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Nanowires of Molecule-Based Charge-Transfer Salts

De Caro Dominique
CNRS-LCC (Laboratoire de Chimie de Coordination), and Université de Toulouse, Toulouse, France

1. Introduction

As we approach the physical limits of conventional silicon-based electronics, there is a clear need for new types of materials that can deliver smaller and smaller devices. A strong candidate in this field is molecular electronics, which uses assemblies (via π−π or van der Waals interactions) of individual molecules (organic or metallo-organic molecules). Organic or metallo-organic molecules should stack in one direction to provide a framework for possible band structure formation. Therefore, the repeat units should preferably have an overall planar geometry. The partial filling of the conduction band (*i.e.* the metallic state) should be ensured either by partial oxidation (mixed-valence salts) or by partial charge transfer (charge-transfer salts). Charge-transfer salts are formed when a number x of donor molecules D jointly donate an electron to a second type of molecule A, to form the compound D_xA; owing to its charge, A is usually referred to as the anion molecule.
Charge-transfer based conductors (exhibiting a semiconducting behaviour, a metal-like conductivity, or a transition to a superconducting state) are more commonly prepared and studied as macroscopic single crystals (prepared by using slow diffusion in organic solution or electrocrystallisation techniques). Micrometer-sized crystals have nevertheless been obtained (Deluzet et al., 2002; Kobayashi et al., 2008; Mas-Torrent & Hadley, 2005). Charge-transfer conductors at the nanoscale have received broad attention in recent years because of their novel properties and potential applications for future electronic devices. However, nanowires of charge-transfer salts are still rare and only few examples have been reported. This chapter presents the most significant results in this area. The first part of this chapter will describe the preparation methods selectively leading to isolated nanowires or nanowire films of charge transfer compounds. The second part will be devoted to the spectroscopic studies of nanowires with a special emphasis on vibrational and photoelectronic techniques. The last part of the chapter will be the description of the physical properties of nanowires.

2. Preparation methods

Preparation methods can be divided into two main categories: vapour phase methods and solution-grown methods. When gas-phase reactions are involved, the most important

characteristic that the precursor molecules should fulfil to be used is their ability to be vaporised. The precursors must also be transported without decomposition from the vaporisation zone to the depositing zone. When a solution-grown technique is involved, soluble precursors are required.

2.1 Vapour phase techniques

Tetrathiafulvalene·7,7,8,8-tetracyano-*p*-quinodimethane (TTF·TCNQ, Fig. 1) is the main charge transfer compound which has been processed as nanowires using vapour phase methods. TTF·TCNQ is the archetype of charge transfer salts. In this compound, TTF and TCNQ molecules are in 1:1 ratio and form separate stacked donor (TTF) columns and stacked acceptor (TCNQ) columns. A partial charge transfer (of about 0.59 electron per molecule) between TTF and TCNQ transforms the molecular stacks into one-dimensional conductive paths *via* the formation of partially filled bands. As single crystals, TTF·TCNQ exhibits a metallic conductivity down to 60 K. Its room-temperature conductivity is of about 600 S cm^{-1} along the *b*-axis of the single crystal.

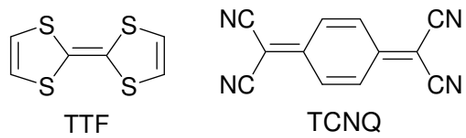


Fig. 1. Molecular structures for TTF and TCNQ.

TTF·TCNQ nanowires can be fabricated by the co-evaporation method in the absence or in the presence of an electric field (Sakai et al., 2003). Two independent crucibles (placed in a vacuum evaporation chamber) are loaded with TTF and TCNQ powders. The sublimation temperatures of the TTF (55 °C) and of the TCNQ (110 °C) are individually controlled. Moreover, a couple of parallel Au/Cr electrodes with a gap of 100 μm are formed on a glass substrate. During the deposition process, the substrate is maintained at temperatures in the 40-45 °C range (deposition rate of about 0.03 nm s^{-1}). In the absence of electric field, randomly oriented nanowires of TTF·TCNQ are formed on the glass substrate, particularly around the electrodes. In the presence of an applied electric field (35 kV cm^{-1}), highly oriented nanowires of TTF·TCNQ (aligned along the electric field) are observed. Using a gap of 20 μm between the two Au/Cr electrodes and a low applied electric field (6 kV cm^{-1}), nanowires may connect the two electrodes.

We have developed an alternative route to TTF·TCNQ nanowires (growing from the edges of a microcrystal) using the chemical vapour deposition (CVD) technique (Wada et al., 2009). TTF·TCNQ nanowires are deposited from TTF and TCNQ, using a conventional hot-wall CVD apparatus. The vaporisation crucibles are charged with about 100 mg of each precursor. The substrates, (001)-oriented intrinsic Si wafers, are placed on top of a glass slide inside the CVD reactor. The precursors are vaporised from the crucibles at low pressures (about 850 Pa), and transported by He carrier gas (flow rate in the 60-80 standard cm^3 min^{-1} range) through heated lines to the mixing zone, and then to the deposition zone (deposition time: 180 min). The lines and mixing zone are set at a higher temperature (170 °C) than the vaporisation zone (78 °C for TTF, and 145 °C for TCNQ) in order to avoid condensation of the starting compounds. The X-ray diffraction pattern recorded on nanowires deposited on (001)-oriented Si wafers only shows the (00*l*), *l* = 2n, lines. This indicates a preferential

orientation of the nanowire films, *i.e.* the *ab*-plane parallel to the substrate surface. Fig. 2 shows that nanowires grow from random branching points on the initial TTF·TCNQ microcrystal. The dimensions of the nanowires are typically 100 nm in diameter and > 5 μm in length. Fig. 2 also evidence that nanowires grow in different orientations leading to a kind of "carnivorous plant".

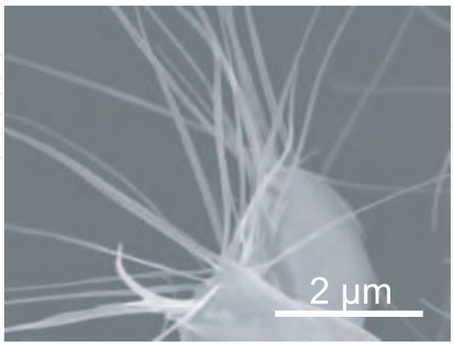


Fig. 2. Nanowires growing from random branching points on a TTF·TCNQ microcrystal

M(TCNQ) (M = Cu, Ag) nanowires can be prepared by organic solid-phase reaction that give good and simple control of the uniformity (Liu et al., 2005). The TCNQ powder is loaded in a ceramic crucible and then placed at the centre of a quartz tube that is inserted into a horizontal tube furnace. A copper or a silver foil is placed on top of the ceramic boat. The TCNQ molecule is then deposited on the surface of the foil (temperature in the 120-150 °C range) for formation of Cu(TCNQ) or Ag(TCNQ) nanowire films. Single Cu(TCNQ) nanowires exhibit a diameter of about 70 nm whereas those of Ag(TCNQ) exhibit a diameter of about 50 nm.

