Molecular Engineering of Organic Semiconductors: Design of Self-Assembly Properties in Conjugated Thiophene Oligomers

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Abstract: In order to analyze the correlation between charge transport and structural properties in conjugated oligomers, sexithiophene, 6T, was substituted by hexyl groups, both on the terminal α positions (α,ωDH6T) and as pendant groups in the β position (β,β′DH6T). Structural characterizations by X-ray diffraction show that vacuum-evaporated thin films of 6T and α,ωDH6T consist of layered structures in a monoclinic arrangement, with all-trans planar molecules standing on the substrate. When compared to 6T, α,ωDH6T is mainly characterized by a very large increase of molecular organization at the mesoscopic level, evidenced by a much longer range ordering. Electrical characterizations indicate that the conductivity of α,ωDH6T is largely anisotropic, with a ratio of 120 in favor of the conductivity parallel to the substrate plane, i.e. along the stacking axis. The charge carrier mobility, determined on field-effect transistors fabricated from these conjugated oligomers, also shows an increase by a factor of 25 when passing from 6T to α,ωDH6T, reaching a value of 5×10^{-2} cm^2 V^{-1} s^{-1}. In contrast, β,β′DH6T presents very low conductivity and mobility, the latter being below detection limit. These results are attributed to the self-assembly properties brought by alkyl groups in the α,ω position.

Introduction

Thin-film devices based on organic materials have been reported in the literature, in which conjugated polymers and oligomers derived from phenylene, phenylenevinylene, or thiophene are used as active semiconducting layers. These devices, including field-effect transistors, FET,[1–5] and light-emitting diodes, LED,[6–8] present a large potential interest, both from a fundamental point of view, for the analysis of the mechanism of charge generation, transport, and recombination in organic materials, and for many envisioned applications in the field of electronics and optoelectronics. When compared to their inorganic counterparts, i.e. classical covalent semiconductors such as Si, organic materials present basic differences. Organic semiconductors are molecular materials, formed by assemblies of molecules held together by weak van der Waals forces, which implies that the properties of the solid are directly governed by those of the individual molecules, which form the elemental bricks of the material, and also by the way these bricks are spatially ordered in the material. These features open very attractive perspectives for controlling the materials properties through the molecular engineering of these assemblies. A fine tuning of the electronic properties of organic molecular semiconductors can be expected through the modification of the chemical structure of their constituting molecules, and many examples in the literature have already revealed the scope of this approach. Thus, the chemical variation of poly(*p*-

phenylenevinylene), either by alkoxyl substitutions or by copolymerization of differently substituted monomers, has been shown to allow the tailoring of the band gap and emission wavelength of electroluminescent diodes based on these materials.[9–11] Similarly, we have shown that the increase of the conjugation length of well-defined conjugated thiophene oligomers leads to a spectacular increase of the charge transport properties of these organic semiconductors, as expressed by the high carrier mobility observed in field-effect transistors based on sexithiophene.[12] Beyond these chemical variations of individual molecules, another key step in the construction of efficient organic semiconductors concerns the control of the spatial arrangement of the molecules in the solid, which also plays a dominant role in the bulk properties. Physical techniques have been developed toward this aim, such as the Langmuir–Blodgett deposition, which enables the ordering of molecules in mono- or multimolecular layers.[4] Although less often described, a chemical route can also be considered, based on self-recognition properties, which can be used as a driving force for inducing a spatial ordering of the constituting molecules, as already reported, for instance, in the case of oligothiophenes or oligoimides, where substitution by alkyl esters[13] or benzenesulfonate groups,[14] respectively, ensures highly organized films. End substitution of thiophene oligomers has recently received increased attention, particularly by the use of trimethylsilyl[15] or 4,5,6,7-tetrahydrobenzo[16] groups. In this paper, we will show how the creation of self-assembly properties in a conjugated sexithiophene oligomer, 6T, by the chemical bonding of alkyl

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groups on its end positions, allows one to control the mesoscopic organization of these molecules by the increase of their stacking properties, and hence to obtain highly ordered films as characterized by X-ray diffraction. We will also show how this chemical engineering of highly ordered films leads to a further improvement of charge transport, as indicated by a large anisotropy of the conductivity and a high field-effect carrier mobility. In contrast, the grafting of hexyl substituents as pendant groups on the β position of 6T leads to a spreading out of the conjugated backbones, as revealed by a large decrease of their conductivity and carrier mobility.

