Construction of conducting bimetallic organic metal chalcogenides via selective metal metathesis and oxidation transformation

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Conducting organic metal chalcogenides (OMCs) have attracted considerable interest for their superior electrical properties and fascinating functions. However, the electronic structural and functional regulation of OMCs are typically limited to the combination of monometallic nodes and graphene-like ligands. Here, we report a family of bimetallic OMCs ([CuAgx(C6S6)]n, x = 4 or 2) synthesized via selective metal metathesis and oxidation transformation. Both OMCs have alternatively stacked one-dimensional (1D) copper-dithiolene chains and 2D Ag-S networks, which can synergistically serve as charge transport pathways, rendering these bimetallic materials highly conductive. The incorporation of heterometallic nodes turned nonmagnetic [Ag5(C6S6)]n into paramagnetic metallic [CuAg4(C6S6)]n, which exhibited a coherence-incoherence crossover in magnetic susceptibility measurements and an unusually large Sommerfeld coefficient, reminiscent of the characteristics of Kondo lattice. This work opens up an avenue for tailoring the electronic structures of OMCs and provides a platform for studying the dichotomy between electronic localization and itinerancy.

Organic metal chalcogenides (OMCs) represent a burgeoning class of organic–inorganic hybrid materials constructed with continuous M-X (X = S, Se, Te) networks that are further covalently connected by organic ligands and extend into periodic one-dimensional (1D), two-dimensional (2D), or three-dimensional (3D) frameworks1,2. Conducting OMCs have currently received significant attention for their tailorability and superior electrical properties3-8 as well as fascinating features of quantum phenomena9-10. Growing efforts have been dedicated to exploring conducting OMCs by varying the organic and metal building blocks. To date, by combining single-metal nodes (e.g., Fe, Ni, Cu, or Ag, etc.) and highly symmetrical aromatic ligands, a large number of conductive OMCs with varying structural topologies have been produced4-10. However, these monometallic OMCs generally impose some unavoidable disadvantages in manipulating their electronic structures and regulating the functions of interest, thus limiting the maximal potential of this emerging class of organic–inorganic hybrid materials.

From the structural perspective, the integration of bimetallic nodes inside OMCs could be an effective method to tailor the targeting structural topologies and introduce additional functionalities.

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However, the kinetic inertness and fast reaction rate of the metal–chalcogen bond formation reaction make the direct synthesis impractical, since the reaction of ligands with different metal ions would inevitably suffer from the separate growth of OMCs in solution. Encouragingly, post-synthetic modification provides an alternative scheme for accessing materials when the direct synthesis route fails. For example, in analogous systems like transition metal dichalcogenides (TMD), doping of TM (Fe, Co, and Ni) atoms has been experimentally demonstrated to be a promising way to achieve functional programming. However, unlike the ionic TMD, OMC is a covalent compound and its skeleton is maintained by robust covalent M-X bonds, which makes the energy barrier of embedding a second metal atom into pristine OMC lattices very steep. Consequently, the synthesis of bimetallic OMCs has been challenging and has not been reported hitherto.

Here, the original bimetallic OMC, [CuAg4(C6S6)]n (CuAg4-BHT, BHT = benzenehexathiol), was synthesized via selective metal metathesis of Ag5BHT, wherein only the square-planar Ag ions were precisely substituted by Cu ions. In particular, under the delicate oxidation regulation, CuAg5BHT can be converted to another bimetallic species, CuAg4-BHT. The crystal structures of both OMCs were solved with atomic resolution, revealing 3D lamellar structures composed of alternatively stacked 1D copper-dithiolene chains and 2D Ag-S networks. Significantly, ultraviolet-photoelectron spectroscopy (UPS) and band structure calculations evidence the intrinsic metallic character of both materials. In addition, combining magnetic susceptibility and specific heat measurements, a coherence-incoherence crossover was observed in CuAg4-BHT, suggesting that this OMC would be an unprecedented candidate for a heavy Fermi liquid with Kondo lattice behavior. Our results open up an avenue for the design of bimetallic OMCs with unusual structural topologies and tailor-made functionalities, and provide an attractive platform to search for exotic states of matter.

