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Christophe Faulmann[1,2]*, Benoît Cormary[1,2], Dominique de Caro[1,2]*, Kane Jacob[1,2], Lydie Valade[1,2], Pascale de Caro[3]

[1]CNRS, LCC (Laboratoire de Chimie de Coordination), Toulouse, France
[2]Université de Toulouse, UPS, INPT, Toulouse, France
[3]Laboratoire de Chimie Agro-Industrielle (LCA), Université de Toulouse, INRA, INPT, Toulouse, France
Email: *christophe.faulmann@lcc-toulouse.fr, *dominique.decaro@lcc-toulouse.fr

Abstract

Nanoparticles of the conductive coordination polymer Ni(tto) have been synthesized under mild conditions in the presence of bio-based polyesters or polyethylene glycol acting as growth controlling agents. With polyesters, aggregates of particles are observed whereas well dispersed nanoparticles are obtained with polyethylene glycol. Indeed, for a Ni^{2+}/polyethylene glycol weight ratio of 0.031, transmission electron micrographs evidence dispersed particles exhibiting sizes in the 3 - 10 nm range. Infrared spectra for nanopowders show two CS stretching modes in the 1100 - 1190 cm^{-1} range, confirming the presence of the tetrathiooxalate ligand coordinated to the nickel center. The room-temperature electrical conductivity for the nanopowder prepared in the presence of polyethylene glycol is about 0.8 S·cm^{-1}, a decent value for tetrathiolate-based polymers. Finally, magnetic susceptibility measurements for well-dispersed Ni(tto) particles evidence a Curie-Weiss law in a large temperature range. Moreover, low temperatures measurement would confirm intra- or interchain interactions between nickel atoms within the Ni(tto) polymer chains.

Keywords

Conductive Coordination Polymers, Tetrathiooxalate, Polyethylene Glycol, Biobased Polyesters, Nanoparticles

1. Introduction

Polymers composed of transition metal ions coordinated to conjugated ligands can possess unfilled molecular orbitals and thus exhibit intrinsic conducting

properties. Among them, poly(nickel tetrathiooxalate), Ni(tto) (**Figure 1**), has an electrical conductivity in the 4 - 20 S·cm^{-1} range. The conductivity value depends on the nature of the starting nickel salt, the solvent and the temperature used for their synthesis [1]. This conducting polymer has been processed as composites with poly(vinyl alcohol) [2], as self-assembled ultrathin films [3] or as coatings on CdS nanocrystals [4].

Poly(nickel ethenetetrathiolate), Ni(ett), another conducting polymer containing the 1,1,2,2-ethenetetrathiolate $C_2S_4^{4-}$ ligand (**Figure 1**), has been obtained as nanoparticles dispersed in poly(vinylidene fluoride) [5]. The particles (sizes in the 230 - 415 nm range) were interconnected with each other to form long chains (>10 μm). Nanoparticles of Ni(ett) stabilized by dodecyltrimethylammonium ions have also been described (average diameter of about 38 nm) [6]. Finally, we have reported the preparation of colloidal solutions of Ni(ett) in methanol [7]. The nanoparticles (sizes in the 5 - 30 nm range) were stabilized by an ionic liquid based on imidazolium cations. However, to our knowledge, the conducting Ni(tto) polymer has never been processed as nanoparticles. In this paper, we describe the growth of Ni(tto) as nano-objects in the presence of two kinds of polymeric size controlling agents. The final goal of this work is to use these nanoparticles for thermoelectric (TE) applications. Nowadays, there is a growing interest in organic thermoelectric (OTE) materials, since they exhibit a low density and can be synthesized under mild conditions. The performance of TE materials can be evaluated by the dimensionless figure of merit ZT, which depends on the Seebeck coefficient, the electrical conductivity and the thermal conductivity. The higher the ZT, the better the thermoelectric performance. Among OTE materials, M(ett) and M(tto) (M = Co, Ni, Cu) are currently taken into consideration, as evidenced by several recent experimental [8]-[14] and theoritical [15] [16] [17] articles (and ref. therein), after a long period of lack of interest in this kind of material. For instance, Yee [10] and Tkachov [12] have published improved and reproducible syntheses of respectively Ni(ett) and Ni(tto) which both exhibit enhanced electrical conductivity, and consequently superior thermoelectric properties, thanks to the control of the synthesis parameters. In the
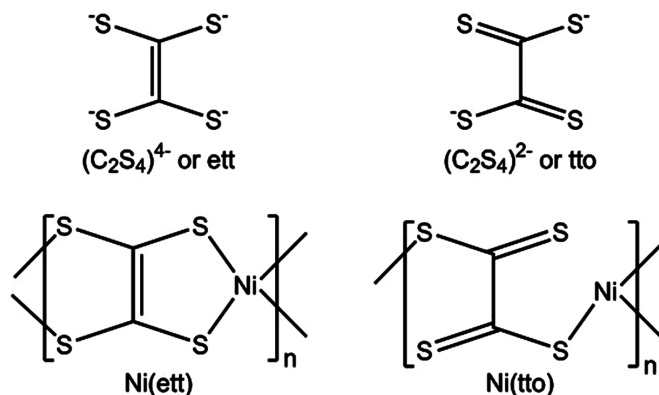

