

# Thin film transistors based on molecular semiconductors

Francis Garnier

Laboratoire des Matériaux Moléculaires, CNRS., 2 rue Henry-Dunant 94320 Thiais  
France

**Abstract** - Electrical properties of thin films of sexithiophene derivatives are directly dependent on the structural order of oligothiophene molecules; the order can be controlled by conditions of film deposition, and chemically by grafting of self-assembling groups. Current densities, switching time and dynamic range of these film transistors make them potentially attractive for use in large scale electronic circuits.

## Introduction

Organic semiconductors have attracted a constant interest since the early fifties, and it has been early shown that metal-semiconductor (MS) and metal-insulator-semiconductor (MIS) structures can be realized with organic materials as active layers. The fundamental studies carried out on these materials have allowed a deeper understanding of charge transport properties in organic semiconductors [1], and even practical applications have even been thought to be within hands in the late seventies, when photovoltaic cells made with merocyanine or phthalocyanines have shown high power efficiencies [2,3]. A second development of organic semiconductors started in the early eighties, with the emergence of conjugated polymers [4]. These polymers, such as polyacetylene, present the unique property of having their conductivity increased by several order of magnitude upon doping, reaching a conductivity close to that of metals [5]. Later, the undoped form of conjugated polymers has been shown to form a new class of organic semiconductors, allowing the realization of various devices, such as light emitting diodes [6] or field-effect transistors [7,8]. This last devices are of particular interest, as the parameters derived from their experimental characterization, conductivity and field-effect mobility, allow to analyze in detail the charge transport properties of the semiconducting materials.

As organic semiconductors, conjugated polymers have been considered attractive, and, among them, polythiophenes [9-11] appeared as particularly promising, owing to the high stability of its semiconducting state. Although the observed field-effect mobility of these macromolecules, of about  $10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , was largely below that of amorphous hydrogenated silicon of about  $10^{-1} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , a large interest has been devoted to organic based thin film transistors, TFTs. As a matter of fact, compared to their inorganic counterparts, organic materials could present the advantages of low cost and room temperature processing, giving access to large area devices, e.g., flat panel displays. An important step has been realized in the late eighties, when it was shown that oligothiophenes, molecular counterparts of polythiophenes, allowed a significant increase, by two orders of magnitude, of the field-effect mobility [12,13]. This result gave hope to further improvement of the electrical properties of thiophene oligomers, which have been found to be very dependent on the purity of the material, and on the method of film preparation. Among organic semiconductors, oligomers appeared also of

particular interest, as the electronic properties of these molecular materials can be easily tailored by subtle chemical modifications performed on the oligomer molecules. Molecular engineering of band level energies appear thus as one of the interesting promises offered by molecular semiconductors.

In the present paper, we describe the fabrication and operating mode of organic thin film transistors, TFTs. With reference to other organic semiconducting materials, a focus will be given on oligothiophenes, for which it has been shown that a strong correlation exists between electrical and structural properties. Thus, it can be expected that the performances of such devices can be improved by an *a priori* chemical or physical control of structural organization of the semiconducting layer.

### Fabrication and Operation Mode of Organic-Based TFTs

The most commonly used TFT structure, Fig. 1, is fabricated according to the field-effect transistor architecture [14]. As the deposition of an insulating layer on top of an organic semiconductor is not easy to perform, inverted structures are used, i.e., built over the gate electrode. The insulator can be silicon oxide, thermally grown on a silicon wafer used as gate electrode, or a thin polymer film. Two gold source and drain electrodes form the ohmic contacts to the semiconducting layer. These electrodes are evaporated either on the insulator prior to the deposition of the active organic semiconducting layer, corresponding to a planar structure depicted on Fig. 1, or on top of the semiconducting layer, corresponding to a staggered structure.

More recently, we have described for the first time an all-organic structure in which the insulator is a spin-coated polymer, poly(methyl methacrylate) or polyimide, on top of a polymer substrate [13,15]. The aluminum gate is evaporated on the substrate before deposition of the insulating layer. Gold source and drain electrodes are then evaporated, followed by the organic semiconductor. One of the main advantage of such all-polymer structure concerns its light weight and mechanical flexibility.