Results

Synthesis and structural characterization

As shown in Fig. 1, both the direct synthesis and post-synthetic metathesis were attempted to synthesize heterometallic OMCs. Under homogeneous solution condition, when BHT reacted with a mixture of the two metal ions, no crystalline product could be isolated (Supplementary Table 1 and Supplementary Fig. 1), due to the divergent OMC formation kinetics of two metal ions with BHT. To achieve controlled incorporation of two metal nodes, we envisioned that the post-synthetic metathesis approach with highly crystalline Ag5BHT and Cu4BHT as the parent frameworks might work, since these two well-defined OMCs possess similar building blocks and coordination geometries (Fig. 1). We screened various synthetic parameters, including temperature, reaction time, stoichiometry, and metal salt types to find optimal conditions. However, due to the appearance of silver metal, the transmetalation reactions of Cu4BHT are always unsuccessful (Supplementary Note 1). Under optimized conditions, the reaction of Ag5BHT with Cu(NO3)2·3H2O could afford a highly crystalline product, CuAg4-BHT (Supplementary Table 2 and Supplementary Fig. 2).

Previous studies have shown that the structural transformation achieved by chemical oxidation was a synthetic shortcut to prepare OMCs. To testify the universality of this chemical transformation strategy for OMCs, valence-variable cerium ammonium nitrate ((NH4)2Ce(NO3)6, CAN) was employed as the oxidizing reagent here (Methods, Supplementary Fig. 6). When two equivalents of CAN were added to CuAg4-BHT, we found that CuAg4-BHT can be completely transformed into another bimetallic species, CuAg2-BHT (Fig. 1), which is evidenced by powder X-ray diffraction (PXRD) and other structural characterizations (see the following section for details).

X-ray photoelectron spectroscopy (XPS) reveals that C, S, Cu, and Ag present within both samples (Supplementary Fig. 7), indicating the absence of solvent molecules or other counterions. The
thermogravimetric analysis shows that CuAg₄BHTs are stable up to 300 °C and solvent molecules are absent in the final products (Supplementary Fig. 8). The energy dispersive spectroscopy disclosed the uniform distribution of S, Cu, and Ag across the samples (Supplementary Fig. 9), suggesting that the samples prepared herein were not physical mixtures of two monometallic OMCs. The inductively coupled plasma optical emission spectrometry (ICP-OES) and Electron Probe Micro-analyzer (EPMA) results indicated that the atomic ratios of this material, rotation electron diffraction (RED) was performed on CuAg₄BHT microcrystals to determine the cell parameter and space group accurately. First, a set of initial unit cells was obtained from the 3D reciprocal lattice reconstructed from the RED data (Supplementary Fig. 10). The results show that CuAg₄BHT crystallizes in the monoclinic P2₁/c space group with cell parameters of a = 4.28 Å, b = 8.75 Å, c = 14.48 Å, and β = 94.3°. Based on this initial unit cell parameters and synchrotron PXRD data, the structure of CuAg₄BHT was solved with the charge flipping algorithm (a detailed description of the structure-solving process is presented in Supplementary Note 2). The final Rietveld refinement converges with Rp = 2.62%, Rwp = 4.64%. The crystal structure of CuAg₄BHT was directly solved based on synchrotron PXRD data with the final Rietveld refinement converging with Rp = 2.21%, Rwp = 2.62%. CuAg₄BHT crystallizes in a triclinic P–1 space group with cell parameters of a = 3.38 Å, b = 8.43 Å, c = 8.80 Å, α = 62.1°, β = 86.1°, and γ = 80.8°. The small differences between the experimental PXRD patterns and the simulated ones (Fig. 2a, b) confirm the accuracy of the crystal structures of CuAg₄BHT. The detailed crystallography data are provided in Table 1 and Supplementary Table 4. In Table 1, no diffraction peaks belonging to crystalline impurities could be observed, and the calculated results are in good agreement with the experimentally observed PXRD data, verifying the phase purity of CuAg₄BHT samples. Additionally, the EPMA, ICP-OES and elemental analysis results of CuAg₄BHT powder samples are highly consistent with the formulas obtained based on crystal structure analysis and further confirmed the purity unambiguously (Supplementary Table 5).

