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Supporting information

A New Semiconducting 1D Cu(I)-Cu(II) Mixed-Valence Coordination Polymer with Cu(II) Dimethylpiperidine-dithiocarbamate and a tetranuclear Cu(I)-Br Cluster Unit

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Experimental Section

Materials. A mononuclear metal complex, $Cu^{II}(dmpip\text{-}dtc)_2$ 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 $[Cu^I_4Cu^{II}Br_4(dmpip\text{-}dtc)_2(C_2H_5CN)]_n$ (1): Coordination Polymer **1** was synthesized by reacting $Cu^{II}(dmpip\text{-}dtc)_2$ (0.044 g, 0.1 mmol) in a CH_2Cl_2 solution (20 mL) with $Cu^IBr{\bullet}S(CH_3)_2$ (0.082 g, 0.4 mmol) in a 4:1 acetone/acetonitrile solution (20 mL). The reaction mixture was filtered and black single crystals suitable for X-ray diffraction were obtained from the filtrate by recrystallization with hexane at room temperature (over a few days). Anal. Calcd for $[Cu^I_4Cu^{II}Br_4(dmpip\text{-}dtc)_2(C_2H_5CN)]_n$ (for $C_{10}H_{17}Br_2Cu_{2.5}N_2S_2$): C, 21.92; H, 3.13; N, 5.11. Found: C, 21.55; H, 3.13; N, 4.88.

Crystal structure determination: Data collection was performed on a Rigaku Saturn724 diffractometer using graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation. The data were collected at a temperature of -173ºC to a maximum 2θ value of 55.0□. A total of 1080 oscillation images were collected. A sweep of data was done using ω scans from -110.0 to 70.0□ in 0.50□ step at χ = 45º and ϕ = 0.0º. The exposure rate was 20.0 [sec./º]. The detector swing angle was -20.15º. A second sweep was performed using ω scans from -110.0 to 70.0º in 0.50º step at χ = 45º and ϕ = 90.0º. The exposure rate was 20.0 [sec./º]. The detector swing angle was -20.15º. Another sweep was parformed using w scans from -110.0 to 70.0º in 0.50º step, at χ = 45.0º and ϕ = 180.0º. The exposure rate was 20.0 [sec./º]. The detector swing angle was -20.15º. The crystal-to-detector distance was 44.93 mm. Readout was performed in the 0.141 mm pixel mode. Of the 9958 reflections were collected, where 3777 were unique (R_{int} = 0.0315). Data were collected and processed using CrystalClear (Rigaku).[2] The linear absorption coefficient, μ, for Mo-Kα radiation is 81.783 cm^{-1}. An empirical absorption correction was applied which relulted in transmission factors ranging from 0.028 to 0.038. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[3] 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[4] on F^2 was based on 3777 observed reflections and 169 variable parameters. All calculations were performed using the CrystalStructure, crystallographic software package. CCDC- 1585395 for **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical measurements : UV–vis–NIR spectra were recorded using a U–4100 UV/VIS/NIR Spectrophotometer (HITACHI). The impedance measurement of a powder-pressed pellet sample sandwiched by brass electrodes (diameter, 13 mm) was carried out using a 6440B (Wayne Kerr Electronics) series precision component analyzer in the frequency range 100 Hz–3 MHz. DC conductivity at room temperature was measured with an ADVANTEST R8340 ultra high resistance meter. Magnetic properties were investigated with a SQUID magnetometer (Quantum Design). Diamagnetic corrections were estimated from Pascal's constants. Photoemission yield spectra were measured using a Surface Analyzer AC-2 (RIKEN KEIKI Co.) at Japan Institute of Science and Technology (JAIST).

