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Nanoparticles of tetrathiafulvalene chloride derivatives grown in the presence of amphiphilic molecules

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ABSTRACT

The work described in this paper is directed towards the electrosynthesis of $\text{TTFCl}_{0.77}$ as spherical nanoparticles by using amphiphilic molecules, behaving as growth-controlling agents. The morphology and the size distribution of the particles were analyzed using transmission electron microscopy and the resulting powders were characterized by infrared and Raman spectroscopy along with X-ray diffraction. In the presence of dodecylamine, electron micrographs evidenced spherical and relatively well-dispersed nanoparticles exhibiting a mean diameter of about 10 nm. However, in the presence of *N*-octylfurfurylimine, a mixture of nanoparticles and sticks were formed. The best results in terms of smallness of particles size and narrowness size distribution were obtained in the presence of 1-octanamine, *N*-(2-thienylmethylene). Spherical nanoparticles exhibiting sizes in the 4–12 nm range with an average size of about 8 nm were observed. The nanoparticles powder exhibited a room temperature conductivity of about 0.01 S.cm^{-1} .

1. Introduction

Mixed valence halide salts of TTF (TTF: tetrathiafulvalene, Fig. 1a) is a famous class of molecular materials. They have attracted increasing attention due to their interesting optical, electrical and thermoelectric properties [1–3]. Exhibiting a simple one dimensional structure [4], TTF halide salts are generally produced as single crystals displaying a needle like morphology. Nanomaterials of those salts have gained increasing interest due to their potential application in nanoscale electronic devices. In the last twenty years, several procedures describing the preparation of TTF halide salts as nano objects have been reported [5–8]. For instance, Ren et al. described the synthesis of $\text{TTFCl}_{0.72}$ nanowires using carbon nanotube electrodes [5]. Moreover, Naka et al. developed an interesting method to self organize $\text{TTFCl}_{0.78}$ nanowires and metallic gold [6]. Furthermore, nanocrystals of TTF bromide TTFBr_x ($x = 0.74–0.79$) were grown as needles on platinum nanoparticles by electrochemical oxidation [7]. Finally, $\text{TTFBr}_{0.59}$ nanosticks were synthesized in the presence of PEDOT (poly(3,4 ethylenedioxythiophene)) behaving as a stabilizing agent [8]. However, despite this variety of synthetic methods aiming at nano structured TTF halide systems, spherical nanoparticles are still very rare [8]. In reality,

spherical nanoparticles are considered as a challenging form because of the one dimensional structure of these materials. Nevertheless, spherical nanoparticles of $\text{TTFCl}_{0.77}$ have been generated by employing a long alkyl chains quaternary ammonium salt $[(\text{CH}_3)_n\text{C}_n\text{H}_{2n+1}\text{N}]\text{Cl}$, behaving as a stabilizing agent [9]. However, these nanoparticles showed a fairly inhomogeneous size distribution, ranging from 50 to 150 nm. In pursuit of reaching nanoparticles exhibiting narrower size distributions and mean diameters less than 20 nm, amphiphilic molecules have been used in the present work. The amphiphilic molecules evaluated include one long alkyl chain amine, i.e., dodecylamine and two long alkyl chain imines, i.e., *N* octylfurfurylimine (Fig. 1b) or 1 octanamine, *N* (2 thienylmethylene) (Fig. 1c).

2. Materials and methods

2.1. Synthesis of $\text{TTFCl}_{0.77}$ nanoparticles

The mixed valence TTF chloride salts are usually produced by the electrocrystallization technique; as it ensures the control of the oxidation degree of TTF along with the generation of high purity crystals [2]. The preparation of the nanoparticles powders was carried out following

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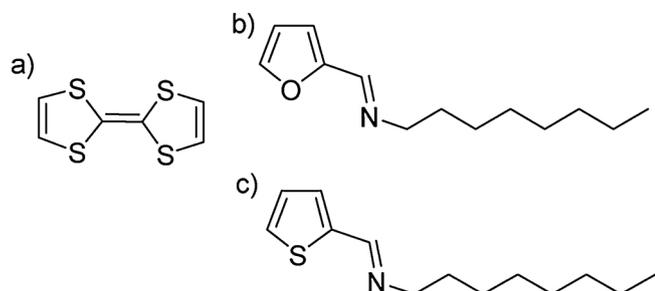


Fig. 1. Molecular formulas for TTF (a), N-octylfurfurylimine (b), and 1-octanamine,N-(2-thienylmethylene) (c).

the procedure described in reference [9]. The tetrabutylammonium chloride salt $[(n\text{C}_4\text{H}_9)_4\text{N}]\text{Cl}$ was used to provide the chloride anion and to serve as an electrolyte support, whereas the amphiphilic molecules were added to the reaction medium, in an attempt to control the growth of $\text{TTFCl}_{0.77}$ as nanoparticles.