Figure 1. Molecular structure of ett^{4-}, tto^{2-}, Ni(ett) and Ni(tto).

same line, theoretical calculations have shown that a weaker electron−phonon coupling results in an improved TE factor, thanks to a suitable frontier molecular orbital alignment and an higher intrinsic mobility. Their results open the way for the design of new thermoelectric polymers [16] [17]. Furthermore, it has also been shown that ZT values are enhanced on nanocrystalline-shaped thermoelectric materials [18]. Therefore, we have undertaken the study of the growth of Ni(tto) as nano-objects.

2. Materials and Methods

2.1. Materials

Solvents are degassed immediately before use. Tetraethylammoniumtetrathiooxalate, $[(C_2H_5)_4N]_2[C_2S_4]$ (or $[NEt_4]_2(tto)$), is prepared following a procedure described previously in [19], using $Na_2S \cdot 9H_2O$, elemental sulfur, tetrachloroethylene and $[NEt_4]Cl$ in a mixture of methanol and acetonitrile (1:7.5 vol./vol.) under reflux for 3h30. $[NEt_4]_2(tto)$ is recrystallized from a mixture of diethylether and acetonitrile (1:2.5 vol./vol.), with a yield of *ca.* 25%.

$Ni(NO_3)_2 \cdot 6 H_2O$ is purchased from Fluka and used without further purification. Polyethylene glycol 400 (PEG400), aconitic acid (**Figure 2**), 1,2,3-propanetriol (glycerol) and 1,4-butanediol are purchased from Sigma-Aldrich and used as received. Infrared spectra of polyesters are taken at room temperature (using the ATR technique) on a Perkin Elmer Spectrum 65 spectrophotometer. Infrared spectra of Ni(tto) are taken at room temperature (in KBr matrix) on a Perkin Elmer Spectrum GX spectrophotometer. For transmission electron microscopy (TEM), the Ni(tto) samples are sonicated, dispersed in acetonitrile, and placed onto a holey carbon-copper grid. TEM experiments are performed on a JEOL Model JEM 1011 operating at 100 kV. Powder conductivity measurements are carried out on pressed pellets of pure powder materials (size: 3.14 mm^2 × 1 mm thick) without any grinding. The cylinders used to press the materials play the electrodes role. Resistance data acquisition is achieved using a Hewlett-Packard model 4263A LCR meter. Magnetic measurements are taken using a MPMS 5 Quantum Design magnetometer. The Ni(tto)/PEG 400 sample (26.4 mg) is placed in a gelatin capsule. The applied magnetic field is 3 kOe.
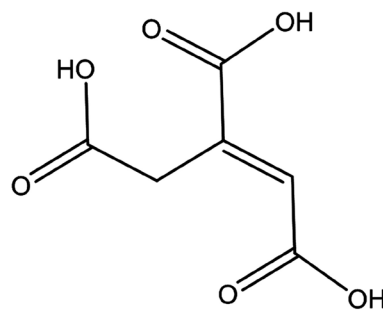

Figure 2. Molecular formula for aconitic acid.

