Supporting Information for

Integrating Multiple Emission Centers for Photoluminescence Regulation in Copper-Antimony/Bismuth Halides

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Supporting Information Contents:

Number of pages: 41

Sections: Experimental section, Crystal structure and Bond length analysis, Figure and Tables.

Number of Figures: 23 (Figure S1 to Figure S23).

Number of Tables: 20 (Table S1 to Table S20).

1. Experimental section

Materials. All purchased reagents were utilized directly without further purification. The detailed information for the reagents is listed as follows: bismuth(III) chloride ($BiCl_3$, 99%, VetecSigma-Aldrich); antimony(III) chloride ($SbCl_3$, 99%, Adamas); bismuth(III) bromide ($BiBr_3$, 99%, Adamas); antimony(III) bromide ($SbBr_3$, 99%, Adamas); copper(I) chloride (CuCl, 98%, Adamas); copper(I) bromide (CuBr, 99%, Adamas); thiomorpholine (C_4H_9NS, 98%, Adamas); hydrochloric acid (HCl, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China); hydrobromic acid (HBr, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China); hypophosphorous acid (H_3PO_2, AR, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China).

X-ray crystallography. A single crystal suitable for single-crystal X-ray diffraction (SCXRD) was selected under an optical microscope. Single crystal X-ray diffraction data were collected with graphite-monochromated Mo*Kα* (λ = 0.71073 Å) and Cu*Kα* (λ = 1.54178 Å) using an XtaLAB Synergy X, HyPix diffractometer at 100 K and 297K. The structure was solved by direct methods and refined with full-matrix least squares on F^2 by the *SHELX2018* package.[1] CCDC NO. 2365627-2365634 and 2391052-2391054 for all compounds contain 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.

Characterization. Powder X-ray diffraction (PXRD) patterns were performed on a Rigaku Miniflex-II diffractometer with Cu*Kα* radiation (λ = 1.54178 Å) in the angular range of 2θ = 5 - 65°. The simulated PXRD pattern is calculated from the SCXRD data using *Mercury* program. Thermogravimetric (TG) analysis was performed on a NETZSCH STA 449F3 unit at a heating rate of 10 K min^{-1} under a nitrogen atmosphere. Solid-state optical diffuse reflectance spectra were recorded on a Shimadzu 2600 UV/vis spectrometer at room temperature (RT) in the range of 800 – 200 nm. A $BaSO_4$ plate is utilized as a standard which possesses 100% reflectance. The absorption data were obtained by converting diffuse reflection spectrum through the Kubelka–Munk function.[2] Photoluminescence excitation (PLE) spectra, photoluminescence (PL) spectra, and time-resolved PL spectra were performed on Edinburgh FLS1000

NV/V/NIR and Edinburgh FLS980 NV/V/NIR fluorescence spectrometer.

Synthesis of $[(Tp)_3CuCl]SbCl_6$. A mixture of thiomorpholine (1.5 mmol), CuCl (0.5 mmol), $SbCl_3$ (0.5 mmol), 3 mL hydrochloric acid and 0.5 mL H_3PO_2 were added to a 20 mL glass vial. The container was sealed and heated at 100 °C for 2 days to completely dissolve to a clear solution. After cooling 1 K/h to room temperature (RT), colorless block-like crystals were obtained. The yield of $[(Tp)_3CuCl]SbCl_6$ was calculated to be nearly 78.90% based on Sb atom. EA: calcd (%): C: 19.32 H: 4.05, N: 5.63. Found: C: 19.50, H: 4.02, N: 5.63.

Synthesis of $[(Tp)_3CuCl]BiCl_6$. The synthetic method is similar to that for $[(Tp)_3CuCl]SbCl_6$, A mixture of thiomorpholine (1.5 mmol), CuCl (0.5 mmol), $BiCl_3$ (0.5 mmol), 3 mL hydrochloric acid and 0.5 mL H_3PO_2 were added to a 20 mL glass vial. The container was sealed and heated at 100 °C for 2 days to completely dissolve to a clear solution. After cooling 1 K/h to room temperature (RT), colorless block-like crystals were obtained. The yield of $[(Tp)_3CuCl]BiCl_6$ was calculated to be nearly 86.91% based on Bi atom. EA: calcd (%): C: 17.30, H: 3.63, N: 5.04. Found: C: 17.42, H: 3.57 N: 5.09.

Synthesis of $[(Tp)_3CuBr]SbBr_6$ and **$[(Tp)_3CuBr]BiBr_6$.** Compounds $[(Tp)_3CuBr]SbBr_6$ and $[(Tp)_3CuBr]BiBr_6$ were synthesized in a similar manner to compounds $[(Tp)_3CuCl]SbCl_6$ and $[(Tp)_3CuCl]BiCl_6$, with the corresponding chlorides replaced with bromides and hydrochloric acid replaced with hydrobromic acid. The yield of $[(Tp)_3CuBr]SbBr_6$ was calculated to be nearly 92.94% based on Sb atom. The yield of $[(Tp)_3CuBr]BiBr_6$ was calculated to be nearly 85.51% based on Bi atom. EA of $[(Tp)_3CuBr]SbBr_6$: calcd (%): C: 13.63, H: 3.86, N: 3.96. Found: C: 12.22, H: 2.71 N:3.51; EA of $[(Tp)_3CuBr]BiBr_6$: calcd (%): C: 12.59, H: 2.64, N: 3.67. Found: C: 11.87, H: 2.64 N:3.42.

Synthesis of $(Tp)_3MX_6$. A mixture of thiomorpholine (1.5 mmol), MX_3 (0.5 mmol), 2 mL hydrohalic acid were added to a 20 mL glass vial. The container was sealed and heated at 100 °C for 1 hour to completely dissolve to a clear solution. After cooling 2 K/h to room temperature (RT), block-like crystals were obtained. The yield of $(Tp)_3SbBr_6$ was calculated to be nearly 92.73% based on Sb atom. The yields of $(Tp)_3BiCl_6$ and $(Tp)_3BiBr_6$ were calculated to be nearly 54.56% and 78.38%,

respectively, based on Bi atom.

Synthesis of (Tp)Br. A mixture of thiomorpholine (1 mmol), 0.7 mL hydrohalic acid, 2 mL ethanol and 2 mL acetonitrile were added to a 20 mL glass vial. The container was sealed and heated at 100 °C for 1 hour. After cooling to room temperature (RT), light-pink block-like crystals were obtained.

Density Functional Theory (DFT) calculation

According to the single-crystal structure refinement results, DFT calculations of $[(Tp)_3CuCl]SbCl_6$, $[(Tp)_3CuBr]SbBr_6$, and $(Tp)_3SbBr_6$ were implemented in the Vienna Ab initio Simulation Package (VASP).[3] Theoretical calculations are processed and analysed using VASPKIT.[4] The generalized gradient approximation (GGA) for the exchange-correlation term with the Perdew–Burke–Ernzerhof (PBE)[5] exchange-correlation functional was applied for electron-electron exchange-correlation processes. To ensure sufficient accuracy, the cut-off energy of 500 eV for the plane wave expansion was chosen, self-consistent field (SCF) computations were set to a convergence criterion of 1×10^{-5} eV and the force criterion was 0.02 eV $Å^{-1}$.

Calculation of distortion in anionic octahedron

Since the luminescence intensity and Stokes shift are different for heterometallic halides at 100 K and 297 K, and previous reports have shown that the Stokes shift is closely related to the degree of distortion of inorganic polyhedron in halides, supramolecular interactions have a strong influence on the distortion of anionic polyhedron.[6-8] Therefore, to evaluate the distortion of the anion $[MX_6]^{3-}$ (*M* = Sb、Bi, *X* = Cl、Br) at 100 K and 297 K, the angle distortion (σ^2) and bond length distortion (Δd) were calculated using the following formulas.[8-10]

Equation S1.

$$\sigma^2 = \frac{1}{11}\sum_{n=1}^{12}(\theta_n - 90°)^2 (six\ coordinated)$$

Equation S2.

$$\Delta d = \frac{1}{6}\sum_{n=1}^{6}[(d_n - d)/d]^2\ (six\ coordinated)$$

Where θ_n denotes the bond angle of each *X*–*M*–*X*, *d* is the average of the *M*–*X* bond distance, and d_n denotes individual *M*–*X* bond length. σ^2 and Δd represent the bond angle variance and bond length distortion level, respectively. The degree of distortion for all compounds is presented in Table S5.

Equation S3. The Huang-Rhys factor equation

The Huang-Rhys factor (*S*) can be obtained by fitting the curve of FWHM *versus* 1/2*kT* using the following formula:

$$FWHM = 2.36\sqrt{S}\hbar\omega\sqrt{\coth\left(\frac{\hbar\omega}{2kT}\right)}$$

where FWHM represents full width at half maximum, $\hbar$ is Planck constant, *ω* is the phonon frequency, $\hbar\omega$ is the longitudinal optical phonon frequency,*k* is the Boltzmann constant (8.617×10^{-5} eV·K^{-1}) and *T* is temperature.[11, 12]

Equation S4. The Toyokawa model equation.

To further discuss electron−phonon coupling interactions, the Toyokawa equation is used to fit the temperature-dependent PL FWHM:

$$\Gamma(T) = \Gamma_0 + \frac{\Gamma_{op}}{e^{\hbar\omega/kT} - 1}$$

where Γ_0 represents the intrinsic line width at absolute 0 K (replaced by the data at 80 K in this work), Γ_{op} is the electron−phonon coupling energy.[13, 14]

Equation S5. the Arrhenius-type equation.

The temperature-dependent PL intensity can be fitted by the Arrhenius-type equation:

$$I_t = \frac{I_0}{1 + Ae^{-E_a/kT}}$$

where I_t represents PL emission intensity at different temperatures, and I_0 represents the intensity at 0 K (replaced by the data at 80 K in this work).[6]

2. Crystal structure and Bond length analysis

All four heterometallic halides $[(Tp)_3CuX]MX_6$ (X = Cl, Br; M = Sb, Bi) were found to be isomorphic and crystallized in the monoclinic space group $P2_1/c$ (Table S1-3 for details). (Tp)Br crystallizes in a triclinic crystal system with space group P-1, and the three monometallic halides crystallize in a monoclinic crystal system, with space groups $P2_1/n$ for $(Tp)_3BiCl_6$ and $C2/c$ for $(Tp)_3SbBr_6$ and $(Tp)_3BiBr_6$ (Table S4). Among them, although $(Tp)_3BiCl_6$ and $(Tp)_3BiBr_6$ are with similar formula, the space groups of their crystallites are not the same (see Table S4 for details).

Analysis of the single-crystal data shows that the heterometallic antimony-based halides $[(Tp)_3CuCl]SbCl_6$ and $[(Tp)_3CuBr]SbBr_6$ show large differences in bond lengths and distortion changes at 100 K and room temperature, whereas the isomorphic heterometallic bismuth-based halides $[(Tp)_3CuCl]BiCl_6$ and $[(Tp)_3CuBr]BiBr_6$ show smaller differences in bond lengths and distortion changes at 100 K and room temperature (Table S5-6). At 100 K, the Sb-Cl bond length of compound $[(Tp)_3CuCl]SbCl_6$ ranged from 2.4954(4) to 2.8994(4) Å, with an average bond length of 2.6711 Å (Figure S3 and Table S7), while the Sb-Br bond length of $[(Tp)_3CuBr]SbBr_6$ ranged from 2.8994(4) Å and 2.8692(8) Å, with an average bond length of 2.8140 Å (Figure S4 and Table S8). The Sb(1)-Cl(3) bond length in $[SbCl_6]^{3-}$ is 2.8994(4) Å, and the Sb(1)-Br(3) bond length in $[SbBr_6]^{3-}$ is 2.9498(4) Å, which are longer than their average bond lengths and the other five Sb-X bond lengths, respectively. Therefore, we can consider the Sb(1)-X(3) bond as a secondary bond.[15] Table S6 shows that they become longer as the temperature decreases, while the other five Sb-X bonds become shorter or have little change in length. The change in bond lengths at different temperatures suggests that the secondary bonds Sb(1)-X(3) are relatively labile and more susceptible to external energies. By contrast, the bond lengths of isomeric bismuth halides change less significantly at low and room temperatures. At 100 K, the Bi-Cl bond lengths in $[(Tp)_3CuCl]BiCl_6$ range from 2.6249 (8) to 2.8060 (7) Å, with an average bond length of 2.7145 Å (Table S9). The Bi-Br bond lengths in $[(Tp)_3CuBr]BiBr_6$ range from 2.7736 (4) to 2.9426 (4) Å, with an average bond length of 2.8594 Å (Figure S4 and Table S10). The Bi(1)-Cl(3) bond length is 2.8060(4) Å,

and the Bi(1)-Br(3) bond length is 2.9378(4) Å, respectively. Analysis of the above bond length data shows that the Bi(1)-X(3) bonds in $[(Tp)_3CuCl]BiCl_6$ and $[(Tp)_3CuBr]BiBr_6$ are not secondary bonds and their bond lengths do not change much at different temperatures. It is noteworthy that the corresponding monometallic halides have no secondary bonds in their structures. The Sb-Br bond lengths in compound $(Tp)_3SbBr_6$ ranged from 2.7173(3) to 2.9169(3) Å with an average bond length of 2.8016 Å (Table S11). The Bi-Cl bond lengths of compound $(Tp)_3BiCl_6$ range from 2.6396(6) to 2.7804(6) Å with an average bond length of 2.7080 Å. The Bi-Br bond lengths in compound $(Tp)_3BiBr_6$ range from 2.8060(5) to 2.9291(5) Å with an average bond length of 2.8563 Å (Figure S4d-f and Table S11-12). Hydrogen bonding data for all title compounds are listed in Tables S13-20. The bond lengths of Bi-*X* and Sb-*X* in all compounds are comparable to those previously reported for antimony and bismuth halides.[16-20]

3. Figures

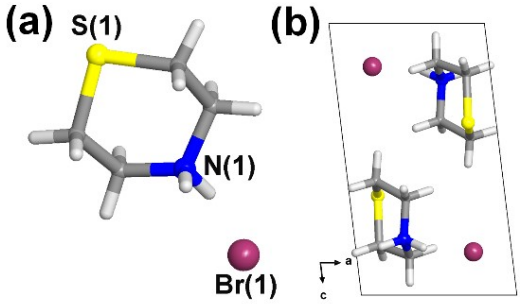

Figure S1 (a) Single-Crystal molecular structural diagram of (Tp)Br. (b) Packing diagram of (Tp)Br viewed along the *b* axis at 298 K.

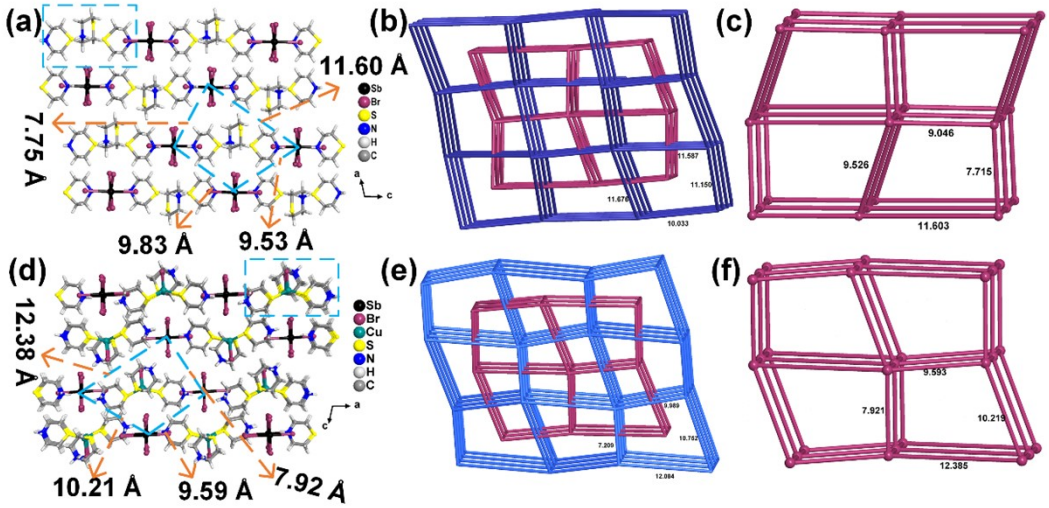

Figure S2 The packing diagram of $(Tp)_3SbBr_6$ (a) and $[(Tp)_3CuBr]SbBr_6$ (d) viewed along the *b* axis (the single-crystal X-ray data collected at 100 K). Topological nets of pcu-type network of $[(Tp)_3CuBr]SbBr_6$ (b) and $[(Tp)_3CuBr]SbBr_6$ (e). Topological nets of pcu-type network of anionic units $[SbBr_6]^{3-}$ of $(Tp)_3SbBr_6$ (c) and $[(Tp)_3CuBr]SbBr_6$ (f). In topological diagrams, the reddish-purple ball represents $[SbBr_6]^{3-}$, the dark blue ball is $(C_4H_{10}NS)_3^{3+}$ and the light blue ball is $[(C_4H_{10}NS))_3CuX]^{3+}$.