Synthesis

The synthesis of unsubstituted sexithiophene I, 6T, and β,β'-dihexyl-substituted sexithiophene II, β,β'DH6T, through oxidative coupling of the corresponding terthiophene derivatives, has been described in previous work.[17,18]

(I)

(II)
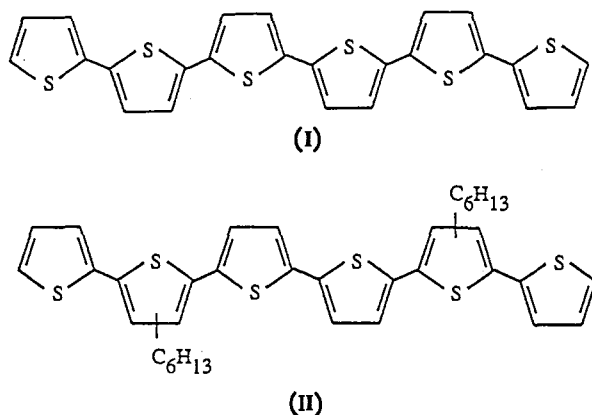
The synthesis of the α,ω-dihexyl-substituted derivative III, α,ωDH6T, was carried out according to the following scheme:

(IV)

(V)

(III)
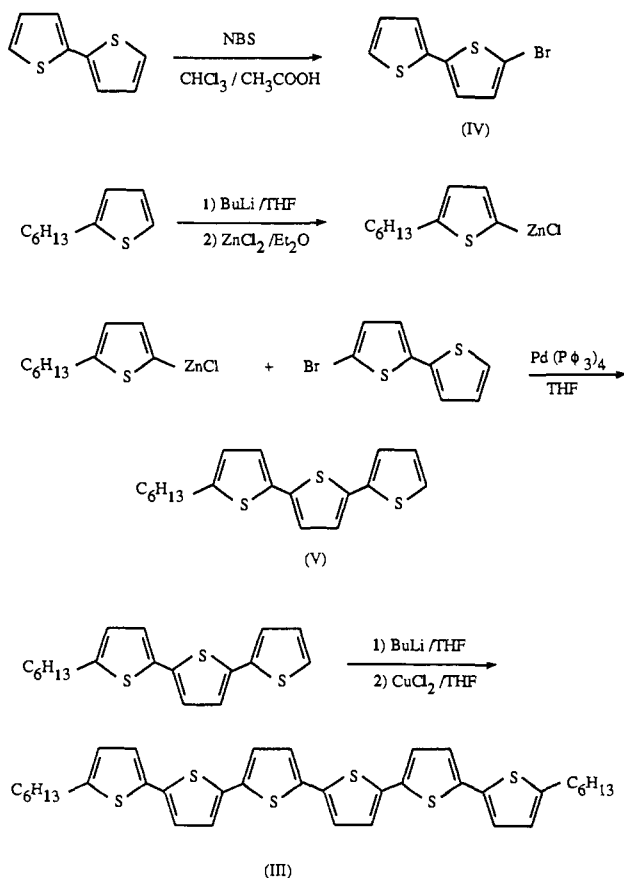
A first monobromination of 2,2'-bithiophene (Aldrich), using N-bromosuccinimide in a 1:1 $CHCl_3$–CH_3CO_2H mixture afforded 2-bromo-5,2'-bithiophene (IV). In a further step, 2-hexylthiophene (Lancaster) (11 mmol) was first lithiated at –70 °C in anhydrous tetrahydrofuran (THF) (30 cm³), by using n-butyllithium (12 mmol of 1.6 M n-BuLi in hexane) and tetramethylenediamine (12 mmol). The resulting solution was stirred at –70 °C for 30 min and then allowed to slowly warm up to room temperature. Zinc chloride (12 mmol of a 1 M solution in diethyl ether) was then added, and the mixture was stirred at room temperature for 1 h. A mixture of IV (10 mmol) and tetrakis(triphenylphosphino)-palladium (0.22 g) in anhydrous THF was then added dropwise and the adduct stirred for 20 h. The reaction mixture was hydrolyzed under acidic pH, and the organic layer was extracted with diethyl ether and washed with water. Purification by column chromatography on SiO_2, with 98:2 heptane–ethyl acetate ↔ eluant, afforded α-hexylterthiophene (V) in 70% yield, which was characterized by mass spectrometry and ^{1}H and ^{13}C NMR spectroscopy. The coupling of two V molecules into α,ωDH6T (III) was realized through the lithiation of V in THF, under the same conditions as above, with the addition of 2 molar equiv of anhydrous copper (II) chloride (Aldrich) at –60 °C. The solution was then slowly warmed up to room temperature with stirring. After 18 h, water was added under acidic pH, leading to a precipitate, which was filtered, washed with water and purified on a Soxhlet with CH_2Cl_2. Derivative III, obtained as an orange powder (yield: 55%), was slightly soluble in CH_2Cl_2 or $CHCl_3$ and has been characterized by electron impact mass spectrometry ($M_w = 664$), ^{13}C NMR ((ppm) 140.400, 136.829, 125.801, 32.642, 24.492, 14.749), UV–vis spectroscopy ((CH_2Cl_2) $\lambda_{max} = 444$ nm), and IR spectroscopy (KBr pellet) (cm⁻¹) 3085 3060, 2956, 2922, 2873, 2855, 1748, 1596, 1538, 1505, 1466, 1442, 1377, 1221, 1206, 1071, 872, 839, 794, 723, 462). The IR spectrum of α,ωDH6T is of particular interest, as it removes some ambiguities concerning the attribution of vibrational bands of the IR absorption spectrum of unsubstituted 6T. As a matter of fact, the high-energy =C—H stretching modes consist of the vibrations associated with hydrogen atoms in the β position, =C—H$_\beta$, as well as those associated with hydrogen atoms in the α position, =C—H$_\alpha$. The absence of these last vibration frequencies has often been invoked as a criterion which characterizes α,α' regularly coupled thiophenes in the corresponding conjugated polymers and oligomers.[19] The unsubstituted 6T oligomer presents four bands, a first set of two bands located at 3048 and 3079 cm⁻¹, which have been attributed to =C—H$_\beta$, and a second set at 3063 and 3101 cm⁻¹, as marks for terminal =C—H$_\alpha$ stretching of hydrogen atoms in the α,ω positions.[20] However, our results disagree with this assignement, as α,ωDH6T, which does not possess hydrogen atoms in the α,ω positions, presents vibration frequencies at 3085 and 3064 cm⁻¹. Thus, the highest and lowest energy frequencies, respectively 3048 and 3101 cm⁻¹, should be considered as marks for terminal =C—H$_\alpha$ groups in conjugated thiophene oligomers and polymers.

