Supporting Information for:

$(BA)_4AgBi_2Br_{19}$: a one-dimensional halide double perovskite with unique Br trimer

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Experimental Section

Materials and Synthesis

AgBr (99.9%, Aladdin), $InBr_3$ (99.9%, Aladdin), $SbBr_3$ (99.9%, Aladdin), $BiBr_3$ (99.9%, Aladdin), $C_4H_{11}N$ (butylamine, 99.9%, Aladdin), and HBr (48% in water by weight, Aladdin) were used for synthesis. All chemicals were used as received without further purification.

$(BA)_4AgBi_2Br_{19}$ were prepared by combining $BiBr_3$ (0.2 mmol), AgBr (0.2 mmol) and $C_4H_{11}N$ (0.5 mmol) in 0.5 mL HBr. A clear solution was obtained after heating and stirring at 100 ºC for 8-10 min. The crystals were obtained by slowly cooling the solution to room temperature with a rate of 2 ℃ per hour. The final products were then obtained by filtering and drying in a vacuum oven. For the known $(BA)_2AgBiBr_8$, the synthetic route is basically the same with that of $(BA)_4AgBi_2Br_{19}$, only with the increased amount of $C_4H_{11}N$, 0.8 mmol. By replacing the $BiBr_3$ with $InBr_3$ and $SbBr_3$, the rod-like crystals were also obtained in Ag-In and Ag-Sb systems.

Characterization

Single crystal X-ray diffractions were conducted on Bruker D8 Venture diffractometer using Mo Kα radiation with λ = 0.7103 Å operating at 50 kV and 1.4 mA. The structure was solved and refined using the OLEX2 package.[1] Powder X-ray diffraction (PXRD) patterns were collected at room temperature on a PANalytical Empyrean diffractometer equipped with Cu Kα radiation (λ = 1.541 Å) operating at 45 kV and 40 mA. The morphology of the samples was observed via scanning electron microscopy (SEM, Regulus8100). The component analysis of elements was measured by energy dispersive X-ray spectroscopy (EDS, Esprit Compact). Optical absorption spectra were obtained using an UV−vis−NIR spectrophotometer (SHIMADZU UV-3600) with $BaSO_4$ serving as a standard. Photoluminescence emission and excitation spectrum were obtained using a PLSP920 fluorescence spectrophotometer equipped with a PMT detector at room temperature and a 150 W Xe900 lamp as the excitation source. Thermogravimetric analysis (TGA) and

differential scanning calorimetry (DSC) were conducted on a Setaram Labsys Evo instrument at a heating rate of ±10 °C/min with a maximum temperature of 600 °C. Approximately 20 mg of each sample was used for the measurement.

Calculation

The theoretical calculations were performed in the density functional theory (DFT) using the Vienna Ab initio Simulation Package (VASP) and the Projector-augmented wave (PAW) scheme.[2-6] The Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) was used for the exchange correlation functional.[7] The wave functions were expanded into plane waves up to a cutoff energy of 600 eV. $1s^1$, $2s^22p^2$, $2s^22p^3$, $5s^14d^{10}$, $6s^26p^3$, $4s^24p^5$ were used as valence electrons for H, C, N, Ag, Bi and Br, respectively. *Γ*-centered *k*-points grids of 4 × 4 × 3 were sampled to calculate the electronic properties of $(BA)_4AgBi_2Br_{19}$.

Table S1. Crystal data and structure refinement for $(C_4H_{12}N)_{10}AgBi_2Br_{19}$ at 293 K.

Empirical formula	$(C_4H_{12}N)_{10}AgBi_2Br_{19}$
Formula weight	2789.57
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	*C*2/*c*
Unit cell dimensions	a = 32.453(2) Å, α = 90°
	b = 8.0862(6) Å, β = 106.856(3)°
	c = 36.082(3) Å, γ = 90°
Volume	9061.9(12) Å^3
Z	4
Density (calculated)	2.045 g/cm^3
Absorption coefficient	12.496 mm^{-1}
F(000)	5240
Crystal size	0.24 × 0.1 ×0.05 mm^3
θ range for data collection	2.359 to 24.998°
Index ranges	$-38 \le h \le 38$, $-9 \le k \le 9$, $-42 \le l \le 42$
Reflections collected	48211
Independent reflections	7933 [R_{int} = 0.0974]
Completeness to θ = 24.998°	99.4%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7933 / 69 / 257
Goodness-of-fit	1.064
Final R indices [$I > 2\sigma(I)$]	R_{obs} = 0.0812, wR_{obs} = 0.1990
R indices [all data]	R_{all} = 0.1179, wR_{all} = 0.2234
Largest diff. peak and hole	2.046 and -1.497 e·Å^{-3}

