Supporting Information

Realization of the transition from an indirect band gap to a direct band gap through halogen regulation in the Cs-Ag-X system

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Experimental Reagents.

CsCl (99.99 %, Aladdin), CsBr (99.99 %, Aladdin), AgCl (99.99 %, Aladdin), and AgI (99.99 %, Aladdin). All chemicals above were used without further purification.

Synthesis.

Single crystals of CsAgICl and Cs_2AgBr_2I were obtained by the high-temperature solid-state method in a vacuum system. A mixture of CsCl (0.17 g) and AgI (0.31 g) (CsBr (0.28 g) and AgI (0.31 g) for Cs_2AgBr_2I) was loaded into a silica tube with an inner diameter of 10 mm. The silica tube was sealed with fire under a high vacuum of 10^{-3} Pa. Then, the tube was placed in a computer-controlled furnace, heated to 220 ℃ in 10 h, dwelled at 220 ℃ for 24 h, cooled to 120 ℃ at a rate of 1 ℃ / h, and cooled to room temperature at a rate of 3 ℃ / h. After that, colorless single crystals were obtained.

Polycrystalline samples of CsAgICl and Cs_2AgBr_2I were obtained by solid-state reaction. A mixture of CsCl (0.28 g) and AgI (0.27 g) (CsBr (0.43 g) and AgI (0.16 g) for Cs_2AgBr_2I) was loaded into a corundum crucible. The crucibles were heated to 320 °C for 10 h, held at this temperature for 12 h, cooled to 120 ℃ at a rate of 1 ℃ / h, and cooled to room temperature at a rate of 3 ℃ / h. Then, the samples were stirred in alcohol. After drying, the polycrystalline samples can be obtained.

Moreover, polycrystalline samples of CsAgICl and Cs_2AgBr_2I can also be prepared by the antisolvent method. A mixture of CsCl (0.14 g) and AgI (0.12 g) (CsBr (0.17 g) and AgI (0.047 g) for Cs_2AgBr_2I) was loaded into a glass bottle. After adding 2 ml of DMSO, it was stirred at 60° for 1 hour. Then, the filtered solution was mixed with 6 ml of isopropanol and centrifuged for 5 minutes at 8000 revolutions per minute. After drying, the polycrystalline samples could be obtained.

Polycrystalline samples of $CsAgCl_2$ were prepared by the supersaturation method. A mixture of CsCl (0.10 g) and AgCl (0.09 g) was loaded into a glass bottle. After adding 4 ml of DMSO, it was stirred at 60° for 1 hour. After a slow cooling process, the micron-sized single crystals crystallized at the bottom of the solution.

Characterization.

The single-crystal X-ray diffraction data were collected by the Bruker D8 Venture diffractometer. The crystal structures were solved and refined by the Apex and Olex2.[1-4] Crystallographic data were contained in CCDC 2519961-2519962 in crystallographic information file format. The elemental analyses were analyzed by the field emission scanning electron microscope (HITACHI Regulus8230) equipped with an energy dispersive X-ray spectroscope (Bruker XFlash Detector 6). The powder X-ray diffraction (PXRD) patterns were measured by the Bruker D8 Advance. The UV-vis optical absorption spectra were measured by the HITACHI-UH4150.

Calculation Methods.

The electronic structures were calculated using first-principles calculations based on density functional theory (DFT) as implemented in the VASP package.[5] The band gap was evaluated using the generalized gradient approximation with the PBE functional (GGA-PBE).[6] For CsAgICl and Cs_2AgBr_2I, the plane-wave energy cutoff was set to 600.0 eV for both compounds, with Monkhorst–Pack *k*-point grid samplings of 6 × 6 × 4 and 3 × 6 × 2, respectively.

Table S1. Crystallographic data.

