ADVANCED MATERIALS

Functionalized Conducting Polymers—Towards Intelligent Materials

Molecular Electronics
Wires, Sensors, Transducers
Polymer Modified Electrodes

By Francis Garnier *

Organic conjugated polymers and oligomers constitute a three-dimensional network of molecular wires, in which all monomeric units can be functionalized with various prosthetic groups. By varying the nature of these groups, specific interactions with external physical or chemical phenomena can be developed in these materials, leading to molecular devices such as sensors, transducers, memories and logic operators. Chemists have already mastered the realization of many of these functional elements, which mimic those existing in organized beings. The further assembly of these elements in multi-functionalized organic conducting polymers and oligomers will represent the next step towards intelligent materials.

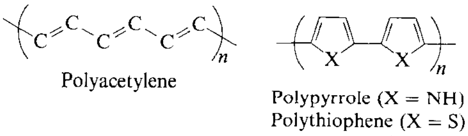
1. Introduction

Inter (between, within), *legere* (to read, to bring together, to choose). The study of all the functions that underlie *intelligence* has long been one of the major goals of science. The analysis of the elements that define organized beings has up to now been the privileged sphere of biology, which has aimed at the understanding, down to the molecular level, of the fundamental processes associated with the faculties of sensing and controlling the environment. On the physical sciences side, electronics is one of the methods developed by men for imitating some of these basic functions in macroscopic devices such as sensors, memories and logic circuits. In these research areas chemistry has mainly had a supporting role, whether conceptual, for explaining the chemical processes involved, or experimental, in the synthesis of model molecules mimicking such biological functions, and also in making the materials needed for electronic devices.

Chemistry has, however, recently developed methods for the a priori control of molecular properties,[1] and a fascinating challenge has now emerged: is it now conceivable to progress beyond the macroscopic approach used in conventional electronics, and also to bypass the inherent complexity of biological systems, in order to build new materials able to perform at a molecular level the basic functions, i.e. recognition, control of chemical processes, memory and logic, which define intelligent structures? Ideas that were regarded a few years ago as long term speculation,[2] are now approaching reality, based on the fact that chemists have learned how to build molecular wires and incorporate into them various types of functions. These new materials are functionalized organic conducting polymers and oligomers, and this article reports on the advances in research which will lead to such molecular devices being constructed in the near future.

2. Molecular Wires

The concept of molecular wires stems from about ten years ago, when it was shown that the individual macromolecular chains of organic conjugated polymers possess a high intrinsic electrical conductivity.[3] These organic conducting polymers have since aroused much interest, and a deep knowledge has been gathered on their physical and chemical properties. The macromolecular chains of these polymers show a regular alternation of single and double bonds, in the manner of the prototype polyacetylene.[4] Other classes of conducting polymers were later synthesized, including polypyrrole,[5] polythiophene,[6] and polyaniline.[7]


Polyacetylene
Polypyrrole (X = NH)
Polythiophene (X = S)

The conjugation of the π-electron system creates a molecular orbital which extends throughout the polymer chain. Using the concept of the one-electron model as a first approximation, these low dimensional materials can be described by a fully occupied valence band and an empty conduction band, formed by the conjugated π and π* systems, respectively. In this state these polymers show semiconducting properties associated with a band gap of about 2 eV. The injection of holes or electrons into these chains, by p-type or n-type doping respectively, leads to electrical conduction, due to the creation of soliton or polaron states in the gap. This doping is performed by the inclusion of electron acceptors, such as halogens, or electron donors, such as alkaline metals, which intercalate between the conjugated polymer chains and lead to their oxidation or reduction, respectively. It must be pointed out that this term of doping is employed

