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Marco Revelli Beaumont, C. Faulmann, Dominique de Caro, Maximilien Cazayous, Yann Gallais, et al.. Reproducible nanostructuration of the superconducting κ -(BEDT-TTF)₂Cu(NCS)₂ phase. *Synthetic Metals*, 2020, 261, pp.116310. 10.1016/j.synthmet.2020.116310 . hal-02611168

HAL Id: hal-02611168

<https://hal.science/hal-02611168>

Submitted on 27 Oct 2020

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Reproducible nanostructuring of the superconducting

κ -(BEDT-TTF)₂Cu(NCS)₂ phase

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Abstract

The synthesis of the superconductor κ -(BEDT-TTF)₂Cu(NCS)₂ is optimized following a two-pot procedure to obtain high quality nanoparticles. This leads to homogeneous sized-nanoparticles, 30 nm diameter, which are further characterized by XRD and Raman spectroscopy. SQUID measurements confirm the occurrence of the superconducting transition at 9.1 K.

Keywords:

BEDT-TTF, nanoparticle, SQUID, superconducting transition

1. Introduction

The κ -(BEDT-TTF)₂Cu(NCS)₂ phase, (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene) prepared as single crystals in 1988, has been intensively studied because it was the first molecule-based superconductor to exhibit a critical temperature higher than 10 K [1]. From the 1990s, thin films [2] and nanorod arrays [3] of κ -(BEDT-TTF)₂Cu(NCS)₂ have also been reported. Some of us have shown that roughly spherical nanoparticles of molecule-based conductors could be prepared either by a chemical or an electrochemical route by adding to the solution a growth controlling agent, such as an amphiphilic molecule, an ionic liquid or a

long alkyl-chain quaternary ammonium salt [4-8]. We have already described the synthesis of nanoparticles of κ -(BEDT-TTF)₂Cu(NCS)₂ by a chemical or an electrochemical route. The chemical method was achieved by refluxing a tetrahydrofuran (THF) solution of BEDT-TTF and Cu(NCS)₂ in the presence of long alkyl-chain aconitate esters [9]. The solid obtained (yield about 70 %) consists in spherical nano-objects which are actually made of aggregated individual small particles ranging from 3 to 10 nm. The electrochemical method was performed in a two-compartment electrochemical cell containing BEDT-TTF, Cu(NCS) and the ionic liquid [EMIM][SCN] (EMIM⁺: ethylmethylimidazolium), acting as supporting electrolyte, provider of an

additional SCN^- ligand, and finally as a growth controlling agent [10]. The solid grown on the anode (yield about 20 %) exhibits well dispersed nanoparticles (mean size: 10 nm). However, this electrochemical route does not show reproducibility. In order to ensure selective and reproducible formation of NPs of the κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ phase, we have explored two synthetic routes using a different stabilizing agent *vs.* the above cited ones, *n*-dodecanoic acid (abbreviated as DA), and performing a one-pot or a new two-pot procedure. We identified a reproducible synthesis of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ nanoparticles and report on their chemical characterisation and super-conductive properties.

2. Results and discussion

The amphiphilic *n*-dodecanoic acid, also called lauric acid has been widely used to control the growth of metal, metal oxide or metal sulphide nanoparticles. It might also have an organizing effect on the nanoparticles [11]. Following the procedure reported in [9] for the synthesis of nanoparticles of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ with aconitate esters *i.e.* by heating a mixture of BEDT-TTF and Cu(NCS) $_2$ at reflux in THF in the presence of 0.3, 0.5, 1, 5, 10 or 20 molar equivalents of DA *vs.* BEDT-TTF, a black solid is obtained (yield in the 40–60 % range). To check sample purity, we focused on infrared transmission spectroscopy analysis. It is a powerful tool to investigate organic conductors quality as it provides a qualitative product characterization to detect unreacted starting compounds and possible impurities [12, 13]. Whatever the molar ratio DA/(BEDT-TTF), the infrared spectrum exhibits four peaks at 2068, 2099, 2110 and 2125 cm^{-1} . The sharp doublet at 2068 and 2110 cm^{-1} is the κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ finger-print that corresponds to two CN stretching modes of the Cu(NCS) $_2$ anions [12, 13], whereas the two other peaks at 2099 and 2125 cm^{-1} are not present in the bulk material and have not been assigned yet.

Electron micrographs of the solids evidence both nanoparticles (sometimes severely aggregated) and micrometre-sized crystals. The lack of selectivity in both the desired phase and the morphology led us to reject this one-pot synthetic route.

