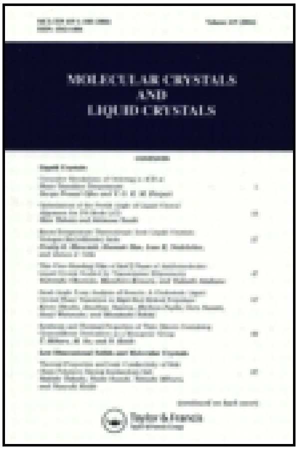

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

From molecule-based (super)conductors to thin films, nanowires and nanorings

Patrick Cassoux [a], Dominique De Caro [a], Lydie Valade [a], Hélène Casellas [a], Barbara Daffos [a] & Maria Elena Sanchez Vergara [a]

[a] Equipe Précurseurs Moléculaires et Matériaux, LCC/CNRS, 205 Route de Narbonne, Toulouse Cedex, F-31077, France

Version of record first published: 18 Oct 2010

To cite this article: Patrick Cassoux, Dominique De Caro, Lydie Valade, Hélène Casellas, Barbara Daffos & Maria Elena Sanchez Vergara (2003): From molecule-based (super)conductors to thin films, nanowires and nanorings, Molecular Crystals and Liquid Crystals, 380:1, 45-52

To link to this article: http://dx.doi.org/10.1080/713738691

Mol. Cryst. Liq. Cryst., Vol. 380, pp. 45-52
Copyright © 2002 Taylor & Francis
1058-725X/02 \$12.00 + .00
DOI: 10.1080/10587250290101351

FROM MOLECULE-BASED (SUPER)CONDUCTORS TO THIN FILMS, NANOWIRES AND NANORINGS

Patrick Cassoux, Dominique De Caro, Lydie Valade,
Hélène Casellas, Barbara Daffos
and Maria Elena Sanchez Vergara
Equipe Précurseurs Moléculaires et Matériaux, LCC/CNRS,
205 Route de Narbonne, F-31077 Toulouse Cedex, France

Thin films of (TTF)(TCNQ) (TTF = tetrathiafulvalene, TCNQ = tetracyanoacyanoquinodimethane) are deposited on Si (001), KBr, and stainless steel conversion coatings (SSCC) using chemical vapor deposition. These films are characterized by IR, XRD, conductivity measurements, and SEM. Conducting nanowires and nanorings of (TTF)(TCNQ) and nanowires of $(TTF)[Ni(dmit)_2]_2$ *(typically, 20 nm × 20 μm) are prepared by successively dipping SSCC in acetonitrile solutions of TTF and TCNQ, or* $(TTF)_3(BF_4)$ *and* $(Bu_4N)[Ni(dmit)_2]$*, respectively. These nanowires are observed by SEM. The (TTF)(TCNQ) nanowires are also observed by TEM and AFM and characterized by current-voltage measurements. Nanowires of* $(TTF)[Ni(dmit)_2]_2$ *are also obtained on silicon conversion coatings (SiCC) and characterized by Raman spectroscopy.*

Keywords: thin films; nanowires; nanorings; chemical vapor deposition; conversion coatings; molecular conductors

INTRODUCTION

A tremendous effort has been devoted in the past two decades to the preparation and study of molecule-based conductors, superconductors. This is what this symposium on "Twenty Years of Organic Superconductors: New Materials – New Insights" within this Pacifichem 2000 conference is all about. A number of contributions are presented at this symposium and a number of reviews and books have appeared on this subject [1–5].

This work implies a close collaboration with L. Aries (CIRIMAT/UPS/CNRS, Toulouse) concerning the conversion coatings, with T. Ondarçuhu and C. Joachim (CEMES/CNRS, Toulouse) for AFM studies, and A. Zwick and R. Carles (LPS/UPS/CNRS, Toulouse) for Raman studies. This work is partly supported by the COST D14 program of the EC and the NOI program of CNRS.