The electrochemical syntheses were performed under an argon atmosphere at room temperature using a potentiostat AMETEK SI model 1480/A. The syntheses were carried out in a H shaped electrocrystallization cell, consisting of two compartments separated by a glass frit in the H cross piece, and equipped with two platinum wire

electrodes. Nanoparticles of $\text{TTFCl}_{0.77}$ were made as follows: 50 mg of TTF (0.245 mmol), 270 mg of the supporting electrolyte $[(n\text{C}_4\text{H}_9)_4\text{N}]\text{Cl}$ and 10 mL of distilled THF were placed into the anodic compartment. Into the cathodic compartment, it was placed the same quantity of $[(n\text{C}_4\text{H}_9)_4\text{N}]\text{Cl}$ and 10 mL of THF. The following amphiphilic molecules were added to the anodic compartment: dodecylamine (136 mg, 0.735 mmol), N octylfurfurylimine (152 mg, 0.734 mmol), 1 octanamine,N (2 thienylmethylene) (167 mg, 0.748 mmol). For duration of 3 days, nanoparticles syntheses were carried out under galvanostatic conditions ($\sim 300\ \mu\text{A}\cdot\text{cm}^2$), and vigorous stirring with a magnetic stirrer. The resulting black solid was collected by filtration from the anodic compartment, rinsed with $2 \times 5\ \text{mL}$ THF, and then dried under vacuum during 10 h (yield: 40%). The black powder thus formed was stable in air.

2.2. Characterization techniques

The morphology and the size distribution of the $\text{TTFCl}_{0.77}$ nanoparticles were investigated by transmission electron microscopy. The TEM micrographs were acquired with the electron microscope JEOL, model: JEM 1011 working at an accelerating voltage of 100 kV. The TEM specimen was prepared as follows: 0.5 mg of the powder was dispersed in 2 mL diethyl ether; the content was then stirred for one minute; afterwards droplets of the suspension were deposited onto