$R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR = \{\Sigma[w(|F_0|^2 - |F_c|^2)^2]/\Sigma[w(|F_0|^4)]\}^{1/2}$ and $w = 1/[\sigma^2(F_0^2) + (0.1001P)^2 + 167.2719P]$, where $P = (F_0^2 + 2F_c^2)/3$.

Table S2. Atomic coordinates (10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $(C_4H_{12}N)_{10}AgBi_2Br_{19}$ at 293 K with estimated standard deviations in parentheses.

Label	x	y	z	Occupancy	U_{eq}^*
Bi(1)	2843(1)	7570(1)	1213(1)	1	53(1)
Ag(1)	2500	2500	0	1	68(1)
Br(1)	3736(1)	7000(2)	1337(1)	1	90(1)
Br(2)	2843(1)	5105(2)	1772(1)	1	82(1)
Br(3)	3032(1)	10168(2)	1768(1)	1	80(1)
Br(4)	2819(1)	9876(2)	611(1)	1	83(1)
Br(5)	1946(1)	8155(2)	1090(1)	1	78(1)
Br(6)	2626(1)	5112(2)	623(1)	1	80(1)
Br(7)	1704(1)	2072(2)	4(1)	1	91(1)
Br(8)	4171(2)	2952(6)	2245(2)	1	214(2)
Br(9)	5000	2931(5)	2500	1	150(2)
Br(1A)	1894(1)	2270(2)	2126(1)	1	83(1)
N(4)	2077(11)	2450(30)	1141(10)	1	200(8)
C(13)	573(11)	2350(30)	804(12)	1	200(8)
C(14)	936(11)	3570(30)	830(11)	1	200(8)
C(15)	1285(12)	2250(40)	961(13)	1	200(8)
C(16)	1699(14)	3350(40)	1035(12)	1	200(8)
N(3)	2219(7)	8290(30)	2168(6)	1	139(4)
C(9)	826(8)	7630(30)	1534(8)	1	139(4)
C(10)	1251(8)	8350(30)	1828(7)	1	139(4)
C(11)	1445(9)	6710(30)	1925(7)	1	139(4)
C(12)	1906(10)	7180(30)	2244(8)	1	139(4)
N(2)	3506(8)	12770(20)	1176(9)	1	155(11)
C(5)	4714(16)	12810(70)	722(18)	1	310(30)
C(6)	4520(20)	11640(70)	960(20)	1	320(30)
C(7)	4179(17)	12710(60)	982(13)	1	230(20)

C(8)	3879(16)	11900(40)	1185(12)	1	194(17)
N(1)	1840(9)	7980(30)	27(8)	1	179(6)
C(1)	453(12)	7700(30)	133(11)	1	179(6)
C(2)	685(10)	7330(40)	-188(10)	1	179(6)
C(3)	1128(10)	7520(40)	113(10)	1	179(6)
C(4)	1412(11)	7170(40)	-136(11)	1	179(6)
N(5)	3779(6)	7180(30)	2323(6)	1	140(8)
C(17)	5021(10)	7390(60)	3434(14)	1	290(20)
C(18)	4809(10)	7820(60)	3061(13)	1	249(15)
C(19)	4388(9)	7470(50)	2878(11)	1	213(13)
C(20)	4180(12)	7890(50)	2509(11)	1	205(13)

*U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table S3. Anisotropic displacement parameters ($Å^2×10^3$) $(C_4H_{12}N)_{10}AgBi_2Br_{19}$ at 293 K with estimated standard deviations in parentheses.