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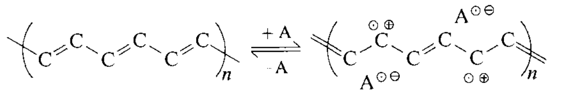
here in a chemical sense and not in the commonly accepted one in solid state physics. The conductivity values depend on the amount of electrons or holes created in the polymer chains, which is determined by the concentration of dopant in the polymer. Very high concentrations of dopants A can be achieved: up to one dopant species for every two or three units of monomer M contained in the polymer, corresponding to $[A]/[M] \approx 0.3-0.5$. The conductivity can reach values as high as that of metals such as Pt or Fe, $\sigma = 2 \times 10^5$ S cm^{-1}, as was recently demonstrated by *Naarmann* et al. in the case of polyacetylene;[8] however, a real metallic state has not yet been obtained as shown by the behavior as a function of temperature.

This doping reaction, which is reversible and can be electrochemically driven, confers on these polymers interesting electroactive properties. It has been shown that even for polymer layers up to hundreds of microns thick the whole polymer is entirely electroactive, implying that the polymer chains stretch throughout these layers. Some defects evidently exist in these chains, such as interruption of conjugation and branching, but interchain hopping of charges allows all the chains to be electroactive. The doping process thus involves every two or three monomer units along all polymer chains, and it can be considered as operating at the molecular level of these conducting polymers (Scheme 1).



Scheme 1. Reversible doping of polyacetylene with an electron acceptor A.

Films of organic conducting polymers behave as organic electrodes, which can be charged and discharged with large amounts of dopants, and this characteristic has been the starting point for numerous studies on "organic batteries",[3] mainly based on polypyrrole and polyaniline and already commercialized, and also on some electrochromic devices.[9] In these applications, the electroactive polymer chains are considered as playing only the passive role of a conducting network for hosting incoming dopant anions, and their potential has thus been largely underestimated. As a matter of fact, these macromolecular conjugated chains, formed by the theoretically infinite coupling of monomer units, possess an intrinsic electrical conduction, and thus represent true molecular wires, i.e. wires consisting of just a one molecule sequence. Furthermore, the fact that every second or third monomer unit along all these wires is involved in the doping–undoping process means that all these monomer units can in theory be individually electrically addressed in the whole polymer layer. This interaction at a molecular level thus opens up the field of molecular devices.

3. Molecular Sensors and Transducers

These molecular wires form unique routes for the reversible transfer of electronic information between an electrode, onto which these polymer chains are grafted, and various prosthetic groups R, which can be covalently bonded as side groups all along the conducting chains (Fig. 1). Depending on the nature of R, these structures can act as molecular sensors or molecular transducers.

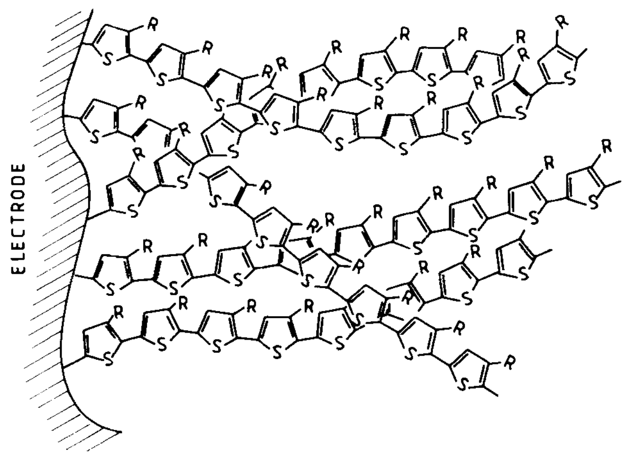


Fig. 1 Three-dimensional distribution of prosthetic groups R along ideally conjugated polythiophene chains grafted onto an electrode.

