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*Electronic supplementary information*

# High-performance, air-stable, n-type thermoelectric films from a water-dispersed nickel-ethenetetrathiolate complex and ethylene glycol

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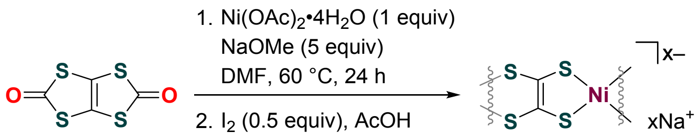
Contents

## 1. General

The NMR measurements were carried out with a JEOL JMTC-400 instrument. Mass spectra were measured on a Shimadzu LCMS-2020 spectrometer or a JEOL JMS-MS700V spectrometer. Electrical conductivity in in-plane direction at room temperature was measured with a Loresta-GX MCP-T700, Mitsubishi Chemical Analytech Co., Ltd. Thermoelectric power factors in in-plane direction at room temperature were measured with an Advance Riko ZEM-3L. Vibration millings with zirconia beads were performed with a MTI MSK-SFM-12M-A-LD. Surface roughness of the thermoelectric films was observed by laser microscopy with an Olympus LEXT OLS4000. Scanning electron microscope (SEM) was performed on JEOL JSM-6610. Samples were previously dried and sputter coated with platinum. Energy-dispersive X-ray spectroscopy (EDX) analyses were performed on the SEM instrument equipped with JED-2300 analyzer. From EDX analyses, the content of elements on the surface was calculated and the maps of the elements were derived. Dynamic light scattering measurements (DLS) were performed with a Malvern Zeta Sizer Nano Series Nano-ZS instrument using a He-Ne laser ($\lambda$ = 633 nm) at 25 °C and a scattering angle of 173°. Sonication was carried out with a Branson 2510J-MT. 1,3,4,6-Tetrathiapentalene-2,5-dione and sodium methoxide (ca. 5 M in methanol) were purchased from Tokyo Chemical Industry Co., Ltd. Nickel(II) acetate tetrahydrate, ethylene glycol, and acetic acid were purchased from Fujifilm Wako Pure Chemical Corporation. Iodine was purchased from Kanto Chemical Co., Inc. Poly(vinylidene fluoride) (average $M_w$ 180,000 by GPC) was purchased from Sigma-Aldrich Co. LLC. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thick silica gel 60F-254 (Merck). All reactions were carried out under a nitrogen atmosphere.

## 2. Synthesis of Ni-ETT 2




**1** **2**

Sodium methoxide (ca. 5 M in methanol) (0.25 mL, ca. 1.25 mmol) was added to a solution of 1,3,4,6-tetrathiapentalene-2,5-dione (**1**) (50 mg, 0.24 mmol) and nickel(II) acetate tetrahydrate (60 mg, 0.25 mmol) in dry DMF (2.5 mL) under a nitrogen atmosphere. After stirring for 24 h, a mixture of acetic acid (0.1 mL) and methanol (1.0 mL) was added. The generated Ni-ETT was subsequently oxidized by adding a solution of iodine (30 mg, 0.12 mmol) in methanol (0.5 mL). After stirring for 24 h, the reaction mixture was transferred to a centrifuging tube. The mixture was purified by repeating the decantation with centrifugation (2900 rpm) to remove all the soluble components in methanol, water, and DMSO. Water was added to the resulting black solids, which were sonicated for 20 min to furnish a water-dispersed Ni-ETT with a concentration of ca. 30 mg/mL.

Note that the synthesis conditions of Ni-ETT complex from compound **1** were carefully investigated by Yee and co-workers.[S1] In this study, we used simple method as shown above with reference to a report, which shows DMF is a suitable solvent for the synthesis of multimetallic gold-complexes.[S2]

## 3. Fabrication of thermoelectric films of Ni-ETT 2

The glass substrate (1.5 cm × 1.5 cm) was washed carefully with water, acetone, and 2-propanol. To the water-dispersed Ni-ETT was added ethylene glycol (EG) at a volume ratio of 10:1 and the resulting mixture was sonicated for 20 min. The thermoelectric film was prepared on the glass substrate by drop-casting the water-dispersed Ni-ETT containing EG (50 μL). The substrate was heated at 70 °C to give a black film, which was further annealed at 210 °C for 30 min under atmospheric conditions.

