Supporting information

Crystal Structure and Carrier Transport Properties of a New Semiconducting 2D Coordination Polymer with 3,5-Dimethylpiperidine Dithiocarbamate Ligand

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Experimental Section

Materials. A mononuclear metal complex, $Cu^{II}(3,5\text{-Dmpip-dtc})_2$ was prepared by a procedure similar to that in the literature.[1] The reagents were purchased from Tokyo Kasei Kogyo Co., Ltd., and Aldrich Chemical Co., Inc. All the chemicals were used without further purification.

Synthesis of $[Cu^{I}_4Cu^{II}I_4(Mo\text{-dtc})_2(CH_3CN)_2]_n$ (1). A 10 ml acetonitrile solution of $CuBr{\bullet}S(CH_3)_2$ (0.041 g, 0.2 mmol) was diluted with 10 ml acetone, and this solution was added to a 20 ml $CHCl_3$ solution of $Cu^{II}(3,5\text{-Dmpip-dtc})_2$ (0.041 g, 0.10 mmol). The reaction mixture was stirred for 5 min and then filtrated. The reaction mixture was filtrated, and the black single crystals suitable for X-ray diffraction were obtained from the mixture in a couple of days by recrystallization with hexane at 40 °C. Anal. Calcd for $[Cu^{I}_3Cu^{II}Br_3(3,5\text{-Dmpip-dtc})_2]_n$ ($C_{16}H_{28}Br_3Cu_4N_2S_4$); C, 22.07; H, 3.24; N,

3.22. Found: C, 22.05; H, 3.21; N, 3.26.

X-ray structure determination. X–ray diffraction measurement of a single crystal of **1** was carried out using a Rigaku Mercury70 diffractometer with graphite-monochromated Mo–Kα radiation. The data were collected at -153 ºC up to a maximum 2θ value of 55.0°. The crystal-to-detector distance was 44.91 mm. The linear absorption coefficient□ for Mo–K□radiation is 87.154 cm^{-1}. A numerical absorption correction was applied which resulted in transmission factors ranging from 0.303 to 0.418. The data were corrected for Lorentz and polarization effects. The structure was solved by direst methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 5565 observed reflections and 262 variable parameters. The crystal parameters and experimental details of data collection are summarized in Table S1. The atomic coordinates, anisotropic displacement parameters, selected bond length, and angles are given in Tables S2–S5.

Physical measurements. UV-vis spectra were monitored on a U-4100 UV/VIS/NIR Spectrophotometer (HITACHI). The impedance measurements were carried out on a pellet of the powder sample sandwiched by 13 mm diameter brass electrodes with a 6440B (Wayne Kerr Electronics) Series Precision Component Analyzer in a frequency range 100 to 3 MHz. Magnetic properties were investigated with a SQUID magnetometer (Quantum Design). For the FP–TRMC measurement, a Nd: YAG laser (third harmonic generation, THG; 355 nm; Spectra Physics, INDY–HG) was used as an excitation light source to generate photo–induced charge carriers. The power density of the laser was tuned at 6.1 mJ cm^{-2} $pulse^{-1}$ (5.6×10^{15} photons cm^{-2} $pulse^{-1}$), and the polarization of the laser pulses was isotropic. Transmittance of the pulses for the samples was measured by PE25 power meter of Ophir Optoronics Ltd. and checked by a spectrophotometer of JASCO V-570. The microwave frequency and power were set at ~ 9.1 GHz and 3 mW, respectively. The conductivity transients in the material were monitored at room temperature.