On the other hand, increasing interest is devoted to the possible use of molecule-based materials for future electronic device applications [6,7]. Research work has been recently directed to the formation and study of thin films of these systems. For example, the use of chemical vapor deposition (CVD) to grow thin films of molecular conductors such as (TTF)(TCNQ) (TTF = tetrathiafulvalene), TCNQ = tetracyanoquinodimethane) has been reported [8,9].

It should be recalled here that (TTF)(TCNQ) was the first reported organic metal [10]. Following this discovery, a large number of charge-transfer conducting and superconducting organic compounds were prepared and studied [1–5]. The first superconductor derived from a metal-organic complex, (TTF)[Ni(dmit)$_2$]$_2$ was characterized in 1984 [11].

The preparation of stainless steel conversion coatings (SSCC) has been recently reported [12]. The interest in using these coatings rests upon their characteristic fractal-like morphology, which induces high adsorption properties. These properties were exploited for improving the adherence of further coatings [13], or for fixing organic dyes [14].

We will review here on the preparation of thin films, nanowires and nanorings of (TTF)(TCNQ) deposited on SSCC using CVD or a dipping process. The designation "nanowire" is mainly used for long, conjugated macromolecules such as for example multi or single-wall carbon nanotubes. The designation "molecular wire" usually refers to conjugated oligomer-like oligothiophene and ladder-like molecules specially designed for tunneling transport studies. This contribution also reports on the use of SSCC and silicon conversion coatings (SiCC) for growing nanowires of (TTF)[Ni(dmit)$_2$]$_2$.

THE FABRICATION OF SSCC AND SiCC

The SSCC substrates are prepared from austenitic stainless steel 1 mm thick sheets[15]. These sheets undergo a surface treatment, which quickens the rate of formation of the SSCC[16]. This treatment may consist in an electrochemical cathodic activation (−1.5 V/SCE) of the surface with H_2 release in a standard three-electrode cell for 30 sec. Alternately, the sheets may undergo a chemical pre-treatment consisting in dipping them in a water/sulfuric acid (50% vol.) bath for 5 sec. The substrates are then dipped in a water/sulfuric acid bath (0.2% vol.) containing sodium thiosulfate (1.5 g L^{-1}) at 57°C for 20 min, whereupon the conversion coatings are formed on the surface. They are finally washed with water and dried before use.

The SSCC show a complex composition characterized by a continuous variation of the components concentration and oxidation states of the

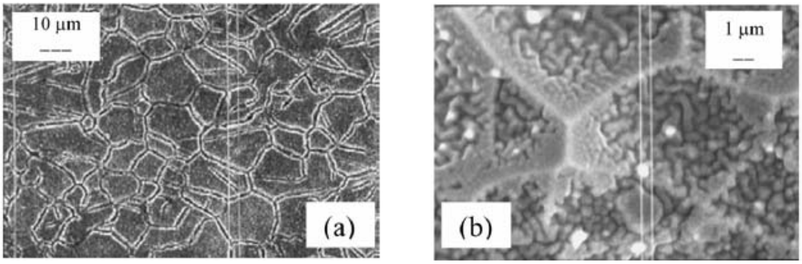

FIGURE 1 SEM images of (a) a stainless steel conversion coating (SSCC) and (b) a silicon conversion coating (SiCC).

metal atoms when going from the outer surface down the interface with the steel. The metal oxides are essentially magnetites (Fe_3O_4) and maghemites (Fe_2O_3) more or less substituted by the component elements of the steel. Scanning electron micrographs (Figure 1a) show that the SSCC surface is composed of grains and cavities separating the grains. The grains are circa 10 μm wide. Inside a grain, smaller grains and cavities are observed, which awards a micro-rough nano-structured fractal-like morphology to the surface. Chemical treatment results in SSCCs growing faster and showing a higher roughness compared to those obtained after electrochemical activation, but the same porosity is observed in both cases[16].