Owing to the richness of chemical synthesis, a large variety of functions can theoretically be incorporated into these conducting polymers by the initial synthesis of a functionalized monomer. This second generation of organic conducting polymers, obtained by their functionalization, has recently excited much interest in view of its great potential, and many experiments have been proposed. This functionalization is experimentally difficult since the steric and electronic properties of most of the interesting substituents on monomers are not easily compatible with the synthesis of a conducting polymer. Thus the electrical conduction in these macromolecular chains requires the stereoregular alternation of single and double bonds, and any structural defect, such as an sp^3 carbon atom or a chain end, is known to result in the interruption of conjugation and hence of conduction. The polymerization reaction is difficult to control, and it has been observed that the more sterically demanding a substituted monomer is, the higher is the concentration of defects in its corresponding polymer. Thus, most of the examples which will be described in the following suffer from a very low electrical conductivity ($\sigma \approx 10^{-4}$ S cm^{-1}). Recently, however, by carefully analyzing the steric and electronic factors which, for a given substituent on a monomer, control the conducting and electroactive properties of the corresponding polymer, we have developed the concept of a "functionalization environment" which allows these problems to be overcome.[10]

Provided that these criteria are fulfilled, substituents can now be envisaged that will give specific interactions with almost any kind of external physical or chemical phenomenon. Examples of *physical quantities* that can be sensed by the use of appropriate R groups are photon fluxes, electric fields and magnetic fields.

The principle of photon sensing has already been demonstrated by the bonding of the well known photoactive metal complex Ru(bpy)$_3^{2\oplus}$ to the monomeric units of polypyrrole.[11] This functionalized polymer has indeed shown a photoresponse, although its intrinsic electronic conduction has not yet been mastered due to the large steric constraints of the metal complex ($\sigma \approx 10^{-4}$ S cm^{-1}). The principle of sensitivity to a magnetic field B has also been proposed recently,[12] using a nitroxide radical grafted on polydiacetylene; the results are, however, a subject of controversy. Even if not yet experimentally demonstrated, the sensitivity to an electric field E is within reach, by substituting a highly polarizable group as already envisioned.[2] The application of an electric field will induce a large dipole moment on the side chain of the conducting system and create electron sinks or electron reservoirs which will lead to a modification of the charge transport properties of the main conducting chain.

Selective chemical interactions with the environment can also be developed in these electroactive polymers by appropriate functionalization. The most significant features which govern fundamental processes in biological systems involve recognition, whether of ions, as in transmembranous transfers, or of optically active species. Both of these recognition phenomena have already been imitated at the molecular level by appropriate functionalization of conducting polymers. Thus, ionic selectivity has been demonstrated in the case of a new class of polymers, the poly(dibenzo crown ethers), which contain crown ethers of variable size.[13] Owing to the well known specific complexation of cations by crown ethers, a highly selective uptake of various cations in solution has been observed with these polymers. A second example relates to the covalent binding of a polyether substituent onto the monomeric units of polypyrrole, which also induce selective complexation of cations such as Li$^{\oplus}$.[14] These last two ion selective materials, however, still suffer from a low electronic conductivity of the polymer backbone, due to the fact that the polymerization reaction is not yet well controlled. On the other hand, by applying the concept of functionalization environment, we were recently able to synthesize polythiophene derivatives substituted with polyether groups, showing both a high electrical conductivity ($\sigma = 10$ S cm^{-1}) and ionic selectivity.[10] The interest in controlling these two properties at the same time arises from the possibility of new materials having both an electronic and an ionic conductivity, which mimic membrane processes and thus open up a large potential in the realization of ion selective electrochemically controlled membranes.