Label	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bi(1)	81(1)	36(1)	44(1)	0(1)	19(1)	-1(1)
Ag(1)	93(2)	56(1)	56(1)	-7(1)	24(1)	-4(1)
Br(1)	88(2)	81(2)	105(2)	3(1)	35(2)	3(1)
Br(2)	121(2)	59(1)	62(1)	-16(1)	19(1)	17(1)
Br(3)	113(2)	56(1)	71(1)	-9(1)	24(1)	-22(1)
Br(4)	116(2)	66(1)	64(1)	-8(1)	20(1)	24(1)
Br(5)	81(2)	71(1)	82(2)	1(1)	26(1)	-2(1)
Br(6)	122(2)	58(1)	61(1)	-9(1)	30(1)	-22(1)
Br(7)	91(2)	74(2)	115(2)	-1(1)	39(2)	4(1)
Br(8)	229(5)	243(4)	166(3)	7(4)	52(3)	-24(3)
Br(9)	223(5)	133(3)	104(3)	0	61(3)	0
Br(1A)	98(2)	68(1)	78(2)	1(1)	20(1)	4(1)
N(4)	260(20)	121(12)	239(19)	-17(10)	105(19)	5(11)
C(13)	260(20)	121(12)	239(19)	-17(10)	105(19)	5(11)

C(14)	260(20)	121(12)	239(19)	-17(10)	105(19)	5(11)
C(15)	260(20)	121(12)	239(19)	-17(10)	105(19)	5(11)
C(16)	260(20)	121(12)	239(19)	-17(10)	105(19)	5(11)
N(3)	146(12)	125(9)	140(10)	11(7)	34(8)	6(7)
C(9)	146(12)	125(9)	140(10)	11(7)	34(8)	6(7)
C(10)	146(12)	125(9)	140(10)	11(7)	34(8)	6(7)
C(11)	146(12)	125(9)	140(10)	11(7)	34(8)	6(7)
C(12)	146(12)	125(9)	140(10)	11(7)	34(8)	6(7)
N(2)	130(20)	55(10)	270(30)	1(11)	50(20)	1(13)
C(5)	160(40)	420(100)	350(80)	-50(50)	60(50)	70(60)
C(6)	210(60)	290(70)	430(100)	30(60)	80(60)	40(70)
C(7)	230(50)	290(60)	170(40)	120(50)	60(40)	10(30)
C(8)	220(50)	130(30)	180(30)	-30(30)	-20(30)	-20(30)
N(1)	173(15)	183(13)	181(15)	-24(11)	52(11)	-33(10)
C(1)	173(15)	183(13)	181(15)	-24(11)	52(11)	-33(10)
C(2)	173(15)	183(13)	181(15)	-24(11)	52(11)	-33(10)
C(3)	173(15)	183(13)	181(15)	-24(11)	52(11)	-33(10)
C(4)	173(15)	183(13)	181(15)	-24(11)	52(11)	-33(10)
N(5)	84(12)	240(20)	92(12)	14(14)	16(9)	3(13)
C(17)	52(17)	470(60)	300(40)	10(30)	-38(19)	-20(40)
C(18)	60(14)	390(40)	270(30)	-20(20)	11(15)	-40(30)
C(19)	70(14)	350(30)	190(20)	-30(20)	-6(13)	-30(20)
C(20)	121(19)	310(30)	170(20)	-50(20)	29(14)	-30(20)