Conversion coatings on silicon (SiCC) have been also recently obtained by a similar procedure[16]. After a standard surface cleaning process, (100) oriented silicon wafers are dipped in a water/sulfuric acid bath (5% vol.) containing sodium thiosulfate ($3\,g\,L^{-1}$) and HF ($2\,mol\,L^{-1}$) at 60°C for 60 min, whereupon the conversion coatings are formed on the non-polished surface of the wafers. Pre-treatment by electrochemical activation is not recommended as it prevents SiCC from growing because of surface passivation. The SiCCs (Figure 1b) show a micro-rough structure uniformly deposited onto the honeycomb network of the non-polished surface of the wafers.

PREPARATION OF THIN FILMS OF (TTF)(TCNQ) ON SSCC

Thin films of (TTF)(TCNQ) are deposited onto SSCC substrates from commercial TTF and TCNQ, using a conventional hot-wall CVD apparatus[9]. The carrier lines and mixing zone are heated at 170°C and the reactor zone at 75°C. TTF and TCNQ are vaporized at 78 and 145°C, respectively, at low pressures (134 Pa), and transported by He carrier gas (flow rate 50 and 70 sccm, respectively) to the deposition zone. The deposition time is 3 h. Simultaneously to SSCC substrates, Si (001) wafers

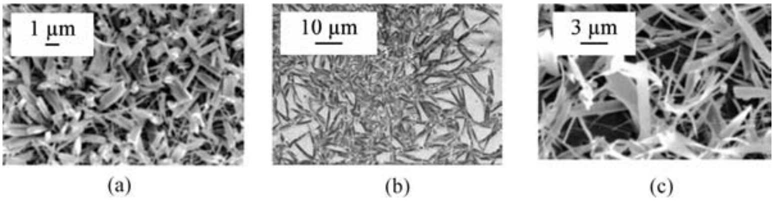

FIGURE 2 SEM images of (TTF)(TCNQ) films grown on (a) SSCC, (b) KBr pellets, and (c) Si (001).

and KBr compressed pellets were used to allow the characterization of the deposits by X-ray diffraction and infrared spectroscopy.

A band attributed to the CN stretching of TCNQ is observed at $2203\,\mathrm{cm}^{-1}$ in the IR spectrum of the films grown on KBr. This vibration frequency, which is characteristic of the formal charge of TCNQ[17], corresponds to a charge transfer from TTF to TCNQ of ≈ 0.57 (compare to 0.59 observed on (TTF)(TCNQ) single crystals)[1]. The X-ray diffraction pattern recorded on the film deposited on Si (001), shows only the (002), (004), and (008) lines of the pattern of polycrystalline (TTF)(TCNQ). This indicates a preferential orientation of the films i.e., *ab* plane parallel to the substrate surface, as previously observed on alkali halides substrates [8]. The room-temperature conductivity of the films deposited on Si (001) and on KBr is in the same range, $16\,\mathrm{S\,cm}^{-1}$ and $3\,\mathrm{S\,cm}^{-1}$, respectively. These values, which may be considered as resulting from a random contribution of the conductivities along the *a* and *b* axes of a single crystal (600 and $1\,\mathrm{S\,cm}^{-1}$, respectively), are consistent with the preferential orientation mentioned above. These values and the semiconductive thermal behavior ($E_a = 0.014\,\mathrm{eV}$) are similar to those previously reported [8].

The films of (TTF)(TCNQ) grown on SSCC uniformly cover the substrate surface (Figure 2a) The films are homogeneous and consist of platelets ($3\,\mu\mathrm{m} \times 1\,\mu\mathrm{m}$) and needles (width $= 0.3\,\mu\mathrm{m}$). The thickness of the films is estimated at $1\,\mu\mathrm{m}$. On KBr pellets, the formation of platelets is favored (Figure 2b), and on Si substrates, platelets and needles are present (Figure 2c). For the same deposition time, the coverage of the surface is much more efficient on SSCC than on Si and KBr substrates.