Due to the shorter Cu–S bond lengths (2.247(8), 2.214(8) Å) in CuAg₄BHT, the substitution of the square-planar Ag atoms leads to an obvious shrink in cell volume for CuAg₄BHT (540.9 Å³) compared to that of Ag₅BHT (551.7 Å³) (Table 1). This also results in a reduction in the crystal symmetry from the I2/m space group to P2₁/c, while the structural topology is almost intact. Thus, similar to that observed in Ag₅BHT, CuAg₄BHT exhibits alternatively stacked 2D Ag-S networks and 1D copper-dithiolene chains (Fig. 3a). Moreover, a graphene-like

Table 1 | Crystallographic details of Ag₅BHT (ref. 19) and CuAg₄BHT obtained from the Rietveld refinement using synchrotron PXRD and RED data

| Formula | Ag₅BHT | CuAg₄BHT | CuAg₂BHT |
|---------|--------|----------|----------|
| Formula weight | 803.77 | 759.44 | 543.71 |
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | P2₁/m | P2₁/c | P–1 |
| a, b, c (Å) | 15.1168, 9.1042, 3.5790 | 4.2776, 4.2773, 8.7547 | 8.4259, 8.7547, 8.8001 |
| a, b, c (°) | 99.1043, 90, 62.09 | 90, 94.31, 90 | 86.14, 80.80 |
| V(Å³) | 551.67 | 540.86 | 231.49 |
| Rexp, Rw | 4.98%, 4.35% | 4.64%, 3.57% | 2.62%, 2.21% |
| GOF | 3.46 | 1.42 | 1.31 |
layer structure formed by the connection of Ag atoms is preserved in the transmetalation product (Fig. 3b), which is further confirmed by the characteristic symmetric vibration signal of Ag-Ag bond in Raman spectrum (Supplementary Fig. 12). In contrast, CuAg2BHT exhibits a Kagome-like lattice when viewed along the a-axis (Fig. 3c), in which the six-coordinated Ag atoms lied between the mean planes defined by the two square-planar metal ions and ligand moieties (Fig. 3d). It is worth noting that the Ag atoms with high coordination numbers are critical for extending bimetallic OMCs into 3D networks (Supplementary Fig. 13 and Fig. 1).

Electrical transport characterizations

The electrical conductivities of Ag5BHT and CuAgxBHT samples were measured on pressed pellets via the four-probe method. At 300 K, all these OMCs exhibited high conductivities, ranging from 10 S cm$^{-1}$ for Ag5BHT and 0.13 S cm$^{-1}$ for CuAg2BHT to 3 S cm$^{-1}$ for CuAg4BHT.

Fig. 3 | Representation of the crystal structures of CuAg$_x$BHTs. a Crystal structure of CuAg$_x$BHT viewed along the a-axis direction. b Honeycomb-like lattice formed by adjacent Ag atoms in CuAg$_x$BHT (viewed along the c-axis). c Top view of the Kagome-like lattice in CuAg$_x$BHT (viewed along the a-axis). d Side view of the layered structure formed by the metals ions with square-planar geometry and the Cu$_6$ moieties in CuAg$_x$BHT (gray: carbon atoms, red: sulfur atoms, blue: copper atoms, violet: silver atoms).