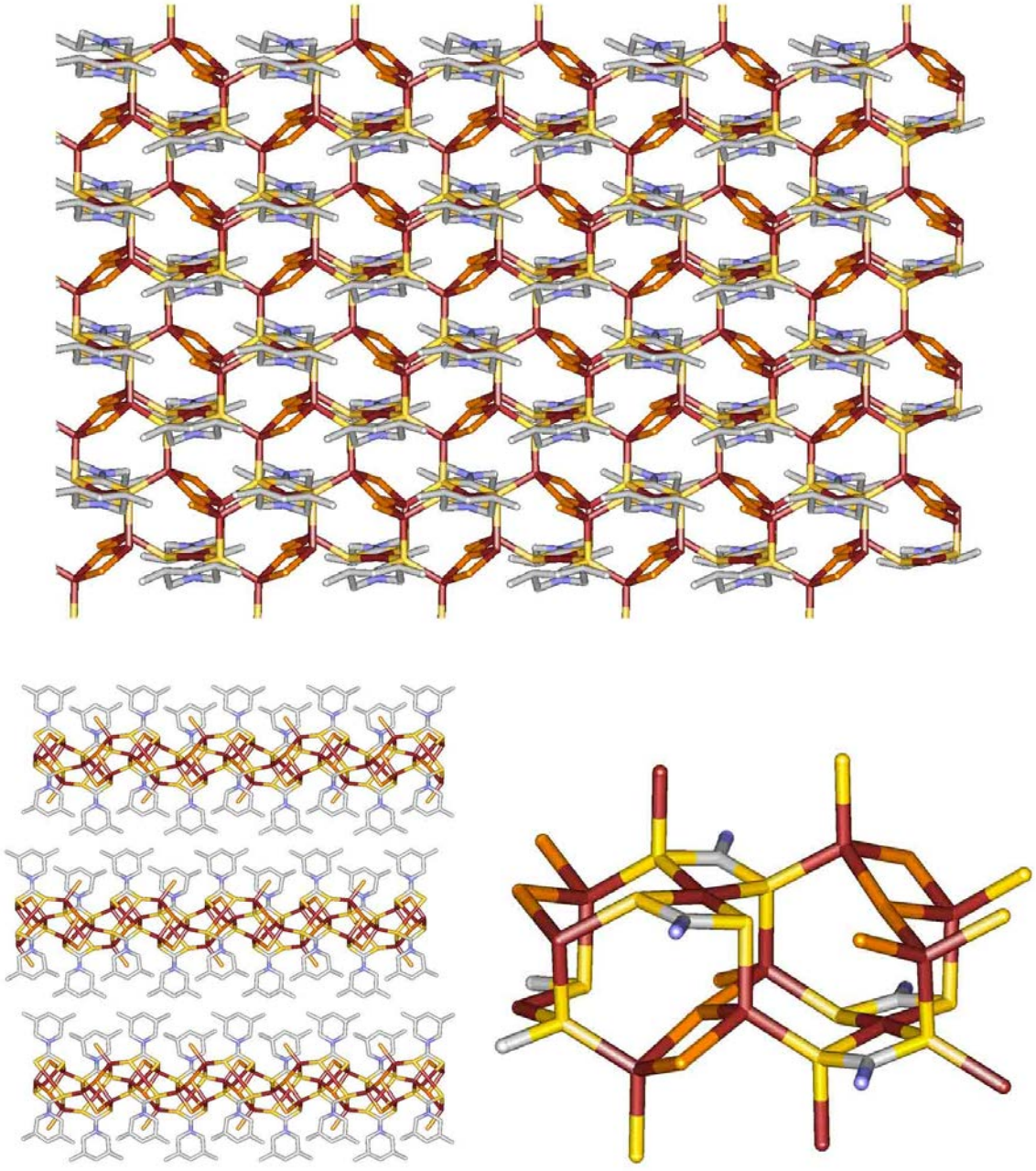

Figure S1. 2D sheet structure of **1** viewed along *c*-axis (a) and *a*-axis (b) for complex **1**: Cu, red-brown; Br, orange; S, yellow; C, white; and N, blue. Hydrogen atoms are omitted for clarity. (c) A unit including two $Cu^{II}(3,5\text{-Dmpip-dtc})_2$ units, where 3,5-dimethylpiperidyl groups are omitted for clarity.