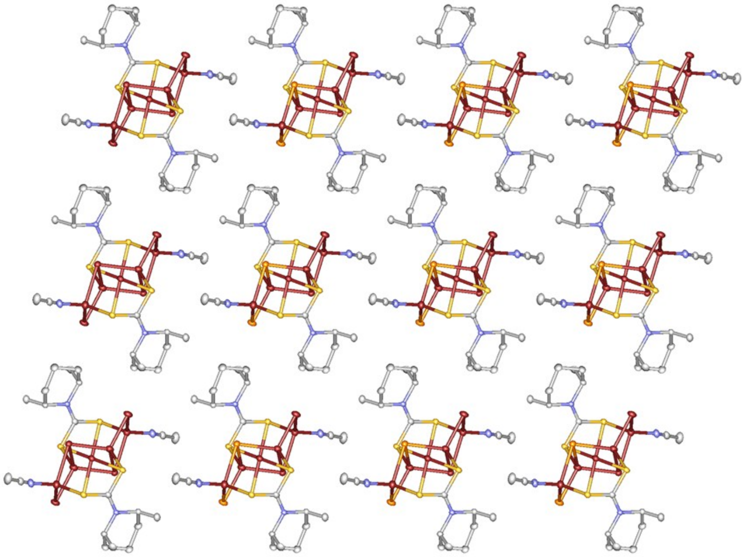

Figure S1. Packing diagram of the mixed-valence Cu(I)-Cu(II) coordination polymer viewed along the *a*-axis. Hydrogen atoms are omitted.

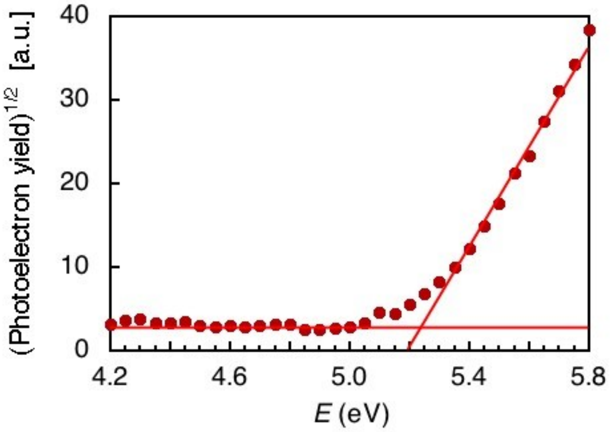

Figure S2. Photoemission yield curves of $[Cu^{I}_4Cu^{II}Br_4(2,6\text{-dmPip-dtc})_2(CH_3CN)_2]_n$ under ambient conditions. The estimated energy levels of the HOMO of $[Cu^{I}_4Cu^{II}Br_4(2,6\text{-dmPip-dtc})_2(CH_3CN)_2]_n$ is –5.23 eV.

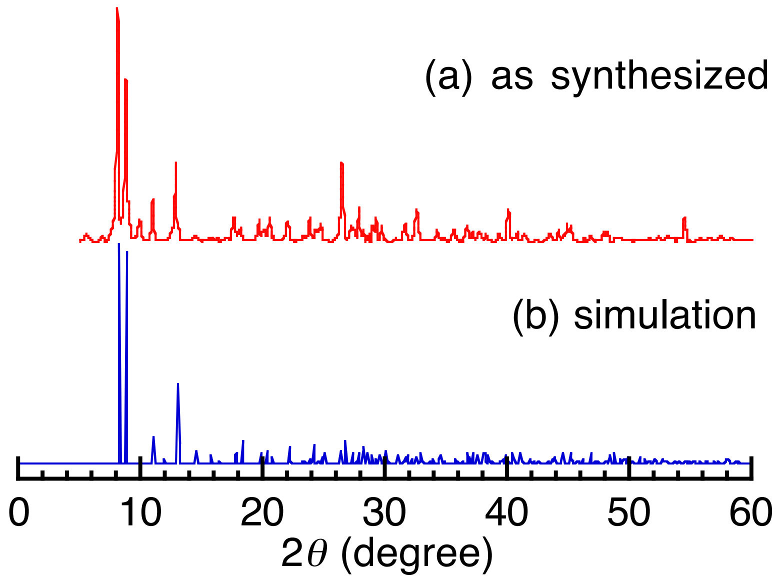

Figure S3. Comparison of XRPD patterns of **1** (a) with the respective calculated ones form the single-crystal data (b).