Whereas sexithiophene substituted with alkyl groups in the β position, β,β'–dihexylsexithiophene (II), shows an extremely high solubility, over 400 g L⁻¹ in $CHCl_3$,[18] 6T and α,ω dihexylsexithiophene (III) appear surprisingly poorly soluble in CH_2Cl_2 or $CHCl_3$, about 1 g L⁻¹. This large decrease in solubility already suggests on one hand that strong intermolecular interactions exist in the solid state of 6T and α,ω substituted 6T, originating from strong π–π interactions, which have already been put forward for explaining the insolubility of conjugated polymers, and on the other hand that β,β'-substituted 6T molecules have gained a large freedom upon β substitution. The melting temperatures observed for these compounds, 80, 280, and 290 °C, respectively, for II, I, and III, confirm that β-alkyl substitution largely increases the degree of freedom of molecule II and that on the other hand α,ω-alkyl substitution enhances the cohesive forces between the conjugated molecules. The presence of terminal alkyl groups appears thus to lead to stronger aggregation of thiophene oligomers, which can be attributed to the hydrophobic–lipophilic interactions existing between alkyl chains.[21] Such intermolecular interactions between alkyl-substituted oligothiophenes can also be expected to take place in the solid state and induce long-range stacking of oligomer molecules in thin films. This should lead to significant modifications of the structural and charge transport properties of these materials. In