We have then explored a two-pot synthetic procedure. A THF solution of Cu(NCS) $_2$ and DA at room temperature is dropwise added to a THF solution of BEDT-TTF and DA at 90°C. For a molar ratio DA/BEDT-TTF of 2, a black solid, further denoted as NPs, precipitates in a 40 % yield. It exhibits two CN vibration modes at 2066 and 2109 cm^{-1} which are the adequate peaks found in the infrared spectrum of microcrystalline κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ [12, 13].

The absence of C=O vibrational modes implies the absence of DA within the solid. Electron micrographs evidence roughly spherical nanoparticles with an average diameter of 28 nm and a standard deviation of 4 nm (Fig. 1).

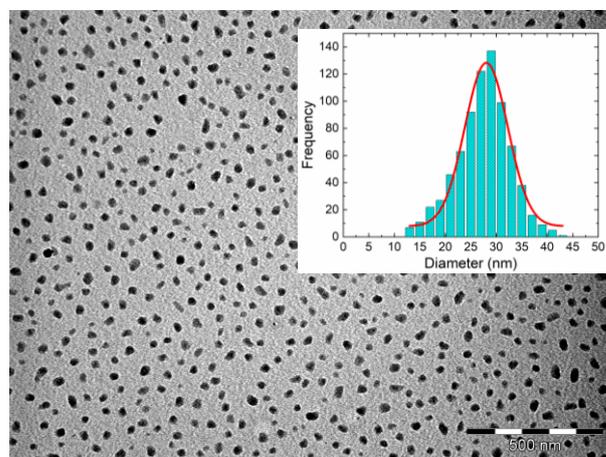
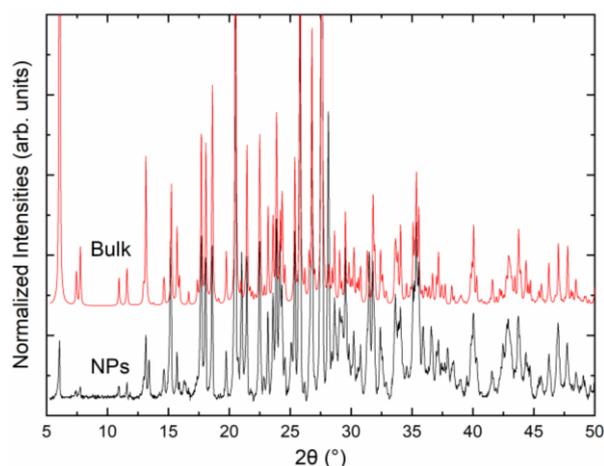


Fig 1. TEM image of NPs. Inset: Size distribution of the nanoparticles, the red line corresponds to a Gauss fit.

Upon dropwise addition, the copper salt Cu(NCS) $_2$ is introduced in a medium where BEDT-TTF is in excess and exhibiting a highly structured environment due to the long alkyl-chain carboxylic acid. Therefore, the germination process is more closely controlled and the growth process is quickly blocked, leading to well dispersed

nanoparticles. Moreover, this synthetic route allowing the preparation of **NPs** is reproducible. To ensure that we synthesized the κ -phase, we performed an XRD measurement of **NPs** and compared it to a **bulk** reference synthesized in the usual electrochemical way [14]. The two spectra are superimposable (Fig. 2), indicating **NPs** is indeed the expected κ -(BEDT-TTF)₂Cu(NCS)₂ phase.

Fig 2. XRD spectra of **NPs** and **bulk**



From the XRD spectrum, it has been possible to estimate the size of the nanoparticles by using Scherrer equation on several diffraction peaks, from 10 to 50° in 2θ . Over this latter range of 2θ , the average size of crystallites is *ca.* 42 nm, whereas it is *ca.* 31 nm between 28° and 50°. These values agree with the size observed by TEM measurements.

To complete the spectroscopic analysis, we also recorded a Raman spectrum at 15 K to compare the **bulk** and the **NPs** (Fig. 3).

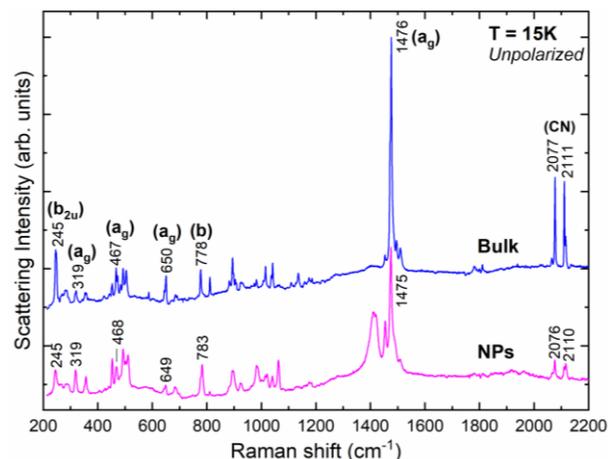


Fig 3. Unpolarized Raman spectra of **NPs** and **bulk** at 15 K in the range of 200 – 2200 cm⁻¹. Some phonons are reported with their corresponding mode.