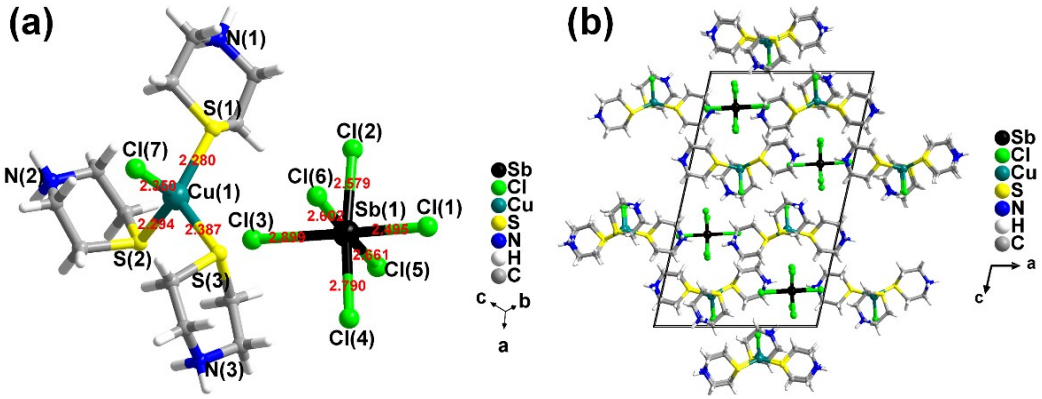

Figure S3 (a) Single-Crystal molecular structural diagram of $[(Tp)_3CuCl]SbCl_6$. (b) Packing diagram of $[(Tp)_3CuCl]SbCl_6$ viewed along the *b* axis at 100 K.

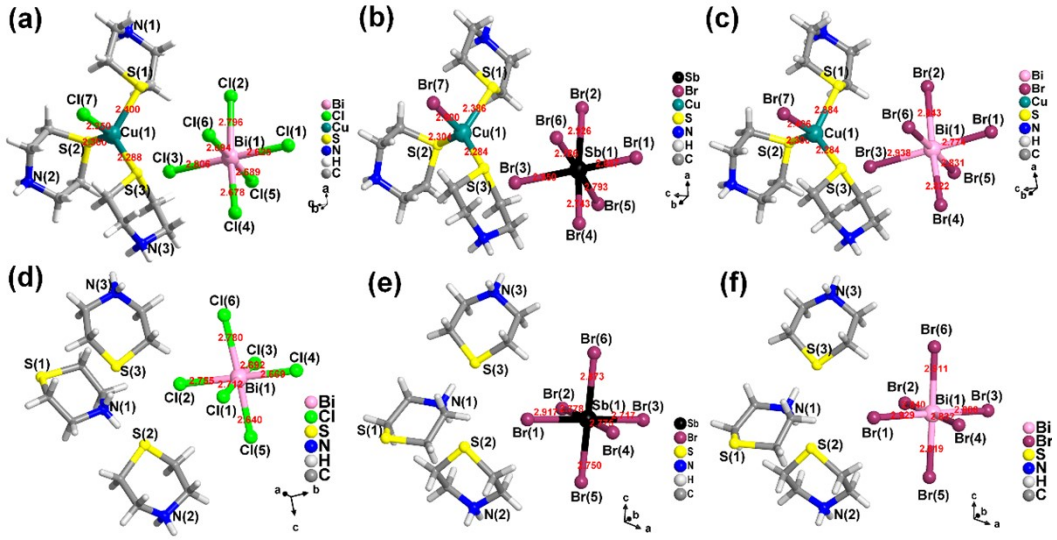

Figure S4 Single-Crystal molecular structural diagrams of $[(Tp)_3CuCl]BiCl_6$ (a), $[(Tp)_3CuBr]SbBr_6$ (b), $[(Tp)_3CuBr]BiBr_6$ (c), $(Tp)_3BiCl_6$ (d), $(Tp)_3SbBr_6$ (e), $(Tp)_3BiBr_6$ (f) (the single-crystal X-ray data of $[(Tp)_3CuBr]SbBr_6$, $[(Tp)_3CuBr]BiBr_6$, $(Tp)_3BiCl_6$, $(Tp)_3SbBr_6$ were collected at 100 K and single-crystal X-ray data of $[(Tp)_3CuCl]BiCl_6$ and $(Tp)_3BiBr_6$ were collected at 297 K and 295 K, respectively).

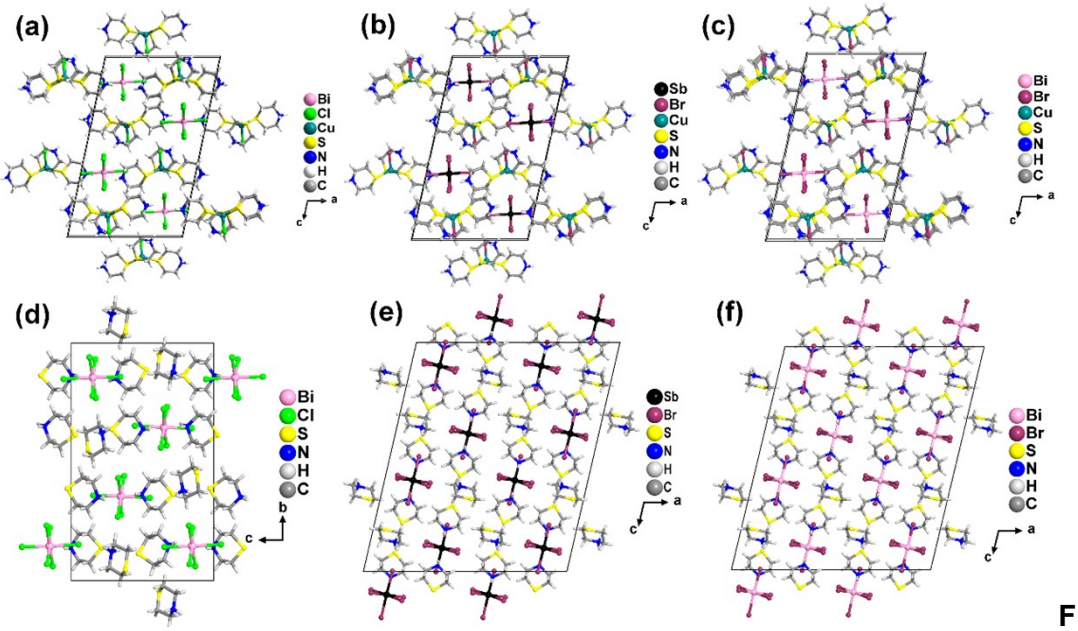

Figure S5 Packing diagrams of $[(Tp)_3CuCl]BiCl_6$ (a), $[(Tp)_3CuBr]SbBr_6$ (b), and $[(Tp)_3CuBr]BiBr_6$ (c) viewed along the *b* axis. (d) Packing diagram of $(Tp)_3BiCl_6$ viewed along the *a* axis. Packing diagrams of $(Tp)_3SbBr_6$ (e) and $(Tp)_3BiBr_6$ (f) viewed along the *b* axis.

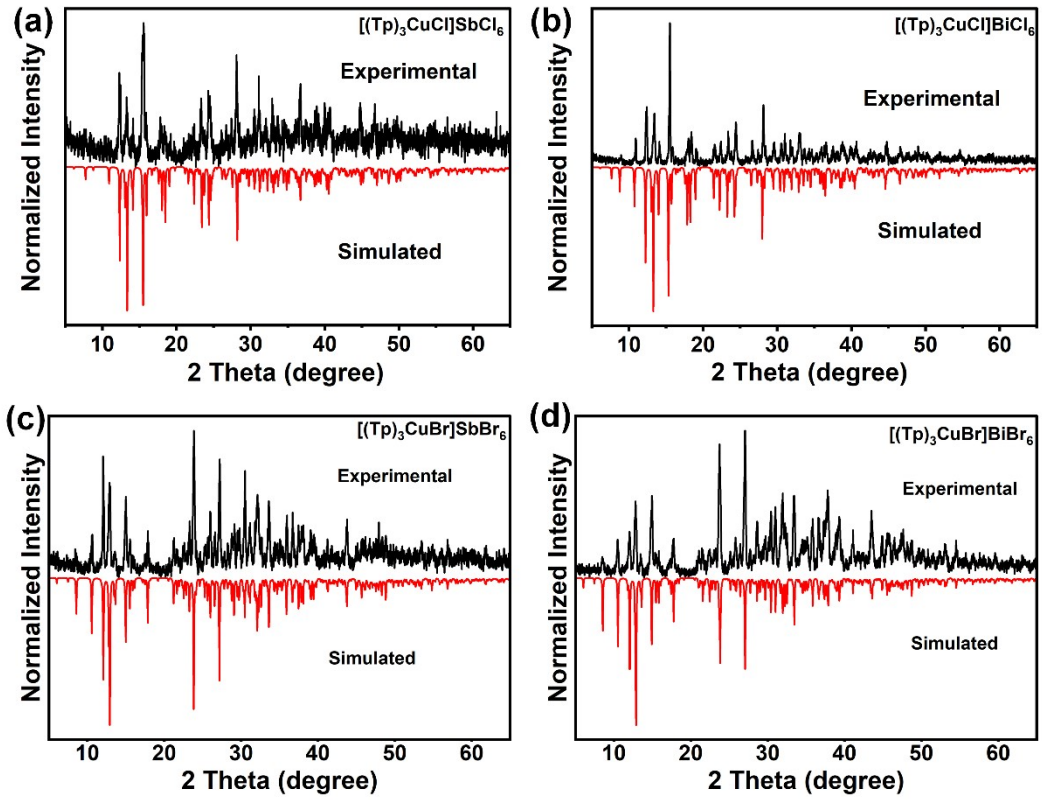

Figure S6 PXRD patterns of $[(Tp)_3CuCl]SbCl_6$ (a), $[(Tp)_3CuCl]BiCl_6$ (b), $[(Tp)_3CuBr]SbBr_6$ (c), and $[(Tp)_3CuBr]BiBr_6$ (d).

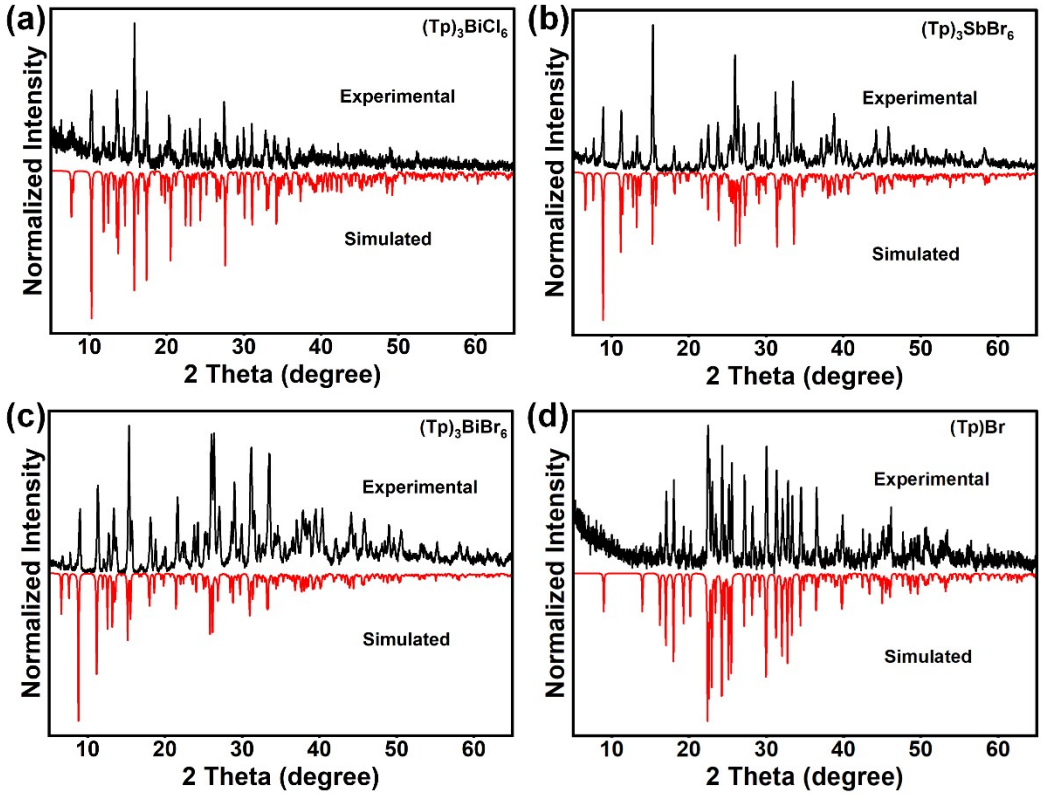

Figure S7 PXRD patterns of $(Tp)_3BiCl_6$ (a), $(Tp)_3SbBr_6$ (b), $(Tp)_3BiBr_6$ (c), and (Tp)Br (d).

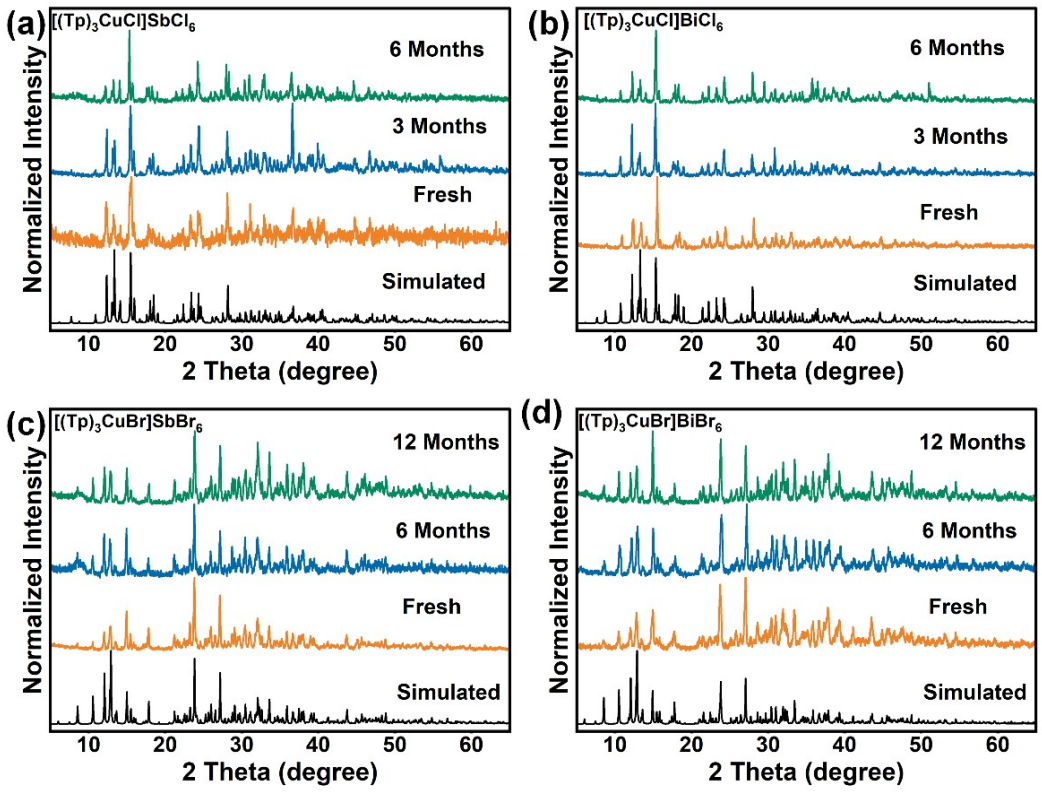

Figure S8 PXRD patterns for $[(Tp)_3CuCl]SbCl_6$ (a) and $[(Tp)_3CuCl]BiCl_6$ (b) fresh samples and samples kept in ambient air for 3 months and 6 months. The PXRD patterns for $[(Tp)_3CuBr]SbBr_6$ (c) and $[(Tp)_3CuBr]BiBr_6$ (d) fresh samples and samples kept in ambient air for 6 months and 12 months.