Empirical formula	CsAgICl	Cs_2AgBr_2I
Formula weight	403.13	660.39
Wavelength (Å)	0.71073	0.71073
Temperature (K)	300	300
Crystal system	Orthorhombic	Orthorhombic
Space group, Z	*Cmcm*, 4	*Pnma*, 4
a (Å)	4.8341(4)	10.0800(16)
b (Å)	15.6709(13)	4.8981(8)
c (Å)	7.6430(5)	19.635(3)
Volume (Å^3)	578.99(8)	969.4(3)
Density (calculated) (g·cm^{-3})	4.6243	4.5245
Absorption coefficient (mm^{-1})	15.300	20.815
F (000)	682.7	1111.5
Theta range for data collection	2.60 to 27.52	2.07 to 27.6
Index ranges	$-6 \le h \le 6$, $-20 \le k \le 20$, $-9 \le l \le 9$	$-13 \le h \le 12$, $-6 \le k \le 6$, $-24 \le l \le 25$
Reflections collected/ unique	3694 / 401 [R(int) = 0.0389]	8177 / 1257 [R(int) = 0.0192]
Completeness (%)	99	99
Data/ restraints/ parameters	401 / 0 / 18	1257 / 0 / 38
Goodness-of-fit on F^2	1.030	1.071
Final R indices [$I > 2$sigma(I)][a]	$R_1 = 0.0228$, $wR_2 = 0.0512$	$R_1 = 0.0173$, $wR_2 = 0.0391$
R indices (all data)[a]	$R_1 = 0.0241$, $wR_2 = 0.0517$	$R_1 = 0.0182$, $wR_2 = 0.0394$
Largest diff. peak and hole (e·Å^{-3})	1.15 and –0.99	0.89 and –0.91

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S2. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($Å^2 \times 10^3$) and bond valence sum (BVS) for CsAgICl and Cs_2AgBr_2I.

	Atom	*x*	*y*	*z*	*U*(eq)	BVS[a]
CsAgICl	Cs1	10000	3964.7(3)	7500	38.51(19)	1.07
	Ag1	5000	3831.7(5)	2500	46.8(2)	1.15
	Cl1	5000	5000	5000	37.2(4)	1.06
	I1	0	2975.5(4)	2500	44.7(2)	1.16
Cs_2AgBr_2I	Cs1	7689.3(4)	7500	4531.85(17)	39.40(10)	1.17
	Cs2	9155.8(4)	7500	7098.24(18)	36.34(10)	1.10
	Ag1	6324.8(5)	2500	6345.5(2)	43.05(12)	1.10
	Br1	8747.5(6)	2500	5730.6(3)	37.49(14)	1.10
	Br2	6804.0(6)	2500	7707.8(3)	37.12(13)	1.07
	I1	5086.9(4)	-2500	5994.54(19)	37.38(10)	1.21

[a]BVS[7] are calculated by using the bond-valence model ($S_i = \exp [(R_o - R_i / b]$, where R_o is an empirical constant with values 2.791 for Cs-Cl bonds, 2.95 for Cs-Br bonds, 3.18 for Cs-I bonds, 2.09 for Ag-Cl bonds, 2.22 for Ag-Br bonds, and 2.38 for Ag-I bonds, R_i is the length of bond *i* (in angstroms), and $b = 0.37$ Å).

Table S3. Selected bond lengths (Å) and bond angles (°) for CsAgICl.