Perhaps the most challenging recognition property concerns enantioselectivity, i.e. the ability to discriminate between optically active substrates. We have recently succeeded in achieving this ultimate type of recognition, by the controlled functionalization of polythiophenes. Thiophene monomers bearing large chiral groups such as R* = (2 *S*)-(+)-$(CH_2)_3OCH(Et)C_6H_5$ were first synthesized, and then electropolymerized as thin films on an electrode. The characterization of the resulting polymer has confirmed that it is chiral (specific rotation = + 3000°), and still conducting ($\sigma = 12$ S cm^{-1}) and electroactive, despite having such bulky substituents. When used as an organic electrode in an electrolytic medium with $ClO_4^{\ominus}$ anions, a reversible, electrochemically driven doping–undoping process is observed. If an optically active anion such as (1 *S*)-(+)-10- or (1 *R*)-(−)-10-camphorsulfonate is used instead of $ClO_4^{\ominus}$, this chiral organic electrode shows a different response depending on the camphorsulfonate enantiomer used (Fig. 2). A ratio of about two has been observed for the oxidation rates at comparable doping levels of the chiral doping matrix, thus defining its selectivity towards these enantiomers.[15] We have also confirmed that when the enantiomer R* = (2 *R*)-(−)-$(CH_2)_3OCH(Et)C_6H_5$ is used as side group on the polythiophene chain, a reverse selectivity is observed for the camphorsulfonate enantiomers.

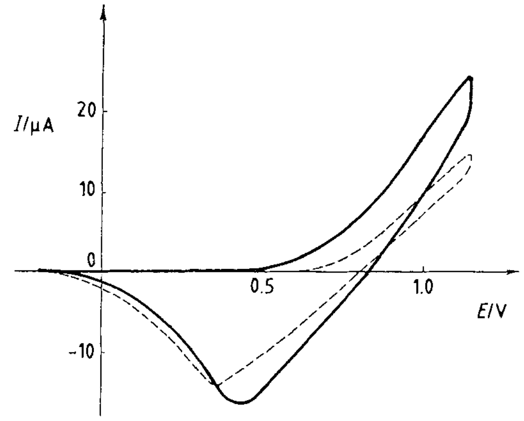


Fig. 2. Cyclic voltammogram of chiral polythiophene using optically active chiral anion as doping agent: (——), (----): (+)- and (−)-10-camphorsulfonate, respectively. E vs. saturated calomel electrode.

This effect has been interpreted on the basis of the chiral environment created by the bulky R* groups around the polythiophene conducting chains. During the doping process, the anions have to percolate through this chiral environment in order to reach the thiophene rings and produce the electronic doping interaction. These results are the first unambiguous evidence that electroactive functionalized polymers are capable of molecular recognition of enantiomers during the electrochemical doping process. This configurational selectivity imposed by the chiral environment appears to mimic the structural control in enzymes caused by the protein subunits surrounding their active site.

4. Molecular Catalysts

The functionalized polymer–enzyme analogy can be carried further, since functionalized conducting polymers are not only able to act as molecular sensors and transducers, but also allow the control of chemical reactions by the incorporation of redox centers or of metallic submicroaggregates able to induce electrocatalytic processes. Thus, many types of redox centers such as metalloporphyrins,[16] ferrocene,[17] metal complexes of bipyridines,[18] and nickel cyclames[19] have already been either covalently bonded or electrostatically included in polypyrrole. Various submicroaggregates of metals such as Pt, Pd, Cu, Ni, Ag have also been incorporated in polythiophenes by an electrochemical deposition method which allows precise control of the size and spatial distribution of these aggregates (Fig. 3).[20] Pt and Cu for instance have been shown by Extended X-Ray Absorption Fine Structure (EXAFS) to exist as coordinated atoms or as small clusters along the individual conducting chains.[21] When the size of the metal particles is increased, aggregates can be visualized by scanning electron microscopy (SEM), appearing then as deposits (size ca. 20 nm) on polymer fibers (diameter ca. 10 nm), in which the disposition of the individual polymer chains is not yet well understood.