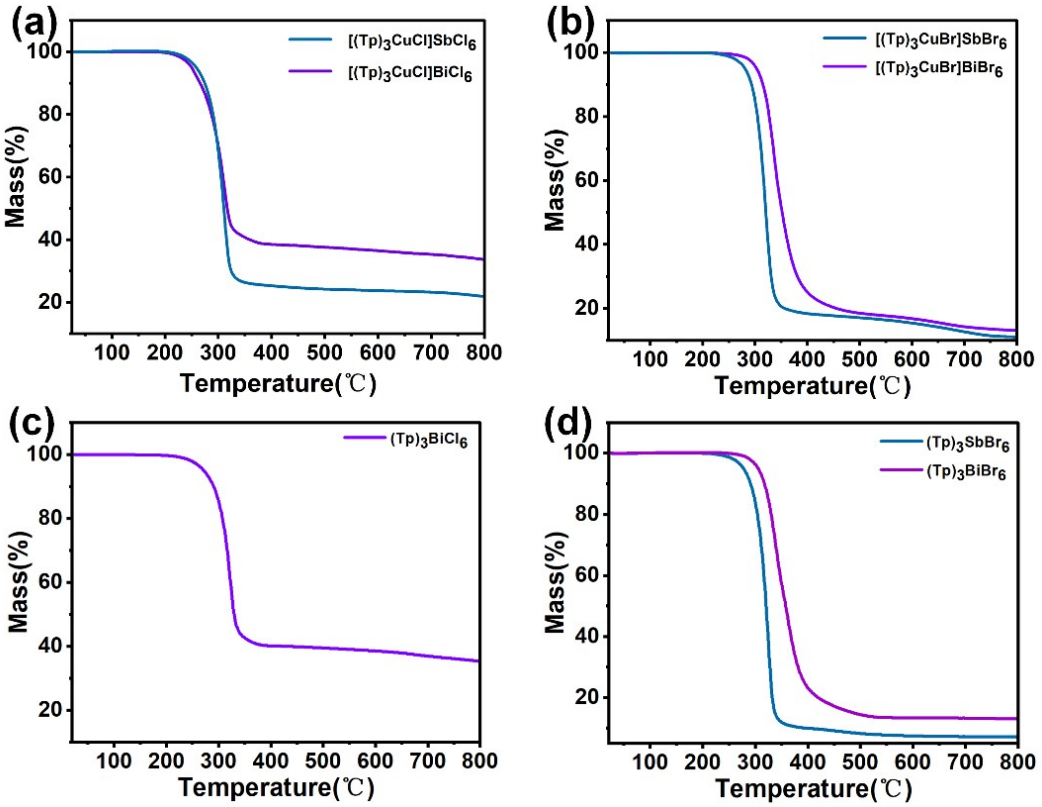

Figure S9 (a) TG curves of $[(Tp)_3CuCl]SbCl_6$ and $[(Tp)_3CuCl]BiCl_6$; (b) TG curves of $[(Tp)_3CuBr]SbBr_6$ and $[(Tp)_3CuBr]BiBr_6$; (c) the TG curve of $(Tp)_3BiCl_6$; (d) TG curves of $(Tp)_3SbBr_6$ and $(Tp)_3BiBr_6$.

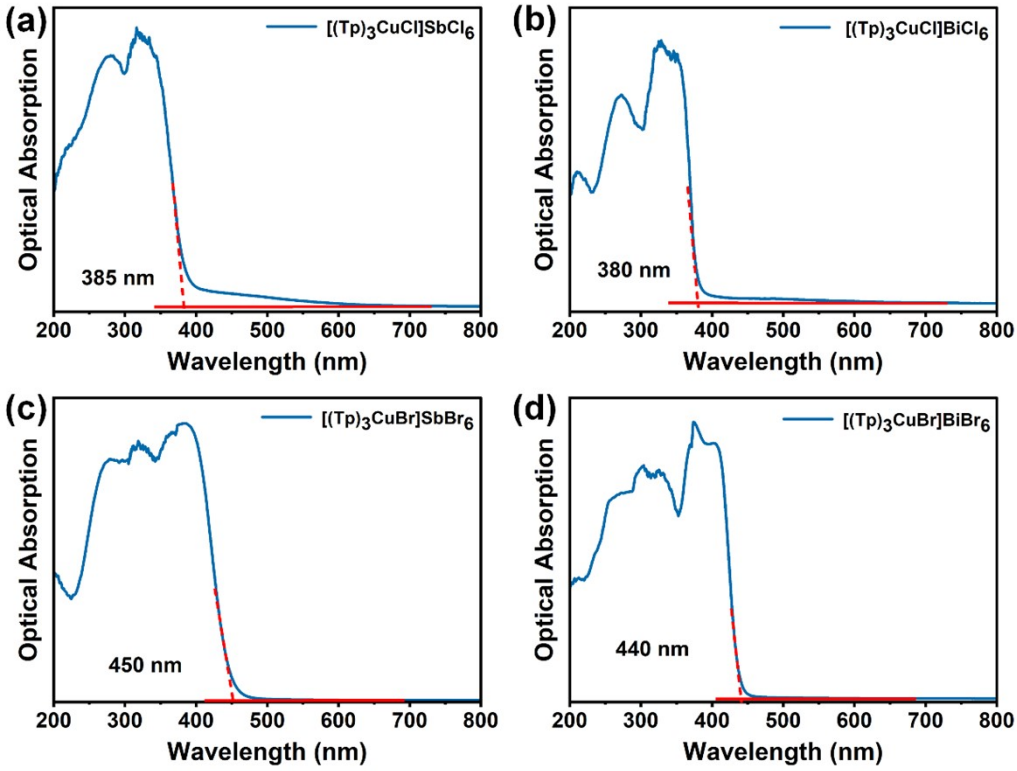

Figure S10 Solid-state optical absorption spectra of $[(Tp)_3CuCl]SbCl_6$ (a), $[(Tp)_3CuCl]BiCl_6$ (b), $[(Tp)_3CuBr]SbBr_6$ (c), and $[(Tp)_3CuBr]BiBr_6$ (d) at ambient conditions.

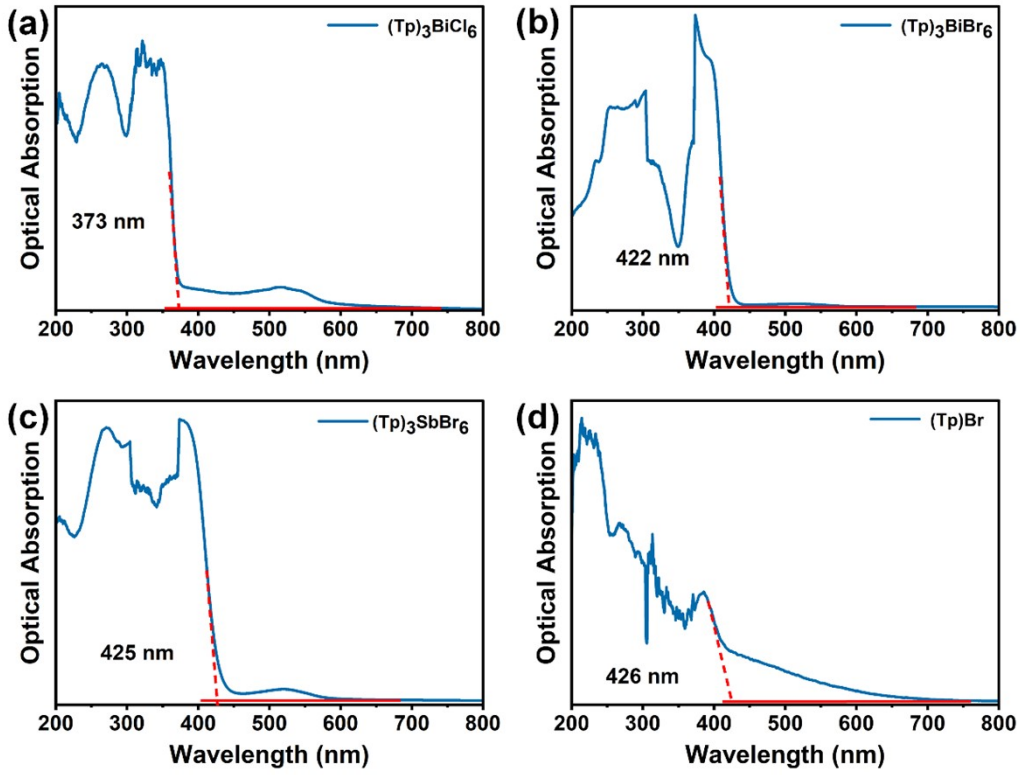

Figure S11 Solid-state optical absorption spectra of $(Tp)_3BiCl_6$ (a), $(Tp)_3BiBr_6$ (b), $(Tp)_3SbBr_6$ (c), and (Tp)Br (d) at ambient conditions.

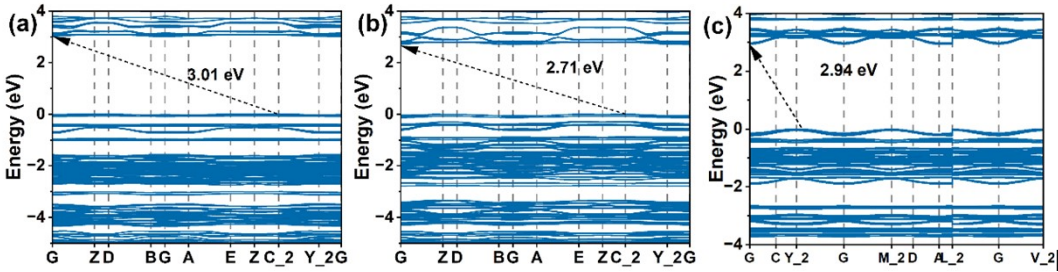

Figure S12 The band structure of $[(Tp)_3CuCl]SbCl_6$ (a), $[(Tp)_3CuBr]SbBr_6$ (b), and $(Tp)_3SbBr_6$ (c).

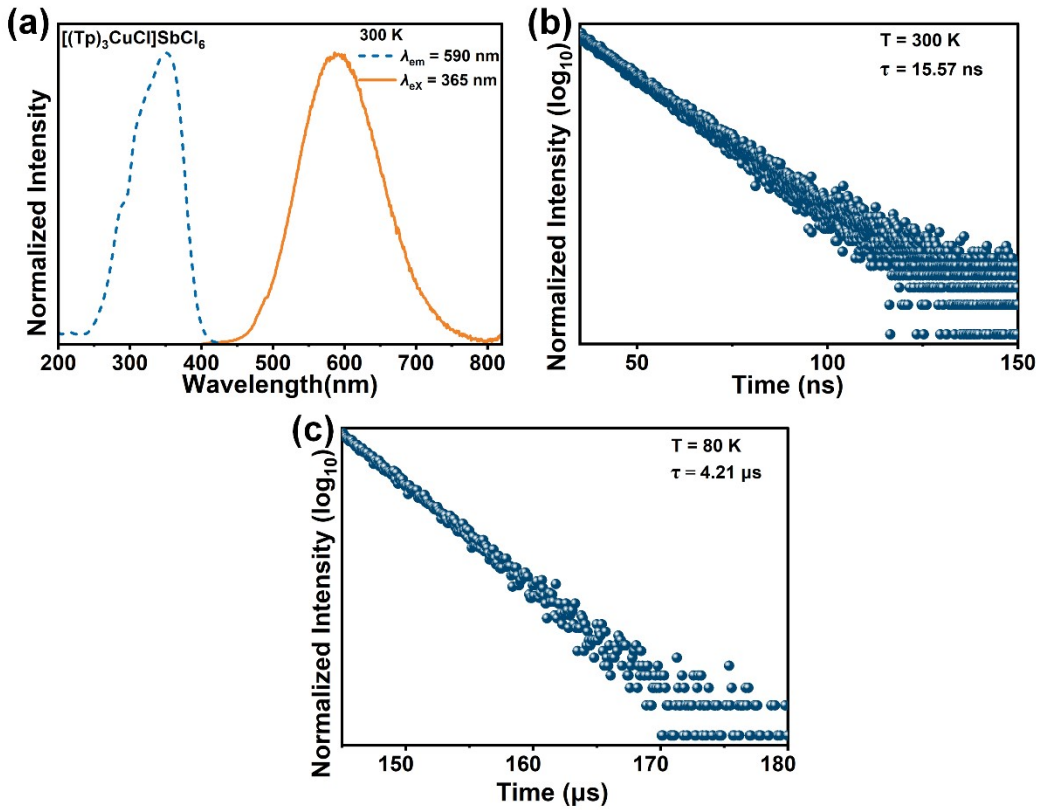

Figure S13 (a) The PLE and PL spectra of $[(Tp)_3CuCl]SbCl_6$ at 300 K. The PL decay spectra of $[(Tp)_3CuCl]SbCl_6$ at 300 K (b) and 80 K (c).

The PL lifetime for $[(Tp)_3CuCl]SbCl_6$ is 15.57 ns at 300 K, while that is 4.21 μs at 80 K (Figure S13b-c).

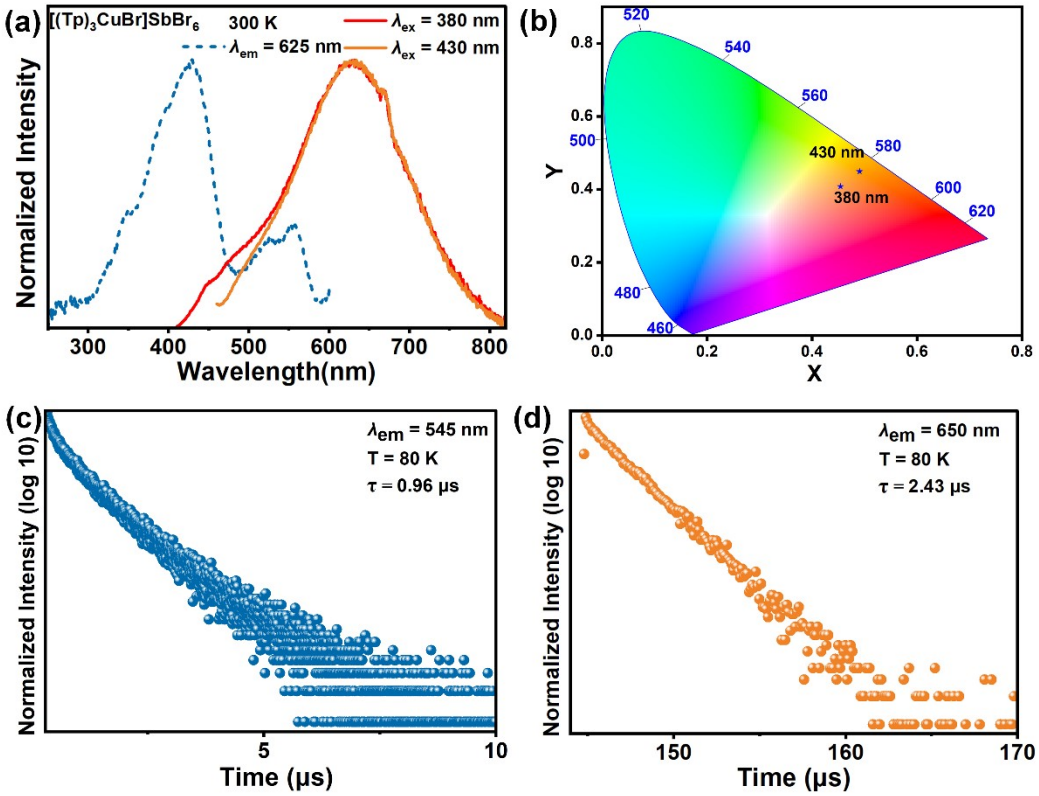

Figure S14 (a) The PLE and PL spectra of $[(Tp)_3CuBr]SbBr_6$ at 300 K. (b) Excitation-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $[(Tp)_3CuBr]SbBr_6$ at 380 and 430 nm at 80 K. PL decay spectra of $[(Tp)_3CuBr]SbBr_6$ at 80 K with emission peaks at 545 nm (c) and 650 nm (d), respectively.