Cs1-Cl1	3.4821(3)	Cs1-I1$^{\#1}$	4.1239(4)	Ag1-Cl1$^{\#1}$	2.6463(5)
Cs1-Cl1$^{\#1}$	3.4821(3)	Cs1-I1$^{\#4}$	3.8841(7)	Ag1-Cl1$^{\#7}$	2.6463(5)
Cs1-Cl1$^{\#2}$	3.4821(3)	Cs1-I1$^{\#5}$	3.8841(7)	Ag1-I1	2.7644(5)
Cs1-Cl1$^{\#3}$	3.4821(3)	Cs1-I1$^{\#6}$	4.1239(4)	Ag1-I1$^{\#1}$	2.7644(5)
Cl1-Cs1-Cl1$^{\#1}$	87.915(2)	Cl1$^{\#1}$-Cs1-I1$^{\#6}$	133.127(2)	I1$^{\#1}$-Cs1-I1$^{\#5}$	72.888(2)
Cl1-Cs1-Cl1$^{\#2}$	66.560(1)	Cl1$^{\#2}$-Cs1-Cl1$^{\#3}$	87.915(2)	I1$^{\#1}$-Cs1-I1$^{\#6}$	135.841(1)
Cl1-Cs1-Cl1$^{\#3}$	124.460(2)	Cl1$^{\#2}$-Cs1-I1$^{\#1}$	133.127(2)	I1$^{\#4}$-Cs1-I1$^{\#5}$	76.967(3)
Cl1-Cs1-I1$^{\#1}$	70.528(2)	Cl1$^{\#2}$-Cs1-I1$^{\#4}$	86.145(3)	I1$^{\#4}$-Cs1-I1$^{\#6}$	72.888(2)
Cl1-Cs1-I1$^{\#4}$	86.145(3)	Cl1$^{\#2}$-Cs1-I1$^{\#5}$	142.813(2)	I1$^{\#5}$-Cs1-I1$^{\#6}$	72.888(2)
Cl1-Cs1-I1$^{\#5}$	142.813(2)	Cl1$^{\#2}$-Cs1-I1$^{\#6}$	70.528(2)	Cl1-Ag1-Cl1$^{\#7}$	92.447(2)
Cl1-Cs1-I1$^{\#6}$	133.127(2)	Cl1$^{\#3}$-Cs1-I1$^{\#1}$	133.127(2)	Cl1-Ag1-I1	109.620(3)
Cl1$^{\#1}$-Cs1-Cl1$^{\#2}$	124.460(2)	Cl1$^{\#3}$-Cs1-I1$^{\#4}$	142.813(2)	Cl1-Ag1-I1$^{\#1}$	109.620(3)
Cl1$^{\#1}$-Cs1-Cl1$^{\#3}$	66.560(1)	Cl1$^{\#3}$-Cs1-I1$^{\#5}$	86.145(3)	Cl1$^{\#7}$-Ag1-I1	109.620(3)
Cl1$^{\#1}$-Cs1-I1$^{\#1}$	70.528(2)	Cl1$^{\#3}$-Cs1-I1$^{\#6}$	70.528(2)	Cl1$^{\#7}$-Ag1-I1$^{\#1}$	109.620(3)
Cl1$^{\#1}$-Cs1-I1$^{\#4}$	142.813(2)	I1$^{\#1}$-Cs1-I1$^{\#4}$	72.888(2)	I1-Ag1-I1$^{\#1}$	121.929(3)
Cl1$^{\#1}$-Cs1-I1$^{\#5}$	86.145(3)				

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$1 + X, Y, Z; $^{\#2}$1 – X, 1 – Y, 1/2 + Z; $^{\#3}$2 – X, 1 – Y, 1/2 + Z; $^{\#4}$1/2 – X, 1/2 – Y, 1/2 + Z; $^{\#5}$3/2 – X, 1/2 – Y, 1/2 + Z; $^{\#6}$1 + X, Y, 1 + Z; $^{\#7}$1 – X, 1 – Y, –1/2 + Z.

Table S4. Selected bond lengths (Å) and bond angles (°) for Cs_2AgBr_2I.