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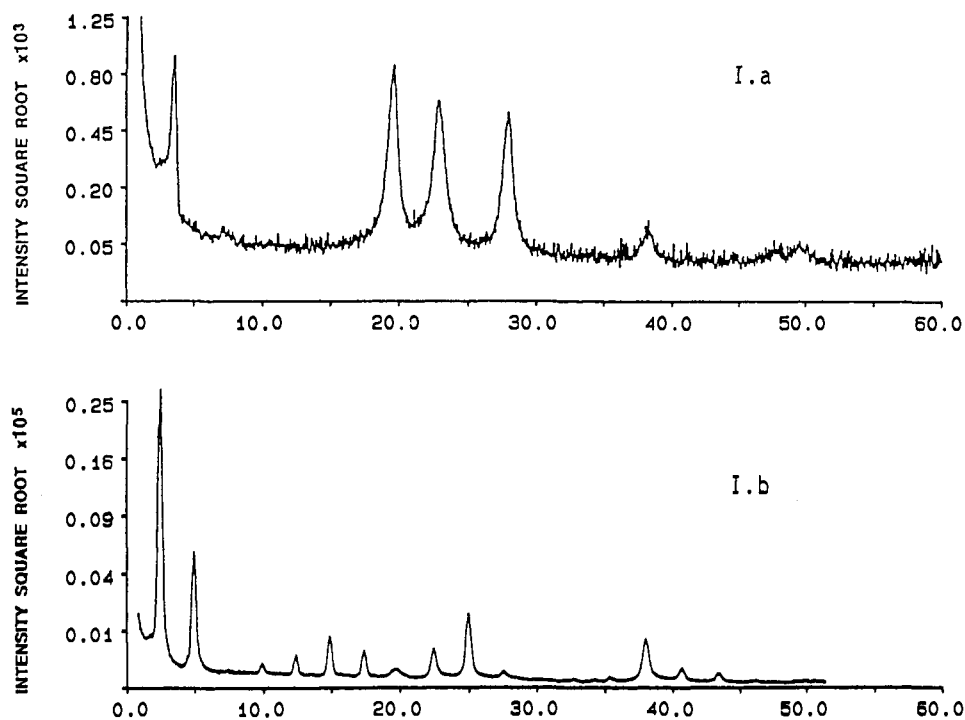
Figure 1. X-ray diffractogram of vacuum-evaporated film of 6T (a) and of α,ωDH6T (b) by θ–2θ scanning in symmetrical reflection mode.
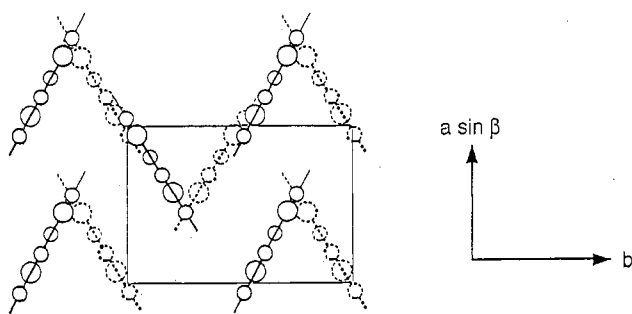

Figure 2. Crystal structure of the vacuum-evaporated film of 6T viewed along the c axis. Sulfur atoms are represented by large circles and carbon atoms by small circles. The unit cell involves four molecules. Molecules in full and dotted lines are located in two adjacent layers.

order to obtain quantitative data, structural characterization of these materials has been made by X-ray diffraction and by electrical measurements.

Structural Characterization

X-ray measurements were carried out at room temperature on films of α,ω-dihexylsexithiophene (**III**) using the same experimental conditions as already recently described for unsubstituted sexithiophene.[22] Films a few microns thick were deposited on the Si substrate by vacuum evaporation at about 350 °C for both 6T and α,ωDH6T. A conventional θ–2θ scanning technique in the symmetrical reflection mode was used, with Cu Kα radiation and a graphite monochromator.

In the case of 6T, the obtained diffraction spectrum (Figure 1a) shows the presence of a layered structure in a monoclinic arrangement with space group $P2_1/c$, in which all-planar 6T molecules are stacked parallel to the long axis of the unit cell.[22] The following cell parameters were calculated, a = 5.98Å, b = 7.80 Å, c = 50.28 Å, β = 111.3°, Z = 4, the molecular planes being rotated by 31° from the $a \sin \beta$ axis, (Figure 2), leading to a classical herringbone structure, which has already been observed for thiophene oligomers.[23,24] These results agree with

packing parameters calculated using packing potential energy calculations[25] and are also consistent with recent structural characterization of sexithiophene by X-ray powder diffraction.[26] In order to obtain a more detailed description of the texture of the present 6T films obtained by thermal evaporation, a pole figure analysis has been carried out, which showed that two possible orientations exist, in fact, for 6T molecules,[22] one in which the molecules stand on the substrate plane with the (a,b) face as contact plane, corresponding to the major population, and another one where 6T molecules have their c axis parallel to the substrate, with the reticular $hk0$ plane as contact plane, which actually corresponds to the thermodynamically favored nucleation of thiophene oligomers on the substrate.