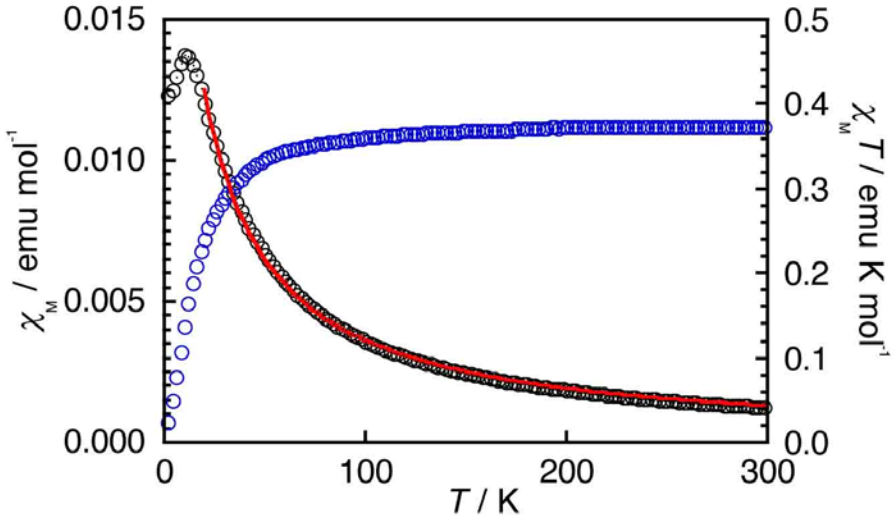

Figure S2. The magnetic susceptibility of a polycrystalline sample of **1** was measured using a SQUID magnetometer at 10 kOe in the temperature range of 2–300K. The effective magnetic moment at 300 K is 1.74 BM, which was comparable to the expected value (1.73 BM) for the copper(II) ions (S = 1/2) in a mononuclear Cu^{II}(3,5-Dmpip-dtc)$_2$ unit. The χ_M values increase with decreasing temperature, reaching a maximum of 0.013443 emu•mol^{-1} at 10 K, and then the values rapidly decreased, which indicated the existence of relatively strong antiferromagnetic interactions between the unpaired electrons in the 2D sheet. The χ_MT values decrease with decreasing temperature at low temperature region. The data in the range of 20–300 K follow the Curie–Weiss law with a Weiss constant (θ = –12.6 K).

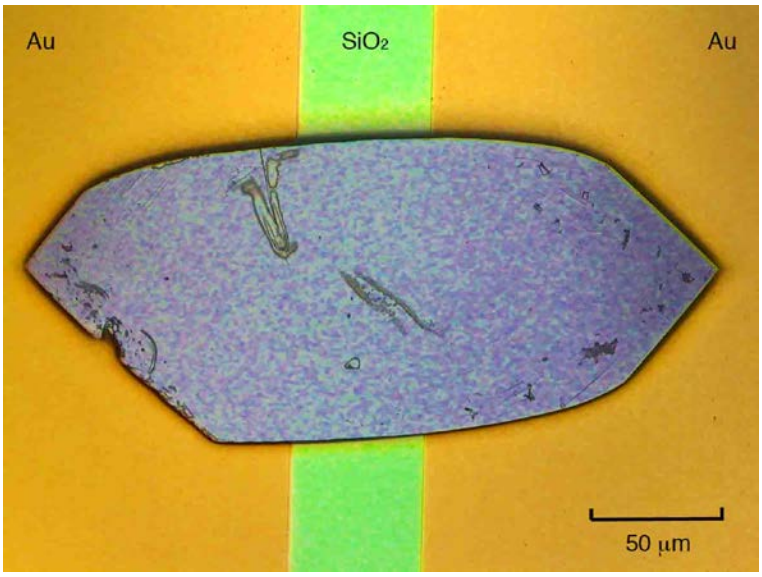

Figure S3. Micrograph of single crystal of **1** on Au electrodes fabricated on SiO_2 substrate, measured by a laser microscope (KEYENCE Co., VK-X200), where the interelectrode gap is 50 μm and the thickness of the single crystal is 6 μm. The DC resistivity was measured with the single crystal covered by gold paste with the interelectrode gap of 50 μm. The estimated conductivity of the single crystal at room temperature is 2.8×10^{-7} S cm^{-1}, which is slightly larger than the value of $\sigma_{300K} = 6.5 \times 10^{-8}$ S cm^{-1} estimated by the impedance measurements.

Table S1. Crystal Data and Structure Refinement Parameters for **1**.

Empirical Formula	$C_{16}H_{28}Br_3Cu_4N_2S_4$
Formula Weight	870.55
Crystal System	monoclinic
Lattice Parameters	a = 7.823(4) Å
	b = 9.518(5) Å
	c = 33.16(2) Å
	β = 98.469(7) º
	V = 2442(2) Å^3
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	2.368 g/cm^3
F_{000}	1692.00
μ(MoKα)	87.117 cm^{-1}
No. Observations (All reflections)	5565
No. Variables	262
Reflection/Parameter Ratio	21.24
Residuals: R_1 ($I > 2.00\ \sigma(I)$) [a]	0.0526
Residuals: wR_2 (All reflections) [b]	0.0981
Goodness of Fit Indicator	1.130
Max Shift/Error in Final Cycle	0.004
Maximum peak in Final Diff. Map	0.87 e/Å^3
Minimum peak in Final Diff. Map	-0.91 e/Å^3

[a] $R_1 = \Sigma\ ||Fo| - |Fc|| / \Sigma\ |Fo|$

[b] $wR_2 = [\ \Sigma\ (\ w\ (Fo^2 - Fc^2)^2\ )/\ \Sigma\ w(Fo^2)^2]^{1/2}$

References

1. Ngo, C.; Banger, K. K.; DelaRosa, M. J.; Toscano, P. J.; Welch, J. T. *Polyhedron* **2003**, *22*, 1575.

2. SHELX97: Sheldrick, G. M. *Acta. Cryst.* 2008, *A64*, 112-122.

3. Least Squares function minimized: (SHELXL97).

$\Sigma w(|F_o| - |F_c|)^2$ where w = least Squares weights.