2.2. Synthesis of Polyester from Aconitic Acid and Glycerol

The schematic procedure for this synthesis is shown in **Figure 3**. Aconitic acid (17.4 g; 0.10 mol) and glycerol (11.1 g; 0.12 mol) are added into a 250 mL round-bottom flask fitted with a condenser at the basis of which molecular sieve is positioned. The polymerization is run at 190˚C for 75 min. under a slow stirring. A yellow transparent solid is collected (23.5 g). About 5 g of water formed during the reaction is absorbed by the molecular sieve. IR data (cm^{-1}): 1710 (s, $\nu_{C=O}$ from ester), 1163 (s, ν_{C-O} from ester).

2.3. Synthesis of Polyester from Aconitic Acid and 1,4-Butanediol

For the synthesis of the polyester with aconitic acid and 1,4-butanediol (**Figure 4**), a synthetic procedure similar to the one described in § 2.2 is carried out using 17.4 g of aconitic acid (0.10 mol) and 10.8 g of 1,4-butanediol (0.12 mol). The polymerization is run at 160˚C for 75 min. A yellow solid is collected (22.5 g). IR data (cm^{-1}): 1709 (s, $\nu_{C=O}$ from ester), 1163 (s, ν_{C-O} from ester).

2.4. Synthesis of Ni(tto) in the Presence of Polyesters

70 mg of [NEt$_4$]$_2$(tto) (0.18 mmol) and 10 mg of polyester (aconitic acid/glycerol or aconitic acid/1,4-butanediol) are added to a double-necked flask containing 15 mL of methanol (**Figure 5**). The mixture is stirred at room temperature until complete dissolution. Meanwhile, a solution of Ni(NO$_3$)$_2$·6H$_2$O (71 mg, 0.24 mmol) in 10 mL methanol is prepared and then dropwise added to the previous solution. The resulting solution is then stirred at 70˚C for 16 h. The black precipitate thus obtained is filtered off, washed with methanol and finally dried under vacuum. Yield in Ni(tto): 10% with aconitic acid/glycerol and 14% with aconitic acid/1,4-butanediol.
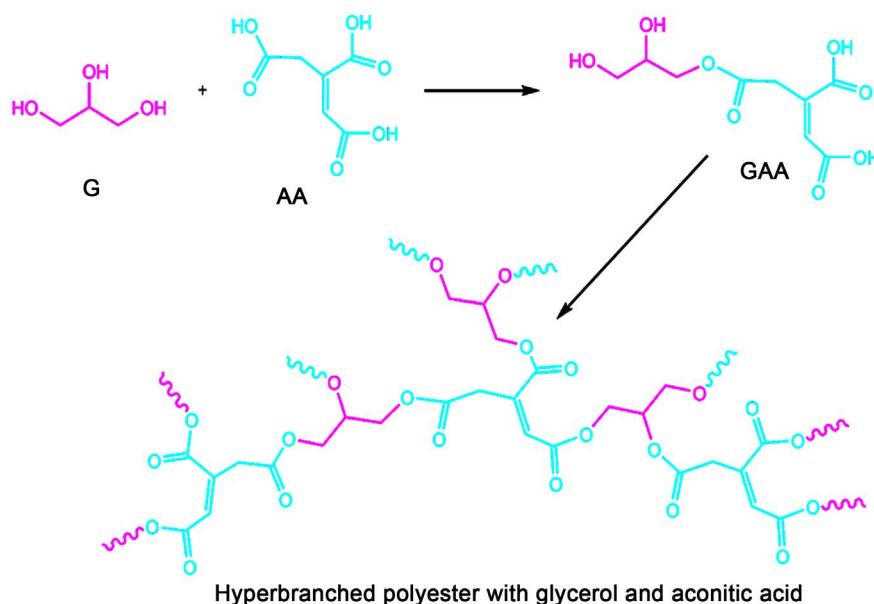