On the other hand, no clear structural organization could be deduced from X-ray analysis of the β-substituted sexithiophene (**II**), β,β'DH6T, which appears to be controlled by the pendant alkyl groups. In contrast, the θ–2θ X-ray diffraction spectrum of a 10-μm-thick film of α,ωDH6T is characterized by a very sharp distribution of X-ray intensities. When using a four-circle diffractometer for adjusting the sample in the θ–2θ technique, the X-ray diffractrogram of α,ωDH6T (Figure 1b) shows that an important degree of crystallinity has been obtained, as confirmed by the numerous high-order 00l (with even l) reflections, up to the 34th order, which are experimentally observed. It must be pointed out that such a highly ordered layered structure of α,ωDH6T is in agreement with structural characterization performed recently on a shorter α,ω dialkylated thiophene oligomer, dimethylquaterthiophene.[25] The X-ray data, which will be discussed in detail in a forthcoming paper,[27] are consistent with a monoclinic arrangement comparable to the one we obtained previously for unsubstituted sexithiophene 6T, with a similar β angle value of 111.3°. A first evaluation of the unit cell parameters led to a = 5.88 Å, b = 7.88 Å, and c = 71.2 Å, the molecular planes being slightly more rotated from the $a \sin \beta$ axis than in the case of 6T. From the sharply resolved diffraction peaks, a

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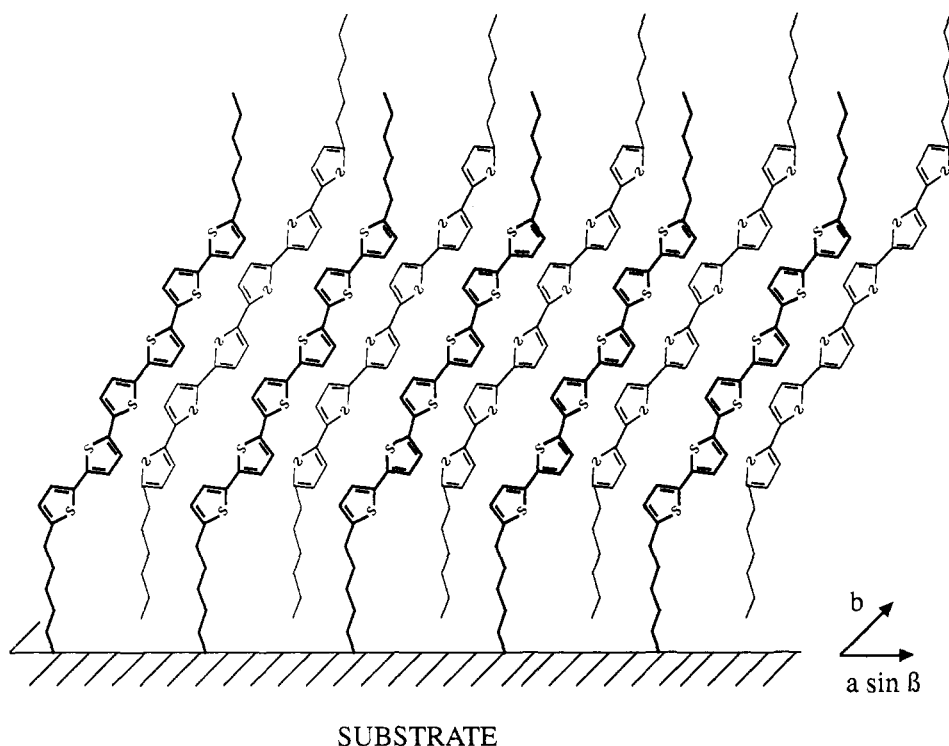

SUBSTRATE

Figure 3. Schematic representation of the α,ωDH6T monolayer on substrate, viewed along the $a \sin \beta$ axis, showing two adjacent rows of oligomers along the b axis.

diffraction spacing of 35.5 Å has been calculated, which corresponds to the monolayer thickness. The α,ωDH6T molecule is composed of a conjugated thiophene core of 20.2 Å and two hexyl groups, each of 9.3 Å when taking into account the van der Waals radius of the terminal CH_3 groups. When assuming a fully extended linear structure, this molecule shows a molecular length of 38.8 Å, leading to a value of 36.2 Å when projected along the $c \sin \beta$ axis, which appears significantly larger than the observed monolayer thickness.