Capacitance-voltage measurements have confirmed that, as most of organic materials, polythiophenes and oligothiophenes are p-type semiconductors, with an accumulation layer formed under applied negative bias. Under positive bias, a depletion layer is observed in case of oligothiophenes, which indicates that the corresponding TFTs will operate under accumulation mode, and also under depletion mode [12]. The characterization of TFTs involves the analysis of the drain current  $I_d$  as a function of the source-drain voltage  $V_d$ , for various source-gate voltages  $V_g$ . A set of such  $I_d$ - $V_d$  curves is shown in Figure 2, which confirms that the device operates both in the accumulation mode, Figure 2a, and also in the depletion mode, Figure 2b. The signs of both  $V_d$  and  $V_g$  are consistent with a p-type semiconductor. In the accumulation mode, the curves can be described by the classical equations (1) derived for inorganic-based TFTs [14].

$$I_d = \frac{W}{L} C_i \mu_{FET} \left[ (V_d - V_t) - \frac{V_d^2}{2} \right] \quad (V_d < V_g) \quad (1a)$$

$$I_{d,sat} = \frac{W}{2L} C_i \mu_{FET} (V_g - V_t)^2 \quad (V_d > V_g) \quad (1b)$$

where  $W$  and  $L$  are the channel width and length respectively,  $C_i$  the insulator

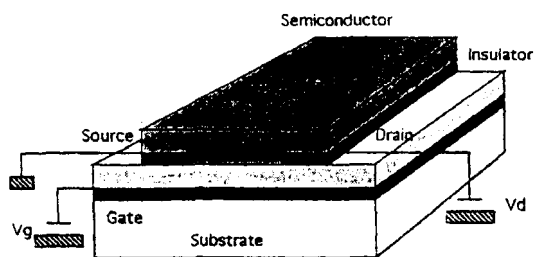


Figure 1. Schematic view of an organic-based thin film transistor.

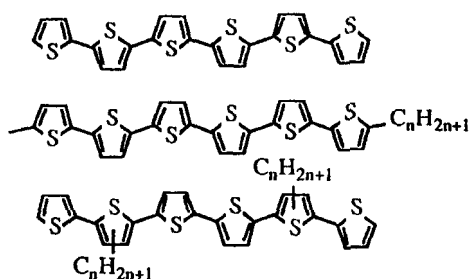


Figure 3. Molecular structure of sexithiophene (top) and its alkyl substituted derivatives, either at end (middle) or at pendent (bottom) positions.

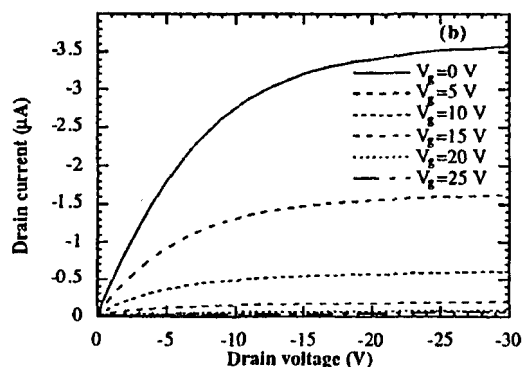
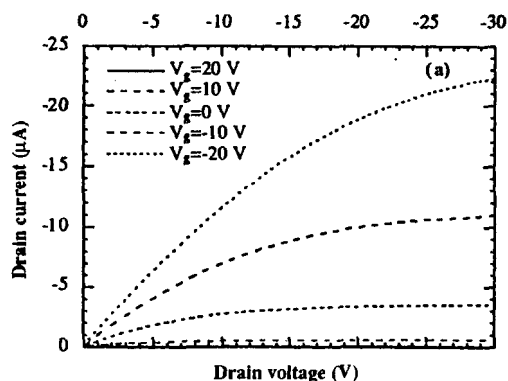


Figure 2. Current voltage curves of a thin film transistor based on sexithiophene, 6T, with a PMMA insulating layer. The device operates in the accumulation (left curves,  $V_g < 0$ ) and depletion (right  $V_g > 0$ ) mode. The TFT characteristics are  $L=50 \mu\text{m}$ ,  $W=5 \text{ mm}$  and  $C_i=10 \text{ nF.cm}^{-2}$ .

capacitance per unit area,  $\mu\text{FET}$  the field-effect mobility and  $V_t$  the threshold voltage. Curves in the accumulation mode allow the calculation of the field-effect mobility, using the linear part of the curve, equation (1a).