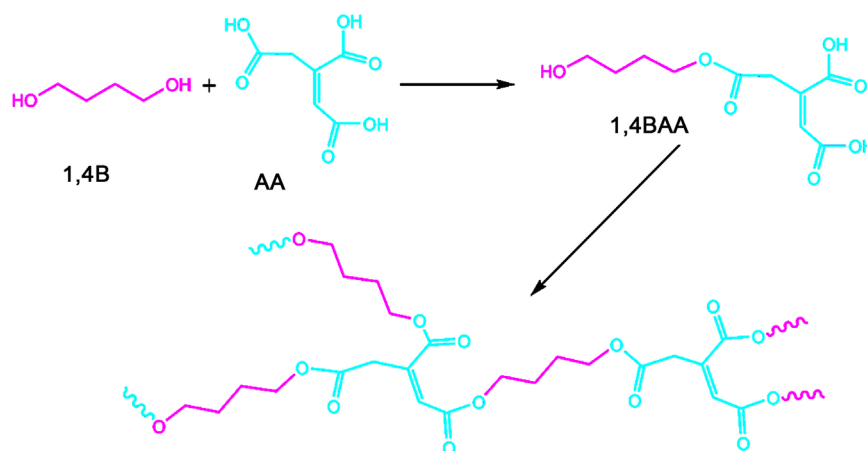**Figure 3.** Synthesis of polyester from aconitic acid and glycerol.

Figure 4. Synthesis of polyester from aconitic acid and 1,4-butanediol.

$$[NEt_4]_2(tto) + Ni(NO_3)_2 \cdot 6H_2O \xrightarrow[\text{or PEG}]{\text{Polyester}} Ni(tto) + 2[NEt_4](NO_3) + 6H_2O$$
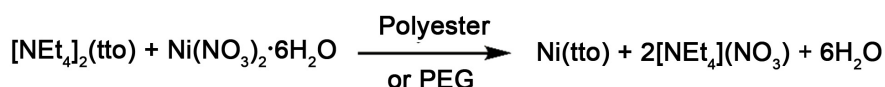
Figure 5. Schematic procedure for the synthesis of nanoparticles of Ni(tto) with polyester or PEG.

2.5. Synthesis of Ni(tto) in the Presence of Polyethylene Glycol

The procedure used for the synthesis of Ni(tto) with polyesters (§2.4) is carried out using 80, 450 or 900 mg of PEG400, instead of polyester. Yield in Ni(tto): 25%.

3. Results

The reaction of $[NEt_4]_2(tto)$ with nickel(II) nitrate under refluxing methanol leads to Ni(tto) polymer whose morphology is characterized by micrometer-sized platelets. To control the growth of Ni(tto) as smaller objects, we have evaluated the use of biobased polyesters. Indeed, polymers are known to sterically control the growth of numerous compounds as nanoparticles but also possibly to stabilize them by forming a protecting shell that prevents agglomeration of individual nanoparticles. Aconitic acid is an organic triacid (Figure 2), which is produced by plants during the Krebs cycle. The main source is found in the sugar cane vinasse. Aconitic acid belongs to the products generally recognized as safe by the Food Drug Administration (FDA). Hyperbranched polyesters of aconitic acid have already been synthesized and studied for their application as scaffolds in tissue engineering [20] [21]. Unlike those previously described, the polyesters of aconitic acid and glycerol or 1,4-butanediol used in this study are prepared in the absence of concentrated sulfuric acid which corresponds to a greener synthesis (see Materials and Methods). Infrared spectra of the synthesized polyesters exhibit strong absorptions at about 1710 cm^{-1} and 1160 cm^{-1} which are assigned to the C=O and C-O modes of esters, respectively. These polyesters are poorly