## 4. Thermoelectric performance of Ni-ETT 2

**Table S1** Thermoelectric performance of the films of Ni-ETT **2** at room temperature

| Entry | Thickness [μm] | $\sigma$ [S cm$^{-1}$] | $S$ [μV K$^{-1}$] | $PF$ [μW m$^{-1}$ K$^{-2}$] |
|---|---|---|---|---|
| 1 | 5.3 | 52 | –79 | 33 |
| 2 | 5.8 | 54 | –76 | 31 |
| 3 | 3.7 | 63 | –65 | 27 |

## 5. Dynamic light scattering (DLS) analysis

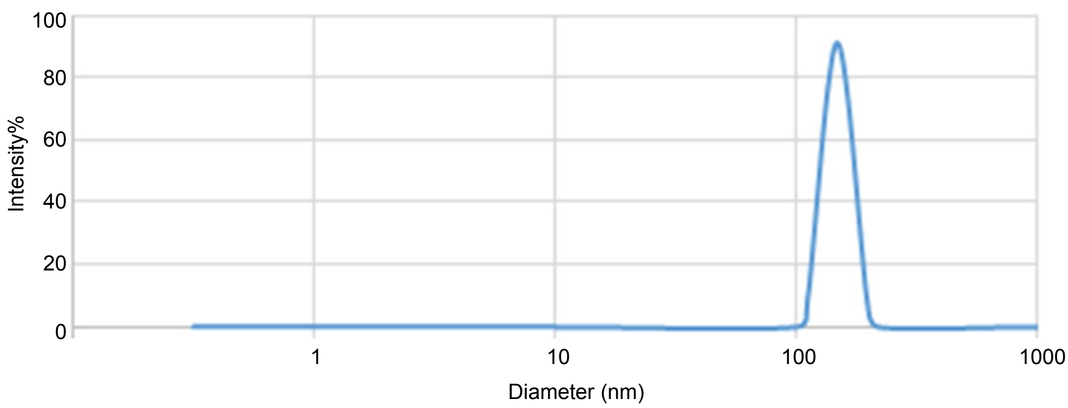



**Fig. S1** Dynamic light scattering (DLS) analysis of the aqueous dispersion of Ni-ETT **2**.

## 6. EDX analysis of the films of Ni-ETT 2

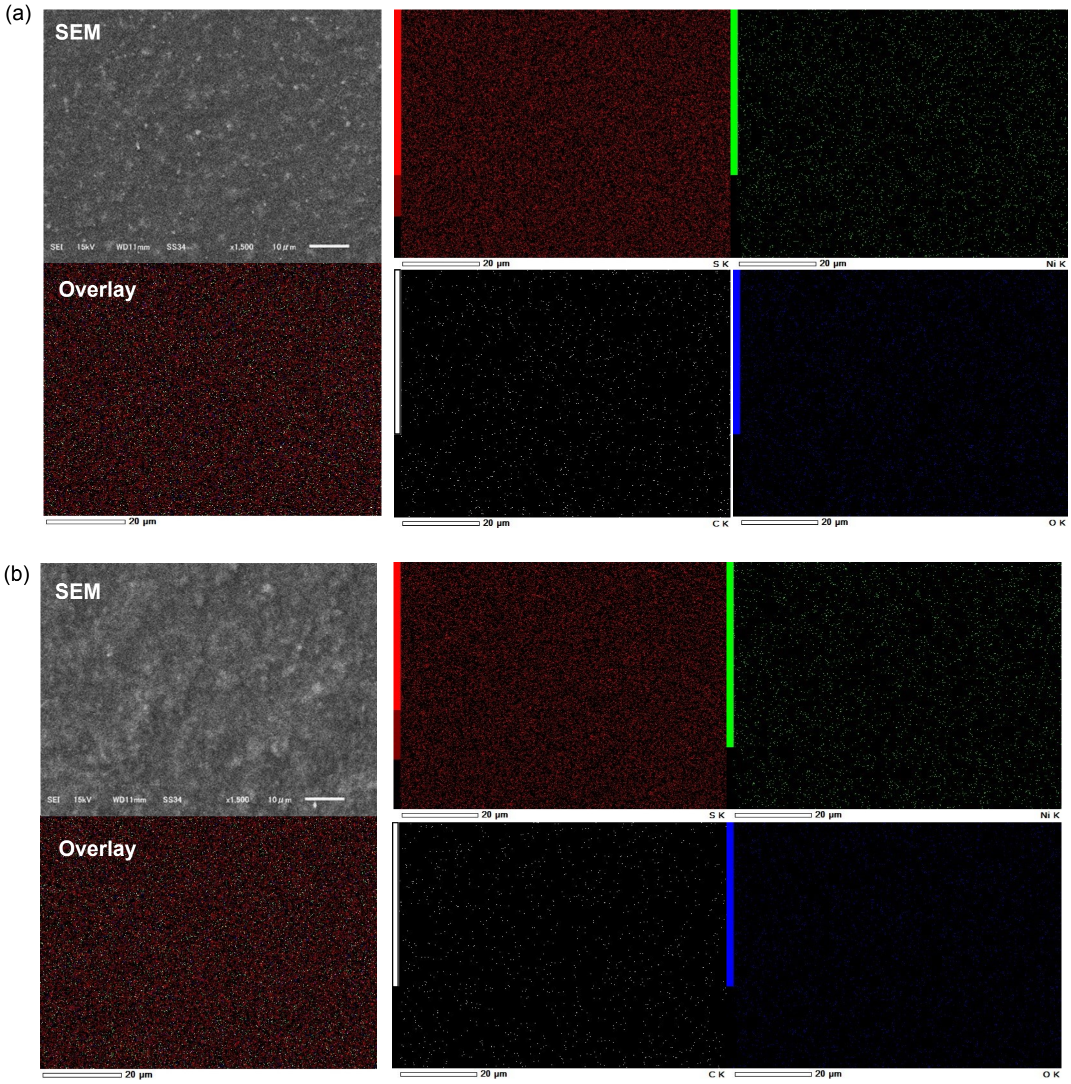



**Fig. S2** SEM images and EDX mappings for the films of Ni-ETT **2** prepared (a) with and (b) without EG as the additive. Individual element distributions are also shown (sulfur: red, nickel: green, carbon: white, and oxygen: blue).

**Table S2** EDX analysis for the films of Ni-ETT **2** prepared with or without EG

| **additive** | **C** (wt%) | **O** (wt%) | **S** (wt%) | **Ni** (wt%) |
|---|---|---|---|---|
| EG | 14.8 | 8.0 | 48.9 | 25.3 |
| – | 18.2 | 4.6 | 48.3 | 25.0 |

