

Supplementary Information

**Thermoelectric power of band-filling controlled organic conductors,  $\beta'$ -(BEDT-TTF) $_3$ (CoCl $_4$ ) $_{2-x}$ (GaCl $_4$ ) $_x$**

*Yasuhiro Kiyota,<sup>a,\*</sup> Tadashi Kawamoto,<sup>a</sup> Hatsumi Mori,<sup>b</sup> and Takehiko Mori<sup>a,\*</sup>*

Corresponding Authors

\*E-mail: kiyota.y.aa@m.titech.ac.jp and mori.t.ae@m.titech.ac.jp

<sup>a</sup> Department of Materials Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

<sup>b</sup> The Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba 277-8581, Japan.

## Sample Preparation

Single crystals were prepared by electrocrystalization.<sup>1</sup> BEDT-TTF was placed in an H-cell together with tetrabutylammonium gallium tetrachloride and tetrabutylammonium cobalt tetrachloride, and dehydrated 1,1,2-trichloroethane was added under argon atmosphere. Samples of various compositions were obtained by changing the nominal anion ratio.<sup>2</sup> In the case of the parent compound, BEDT-TTF was placed in the presence of tetramethylammonium manganese tetrachloride in dehydrated benzonitrile.<sup>3</sup> After a current of  $1 \mu\text{A}$  was applied to platinum electrodes for about one week, black needle or plate crystals were obtained.

Several different crystal phases were obtained at the same time. The  $\beta'$ -phase crystals were distinguished from the black and small stick-like appearance. The typical size was as follows: length( $L$ )  $\sim 0.3$  mm, width( $W$ ) and height( $H$ )  $\sim 0.03$  mm. Crystal phases were determined from the lattice constants using an X-ray diffractometer: a RIGAKU R-AXIS RAPID II imaging plate with Cu-K $\alpha$  radiation from a rotation anode source with a confocal multilayer X-ray mirror (RIGAKU VM-spider,  $\lambda = 1.54187 \text{ \AA}$ ).

Since the composition potentially changes from crystal to crystal, the X-ray,  $\sigma$ ,  $S$ , and EPMA measurements were carried out using the same crystal.

## Electrical conductivity

Sample resistance ( $R$ ) was measured by the conventional four-probe technique from room temperature to lower temperatures. Applying an ac current, voltage measurement was carried out by a lock-in amplifier (Stanford Research Systems SR830). The measurement was continued down to the temperature at which the resistance becomes too large for this lock-in technique. This sometimes happened when the resistance jumped to some extent. The electrical resistivity ( $\rho$ ) and conductivity ( $\sigma$ ) were derived from the following equation.

$$\rho = R \frac{WH}{L} = \frac{1}{\sigma} \quad (1)$$

## Thermopower

Sample setting is illustrated in Fig. S1. The sample was attached to copper blocks via gold foils by carbon paste, and the copper blocks were alternately heated by applying voltages to the resistors to generate a temperature gradient  $\Delta T$  of less than 1 K.  $\Delta T$  was measured by an Au0.07% Fe vs. chromel thermocouple. The thermopower  $S = \Delta V / \Delta T$  was evaluated from the  $\Delta V$ - $\Delta T$  plot in the linear region using the average of the heating and cooling cycles.

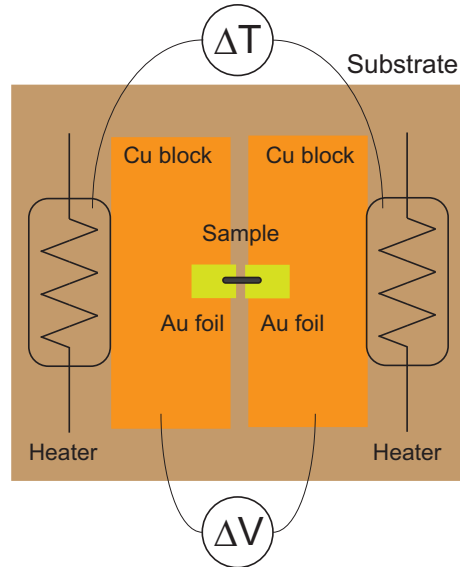


Fig. S1: An illustration of the sample stage for thermopower measurement.

## Electron Probe Micro Analyzer

EPMA measurement was performed on JEOL JXA-8200 to determine the composition after the electrical transport measurements. The sampling area was  $\sim 1 \mu\text{m}^2$  near the surface. The ratio between Co and Ga was measured at more than three positions, and the ratio was obtained from the average.

## Band Calculation

In order to explain the nontrivial behavior of thermopower, we have calculated the thermopower from the band structure.<sup>4,5</sup> The molecular orbital of a single BEDT-TTF molecule in  $\beta'$ -(BEDT-TTF)<sub>3</sub>(MnCl<sub>4</sub>)<sub>2</sub> was calculated.<sup>3</sup> Then, intermolecular overlap integrals of the highest occupied molecular orbital (HOMO) of the BEDT-TTF molecules were calculated as listed in Table 1. The band structure calculation was carried out based on the tight-binding method. For the thermopower calculation, the energies were calculated for  $100 \times 100$  mesh points in the  $k$ -space.

## References

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