2.2 Solution-grown techniques

As described above, vapour phase methods require vaporizable precursors. These techniques are therefore restricted to only neutral molecules. Charge transfer salts are mostly prepared in organic solution, medium in which both neutral and ionic precursors are soluble. Moreover, a wide variety of charge transfer salts are obtained by electrochemical oxidation of the donor molecule in the presence of a supporting electrolyte. These systems are then not accessible to gas-phase techniques. In the first part of this paragraph, we will describe the preparation of nanowires of charge transfer salts for which there is a direct chemical reaction between the donor and the acceptor molecule. The second part of this paragraph will be devoted to the preparation of nanowires of charge transfer compounds in which the oxidation of the donor molecule is current-induced.

2.2.1 Nanowires of TTF·TCNQ and TTF[Ni(dmit)$_2$]$_2$

TTF·TCNQ can easily be prepared by slow addition of an organic solution of TTF into an organic solution of TCNQ. Electron micrograph images of the resulting powder show long micrometer-sized needles (typical sizes: 1-2 μm wide and > 5 μm long). To constrain the growth as nanowires, two synthetic strategies have been developed: a two-phase method and a dipping process on an oxide conversion coating onto a stainless steel substrate.

TTF·TCNQ nanowires can be grown in organic solution using the two-phase method (Liu et al., 2007). TTF solutions are prepared by dissolving TTF in hexane and TCNQ solutions by

dissolving TCNQ in acetonitrile. The TCNQ solution is dripped into the TTF solution at various rates (in the 1-500 μL s^{-1} range) under stirring. The morphology and the state of dispersion of the nanowires is dripping-rate dependent: straight nanowires (at 1 μL s^{-1}), helical nanowires (at 20 μL s^{-1}), helical dendrites (at 40 μL s^{-1}), and complicated helical dendrites (at 500 μL s^{-1}). The faster growth rate along the *b*-axis is due to the π−π stacking interaction for inducing the formation of TTF·TCNQ nanowires at the hexane-acetonitrile interface. However, using this two-phase technique, diameters lower than 100 nm is never observed.

We have developed an easy route to the formation of TTF·TCNQ nanowires exhibiting diameters lower than 80 nm, and well dispersed on a surface from which they can easily be removed (Savy et al., 2007). The substrate on which nanowires are formed is an oxide conversion coating onto stainless steel (stainless steel conversion coating, abbreviated SSCC). The SSCC substrates are prepared from austenitic stainless steel dipped in an aqueous sulphuric acid bath (0.2 % vol.) containing sodium thiosulfate (0.01 mol L^{-1}) at 45 °C. After an electrolytic activation (− 1.5 V/SCE) for 2 min, the conversion coating grows by chemical treatment in the same bath. The resulting coatings are identified as magnetite and maghemite phases. They are known for showing advanced adsorption properties due to their fractal-like nanostructured surface. TTF·TCNQ nanowires are prepared by successive immersion of the SSCC substrate in acetonitrile solutions of TTF (10^{-2} mol L^{-1}) and TCNQ (10^{-2} mol L^{-1}). Adsorption of TTF is realised at first. Then, immersion of the TTF-containing oxide surface in the TCNQ solution results in the formation of TTF·TCNQ nanowires. Nanowires uniformly cover the substrate surface and a large amount of them bridge the cracks of the conversion coating (Fig. 3). Efficient adsorption of the TTF moiety onto the surface is not surprising because SSCC substrates are known to adsorb π-electron-rich planar molecules. Further formation of TTF·TCNQ as nanowires and not as a continuous film could be explained by the 1D-character of the charge transfer salt. Individual nanowires can be collected using a micropipette (diameter < 1 μm) gently scanned with a micro-manipulator inside the cracks of the conversion coating.

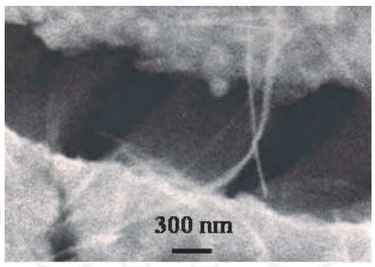
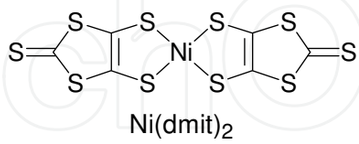


Fig. 3. TTF·TCNQ nanowires on a SSCC substrate.

Certain kind of metal complexes have been regarded as promising molecule-based conductors, because they combine a metal ion surrounded by ligands which exhibit a more or less extended π system. Among them and due to their remarkable coordination properties, dithiolene ligands have been intensively studied. TTF$[Ni(dmit)_2]_2$ combine the TTF donor molecule and the $[Ni(dmit)_2]^{\delta-}$ acceptor bis-dithiolene complex (Fig. 4, the non integer δ value, *i.e.*, the incommensurable character of the system will be discussed in part 3). It results from the reaction of the $(TTF)_3(BF_4)_2$ salt with $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$ in organic solution. The reaction leads to the formation of a 1:2 adduct where TTF and $Ni(dmit)_2$ species are partially oxidised. Within the final material, the charge transfer between the TTF

donor molecule and the $Ni(dmit)_2$ acceptor complex is found to be 0.80 from diffuse X-ray scattering experiments and band structure calculations. The structure of $TTF[Ni(dmit)_2]_2$ consists of segregated stacks of TTF and $Ni(dmit)_2$ units. On single crystals, its room-temperature conductivity is about 300 S cm^{-1} along the *b*-axis. The conductivity behaviour is metallic down to 4 K at ambient pressure. Moreover, this compound undergoes a complete transition to a superconducting state at 1.62 K under a hydrostatic pressure of 7 kbar.



$Ni(dmit)_2$

Fig. 4. Molecular structure for $Ni(dmit)_2$.

The slow addition of an organic solution of $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$ in an organic solution of $(TTF)_3(BF_4)_2$ leads to $TTF[Ni(dmit)_2]_2$ as long micrometer-sized needles (typical sizes: 1-2 μm wide and > 5 μm long). $TTF[Ni(dmit)_2]_2$ nanowire films are prepared by successive immersion of the SSCC substrate in an acetonitrile solution of $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$ (3.54 g L^{-1}) and in an acetonitrile solution of $(TTF)_3(BF_4)_2$ (2.04 g L^{-1}) (Valade et al., 2002). The diameters of the nanowires lie from 50 to 250 nm (Fig. 5). By changing the order of immersion, *i.e.* $(TTF)_3(BF_4)_2$ first and then $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$, no nanowire is obtained on the SSCC surface. Tetraalkylammonium cations have a strong affinity for oxide surfaces. The adsorption of $[R_4N]^+$ cations originates in their interaction with the dipoles of the oxide species. A hydrophilic surface, such as SSCC, also facilitates this adsorption. This could explain that $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$ is strongly anchored onto the SSCC substrate and reacts with $(TTF)_3(BF_4)_2$ to form $TTF[Ni(dmit)_2]_2$ as nanowires.

