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Crystal structure and carrier transport properties of a new semiconducting 2D coordination polymer with a 3,5-dimethylpiperidine dithiocarbamate ligand† ‡

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A novel mixed-valence Cu(I)–Cu(II) coordination polymer with an infinite two-dimensional structure, $[Cu_3{}^{I}Cu^{II}Br_3(3,5\text{-Dmpip-dtc})_2]_n$ (3,5-Dmpip-dtc$^-$ = 3,5-dimethylpiperidine dithiocarbamate), was prepared, and its structure was characterized by X-ray diffraction. It shows semiconducting behavior with a relatively small activation energy and high carrier mobility, which were investigated using impedance spectroscopy and flash photolysis time-resolved microwave conductivity measurements, respectively.

Coordination polymers have attracted a considerable amount of interest as a new class of organic–inorganic hybrid materials, owing to their unique infinite structures and electronic states formed by the combination of metal ions with versatile coordination architectures and a variety of organic bridging ligands. Conducting coordination polymers[1] are of particular importance and interest both in terms of fundamental knowledge[2] and for a variety of technological applications in novel optoelectronic devices such as electroluminescent (EL) devices, field-effect transistors (FETs), and solar cells.[3] Dithiocarbamate derivatives are promising bridging ligands for the formation of coordination polymers that have potential as conducting materials,[4] because the overlap of the d-orbitals and HOMOs and/or LUMOs of the ligands in Cu(II)–dithiocarbamate coordination polymers causes the formation of narrow conduction and/or valence bands, which induce strong magnetic interactions and conducting properties. For example, the three-dimensional coordination polymer $\{[Cu_4{}^{I}Cu_2{}^{II}Br_4(\text{Pyr-dtc})_4]\cdot CHCl_3\}_n$ (Pyr-dtc$^-$ = pyrrolidine dithiocarbamate) shows a relatively high carrier mobility ($\Sigma\mu$ = 0.4 cm^2 V^{-1} s^{-1}),[4b] which is comparable to those of the organic semiconductors used in devices, such as P3HT (0.12 cm^2 V^{-1} s^{-1}),[5a] MEH-PPV (0.43 cm^2 V^{-1} s^{-1}),[5b] and pentacene (>0.7 cm^2 V^{-1} s^{-1}).[5c] However, conductive coordination polymers have not been studied in as much detail as organic semiconductors, although coordination polymers, which are a class of organic–inorganic hybrid materials, have many advantages as new semiconducting materials in terms of their diversity, designability, and possibilities as new functional materials. In particular, reports on the carrier mobilities of coordination polymers are quite limited,[4b,6] despite the fact that carrier mobility is an important parameter for the design of new optoelectronic devices based on semiconducting coordination polymers. Therefore, we are focusing on the creation of new semiconducting coordination polymers based on dithiocarbamate derivatives and the clarification of their carrier transport properties by using impedance measurements and flash photolysis time-resolved microwave conductivity (FP-TRMC) measurements. In this communication, we report a new mixed-valence coordination polymer containing a dithiocarbamate ligand and Br anions, $[Cu_3{}^{I}Cu^{II}Br_3(3,5\text{-Dmpip-dtc})_2]_n$ (**1**) (3,5-Dmpip-dtc$^-$ = 3,5-dimethylpiperidine dithiocarbamate), showing semiconducting properties with a relatively small activation energy and high carrier mobility in a new 2D coordination network.

Complex **1** was synthesized through the reaction of a $CHCl_3$ solution of $Cu^{II}(3,5\text{-Dmpip-dtc})_2$ with an acetone–acetonitrile solution of $Cu^{I}Br\cdot S(CH_3)_2$. The reaction mixture was filtered, and 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.