Fig. 4 | Electrical transport characterizations. a–c Electrical conductivities of three materials as a function of temperature from 2 to 400 K. Inset, plots of ln(σ) versus $T^{-1/4}$ over the temperature region of 100–250 K. d UPS data for the valence band region of three samples acquired at 300 K, and the Fermi edge was shown by the pink dotted line. Source data are provided as a Source Data file.
(Fig. 4a–c and Supplementary Table 6). These conductivities are among the highest values ever reported for conductive coordination polymers (Supplementary Table 7). The conductivity is positively correlated with temperature, suggesting the thermally activated transport. The plot of ln(σ) versus 1/T (Fig. 4a–c, inset) suggests an activated behavior with an activation energy of 0.25 eV in the temperature range of 100–400 K. The Seebeck coefficients of all three materials as a function of temperature from 300 to 400 K are shown in Supplementary Table 8. 

The Seebeck coefficients of CuAg4BHT and CuAg5BHT are nearly identical, while CuAg2BHT displays a significantly higher Seebeck coefficient. Notably, a bipolaron effect could be observed in CuAg5BHT, with the Seebeck coefficient reaching a maximum value (~74 μV K⁻¹) at 350 K and decreasing with increasing temperature from 350 to 400 K, suggesting the contribution of the minority carriers increases with raising temperature.

As shown in Supplementary Fig. 17a–d, for monometallic Ag5BHT, the DOS near the Fermi level mainly derived from the Ag-d orbitals and S-p orbitals, suggesting that the 2D Ag-S network is the preferred charge transport route. Due to the different coordination geometries and chemical environments of Ag1 and Ag2 in Ag5BHT (Ag1 refers to the six-coordinated Ag atoms with distorted octahedral geometry and Ag2 features a square-planar coordination mode), the d-orbitals splitting of Ag1 and Ag2 is expected to be different, which makes the orbital compositions of Ag1 and Ag2 different in PDOS. The Ag1dxy, Ag1dyz, and Ag2dyz, dyz orbitals contribute the most to PDOS near the Fermi level, whereas for CuAg5BHTs, due to copper incorporating into the framework matrix, the PDOS near the Fermi level is dominated by contributions from the d orbitals of Cu and Ag and p orbitals of S. It should be noted that for CuAg5BHT, the DOS derived from Ag d-orbitals is different from that of Ag in Ag5BHT, while the PDOS contribution from CuAg5BHT is similar to that of Ag in Ag5BHT. The p-orbital composition of S atoms also changes after the metal atom substitution (Supplementary Fig. 17b, f), which is ascribed to the charge redistribution in this M3BHT system (M refers to the metal ions). After the chemical oxidation transformation, significant variations in the PDOS composition of the d orbitals of metal atoms and the p orbitals of C and S atoms can be observed near the Fermi level (Supplementary Fig. 17i–l). All these results elucidate that the introduction of bimetallic nodes can synergistically tailor the electronic structures of the OMCs, thereby modulating the corresponding charge transport behavior.

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**Fig. 5 | Calculated electronic structures and Seebeck coefficient measurements.** a–c Calculated band structures and DOS for Ag5BHT (a), CuAg5BHT (b), and CuAg4BHT (c). The high-symmetry K points in the first Brillouin zone are provided in Supplementary Table 8. d Seebeck coefficients of three materials as a function of temperature from 300 to 400 K. Source data are provided as a Source Data file.
EPR and magnetic studies

Electron paramagnetic resonance (EPR) measurements were performed to investigate electron configurations of these materials. For CuAg₄BHT, no EPR signal was detected even when cooled down to 10 K, suggesting its diamagnetic nature. After metal metathesis, a nearly isotropic signal contributed by the Cu²⁺ with $g = 2.053$ was observed (Fig. 6a), which is consistent with the Cu 2p XPS analysis in CuAg₄BHT (Supplementary Fig. 18). As for CuAg₂BHT, only a very weak EPR signal was observed (Supplementary Fig. 19). The signal intensity is temperature dependent and almost diminishes at room temperature, which indicates that it does not originate from an organic radical. As this EPR signal was broad and asymmetrical, it can be attributed to a small amount of leftover Cu²⁺ during oxidation, while the dominant Cu ions became EPR silent, supporting that the oxidation state of Cu in CuAg₂BHT was +1 (Supplementary Fig. 18).