PREPARATION OF NANOWIRES AND NANORINGS OF (TTF)(TCNQ) ON SSCC

The adsorption properties of SSCC substrates were also further exploited for depositing (TTF)(TCNQ) by using a dipping process. Successive dipping of SSCC substrates in TTF and TCNQ solutions did not lead to the

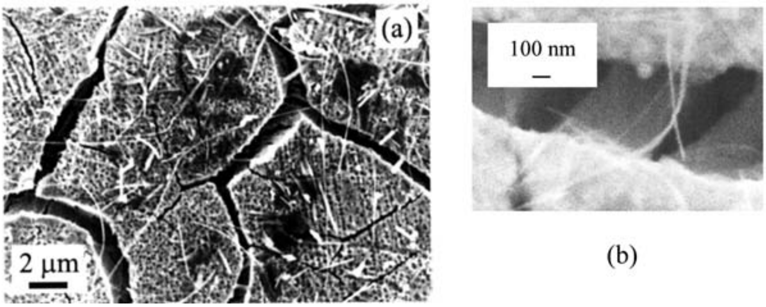

FIGURE 3 SEM images of a SCCC surface with (TTF)(TCNQ) nanowires.

formation of a (TTF)(TCNQ) thin films, but to the growth of nanowires (Figure 3a). These nanowires are anchored on the SSCC surface, and some of them bridge grains above the cavities of the conversion coating (Figure 3b).

The nanowires are collected using a micropipette moving inside the cavities between the grains and transferred onto a carbon-coated grid for Transmission Electron Microscopy (TEM) studies (Figure 4a and 4b), or onto a silica surface for Atomic Force Microscopy (AFM) observations (Figure 4c). The wires actually are ribbons having an average thickness of 20 nm and a width between 20 nm and 200 nm. These ribbons can be 20 μm long. Occasionally, nanorings were also observed.

The current-voltage characteristics were measured for a bundle of nanowires deposited on a metal-insulator-metal nanojunction. For technical

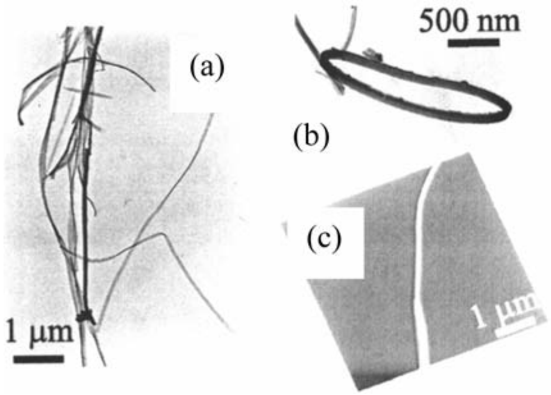

FIGURE 4 TEM image of a bundle of (a) nanowires and (b) a nanoring, and (c) 3D representation of a tapping mode AFM image of a nanowire.

reasons, the bundles could not be positioned parallel to the electrodes, and the value of the conductivity, $\approx 1\,\mathrm{S\,cm^{-1}}$, inferred from the curve is dominated by the perpendicular conductivity. This value is comparable to that determined by STM along the ***b*** axis of single crystals of (TTF)(TCNQ) deposited on an alkali halide [18].

PREPARATION OF NANOWIRES OF (TTF)[NI(DMIT)$_2$]$_2$ ON SSCC AND SICC

The results described above proved the feasibility of the deposit of nanowires of (TTF)(TCNQ) onto conversion coatings. Extension to other molecule-based conductors, such as for example (TTF)[Ni(dmit)$_2$]$_2$, could be then envisioned. On the other hand, stainless steel-based substrates are not most appropriate for electronic device applications, and it seemed interesting to evaluate the use of silicon-based substrates.