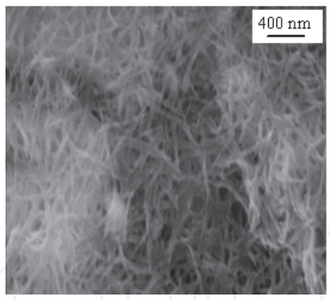


Fig. 5. $TTF[Ni(dmit)_2]_2$ nanowires on a SSCC substrate.

2.2.2 Nanowire films prepared by the Langmuir-Blodgett technique

The Langmuir-Blodgett (LB) technique has been successfully applied to form nanowire films of charge transfer-based conductors (Miyata et al., 2003). The donor molecule is a didecyl derivative of a bis-tetrathiafulvalene substituted macrocycle (bis-TTF-$(C_{10}H_{21})_2$), and the acceptor molecule is the tetrafluorotetracyanoquinodimethane (F_4TCNQ). A conventional LB trough is used for monolayer formation and LB film deposition. A KCl aqueous solution (0.01 mol L^{-1}) is used as a subphase, and a mixture of chloroform/acetonitrile (9:1) is used as a spreading solvent. One equivalent of the bis-TTF-$(C_{10}H_{21})_2$ molecule and two equivalent of F_4TCNQ are combined in the spreading solution. Monolayers are transferred on freshly cleaved mica substrates by the vertical dipping method with the deposition speed of 10 mm

min^{-1} at 17 °C. Atomic force microscopy images of transferred films exhibit nice extended nanowire network structures on mica surface. The majority of the nanowires (typical diameters: 70-100 nm) orient specific direction reflecting the lattice of mica surface. The orientation of six-fold symmetry should be due to the recognition of K^+ array on mica surface by nanowires upon the deposition of monolayers.

2.2.3 Electrochemically-grown nanowires of charge-transfer salts

The electrochemical method is the most widely used technique to grow conductive molecular salts. During electrocrystallisation, compounds are intended to grow attached to the electrode surface, which is usually a platinum or a gold wire. However, it is clear that only conductive species may be considered, as the covered electrode should retain a high enough conductivity at any time during the process. An electrochemical synthesis may be conducted either under potentiostatic or galvanostatic conditions. The growth rate is highly important to control the size, the morphology, and the quality of crystals. For this reason, galvanostatic conditions are preferably applied for electrosynthesis of charge transfer salts. On platinum or gold wire-like electrodes, macroscopic needles or platelets of molecule-based conductors are commonly obtained. To constrain the growth as nanowires, two different strategies have been developed:

- The use of a pre-treated Si wafer, used as an anode,
- The use of an electrode functionalised by a membrane.

Flat metallic electrode (*e.g.* a Pt foil) have been used to grow thin films of charge transfer salts. However, in the conditions explored, nanowires have never been observed. We have developed the use of a semiconducting electrode, namely silicon, to process nanowire films (Savy et al., 2007). Silicon is the substrate of choice in the electronic domain. It is easily available, cheap, and has a high enough conductivity to be used as an electrode (conductivity of about 5×10^{-3} S cm^{-1} at room temperature). A pre-treatment of the intrinsic silicon wafer is required to generate nanocavities, which will act as nanoflasks from which the growth as nanowires will be initiated. The pre-treatment consists in dipping the Si wafer in a mixture of H_2SO_4/H_2O_2 (1:1 v/v) for 10 min. The Si wafer is then dipped in a mixture of H_2O/HF (9:1 v/v) for 10 min, and finally dipped in a mixture of H_2SO_4/H_2O_2 (1:1 v/v) for 10 min. After these three aqueous treatments, the silicon wafer is rinsed (10 min) in the organic solvent in which the electrosynthesis will be carried out. The silicon surface thus obtained exhibits nanocavities (Fig. 6).

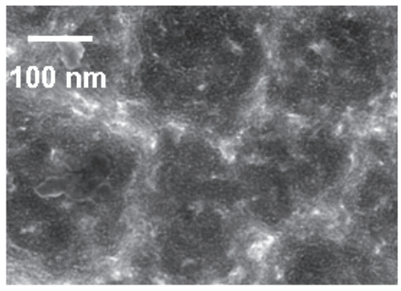


Fig. 6. Nanocavities on a treated intrinsic silicon wafer.

Charge-transfer salts combining an electron organic donor (D) and a [M(dithiolate)$_2$] complex are grown as nanowires on the silicon electrode described above, used as an anode in a conventional electrochemical cell. The electrochemical reaction leading to D_n[M(dithiolate)$_2$]$_m$

charge-transfer salts, involves the oxidation of the donor in the presence of the $[M(dithiolate)_2]^-$ salt which plays the role of both the acceptor and the supporting electrolyte:
Electrochemical step: $D \rightarrow D^+ + e^-$
Chemical step: $n\ D^+ + m\ [M(dithiolate)_2]^- \rightarrow (D^{+\delta/m})_n\ \{[M(dithiolate)_2]^{-\delta/n}\}_m$
$TTF[Ni(dmit)_2]_2$ nanowires are electrodeposited on a pre-treated Si anode from TTF (3 mmol L^{-1} in acetonitrile) and $[(n\text{-}C_4H_9)_4N][Ni(dmit)_2]$ (1 mmol L^{-1} in acetonitrile) starting materials in a one-compartment electrochemical cell, under galvanostatic conditions (about 6 μA cm^{-2}). Nanowires obtained exhibit diameters in the 50-300 nm range (Fig. 7).

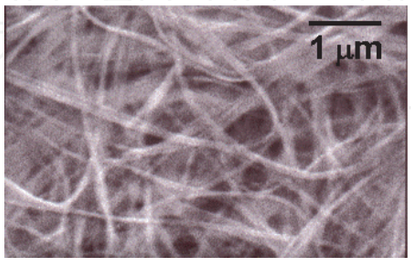


Fig. 7. $TTF[Ni(dmit)_2]_2$ nanowires grown on a pre-treated intrinsic silicon wafer, used as an anode.