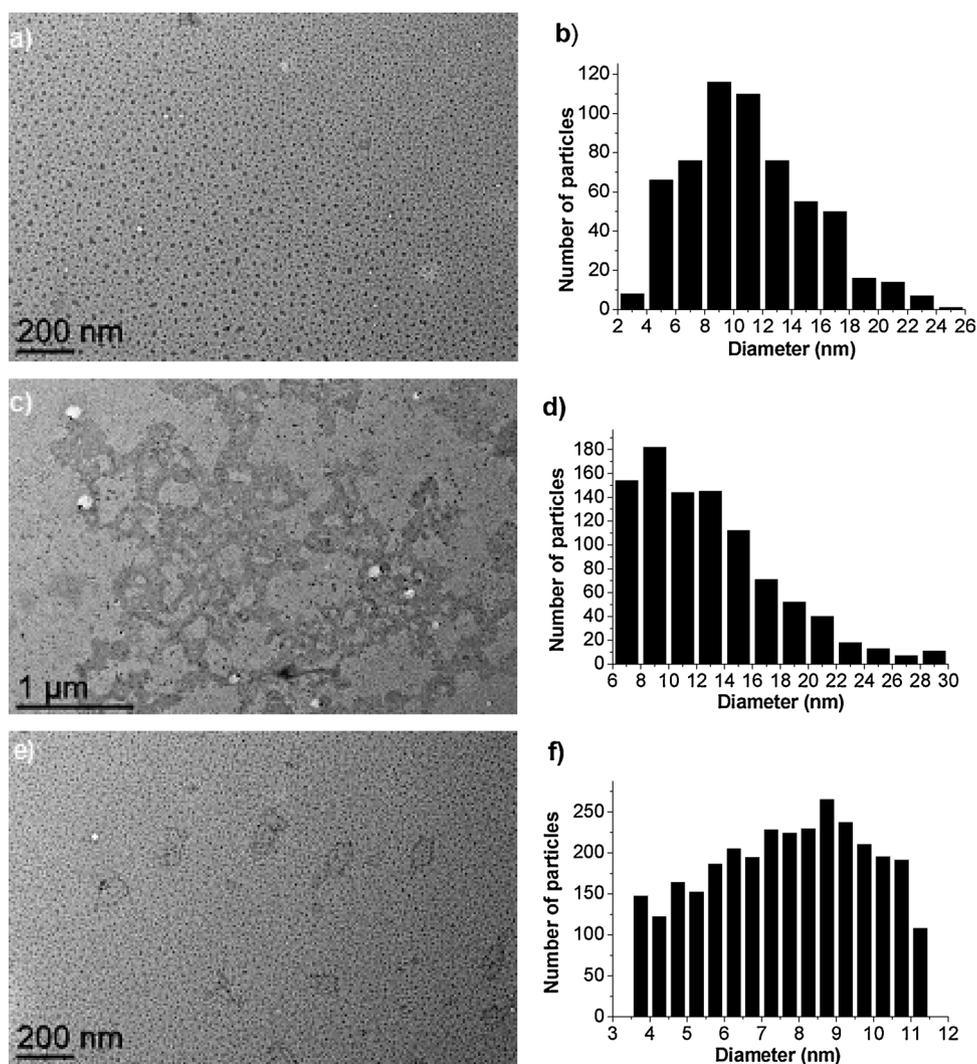


Fig. 2. Electron micrographs and histograms of particle size for $\text{TTFCl}_{0.77}$ grown in the presence of 3 M eq. of dodecylamine (a, b), N-octylfurfurylimine (c, d), and 1-octanamine,N-(2-thienylmethylene) (e, f).

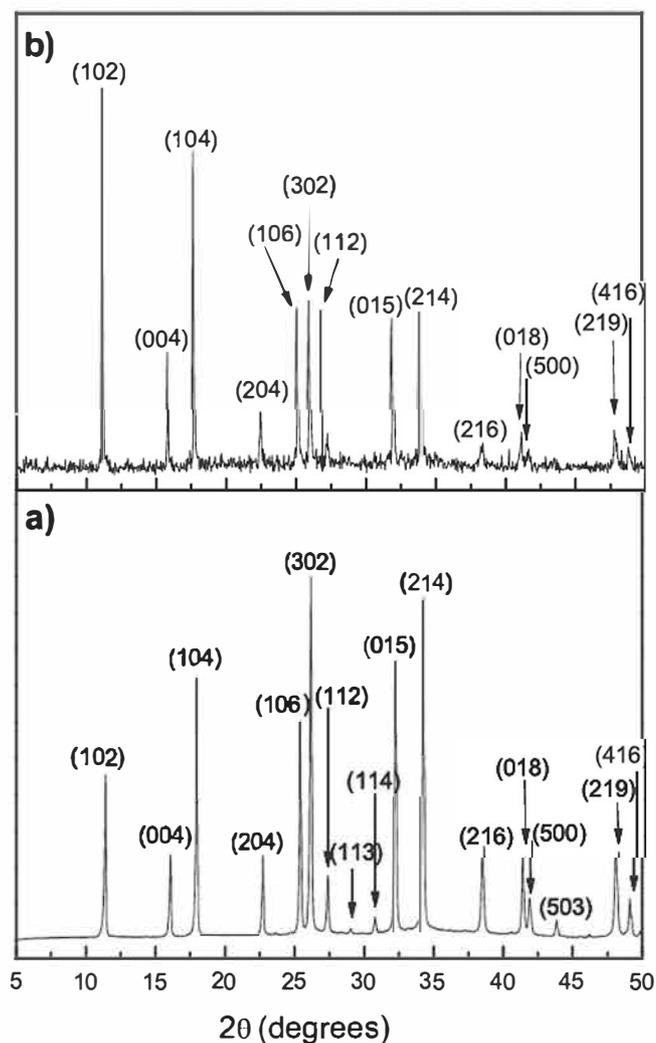


Fig. 3. XRD patterns for $\text{TTFCl}_{0.77}$ nanoparticles prepared in the presence of (a) $[(\text{CH}_3)(n\text{-C}_8\text{H}_{17})_3\text{N}]\text{Cl}$ [9], and (b) 1-octanamine,*N*-(2-thienylmethylene).

carbon supported copper grids; ultimately, the diethyl ether was evaporated. Infrared spectra (in KBr matrix) were acquired using a Perkin Elmer Spectrum GX spectrophotometer. Raman analysis was performed at 80 K by employing a DILOR XY micro Raman (laser wavelength: 785 nm). X ray data were collected on a Siemens D5000 diffractometer in the Bragg Brentano geometry (θ 2 θ mode) using monochromatized $\text{Cu K}\alpha$ (1.54056 Å). The electrical conductivity at room temperature was measured by the two probe technique, using a digital multimeter KEITHLEY 2001.

