the charge has to hop, and iii) the long range ordering of conjugated segments in the organic semiconducting layer. The precise analysis of these parameters and the determination of their respective contributions in the transport of charge carriers appears almost out of reach in the case of conjugated polymers, owing to the very poor definition of these materials. On the other hand, short

conjugated oligomers present the advantage of being well defined and almost defect free molecules, and thus perfectly adapted for such studies, and, in this paper, we will report on a first approach on the effects of conjugation length, interchain spacing and long range ordering on the transport efficiency, expressed through the field-effect mobility,  $\mu_{\text{FET}}$ , determined on FET devices. Conjugation length is analyzed by considering thiophene oligomers ranging from the trimer to the hexamer, (I), whereas the interchain spacing has been varied by alkyl substitution on the  $\beta$  position of thiophene units along the oligomer chain, (II), and finally an attempt to induce long range order in thin layers of oligomers has been performed through alkyl substitution at the both  $\alpha$  ends of an oligomer, sexithienyl, (III), considering that the recognition property between the alkyl chains of adjacent oligomers could produce a driving force for such a structured packing.



## EXPERIMENTAL

The synthesis of  $\alpha$  quaterthiophene, 4T, and  $\alpha$  quinquethiophene 5T, has been already described.<sup>2</sup>  $\alpha$  Sexithiophene, 6T, has been obtained by oxidative coupling of the commercially available thiophene trimer,  $\alpha$  3T (Aldrich). The field-effect transistors were fabricated according to a thin film architecture, TFT, on Si/SiO<sub>2</sub> substrate, which has revealed to afford highly reproducible values for field-effect mobility,  $\mu_{\text{FET}}$ . The insulator is silicon oxide, 200 to 300 nm thick, thermally grown on a highly doped n-type silicon wafer, with resistivity of 0.002  $\Omega$  cm. The gate electrode is made of gallium-indium alloy rubbed on the oxide-free rear side of the wafer. The oligomer layer (20 to 100 nm thick), is deposited on SiO<sub>2</sub> film by vacuum evaporation, carried out by heating the powdered compound in a tungsten boat under reduced pressure (ca  $5 \times 10^{-3}$  Pa). The device is then completed by evaporating two gold contacts forming the the source and drain electrodes, with a channel length and width of 50  $\mu\text{m}$  and 0.5 mm respectively. All electrical measurements were accomplished in a metal box providing electrical and optical shielding. Contacts to source and drain were made with tungsten microprobes. Current-voltage characteristics were measured with a Hewlett Pacard 4140 picoameter/dc voltage source and capacitance measurements with a Hewlett Packard HP 4192 impedance analyzer.

## RESULTS AND DISCUSSION

Contrary to conventional field effect transistors, organic based TFT operate in the accumulation regime. When an appropriate negative voltage  $V_G$  is applied between source and gate electrodes, an accumulation layer forms at the interface between this p-type organic semiconductor and the insulator. At small source-gate voltage  $V_D$ , a drain current  $I_D$  proportional to  $V_D$  will flow in this conducting channel. As  $V_D$  increases, the channel depth decreases near the drain electrode, until the pinch-off voltage is reached, at which  $I_D$  saturates to  $I_{D,sat}$ , which is given by the relation (1)

$$I_{D,sat} = (W/2L)C_i\mu_{FET}(V_G - V_t)^2 \quad (1)$$

where  $C_i$  is the capacitance per unit area of the insulator and  $V_t$  a threshold voltage. This equation shows that  $\mu_{FET}$  can be calculated from the slope of the  $(I_{D,sat})^{1/2}$  vs  $V_G$  plot.

### 1. Effect of conjugation length

Results on thiophene oligomers (I), Table I, show a gradual increase of the conductivity  $\sigma$  and field-effect mobility  $\mu_{FET}$ , determined on  $SiO_2$  insulating layer, as the conjugation length increases up to the hexamer. The steepness of the variation in  $\mu_{FET}$  clearly expresses the importance of conjugation length in the transport of charge carriers.

TABLE I Conductivities and field-effect mobilities of thiophene oligomers (I).