From the first generation of Ag₅BHT (coordination assembly), to the second generation of CuAg₄BHT (metal metathesis), and then to the third generation of CuAg₄BHT (oxidation regulation) (Fig. 1), the non-innocent ligand shows multiple accessible redox states that are responsible for electrically neutral networks. During the metathesis process, we found that only the square-planar Ag atoms of Ag₅BHT could be replaced by Cu(II) ions, even by raising the reaction temperature or prolonging the duration. Generally, longer bond length refers to lower bond energy, so it can be expected that the bond energy of Ag-S bond (231.3–202.1 kJ mol⁻¹) is lower than that of Cu-S bond (274.5 kJ mol⁻¹). Thus, the precise exchange result can be attributed to the labile tetra-coordinated [AgS₄] cores (Supplementary Fig. 13), which has also been verified by other studies²⁶,²⁸, whereas Ag atoms with non-coplanar coordination geometry were stabilized by the formation of Ag-Ag bond, preventing their substitution by Cu atoms. Furthermore, the total energy of Ag₅BHT (−122.4 eV) calculated with DFT method is higher than that of CuAg₅BHT (−125.6 eV), indicating this selective metal metathesis reaction is a thermodynamically favored process.

The precise substitution of the Ag⁺ ions by Cu²⁺ ions turns the nonmagnetic Ag₅BHT into a paramagnetic conducting material. The coexistence of local spins and conducting electrons reminds us of the research on molecular Kondo system⁶. Remarkably, searching for Kondo systems in 3d-electron compounds has attracted immense interest in condensed matter physics⁷. Considering that Cu²⁺ ions with localized magnetic moments are periodically arranged in the network having itinerant d-p-π electrons, Kondo lattice scenario arising from the interaction between localized spins and conduction electrons in CuAg₄BHT could be expected.

Thus, the magnetic susceptibility measurements were carried out first. As shown in Fig. 6c, $M/H$ increases with decreasing temperatures and displays a broad peak around 12 K. A significant downward trend occurs as the temperature decreases, and the $M(T)_{\mu B}$ curve starts to increase again below 5 K. This upturn is typical of heavy Fermi liquids and reveals the presence of a small amount of magnetic or paramagnetic impurities/defects⁸,⁹. Actually, we noticed such paramagnetic impurities originating from the surface contamination or defects, and a calibration procedure was carried out to eliminate the interference signal. Meanwhile, in order to ensure the dominant source of magnetic properties of CuAg₄BHT, the possible influence of extrinsic oxides was excluded by synchrotron PXRD and temperature variable EPR measurements (Supplementary Figs. 19 and 20). Therefore, the intrinsic magnetic susceptibility of CuAg₄BHT was precisely determined by analyzing the magnetic isotherms $M(H)_{\mu B}$ at different temperatures (Fig. 6b) instead of $M(T)_{\mu B}$ curve⁹. The derived intrinsic susceptibilities were represented by the blue symbols in Fig. 6c, and followed the Curie–Weiss law in the high $T$ region. The Curie–Weiss fitting from 100 to 300 K afforded a Curie constant of $C = 0.376$ emu K mol⁻¹ and Curie–Weiss temperature of $\theta = −5.6$ K. The calculated effective moment ($\mu_{eff}$) for each Cu ion in the formula CuAg₄C₆S₆ equals 1.74 $\mu_B$, which was reasonably close to that expected for Cu(II) ($S = 1/2$, $\mu_{eff} = 1.73 \mu_B$). The negative Curie–Weiss temperature indicated the
presence of antiferromagnetic interactions between the magnetic moments. Besides, the measured susceptibility shows no sign of a magnetic ordering transition down to 2 K, but a clear deviation from Curie–Weiss behavior appears below $T < 12$ K. As the temperature decreases, the intrinsic susceptibility of CuAg$_4$BHT reaches a broad hump around 10 K and then decreases when $T < 8$ K, while its intrinsic susceptibility remains quite large, equal to $1.8 \times 10^{-4}$ emu mol$^{-1}$ toward the $T = 0$ limit. Such magnitude and $T$ dependence of susceptibility$^{34,41}$ provides a crude estimation of the coherence temperature $T$ (refs. 42, 43). Below the $T$ of ~8–10 K, the susceptibility evolving becomes visible, indicating the emergence of the interaction of local Cu$^{2+}$ spins and conduction $d$-$p$-$\pi$ electrons. Therefore, the observable decrease in intrinsic susceptibility when $T < 8$ K is attributed to the Kondo scenario, in which localized magnetic moments are screened by itinerant electrons. Thus, with decreasing temperature, a crossover from a paramagnetic state with localized moments to renormalized Fermi liquid state with coherent Kondo lattice was suggested in CuAg$_4$BHT.