Cs1-Br1	3.5603(6)	Cs1-I1$^{\#5}$	3.8597(6)	Cs2-Br2$^{\#7}$	3.6426(7)
Cs1-Br1$^{\#1}$	3.5603(6)	Cs2-Br1	3.6576(7)	Cs2-I1$^{\#6}$	3.8606(8)
Cs1-Br1$^{\#2}$	3.6285(9)	Cs2-Br1$^{\#1}$	3.6576(7)	Ag1-Br1	2.7242(9)
Cs1-Br2$^{\#3}$	3.6178(9)	Cs2-Br2	3.6125(6)	Ag1-Br2	2.7181(8)
Cs1-I1$^{\#1}$	3.8897(7)	Cs2-Br2$^{\#1}$	3.6125(6)	Ag1-I1	2.8337(5)
Cs1-I1$^{\#4}$	3.8597(6)	Cs2-Br2$^{\#6}$	3.6426(7)	Ag1-I1$^{\#1}$	2.8337(5)
Br1-Cs1-Br1$^{\#1}$	86.925(4)	Br2$^{\#3}$-Cs1-I1$^{\#4}$	80.634(7)	Br2-Cs2-Br2$^{\#1}$	85.365(4)
Br1-Cs1-Br1$^{\#2}$	78.307(8)	Br2$^{\#3}$-Cs1-I1$^{\#5}$	80.634(7)	Br2-Cs2-Br2$^{\#6}$	89.453(10)
Br1-Cs1-Br2$^{\#3}$	127.748(8)	I1$^{\#1}$-Cs1-I1$^{\#4}$	73.067(6)	Br2-Cs2-Br2$^{\#7}$	154.430(5)
Br1-Cs1-I1$^{\#1}$	73.376(7)	I1$^{\#1}$-Cs1-I1$^{\#5}$	73.067(6)	Br2-Cs2-I1$^{\#6}$	80.686(9)
Br1-Cs1-I1$^{\#4}$	87.580(9)	I1$^{\#4}$-Cs1-I1$^{\#5}$	78.769(4)	Br2$^{\#1}$-Cs2-Br2$^{\#6}$	154.430(5)
Br1-Cs1-I1$^{\#5}$	146.174(5)	Br1-Cs2-Br1$^{\#1}$	84.068(4)	Br2$^{\#1}$-Cs2-Br2$^{\#7}$	89.453(10)
Br1$^{\#1}$-Cs1-Br1$^{\#2}$	78.307(8)	Br1-Cs2-Br2	73.470(8)	Br2$^{\#1}$-Cs2-I1$^{\#6}$	80.686(9)
Br1$^{\#1}$-Cs1-Br2$^{\#3}$	127.748(8)	Br1-Cs2-Br2$^{\#1}$	128.560(4)	Br2$^{\#6}$-Cs2-Br2$^{\#7}$	84.495(4)
Br1$^{\#1}$-Cs1-I1$^{\#1}$	73.376(7)	Br1-Cs2-Br2$^{\#6}$	73.085(8)	Br2$^{\#6}$-Cs2-I1$^{\#6}$	73.765(7)
Br1$^{\#1}$-Cs1-I1$^{\#4}$	146.174(5)	Br1-Cs2-Br2$^{\#7}$	127.546(4)	Br2$^{\#7}$-Cs2-I1$^{\#6}$	73.765(7)
Br1$^{\#1}$-Cs1-I1$^{\#5}$	87.580(9)	Br1-Cs2-I1$^{\#6}$	137.689(8)	Br1-Ag1-Br2	106.071(23)
Br1$^{\#2}$-Cs1-Br2$^{\#3}$	73.719(15)	Br1$^{\#1}$-Cs2-Br2	128.560(4)	Br1-Ag1-I1	106.676(8)
Br1$^{\#2}$-Cs1-I1$^{\#1}$	140.573(16)	Br1$^{\#1}$-Cs2-Br2$^{\#1}$	73.470(8)	Br1-Ag1-I1$^{\#1}$	106.676(8)
Br1$^{\#2}$-Cs1-I1$^{\#4}$	132.817(8)	Br1$^{\#1}$-Cs2-Br2$^{\#6}$	127.546(4)	Br2-Ag1-I1	108.516(8)
Br1$^{\#2}$-Cs1-I1$^{\#5}$	132.817(8)	Br1$^{\#1}$-Cs2-Br2$^{\#7}$	73.085(8)	Br2-Ag1-I1$^{\#1}$	108.516(8)
Br2$^{\#3}$-Cs1-I1$^{\#1}$	145.708(15)	Br1$^{\#1}$-Cs2-I1$^{\#6}$	137.689(8)	I1-Ag1-I1$^{\#1}$	119.598(4)