At 80 K, the PL lifetime of $[(Tp)_3CuBr]SbBr_6$ is 0.96 μs at 545 nm and 2.43 μs at 650 nm (Figure S14c-d).

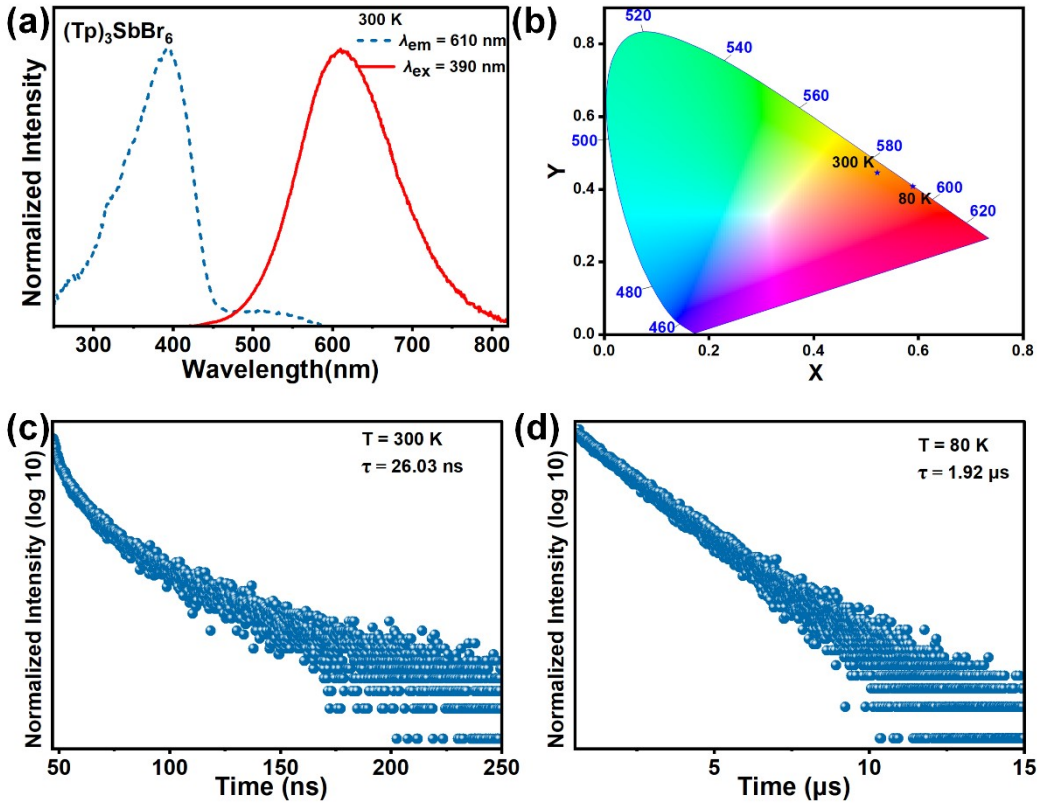

Figure S15 (a) The PLE and PL spectra of $(Tp)_3SbBr_6$ at 300 K. (b) Temperature-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $(Tp)_3SbBr_6$ at 300 and 80 K. The PL decay spectra of $(Tp)_3SbBr_6$ at 300 K (c) and 80 K (d).

The PL lifetime for $(Tp)_3SbBr_6$ is 26.03 ns at 300 K, while that is 1.92 μs at 80 K (Figure S15c-d).

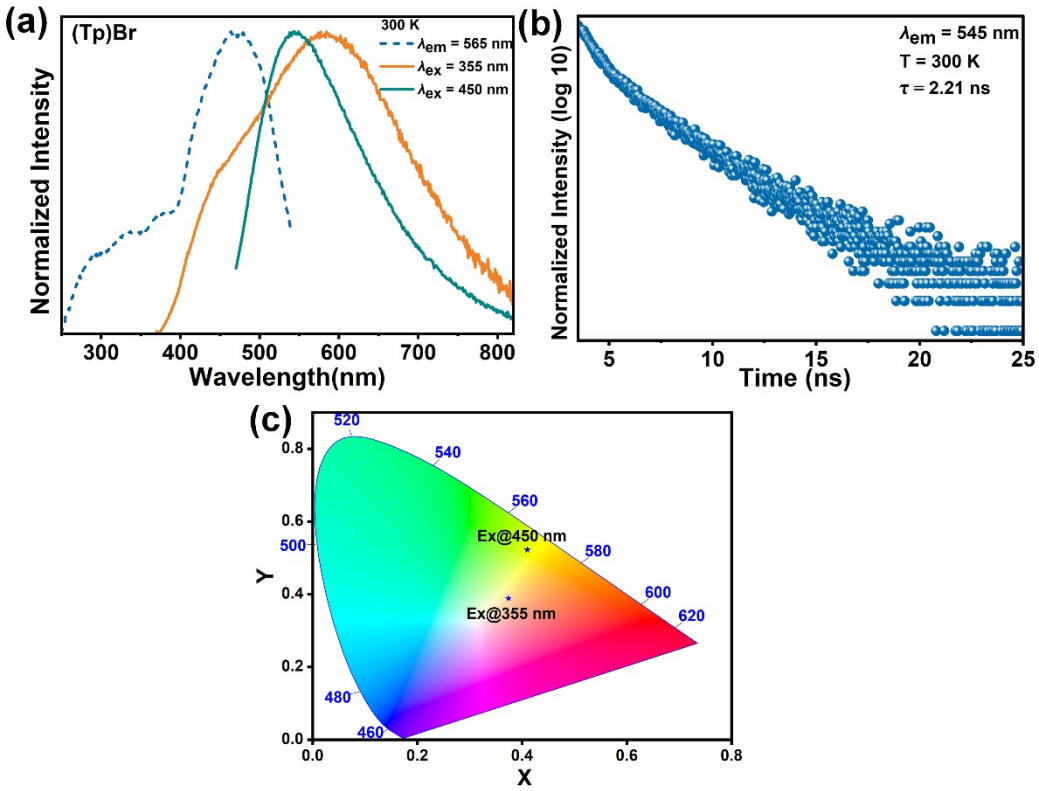

Figure S16 (a) The PLE and PL spectra of (Tp)Br at 300 K. (b) The PL decay spectra of (Tp)Br at 300 K. (c) Excitation-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of (Tp)Br at 300 K.

The PL lifetime for (Tp)Br is 2.21 ns at 300 K (Figure S16b).

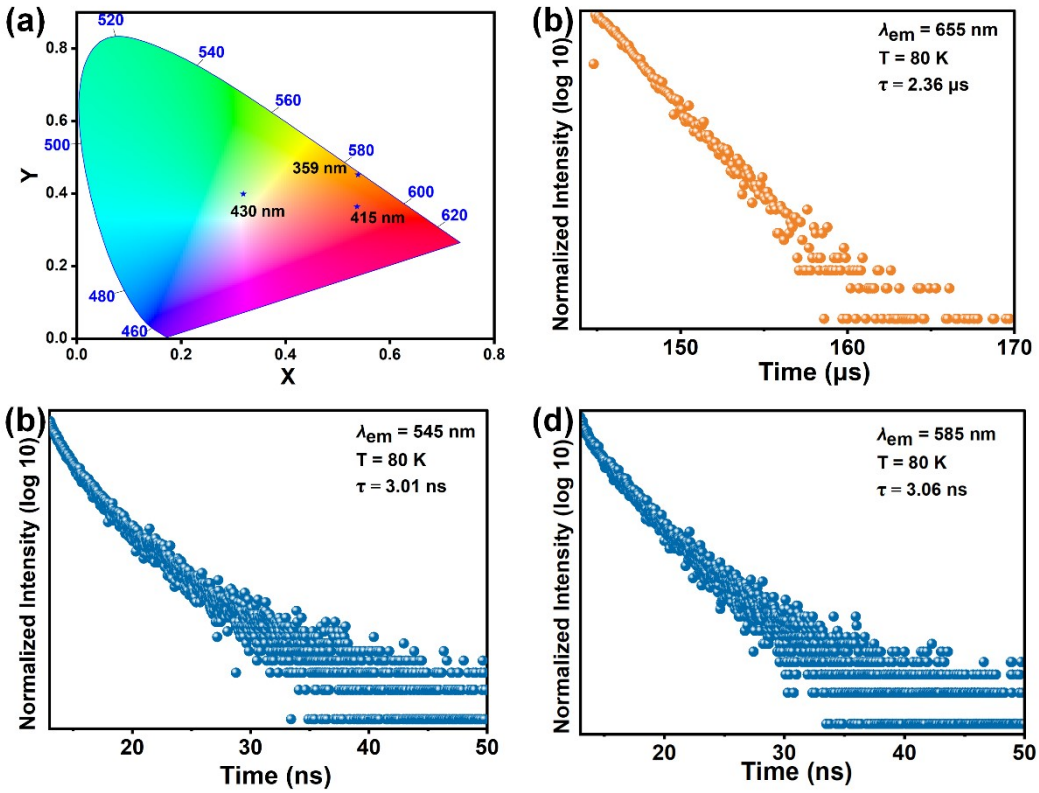

Figure S17 (a) Excitation-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $[(Tp)_3CuBr]BiBr_6$ at 80 K. (b) The PL decay spectra of $[(Tp)_3CuBr]BiBr_6$ (545 nm) at 80 K. (c) The PL decay spectra of $[(Tp)_3CuBr]BiBr_6$ (650 nm) at 80 K. (d) The PL decay spectra of $(Tp)_3BiBr_6$ (585 nm) at 80 K.

At 80 K, the PL lifetime of $(Tp)_3BiBr_6$ is 3.06 ns at 585 nm, while the PL lifetime of $[(Tp)_3CuBr]BiBr_6$ is 3.01 ns at 545 nm and 2.35 μs at 655 nm (Figure S17b-d).

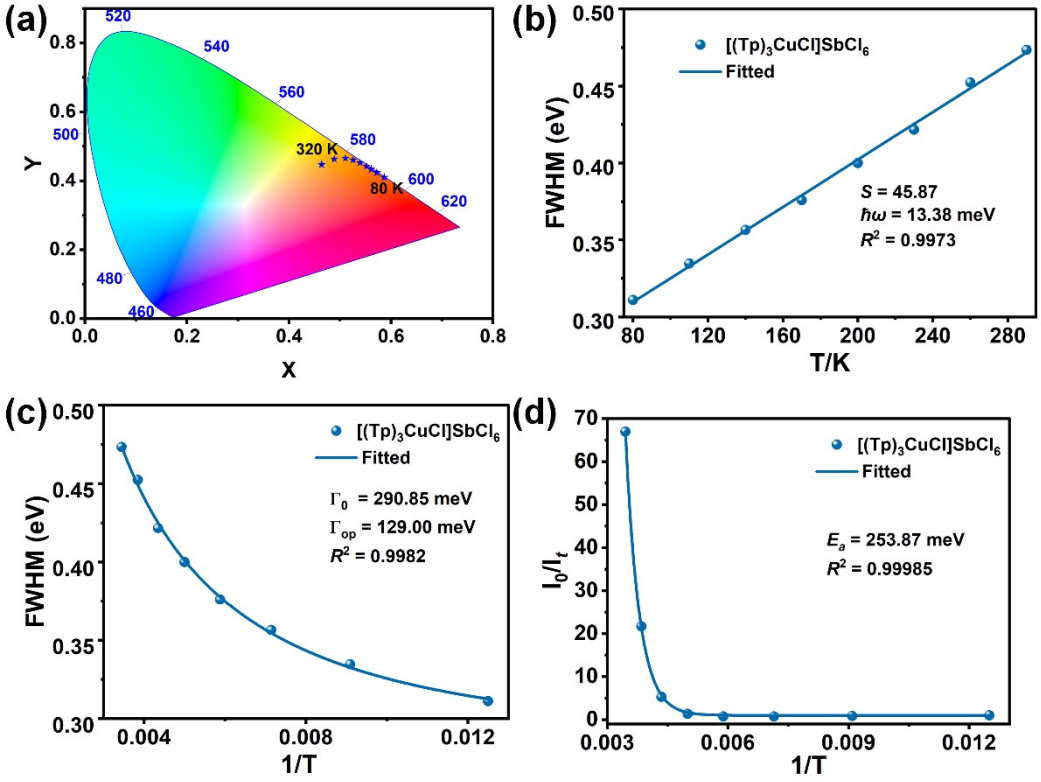

Figure S18 (a) Temperature-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $[(Tp)_3CuCl]SbCl_6$ in the temperature range from 80-320 K. (b) FWHM *vs* temperature fitted by Equation S2 for $[(Tp)_3CuCl]SbCl_6$. (c) FWHM *vs* 1/T fitted by Equation S3 for $[(Tp)_3CuCl]SbCl_6$. (d) PL intensity I_0/I_t vs $1/T$ fitted by Equation S4 for $[(Tp)_3CuCl]SbCl_6$.

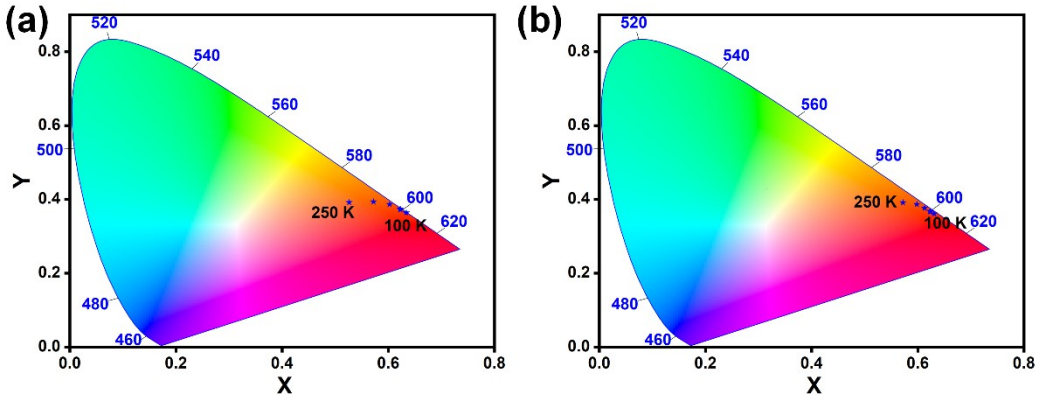

Figure S19 Temperature-dependent Commission Internationale de l´Eclairage (CIE) coordinates diagram of $[(Tp)_3CuBr]SbBr_6$ (a) and $[(Tp)_3CuBr]BiBr_6$ (b) from 100-250 K;

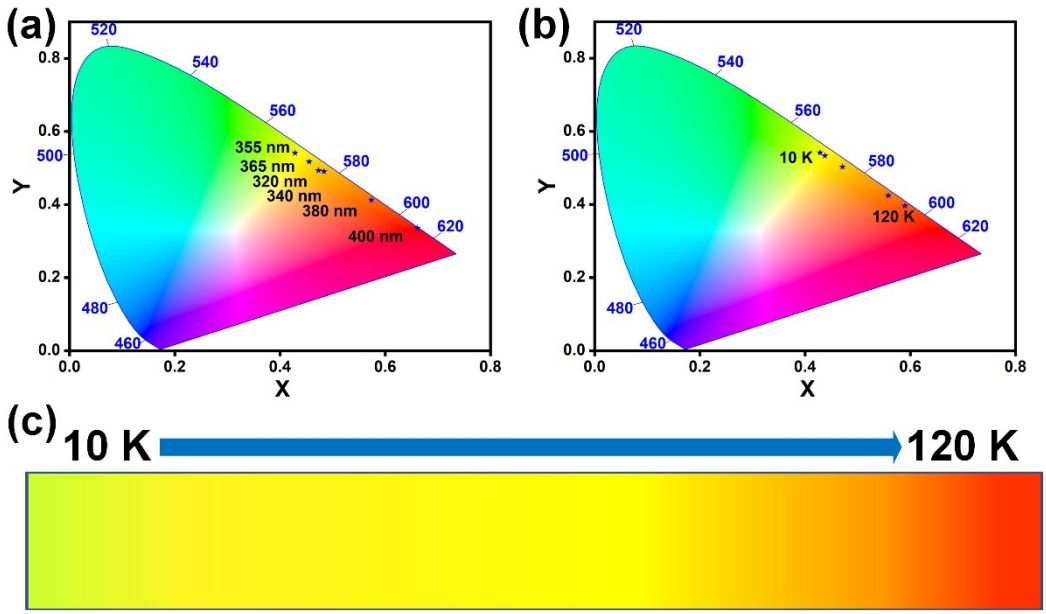

Figure S20 (a) Temperature-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $[(Tp)_3CuBr]SbBr_6$ from 10-120 K. (b) Excitation-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $[(Tp)_3CuBr]SbBr_6$ at 10 K. (c) The visualization of the multi-color emission of $[(Tp)_3CuBr]SbBr_6$ in the temperature range of 10-120 K.