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

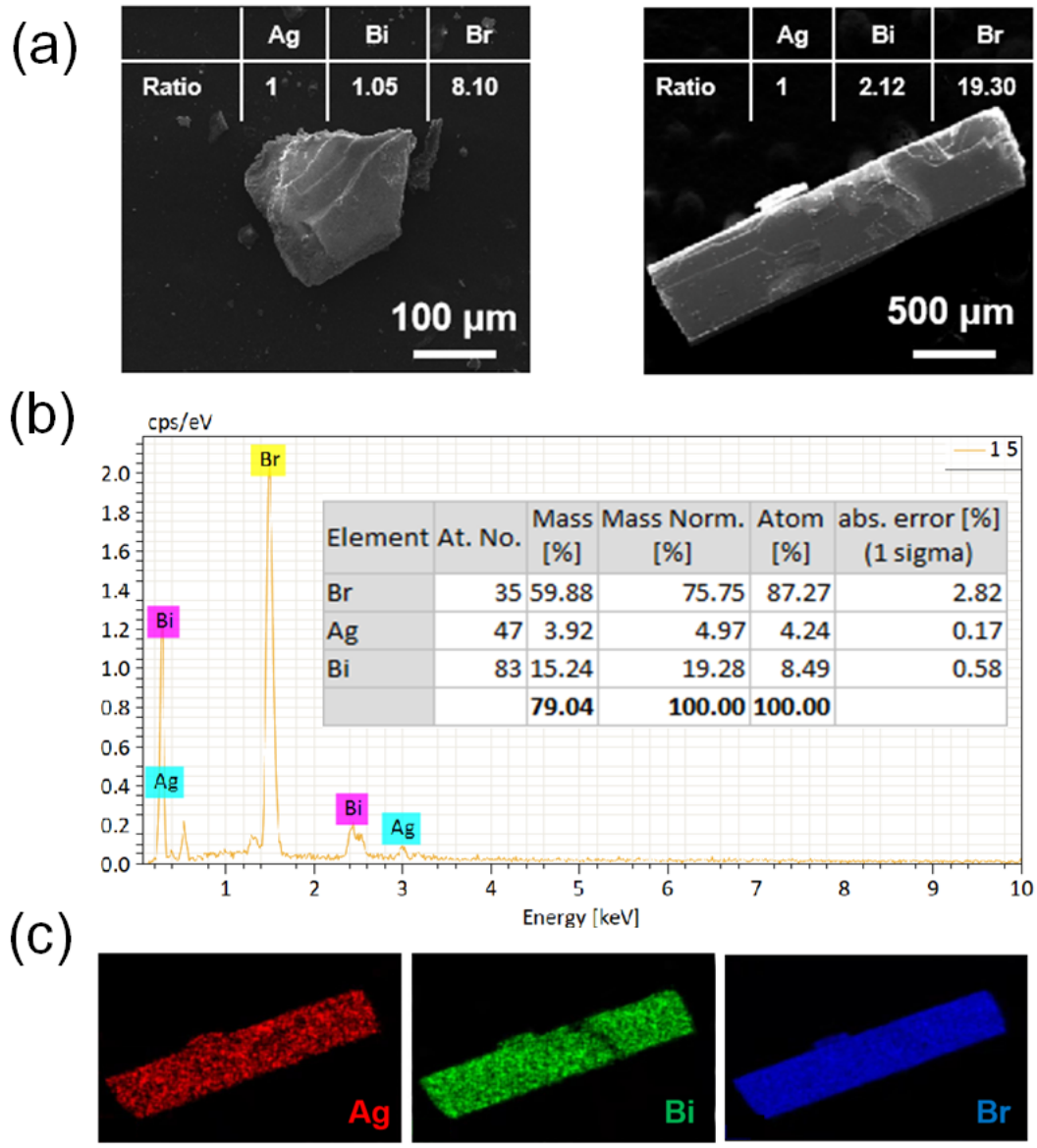


Figure S1. (a) SEM images of $(BA)_4AgBiBr_8$ and $(BA)_{10}AgBi_2Br_{19}$ with the normalized molar ratio of Ag, Bi and Br from EDS. (b) EDS spectrum and (c) elemental mapping for $(BA)_{10}AgBi_2Br_{19}$.

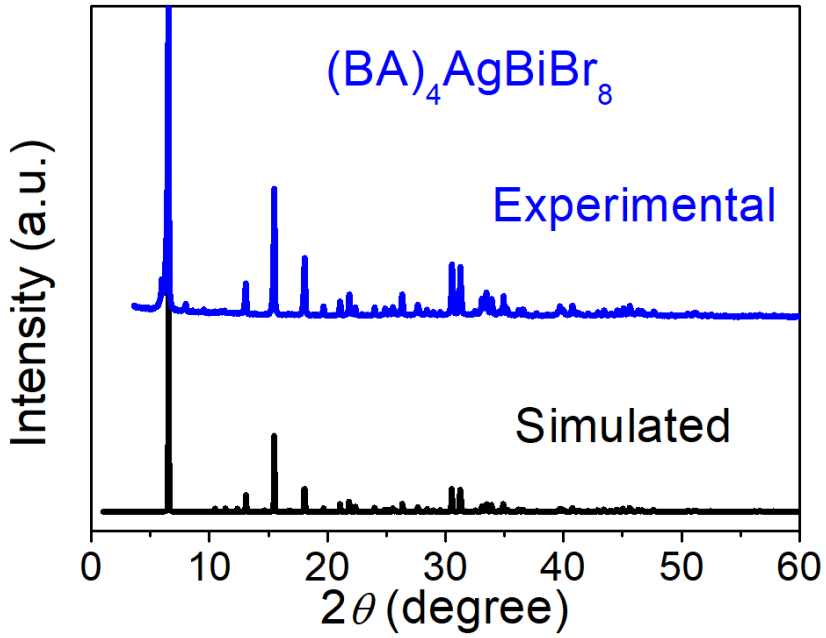


Figure S2. Experimental and calculated PXRD patterns of $(BA)_4AgBiBr_8$.