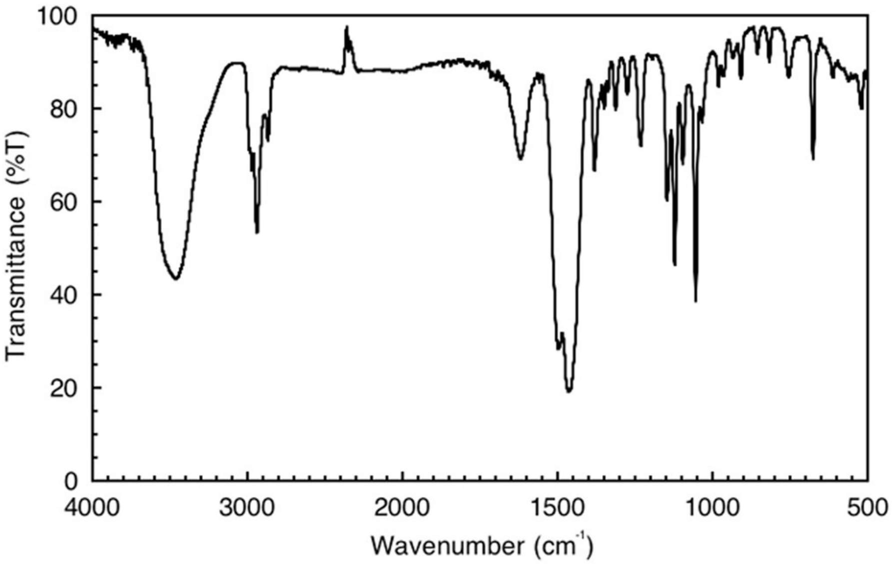

Figure S4. IR spectrum of **1**.

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

Empirical Formula	$C_{20}H_{34}Br_4Cu_5N_2S_4$
Formula Weight	1096.10
Crystal System	triclinic
Lattice Parameters	a = 7.6203(9) Å
	b = 10.1947(13) Å
	c = 11.2268(11) Å
	α = 79.856(4)
	β = 77.927(4)
	γ = 83.881(4)
	V = 837.35(17) Å^3
Space Group	P-1 (#2)
Z value	1
D_{calc}	2.174 g/cm^3
F_{000}	531.00
μ(MoKα)	81.783 cm^{-1}
No. Observations (All reflections)	3777
No. Variables	169
Reflection/Parameter Ratio	22.35
Residuals: R ($I > 2.00\ \sigma(I)$)[a]	0.0191
Residuals: wR_2 (All reflections)[b]	0.0455
Goodness of Fit Indicator	0.947
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	0.58 e/Å^3
Minimum peak in Final Diff. Map	-0.46 e/Å^3

[a] $R = \Sigma\ ||F_o| - |F_c|| / \Sigma\ |F_o|$

[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$

Table S2. Estimated parameters (R_1, CPE$_1$-A, CPE$_1$-α, R_2, CPE$_2$-A and CPE$_2$-α) by the fittings to the impedance data of $[\mathrm{Cu^I}_4\mathrm{Cu^{II}Br_4(2,6\text{-}dmPip\text{-}dtc)_2(CH_3CN)_2}]_n$ at different temperatures with the equivalent circuit in the inset of Figure 7 (a) using ZView software, where R_1 and R_2 are the resistances, CPE$_1$-A and CPE$_2$-A are the parameters concerned with the capacitances, and CPE$_1$-α and CPE$_2$-α are corresponding to the dispersion of the relaxation time of the bulk sample and electrode interface, respectively; the CPE impedance is given by the relationship: $Z_{\mathrm{CPE}} = 1/[A(j\omega)^{\alpha}]$, and for $\alpha = 1$ the CPE describes an ideal capacitor ($A = C$).