Oligomer	Conductivity $\sigma$ (S cm <sup>-1</sup> )	Field-effect mobility $\mu_{FET}$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
Trimer, 3T	10 <sup>-10</sup>	not measurable
Tetramer, 4T	10 <sup>-9</sup>	2 x 10 <sup>-7</sup>
Pentamer, 5T	10 <sup>-8</sup>	10 <sup>-5</sup>
Hexamer, 6T	10 <sup>-7</sup>	2 x 10 <sup>-3</sup>

An important point concerns the existence of a threshold in conjugation length for observing a field-effect, which appears for the tetramer 4T. This result can be explained by considering the mechanism of carrier generation in  $\pi$ -conjugated oligomers. It is generally accepted that carriers in conjugated polymers are associated with self-localized defects, such as polarons or excitons. On an as short oligomer as 3T, such defects would be more appropriately termed as radical cations, 3T<sup>+</sup>, which are known to be the more short lived and reactive as the  $\pi$  conjugated system is shorter. The lifetime of the radical cation 3T<sup>+</sup>, which is inversely correlated with its chemical reactivity, can reach a too low value in the

case of  $3T^+$  for allowing the charge to be transferred to another molecule. The direct determination of the radical lifetime, actually under way by the use of time resolved laser spectroscopy, will allow a more quantitative description of the correlation between radical properties and field effect mobility. A second significant point deserving attention concerns the effect of the nature of dielectric layer on the observed field-effect mobility, Table II. As already described<sup>3</sup>, the use of various organic and inorganic insulating layers leads to a drastic variation in  $\mu_{\text{FET}}$ , reaching values as high as  $4 \times 10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for sexithiophene when deposited on cyanoethylpullulan, CYEPL.<sup>4</sup> This very large dependence of  $\mu_{\text{FET}}$  of a same organic semiconductor on the nature of the insulating layer can be related to its dielectric constant, which passes from 3.5 to 18.5 when going from  $\text{SiO}_2$  to CYEPL. It can be suggested that a polarizing effect is exerted by the surface of the insulator during the deposition of the oligomer layer, contributing to a better ordering of the conjugated molecules, at least for the first monolayers which will form the conducting channel during the FET operation.

TABLE II Field-effect mobility of sexithiophene,  $\mu_{\text{FET}}$ , as function of the insulator used in the fabrication of the TFT.

Insulator	Dielectric constant	Field-effect mobility $\mu_{\text{FET}} (\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$
$\text{SiO}_2$	3.9	$2 \times 10^{-3}$
AlN	9	$2.5 \times 10^{-2}$
Polyvinylchloride	4.6	$2 \times 10^{-5}$
Polyvinylalcohol	7.8	$10^{-3}$
Cyanoethylpullulan	18.5	$4 \times 10^{-1}$

This result underlines that various degree of structural organization of the organic semiconductor can be achieved, leading to very significant variations in the charge transport properties.

## 2. Effect of interchain spacing

X ray characterization of thin films of conjugated thiophene oligomers have already indicated that, whatever the deposition method used, these molecular materials show the tendency to align themselves almost perpendicular to the surface of the substrate.<sup>5,6</sup> The obtained structures correspond to an orthorhombic cell unit, with *Pbca* space group. This result confirms first the importance of self-organization of thiophene oligomers, which contribute to the very high carrier mobilities obtained with these organic materials. This observation opens also an elegant way for varying the spacing between adjacent

conjugated oligomer chains. Indeed, the chemical substitution of alkyl groups on the  $\beta$  position of thiophene units along the oligomer chain allows to vary, in a controlled manner, the closest possible distance between oligomers. With this aim, decyl  $\beta$  substituted thiophene oligomers (IIa, b) were synthesized and characterized. The results, Table III, show that this substitution leads to very large variations in the carrier mobility, none being observed for the alkylated sexithiophene (II a). Only a large increase in conjugation length, by going to the alkylated duodecithiophene (II b), allows to restore some field-effect mobility.

TABLE III Field-effect mobility of alkylated thiophene oligomers (II) and (III).