Single-crystal X-ray analysis of complex **1** reveals the formation of a coordination polymer $[Cu_4Br_3(3,5\text{-Dmpip-dtc})_2]_n$ having an infinite 2D sheet structure. The asymmetric unit of the coordination polymer **1** consists of four crystallographically independent copper ions, two 3,5-Dmpip-dtc$^-$ ligands, and three bromide anions (Fig. 1a). The mononuclear copper units, Cu^{II}(3,5-Dmpip-dtc), are connected by a trinuclear Cu unit of Cu_3Br_3 consisting of three tetrahedral copper ions (Cu(2), Cu(3), and Cu(4)), two bridging bromide ions (Br(1) and Br(2)), and one terminal bromide anion (Br(3)), forming an infinite 2D sheet, as shown in Fig. 1b. The copper ion of the mononuclear unit, Cu(1), has a square-planar coordination geometry wherein the 3,5-Dmpip-dtc$^-$ ligands coordinate with the copper ion to form a four-membered chelate ring. Usually, the oxidation states of Cu complexes with dithiocarbamate ligands can be determined from

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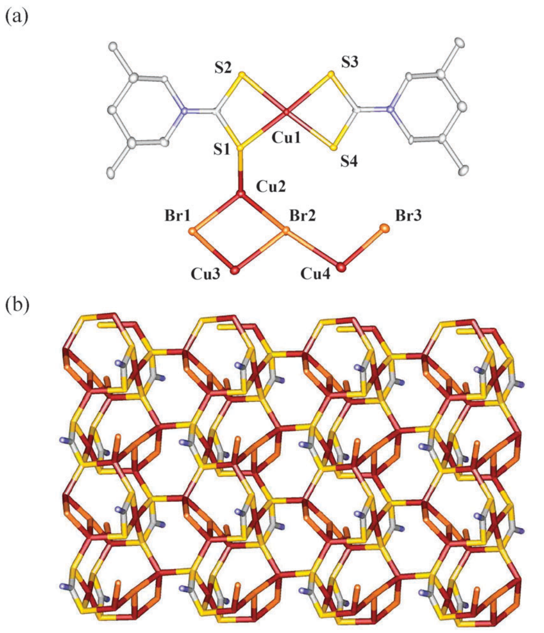

Fig. 1 (a) Asymmetric unit of **1** (hydrogen atoms are omitted for clarity). (b) 2D sheet structure of **1** viewed along the *c*-axis; 3,5-dimethylpiperidyl groups are omitted for clarity: Cu, red-brown; Br, orange; S, yellow; C, white; and N, blue.

the Cu–S distances. In the mononuclear Cu(3,5-Dmpip-dtc)$_2$ unit of the coordination polymer **1**, the average Cu–S distance (2.317(2) Å) is similar to the reported average Cu(II)–S distances in Cu(II)–dithiocarbamate complexes such as Cu^{II}(Et$_2$dtc)$_2$ (2.312(1) Å), Cu(i-Pr$_2$dtc)$_2$ (2.2884(7) Å) and Cu^{II}(*n*-Bu$_2$dtc)$_2$ (2.308(1) Å).[7] The Cu(2), Cu(3), and Cu(4) ions in the trinuclear units have distorted tetrahedral coordination geometries, which are typical for Cu(I) ions. On the basis of its charge neutrality, it is concluded that complex **1** is in a mixed-valence state and has the chemical formula [Cu$_3^I$Cu^{II}Br$_3$(3,5-Dmpip-dtc)$_2$]$_n$.

Fig. 2a shows the diffuse-reflection spectra converted from diffusion-reflectance (R) using the Kubelka–Munk function: $f(R) = (1 - R)^2/2R$.[8] The large absorption bands of the mononuclear complex Cu^{II}(3,5-Dmpip-dtc)$_2$ are attributed to a ligand-to-metal charge transfer (MLCT) process and the transition of the d-electron of the copper(II) ion, wherein the absorption is enhanced by the mixing of the d-orbitals of the copper(II) ion and the HOMOs of the dithiocarbamate ligands. The coordination polymer **1** exhibits a broad absorption in the UV to NIR region, which may be due to the d–d transition of the Cu(II) ion. For the determination of the HOMO–LUMO gaps (E_g) of Cu^{II}(3,5-Dmpip-dtc)$_2$ and **1**, the Kubelka–Munk plots of $(f(R)\cdot E)^{1/2}$ *versus* E were employed (Fig. 2b). E_g corresponds to the intersection point between the baseline along the energy axis and a line extrapolated from the linear portion of the threshold. Thus, the E_g values of Cu^{II}(3,5-Dmpip-dtc)$_2$ and **1** were determined to be 1.25 and 1.06 eV, respectively, indicating that the decrease in E_g for the coordination polymer **1** is due to the formation of the energy band structure based on the overlap of the HOMOs and/or LUMOs in the infinite 2D sheet.