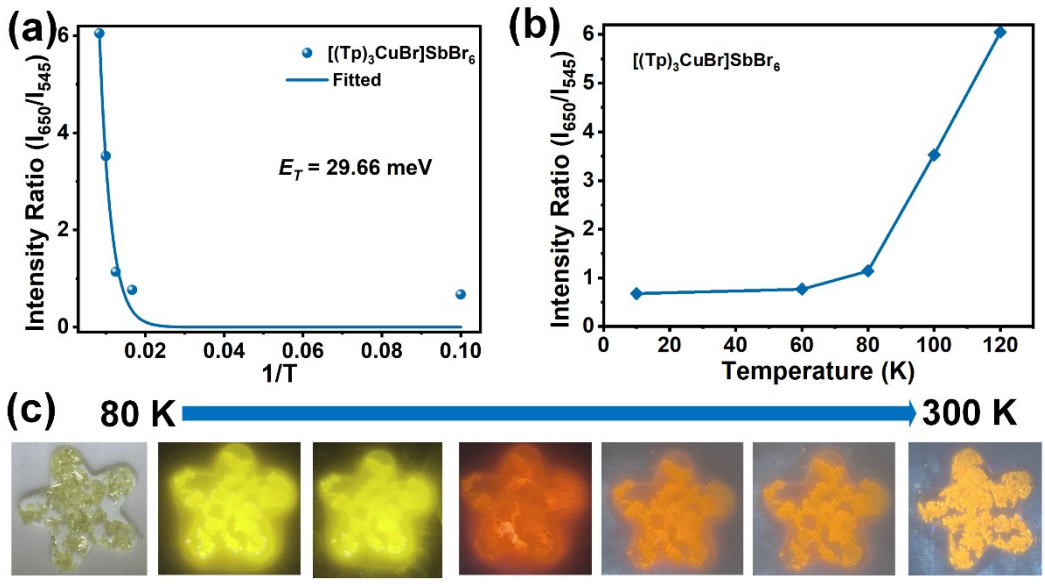

Figure S21 (a) The PL intensity ratio (I_{650}/I_{545}) *vs* $1/T$ fitted by Equation 1 for $[(Tp)_3CuBr]SbBr_6$ in the temperature range of 10-120 K under 355 nm excitation. (b) The PL intensity ratio (I_{650}/I_{545}) *vs* T for $[(Tp)_3CuBr]SbBr_6$ in the temperature range of 10-120 K and under 355 nm excitation. (c) Luminescence of $[(Tp)_3CuBr]SbBr_6$ under UV lamps at 365 nm from 80-300 K.

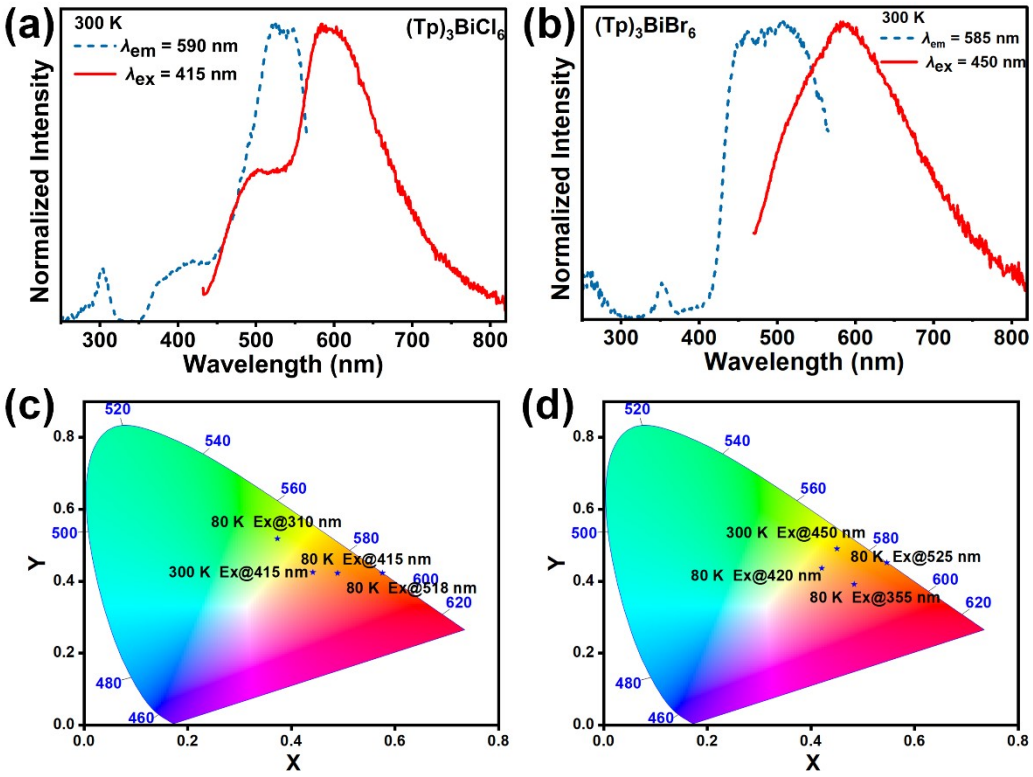

Figure S22 The PLE and PL spectra of $(Tp)_3BiCl_6$ (a) and $(Tp)_3BiBr_6$ (b) at 300 K. Excitation-dependent Commission Internationale de l´Eclairage (CIE) coordinate diagram of $(Tp)_3BiCl_6$ (c) and $(Tp)_3BiBr_6$ (d) at 300 and 80 K.

The $(Tp)_3BiCl_6$ has a maximum emission peak of 590 nm at 300 K under 415 nm excitation and a shoulder peak of 500 nm (Figure S22a). At 300 K, the isomeric bromide $(Tp)_3BiBr_6$ has the highest emission peak at 585 nm under 450 nm excitation (Figure S22b). The emission peak of $(C_4H_{10}NS)Br$ at 575 nm at 300 K (Figure S16a) is very similar to that of $(Tp)_3BiCl_6$ and $(Tp)_3BiBr_6$ around 575 nm. Therefore, it can be assumed that the 575 nm emission of compounds $(Tp)_3BiCl_6$ and $(Tp)_3BiBr_6$ is from the cationic ligand.

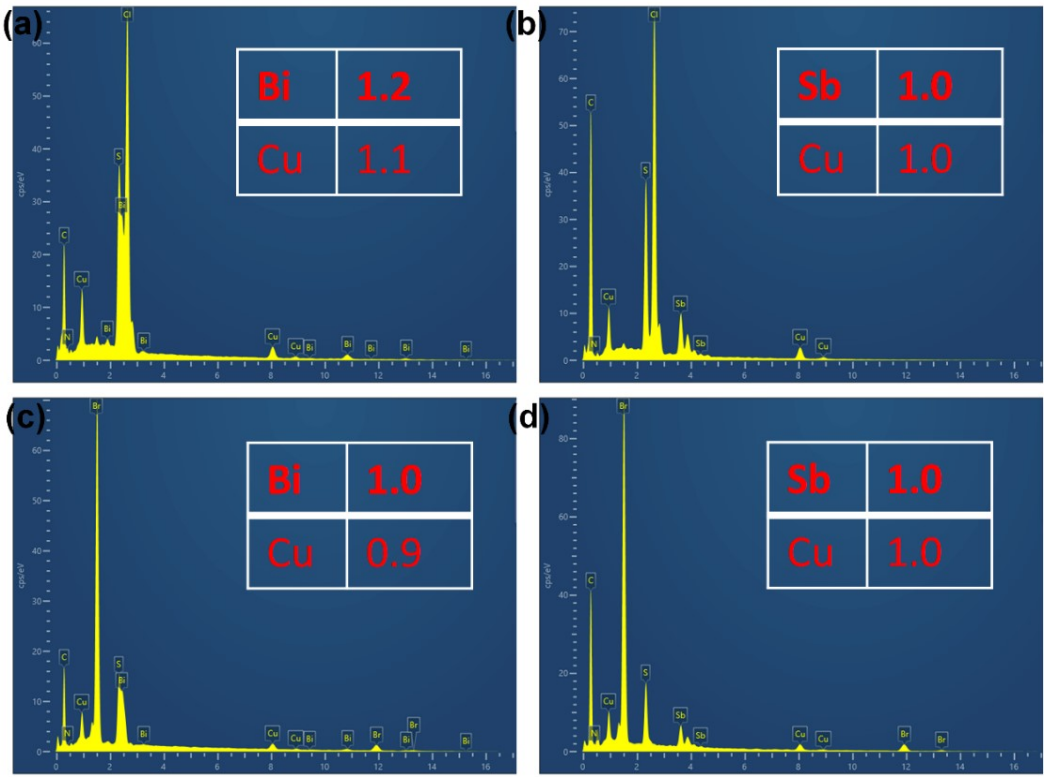

Figure S23 The EDS analysis results of $[(Tp)_3CuCl]BiCl_6$ (a), $[(Tp)_3CuCl]SbCl_6$ (b), $[(Tp)_3CuBr]BiBr_6$ (c) and $[(Tp)_3CuBr]SbBr_6$ (d).

The Energy Dispersive Spectrometer (EDS) analysis was carried out for four cases of heterometallic halides. It can be seen that the ratio of Cu and Sb/Bi in these compounds are close to 1:1.

4. Tables

Table S1. Crystal data and structure refinement for compounds $[(Tp)_3CuCl]SbCl_6$-100 K, $[(Tp)_3CuCl]SbCl_6$-297 K and $[(Tp)_3CuCl]BiCl_6$-100 K, respectively.

Compound	$[(Tp)_3CuCl]SbCl_6$-100 K	$[(Tp)_3CuCl]SbCl_6$-297 K	$[(Tp)_3CuCl]BiCl_6$-100 K
CCDC number	2365632	2391053	2365634
Empirical formula	$C_{12}H_{30}Cl_7CuN_3S_3Sb$	$C_{12}H_30Cl_7CuN_3S_3Sb$	$C_{12}H_{30}BiCl_7CuN_3S_3$
Formula weight	746.01	746.01	833.24
Temperature/K	100(2)	297.00	297.00
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	14.6738(4)	14.7389(4)	14.7695(4)
b/Å	7.5920(2)	7.6456(2)	7.6398(2)
c/Å	23.4189(6)	23.5074(6)	23.5904(6)
α/°	90	90	90
β/°	102.617(3)	102.041(3)	101.894(3)
γ/°	90	90	90
Volume/Å^3	2545.95(12)	2590.71(12)	2604.70(12)
Z	4	4	4
ρ_{calc} g/cm^3	1.946	1.913	2.125
μ/mm^{-1}	2.884	18.246	8.529
F(000)	1480.0	1480.0	1608.0
Crystal size/mm^3	0.25×0.20×0.20	0.25 × 0.10 × 0.10	0.15×0.15×0.10
Radiation/Å	λ = 0.71073	λ = 1.54178	λ = 0.71073
2θ range for data collection/°	5.024 to 61.686	6.132 to 151.78	4.95 to 61.682
Index ranges	-19 ≤ h ≤ 20, -9 ≤ k ≤ 10, -31 ≤ l ≤ 30	-18 ≤ h ≤ 18, -9 ≤ k ≤ 6, -29 ≤ l ≤ 29	-20 ≤ h ≤ 19, -10 ≤ k ≤ 8, -32 ≤ l ≤ 29
Reflections collected	30119	26281	30683
Independent reflections	6753 [R_{int}= 0.0295]	5245 [R_{int} = 0.0615]	6858 [R_{int} = 0.0417]
Data/restraints/parameters	6753/0/244	5245/0/245	6858/0/244
Goodness-of-fit on F^2	1.038	1.031	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0195, wR_2 = 0.0391	R_1 = 0.0393, wR_2 = 0.1061	R_1 = 0.0261, wR_2 = 0.0482
Final R indexes [all data]	R_1 = 0.0248, wR_2 = 0.0403	R_1 = 0.0404, wR_2 = 0.1073	R_1 = 0.0399, wR_2 = 0.0512
Largest diff. peak and hole /e Å^{-3}	0.48/-0.42	2.37/-2.07	0.70/-0.81

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S2. Crystal data and structure refinement for compounds $[(Tp)_3CuBr]SbBr_6$-100 K, $[(Tp)_3CuBr]SbBr_6$-297 K,and (Tp)Br respectively.

Compound	$[(Tp)_3CuBr]SbBr_6$-100 K	$[(Tp)_3CuBr]SbBr_6$-298 K	(Tp)Br
CCDC number	2365629	2391054	2365630
Empirical formula	$C_{12}H_{30}SbBr_7CuN_3S_3$	$C_{12}H_{30}SbBr_7CuN_3S_3$	$C_4H_{10}BrNS$
Formula weight	1057.23	1057.23	184.10
Temperature/K	100(2)	298.20	298(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	14.9299(4)	14.99470(10)	5.71440(10)
b/Å	7.82639(19)	7.88280(10)	6.44290(10)
c/Å	24.0784(6)	24.1569(2)	9.9434(2)
α/°	90	90	85.824(2)
β/°	102.570(3)	102.2670(10)	82.560(2)
γ/°	90	90	79.701(2)
Volume/Å^3	2746.06(12)	2790.16(5)	356.695(11)
Z	4	4	2
ρ_{calc} g/cm^3	2.557	2.517	1.714
μ/mm^{-1}	12.179	22.522	9.705
F(000)	1984.0	1984.0	184.0
Crystal size/mm^3	0.20 × 0.20 × 0.10	0.10 × 0.10 × 0.10	0.30 × 0.20 × 0.20
Radiation/Å	λ = 0.71073	λ = 1.54178	λ = 1.54178
2θ range for data collection/°	3.466 to 58.158	6.032 to 149.814	8.98 to 157.814
Index ranges	-19 ≤ h ≤ 18, -10 ≤ k ≤ 9, -30 ≤ l ≤ 30	-18 ≤ h ≤ 18, -9 ≤ k ≤ 9, -27 ≤ l ≤ 30	-6 ≤ h ≤ 7, -8 ≤ k ≤ 8, -12 ≤ l ≤ 12
Reflections collected	31403	27142	7009
Independent reflections	6429 [R_{int} = 0.0501]	5590 [R_{int} = 0.0453	1464 [R_{int} = 0.0364]
Data/restraints/parameters	6429/0/245	5590/0/245	1464/0/71
Goodness-of-fit on F^2	1.038	1.023	1.062
Final R indexes [I>=2σ (I)]	R_1 = 0.0283, wR_2 = 0.0585	R_1 = 0.0325, wR_2 = 0.0841	R_1= 0.0378, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0401, wR_2 = 0.0619	R_1 = 0.0348, wR2 = 0.0860	R_1 = 0.0388, wR_2 = 0.0979
Largest diff. peak and hole /e Å^{-3}	0.86/-1.08	1.22/-1.45	0.96/-1.02

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S3. Crystal data and structure refinement for compounds $[(Tp)_3CuBr]BiBr_6$-100 K, $[(Tp)_3CuBr]BiBr_6$ -298 K,respectively.