Following a similar procedure as that employed for (TTF)(TCNQ), (TTF)[Ni(dmit)$_2$]$_2$ nanowires are grown by dipping SCCC substrates successively in acetonitrile solutions of (TTF)$_3$(BF$_4$)$_2$ ($2.04\,\mathrm{g\,L^{-1}}$) and (Bu$_4$N[Ni(dmit)$_2$]$_2$ ($3.54\,\mathrm{g.L^{-1}}$)[16]. A high concentration of tangled up nanowires is observed in places on the SCCC. These nanowires have a diameter of 50–150 nm (Figure 5a). Likewise, tangled up (TTF)[Ni(dmit)$_2$]$_2$ nanowires with similar dimensions are grown by dipping SiCC substrates successively in the same starting solutions as above (Figure 5b). In this case, the nanowires are more uniformly scattered on the surface.

Raman spectroscopy studies on the (TTF)[Ni(dmit)$_2$]$_2$ nanowires were carried out using a Raman microprobe. The spectrum obtained when focusing the laser beam on bundles of nanowires is shown in Figure 6. The eight most intense observed bands could be assigned to the A_g mode vibrations of the D_{2h} Ni(dmit)$_2$ moiety by comparison with previously studied Ni(dmit)$_2$]$_2$-based compounds[19]. This spectrum is similar (though better

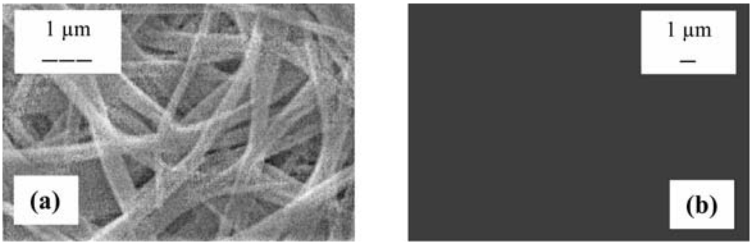

FIGURE 5 SEM images of (TTF)[Ni(dmit)$_2$]$_2$ nanowires grown on (a) SSCC and (b) SiCC.

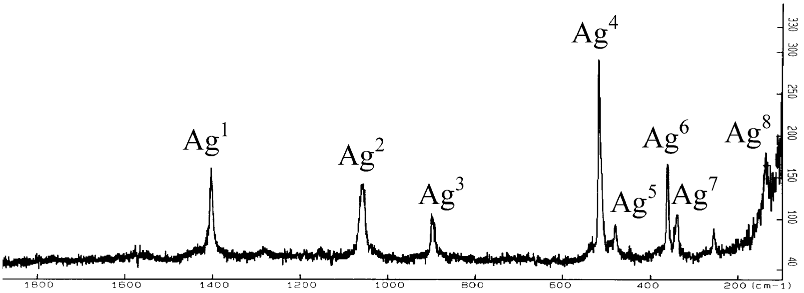

FIGURE 6 The Raman spectrum of (TTF)[Ni(dmit)$_2$]$_2$ nanowires.

resolved) to that of a polycrystalline sample of (TTF)[Ni(dmit)$_2$]$_2$ independently prepared in solution. Surprisingly however, in both spectra the C=C and C-S stretching vibration of the TTF moiety are not observed, possibly indicating a coupling of the stretching vibrations of both TTF and Ni(dmit)$_2$ moieties.

CONCLUSION

Because of the high adsorption properties of SSCC (previously described) and SiCC (reported here for the first time), good quality thin films and nanowires of the (TTF)(TCNQ) and (TTF)[Ni(dmit)$_2$]$_2$ molecule-based conductors can be obtained when using these substrates. Nevertheless, much work remains to be done for a better characterization of these fascinating, but difficult to deal with, objects, and for their possible use in the making of electronic devices.

REFERENCES

[1] Ferraro, J. R., & Williams, J. M. (1987). *Introduction to synthetic electrical conductors*, Academic Press, San Diego, CA.