In order to determine precisely the conformation of the α,ωDH6T molecule, segregation phenomena of molecular fragments, as well as molecular restrictions on packing, have to be considered. Indeed, this molecule is composed of two different subunits, a π-conjugated sexithiophene rigid core and flexible alkyl chains, each one obeying particular rules for their stacking. The piling up of rigid conjugated subunits and the aggregation of lipophilic groups have been long recognized as determining the construction of molecular assemblies.[28] The thermodynamics of the free energy of mixing, as well as van der Waals interaction considerations, indicates that units of the same chemical nature tend to associate in order to form homogeneous microdomains, as shown for instance by group molar attraction constants calculated from vapor pressure measurements.[29] In the present case, it is apparent that incommensurability between the rigid conjugated core of the sexithiophene moiety and the flexible hexyl side chains will lead to segregation of these subunits. The closest packing of such biphasic molecules must take into account the closest intermolecular distance between the conjugated π systems, 4.79 Å between edge and center of the unit cell, and the intermolecular distance between alkyl chains, on the order of 5.0 Å as derived from the structural characterization of paraffins.[30] The minimization of empty spaces requires a tilting angle γ between the conjugated core and the paraffinic chains,[31] such that $\cos \gamma = (4.79/5.0)$ or $\gamma = 16°$. Taking into account this

tilting angle, the length of the α,ωDH6T molecule projected on its long axis becomes $20.2 + 2(9.3 \cos 16) = 38.1$ Å. The monolayer thickness is then given by the projection on the $c \sin \beta$ axis, leading to $38.1 \sin 111.3 = 35.5$ Å, which appears to be in excellent agreement with the value determined from the X-ray diffractogram.

As in the case of 6T, a description of the structural organization of α,ωDH6T films at the mesoscopic scale has been obtained through X-ray pole figure characterization. The results showed that only one spatial orientation is obtained in the case of α,ωDH6T, corresponding to microcrystals having the (a,b) plane in contact with the substrate. The schematic representation depicted in Figure 3 can be proposed for a α,ωDH6T monolayer.

Alkyl substitution in the terminal position of sexithiophene leads thus to important effects on the structure of vacuum-evaporated films. The geometry of the unit cell appears modified, with a lengthening of the b parameter and a shortening of the $a \sin \beta$ parameter in a monoclinic cell structure. These variations in fact lead to an almost similar value for the closest distance between molecular planes, between edge and center of unit cell, which reaches 4.794 ± 0.005 Å for both molecules. The most remarkable effect observed when passing from 6T to α,ωDH6T concerns the very high increase in structural ordering of the films. Only one population of molecules is experimentally evidenced for α,ωDH6T films, standing up on the substrate with with (a,b) plane as contact plane. This almost complete structuration of molecular layers must be associated with the stacking properties brought by the terminal alkyl groups, which are already known for inducing long-range ordering and even mesophases, as observed in the case of alkyl-substituted phthalocyanines, these effects being interpreted on the basis of strong liphophilic–hydrophobic interactions. Molecular engineering of conjugated oligomers by alkyl substitution appears thus as an elegant and powerful way for creating self-assembly properties, allowing control of the mesoscopic organization of molecular layers. These effects can be expected to largely govern the charge transport properties of these materials, which will be examined in the following section by the analysis of their electrical properties, i.e. conductivity and field-effect mobility.

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Table I. Electrical Properties of Dialkyl-Substituted Sexithiophene

	conductivity		field-effect mobility
oligomer	$\sigma_\parallel$ (S cm^{-1})	$\sigma_\perp$ (S cm^{-1})	μ_{FET} (cm^2 V^{-1} s^{-1})
6T	2×10^{-7}	1×10^{-6}	2×10^{-3}
α,ωDM6T[a]			10^{-2} [b]
α,ωDH6T	5×10^{-7}	6×10^{-5}	5×10^{-2}
β,β'DH6T	10^{-13}	10^{-13}	$<10^{-7}$

[a] Dimethyl-substituted sexithiophene. [b] Values taken from ref 35.