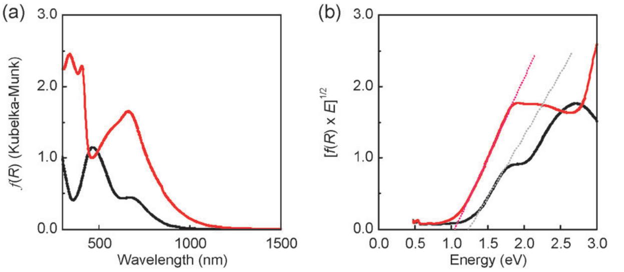

Fig. 2 (a) Diffuse-reflection spectra of mononuclear complex Cu^{II}(3,5-Dmpip-dtc)$_2$ and **1** (0.01 mmol) doped in MgO powder (80 mg) obtained through Kubelka–Munk analysis of reflectance spectra. (b) Plot of modified Kubelka–Munk function *versus* energy of exciting light.

Complex impedance spectroscopy ($Z^* = Z' - jZ''$, where $j = (-1)^{1/2}$) gives the electrical conductive properties of materials as a function of temperature and frequency.[9] The impedance measurements were performed using a pressed powder pellet sample sandwiched by brass electrodes (diameter: 13 mm); the thickness of the pellet sample of **1** was 0.357 mm. Fig. 3a shows the complex impedance spectra over a wide range of frequencies in the temperature range 300–350 K. In these plots, parts of semicircular arcs are seen, and the diameters of curvature decrease with increasing temperature; this means that this complex has typical semiconducting properties, *i.e.*, a negative temperature coefficient of resistance (NTCR).

In general, the complex modulus spectrum ($M^* = M' + jM'' = 1/\varepsilon^* = j\omega C_0 Z^*$, where ε^* is the complex dielectric permittivity, $\omega = 2\pi f_r$ (f_r = resonance frequency), and C_0 is the vacuum capacitance of the circuit elements) shows a marked change in its shape with an increase in temperature, indicating a probable change in the capacitance values of materials as a function of temperature. Fig. 3b shows the complex electric modulus spectra of the coordination polymer **1** at different temperatures. Depressed semicircular arcs are observed in the high-frequency region (right arcs) and parts of semicircular arcs are observed in the low-frequency region (left arcs). The asymmetrical depressed semicircles in the high-frequency region indicate the existence of several components having different resistances and capacitances, and the parts of semicircular arcs in the low-frequency region are derived from the contact resistivity at the electrode interface. The diameters of the right arcs did not change with temperature, which implies a

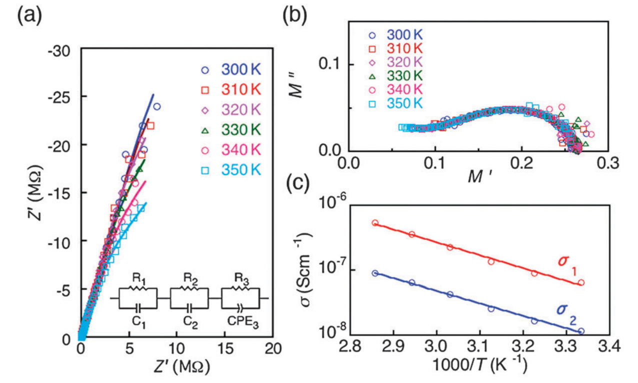

Fig. 3 (a) Complex impedance Z'–Z'' plots of **1** at selected temperatures. The solid lines represent the fits using the equivalent circuit shown in the inset. (b) Complex modulus plots of **1** at selected temperatures. (c) Arrhenius plots of DC conductivities σ_1 (bulk) and σ_2 (grain boundary) estimated by fitting to the equivalent circuit (shown in the inset of (a)), against inverse temperatures.

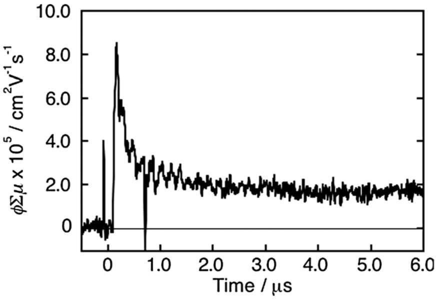

Fig. 4 Transient conductivity signal of $\phi\Sigma\mu$ obtained by FR-TRMC measurements under 355 nm laser pulse excitation at 6.1 mJ cm^{-2}.

temperature-independent capacitance and indicates conductivity relaxation, suggesting impedance behavior in this system.