[2] Williams, J. M., Ferraro, J. R., Thorn, R. J., Carlson, K. D., Geiser, U., Wang, H. H., Kini, A. M., & Whangbo, M. H. (1992). *Organic superconductors (Including Fullerenes)*, Prentice Hall, Englewood Cliffs, N. J.

[3] Cassoux, P., & Valade, L. (1996). In D. W. Bruce, & D. O'Hare (Eds.), *Inorganic Materials*, (2nd Ed.) (1–63). John Wiley & Sons, London.

[4] Cassoux, P., & Miller, J. S. (1997). In L. V. Interrante, & M. Hampden-Smith (Eds.), *Chemistry of Advanced Materials: An Overview*, (19–72). VCH Publishers.

[5] Kobayashi, H., Kobayashi, A., & Cassoux, P. (2000). *Chem. Soc. Rev.*, *29*, 325.

[6] Carter, F. L., Siatkowski, R. E., & Wohltjen, H. (1988). *Molecular Electronic Devices*, North Holland, New York.

[7] Garnier, F., Horrowitz, G., Peng, X., & Fichou, D. (1990). *Adv. Mat., 2*, 592–4.

[8] Caro, J., Garelik, S., & Figueras, A. (1996). ***Chem. Vap. Deposition***, ***2***, 251; Figueras, A., Garelik, S., Caro, J., Cifre, J., Veciana, J., Rovira, C., Ribera, E., Canadell, E., Seffar, A. (1996). ***J. Cryst. Growth***, ***166***, 798.

[9] de Caro, D., Sakah, J., Basso-Bert, M., Faulmann, C., Legros, J.-P., Ondarçuhu, T., Joachim, C., Aries, L., Valade, L., & Cassoux, P. ***C. R. Acad. Sci. (Paris) Ser., 2***, in the press.

[10] Epstein, A. J., Etemad, S., Garito, A. F., & Heeger, A. J. (1972). ***Phys. Rev. B***, ***5***, 952; Coleman, L. B., Cohen, M. J., Sandman, D. J., Yamagishi, F. G., Garito, A. F., & Ferraris, A. J. (1973). ***Solid State Commun.***, ***12***, 1125.

[11] Brossard, L., Ribault, M., Bousseau, M., Valade, L., & Cassoux, P. (1986). ***C. R. Acad. Sci. (Paris) Ser., 2***, 302, 205; Brossard, L., Ribault, M., Valade, L., & Cassoux, P. (1986). ***Physica B&C (Amsterdam)***, ***143***, 378.

[12] Aries, L., Roy, J., Bouissou, T., & Sempere, R. (1991). ***Mat. Sci. Technol.***, ***7***, 24.

[13] Aries, L. (1994). ***J. Appl. Electrochem.***, ***24***, 554.

[14] Aries, L., & Traverse, J.-P. (1987). European Patent 87 4000 318.

[15] Austenitic Steel (304L, bright) is a stainless steel with a low carbon content (composition (%): C, 0.03; Al, 0.1; Cr, 17.4; Cu, 0.135; Mn, 1.78; Mo, 0.15; Ni, 9.41; P, 0.025; S, 0.04; Si, 0.45; V, 0.075; Fe, 70.495).

[16] Daffos, B., Diplome d'Etudes Supérieures d'Université, Toulouse, October 24, 2000. L. Aries, B. Daffos, H. Casellas unpublished results.

[17] Chappell, J. S., Bloch, A. N., Bryden, W. A., Maxfield, M., Poelher, T. O., & Cowan, D. O. (1981). ***J. Amer. Chem. Soc.***, ***103***, 2442.

[18] Ara-Kato, N., Yase, K., Shigekawa, H., Yoshimura, M., & Kawasu, A. (1995). ***Synth. Met.***, ***70***, 1245.

[19] Pokhodnya, K. I., Faulmann, C., Malfant, I., Andreu-Solano, R., Cassoux, P., Mlayah, A., Smirnov, D., & Leotin, J. (1999). ***Synth. Met.***, ***103***, 2016.