In the depletion mode, the curves show that the semiconducting layer can be fully depleted, when the width of the depletion layer equals that of the semiconducting layer. This occurs when the gate voltage equals the pinch-off voltage  $V_p$ , given by equation (2).

$$V_p = \frac{qNd^2}{2e_s e_0} \left( 1 + 2 \frac{C_s}{C_i} \right) \quad (2)$$

where  $q$  is the electron charge,  $N$  the dopant concentration,  $d$  the thickness of the semiconductor,  $e_s$  its dielectric constant,  $e_0$  the permittivity of free space, and  $C_s$  the dielectric capacitance of the semiconducting layer ( $C_s = e_s e_0 / d$ ). These equations can thus be used for calculating the doping level  $N$  of the organic semiconductor.

Various types of molecular materials have been used in the literature for organic-based TFTs, involving conjugated oligomers as well as other conjugated molecules. Among oligomers, oligothiophenes  $nT$ , where  $n$  represents the number of thiophene units, are actually the most studied ones [16]. Homogeneous films of oligothiophenes can be realized under mild conditions on different substrates by vacuum evaporation. The most widely used oligothiophene is sexithiophene, as well as its substituted derivatives, Fig. 3.

Other conjugated molecule, such as pentacene [17] and also various phthalocyanines [18], which are also mainly p-type semiconductors, have been used for realizing organic TFTs. More recently, interesting work have concerned the development of n-type organic semiconductors, such as tetracyanoquinodimethane (TCNQ) [19], perylene derivatives [20], and fullerenes C<sub>60</sub> [21].

### Characteristics of Organic -Based TFTs

Whereas conjugated polymers showed field-effect mobilities in the range of 10<sup>-5</sup> to 10<sup>-4</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, oligothiophenes on the other hand presented a significant increase of mobility, up to 2x10<sup>-3</sup> cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>[8]. This result has been ascribed to a higher purity of the materials, and also to a much better defined structural organization of molecules in the film. Furthermore, oligomers, as molecular materials, offer the possibility to rationalize the effect of structural organization on the electrical properties of the corresponding films. The structural variations which have been studied will be gathered in terms of conjugation length, of chemical substitutions, and of structural organization of molecules in the film.

#### *Effect of the length of the oligomer*

The conductivity and field-effect mobility of vacuum evaporated oligothiophenes, from terthiophene (3T) up to octithiophene (8T), Table 1, indicates a huge increase of the mobility, up to sexithiophene 6T [17]. The further decrease of mobility observed for octithiophene 8T may not be significant, as the purity of 8T films is still debated. It is noteworthy to mention that mobility increases much faster than the conductivity. The conductivity of oligothiophenes is anisotropic, which confirms that charge transport is favored in the direction parallel to the film, along the stacking axis of the oligothiophene molecules.

#### *Effect of substitutions*

Substitution on the oligomer can be performed either at the end positions of the backbone, or as pendent groups [22]. End substitution, Table 2, results in an increase by a factor of 100 of the field-effect mobility, whereas the conductivity remains practically unchanged [23].

Substitution by pendent groups, Table 3, leads to insulating materials. Conductivity and mobility could be determined only on a very long oligomer, the tetradecyl substituted dodecamer, TD12T, where they reach those of the parent polymer.

TABLE 1. Conductivity and field effect mobility of vacuum evaporated unsubstituted oligothiophenes nT

Oligomer	Conductivity (S.cm <sup>-1</sup> )		Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
	perpendicular	parallel	
3T	10 <sup>-10</sup>		<10 <sup>-7</sup>
4T	10 <sup>-9</sup>		2x10 <sup>-7</sup>
5T	10 <sup>-8</sup>	10 <sup>-6</sup>	2.5x10 <sup>-5</sup>
6T	2x10 <sup>-7</sup>	10 <sup>-6</sup>	2x10 <sup>-3</sup>
8T	10 <sup>-7</sup>		2x10 <sup>-4</sup>

TABLE 2. Conductivity and field-effect mobility of oligothiophenes substituted with ethyl, E, and hexyl, H, chains at the end positions.