soluble in methanol, the solvent used for the synthesis of Ni(tto) polymers. We have then explored the preparation of Ni(tto) at the limit of solubility of polyesters in methanol, *i.e.* 0.4 mg·mL^{-1}. The reaction of [NEt$_4$]$_2$(tto) with nickel(II) nitrate in the presence of polyester (weight ratio Ni^{2+}/polyester of 1.40) in methanol at reflux leads to a very fine black powder of Ni(tto). Infrared spectra do not show the C=O stretching mode for esters, implying the absence of polyesters within the powder. Observed vibration modes of the powder are mainly due to the coordinated tto ligand (**Figure 6**).

CS stretching frequencies are located at 1182 (s) and 1155 (sh) cm^{-1}. These values are very close or similar to those reported for Ni(tto) capped CdSnanocrystals (1182 and 1151 cm^{-1}) [4]. Moreover, the mode at 1019 cm^{-1} in the IR spectrum of our samples is also present in the spectrum for ultrathin Ni(tto) films (1025 cm^{-1}) [22]. When the synthesis of Ni(tto) is carried out in the presence of the polyester with aconitic acid and 1,4-butanediol, electron micrographs show severely aggregated nanoparticles (**Figure 7**). Sizes of individual nanoparticles within the agglomerates are difficult to quantify. In the presence of the polyester with aconitic acid and glycerol, aggregates of nanoparticles are also observed (**Figure 7**). In some areas of the aggregates, sizes of individual roughly spherical nanoparticles can be measured and are found in the 15 - 35 nm range. When the synthesis of Ni(tto) is conducted in the absence of structuring agent, the isolated powder only contains microsize platelets. Therefore, although polyesters are not present in the powders, their presence in the reaction medium prevents the formation of platelets of Ni(tto). However, in the conditions explored, these hyperbranched biobased polyesters, characterized by a strong steric hindrance, do not prevent aggregation of particles.

A previous work has shown that PEG could control the growth of molecule-based conductors as nanocrystals. For instance, tetrathiafulvalene·tetracyanoquinodimethane (TTF·TCNQ) nanoparticles have been grown in
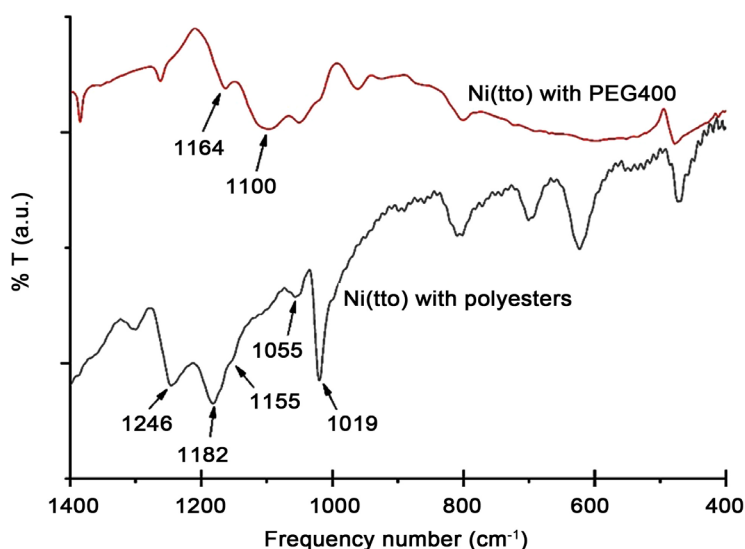