Electrical Characterization

Once a positive charge is injected in these molecular materials from an electrode, a polaronic type radical cation is created on a π-conjugated oligomer molecule, and the hopping of this positive charge between adjacent molecules in the material generates the overall charge transport process. This mechanism is similar to the one already largely described in the case of molecular crystals based on condensed aromatic hydrocarbons such as anthracene.[32] It has been shown that the charge transport efficiency in these materials, as expressed by the carrier mobility, is highly dependent on the perfection of structural organization, mobilities reaching the range of 1–10 cm^2 V^{-1} s^{-1} at room temperature for perfect crystals. This feature underlines the importance of avoiding structural defects and grain boundaries for improving charge transport in these molecular materials. This requirement of enhanced long-range molecular organization has been already recognized in previous work on field-effect mobility shown by thiophene oligomers, which was observed to be strongly influenced by the dielectric characteristics of the insulating substrate in field-effect transistors.[33] At a molecular level, charge hopping between adjacent thiophene oligomers will depend on the intermolecular distance and on their π molecular orbital overlap, thus on the structural factors which maximize the intermolecular interaction. In this arrangement the charges are to a great extent constrained to move along the stacking axis of the π systems, i.e. perpendicular to the π molecular systems, leading to a high degree of anisotropy in conductivity. In the present case of thin films of thiophene oligomers, the large increase of structural organization observed when passing from 6T to α,ωDH6T suggests that the charge transport properties should also be significantly improved, and more precisely along the stacking axis of the molecules, i.e. parallel to the substrate plane on which the oligomer is deposited. Although charge transport in the oligomer films studied here will be controlled by defects and grain boundaries, it appears tempting to analyze the relation between electrical properties and structure of these molecular materials.

Conductivity measurements have been performed on oligomer films, both in the parallel, $\sigma_\parallel$, and perpendicular, $\sigma_\perp$, directions, as referred to the substrate plane. A planar geometry was used for the measurement of $\sigma_\parallel$, with vacuum-evaporated gold electrodes. We confirmed experimentally that the same parallel conductivity is obtained using either a four- or two-point probe technique, which indicates that charge injection is not limiting. A film was sandwiched between two vacuum-evaporated gold contacts for that of $\sigma_\perp$. Variation of σ from one sample to another is less than 25%. The conductivity in the 6T film, Table I, appeared to be slightly anisotropic, the conductivity parallel to substrate, $\sigma_\parallel = 1 \times 10^{-6}$ S cm^{-1}, being higher than the perpendicular one, $\sigma_\perp = 2 \times 10^{-7}$ S cm^{-1}. In the case of β,β'DH6T, a very low conductivity has been obtained, $\sigma = 10^{-13}$ S cm^{-1}, confirming that the conjugated sexithiophene chains are pulled apart from each other when substituted in the β position with pendant hexyl groups. On the other hand, α,ωDH6T shows a large increase of conductivity in the direction parallel to the substrate, $\sigma_\parallel = 6 \times 10^{-5}$ S cm^{-1}, together with an important anisotropy, $\sigma_\perp = 5 \times 10^{-7}$ S cm^{-1}. It must be pointed out that a high anisotropy of
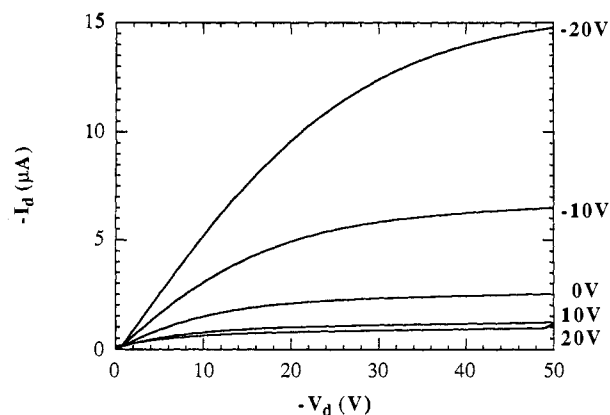

Figure 4. Drain current vs drain voltage characteristics of a α,ωDH6T–polyimide field-effect

conductivity has also been reported by S. Hotta et al. on crystals of α,ω dimethylquaterthiophene doped with iodine, which appeared comparable to the one observed with charge-transfer complexes such as bis(ethylenedithio)tetrafulvalene with iodine.[25] The increase of the electrical conductivity, together with its much larger anisotropy, brings a confirmation that vacuum-evaporated thin films of α,ωDH6T possess a much better layered structure and much longer range order than 6T ones, these better stacking properties being associated with the presence of alkyl groups, in agreement with the preceding conclusions from structural characterizations.