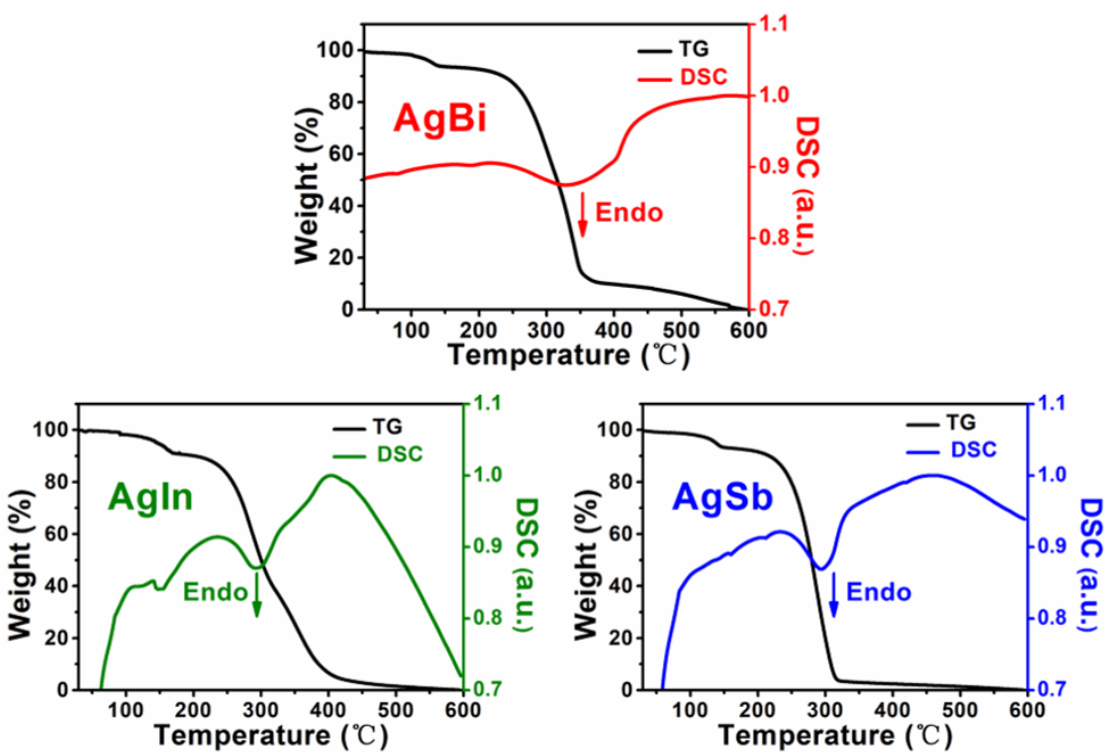


Figure S3. Thermogravimetric analysis (TGA)-Differential scanning calorimetry (DSC) data for $(BA)_{10}AgBi_2Br_{19}$, and analogous 1D crystals in Ag-In and Ag-Sb systems.

