



# Electrical conduction and thermoelectric properties of tetrathiafulvalene-tetracyanoquinodimethane cast films prepared with *N,N*-dimethylacetamide



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## ABSTRACT

We evaluated the effect of an amide compound bearing methyl groups on the properties of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) cast films. The spontaneous electron transfer between *N,N*-dimethylacetamide (DMA) and the TCNQ complex is expected to change the casting condition. Then, we obtained a higher density of nanofibers in TTF-TCNQ films using DMA. The electrical conduction of TTF-TCNQ films using DMA was 58.0 S/cm, which is twice that of previously reported polycrystalline films. We measured the Seebeck coefficients of the films for their future possible use as thermoelectric materials. The Seebeck coefficient and power factor of the films prepared with DMA were 32.3  $\mu\text{V/K}$  and 6.05  $\mu\text{W/mK}^2$ , respectively.

## 1. Introduction

Studies of functional organic materials with higher electrical conduction have been performed to provide new organic electric devices such as thermoelectric (TE) devices, organic transistors, and organic solar cells [1]. For example, the *p*-type organic material PEDOT:PSS has been investigated as a TE material and its high TE conversion performance was confirmed [2–5]. The TE module configuration must also be considered for fabricating organic TE modules with a higher TE conversion efficiency. For example, a conventional TE module has a  $\pi$ -type structure that combines *p*- and *n*-type materials. However, for organic semiconductors, there are few reports of good *n*-type TE materials [6,7], compared with the number of reports of carbon nanotube TE materials [8,9]. Therefore, it is important to develop *n*-type organic TE materials.

The organic charge-transfer complex tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) is a widely studied organic conductor. The material has a negative Seebeck coefficient at room temperature along its *b*-axis, suggesting that this material could be used as an *n*-type TE material (Fig. 1(a)) [10]. The electrical conductivities of single-crystal and polycrystalline film TTF-TCNQ complexes are approximately 400–500 [11] and 5–30 S/cm [12,13], respectively. A TTF-TCNQ complex film with a higher electrical conductivity and larger Seebeck coefficient would be a promising candidate *n*-type TE material for fabricating organic  $\pi$ -type TE modules.

The electrical conductivity in TTF-TCNQ poly-crystalline film could

be increased by changing the micro/nanostructures of TTF-TCNQ films or by increasing the charge transfer degree between TTF and TCNQ. It is well-known that TTF-TCNQ nanocrystals form nanofibers in the films prepared by the drop-casting process [14]. We expect that the density of nanofibers of TTF-TCNQ at the surface could be controlled by changing the casting conditions, such as the solvent species etc. Interestingly, an electron transfer [15,16] or additional reaction [17] between nitrogen-bearing molecules (amides or amines) and a TCNQ has been reported. Using an amide with a short alkyl chain as a solvent the electron transfer between TCNQ and the amide is highly expected (Fig. 1(b)). By using such an electrically charged molecular species, we expect to change the density of nanofibers and increase the charge transfer degree simultaneously, because a difference in electrical charge in solution could affect both the electrical properties of the film and the casting conditions that determine the film structure.

In this study, we report the preparation of TTF-TCNQ polycrystalline films by the drop-cast method using *N,N*-dimethylacetamide (DMA) with short alkyl chains (methyl groups) before casting. We succeeded in obtaining a higher electrical conductivity of 58.0 S/cm, which was twice that of previously reported TTF-TCNQ polycrystalline films. In addition, we evaluated the TE properties of the TTF-TCNQ films by measuring their Seebeck coefficients.