Compound	$[(Tp)_3CuBr]BiBr_6$-100 K	$[(Tp)_3CuBr]BiBr_6$-298 K
CCDC number	2365628	2391052
Empirical formula	$C_{12}H_{30}BiBr_7CuN_3S_3$	$C_{12}H_{30}BiBr_7CuN_3S_3$
Formula weight	1144.46	1144.46
Temperature/K	100(2)	298.20
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	14.9370(3)	15.00940(10)
b/Å	7.8349(2)	7.91280(10)
c/Å	24.1909(6)	24.2673(2)
α/°	90	90
β/°	102.411(2)	102.0800(10)
γ/°	90	90
Volume/Å^3	2764.90(11)	2818.32(5)
Z	4	4
ρ_{calc} g/cm^3	2.749	2.697
μ/mm^{-1}	17.475	26.810
F(000)	2112.0	2112.0
Crystal size/mm^3	0.15 × 0.10 × 0.10	0.20 × 0.20 × 0.20
Radiation/Å	λ = 0.71073	λ = 1.54178
2θ range for data collection/°	3.448 to 58.34	6.022 to 150.43
Index ranges	-20 ≤ h ≤ 19, -9 ≤ k ≤ 10, -30 ≤ l ≤ 32	-18 ≤ h ≤ 18, -9 ≤ k ≤ 8, -30 ≤ l ≤ 28
Reflections collected	31581	27376
Independent reflections	6576 [R_{int} = 0.0534]	5676 [R_{int} = 0.0571]
Data/restraints/parameters	6576/0/244	5676/0/244
Goodness-of-fit on F^2	1.025	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0284, wR_2 = 0.0543	R_1 = 0.0316, wR_2 = 0.0824
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.0579	R_1 = 0.0341, wR_2 = 0.0844
Largest diff. peak and hole /e Å^{-3}	1.05/-1.21	1.10/-1.38

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S4. Crystal data and structure refinement for compounds $(Tp)_3BiCl_6$-100 K, $(Tp)_3SbBr_6$-100 K and $(Tp)_3BiBr_6$-295 K, respectively.

Compound	$(Tp)_3BiCl_6$-100 K	$(Tp)_3SbBr_6$-100 K	$(Tp)_3BiBr_6$-295 K
CCDC number	2365627	2365633	2365631
Empirical formula	$C_{12}H_{30}BiCl_6N_3S_3$	$C_{12}H_{30}SbBr_6N_3S_3$	$C_{12}H_{30}BiBr_6N_3S_3$
Formula weight	734.25	913.78	1001.01
Temperature/K	100(2)	100(2)	295(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$C2/c$
a/Å	8.0704(2)	23.7563(6)	23.9911(8)
b/Å	22.4062(5)	8.2107(2)	8.3716(3)
c/Å	13.7318(3)	27.3933(7)	27.6023(9)
α/°	90	90	90
β/°	101.415(2)	103.077(2)	103.520(3)
γ/°	90	90	90
Volume/Å^3	2433.96(10)	5204.7(2)	5390.1(3)
Z	4	8	8
ρ_{calc} g/cm^3	2.004	2.332	2.467
μ/mm^{-1}	8.164	10.519	15.675
F(000)	1424.0	3456.0	3712.0
Crystal size/mm^3	0.15 × 0.10 × 0.10	0.15 × 0.15 × 0.10	0.15 × 0.15 × 0.05
Radiation/Å	λ = 0.71073	λ = 0.71073	λ = 0.71073
2θ range for data collection/°	3.53 to 61.6	4.104 to 61.476	4.056 to 61.6
Index ranges	-11 ≤ h ≤ 10, -31 ≤ k ≤ 31, -17 ≤ l ≤ 19	-32 ≤ h ≤ 27, -11 ≤ k ≤ 11, -34 ≤ l ≤ 38	-29 ≤ h ≤ 32, -11 ≤ k ≤ 11, -34 ≤ l ≤ 38
Reflections collected	28445	31135	32707
Independent reflections	6245 [R_{int} = 0.0343]	6655 [R_{int} = 0.0305]	6973 [R_{int} = 0.0335]
Data/restraints/parameters	6245/0/226	6655/7/254	6973/1/254
Goodness-of-fit on F^2	1.055	1.017	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0201, wR_2 = 0.0355	R_1 = 0.0237, wR_2 = 0.0402	R_1 = 0.0329, wR_2 = 0.0547
Final R indexes [all data]	R_1 = 0.0277, wR_2 = 0.0366	R_1 = 0.0340, wR_2 = 0.0419	R_1 = 0.0500, wR_2 = 0.0582
Largest diff. peak and hole /e Å^{-3}	0.67/-0.62	0.58/-0.76	0.95/-0.76

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$, [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$

Table S5. The distortion data for all title compounds.

Compounds	σ^2	$\Delta d/\times 10^{-4}$
$[(Tp)_3CuCl]SbCl_6$-100 K	14.70	25.79
$[(Tp)_3CuCl]SbCl_6$-297 K	11.75	21.63
$[(Tp)_3CuCl]BiCl_6$-297 K	10.87	5.77
$[(Tp)_3CuBr]SbBr_6$-100 K	8.30	11.26
$[(Tp)_3CuBr]SbBr_6$-297 K	7.25	10.54
$[(Tp)_3CuBr]BiBr_6$-100 K	8.57	4.63
$[(Tp)_3CuBr]BiBr_6$-297 K	7.56	4.49
$(Tp)_3BiCl_6$-100 K	15.68	3.17
$(Tp)_3SbBr_6$-100 K	9.37	6.23
$(Tp)_3BiBr_6$-295 K	11.88	2.66

Table S6. List of average bond lengths and *M*(1)-*X*(3) bond lengths of $[MX_6]^{3-}$ units in all title compounds.

Compound	Average bond length (Å)	$M(1)$-$X(3)$ bond length (Å)
$[(Tp)_3CuCl]SbCl_6$-100 K	2.6711	2.8894
$[(Tp)_3CuCl]SbCl_6$-297 K	2.6690	2.8692
$[(Tp)_3CuCl]BiCl_6$-297 K	2.7145	2.8060
$[(Tp)_3CuBr]SbBr_6$-100 K	2.8140	2.9498
$[(Tp)_3CuBr]SbBr_6$-297 K	2.8132	2.9390
$[(Tp)_3CuBr]BiBr_6$-100 K	2.8594	2.9378
$[(Tp)_3CuBr]BiBr_6$-297 K	2.8596	2.9349
$(Tp)_3BiCl_6$-100 K	2.7080	-
$(Tp)_3SbBr_6$-100 K	2.8016	-
$(Tp)_3BiBr_6$-295 K	2.8563	-

Notes: $[MX_6]^{3-}$ (*X* = Cl, Br; *M* = Sb, Bi); *M(1)-X(3) refers to a bond between a trivalent metal and a halogen, which is located directly behind the Cu atom and in the vicinity of the Cu atom.*

Table S7 Selected bond lengths (Å) and bond angles (°) for $[(Tp)_3CuCl]SbCl_6$-100 K and $[(Tp)_3CuCl]SbCl_6$-297 K.

$[(Tp)_3CuCl]SbCl_6$-100 K		$[(Tp)_3CuCl]SbCl_6$-297 K	
Sb(1)−Cl (1)	2.4954(4)	Sb(1)−Cl (2)	2.5817(9)
Sb(1)−Cl (2)	2.5787(4)	Sb(1)−Cl (3)	2.5085(8)
Sb(1)−Cl (3)	2.8994(4)	Sb(1)−Cl (4)	2.6503(9)
Sb(1)−Cl (4)	2.7895(4)	Sb(1)−Cl (5)	2.7928(9)
Sb(1)−Cl (5)	2.6613(4)	Sb(1)−Cl (6)	2.8692(8)
Sb(1)−Cl (6)	2.6021(4)	Sb(1)−Cl (7)	2.6113(8)
Cu(1)−Cl (7)	2.3499(4)	Cu(1)−Cl (1)	2.3491(9)
Cu(1)−S(1)	2.2802(4)	Cu(1)−S(1)	2.2898(9)
Cu(1)−S(2)	2.2943(4)	Cu(1)−S(2)	2.3019(10)
Cu(1)−S(3)	2.3868(4	Cu(1)−S(3)	2.4007(9)
Cl(2)−Sb(1)−Cl(1)	87.900(13)	Cl(1)−Sb(1)−Cl(2)	88.38(3)
Cl(3)−Sb(1)−Cl(1)	178.198(13)	Cl(5)−Sb(1)−Cl(2)	92.03(3)
Cl(3)−Sb(1)−Cl(2)	90.688(12)	Cl(5)−Sb(1)−Cl(1)	89.52(3)
Cl(4)−Sb(1)−Cl(1)	83.542(12)	Cl(4)−Sb(1)−Cl(2)	170.33(3)
Cl(4)−Sb(1)−Cl(2)	169.254(13)	Cl(4)−Sb(1)−Cl(1)	83.86(3)
Cl(4)−Sb(1)−Cl(3)	97.987(11)	Cl(4)−Sb(1)−Cl(5)	93.67(3)
Cl(5)−Sb(1)−Cl(1)	89.136(14)	Cl(3)−Sb(1)−Cl(2)	91.22(3)
Cl(5)−Sb(1)−Cl(2)	91.680(13)	Cl(3)−Sb(1)−Cl(1)	178.03(3)
Cl(5)−Sb(1)−Cl(3)	89.788(12)	Cl(3)−Sb(1)−Cl(5)	88.57(3)
Cl(5)−Sb(1)−Cl(4)	94.668(12)	Cl(3)−Sb(1)−Cl(4)	96.72(2)
Cl(6)−Sb(1)−Cl(1)	90.301(13)	Cl(6)−Sb(1)−Cl(2)	85.77(3)
Cl(6)−Sb(1)−Cl(2)	85.279(12)	Cl(6)−Sb(1)−Cl(1)	90.44(3)
Cl(6)−Sb(1)−Cl(3)	90.697(12)	Cl(6)−Sb(1)−Cl(5)	177.80(3)
Cl(6)−Sb(1)−Cl(4)	88.270(12)	Cl(6)−Sb(1)−Cl(4)	88.51(3)
Cl(6)−Sb(1)−Cl(5)	176.926(13)	Cl(6)−Sb(1)−Cl(3)	91.45(3)
S(1)−Cu(1)−Cl(7)	96.041(15)	Cl(7)−Cu(1)−S(1)	95.70(3)
S(2)−Cu(1)−Cl(7)	119.855(16)	S(2)−Cu(1)−Cl(7)	120.59(3)
S(2)−Cu(1)−S(1)	125.288(16)	S(1)−Cu(1)−S(2)	124.63(4)
S(3)−Cu(1)−Cl(7)	95.094(15)	S(3)−Cu(1)−Cl(7)	94.89(3)
S(3)−Cu(1)−S(1)	116.863(16)	S(3)−Cu(1)−S(1)	117.44(3)
S(3)−Cu(1)−S(2)	100.604(15)	S(2)−Cu(1)−S(3)	100.72(3)

Table S8 Selected bond lengths (Å) and bond angles (°) for $[(Tp)_3CuBr]SbBr_6$-100 K and $[(Tp)_3CuBr]SbBr_6$-298 K.

$[(Tp)_3CuBr]SbBr_6$-100 K		$[(Tp)_3CuBr]SbBr_6$-298 K	
Sb(1)−Br (1)	2.6869(4)	Sb(1)−Br (1)	2.6927(5)
Sb(1)−Br (2)	2.9261(4)	Sb(1)−Br (2)	2.9287(5)
Sb(1)−Br (3)	2.9498(4)	Sb(1)−Br (3)	2.9390(5)
Sb(1)−Br (4)	2.7426(4)	Sb(1)−Br (4)	2.7415(5)
Sb(1)−Br (5)	2.7925(4)	Sb(1)−Br (5)	2.7869(5)
Sb(1)−Br (6)	2.7862(4)	Sb(1)−Br (6)	2.7903(5)
Cu(1)−Br (7)	2.4999(6)	Cu(1)−Br (7)	2.4983(8)
Cu(1)−S(1)	2.3862(9)	Cu(1)−S(1)	2.3961(12)
Cu(1)−S(2)	2.3040(10)	Cu(1)−S(2)	2.3140(15)
Cu(1)−S(3)	2.2843(10)	Cu(1)−S(3)	2.2940(11)
Br(1)−Sb(1)−Br(2)	84.614(12)	Br(1)−Sb(1)−Br(2)	84.782(16)
Br(1)−Sb(1)−Br(3)	179.127(13)	Br(1)−Sb(1)−Br(3)	178.521(17)
Br(1)−Sb(1)−Br(4)	89.306(13)	Br(1)−Sb(1)−Br(4)	89.729(18)
Br(1)−Sb(1)−Br(5)	90.392(13)	Br(1)−Sb(1)−Br(5)	90.654(19)
Br(1)−Sb(1)−Br(6)	91.611(13)	Br(1)−Sb(1)−Br(6)	91.524(18)
Br(3)−Sb(1)−Br(2)	94.876(12)	Br(3)−Sb(1)−Br(2)	94.225(14)
Br(4)−Sb(1)−Br(2)	172.073(13)	Br(4)−Sb(1)−Br(2)	172.791(19)
Br(4)−Sb(1)−Br(3)	91.263(12)	Br(4)−Sb(1)−Br(3)	91.349(15)
Br(4)−Sb(1)−Br(5)	92.398(13)	Br(4)−Sb(1)−Br(5)	92.488(16)
Br(4)−Sb(1)−Br(6)	85.753(12)	Br(4)−Sb(1)−Br(6)	86.081(16)
Br(5)−Sb(1)−Br(2)	92.726(12)	Br(5)−Sb(1)−Br(2)	92.244(15)
Br(5)−Sb(1)−Br(3)	88.924(12)	Br(5)−Sb(1)−Br(3)	88.288(17)
Br(5)−Sb(1)−Br(6)	89.330(12)	Br(5)−Sb(1)−Br(6)	177.388(17)
Br(6)−Sb(1)−Br(2)	89.091(12)	Br(6)−Sb(1)−Br(2)	89.391(15)
Br(6)−Sb(1)−Br(3)	177.256(13)	Br(6)−Sb(1)−Br(3)	89.561(15)
S(1)−Cu(1)−Br (7)	94.94(3)	S(1)−Cu(1)−Br (7)	94.96(4)
S(2)−Cu(1)−Br (7)	117.01(3)	S(2)−Cu(1)−Br (7)	117.68(4)
S(2)−Cu(1)−S(1)	101.35(3)	S(2)−Cu(1)−S(1)	101.26(4)
S(3)−Cu(1)−Br(7)	94.71(3)	S(3)−Cu(1)−Br(7)	94.73(4)
S(3)−Cu(1)−S(1)	117.83(4)	S(3)−Cu(1)−S(1)	118.65(5)
S(3)−Cu(1)−S(2)	127.03(4)	S(3)−Cu(1)−S(2)	126.00(5)

Table S9 Selected bond lengths (Å) and bond angles (°) for $[(Tp)_3CuCl]BiCl_6$-297 K.

$[(Tp)_3CuCl]BiCl_6$-297 K			
Bi(1)−Cl (1)	2.6249(8)	Bi(1)−Cl (6)	2.6939(8)
Bi(1)−Cl (2)	2.7960(8)	Cu(1)−Cl (7)	2.3498(9)
Bi(1)−Cl (3)	2.8060(7)	Cu(1)−S(1)	2.4001(8)
Bi(1)−Cl (4)	2.6776(8)	Cu(1)−S(2)	2.3003(9)
Bi(1)−Cl (5)	2.6886(8)	Cu(1)−S(3)	2.2883(9)
Cl(1)−Bi(1)−Cl(2)	84.20(3)	Cl(5)−Bi(1)−Cl(3)	88.35(3)
Cl(1)−Bi(1)−Cl(3)	177.60(3)	Cl(5)−Bi(1)−Cl(6)	179.32(3)
Cl(1)−Bi(1)−Cl(4)	88.65(3)	Cl(6)−Bi(1)−Cl(2)	88.05(2)
Cl(1)−Bi(1)−Cl(5)	89.32(3)	Cl(6)−Bi(1)−Cl(3)	91.59(2)
Cl(1)−Bi(1)−Cl(6)	90.74(3)	Cl(7)−Cu(1)−S(1)	94.24(3)
Cl(2)−Bi(1)−Cl(3)	95.33(2)	S(2)−Cu(1)−Cl(7)	120.15(3)
Cl(4)−Bi(1)−Cl(2)	170.33(2)	S(2)−Cu(1)−S(1)	100.55(3)
Cl(4)−Bi(1)−Cl(3)	92.08(3)	S(3)−Cu(1)−Cl(4)	95.98(3)
Cl(4)−Bi(1)−Cl(5)	93.79(3)	S(3)−Cu(1)−S(1)	117.88(3)
Cl(4)−Bi(1)−Cl(6)	85.53(3)	S(3)−Cu(1)−S(2)	124.91(4)
Cl(5)−Bi(1)−Cl(2)	92.63(3)		

Table S10 Selected bond lengths (Å) and bond angles (°) for $[(Tp)_3CuBr]BiBr_6$-100 K and $[(Tp)_3CuBr]BiBr_6$-298 K.