Main phonons are reported with their corresponding modes. Differences in intensities between the **bulk** and the **NPs** are due to random orientation of the **NPs**. In particular, the peaks at 1411 and 1454 cm⁻¹ are strongly enhanced for the **NPs** [15]. Indeed, the phonon intensities between **NPs** and bulk are different. Bulk is oriented so Raman selection rules can be applied. **NPs** are oriented in all directions, as if it was a polycrystalline bulk, and Raman selection rules cannot be used to select specific phonon modes. Phonons **NPs** intensities are then an averaged response (of all possible bulk orientations). We also notice peak broadening for **NPs**. The two lines at 2076 and 2110 cm⁻¹ are due to distinct CN environments in the unit cell [16], in agreement with infrared measurements. The most intense band at 1476 cm⁻¹ is assigned to the C=C stretching vibration of the central carbon atoms of the BEDT-TTF molecule [17]. Despite intensities variations and broadening of phonons peaks, there are no main differences in peaks positions between the **NPs** and the **bulk**.

Raman measurements show that the structural properties of the bulk are preserved at the nanoscale.

Finally, in order to investigate the superconductivity of the **NPs** we performed d.c. magnetization measurements in a SQUID magnetometer. The temperature

dependence of the d.c. volume susceptibility of the NPs is shown in Fig. 4.

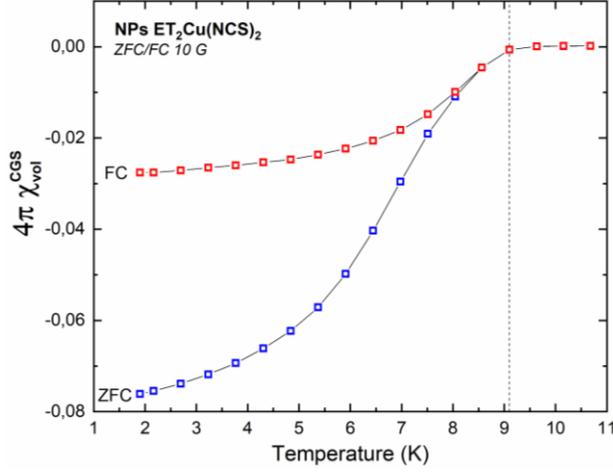


Fig 4. Temperature dependence (in blue) of the zero-field cooling (ZFC) and (in red) of the field cooling (FC) of the NPs. The dash line indicates $T_c = 9.1K$.

Volume susceptibility was derived using the following formulas:

$$\chi_{vol}^{MKS} = 4\pi \chi_{vol}^{CGS} \quad \chi_{vol}^{CGS} = \chi_{mass}^{CGS} \cdot \rho$$

$$\chi_{mass}^{CGS} = \frac{M^{CGS}(emu)}{H(Oe)}$$

$$\rho = \frac{M(g \cdot mol^{-1})}{N_A(mol^{-1})V_{cell}(cm^{-3})}$$

with χ_{vol} the volume susceptibility (dimensionless), χ_{mass} the mass susceptibility, M^{CGS} the measured magnetization, ρ the density and V_{cell} the volume of a unit cell.

In blue, we plot the effect of diamagnetic shielding, *i.e.* zero-field cooling (ZFC) and in red, the effect of magnetic flux expulsion, the Meissner effect, *i.e.* field cooling (FC). The two curves were recorded in the temperature range from 1.9 to 10.7 K. The dash line indicates the temperature where the magnetization starts to decrease, which is the signature of the superconducting transition for the NPs, $T_c = 9.1$ K. This temperature is close to the one observed in the **bulk** ($T_c \approx 9.5$ K). The ratio between Meissner susceptibility (FC) and shielding susceptibility (ZFC) is a lower bound to the

superconducting volume fraction. From $\frac{\chi_{vol}^{MKS}(FC)}{\chi_{vol}^{MKS}(ZFC)}$, measured at $H = 10$ G and $T = 1.9$ K, we estimate a superconducting fraction of 40%, in agreement with bulk measurements [18, 19]. This is a rough estimate since the anisotropy and demagnetization factors may modify the basic formula of the superconducting volume fraction.

Therefore, superconductivity in the NPs of typical diameter 30 nm is still present with a critical temperature of the same order of magnitude as in a bulk sample. Superconductivity in the NPs also indicates that the coherence length is shorter than 30 nm (in agreement with values of the bulk where the in-plane coherence length is $\xi_{//} \approx 7.5$ nm and the out-of-plane coherence length is $\xi_{\perp} \approx 0.5$ nm) [20].