Figure 6. Infrared spectra for Ni(tto) prepared in the presence of polymers.
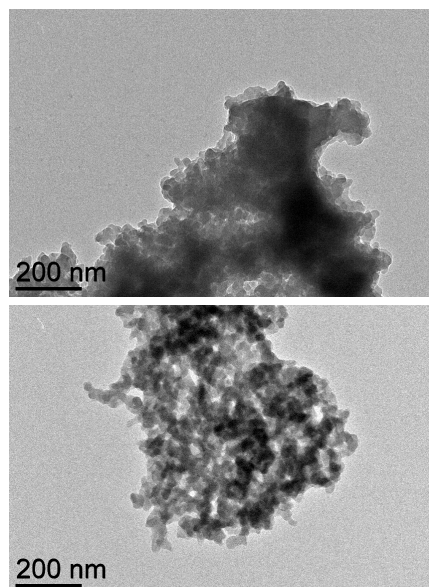
Figure 7. TEM images for Ni(tto) prepared in the presence of polyesters (top: aconitic acid/1,4-butanediol; bottom: aconitic acid/glycerol).

an acetone/acetonitrile solution of PEG [23]. PEG served as a growth controlling agent. However, it was not present at the particles surface. In the present work, we have evaluated the use of PEG to control the growth of Ni(tto) as nano-objects. The reaction of $[NEt_4]_2(tto)$ with nickel(II) nitrate in the presence of PEG 400 in refluxing methanol leads to a black powder. We have investigated three different weight ratios Ni^{2+}/PEG 400: 0.175, 0.031 and 0.016. Infrared spectra exhibit CS stretching modes at 1164 and 1100 cm^{-1} (**Figure 6**). These values are similar to those for bulk Ni(tto) (1168 and 1113 cm^{-1}) [4]. IR spectra do not show bands assigned to PEG. For weight ratios of 0.175 and 0.016, transmission electron micrographs show platelets of Ni(tto). Thus, for these weight ratios, the PEG present in solution has no structuring effect, and bulk Ni(tto) has been grown. For a weight ratio of 0.031, a typical image is shown on **Figure 8**. We observe nanoparticles of Ni(tto) (sizes in the 3 - 10 nm range) dispersed in a Ni(tto) matrix. We note that, in these conditions (Ni^{2+}/PEG400 = 0.031), the PEG does not allow the selective growth of Ni(tto) as well dispersed nanoparticles. However, these latter are surprisingly embedded in a matrix of the same chemical nature.

Ni(tto) polymers prepared in the presence of biobased polyesters (with aconitic acid/glycerol or aconitic acid/1,4-butanediol) exhibit room-temperature conductivity values of about 5×10^{-6} S·cm^{-1}, several orders of magnitude lower than those for bulk Ni(tto) (4 - 20 S·cm^{-1}) [1]. Although not detected by infrared spectroscopy, traces of polyester adsorbed onto the particles surface could break conduction pathways between the grains which might explain the poor transport properties of these materials. For the sample exhibiting nanoparticles embedded
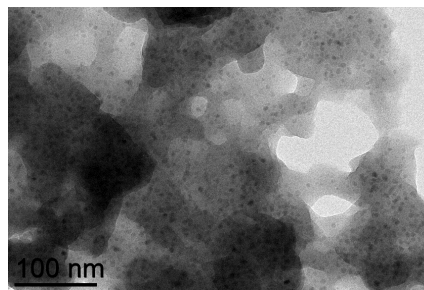
Figure 8. TEM image for Ni(tto) prepared in the presence of PEG with a weight ratio Ni^{2+}/PEG 400 of 0.031.

in a Ni(tto) matrix, the conductivity at room temperature is *ca.* 0.8 S·cm^{-1}, a value slightly lower than that for bulk Ni(tto). In this sample, nanoparticles are not in close contact (lack of conduction pathways). Thus, the conduction process is presumably due to the continuous Ni(tto) matrix and the conductivity value measured on this sample is logically close to that of the bulk.