Another charge-transfer salt based on a metal bis(dithiolene) complex can be processed as a nanowire film onto Si substrates: $(Per)_2[Au(mnt)_2]$ where Per stands for the perylene molecule, $C_{20}H_{12}$ (Fig. 8). The interest of $(Per)_2[M(mnt)_2]$ (M = Fe, Co, Ni, Pd, Pt, Cu, Au) compounds resides upon the coexistence in the same system of delocalized electron chains (perylene molecules) and chains of localized spins, *via* the $[M(mnt)_2]^-$ units. Though diamagnetic (Au^{3+} square planar d^8 configuration), the $[Au(mnt)_2]$-based charge-transfer salt has been selected due to its high room-temperature conductivity value (700 S cm^{-1} along the stacking *b* axis). Moreover, it can be easily studied by X-ray photoelectron spectroscopy (see paragraph 3) due to the presence of a relatively intense Au 4f line whose position is sensitive towards the formal oxidation number of the gold centre and towards electronic delocalization through mnt ligands. $(Per)_2[Au(mnt)_2]$ nanowires are electrodeposited on a pre-treated Si anode from perylene (6 mmol L^{-1} in dichloromethane) and $[(n\text{-}C_4H_9)_4N][Au(mnt)_2]$ (1.5 mmol L^{-1} in dichloromethane) starting materials in a two-compartment electrochemical cell, under galvanostatic conditions (about 0.3 μA cm^{-2}). Electron micrographs reveal that the film coated on the Si surface consists of large-scale $(Per)_2[M(mnt)_2]$ nanowires (Fig. 9). Diameter of individual nanowires is in the narrow range of 35-55 nm.
One interest of processing a nanowire film onto an intrinsic silicon wafer is that it is not necessary to remove it from the surface to investigate the transport properties (resistivity *vs.* temperature for example). Silicon has a conductivity value (about 5×10^{-3} S cm^{-1} at 25 °C) which is lower than that of the deposited material itself. Electrical contacts can then be drawn on a nanowire film as prepared.

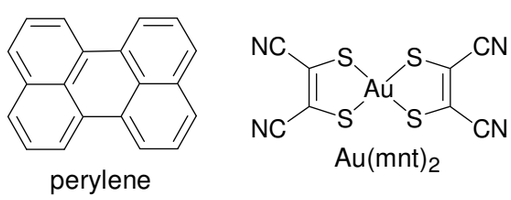


Fig. 8. Molecular structures for perylene and $Au(mnt)_2$

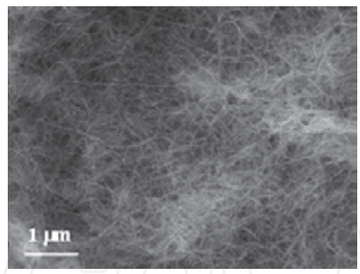


Fig. 9. $(Per)_2[Au(mnt)_2]$ nanowires grown on a pre-treated intrinsic silicon wafer, used as an anode.

Nanowire of charge transfer salts can also be prepared by electrocrystallisation using a functionalised electrode: a porous anodic aluminium oxide (AAO) coated with a gold film, or a Si-supported multilamellar membrane. The use of the first type of electrode leads to nanowire arrays, whereas the second type of electrode leads to nanowire films.

1D nanostructured arrays of $(BEDT\text{-}TTF)_4[H_2O{\cdot}Fe(C_2O_4)_3]{\cdot}C_6H_5NO_2$ where BEDT-TTF stands for bis(ethylenedithio)tetrathiafulvalene (Ji et al., 2006) and $[(CH_3)_4][Ni(dmit)_2]_2$ (Cui et al., 2004) are grown on a AAO-coated gold electrode, the porous AAO acting as a template which serves as an ideal host for the synthesis of the material of sub-micrometer dimensions. The preparation of $(BEDT\text{-}TTF)_4[H_2O{\cdot}Fe(C_2O_4)_3]{\cdot}C_6H_5NO_2$ as nanowire arrays can be divided into two steps. The first step is electrocrystallisation in organic medium. The AAO template, coated on one side with a gold film serving as the anode, and a platinum sheet serving as the cathode, are immersed in the electrolyte solution that consists of BEDT-TTF, $K_3[Fe(C_2O_4)_3]$, 18-crown-6 ether (used to coordinate potassium cations), and nitrobenzene as a solvent. The nanowire arrays grow along the channels of the AAO template at a constant current density of 1 µA cm^{-2} for 72 hours. In the second step, selective etching of the alumina template results in a freestanding $(BEDT\text{-}TTF)_4[H_2O{\cdot}Fe(C_2O_4)_3]{\cdot}C_6H_5NO_2$ charge-transfer salt nanowire array. The preparation of the mixed-valence compound $[(CH_3)_4][Ni(dmit)_2]_2$ follows a similar procedure (electrolyte solution: $[(CH_3)_4][Ni(dmit)_2]$, $[(CH_3)_4]ClO_4$ as a supporting electrolyte, acetonitrile). The nanowires obtained fit perfectly the pore diameters of the AAO template (in the 32-49 nm range). These nanowire arrays are highly textured in the direction of higher conductivity. However, the preparation of the porous alumina template is not straightforward. Furthermore, the prepared AAO membrane has to be metallated to be used as a working electrode. We have preferred to use another type of template, *i.e.*, a Si-supported phospholipidic-based multilamellar membrane. These well-ordered multilamellar membranes (thickness ~ 2.5 µm) are easily produced by spreading small drops of a lipidic solution on Si surfaces and letting the solvent (methanol/chloroform) evaporate slowly. The phospholipid used (DC8,9PC; Fig. 10) contains a zwitterion type headgroup and two long alkyl chains. Each alkyl chain has two conjugated carbon-carbon triple bonds which can polymerise by irradiating with a UV light. This template, used as a working electrode, preserves its lamellar structure in the electrolyte solution. This template-modified anode is advantageously used for growing a nanowire film of $(EDT\text{-}TTFVO)_4(FeCl_4)_2$ (EDT-TTFVO: ethylenedithiotetrathiafulvalenquinone-1,3-dithiomethide, Fig. 10). A solution of EDT-TTFVO (0.4 mmol L^{-1}) and $[(C_2H_5)_4N]FeCl_4$ (15 mmol L^{-1}) is electrolysed in a two-

compartment electrochemical cell in a mixture of chlorobenzene/ethanol (9:1 v/v) at constant current density (0.15 μA cm^{-2}) for 10 days. A nanowire film is obtained in which individual nanowires exhibit diameter ≤ 20 nm (Fig. 11). Using a Si-supported multilamellar membrane as electrode, growth as nanowires is conceivable as follows: EDT-TTFVO molecules migrate from the solution/membrane interface to the substrate surface *via* the channels delimited by the long alkyl chains. They are oxidized and produce the conducting salt by combination with $FeCl_4^-$ ions, largely present at the vicinity of the hydrophilic silicon surface. As the growing salt is in contact with $FeCl_4^-$ ions located in interheadgroup areas, the growth can continue but should adapt to nanometric size of the channels. Even when the growing salt reaches the membrane surface, the growth still continues towards the formation of long nanowires lying parallel to the membrane surface, as evidenced on Fig. 11.