Oligomer	Conductivity (S.cm <sup>-1</sup> )		Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
	perpendicular	parallel	
DE3T <sup>a</sup>			2x10 <sup>-7</sup>
DE4T <sup>a</sup>			5x10 <sup>-5</sup>
DE5T <sup>a</sup>			9x10 <sup>-4</sup>
DH6T	5x10 <sup>-7</sup>	6x10 <sup>-5</sup>	8x10 <sup>-2</sup>
DH8T	5x10 <sup>-7</sup>	4x10 <sup>-4</sup>	10 <sup>-2</sup>

<sup>a</sup>: values taken from ref. [24]

TABLE 3. Conductivity and field-effect mobility of oligothiophenes substituted with pendent decyl, D, chains.

Oligomer	Conductivity (S.cm <sup>-1</sup> )	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
DD6T	10 <sup>-13</sup>	<10 <sup>-7</sup>
TD12T	10 <sup>-9</sup>	5x10 <sup>-6</sup>

TABLE 4. Conductivity, mobility and doping level of polythiophene and different forms of sexithiophene

Material	Conductivity (S.cm <sup>-1</sup> )	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
Polythiophene	10 <sup>-7</sup> - 10 <sup>-6</sup>	10 <sup>-5</sup> - 10 <sup>-4</sup>
6T (substrate at 25°C)	1.5x10 <sup>-6</sup>	3x10 <sup>-3</sup>
6T (substrate at 280°C)	1.2x10 <sup>-7</sup>	2.5x10 <sup>-2</sup>
6T (annealed) <sup>a</sup>	-----	1.5x10 <sup>-2</sup>
6T (single crystal)	< 10 <sup>-10</sup>	(10 <sup>-1</sup> )
DH6T	6x10 <sup>-5</sup>	8x10 <sup>-2</sup>

<sup>a</sup>: value taken from ref. [26]

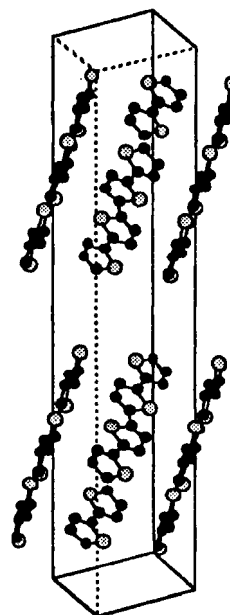


Figure 5. Crystal structure of sexithiophene

#### Effect of structural organization

Structural order has revealed the most interesting parameter, allowing a more general discussion on the charge transport properties of these materials. As a matter of fact, on one hand the structural organization of molecular materials can be varied by the use of various physical and chemical methods, and among them, i) the substrate temperature and rate of evaporation during film deposition, ii) annealing of the films, iii) chemical substitution by self-assembling groups, and finally iv) growth of single crystals of oligothiophene, as ultimate organized structure. On the other hand, many techniques can be used for a precise determination of structural organization at a mesoscopic scale, such as X-ray diffraction, optical dichroism and electron microscopies. A detailed study has been achieved on these points, focussed on sexithiophene oligomer, 6T. By varying the temperature of substrate, from 77 K to 280 °C, and rate of evaporation during deposition of films of 6T, it has been shown that 6T is a polymorphic material, with various structural phases, which have been characterized by X ray diffraction [25]. Highly structured and long range ordered films can be obtained when heating the substrate at 280 °C and lowering the rate of evaporation. It must be noted that annealing of a 6T film, performed by short thermal pulses, has also been shown to lead to polycrystalline films [26]. This increase of ordering can also be easily achieved by a chemical route, through the chemical bonding of substituents showing self-assembling properties. This has been achieved by the covalent bonding at the  $\alpha,\omega$  end positions of 6T by hexyl groups, DH6T [23], which has been described in the previous paragraph. End substituted oligothiophene present a two dimensional structure, where layers of thiophene chains alternate with alkyl layers. Such extended two dimensional structure, almost similar to a liquid crystalline phase, has been suggested by X-ray diffraction measurements on films of DH6T evaporated on room temperature substrate.

Finally single crystals of 6T have also been grown, which represent the ultimate organized structure of 6T oligomer [27]. The unit cell, Figure 5, is monoclinic, and contains four molecules arranged in a herringbone close-packing.