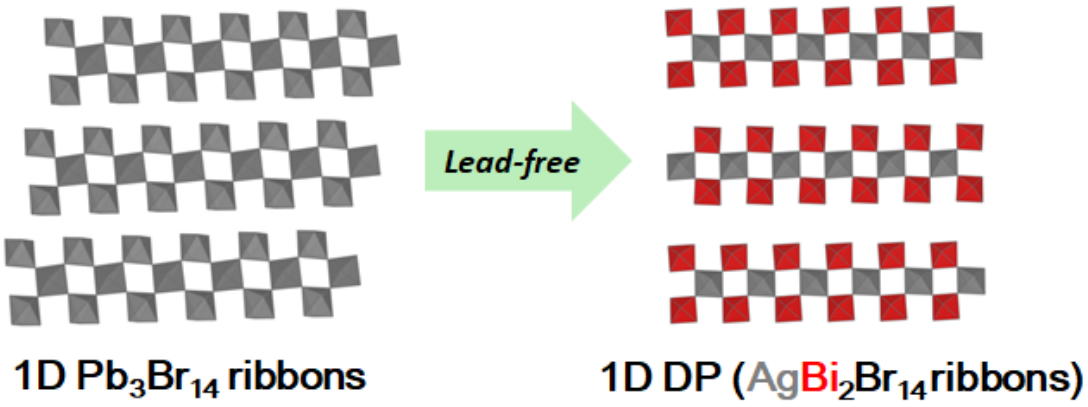


Figure S4. The inorganic frameworks in $(L\text{-}H_2Orn)_4[Pb_3Br_{14}]2H_2O$ as 1D Pb_3Br_{14} ribbons compared with the 1D $AgBi_2Br_{14}$ ribbons in $(BA)_{10}AgBi_2Br_{19}$.

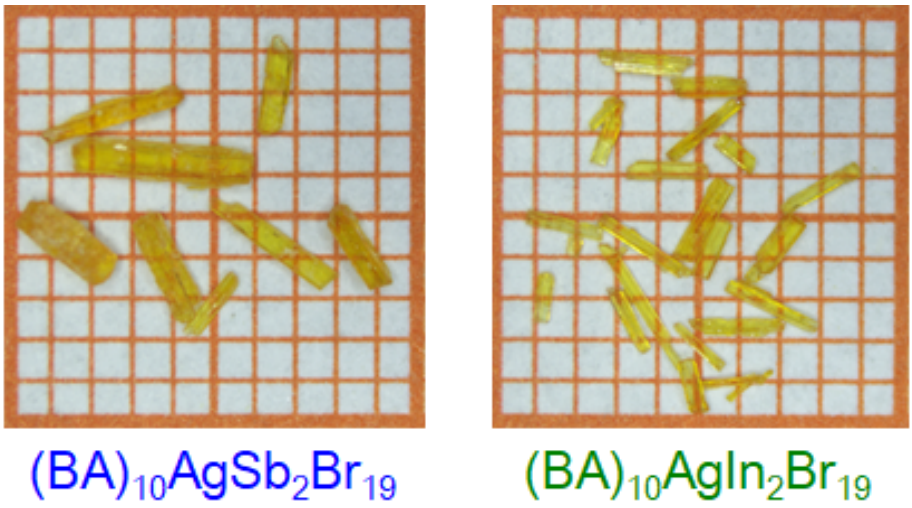
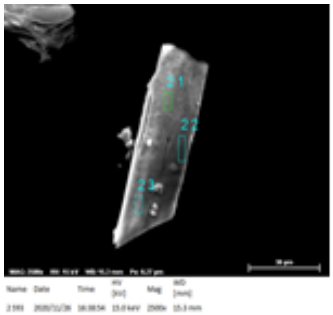


Figure S5. Optical photograph of the 1D crystals in Ag-Sb and Ag-In systems.



Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Br	35	70.53	80.19	85.56	3.31
Ag	47	5.57	6.33	5.00	0.22
Sb	51	11.86	13.48	9.44	0.40
		87.95	**100.00**	**100.00**	

Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)
Br	35	74.65	83.47	87.66	3.52
Ag	47	4.85	5.42	4.22	0.21
In	49	9.94	11.11	8.12	0.36
		89.44	**100.00**	**100.00**	

Figure S6. The molar ratio of Ag, Sb(In) and Br in the 1D crystals in Ag-Sb and Ag-In systems based on EDS measurements.