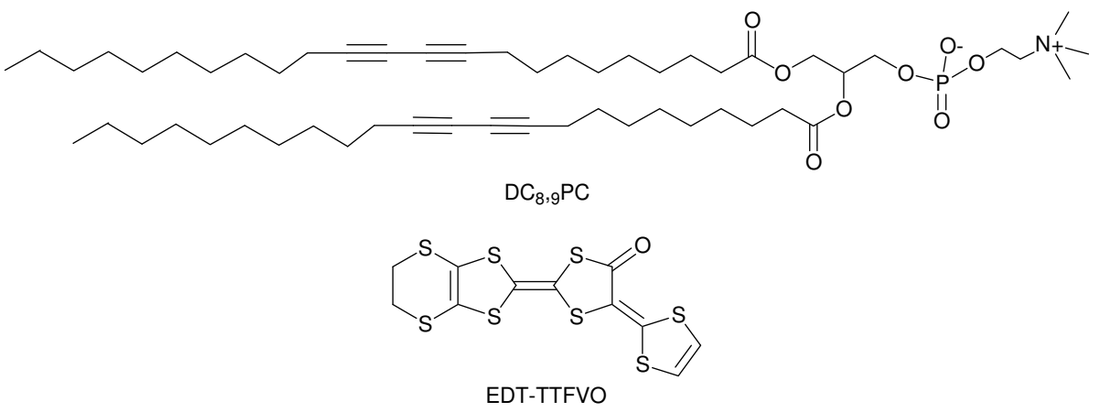


Fig. 10. Molecular structures for DC8,9PC and EDT-TTFVO.

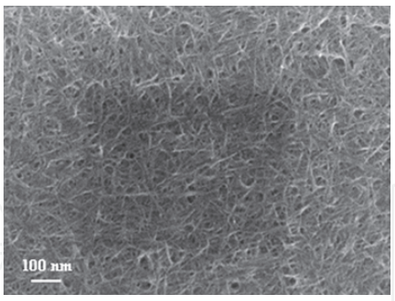


Fig. 11. Nanowires of $(EDT\text{-}TTFVO)_4(FeCl_4)_2$ electrochemically grown on a Si-supported multilamellar membrane, used as an anode.

3. Spectroscopic studies of charge-transfer salt-based nanowires

Infrared, Raman, and X-ray photoelectron spectroscopy are the most widely used techniques to characterize nanowires of charge transfer salts. The two first techniques allow the determination of the amount of charge transfer between the donor and the acceptor molecule. X-ray photoelectron spectroscopy provides both stoichiometry and formal charge borne by the moieties within the nanowires.

Infrared is particularly suitable for molecules bearing polar groups such as cyano groups (*e.g.* TCNQ, see Fig. 1). On the infrared spectrum of TTF·TCNQ nanowires (grown on Si using a vapour phase technique), a band attributed to the CN stretching mode (ν_{CN}) of TCNQ appears at 2203 cm^{-1}. The vibration frequency of the CN groups of TCNQ is characteristic of the formal charge of TCNQ, thus of the charge transfer between TTF and TCNQ moieties. In the case of the nanowires, it corresponds to a TTF·TCNQ phase with a charge transfer of $\rho = 0.57$, consistent with that observed on single crystals ($\rho = 0.59$).

Raman spectroscopy is particularly suitable to investigate polarisable molecules. It is a technique of choice for studying molecules exhibiting large delocalised π systems, which is the case for most of the molecules cited in this chapter. The Raman spectrum for TTF·TCNQ nanowires (grown on SSCC in acetonitrile) is shown on Fig. 12. In the 1400-1600 cm^{-1} range, the Raman spectrum exhibits three lines, all related to C=C modes. The first line, exhibiting two maxima at 1413 and 1418 cm^{-1}, corresponds to the ν_4 a_g mode in TCNQ. Using the linear relation of the TCNQ ν_4 frequency *vs.* ρ (amount of charge transfer), we determine a degree of charge transfer ranging from 0.65 to 0.60, in good agreement with 0.59 on single crystals. The second line (1512 cm^{-1}) is due to the ν_2 a_g mode in TTF. Its position is intermediate between neutral TTF (1555 cm^{-1}) and TTF^+ (1505 cm^{-1}). The third frequency (1600 cm^{-1}) is assigned to the ν_3 a_g mode in TCNQ, which is less sensitive to charge-transfer change (1602 cm^{-1} for neutral TCNQ and 1595 cm^{-1} for $TCNQ^-$). TTF·TCNQ nanowires grown on SSCC can then be written as: $[TTF^{\delta+}][TCNQ^{\delta-}]$ with $0.60 \leq \delta \leq 0.65$.

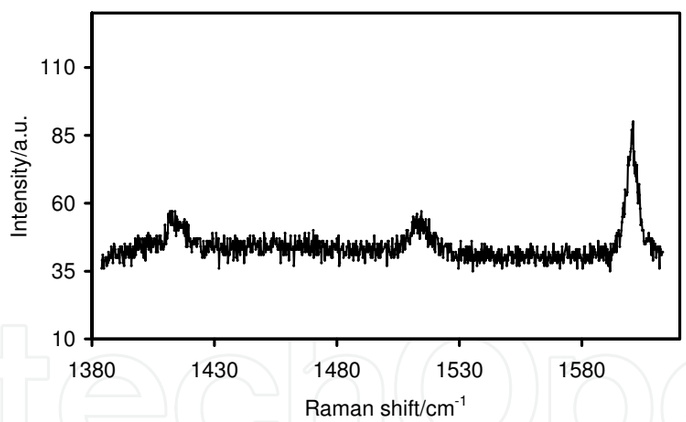


Fig. 12. Raman spectrum recorded on TTF·TCNQ nanowires grown on SSCC dipped in an acetonitrile solution of TTF and in an acetonitrile solution of TCNQ, respectively.

$TTF[Ni(dmit)_2]_2$ (either grown on SSCC or electrodeposited on Si) are also investigated by Raman spectroscopy (Fig. 13). In the low frequency region (not shown on Fig. 13), bands at 362 (weak), 496 (strong) and 510 (medium) cm^{-1} are assigned to ν_{Ni-S}, ν_{C-S} for TTF, and ν_{C-S} for $Ni(dmit)_2$, respectively. In the high frequency region (1300-1550 cm^{-1}), two strong C=C stretching modes are observed at 1436 (ν_3 a_g for TTF) and 1511 (ν_2 a_g for TTF) cm^{-1}. The low intensity line at 1475 cm^{-1} corresponds to the second overtone of the stretching ν_{C-S} for TTF. The ν_3 a_g mode for TTF is the most sensitive to the amount of charge transfer between the TTF donor and the $Ni(dmit)_2$ acceptor molecule, because it corresponds to a contribution of

about 71 % of the central C=C bond in the TTF moiety (highly symmetrical mode). Using the linear correlation between the ν_3 a_g position *vs.* the degree of charge transfer (ρ), a value of about ρ = 0.86 can be extracted, in excellent agreement with that found on TTF[Ni(dmit)$_2$]$_2$ single crystals (ρ = 0.80). TTF[Ni(dmit)$_2$]$_2$ nanowires can then be written as: [TTF$^{0.86+}$]{[Ni(dmit)$_2$]$^{0.43-}$]$_2$.