## 7. Air-stability of the thermoelectric performance

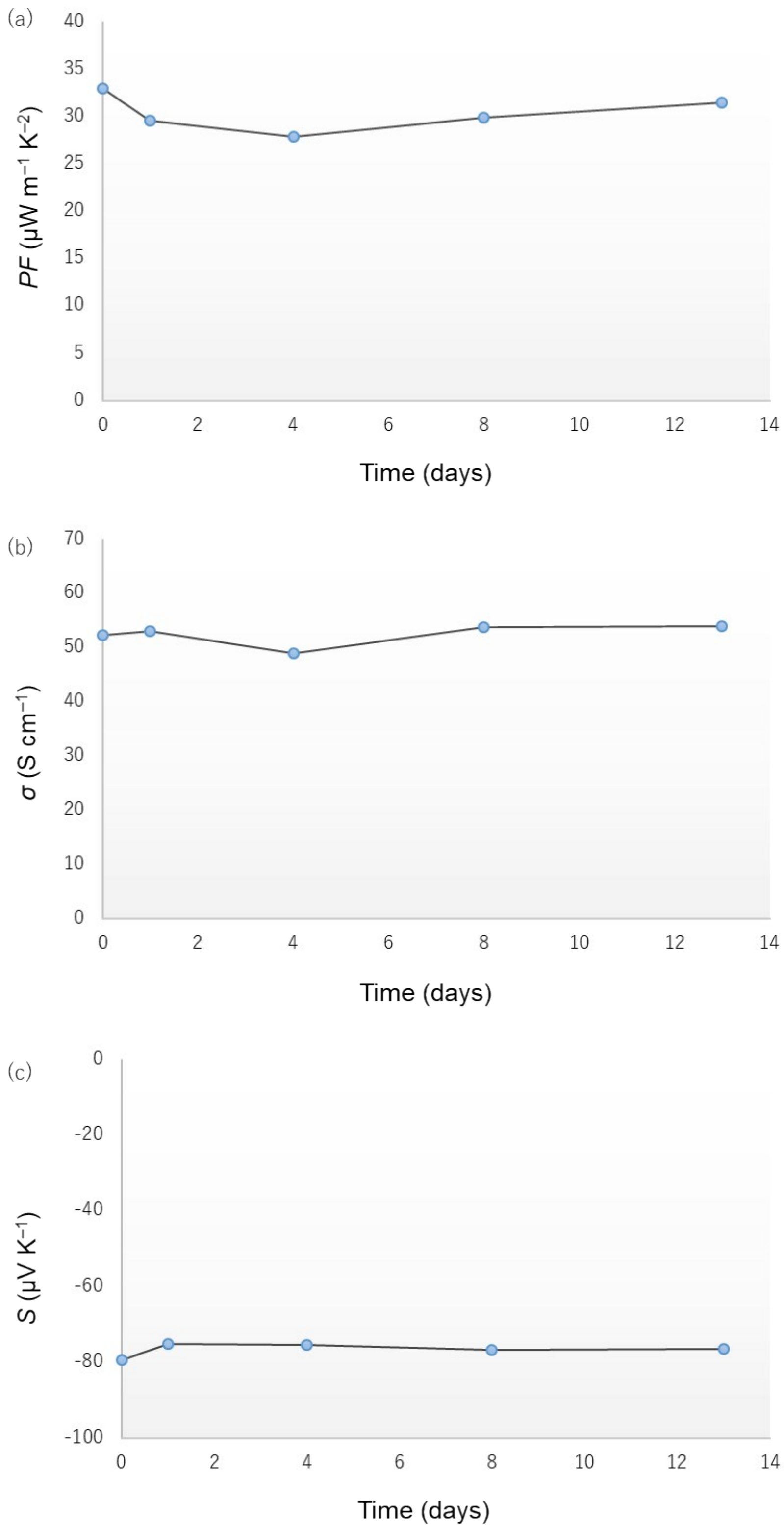



**Fig. S3** Air-stability of (a) power factor, (b) electrical conductivity, and (c) Seebeck coefficient of a film of Ni-ETT **2** under atmospheric conditions at room temperature.

## 8. GIWAXD measurements

Grazing incidence wide-angle X-ray diffraction (GIWAXD) measurements were performed on the BL40B2 beamline at the SPring-8 facility in Hyogo, Japan, using an incident X-ray wavelength ($\lambda$) of 0.1 nm and incidence angle of 0.12°. The incidence angle was selected to be between the critical angle of the thermoelectric film and the substrate. The scattering vector, $\mathbf{q} = (4\pi/\lambda) \sin \theta$, where $\theta$ is the Bragg angle, is defined as $2\pi(\mathbf{s}_1 - \mathbf{s}_0)$, where $\mathbf{s}_0$ is a vector parallel to the incident X-ray, $\mathbf{s}_1$ is the vector