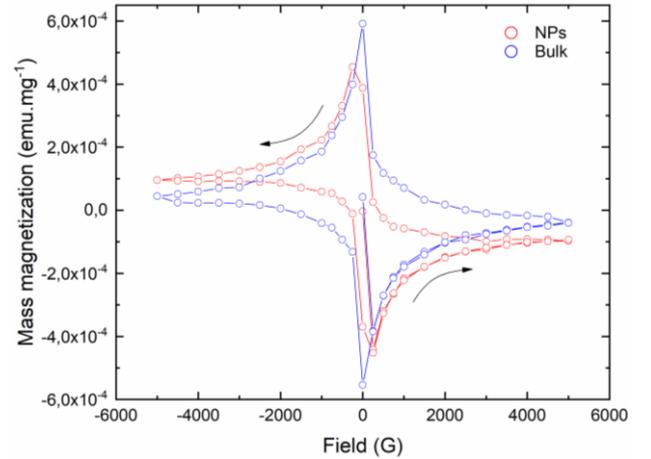


Fig 5. Isothermal magnetization at 1.9K for the NPs (in red) and the bulk (in blue).

Figure 5 shows a clear magnetization loop characteristic of a superconductor in both cases. For NPs, the hysteresis loop is of smaller area as compared to the bulk one suggesting a lower critical current.

In this work, 30 nm diameter nanoparticles of the superconducting phase κ -(BEDT-TTF)₂ Cu(NCS)₂ have been synthesized in a reproducible manner using lauric acid in a two-pot procedure. The one-pot synthesis, using the same reactants leads to inhomogeneous nanoparticles, whose IR spectrum does not correspond to the bulk. In

addition to reproducibility of the synthesis, it is confirmed that superconductivity occurs in nanoparticles of κ -(BEDT-TTF)₂Cu(NCS)₂ at size down to 30 nm, since the isolated nanoparticles exhibit a T_c of 9.1 K, *i.e.* in the same range as the bulk. Nevertheless, since both Raman and SQUID measurements show some small discrepancies between **NPs** and **bulk**, works are in progress to investigate more carefully these nanoparticles.

3. Experimental section

3.1. Chemical preparation of κ -(BEDT-TTF)₂Cu(NCS)₂ nanoparticles

Solution A: Cu(NCS)₂ (20 mg, 0.11 mmol) and *n*-dodecanoic acid (40 mg, 0.20 mmol) are dissolved by stirring for 15 min in 50 mL THF at 25°C. Solution B: BEDT-TTF (80 mg, 0.21 mmol) and *n*-dodecanoic acid (40 mg, 0.20 mmol) are dissolved by stirring for 15 min in 50 mL THF at 90°C. Solution A is dropwise added to solution B at 90°C with a flow rate of 1.5 mL.min⁻¹. After stirring at reflux for 30 min, a black solid is filtered off, washed with 3 × 10 mL hot THF, 10 mL diethyl ether, and finally dried under vacuum (yield: 40 %). Elemental analyses are in agreement between the calculated percentages and those of a raw powder obtained by direct precipitation without any recrystallisation. Calculated for C₂₂H₁₆CuN₂S₁₈: C, 27.8 %; H, 1.7 %; N, 3.0 %. Found: C, 27.1 %; H, 1.3 %; N, 3.5 %.

3.2. Characterization techniques

For transmission electron microscopy observation, powder (about 0.5 mg) is dispersed in diethyl ether (2 mL) under slow stirring for 1 min. The TEM specimens are then prepared by evaporation of droplets of the suspension deposited on carbon-supported copper grids. The experiments are performed on a JEOL Model JEM 1011 operating at 100 kV.

Infrared spectra (in KBr matrix) are registered at room temperature on a Perkin Elmer Spectrum GX spectrophotometer.

X-ray diffraction data are collected at room temperature with a Bruker D8 Advance diffractometer working in the Bragg-Brentano configuration (θ - θ) using Ni filtered CuK α radiation (0.15418 nm) and fitted with a SuperSpeedVantec Detector.

Raman spectra are obtained using a triple subtractive T-64000 Jobin-Yvon spectrometer with a cooled CCD detector. An unpolarized 532 nm laser line (green) from an Oxixus-Slim solid state laser is used.

Magnetic susceptibility is measured using a Quantum design MPMS XL-7, operating at an external magnetic field $H = 10$ G on a 5 mg **NPs** sample. Measurements are done in primary vacuum with a helium gas exchange for thermalization.

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