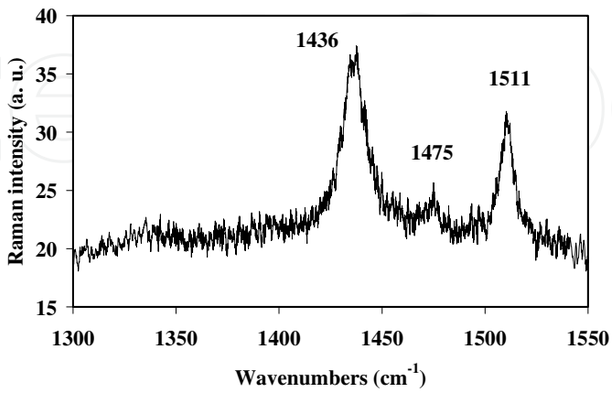


Fig. 13. Raman spectrum recorded on TTF[Ni(dmit)$_2$]$_2$ nanowires (grown on SSCC or on silicon wafers).

Nanowires of metal bis(dithiolene) complexes-based charge transfer salts are also characterized by X-ray photoelectron spectroscopy (XPS). XPS is a powerful technique to investigate the stoichiometry (donor/acceptor) within the nanowire films. In TTF[Ni(dmit)$_2$]$_2$, the TTF and the Ni(dmit)$_2$ moieties both contain sulphur atoms (see Fig.1 and Fig. 4). However, their chemical environment is different. Taking into account the presence of 2 [Ni(dmit)$_2$] and 1 TTF, 12 sulfur atoms are bound to two different sp^2 carbons (C−S−C), 8 sulfur atoms are bound to a nickel and a sp^2 carbon (C−S−Ni), and, finally, 4 sulfur atoms are bound to one sp^2 carbon (C=S). Atomic ratios are therefore 3:2:1. The X-ray photoelectron spectroscopy S2p line can be satisfactorily decomposed in three contributions (Fig. 14). According to their relative intensities, the most intense line, with a binding energy of 163.5 eV, corresponds to C−S−C bonds. Lines at 161.8 and 165.3 eV correspond to C−S−Ni and C=S bonds, respectively. The experimental intensity ratio between the C−S−C and C−S−Ni contributions is 1.4, in excellent agreement with the nominal 1.5 (3/2) value.
Nanowires of (Per)$_2$[Au(mnt)$_2$] are also studied by the XPS technique. Also the sulphur, nitrogen and gold have binding energies and lineshapes which are very sensitive to their formal charges. Fig. 15 shows the Au4f (a) and N1s (b) XPS lines measured on a Per$_2$[Au(mnt)$_2$] naowire film, respectively. The binding energy of the Au4f$_{7/2}$ peak is 86.1 eV, which can be associated to a formal Au(III) oxidation state. The shape of the lines (essentially symmetric) together with their small Full Width at Half Maximum (FWHM), 0.8 eV, strongly suggest that the dominant contribution corresponds to Au(III) and that other non-zero oxidation states of gold contribute negligibly to the signal, *e.g.*, absence of mixed-valency. The N1s line is composed of a main peak located at 398.2 eV binding energy and a shoulder at *ca.* 401 eV. The lineshape is characteristic of the presence of the cyano group, with a main peak and a (shake-up) satellite. The satellite arises from the energy loss (about 3 eV) of electrons associated to the occupied-unoccupied CN-related states, a known feature previously evidenced in neutral TCNQ: the inset in Fig. 15 (b) shows the XPS spectrum of the N1s line of neutral TCNQ taken at high resolution in which the observation of the satellite is more evident.

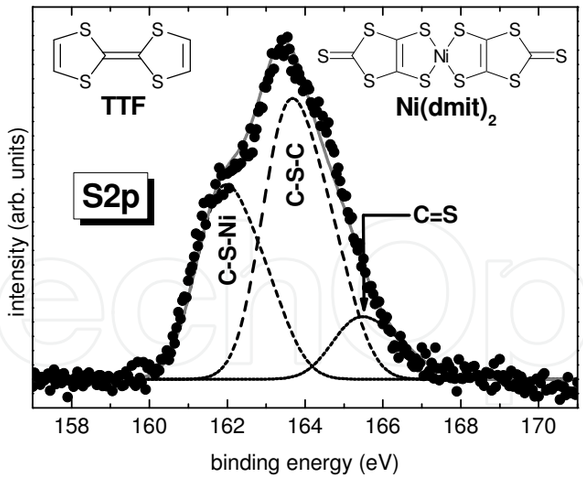


Fig. 14. S2p line in the XPS spectrum of TTF[Ni(dmit)$_2$]$_2$ nanowires (grown on silicon wafers).

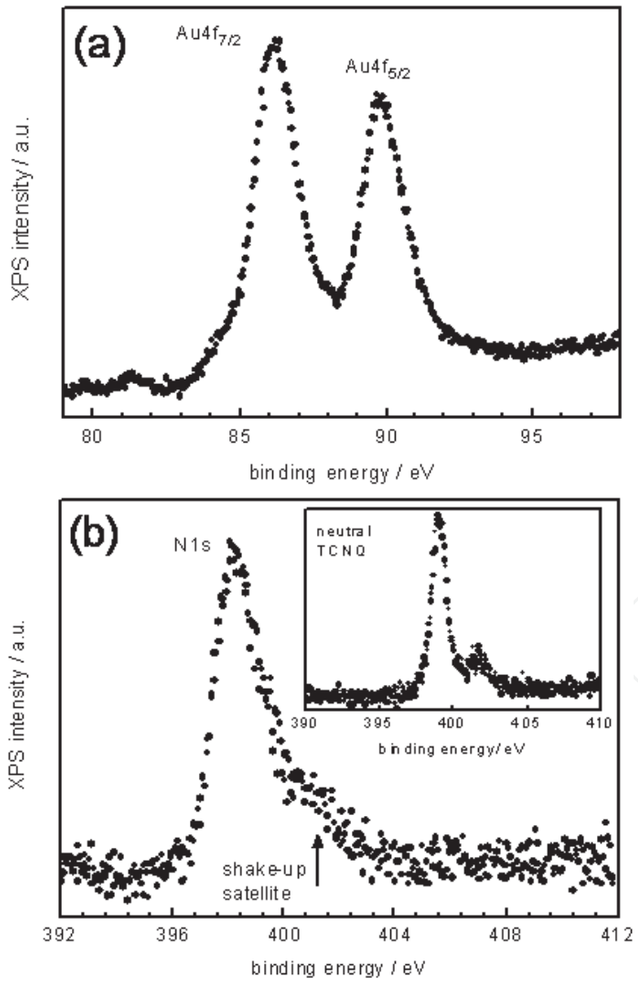


Fig. 15. Au4f (a) and N1s (b) lines in the XPS spectrum of (Per)$_2$[Au(mnt)$_2$] nanowires (grown on silicon wafers).

4. Physical properties of charge-transfer salt-based nanowires

4.1 Conductivity measurements

All charge-transfer salts described in this chapter are conducting materials as single crystals. At room temperature, their conductivity values range from 1 to about 10^3 S cm^{-1} along the molecular stacking direction. Conductivity measurements on single crystals are performed using the standard four-probe method: four electrical contacts are drawn on the single crystal using a conductive paste, such as gold, silver or graphite paste. Electrical current is passed between two of the contacts and the voltage created is measured between the other two contacts. The resistance can be calculated from the measured values of current and voltage. Knowing the dimensions of the single crystal and the distance between the electrical contacts, resistivity ρ (or conductivity, $\sigma = 1/\rho$) values can be calculated. The same four-probe technique is successfully applied to measure the conductivity on nanowire films.