## 2. Experimental section

Acetone and acetonitrile (AN) were purchased from Kanto Chemical

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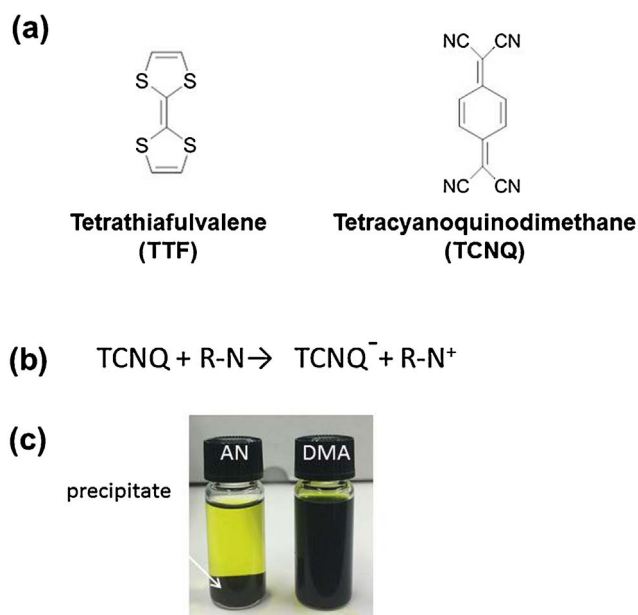


Fig. 1. (a) Chemical structures of TTF and TCNQ; and (b) Scheme of electron transfer between TCNQ and a nitrogen-containing molecule. (c) a picture of TTF-TCNQ solvents: left in AN and right in DMA.

**Table 1**  
Reaching solvent temperatures and solution state after mixing process of TTF and TCNQ.

Solvent	Temperature (°C)	Solution state
AN	72	Precipitation formed
DMA	83	Suspension
5% DMA	72	Precipitation formed
10% DMA	72	Precipitation formed
20% DMA	73	Precipitation formed
50% DMA(1:1)	73	Precipitation formed

Co., Inc. DMA was purchased from Wako Pure Chemical Industries, Ltd. TTF and TCNQ were purchased from Tokyo Chemical Industry Co., Ltd. Glass substrates (S1126, Matsunami Glass Industry Ltd.) were cleaned by sonication with acetone for 10 min, rinsed with acetone thoroughly, and air dried. Before TTF-TCNQ complex crystallization, TCNQ was dissolved in AN, DMA, or 4 kinds of mixtures of AN and DMA. The concentrations of DMA in the mixed solvents were 5%, 10%, 20% and 50%. These solutions are heated on the hot plate (set at 95 °C) in an air atmosphere for 10 min to induce the charge transfer or reaction. The humidity is in the between 50 and 60%. The reaching temperatures of all the solutions are listed in Table 1. TTF was dissolved in the same solvent. The TTF-TCNQ complexes were synthesized by mixing TTF and TCNQ solutions (10 mg/mL, 1:1), at 20–25 °C without a stirring, in an air atmosphere and under the humidity in the between 50 and 60%. The solution states are also listed in Table 1. We observed the formation of the precipitation in AN (see Fig. 1c) and other four mixed solutions. On the other hand, only in DMA, we observed the formation of suspension (see Table 1 and Fig. 1c).

To concentrate TTF-TCNQ-based product, we used a centrifuge (MCF-2360, LMS Co., Ltd.). The rotation speed was at 6600 rpm. We used the concentrate TTF-TCNQ-based product at the bottom of the tube that allowed them to remove excess of the solvent for film formation. To obtain high-quality cast film, the glass substrate was rinsed thoroughly with pure AN, and the TTF-TCNQ complexes rich part suspended in AN were drop-cast on the substrate and dried at room temperature.

The UV/vis absorption spectra of the TCNQ solutions were recorded between 300 and 800 nm (UV-2450, Shimadzu). The thicknesses of the TTF-TCNQ films were measured with a microfigure measuring instru-

ment (Surfcorder ET200, Kosaka Laboratory Ltd.). The conductivities of the cast films were measured with a four-probe conductivity test meter (MCP-T600, Mitsubishi Chemical Corporation). To estimate the crystallite size and orientation of TTF-TCNQ crystals, X-ray diffraction (XRD) measurements were performed with CuK $\alpha$  radiation (RINT 2100, Rigaku Corporation). Scanning electron microscopy (SEM; S-4800, Hitachi) was used to check the morphology of the TTF-TCNQ films. The accretion energy of the electrons was 3.0 kV. The fiber densities were estimated using SEM images. We counted the fiber numbers in the  $20 \times 20 \mu\text{m}^2$  of 5 places in the SEM images and used the average value.