The sample exhibiting the higher room-temperature conductivity, *i.e.* Ni(tto) prepared in the presence of PEG400, has been investigated by magnetic measurements. The magnetic susceptibility (χ_m) at 3 kOe is measured in the 2 - 300 K temperature range, indicating a paramagnetic behaviour. Occurrence of unpaired electron is not surprising in this kind of materials, although it concerns formally square-planar Ni^{2+} entities and neutral Ni(tto). Indeed, traces of counter ion as $(NEt_4)^+$ is still possible, alike traces of K^+ in poly[Ni-tto] (P3) in [12], which will induce slight changes in the electronic structure of the Ni(tto) fragment. Moreover, electron transfer between metal and ligand is not rare within the $Ni(C_2S_4)$ fragment, whatever its native degree of charge of the metal or the ligand (tto^{2-} or ett^{4-}) [24] [25] [26].

The plots of $\chi_m T$ *vs*. T and $(\chi_m)^{-1}$ *vs* T (inset) are shown on **Figure 9**. $\chi_m T$ values are roughly constant in a large temperature range, in agreement with a Curie-Weiss law (C = 0.272 and θ = −4.26 K). At low temperatures, $\chi_m T$ significantly decreases. A similar magnetic behavior has been observed for bimetallic dithiooxalate complexes [27] [28].

The authors of this article assigned the decrease of $\chi_m T$ *vs*. T to interchain antiferromagnetic couplings. Furthermore, bulk Ni(tto) also presents antiferromagnetic exchange interactions for T < 40 K [1]. In our case, such antiferromagnetic couplings between nickel ions could also explain the decrease of $\chi_m T$ values at low temperatures. Without any structural data (except the first theoritical model for the bulk ett polymer in 1987 [29] and those recently reported by Tkachov *et al*. [12]), it does not seem pertinent to elaborate any hypothesis concerning the nature of this antiferromagnetic coupling (intra- or interchain interactions).

4. Conclusion

In this paper, we have described the first nanoparticles of the conducting Ni(tto)
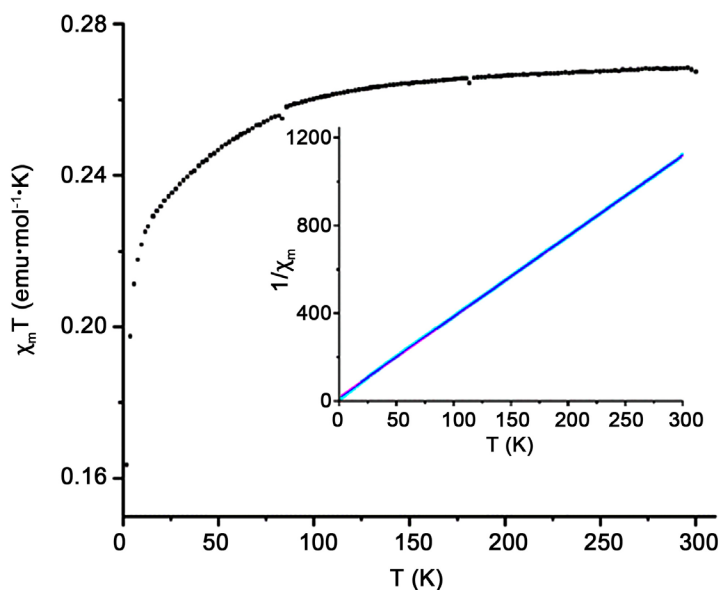
Figure 9. Magnetic behaviour of Ni(tto) (inset: experimental points in cyan, fit in magenta).

polymer. The growth controlling agents evaluated in this study, *i.e.* hyperbranched bio-based polyesters and polyethylene glycol, prevented the growth of Ni(tto) as micrometre-sized platelets. In the presence of hyperbranched bio-based polyesters, aggregated nanoparticles have been obtained. In the presence of polyethylene glycol, Ni(tto) nanoparticles have been grown in a Ni(tto) matrix. Despite a lower or similar electrical conductivity compared with the bulk Ni(tto) polymer, these materials might have potential applications in thermoelectricity since their morphology should favor a lower thermal conductivity thanks to the nanometric size of the particles, and then this should increase the ZT factor. Works are currently in progress to determine these thermoelectrical parameters.

Acknowledgements

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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