Nanowire films of TTF·TCNQ (prepared by CVD), TTF[Ni(dmit)$_2$]$_2$ (electrochemically grown on Si), and (Per)$_2$[Au(mnt)$_2$] (electrochemically grown on Si) all exhibit a semiconducting behaviour (conductivity σ increases with temperature). Room-temperature conductivities are 0.5, 9, and 0.02 S cm^{-1}, respectively. These values are at least one order of magnitude less those on single crystals. Within single crystals, the stacking axis is the direction of highest conductivity. The contributions of other directions due to random orientation of the nanowires on the surface, and the presence of inter-nanowire contacts which are presumably more resistive than the material itself, account for the lower conductivity value of the nanowire film *vs*. that of single crystals. For a semiconductor, the logarithm of the conductivity follows a linear relationship *vs*. the reciprocal temperature, the activation energy being extracted from the slope (Fig. 16). Activation energies in the 0.2-0.8 eV range are obtained for nanowire films of TTF·TCNQ, TTF[Ni(dmit)$_2$]$_2$, and (Per)$_2$[Au(mnt)$_2$].

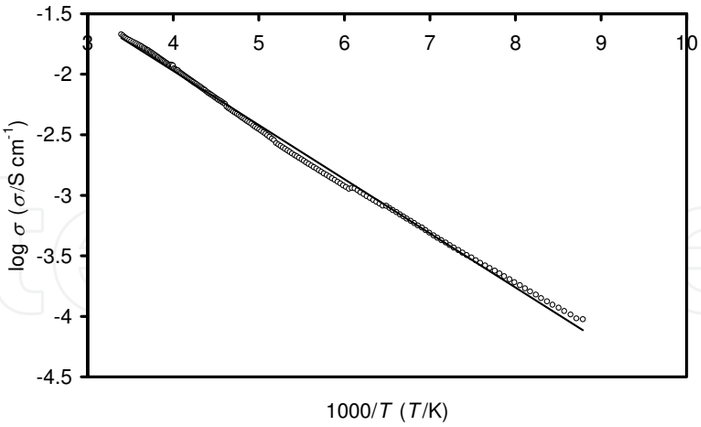


Fig. 16. Conductivity as a function of reciprocal temperature for electrodeposited (Per)$_2$[Au(mnt)$_2$] nanowire films.

Very interesting conductivity investigations have been done on isolated TTF·TCNQ nanowires synthesized under an electric field (Phanindra Sai & Raychaudhuri, 2010). The TTF·TCNQ nanowires are prepared by the thermal evaporation method (using TTF·TCNQ powdered material as a source) on SiO_2 substrates, on which electrodes were prefabricated using

electron-beam lithography and the lift-off process. Recall that TTF·TCNQ single crystals exhibit a metal-like conductivity at high temperatures. However, the metal-like conductivity is suppressed by two successive Peierls transitions on the TCNQ and TTF stacks at 54 K and 38 K, respectively. A single TTF·TCNQ nanowire (vapour-phase grown in an electric field) shows a semiconductor-like behaviour. It does not show the metallic behaviour, as the stoichiometry of the nanowires does not remain 1:1 due to different vapour pressures of TTF and TCNQ molecules and these nanowires are generally TCNQ-rich. The temperature dependence of the resistivity is found to obey an activated behaviour. The plot of the logarithm of ρ versus $T^{-1/2}$ clearly evidences change in slopes at 55 and 37 K, the region where the Peierls transition occurs. Moreover, the conductivity value on an isolated nanowire is about 12 S cm^{-1}, much lower than that for a single crystal along the *b* stacking direction (600 S cm^{-1}). This arises presumably from the disorder in the stacking sequences of TTF and TCNQ.

4.2 Current-voltage curves on TTF·TCNQ isolated nanowires

Recall that TTF·TCNQ nanowires exhibiting diameters lower than 70 nm can be prepared on an oxide layer chemically grown on stainless steel (SSCC, *i.e.* stainless steel conversion coating). They can be removed from the substrate surface by moving a micropipette inside the cracks of the SSCC. Fig. 17 evidences a nanowire deposited on a copper grid covered by a carbon layer for transmission electron microscopy measurements, whereas Fig. 18 shows an atomic force microscopy image of an individual nanowire deposited on a silica surface.

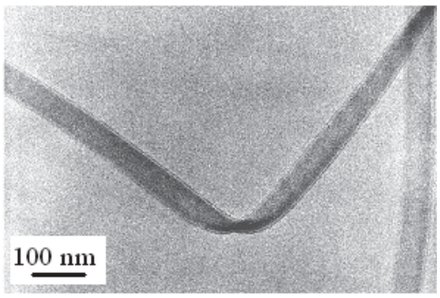


Fig. 17. Transmission electron micrograph of a TTF·TCNQ nanowire, grown by the dipping method.

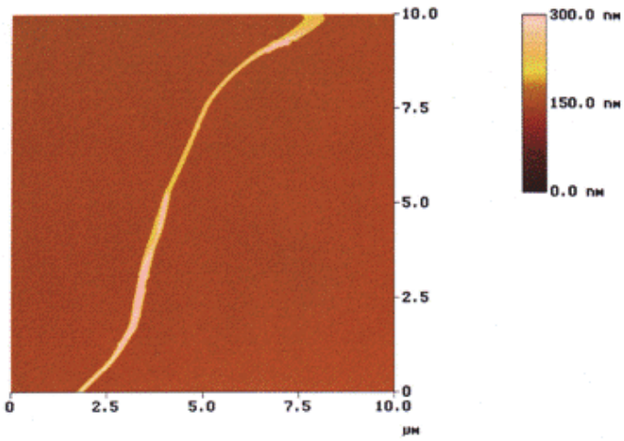


Fig. 18. Atomic force microscopy image of a TTF·TCNQ nanowire, grown by the dipping method.

To plot the current-voltage (I−V) response for TTF·TCNQ nanowires, they are placed between two electrodes of a metal-insulator-metal nanojunction fabricated on a silica surface. The non linearity of the I−V curve (Fig. 19) is attributed to the non-ohmic character of the contacts which is possibly due to an imperfect interface between the electrodes and the nanowire. The existence of a tunnel junction at the electrode−TTF·TCNQ nanowire junction is therefore highly possible. Indeed, the observed gap of about 0.6 eV is compatible with values obtained by scanning tunnelling spectroscopy and photoemission measurements performed on TTF·TCNQ single crystals.