The carrier mobility was determined by characterizing field-effect transistors, FET, fabricated from oligomers, which afford the field-effect mobility μ_{FET}. The realization and mode of operation of these organic-based FETs have been already described in the literature.[5] We have also shown the potential interest of using organic materials as an insulating layer, among which polyimide appears to be very promising, owing to its high resistivity and high dielectric strength. FETs were fabricated on a glass substrate, by successive deposition of a gold contact as gate electrode, G, a 500-nm-thick polyimide film as an insulating layer, a 70-nm-thick layer of oligothiophene as a semiconducting layer, and finally two 5-mm-long gold electrodes forming source, S, and drain, D, electrodes, separated by a channel length of either 25 or 50 μm. Typical amplification curves, $I_{SD} = f(V_{SD})$ at different gate biases, Figure 4, show low I_{off} current and very clear saturation characteristics, with currents of a few tens of microamperes, which confirm the significance and potential interest of these organic-based devices. The field-effect mobilities, μ_{FET}, can be calculated from these amplification characteristics, by using the classical equations describing field-effect transistors.[34] The obtained mobility values (Table I) $\mu_{FET(6T)} = 2 \times 10^{-3}$ cm^2 V^{-1} s^{-1} and $\mu_{FET(\alpha,\omega DH6T)} = 5 \times 10^{-2}$ cm^2 V^{-1} s^{-1} show that an important increase in mobility is obtained by the end substitution of sexithiophene with hexyl groups.

The values of field-effect mobility are listed in Table I, together with the one recently reported by S. Hotta et al. on the very similar α,ω dimethylsexithiophene, using a SiO$_2$ insulating layer.[35] The agreement of field-effect mobilities, determined independently for alkyl-substituted sexithiophene, brings a clear confirmation of the considerable improvement in charge transport efficiency obtained when passing from 6T to α,ωDH6T. In contrast, the mobility of the β,β'-dihexyl-substituted sexithiophene (**II**) stands below the detection limit. For interpreting these effects, one has to determine precisely the mode of operation of these devices on the basis of π-type organic semiconductors. As a matter of fact, we have already shown that these metal–insulator–semiconductor

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field-effect transitors, MISFET, operate in an accumulation regime, through the formation of a thin channel between source and drain electrodes under negative gate bias, the saturation of the channel current appearing at pinchoff of the channel near the drain contact for sufficiently high values of drain voltage. Under these working conditions, the privileged direction for flow of source–drain current is parallel to the substrate plane. The increase observed in field-effect mobility from 6T to α,ωDH6T expresses the enhancement of charge transport efficiency parallel to the substrate plane, thus in complete agreement with the preceding conductivity results. The well-layered structures, showing improved intermolecular interactions between the conjugated sexithiophene backbones, together with the long-range stacking, which have been realized through alkyl susbtitution, are directly responsible for the remarkable characteristics observed for α,ωDH6T-based FET devices. On the other hand, the unmeasurable field-effect mobility of β-substituted sexithiophene (**II**) appears in agreement with the extremely low conductivity of this material.

Conclusions

Crystalline structure and long-range order appear thus to be key factors in the charge transport properties of conjugated materials. Literature results on FETs fabricated from conjugated polymers, such as polyacetylene or polyalkylthiophenes, mostly agree with mobility values on the order of 10^{-5}–10^{-4} cm^2 V^{-1} s^{-1}. These low values can probably be associated with the mostly amorphous state of these materials, originating from a noncontrolled polymerization reaction which leads to spatially disordered polymer chains, involving a large distribution of conjugated segments linked through chain defects, mainly sp^3 carbon atoms. A first significant step toward high charge transport properties has been recently accomplished by the use of well defined conjugated oligomers such as oligothiophenes and particularly sexithiophene 6T. The monodisperse definition of conjugation length of these almost defect-free molecules allows them to organize in well layered structures, when deposited as thin films, and thus to bring a first answer to the requirements for improved charge transport. A further increase can be expected through a deeper control of molecular organization, for instance by the use of a sophisticated deposition technique such as Langmuir Blodgett one. However, another approach to the structuration of organic layers can be proposed, through the chemical engineering of their constituting molecules. Self-assembly properties can be generated by the grafting of adequate chemical substituents, e.g. alkyl groups, which leads to a remarkable improvement of the structural organization of molecules at the mesoscopic level. Alkyl-alkyl recognition phenomena, based on hydrophobic-lipophilic interactions, are strong enough to ensure the long range order required for high charge transport properties.