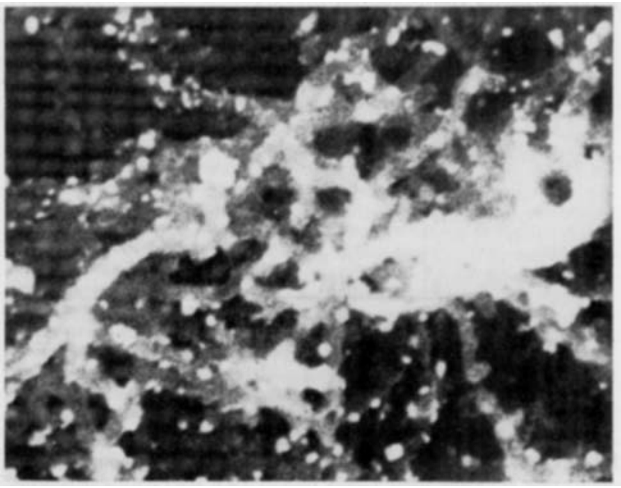


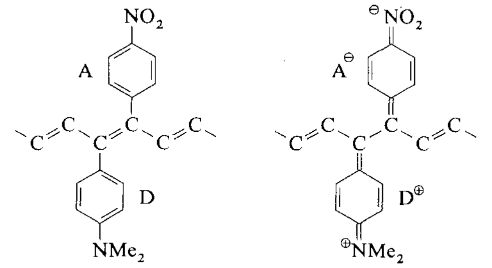
Fig. 3. Scanning electron micrograph of silver aggregates deposited along the conducting fibers of polymethylthiophene. Enlargement: 30000 ×.

These redox and metal centers can be electrochemically addressed through the conducting chains of the polymer, allowing the controlled triggering of fundamental chemical processes such as the reduction of $H^{\oplus}$,[20] CO_2[19] or O_2,[20] or the oxidation of H_2O[22] or ROH.[23] High catalytic activity has been demonstrated,[20] resulting from the molecular distribution of these catalytic centers in three-dimensional materials of hundreds of microns in thickness. Furthermore, the regioselectivity observed, e.g. in the catalytic hydrogenation of unsaturated compounds with substituted polypyrroles,[24] indicates that the reactions proceed under a stereochemical control exerted by the environment of the catalytic centers in the conducting polymers. This result is very promising in relation to the possibility of using conducting polymers with chiral substituents such as those described in the previous section, for inducing asymmetry during these catalytic reactions through a template effect, although such an effect has still to be experimentally demonstrated.

These few examples show how far chemists have already gone in the realization of molecular materials capable to perform physical and chemical recognition, to transfer molecular signals, and to induce electrocatalytic reactions. Of course, the phenomena of molecular recognition, signal transfer and catalytic control are also known for individual molecules and supramolecules in homogeneous phases.[1] The important step achieved with functionalized conducting polymers is the assembly of these functional elements in a three-dimensional architecture based on a network of molecular wires able to carry electronic information to and from these elements. There is still a long way to go before these elaborate structures can be addressed at a molecular level.

5. Molecular Electronics

The introduction of memory effects and logic functions in these materials is the field of molecular electronics. In molecular wires switching, gating and amplification functions result from the ability to modulate their charge transfer properties, and memory effects are directly related to bistability phenomena. For example, donor (D)–acceptor(A) systems in which a charge separation can be photochemically induced can be covalently bonded as side groups along the conducting chains; by altering the amount of charge transfer between D and A the extent of conjugation, and thus the charge transport properties of the chains, can be modified. Such a type of "push-pull" mechanism[2] is depicted in Scheme 2.



Scheme 2. Left: conjugated conducting chain of polyacetylene; right: interruption of conjugation and conduction due to charge transfer D → A.

If we use a D–A system in which the extent of charge transfer is controlled by an external variable such as light intensity, the charge transport properties of the conducting polymer chains can be modulated ("molecular modulation" of a signal). If a very large variation of this charge transfer is imposed, electron sinks will be created along the conducting chains which will hinder any conduction, thus leading to molecular switches. Considerable knowledge of such D–A systems is already available, e.g. in dye chemistry. As a consequence of the very short time scale associated with light excitation phenomena, which typically lies in the order of 10^{-15} s for reaching Franck–Condon states, ultra-fast modulation and switching can be expected with these new molecular structures.