T (K)	R_1 (Ω)	CPE$_1$-A	CPE$_1$-α	R_2 (Ω)	CPE$_2$-A	CPE$_2$-α
320	85007	6.90E-10	0.927	1.33E+08	1.03E-10	0.913
325	47515	5.24E-10	0.973	1.08E+08	1.12E-10	0.905
330	40967	5.81E-10	0.965	9.49E+07	1.15E-10	0.905
335	31728	5.55E-10	0.971	7.40E+07	1.17E-10	0.905
340	20311	5.04E-10	1.000	6.97E+07	1.25E-10	0.900
345	17914	4.79E-10	1.000	5.85E+07	1.26E-10	0.900
350	14889	5.25E-10	0.998	5.36E+07	1.30E-10	0.899
355	11466	5.99E-10	1.000	4.62E+07	1.34E-10	0.897
360	9119	6.68E-10	1.000	4.23E+07	1.38E-10	0.896
365	6990	8.07E-10	1.000	3.78E+07	1.43E-10	0.894
370	4433	1.19E-09	1.000	3.45E+07	1.50E-10	0.890

Table S3. Calculated electric conductivity σ and dielectric constant ε' from the parameters in Table S1 by using the following relationships: $\sigma = 1/R \times d/S$ and $\varepsilon' \approx \mathrm{A}/\varepsilon_0 \times d/S$, where d is the thickness of the pellet sample, S is the electrode area and ε_0 is the permittivity of vacuum, 8.854×10^{-12} F/m. The σ_1 and σ_2 values are corresponding to the electric conductivity of the bulk sample and electrode interface, respectively.

T (K)	σ_1 (S/cm)	ε_1'	σ_2 (S/cm)	ε_2'
320	1.19E-07	78.5	7.58E-11	11.72

325	2.12E-07	59.6	9.33E-11	12.74
330	2.46E-07	66.1	1.06E-10	13.09
335	3.18E-07	63.1	1.36E-10	13.31
340	4.96E-07	57.4	1.45E-10	14.22
345	5.62E-07	54.5	1.72E-10	14.34
350	6.77E-07	59.7	1.88E-10	14.79
355	8.79E-07	68.2	2.18E-10	15.25
360	1.10E-06	76.0	2.38E-10	15.70
365	1.44E-06	91.8	2.67E-10	16.27
370	2.27E-06	135.4	2.92E-10	17.07

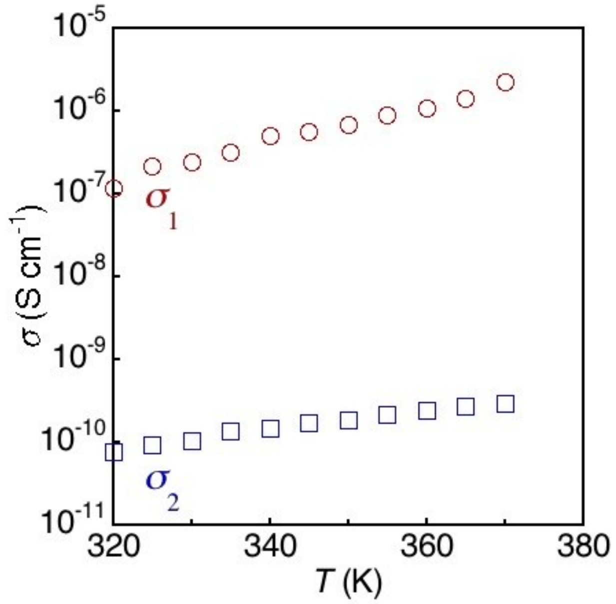

Figure S5. Temperature dependence of the electric conductivity of $[\mathrm{Cu^{I}_4Cu^{II}Br_4(2,6\text{-}dmPip\text{-}dtc)_2(CH_3CN)_2}]_n$ estimated in Table S3. The activation energy, $E_a = 0.544$ eV, for the bulk sample is estimated by the fitting to the σ_1 values with the following relation: $\sigma_1 = \sigma_0\exp(-E_a/kT)$, where k is the Boltzmann constant.

References

1. Ngo, C.; Banger, K. K.; DelaRosa, M. J.; Toscano, P. J.; Welch, J. T. *Polyhedron* **2003**, *22*, 1575.
2. CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2015). Tokyo 196-8666, Japan.
3. SIR2008: Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. Siliqi, D. and Spagna R. (2007). J. Appl. Cryst. 40, 609-613.
4. Least Squares function minimized: (SHELXL97).
   $\Sigma w(|F_o| - |F_c|)^2$ where w = least Squares weights.