Symmetry transformations used to generate equivalent atoms:
$^{\#1}$X, 1 + Y, Z; $^{\#2}$2 – X, 1/2 + Y, 1 – Z; $^{\#3}$3/2 – X, 1 – Y, –1/2 + Z; $^{\#4}$1 – X, 1/2 + Y, 1 – Z; $^{\#5}$1 – X, 3/2 + Y, 1 – Z; $^{\#6}$1/2 + X, 1/2 – Y, 3/2 – Z; $^{\#7}$1/2 + X, 3/2 – Y, 3/2 – Z.

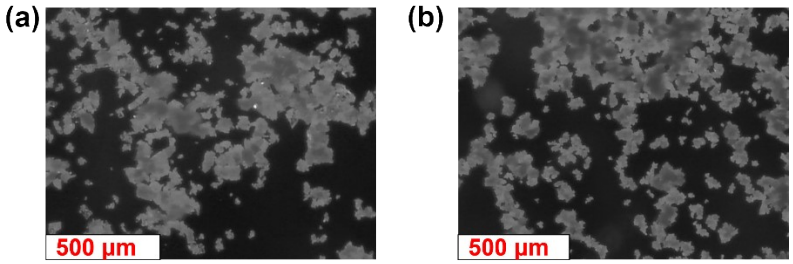

Figure S1. Microscopic morphology: (a) CsAgICl; (b) Cs_2AgBr_2I.

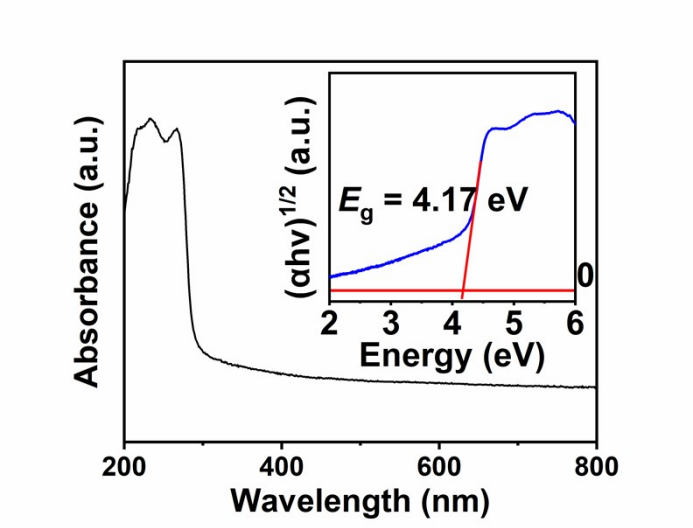

Figure S2. UV-vis optical absorption spectrum of $CsAgCl_2$.

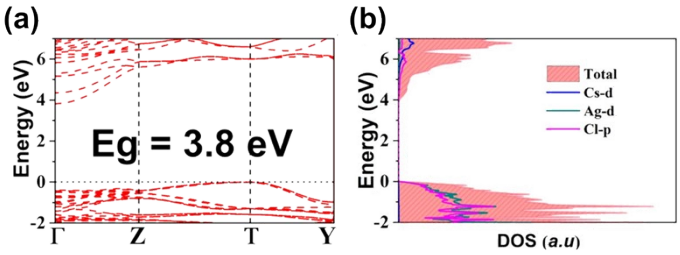

Figure S3. (a) Calculated band gap and (b) calculated density of states of $CsAgCl_2$.[8] Copyright 2021, American Chemical Society.

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