Memory effects will be obtained if bistable structures showing some hysteresis can be produced. Bistability is already a well studied phenomenon, and molecular systems exhibiting this effect have been proposed, based, for example, on an antiferroelectric to ferroelectric transition induced by the application of an external field,[25] on a ferrimagnetic to ferromagnetic transition in heterobimetallic complexes,[26] or on the more familiar modification of optical properties that occurs in photochromic molecules following a light pulse.

Unlike inorganic semiconductors, where the semiconducting properties are associated with a macroscopic solid state, whether crystalline or amorphous, in organic molecules the properties are intrinsic to the molecules. The new concept of molecular semiconductors opens up a new field, both theoretically and with regard to applications.[27] The semiconducting properties of undoped conjugated polymers such as polyacetylene and polythiophene have been used in various devices, such as Schottky junctions,[29] homo- and heterojunctions,[29] organic–inorganic junctions,[30] and field-effect transistors.[31] Although the results are promising, it has been acknowledged in all these investigations that the devices suffer from the very poor semiconducting properties of these conjugated polymers. As already observed for most organic semiconductors, these materials have large concentrations of structural defects and impurities, which create efficient traps and recombination centers. Thus the carrier mobility which is one of the most important characteristics for a semiconductor, is very low, rarely exceeding 10^{-5} cm^{2}V^{-1}s^{-1}, a value which has to be compared with about 1 cm^{2}V^{-1}s^{-1} for a classical amorphous inorganic semiconductor such as Si, and more than 10^2 cm^{2}V^{-1}s^{-1} for monocrystalline Si. A large improvement in the semiconducting properties of these organic materials thus appeared essential in order to consider them for electronics applications. An important achievement has been the use of conjugated oligomers instead of the corresponding polymers. Oligomers can be synthesized as chemical compounds with a well defined structure and a much lower concentration of defects and impurities than the corresponding polymers. By controlling the conjugation length, it is possible to prepare oligomers showing almost the same band-gap energy as the parent polymers, and their solubility and low molecular weight allow them to be easily processed by vacuum or by Langmuir–Blodgett techniques. The most important advantage is their structural homogeneity, which leads to carrier mobility values as high as 2×10^{-2} cm^{2}V^{-1}s^{-1} in the case of thiophene oligomers.[32] This spectacular increase in mobility underlines the major role played by structural defects for limiting the charge transport properties in polymer chains. Thus, conjugated oligomers, which can be functionalized in the same way with prosthetic groups R, appear to be promising in meeting the requirements for applications in electronics.

A last important aspect which deserves attention concerns the tunability of the electronic properties of these organic semiconductors compared to inorganic semiconductors. Indeed, the characteristics of electronic devices, junctions and transistors, are mainly determined by the intrinsic electronic properties of their n- and p-type semiconducting components. The common inorganic semiconductors, such as Si, GaAs and InP, have discrete band energy values, which impose limits on the characteristics of the corresponding devices. On the other hand, in organic materials which are capable of either large or subtle chemical modifications, these band energy values can be controlled over a wide range, and can thus be tuned in order to achieve almost any desired characteristic. Functionalized organic conjugated polymers and oligomers will thus be able to perform memory and logic functions. Compared to conventional inorganic materials, the easy tuning of their electronic properties offers a promise as great as the first proposals, some decades ago, for using polymers instead of metals.

Received: November 21, 1988

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[1] J. M. Lehn, *Angew. Chem. 100* (1988) 91; *Angew. Chem. Int. Ed. Engl. 27* (1988) 89; D. J. Cram, *ibid. 100* (1988) 1041 and *27* (1988) 1009; C. J. Pedersen, *ibid. 100* (1988) 1053 and *27* (1988) 1021.

[2] F. Carter (Ed.): *Molecular Electronic Devices*, Marcel Dekker, New York 1982.

[3] T. A. Skotheim (Ed.): *Handbook of Conducting Polymers*, Marcel Dekker, New York 1986.

[4] H. Shirakawa, E. Louis, A. MacDiarmid, C. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun. 1977*, 758.