3. Results and discussion

3.1. TEM analysis

The galvanostatic oxidation of TTF has been performed in the presence of dodecylamine, *N* octylfurfurylimine, or 1 octanamine,*N* (2 thienylmethylene) behaving as growth controlling agents. After an electrolysis duration of three days, a shiny black powder was collected from the anodic compartment.

The results obtained by TEM analysis along with the size histograms have been shown in Fig. 2. TEM micrographs of the sample elaborated in the presence of 3 M eq. of dodecylamine vs. TTF (Fig. 2a) evidenced the presence of relatively well dispersed spherical nanoparticles with diameters ranging from 2 to 24 nm (Fig. 2b). This result was quite satisfactory in terms of smallness of particle sizes. It should be noted that,

the particles thus prepared exhibited diameters much smaller than those for the molecular superconductor $(\text{TMTSF})_2\text{ClO}_4$ (40–60 nm) elaborated in the presence of 3 M eq. of dodecylamine vs. TMTSF [10]. Exploring other electro-synthesis condition based on reducing the amount of dodecylamine, i.e. 1 M eq. of dodecylamine vs. TTF, it was found that the dispersion state of the particles was altered, giving rise to highly agglomerated nanoparticles. Hence, it can be stated that the dispersion state of the particles could be improved with the use of dodecylamine in an appropriate concentration. On the other hand, the use of 3 M eq. of *N* octylfurfurylimine vs. TTF led to the genesis of a black powder consisting of a mixture of dispersed nanoparticles (6–30 nm in diameter, Fig. 2c d) and sticks (length: 0.1–0.4 μm). It is worth mentioning that the amphiphilic molecule *N* octylfurfurylimine, employed in those conditions, did not act as an efficient growth controlling agent as it did for the metallo-organic based conductor $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$ [11]. In this latter case, the use of the same amount of *N* octylfurfurylimine vs. TTF allowed access to only spherical and well dispersed nanoparticles of $\text{TTF}[\text{Ni}(\text{dmit})_2]_2$, exhibiting a mean diameter of about 12 nm [11]. Samples prepared by using either lower or higher amount of *N* octylfurfurylimine, such as 1 or 10 M eq. vs. TTF, showed various morphologies including sticks and irregularly shaped microcrystals. In fact, the growth controlling process for *N* octylfurfurylimine seemed analogous to that for imidazolium salts used to prepare $\text{TTF}\text{-TCNQ}$ nanoparticles [12]. In other words, when the growth controlling agent was used in either small or large quantities compared to TTF, sticks were favored, while nanoparticles were preferred for intermediate amounts of the imidazolium salt [12]. In contrast, the best results were obtained in the presence of 1 octanamine,*N* (2 thienylmethylene) by using 3 M eq. vs. TTF. TEM images showed well dispersed spherical nanoparticles exhibiting diameters as small as 4 to 12 nm with an average size of 8 nm (Fig. 2e f). This result was considered as the most satisfactory owing to the fact that the particles showed the smallest sizes ever published for the TTF halide salts. The long alkyl chain amphiphilic molecule, 1 octanamine,*N* (2 thienylmethylene), authorized access to small and dispersed spherical nanoparticles most likely via an efficient π stacking with cycles of TTF and effective S...S van der Waals interactions between the sulfur atoms of the 1 octanamine,*N* (2 thienylmethylene) and those of the TTF cycles.