To distinguish the parameters of bulk conductivity from the total AC conductivity of complex **1**, we used the equivalent circuit model (Fig. 1a) of the ZView software,[10] where the equivalent circuit consisted of three resistances (R_1, R_2, and R_3), two capacitances (C_1 and C_2), and one constant phase element (CPE3); the R_1–C_1, R_2–C_2, and R_3–CPE$_3$ parallel circuits represent the resistances and capacitances of the bulk sample, grain boundary, and electrode interfaces, respectively. The DC conductivities of the bulk sample and grain boundary were calculated using R_1 and R_2. The activation energies were estimated from the variations in σ_{dc} as a function of temperature (Fig. 3c) using the relation $\sigma_{dc} = \sigma_0\exp(-E_a/kT)$. The conductivities of the bulk sample and grain boundary at 300 K were 6.5×10^{-8} and 1.2×10^{-8} S cm^{-1}, respectively, and the estimated activation energies were 0.39 and 0.38 eV, respectively, which were smaller than those of 1D coordination polymers $[Cu_2{}^{I}Cu^{II}X_2(Hm\text{-}dtc)_2(CH_3CN)_2]_n$ (E_a = 0.56 eV (X = Br$^-$); E_a = 0.48 eV (X = I$^-$)) and larger than that of the 3D coordination polymer $\{[Cu_4{}^{I}Cu_2{}^{II}Br_4(Pyr\text{-}dtc)_4]\cdot CHCl_3\}_n$ (E_a = 0.29 eV (bulk)) containing dithiocarbamate ligands.

In order to estimate the carrier mobility of the coordination polymer **1**, we performed FP-TRMC measurements,[11] the results of which provided information on the behaviors of mobile charge carriers over a short distance (<10 nm) in the bulk sample. The transient conductivity signal of $\phi\Sigma\mu$ obtained from the FP-TRMC measurements upon exposure to a 355 nm laser is shown in Fig. 4; the transient signal consisting of the photocarrier generation yield (quantum efficiency) and the sum of the mobilities of negative and positive carriers is related to the transient photoconductivity $\Delta\sigma = eN\phi\Sigma\mu$, where e and N are the elementary charge of an electron and the number of absorbed photons per unit volume, respectively. The carrier mobility $\Sigma\mu$ was estimated to be $\approx$0.2 cm^2 V^{-1} s^{-1} with a maximum transient conductivity of 9.0×10^{-5} cm^2 V^{-1} s^{-1}. Here, a value of 5×10^{-4} was used as the photocarrier generation yield ϕ on the basis of the assumption that the photocarrier generation yield is comparable to that of the 3D coordination polymer $\{[Cu_4{}^{I}Cu_2{}^{II}Br_4(Pyr\text{-}dtc)_4]\cdot CHCl_3\}_n$, since both coordination polymers have similar local structures consisting of Cu(II)–dithiocarbamate and bridging Cu(I)–Br units.[4b] The $\Sigma\mu$ value of **1** is comparable to those of organic semiconducting polymers such as P3HT (0.12 cm^2 V^{-1} s^{-1})[5a] and MEH-PPV (0.43 cm^2 V^{-1} s^{-1}).[5b] Generally, the carrier mobilities of semiconductors are concerned with the transfer integrals, which are related to the overlap of HOMOs and/or LUMOs. The coordination polymer **1** has a 1D zigzag$\cdots$Cu(dtc)$_2$–Cu(I)–Cu(dtc)$_2$–Cu(I)$\cdots$chain in the 2D sheet, which might be a good conductive pathway in this coordination polymer because of the large overlaps of the HOMOs and/or LUMOs between the Cu(3,5-Dmpip-dtc)$_2$ unit and the Cu(I) ion.

In summary, we have synthesized a new mixed-valence Cu(I)–Cu(II) coordination polymer with an infinite 2D sheet structure. This complex forms its energy band structure on the basis of the overlap of the HOMOs and/or LUMOs in the infinite 2D sheet, which induces thermally activated conducting properties with a small activation energy. FP-TRMC measurements revealed that this coordination polymer has a high carrier mobility, which might be caused by the large overlap integrals of the orbitals of the Cu(II)(3,5-Dmpip-dtc)$_2$ unit and Cu(I) ion.

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