$[(Tp)_3CuBr]BiBr_6$-100 K		$[(Tp)_3CuBr]BiBr_6$-298 K	
Bi(1)−Br (1)	2.7736(4)	Bi(1)−Br (1)	2.7793(6)
Bi(1)−Br (2)	2.9426(5)	Bi(1)−Br (2)	2.9461(5)
Bi(1)−Br (3)	2.9378(4)	Bi(1)−Br (3)	2.9349(5)
Bi(1)−Br (4)	2.8217(5)	Bi(1)−Br (4)	2.8209(6)
Bi(1)−Br (5)	2.8313(4)	Bi(1)−Br (5)	2.8292(6)
Bi(1)−Br (6)	2.8496(4)	Bi(1)−Br (6)	2.8529(5)
Cu(1)−Br (7)	2.4957(7)	Cu(1)−Br (7)	2.4976(9)
Cu(1)−S(1)	2.3835(13)	Cu(1)−S(1)	2.3968(14)
Cu(1)−S(2)	2.3004(12)	Cu(1)−S(2)	2.3165(18)
Cu(1)−S(3)	2.2837(12)	Cu(1)−S(3)	2.2937(14)
Br(1)−Bi(1)−Br(2)	84.703(13)	Br(1)−Bi(1)−Br(2)	84.834(18)
Br(1)−Bi(1)−Br(3)	178.550(15)	Br(1)−Bi(1)−Br(3)	177.994(17)
Br(1)−Bi(1)−Br(4)	89.594(14)	Br(1)−Bi(1)−Br(4)	89.913(19)
Br(1)−Bi(1)−Br(5)	90.092(14)	Br(1)−Bi(1)−Br(5)	90.36(2)
Br(1)−Bi(1)−Br(6)	91.699(13)	Br(1)−Bi(1)−Br(6)	91.494(19)
Br(3)−Bi(1)−Br(2)	94.240(13)	Br(3)−Bi(1)−Br(2)	93.714(16)
Br(4)−Bi(1)−Br(2)	171.758(13)	Br(4)−Bi(1)−Br(2)	172.457(19)
Br(4)−Bi(1)−Br(3)	91.559(13)	Br(4)−Bi(1)−Br(3)	91.662(17)
Br(4)−Bi(1)−Br(5)	93.719(13)	Br(4)−Bi(1)−Br(5)	93.529(18)
Br(4)−Bi(1)−Br(6)	85.440(13)	Br(4)−Bi(1)−Br(6)	85.852(17)
Br(5)−Bi(1)−Br(2)	92.240(13)	Br(5)−Bi(1)−Br(2)	91.917(16)
Br(5)−Bi(1)−Br(3)	88.958(13)	Br(5)−Bi(1)−Br(3)	88.304(18)
Br(5)−Bi(1)−Br(6)	178.016(14)	Br(5)−Bi(1)−Br(6)	178.044(18)
Br(6)−Bi(1)−Br(2)	88.779(13)	Br(6)−Bi(1)−Br(2)	88.871(16)
Br(6)−Bi(1)−Br(3)	89.268(13)	Br(6)−Bi(1)−Br(3)	89.860(16)
S(1)−Cu(1)−Br (7)	94.64(3)	S(1)−Cu(1)−Br (7)	94.72(4)
S(2)−Cu(1)−Br (7)	116.87(4)	S(2)−Cu(1)−Br (7)	117.54(5)
S(2)−Cu(1)−S(1)	101.22(4)	S(2)−Cu(1)−S(1)	101.23(5)
S(3)−Cu(1)−Br(7)	95.18(3)	S(3)−Cu(1)−Br(7)	95.20(4)
S(3)−Cu(1)−S(1)	117.96(4)	S(3)−Cu(1)−S(1)	118.76(6)
S(3)−Cu(1)−S(2)	126.95(5)	S(3)−Cu(1)−S(2)	125.80(6)

Table S11 Selected bond lengths (Å) and bond angles (°) for $(Tp)_3BiCl_6$-100 K and $(Tp)_3SbBr_6$-100 K.

$(Tp)_3BiCl_6$-100 K		$(Tp)_3SbBr_6$-100 K.	
Bi(1)−Cl (1)	2.7118(6)	Sb(1)−Br (1)	2.9169(3)
Bi(1)−Cl (2)	2.7550(6)	Sb(1)−Br (2)	2.7780(3)
Bi(1)−Cl (3)	2.6916(6)	Sb(1)−Br (3)	2.7173(3)
Bi(1)−Cl (4)	2.6689(6)	Sb(1)−Br (4)	2.7747(3)
Bi(1)−Cl (5)	2.6396(6)	Sb(1)−Br (5)	2.7503(3)
Bi(1)−Cl (6)	2.7804(6)	Sb(1)−Br (6)	2.8726(3)
Cl(1)−Bi(1)−Cl(2)	95.380(18)	Br(2)−Sb(1)−Br(1)	93.435(9)
Cl(1)−Bi(1)−Cl(6)	94.655(18)	Br(2)−Sb(1)−Br(6)	88.774(9)
Cl(2)−Bi(1)−Cl(6)	87.336(18)	Br(3)−Sb(1)−Br(1)	177.987(10)
Cl(3)−Bi(1)−Cl(1)	175.029(18)	Br(3)−Sb(1)−Br(2)	84.983(9)
Cl(3)−Bi(1)−Cl(2)	83.780(18)	Br(3)−Sb(1)−Br(4)	95.192(9)
Cl(3)−Bi(1)−Cl(6)	90.204(17)	Br(3)−Sb(1)−Br(5)	90.074(9)
Cl(4)−Bi(1)−Cl(1)	85.376(18)	Br(3)−Sb(1)−Br(6)	89.066(9)
Cl(4)−Bi(1)−Cl(2)	179.206(18)	Br(4)−Sb(1)−Br(1)	86.334(9)
Cl(4)−Bi(1)−Cl(3)	95.488(18)	Br(4)−Sb(1)−Br(2)	177.511(10)
Cl(4)−Bi(1)−Cl(6)	92.362(18)	Br(4)−Sb(1)−Br(6)	93.711(9)
Cl(5)−Bi(1)−Cl(1)	85.686(19)	Br(5)−Sb(1)−Br(1)	88.641(8)
Cl(5)−Bi(1)−Cl(2)	90.165(18)	Br(5)−Sb(1)−Br(2)	88.608(9)
Cl(5)−Bi(1)−Cl(3)	89.414(18)	Br(5)−Sb(1)−Br(1)	88.909(9)
Cl(5)−Bi(1)−Cl(4)	90.135(18)	Br(5)−Sb(1)−Br(6)	177.306(9)
Cl(5)−Bi(1)−Cl(6)	177.499(18)	Br(6)−Sb(1)−Br(1)	92.148(9)

Table S12 Selected bond lengths (Å) and bond angles (°) for $(Tp)_3BiBr_6$-295 K.

$(Tp)_3BiBr_6$-295 K.			
Bi(1)−Br (1)	2.9291(5)	Bi(1)−Br (4)	2.8323(5)
Bi(1)−Br (2)	2.8404(5)	Bi(1)−Br (5)	2.8189(5)
Bi(1)−Br (3)	2.8060(5)	Bi(1)−Br (6)	2.9109(5)
Br(2)−Bi(1)−Br(1)	94.146(15)	Br(4)−Bi(1)−Br(2)	178.407(17)
Br(2)−Bi(1)−Br(6)	88.268(16)	Br(4)−Bi(1)−Br(6)	93.089(15)
Br(3)−Bi(1)−Br(1)	178.000(16)	Br(5)−Bi(1)−Br(1)	88.544(14)
Br(3)−Bi(1)−Br(2)	84.554(16)	Br(5)−Bi(1)−Br(2)	89.115(16)
Br(3)−Bi(1)−Br(4)	96.282(16)	Br(5)−Bi(1)−Br(1)	89.530(15)
Br(3)−Bi(1)−Br(5)	89.914(15)	Br(5)−Bi(1)−Br(6)	177.376(15)
Br(3)−Bi(1)−Br(6)	89.638(15)	Br(6)−Bi(1)−Br(1)	91.845(14)
Br(4)−Bi(1)−Br(1)	84.981(15)		

Table S13 Hydrogen bonding data for $[(Tp)_3CuCl]SbCl_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···Cl(1)#1	0.91	2.48	3.3619(15)	162.1
N(1)−H(1A)···Cl(2)#1	0.91	2.79	3.2706(14)	114.3
N(1)−H(1B)···Cl(5)#2	0.91	2.36	3.1766(15)	149.4
N(2)−H(2A)···Cl(7)#3	0.91	2.22	3.1323(14)	176.4
N(2)−H(2B)···Cl(2)#4	0.91	2.94	3.6388(14)	134.5
N(2)−H(2B)···Cl(3)#4	0.91	2.34	3.0952(14)	139.8
N(3)−H(3A)···Cl(4)#5	0.91	2.30	3.2085(14)	173.3
N(3)−H(3B)···Cl(5)#6	0.91	2.39	3.1678(14)	143.7
N(3)−H(3B)···Cl(6)#5	0.91	2.73	3.2572(13)	118.0
C(1)−H(1C)···Cl(1)	0.99	2.84	3.6343(17)	138.3
C(1)−H(1C)···Cl(5)	0.99	2.89	3.5922(16)	128.7
C(1)−H(1D)···Cl(1)#1	0.99	2.93	3.7520(17)	140.8
C(3)−H(3C)···Cl(2)#1	0.99	2.96	3.5871(17)	121.9
C(3)−H(3C)···Cl(3)#2	0.99	2.92	3.4675(16)	116.1
C(3)−H(3D)···Cl(1)#2	0.99	2.77	3.7442(18)	166.6
C(4)−H(4B)···Cl(2)#7	0.99	2.97	3.9174(17)	159.9
C(6)−H(6B)···Cl(1)#1	0.99	2.88	3.4701(16)	119.3
C(7)−H(7A)···Cl(4)#4	0.99	2.73	3.5841(17)	145.1
C(7)−H(7B)···Cl(7)	0.99	2.88	3.7585(18)	148.8
C(9)−H(9A)···Cl(7)	0.99	2.91	3.4355(15)	114.2
C(10)−H(10A)···Cl(4)#6	0.99	2.71	3.6685(17)	163.0
C(12)−H(12A)···S(2)	0.99	2.80	3.5369(16)	132.1
C(12)−H(12B)···Cl(4)	0.99	2.78	3.6203(17)	142.6

Symmetry transformations used to generate equivalent atoms:

#1 -*x*,-1/2+*y*,1/2-*z*;#2 -*x*,1/2+*y*,1/2-*z* ;#3 +*x*,-1+*y*,+*z*; #4 +*x*,3/2-*y*,1/2+*z*; #5 1-*x*,-1/2+*y*,1/2-*z*; #6 1-*x*,1/2+*y*,1/2-*z*;#7 +*x*,5/2-*y*,1/2+*z*

Table S14 Hydrogen bonding data for $[(Tp)_3CuCl]BiCl_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···Cl(3)#1	0.89	2.49	3.233(3)	141.7
N(1)−H(1A)···Cl(6)#2	0.89	2.71	3.251(3)	120.3
N(1)−H(1B)···Cl(2)#2	0.89	2.35	3.236(3)	174.7
N(2)−H(2A)···Cl(7)#3	0.89	2.25	3.141(3)	175.5
N(2)−H(2B)···Cl(1)#4	0.89	2.90	3.587(3)	134.7
N(2)−H(2B)···Cl(5)#4	0.89	2.45	3.157(3)	136.9
N(3)−H(3A)···Cl(1)#5	0.89	2.84	3.292(3)	112.8
N(3)−H(3A)···Cl(4)#5	0.89	2.58	3.438(3)	161.2
N(3)−H(3B)···Cl(3)#6	0.89	2.52	3.302(3)	147.4
C(1)−H(1C)···Cl(2)	0.97	2.79	3.631(3)	145.1
C(1)−H(1D)···S(2)	0.97	2.87	3.585(3)	131.3
C(3)−H(3D)···Cl(2)#1	0.97	2.75	3.691(3)	164.6
C(4)−H(4B)···Cl(7)	0.97	2.91	3.433(3)	115.1
C(6)−H(6A)···Cl(7)	0.97	2.95	3.815(3)	148.3
C(6)−H(6B)···Cl(2)#4	0.97	2.79	3.619(3)	144.0
C(7)−H(7A)···Cl(4)#5	0.97	2.88	3.444(4)	118.2
C(9)−H(9A)···Cl(1)#7	0.97	2.92	3.848(3)	159.7
C(10)−H(10A)···Cl(4)#6	0.97	2.90	3.835(4)	161.4
C(10)−H(10B)···Cl(1)#5	0.97	2.96	3.588(4)	123.2
C(10)−H(10B)···Cl(5)#6	0.97	2.97	3.467(3)	112.8
C(12)−H(12A)···Cl(4)#5	0.97	2.91	3.744(3)	144.4
C(12)−H(12B)··· Cl(4)	0.97	2.87	3.649(3)	137.7

Symmetry transformations used to generate equivalent atoms:

#1 -*x*,-1/2+*y*,1/2-*z*;#2 -*x*,1/2+*y*,1/2-*z* ;#3 +*x*,-1+*y*,+*z*; #4 +*x*,3/2-*y*,1/2+*z*; #5 1-*x*,-1/2+*y*,1/2-*z*; #6 1-*x*,1/2+*y*,1/2-*z*;#7 +*x*,5/2-*y*,1/2+*z*

Table S15 Hydrogen bonding data for $[(Tp)_3CuBr]SbBr_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···Br(2)#1	0.91	2.46	3.362(3)	172.7
N(1)−H(1A)···Br(3)#2	0.91	2.58	3.347(3)	142.5
N(1)−H(1B)···Br(6)#1	0.91	2.77	3.341(3)	121.6
N(2)−H(2A)···Br(1)#3	0.91	3.08	3.750(3)	131.9
N(2)−H(2B)···Br(5)#3	0.91	2.52	3.266(3)	139.4
N(2)−H(2B)···Br(7)#4	0.91	2.37	3.283(3)	176.2
N(3)−H(3A)···Br(3)#5	0.91	2.63	3.418(3)	145.4
N(3)−H(3A)···Br(1)#6	0.91	2.95	3.413(3)	113.0
N(3)−H(3B)···Br(4)#6	0.91	2.72	3.592(3)	161.8
C(1)−H(1C)···Br(2)	0.99	2.90	3.718(4)	140.4
C(1)−H(1D)···S(2)	0.99	2.88	3.602(3)	130.7
C(3)−H(3C)···Br(5)#2	0.99	3.14	3.852(4)	130.5
C(3)−H(3D)···Br(2)#2	0.99	2.80	3.744(3)	159.9
C(4)−H(4B)···Br(7)	0.99	2.93	3.496(3)	117.5
C(6)−H(6A)···Br(7)	0.99	2.92	3.787(3)	146.6
C(6)−H(6B)···Br(2)#3	0.99	2.85	3.677(3)	141.7
C(7)−H(7A)···Br(4)#+	0.99	2.97	3.499(4)	114.7
C(9)−H(9A)···Br(1)#7	0.99	3.00	3.911(4)	153.8
C(9)−H(9A)···Br(7)	0.99	3.10	3.718(4)	121.8
C(10)−H(10A)···Br(4)#5	0.99	2.95	3.894(4)	159.8
C(10)−H(10B)···Br(1)#6	0.99	3.05	3.702(4)	124.4
C(10)−H(10B)···Br(5)#5	0.99	3.05	3.545(4)	112.0
C(12)−H(12A)···Br(4)#6	0.99	3.05	3.905(4)	145.2
C(12)−H(12B)··· Br(3)	0.99	3.05	3.690(3)	123.7
C(12)−H(12B)··· Br(4)	0.99	2.93	3.732(4)	138.4
C(12)−H(12B)··· Br(6)	0.99	3.03	3.737(3)	129.2

Symmetry transformations used to generate equivalent atoms:

#1 1-*x*,1/2+*y*,1/2-*z*; #2 1-*x*,-1/2+*y*,1/2-*z*;#3 +*x*,3/2-*y*,1/2+*z*; #4 +*x*,1+*y*,+*z*; #5 -*x*,-1/2+*y*,1/2-*z*; #6 -*x*,1/2+*y*,1/2-*z*; #7 +*x*,1/2-*y*,1/2+*z*