3.2. X Ray diffraction

The X ray diffraction patterns for samples prepared in the presence of dodecylamine, *N* octylfurfurylimine and 1 octanamine,*N* (2 thienylmethylene) were almost identical. Only the X ray diffraction pattern of the powder obtained using 1 octanamine,*N* (2 thienylmethylene) has been illustrated in Fig. 3b, as this amphiphilic molecule allowed the preparation of the smallest nanoparticles. Diffraction peaks depicted in Fig. 3b were in excellent agreement with those related to $\text{TTFCl}_{0.77}$ nanoparticles obtained using $[(\text{CH}_3)(n\text{-C}_8\text{H}_{17})_3\text{N}]\text{Cl}$ as a growth controlling agent (Fig. 3a) [9]. Hence, XRD patterns confirmed unambiguously that the phase which has been prepared with the aid of long alkyl chains amphiphilic molecules is the mixed valence compound $\text{TTFCl}_{0.77}$.

3.3. Infrared and Raman spectroscopy

Whatever the nature of the amphiphilic molecule used, infrared and Raman spectra were very similar. Those for the nanopowder prepared in the presence of 1 octanamine,*N* (2 thienylmethylene) were shown on Figs. 4 and 5, and the assignments of the corresponding signals were registered in Tables 1 and 2. Both spectra corroborated the presence of the TTF moiety within the nanoparticle powders. In the region above 3000 cm^{-1} , infrared spectrum revealed two absorptions at 3056 (ν_{2u}) and 3078 (ν_{1u}) cm^{-1} , which were ascribed to $\text{Csp}^2\text{-H}$ stretching vibrations. Fifth further TTF absorptions available at 1237 (ν_{2u}), 1072 (ν_{1u}), 829 (ν_{1u}), 817 (ν_{2u}), and 453 (ν_{1u}) cm^{-1}

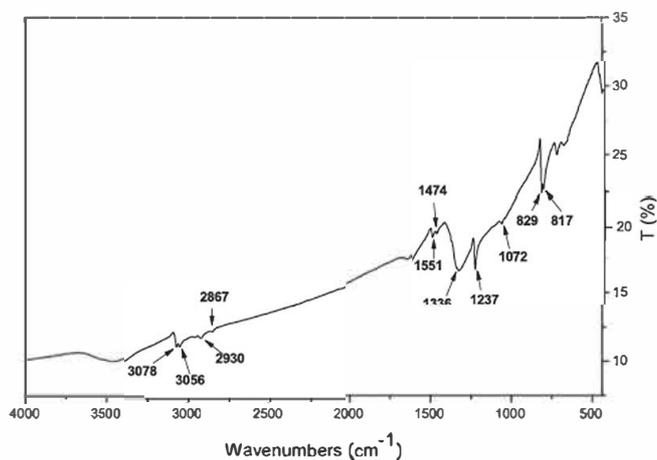


Fig. 4. Infrared spectrum for TTFCl_{0.77} nanoparticles prepared in the presence of 1-octanamine,N-(2-thienylmethylene).

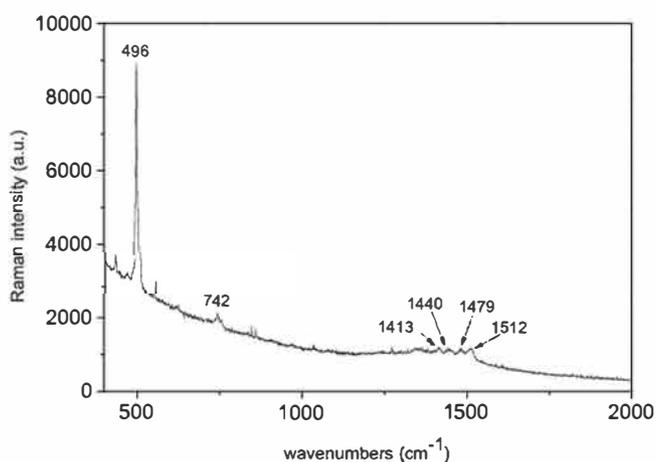


Fig. 5. Raman spectrum for TTFCl_{0.77} nanoparticles prepared in the presence of 1-octanamine,N-(2-thienylmethylene).

Table 1

Assignments of infrared signals of TTFCl_{0.77} nanoparticles prepared in the presence of 1-octanamine,N-(2-thienylmethylene).

ν (cm ⁻¹)	Attribution
3056	b _{2u} ν_{22} (ν_C H)
3078	b _{1u} ν_{13} (ν_C H)
1551	b _{1u} ν_{14} (ν_C C)
1237	b _{2u} ν_{23}
1072	b _{1u} ν_{15}
829	b _{1u} ν_{16} (ν_C S)
817	b _{2u} ν_{25}
453	b _{1u} ν_{18}

Table 2

Assignments of Raman signals for TTFCl_{0.77} nanoparticles prepared in the presence of 1-octanamine,N-(2-thienylmethylene).