The crystal arrangement of 6T shows remarkable features. Molecules are rigorously planar and strictly parallel to each other. Moreover, the inter-molecular  $\pi$ -orbital overlap is maximum, which can account for that charge transport is favored along the  $\pi$ -stacking direction. On the other hand, the crystal structure of sexithiophene substituted by pendent butyl chains shows a shift of the nearest neighbour thiophene chains, which results in a dramatic decrease of the  $\pi$ -overlap. This can account for the very low conductivity and mobility of this compound. The electrical properties of these films are reported in Table 4. The field-effect mobility for single crystals of 6T is not yet ascertained, as it has been determined on a staggered TFT structure, where important ohmic losses may have altered the characterization.

These results show that the large increase in carrier mobility observed with oligothiophenes is directly related to the mesoscopic structural organization of molecules in the film, which can be controlled by the experimental conditions used for film deposition. An even better control can be exerted by a chemical approach, involving the end-substitution of alkyl groups, which bring self-assembling properties to the oligothiophene molecules, leading to particular liquid-crystal-like structure, with low structural defects in the film [23]. Thus DH6T shows a mobility which almost equals that of single crystal of unsubstituted 6T.

### State of Art on Organic TFTs

Main results from literature show that organic thin film transistors, TFTs, can be realized by simple processes, on various types of substrates, silicon, glass or polymer. Masking techniques have been used, leading to oversized device geometries, with channel length and width of the order of tenths of microns and millimeters respectively. Micron sized devices have also been achieved, by the use of conventional microlithographic techniques for realizing the gate, source and drain electrodes, with conventional channel length of some microns and channel width of some hundred microns. The organic semiconductor is then simply evaporated, in a last step, on top of this structure, at room temperature.

Characterization of organic TFTs have been carried out on devices, based, both on p-type and on n-type organic semiconductors. The most interesting characteristics have been obtained with sexithiophene, 6T, and dihexylsexithiophene, DH6T. Field-effect mobilities in the range of  $10^{-2}$  to  $10^{-1}$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  have been obtained, the highest value being observed with DH6T deposited at room temperature, of the same order as that observed with single crystal of 6T. Switching times of the order of 10  $\mu\text{s}$  have been determined, which appear to be limited by resistance-capacitance time constants. The characteristics of the dynamic range,  $I_{\text{on}}/I_{\text{off}}$ , are highly dependent on the purity and on the thickness of the film., values higher than  $10^6$  being obtained.  $I_{\text{on}}$  values typically reach some tenths of  $\mu\text{A}$ , and  $I_{\text{off}}$  values, of the order of some tenths of pA, can be obtained at 0 V gate voltage for very thin films of pure 6T, and appear to be limited by current leakages through the insulating layer. Long term stability tests, carried out under ambient conditions on non-encapsulated devices, have shown stabilities exceeding  $10^4$  hours under constant operation, without any modification of characteristics. These values appear to already meet the requirements for various applications in electronic circuits.

TFTs based on n-type semiconductors have been more recently described, based on TCNQ, perylenes and C<sub>60</sub>, this latter compound showing stability problems toward air. The obtained mobilities are of the order of  $10^{-5}$  to  $10^{-2}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, and progresses can be expected which will enable to demonstrate soon the applicability of heterojunction concepts to organic semiconductors. Main results from literature show that organic Thin Film Transistors can be realized by simple processes, on various types of substrates, silicon, glass or polymer. Masking techniques have been used, leading to oversized device geometries, with channel length and width of the order of tenths of microns and millimeters respectively. Micron sized devices have also been achieved, by the use of conventional microlithographic techniques for realizing the gate, source and drain electrodes with conventional channel length of some microns and channel width of some hundred microns.

### Conclusion

Thin film of sexithiophene derivatives have been characterized for their structural and electrical properties. It has been shown that structural order of oligothiophene molecules in these films can be controlled by modifying the experimental conditions of film deposition. A chemical approach, based on the grafting of self-assembling groups on the molecule, has revealed even more powerful for inducing long range order in these organic films. As expected, electrical properties of these films are directly dependent on the structural order. Current densities, switching time and dynamic range have been determined on thin film transistors based on sexithiophene. The obtained experimental data are actually considered as good enough for envisioning practical applications in large-area electronic circuits.

Acknowledgements are made to Dr. G. Horowitz for helpfull discussions.