parallel to the diffracted X-ray, and $|\mathbf{s}_0| = |\mathbf{s}_1| = 1/\lambda$. Diffraction peaks from both in-plane and out-of-plane directions were detected with PILATUS3 2M (253.7 mm × 288.8 mm with a pixel size of 172 μm × 172 μm). The sample-to-IP detector distance was calibrated with silver behenate standard and fixed at 337 mm. Samples for the GIWAXD measurements were prepared by drop-casting onto a silicone substrate under the atmospheric conditions.

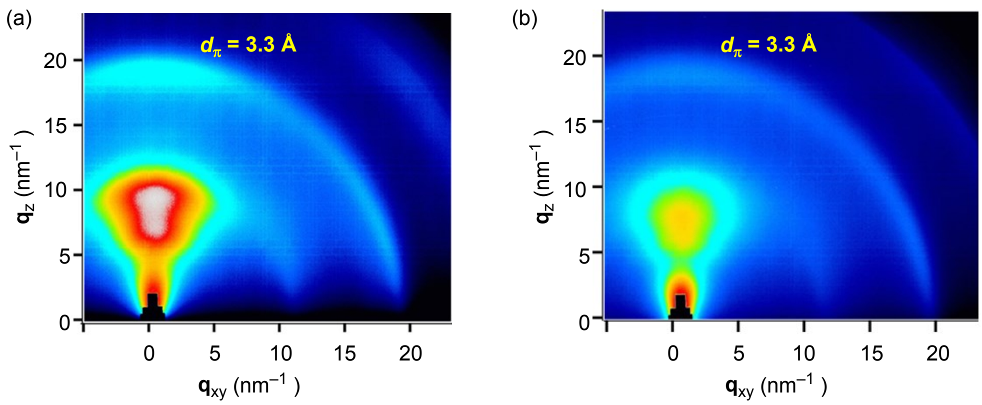



**Fig. S4** GIWAXD patterns of the films of Ni-ETT **2** fabricated on a silicone substrate (a) with and (b) without EG as the additive.

## 9. References


S1) A. K. Menon, R. M. W. Wolfe, S. R. Marder, J. R. Reynolds and S. K. Yee, *Adv. Funct. Mater.*, 2018, **28**, 1801620.

S2) M. Murata, S. Kaji, H. Nishimura, A. Wakamiya and Y. Murata, *Eur. J. Inorg. Chem.*, 2016, **2016**, 3228.