In addition, since CuAg$_4$BHT is isostructural with Ag$_5$BHT, the comparison of their specific heat data can reveal the influence of Cu ion introduction. In the temperature range from 2 to 8 K, the specific heat data are well represented by the relation of $C_v = \gamma + \beta T^2$ (Fig. 6d). A linear fit of $C_v/T$ to $T^2$ plot yields a Sommerfeld coefficient $(\gamma) = 2.2$ mJ K$^{-2}$ mol$^{-1}$. For CuAg$_4$BHT, which is more than ten times higher than that of Ag$_5$BHT (Supplementary Fig. 21). Such unusually large value also proves the existence of heavy-mass quasiparticle states$^{14,45}$, supporting the observed susceptibility anomaly. Furthermore, anomalously large Seebeck coefficient in metallic CuAg$_4$BHT provides another hint for the existence of a large effective electron mass. Finally, we realized that CuAg$_4$BHT has a triangular lattice of Cu(II) cations (Supplementary Fig. 22). The origin of the heavy quasiparticle mass could be closely linked with the geometrical frustration, as also demonstrated in d-electron LiV$_2$O$_4$ spinel$^{46}$. To gain in-depth insight into the complex Kondo physics, the preparation of bulk single-crystal sample (>50 μm) and ultralow temperature measurements are further demanded, and will be performed on this OMC in the near future.

### Discussion

In summary, we have rationally designed and synthesized a family of bimetallic OMCs, CuAg$_n$BHTs, via selective metal metathesis and delicate oxidation regulation. Both crystal structures have been well characterized by PXRD and RED techniques, revealing atomically precise structures composed of alternatively stacked 1D copper-dithiolene chains and 2D Ag-S networks. As suggested by band structure calculations, the bimetals(bis(dithiolene) moieties can synergistically regulate the electronic structures of these OMCs, which accounts for the high electrical conductivity observed in 3D OMCs. In addition, the susceptibility anomaly and other measurements suggested that CuAg$_n$BHT was a candidate for a heavy Fermi liquid with Kondo lattice. We expect that our experimental results will motivate theoretical efforts on this intriguing subject in the future. More importantly, the development of bimetalllic OMCs may synergistically regulate the electronic structures of these OMCs, the preparation of dithiolene chains and 2D Ag-S networks. As suggested by band structure calculations, the bimetal-bis(dithiolene) moieties can synergistically regulate the electronic structures of these OMCs.

### Methods

#### Synthesis of CuAg$_n$BHT

Under argon atmosphere, Cu(NO$_3$)$_2$·3H$_2$O (470 mg, 1.94 mmol) was dissolved in 160 mL degassed ethanol, and then Ag$_5$BHT (100 mg, 0.124 mmol) was added. The mixture was sonicated for 5 min, and subsequently heated to 80 °C with constant stirring for 72 h to form a gray-black powder, followed by natural cooling to room temperature. The obtained powder was filtered, washed with water, ethanol, acetone, and diethyl ether in sequence, and then dried at 80 °C under vacuum for 24 h. Yield: 82 mg (87%).