### References.

1. Pope, M. and Swenberg, C.E. *Electronic Processes in Organic Crystals*, Oxford University Press, New York, 1982.
2. Ghosh, A.K. and Feng, T., *J. Appl. Phys.* 49, 1978, 5982.
3. R.O. Loutfy, J.H. Sharp, C.K. Hsiao, R. Ho, *J. Appl. Phys.*, 52, 1981, 5218
4. T.J. Skoktheim, *Handbook of Conducting Polymers*, Wiley and Sons, New York, 1985.
5. Basescu, N., Liu, Z.X., Moses, D., Heeger, A.J., Naarman, H. and Theophilou, N., *Nature*, 327, 1987, 403.
6. Burroughes, J.H., Bradley, D.C.C., Brown, A.R., Marks, R.N., McKay, K., Friend, R.H., Burns, P.N. and Holmes, R.B. *Nature*, 341, 1990, 539.
7. Tsumura, A., Koezuka, H. and Ando, Y., *Synthet. Metal.* 25, 1988, 11.
8. Horowitz, G., Fichou, D., Peng, X.Z., Xu, Z.G. and Garnier, F., *Solid State Commun.* 72, 1989, 381.
9. Assadi, A., Svensson, C., Willander, M. and Inganäs, O., *Appl. Phys. Lett.* 53, 1988, 195.
10. Paloheimo, J., Kuivalainen, P., Stubb, H., Vuorimaa, E. and Yli-Lahti, P., *Appl. Phys. Lett.* 56, 1990, 1157.

11. Xie, Z., Abdou, M.S.A., Lu, X., Deen, M.J. and Holdcroft, S. , *Can. J. Phys.* 70, 1992, 1171.
12. Horowitz, G., Peng, X.Z., D. Fichou , D. and Garnier, F., *J. Appl. Phys.* 67, 1990, 528.
13. Garnier, F., Horowitz, G., Peng, X.Z. and Fichou, D., *Adv. Mater.*, 2, 1990, 592.
14. Sze, S.M., *Physics of Semiconductor Devices*, John Wiley, New York, 1981.
15. Garnier, F., Hajlaoui, R., Yassar, A. and Srivastava, P., *Science* 265, 1994, 1684.
15. Akimichi, H., Waragai, K., Hotta, S., Kano, H. and Sakati, H. , *Appl. Phys. Lett.* 58, 1991, 1500.
16. Hotta, S. and Waragai, K. *J. Mater. Chem.* 1, 1991, 835.
17. Horowitz, G., Deloffre, F., Garnier, F., Hajlaoui, R., Hmyene, M. and Yassar, A., *Synthet. Metal.* 54, 1993, 435.
18. Guillaud, G., Al Sadoun, M., Maitrot, M., Simon, J. and Bouvet, M., *Chem. Phys. Lett.* 167, 1990, 503.
19. Brown, A.R., Deleeuw, D.M., Lous, E.J. and Havinga, E.E. , *Synthet. Metal.* 66, 1994, 257.
20. Garnier F., Horowitz G., Fichou D., and Sperman P., to be published.
21. Hoshimono, K., Fujimori, S., Fujita, S. and Fujita, S., *Jpn. J. Appl. Phys. Pt 2* 32, 1993, L1070.
22. Delabouglise, D., Hmyene, M., Horowitz, G., Yassar, A. and Garnier, F., *Adva Mater.* 4, 1992, 107.
23. Garnier, F., Yassar, A., Hajlaoui, R., Horowitz, G., Deloffre, F., Servet, B., Ries, S. and Alnot, P. *J. Am. Chem. Soc.* 115, 1993, 8716.
24. Waragai, K., Akamichi, H., Hota, S., Kano, H. and Saraki, H., *Synth. Met.*, 57, 1993, 4053.
25. Servet, B., Horowitz, G., Ries, S., Lagorsse, O., Alnot, P., Yassar, A., Deloffre, F., Srivastava, P., Hajlaoui, R., Lang, P. and Garnier, F. , *Chem. Mater.* 6, 1994, 1809.
26. Dodabalapur, A., Torsi, L. and Katz, H.E. , *Science* , 268, 1995, 270.
27. Horowitz, G., Bachet, B., Yassar, A., Lang, P., Demanze, F., Fave, J.L and Garnier, F., *Chem. Mater.*, 1995, in press.