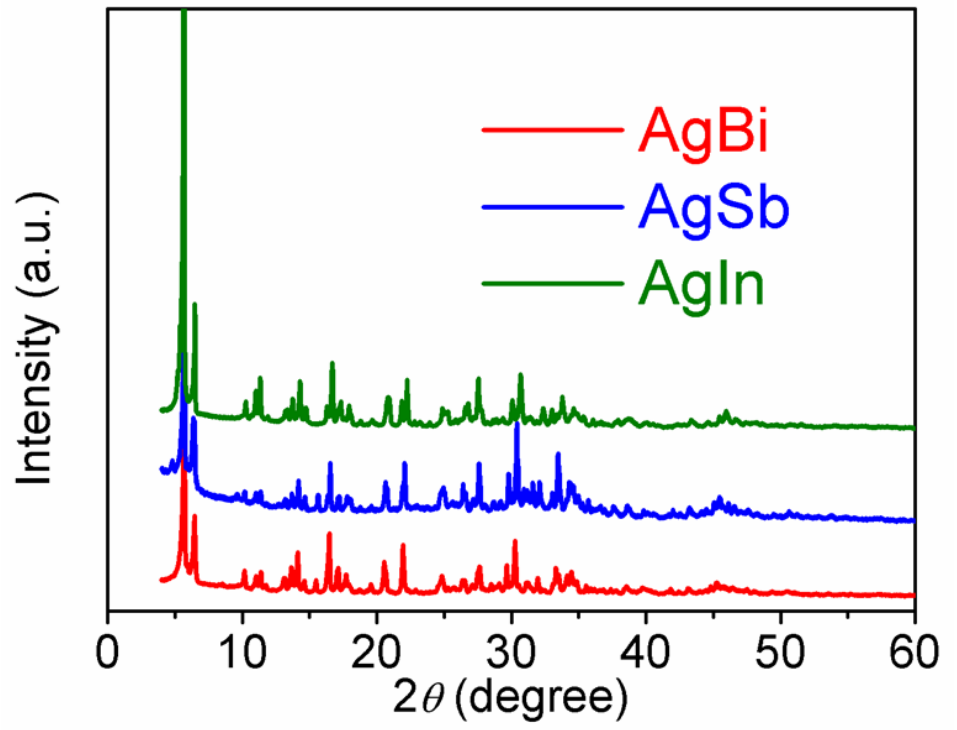


Figure S7. PXRD patterns of the 1D crystals in Ag-Sb and Ag-In systems, compared to the pattern of $(BA)_{10}AgBi_2Br_{19}$.

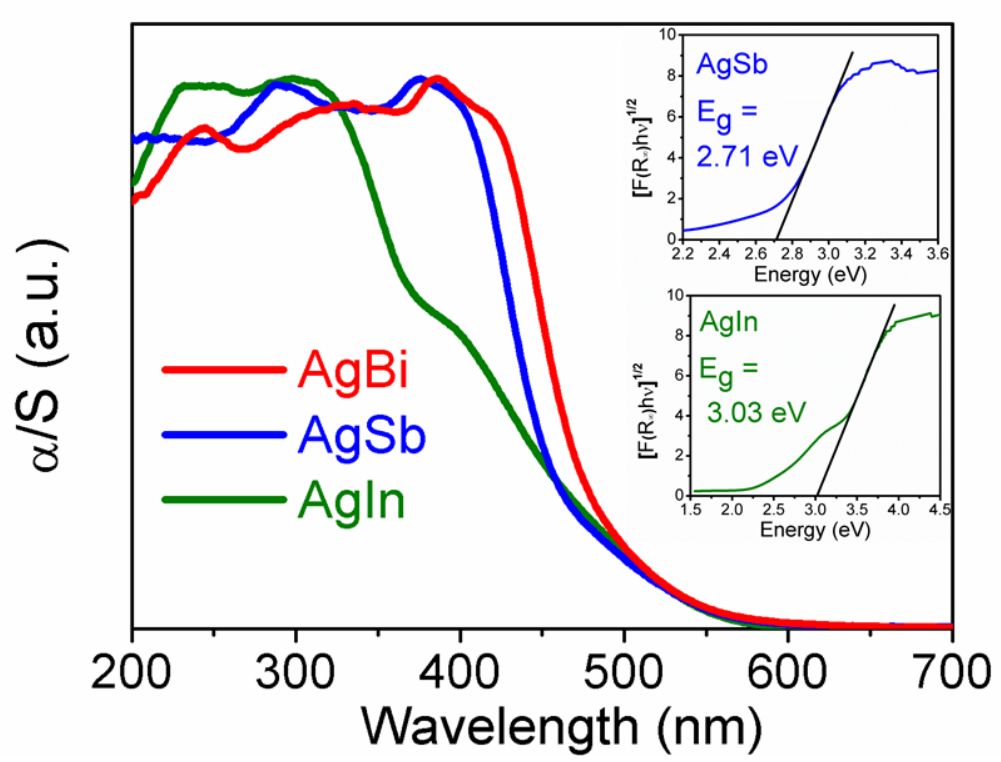


Figure S8. UV-vis diffuse-reflectance spectrum for 1D crystals in Ag-Sb and Ag-In systems, compared to the spectrum of $(BA)_{10}AgBi_2Br_{19}$ (the same one with that used in main text).

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