#### Trials for the oxidation regulation of CuAg$_n$BHT

Under argon atmosphere, different amounts of Ce(NH$_4$)$_2$(NO$_3$)$_3$ (0.5–6 equiv. to CuAg$_n$BHT) were dissolved in 100 mL degassed acetonitrile, and then CuAg$_4$BHT (76 mg, 0.1 mmol) was added. The mixture was stirred at room temperature for 12 h. The obtained powder was filtered, washed with water, CH$_3$CN, acetone, and diethyl ether in sequence, and then dried at 80 °C under vacuum for 24 h.

#### Optimized synthetic condition of CuAg$_n$BHT

Under argon atmosphere, Ce(NH$_4$)$_2$(NO$_3$)$_3$ (220 mg, 0.4 mmol) was dissolved in 150 mL degassed acetonitrile, and then CuAg$_4$BHT (152 mg, 0.2 mmol) was added. The mixture was stirred at room temperature for 24 h. The obtained powder was filtered, washed with water, CH$_3$CN, acetone, and diethyl ether in sequence, and then dried at 80 °C under vacuum for 24 h. Yield: 48 mg (88%).

#### SEM and TEM characterizations

SEM images were obtained using a Topcon SU8000-SEM with an acceleration voltage of 10 kV. TEM images were acquired using a JEOL JEM-2100F-TEM with an acceleration voltage of 100 kV. The electrical conductivities were measured on the pelletized samples via a four-probe method in a Physical Property Measurement Systems (PPMS-9, Quantum design). About 5 mg samples were compressed into a cuboid pellet under a pressure of 10 MPa. Then four parallel gold electrodes were deposited on the pellet by vacuum evaporation to form a-four-electrode device. The Seebeck coefficients were measured using the SB-100 Seebeck Measurement System (MMR Tech.) under a vacuum environment below 18 mTorr.

#### Details of physical property measurements

The DC magnetic susceptibility measurement under 2–300 K was conducted in a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design). Zero field cooling and field cooling measurements were performed under an applied field of 1000 Oe. Diamagnetic correction was applied using Pascal’s constant. The temperature variable EPR spectrum were collected using a Bruker Petas2.0.

#### Electrical property measurement

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#### SEM and TEM characterizations

In a high vacuum environment, EPR spectra were collected using a Bruker Petas2.0.

#### Electrical property measurement

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temperature heat capacity measurements were also performed in PPMS.

**Data availability**

The crystallographic information obtained by Rietveld refinement of PXRD data has been deposited in the Cambridge Crystallographic Data Centre under accession codes CCDC 2143107 (CuAg2BHT) and CCDC 2143106 (CuAg4BHT) [https://www.ccdc.cam.ac.uk/structures/?]. All data generated and analyzed in this study are included in the article and its Supplementary Information, and are also available from the authors upon request. The source data generated in this study are provided in the Source Data file. Source Data are provided with this paper.

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Author contributions
W.X. planned and designed the research project. Y.G.J. executed the syntheses, chemical, spectroscopic and electrical characterization. Y.H.F. performed and analyzed temperature variable EPR data. X.H. and B.G. obtained and analyzed the transmission electron microscopy data. C.M.L. performed and analyzed the magnetic susceptibility measurements. Y.L., Z.L., and S.W. collected the PXRD data. Y.M.S. contributed to the Seebeck coefficient measurements and analysis. X.J.D. and Y.Z. performed and analyzed electrical conductivity experiments and UPS characterizations. B.W.W. performed and analyzed the specific heat data. F.H. and W.X. performed the DFT calculation and crystal structure-solving works. Y.G.J. and W.X. wrote the manuscript. All authors participated in the discussion and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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