[5] A. F. Diaz, K. K. Kanazawa, J. P. Gardini, *J. Chem. Soc. Chem. Commun. 1979*, 635.

[6] G. Tourillon, F. Garnier, *J. Electroanal. Chem. 135* (1982) 173.

[7] A. G. MacDiarmid, J. C. Chiang, M. Halpern, W. S. Huang, S. L. Mu, N. D. L. Somasiri, W. Wu, S. Yaniger, *Mol. Cryst. Liq. Cryst. 121* (1985) 173.

[8] N. Basescu, Z. X. Liu, D. Moses, A. J. Heeger, H. Naarmann, H. Teophilou, *Nature (London) 327* (1987) 403.

[9] F. Garnier, G. Tourillon, M. Garzard, J. C. Dubois, *J. Electroanal. Chem. 148* (1983) 299.

[10] J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, M. Lemaire, *Synth. Met. 28* (1989) C341.

[11] G. Bidan, A. Deronzier, J. C. Moutet, *Nouv. J. Chim. 8* (1984) 501.

[12] Y. K. Korshak, T. V. Medvedeva, A. A. Ovchinnikov, V. N. Spector, *Nature (London) 326* (1987) 370.

[13] V. Leberre, L. Angely, N. Simonet-Gueguen, J. Simonet, *J. Electroanal. Chem. 206* (1986) 115.

[14] M. G. Minett, J., R. Owen, *Synth. Met. 28* (1989) C211.

[15] J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, M. Lemaire, *Makromol. Chem. Makromol. Symp. 20* (1988) 601.

[16] A. Bettelheim, B. A. White, S. A. Ratbuck, R. W. Murray, *Inorg. Chem. 26* (1987) 1009.

[17] J. G. Eaves, H. S. Munro, D. Parker, *Synth. Met. 26* (1986) 123.

[18] F. Daire, F. Bedioui, J. Devynck, C. Bied Charreton, *J. Electroanal. Chem. 205* (1986) 309; R. A. Bull, F. R. Fan, A. J. Bard, *J. Electrochem. Soc. 131* (1984) 687.

[19] J. P. Collin, J. P. Sauvage, *J. Chem. Soc. Chem. Commun. 1987*, 1075.

[20] G. Tourillon, F. Garnier, *J. Phys. Chem. 88* (1984) 5281; A. Yassar, J. Roncali, F. Garnier, *J. Electroanal. Chem. 255* (1988) 53.

[21] D. Gourier, G. Tourillon, *J. Phys. Chem. 90* (1986) 5561.

[22] D. Gningue, H. Horowitz, F. Garnier, *J. Electrochem. Soc. 135* (1988) 1695.

[23] A. Deronzier, L. Coche, J. C. Moutet, *J. Electroanal. Chem. 198* (1986) 187.

[24] L. Coche, J. C. Moutet, *J. Am. Chem. Soc. 109* (1987) 6887.

[25] J. Malthete, A. Collet, *J. Am. Chem. Soc. 109* (1987) 7544.

[26] O. Kahn, Y. Pei, M. Verdaguer, J. P. Renard, J. Sletten, *J. Am. Chem. Soc. 110* (1988) 782.

[27] J. Simon, J. J. André: *Molecular Semiconductors*, Springer, Berlin 1985.

[28] S. Glenis, G. Tourillon, F. Garnier, *Thin Solid Films 139* (1986) 221.

[29] T. Wada, A. Takeno, M. Iwaki, H. Sasabe, Y. Kobayashi, *J. Chem. Soc. Chem. Commun. 1985*, 1194.

[30] G. Horowitz, F. Garnier, *Chemtronics 1* (1986) 80.

[31] A. Tsumura, H. Koezuka, S. Tsunada, T. Ando, *Chem. Lett. 1986*, 863.

[32] F. Garnier, G. Horowitz, D. Fichou, *Synth. Met. 28* (1988) 705.