Oligomer	Field-effect mobility $\mu_{\text{FET}}$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )
$\beta$ didecyl 6T, (IIa)	not measurable
$\beta$ tetradecyl 12T, (IIb)	$5 \times 10^{-6}$
$\alpha$ dihexyl 6T, (III)	$2 \times 10^{-2}$
$\alpha$ diethyl 5T <sup>(a)</sup>	$9 \times 10^{-4}$
$\alpha$ diethyl 4T <sup>(a)</sup>	$5 \times 10^{-5}$
$\alpha$ diethyl 3T <sup>(a)</sup>	$1.9 \times 10^{-7}$

<sup>(a)</sup> : taken from reference (7)

This observation confirms on one hand the importance of interchain spacing for the efficiency of charge hopping between conjugated chains, and on the other hand the steady rise of field-effect mobility which can be expected by the increase of the conjugation length of thiophene oligomers, beyond the hexamer.

### 3. Long range order of organic semiconducting layer

As already largely demonstrated in the literature concerning organic crystals, long range order in the packing of molecules constitutes one of the key parameter governing the charge transport properties in organic solids. With this aim, a promising way could involve molecular recognition between neighbouring oligomers as a driving force for inducing such structural organization, this recognition property being created by the binding of alkyl groups in the  $\alpha$  positions of conjugated oligomer. An alkylated sexithiophene oligomer, (III), has thus been synthesized and characterized. A very significant increase in field-effect mobility is observed when passing from the unsubstituted sexithiophene to the  $\alpha \alpha'$  dihexylsexithiophene, by a factor of about 10, Table III, these results being in agreement with recent work on shorter conjugated oligomers.<sup>7</sup> A quantitative interpretation of this effect, which we attribute to higher long

range ordering, requires a structural characterization of thin films of (I), (II) and (III), and X-ray characterizations are actually under way in this direction. This improvement in  $\mu_{\text{FET}}$  shows that alkyl substitution of conjugated oligomers in their  $\alpha$  positions, as in (III), represents a very efficient way for controlling and increasing their field effect mobility. These results on structure effects on field-effect mobility of conjugated oligomers can be rationalized by the use of the inverse of conjugation length,  $1/n$ , which has been shown, both experimentally and theoretically, to express the electronic properties of these conjugated materials.<sup>8</sup>

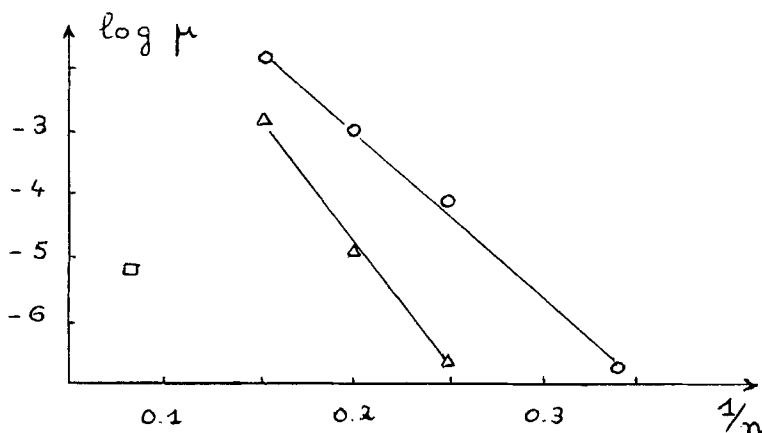


FIGURE 1 Field-effect mobility of conjugated thiophene oligomers as function of inverse of chain length  $1/n$ .  $\Delta$ , unsubstituted;  $\square$ ,  $\beta$  alkylated;  $\circ$ ,  $\alpha$  alkylated oligomers.

The obtained relationships, which also include literature results on  $\alpha$  diethyl substituted thiophene oligomers, show indeed that linear correlation exists between  $\mu_{\text{FET}}$  and  $1/n$ , and that extrapolation to longer conjugated oligomers opens new routes for a further improvement of the charge transport properties of conjugated materials.

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