The film surfaces were characterized by X-ray photoelectron spectroscopy (XPS; Theta Probe, Thermo Fisher Scientific) with a focused monochromatic Al-K $\alpha$  X-ray source (1486.6 eV). Raman spectra of cast films were recorded with a Raman spectrometer (NRS-2100, JASCO) with a 514 nm laser as an excitation light source. We used a homemade Seebeck coefficient measurement system [4] with a humidity of less than 30%. A sample holder with two Peltier units (UT40U100F, Ampere) was placed in air. The temperatures of the two Peltier units were controlled independently. The temperature difference ( $\Delta T$ ) of the sample and the electromotive force ( $\Delta V$ ) were measured simultaneously by two thermocouple probes with a digital multimeter. The Seebeck coefficient,  $S$ , was measured for  $T$  between 0 and 8 °C. The slopes of plots of  $\Delta V$  versus  $\Delta T$  gave  $S$ .

### 3. Results and discussion

To check the electronic structure of TCNQ, the authors measured UV–vis spectra of TCNQ heated in the solvents used. In AN, one absorption around 400 nm corresponding to TCNQ was observed (Fig. 2(a)). In the 1:1 mixture (50%, Fig. 2(b)) and in DMA (Fig. 2(c)), the intensity of the TCNQ peak at 400 nm decreased and new absorptions appeared between 600 and 950 nm after 10 min heating. The new absorption peaks were assigned as an anionic TCNQ moiety (TCNQ $^-$ ) [15]. Furthermore, the absorption peak of unreacted TCNQ at around 400 nm shifted to a longer wavelength. To show the direct evidence of TCNQ anion formation, we measured TCNQ in DMA solution after 1 h heating (cf. Fig. 2(d)). The spectrum is almost the same as that of TCNQ anion [15]. From the UV–vis spectra, we confirmed that electron transfer occurred between the amide solvent and TCNQ moiety.

We further checked whether the TTF-TCNQ nanocrystals will dissolve or not in the solvent. In AN, since the TTF and TCNQ are very reactive, they react quickly to form a precipitate (cf. Fig. 1(c) left). On the other hand, when the TTF and TCNQ were reacted in DMA, no precipitate was formed (cf. Fig. 1(c) right). This indicated that TTF-TCNQ particles are well dispersed in DMA. Since the pKa of the solvent has to play a principal role in the solubility of TTF-TCNQ, we estimated the pKa values of pure AN and DMA. The pKa values of AN and DMA are estimated to be ca. 11.0 and 15.0, respectively. We consider that the higher pKa of the DMA is enabled us to form the suspension of TTF-TCNQ.

Since the reaction of TTF-TCNQ is expected to be fast, nanocrystals are formed at the stage of mixing. In the case of the suspension in DMA, the collision frequency of the nanocrystals is sufficiently increased, the density of nanocrystals on the substrates expected to be higher. Thus, the density of nanocrystals should be higher. However, in cases of other solvents, the drying of the solvent from the precipitation is dominant, and the structure formed at the time of the reaction only aggregates, so the density of nanocrystals on the substrates is expected to be low.

The amount of TCNQ anions estimated using UV–vis data in a 1:1 mixture of AN/DMA and DMA only solutions are 1.65% and 11.5%, respectively. We consider that the formation of TCNQ anions is enough high to change the properties of TTF-TCNQ film, such as crystal orientation and the charge transfer degree etc.

We examined the dependence of the electrical conduction of TTF-TCNQ cast films on the solvents (Fig. 3). All the TTF-TCNQ films

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