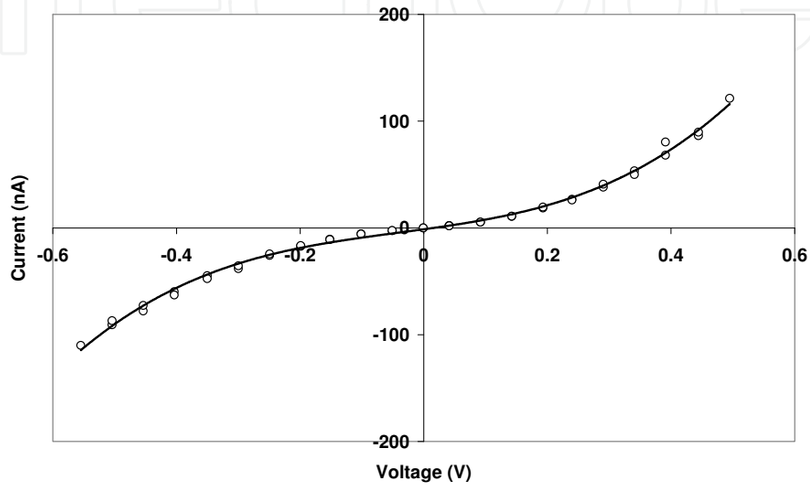


Fig. 19. I−V curve on TTF·TCNQ nanowires.

As the nanowires are not parallel to the electrodes, the conductivity value deduced from the curve is dominated by the perpendicular conductivity. The conductivity found is about 1 S cm^{-1}, a value which is comparable to the conductivity value along the *a* axis on single crystals (recall that the conductivity value along the *b* axis is about 600 S cm^{-1}, the *b* axis being the molecular stacking axis). For TTF·TCNQ nanowires (prepared by the two-phase technique, Liu et al., 2007), in which the contacts are made on the side wall of a nanowire, the carriers need to overcome the energy barrier between TTF·TCNQ columns for current transport. So, the conductance of the nanowire in this configuration is very small. However, when the electrodes make a direct contact with the TTF·TCNQ tunnelling channel, the conductance of the nanowire is much higher (increasing intensity by a factor of about 4000).

5. Conclusion and perspective work

The interest of using molecule-based charge-transfer compounds for future electronic device applications is well established. Organic field effect transistors (OFETs) in which materials for source and drain electrodes are made of a TTF-based conductor, are currently studied. The TTF·TCNQ complex can also been used as an active component in the fabrication of new electrodes for amperometric detection of glucose. Charge-transfer conductors are usually prepared under mild conditions whereas commonly-used metals and semiconductors are elaborated by metallurgical procedures. Moreover, slight changes in the molecular structure on either the donor or the acceptor molecule can drastically influence the physical properties.

Methods described in this chapter allow the preparation of individual nanowires, bundles of nanowires, or nanowire films. Vapour-phase techniques can lead to nanowires whose diameters are well controlled. However, the experimental set-up can be relatively sophisticated (use of ultra high vacuum, presence of an electric field) and vapour-phase techniques can not be applied to ionic precursors (non-volatile precursors). Solution-grown methods are much easy to implement and can be applied to large variety of precursors (neutral molecules, ionic species, compounds bearing a long-alkyl chain). Two-phase and dipping methods allow the formation of nanowires of TTF-based conductors exhibiting a narrow diameter distribution. Electrochemical techniques are the more promising methods. Indeed the application of a current is required to oxidize the majority of donor molecules. These electrochemical techniques require the use of a specific electrode on which the growth as nanowires can be initiated. Functionalised or nano-rough surfaces have then been developed. Nanowire films (made of randomly distributed nanowires) can be processed on a nano-rough intrinsic silicon electrode, used as an anode. Nanowire arrays (made of highly oriented nanowires) can be fabricated on electrodes functionalised by a nanoporous alumina membrane.

Individual nanowires and nanowire films have also been studied by spectroscopic methods, namely, infrared, Raman, and X-ray photoelectron spectroscopy. Such techniques have shown their potentiality in determining the amount of charge transfer between the donor and the acceptor molecule within nanowires. It has been shown that amount of charge transfer calculated on nanowires is similar to that on macroscopic single crystals.

Nanowires usually exhibit a semiconducting behaviour. However, calculated activation energies are relatively low, which is satisfactory taking into account the large number of inter-wire contacts and the presence of an imperfect interface between the nanowire and the electrode. However, a lot of work remains to be done in studying the transport properties of charge-transfer salts-based nanowires.

Finally, new synthetic challenges are offered to chemists: the preparation of nanowires, nanosticks or nanoparticles of molecule-based charge-transfer compounds embedded in a polymer matrix, dispersed in a micellar medium, or stabilized by an amphiphilic molecule. Poly(3,4-ethylenedioxythiophene), abbreviated PEDOT (Fig. 20), is a conducting polymer with small band gap allowing high optical transparency in the doped, conducting state (conductivity value of about 5×10^{-3} S cm^{-1}). To further increase the conductivity of the polymer material, it can be doped by adding a molecule-based salt, such as $(TTF)A_x$, where A stands for a monoanionic species (Cl^-, Br^-, ClO_4^-). For instance, we have recently prepared nanosticks of $(TTF)Br_{0.59}$ dispersed in a PEDOT matrix (Fig. 21). The PEDOT acts as a stabilizing agent around each $(TTF)Br_{0.59}$ nanostick and the conductivity value is increased to about 0.25 S cm^{-1} (Souque, 2011). We have also recently prepared nanoparticles of molecule-based charge-transfer salts which can, under certain conditions, organize as elongated nanostructures. For example, TTF·TCNQ nanoparticles organized in nanosticks or nanowires have recently been prepared (Souque, 2011). Acicular-shaped nanoparticles are prepared by adding a solution of TTF in a solution of TCNQ in the presence of a mixture of solvents, *i.e.*, acetonitile/ionic liquid (imidazolium salt). Moreover, nanoparticle-made nanowires are obtained by mixing TTF and TCNQ solutions in the presence of a long-chain carboxylic acid (amphiphilic molecule), used as a stabilizing agent. Changing the nature and the amount of the amphiphilic molecule allows the formation of either isolated nanowires or nanodendrites structures.

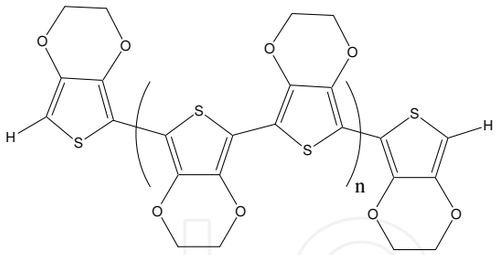


Fig. 20. Molecular formula for PEDOT.

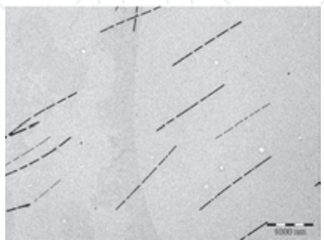


Fig. 21. Nanosticks of $TTFBr_{0.59}$ dispersed in a PEDOT matrix (bar = 1000 nm).

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