ν (cm ⁻¹)	ν (cm ⁻¹) in Ref. [9]	Assignment according to [13]
496	495	a _g ν_6 (ν_C S)
742	755	a _g ν_5
1440	1447	a _g ν_3
1479	1484	a _g 3 \times ν_6
1512	1514	a _g ν_2 (ν_C C)

seemed analogous to those recorded for TTFCl_{0.77} nanoparticles grown in the presence of [(CH₃)_n(C₈H₁₇)₃N]Cl [9]. Besides, infrared spectrum revealed the presence of traces of the long alkyl chain imine in the final compound. Signals available at 2867 2930 cm⁻¹ and 1474 cm⁻¹ were attributed to the C-H stretching modes and the CH₂ bending mode, respectively. Comparing the intensities of the Csp³ H stretching vibrations of the alkyl chains of 1 octanamine,N (2 thienylmethylene) (at 2867 and 2930 cm⁻¹) and the Csp² H stretching vibrations related to TTF in TTFCl_{0.77} powder (at 3056 and 3078 cm⁻¹), it was noticeable that the former vibrations had intensities lower than the latter, which indicated that the amphiphilic molecule might wrap the TTFCl_{0.77} particle as a very thin shell.

The presence of the mixed valence salt TTFCl_{0.77} in the nanoparticles powder was equally confirmed by Raman spectroscopy (Fig. 5, Table 2). Signals located at 496 (ν_C S, a_g ν_6), 742 (a_g ν_5), 1440 (a_g ν_3), 1479 (a_g 3 \times ν_6), and 1512 (ν_C C, a_g ν_2) cm⁻¹ were attributed according to reference [13] and were similar to those for TTFCl_{0.77} in reference [9].

3.4. Conductivity

The electrical conductivity was assessed, at room temperature, on pellets obtained by compression of the TTFCl_{0.77} nanopowder. Regardless of the nature of the amphiphilic molecule employed, as a growth controlling agent, the values obtained were of about 0.01 S. cm⁻¹. These conductivity measurements were deemed less lower than those reported for the TTFCl_{0.65-0.72} microcrystalline powders (about 0.6 S. cm⁻¹) [14]. It was worth pointing out that, powders made of TTF TCNQ nanoparticles, stabilized by the amphiphilic molecule octylamine, exhibited conductivity values lower than those of the microcrystalline TTF TCNQ powders, formed in absence of any stabilizer [15]. The former powders exhibited electrical conductivities in the 0.01 0.1 S. cm⁻¹ range, while the latter afford values of about 10 S. cm⁻¹ [15]. Note that, the octylamine affected slightly the overall conductivity, which mainly originated from the TTF TCNQ particles, the traces of octylamine remained at the particles surface besides to the boundaries between them. In that respect, our slightly lower conductivity value might evidence that the particles were made of a TTFCl_{0.77} core covered by the amphiphilic molecule, presumably as a thin shell at the particle surface (as previously evidenced by infrared spectroscopy), thus increasing interparticle resistances in comparison to the microcrystalline powders. However, in long alkyl chain ammonium stabilized nanoparticles of TTFCl_{0.77} [9], the ionic conductive shell existing at the particles surface affected slightly the total conductivity (0.15 0.25 S. cm⁻¹) compared to the neutral insulating shell at the surface of the TTFCl_{0.77} particles, stabilized by the long alkyl chain amine or imine (\sim 0.01 S. cm⁻¹).

4. Conclusion

In conclusion, the use of neutral amphiphilic molecules, bearing a long alkyl chain, a nitrogen atom in either an amino or an imino function, and possibly a heterocycle, played an efficient role in controlling the growth of TTFCl_{0.77} as nanoparticles. The smallest and the most homogeneously distributed spherical particles were obtained in the presence of 1 octanamine,N (2 thienylmethylene). Nanoparticles with an average size of about 8 nm were grown. The chemical nature of the nanoparticles was confirmed by X ray diffraction, infrared and Raman spectroscopy. The nanopowders thus elaborated, exhibiting an electrical conductivity of about 10⁻² S. cm⁻¹, will be prepared at the gram level in order to prepare composites at present.

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