Table S16 Hydrogen bonding data for $[(Tp)_3CuBr]BiBr_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···Br(2)#1	0.91	2.59	3.349(4)	141.8
N(1)−H(1A)···Br(3)#2	0.91	2.76	3.329(4)	122.0
N(1)−H(1B)···Br(6)#1	0.91	2.46	3.367(3)	172.9
N(2)−H(2A)···Br(1)#3	0.91	3.06	3.727(4)	131.6
N(2)−H(2B)···Br(5)#3	0.91	2.55	3.281(4)	137.5
N(2)−H(2B)···Br(7)#4	0.91	2.37	3.277(4)	176.1
N(3)−H(3A)···Br(3)#5	0.91	2.67	3.454(4)	144.4
N(3)−H(3A)···Br(1)#6	0.91	2.69	3.565(4)	161.7
N(3)−H(3B)···Br(4)#6	0.99	2.90	3.710(4)	140.2
C(1)−H(1C)···Br(2)	0.99	2.89	3.614(5)	130.5
C(1)−H(1D)···S(2)	0.99	3.12	3.886(4)	135.6
C(3)−H(3C)···Br(5)#2	0.99	3.13	3.844(4)	129.8
C(3)−H(3D)···Br(2)#2	0.99	2.81	3.753(4)	160.5
C(4)−H(4B)···Br(7)	0.99	2.93	3.495(5)	117.2
C(6)−H(6A)···Br(7)	0.99	2.94	3.803(4)	145.6
C(6)−H(6B)···Br(2)#3	0.99	2.86	3.694(4)	142.2
C(7)−H(7A)···Br(4)#+	0.99	2.96	3.473(4)	113.6
C(9)−H(9A)···Br(1)#7	0.99	2.97	3.888(4)	154.4
C(9)−H(9A)···Br(7)	0.99	3.10	3.719(4)	121.5
C(10)−H(10A)···Br(4)#5	0.99	2.99	3.933(4)	160.6
C(10)−H(10B)···Br(1)#6	0.99	3.04	3.697(4)	125.0
C(10)−H(10B)···Br(5)#5	0.99	3.07	3.564(4)	112.4
C(12)−H(12A)···Br(4)#6	0.99	3.01	3.868(4)	145.4
C(12)−H(12B)··· Br(3)	0.99	3.10	3.731(5)	122.9
C(12)−H(12B)··· Br(4)	0.99	2.94	3.728(4)	137.2
C(12)−H(12B)··· Br(6)	0.99	3.03	3.735(4)	129.3

Symmetry transformations used to generate equivalent atoms:

#1 1-*x*,1/2+*y*,1/2-*z*; #2 1-*x*,-1/2+*y*,1/2-*z*;#3 +*x*,3/2-*y*,1/2+*z*; #4 +*x*,1+*y*,+*z*; #5 -*x*,-1/2+*y*,1/2-*z*; #6 -*x*,1/2+*y*,1/2-*z*; #7 +*x*,1/2-*y*,1/2+*z*

Table S17 Hydrogen bonding data for $(Tp)_3BiCl_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···S(3)	0.91	2.65	3.516(2)	160.2
N(1)−H(1B)···Cl(6)#1	0.91	2.48	3.195(2)	135.5
N(1)−H(1B)···S(2)	0.91	2.84	3.362(2)	118.0
C(1)−H(1C)···S(2)#2	0.99	2.98	3.745(2)	135.2
C(1)−H(1D)···Cl(1)#2	0.99	2.72	3.421(2)	128.1
C(1)−H(1D)···Cl(2)	0.99	2.73	3.509(2)	135.4
C(2)−H(2D)···Cl(5)#3	0.99	2.84	3.522(3)	127.1
C(3)−H(3D)···Cl(5)#4	0.99	2.72	3.689(2)	167.6
C(4)−H(4A)···Cl(3)#4	0.99	2.82	3.545(2)	130.2
N(2)−H(2A)···Cl(1)#1	0.91	2.76	3.413(2)	129.5
N(2)−H(2A)···Cl(4)#1	0.91	2.57	3.340(2)	142.6
N(2)−H(2B)···Cl(2)#5	0.91	2.93	3.646(2)	137.0
N(2)−H(2B)···Cl(3)#5	0.91	2.54	3.264(2)	136.3
C(5)−H(5A)···Cl(6)#5	0.99	2.96	3.670(3)	129.4
C(5)−H(5B)···Cl(3)#5	0.99	2.97	3.485(3)	113.2
C(6)−H(6A)···Cl(3)#4	0.99	2.95	3.669(2)	130.2
C(6)−H(6B)···Cl(4)#1	0.99	2.95	3.680(3)	130.9
C(7)−H(7A)···Cl(6)#1	0.99	2.73	3.643(3)	153.1
C(7)−H(7B)···Cl(5)	0.99	2.77	3.659(2)	150.4
C(8)−H(8A)···Cl(1)#1	0.99	2.91	3.469(3)	116.5
C(8)−H(8B)···Cl(6)#5	0.99	2.92	3.638(3)	129.7
N(3)−H(3A)···Cl(2)#6	0.91	2.73	3.417(2)	133.5
N(3)−H(3A)···Cl(3)#6	0.91	2.61	3.327(2)	136.1
N(3)−H(3B)···Cl(1)#3	0.91	2.44	3.298(2)	157.2
C(9)−H(9A)···Cl(6)	0.99	2.90	3.615(2)	129.7
C(10)−H(10A)···Cl(5)#6	0.99	2.75	3.704(3)	162.4
C(11)−H(11B)···Cl(3)#6	0.99	2.89	3.581(3)	127.8
C(12)−H(12A)···Cl(5)#3	0.99	2.79	3.536(3)	132.3
C(12)−H(12B)··· Cl(4)#3	0.99	2.80	3.526(2)	130.9

Symmetry transformations used to generate equivalent atoms:

#1 1/2+*x*,1/2-*y*,1/2+*z*; #2 1+*x*,+*y*,+*z*; #3 1/2+*x*,1/2-*y*,-1/2+*z*; #4 3/2-*x*,-1/2+*y*,3/2-*z*; #5 -1/2+*x*,1/2-*y*,1/2+*z*; #6 -1/2+*x*,1/2-*y*,-1/2+*z*

Table S18 Hydrogen bonding data for $(Tp)_3SbBr_6$-100 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1B)···S(2)	0.91	2.56	3.414(2)	157.0
N(1)−H(1C)···S(3)	0.91	2.64	3.365(2)	137.4
N(1)−H(1C)···S(3)	0.91	2.64	3.365(2)	137.4
N(1)−H(1D)···Br(6)#1	0.91	2.54	3.415(2)	160.4
N(1)−H(1D)···Br(6)#1	0.91	2.54	3.415(2)	160.4
C(4)−H(4C)···Br(3)#2	0.99	2.79	3.552(3)	134.2
C(1)−H(1E)···Br(1)	0.99	3.13	3.886(3)	134.4
C(1)−H(1E)···Br(2)#3	0.99	2.69	3.430(3)	132.1
C(1)−H(1F)···Br(6)#1	0.99	2.98	3.546(3)	117.1
C(2)−H(2C)···Br(2)#3	0.99	2.95	3.497(6)	115.7
C(2)−H(2C)···S(2)#3	0.99	3.02	3.797(6)	136.6
C(2)−H(2D)···Br(5)#4	0.99	2.81	3.747(5)	159.1
C(3)−H(3D)···Br(5)#2	0.99	2.98	3.972(4)	175.3
C(1B)−H(1G)···Br(1)	0.99	2.79	3.561(10)	135.1
C(1B)−H(1G)···Br(2)#3	0.99	2.85	3.579(10)	131.2
C(1B)−H(1H)···Br(5)#4	0.99	2.90	3.799(11)	151.2
C(1B)−H(1H)···S(2)	0.99	3.02	3.568(10)	116.3
C(2B)−H(2E)···S(3)#3	0.99	2.85	3.45(2)	119.3
C(2B)−H(2F)···Br(2)#3	0.99	2.93	3.55(2)	121.3
C(3B)−H(3E)···Br(5)#2	0.99	2.91	3.872(12)	163.1
C(3B)−H(3F)···Br(4)#2	0.99	2.63	3.381(12)	133.0
N(2)−H(2A)···Br(1)#5	0.91	2.77	3.489(2)	137.0
N(2)−H(2A)···Br(4)#5	0.91	2.92	3.565(2)	129.6
N(2)−H(2A)···Br(5)#5	0.91	3.08	3.620(2)	119.4
N(2)−H(2B)···Br(2)#4	0.91	2.77	3.512(2)	139.8
N(2)−H(2B)···Br(3)#4	0.91	2.88	3.594(2)	136.5
C(6)−H(5A)···Br(3)#4	0.99	3.13	3.823(3)	128.4
C(6)−H(5A)···Br(5)#4	0.99	3.04	3.928(3)	149.2
C(5)−H(6A)···Br(4)#5	0.99	2.97	3.589(3)	121.8
C(5)−H(6B)···Br(5)#5	0.99	3.04	3.721(3)	127.0
C(7)−H(7A)···Br(1)	0.99	2.97	3.759(3)	137.0
C(7)−H(7A)···Br(5)	0.99	3.03	3.836(3)	139.4
C(7)−H(7B)···Br(5)#4	0.99	3.00	3.895(3)	150.4
N(3)−H(3A)···Br(1)#1	0.91	2.83	3.535(2)	135.6
N(3)−H(3A)···Br(4)#1	0.91	2.84	3.558(2)	136.5
N(3)−H(3B)···Br(2)#6	0.91	2.86	3.593(2)	138.7
N(3)−H(3B)···Br(3)#6	0.91	2.86	3.538(2)	131.9
N(3)−H(3B)···Br(6)#6	0.91	3.04	3.579(2)	119.3
C(9)−H(9A)···Br(1)#1	0.99	3.12	3.632(3)	113.4
C(9)−H(9B)···Br(6)#6	0.99	3.07	3.738(2)	125.7
C(10)−H(10A)···Br(6)#1	0.99	2.93	3.790(3)	146.4
C(10)−H(10B)···Br(1)	0.99	3.08	3.801(2)	130.8

C(10)−H(10B)···Br(3)#2	0.99	3.01	3.798(3)	137.1
C(11)−H(11A)···Br(3)#2	0.99	3.12	3.839(3)	130.8
C(11)−H(11A)···Br(4)#7	0.99	3.13	3.836(3)	129.6
C(11)−H(11B)···Br(4)#1	0.99	3.08	3.781(3)	128.9
C(11)−H(11B)···Br(6)#1	0.99	3.11	3.939(3)	141.9
C(12)−H(12A)···Br(6)#6	0.99	3.04	3.715(3)	126.6
C(12)−H(12B)···Br(3)#6	0.99	3.05	3.644(3)	119.6
C(12)−H(12B)···Br(4)#1	0.99	3.12	3.605(3)	112.0

Symmetry transformations used to generate equivalent atoms:
#1 3/2-*x*,3/2-*y*,1-*z*; #2 -1/2+*x*,-1/2+*y*,+*z*; #3 +*x*,-1+*y*,+*z*; #4 3/2-*x*,-1/2+*y*,1/2-*z*; #5 3/2-*x*,1/2+*y*,1/2-*z*; #6 3/2-*x*,5/2-*y*,1-*z*; #7 -1/2+*x*,1/2+*y*,+*z*

Table S19 Hydrogen bonding data for $(Tp)_3BiBr_6$-295 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1B)···S(2)	0.89	2.66	3.490(4)	156.0
N(1)−H(1C)···S(3)	0.89	2.71	3.389(4)	134.1
N(1)−H(1C)···S(3)	0.89	2.71	3.389(4)	134.1
N(1)−H(1D)···Br(6)#1	0.89	2.58	3.450(4)	166.4
N(1)−H(1D)···Br(6)#1	0.89	2.58	3.450(4)	166.4
C(4)−H(4C)···Br(3)#2	0.97	2.86	3.638(6)	138.3
C(1)−H(1E)···Br(2)#3	0.97	2.74	3.467(8)	131.8
C(1)−H(1F)···Br(6)#1	0.97	2.96	3.544(10)	119.5
C(2)−H(2C)···Br(2)#3	0.97	2.95	3.50(2)	117.4
C(2)−H(2D)···Br(5)#4	0.97	2.83	3.761(19)	161.0
C(3)−H(3D)···Br(5)#2	0.97	3.03	3.988(16)	170.6
C(1B)−H(1G)···Br(1)	0.97	2.97	3.672(11)	130.3
C(1B)−H(1G)···Br(2)#3	0.97	2.86	3.621(12)	136.3
C(1B)−H(1H)···Br(5)#4	0.97	2.96	3.836(16)	150.4
C(2B)−H(2E)···S(3)#3	0.97	2.89	3.59(3)	129.9
C(3B)−H(3E)···Br(5)#2	0.97	3.04	3.98(2)	165.4
C(3B)−H(3F)···Br(4)#2	0.97	2.90	3.617(17)	131.4
N(2)−H(2A)···Br(1)#5	0.89	2.83	3.552(4)	139.2
N(2)−H(2A)···Br(4)#5	0.89	2.97	3.606(4)	129.8
N(2)−H(2B)···Br(2)#4	0.89	2.89	3.610(4)	139.2
N(2)−H(2B)···Br(3)#4	0.89	2.92	3.622(4)	137.2
C(5)−H(6A)···Br(4)#5	0.97	3.00	3.619(5)	122.6
C(5)−H(6B)···Br(5)#5	0.97	3.09	3.784(6)	129.8
C(7)−H(7A)···Br(1)	0.97	3.03	3.814(5)	138.4
C(7)−H(7A)···Br(5)	0.97	3.11	3.885(5)	138.2
C(7)−H(7B)···Br(5)#4	0.97	3.07	3.956(5)	153.3
N(3)−H(3A)···Br(1)#1	0.89	2.93	3.617(4)	135.8
N(3)−H(3A)···Br(4)#1	0.89	2.86	3.573(4)	138.4
N(3)−H(3B)···Br(2)#6	0.89	2.93	3.643(4)	138.8
N(3)−H(3B)···Br(3)#6	0.89	2.91	3.567(3)	131.8

N(3)−H(3B)···Br(6)#6	0.89	3.13	3.655(4)	119.5
C(9)−H(9B)···Br(6)#6	0.97	3.13	3.801(4)	127.3
C(10)−H(10A)···Br(6)#1	0.97	2.99	3.852(5)	148.7
C(10)−H(10B)···Br(1)	0.97	3.09	3.818(4)	132.5
C(10)−H(10B)···Br(6)	0.97	3.07	3.835(5)	136.5
C(11)−H(11A)···Br(3)#2	0.97	3.13	3.831(5)	130.0
C(11)−H(11B)···Br(4)#1	0.97	3.11	3.804(5)	130.0
C(12)−H(12A)···Br(6)#6	0.97	3.11	3.781(5)	127.9
C(12)−H(12B)···Br(3)#6	0.97	3.07	3.665(5)	121.0
Symmetry transformations used to generate equivalent atoms:				
#1 3/2-*x*,3/2-*y*,1-*z*; #2 -1/2+*x*,-1/2+*y*,+*z*; #3 +*x*,-1+*y*,+*z*; #4 3/2-*x*,-1/2+*y*,1/2-*z*; #5 3/2-*x*,1/2+*y*,1/2-*z*; #6 3/2-*x*,5/2-*y*,1-*z*;				

Table S20 Hydrogen bonding data for (Tp)Br-298 K.

D−H···A	D−H (Å)	H···A (Å)	D···A (Å)	<(DHA) (°)
N(1)−H(1A)···Br(1)#1	0.89	2.66	3.490(4)	156.0
N(1)−H(1B)···Br(1)	0.89	2.71	3.389(4)	134.1
C(2)−H(2A)···Br(1)#1	0.89	2.71	3.389(4)	134.1
C(4)−H(4A)···Br(1)#2	0.89	2.58	3.450(4)	166.4
C(4)−H(4B)···Br(1)#3	0.89	2.58	3.450(4)	166.4
Symmetry transformations used to generate equivalent atoms:				
#1 1+*x*,+*y*,+*z*; #2 +*x*,1+*y*,+*z*; #3 1-*x*,1-*y*,-*z*				

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