Electronic Supplementary Information for

Dimensionality-driven photoluminescence enhancement in Cl/Br mixed-halide organic–inorganic hybrid cadmium halides

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Table S1. Crystallographic data for compounds with Cl ratios of 0%, 50%, 80%, and 100%.

Cl amount (%)	0% (pure Br)	50%	80%	100%
Formula	$C_7H_{12}N_2CdBr_4$	$C_7H_{12}N_2CdBr_2Cl_2$	$C_{28}H_{48}N_8Cd_5Br_4Cl_{14}$	$C_{28}H_{48}N_8Cd_5Cl_{18}$
F.W.	556.23	466.30	1872.58	1696.84
T [K]	298(2)	299(2)	293(2)	299(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.2195(2)	6.5194(2)	7.5987(2)	7.5301(4)
b [Å]	21.8680(6)	9.2971(3)	11.7771(3)	11.6305(6)
c [Å]	9.3469(2)	11.4021(3)	15.6318(3)	15.4375(8)
α [°]	90	87.5680(10)	93.7070(10)	93.423(2)
β [°]	103.1430(10)	87.9350(10)	90.9100(10)	91.204(2)
γ [°]	90	84.4990(10)	101.3830(10)	100.372(2)
V [Å^3]	1437.00(6)	686.94(4)	1367.93(6)	1326.84(12)
Z	4	2	1	1
$R(F)$[a]	0.0564	0.0287	0.0502	0.0457
$R_w(F_o^2)$ [b]	0.1434	0.680	0.1390	0.928

[a] $R(F) = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$. [b] $R_w(F_o^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

Table S2. Cd–Br bond lengths (Å) and bond angles (°) for pure Br compound.

Bond	Length	Bond	Angle
Cd(1)-Br(2)	2.5769(10)	Br(2)-Cd(1)-Br(3)	108.90(3)
Cd(1)-Br(3)	2.5855(9)	Br(2)-Cd(1)-Br(1)	116.69(4)
Cd(1)-Br(1)	2.5871(9)	Br(3)-Cd(1)-Br(1)	106.43(3)
Cd(1)-Br(4)	2.6014(9)	Br(2)-Cd(1)-Br(4)	104.16(3)
		Br(3)-Cd(1)-Br(4)	111.59(3)
		Br(1)-Cd(1)-Br(4)	109.17(3)

Table S3. Cd–X (X = Br/Cl) bond lengths (Å) and bond angles (°) for Cl 50% compound.

Bond	Length	Bond	Angle
Cd(1)-X(1)	2.5231(6)	X(1)-Cd(1)-X(3)	106.64(2)
Cd(1)-X(2)	2.5112(7)	X(2)-Cd(1)-X(1)	117.95(3)
Cd(1)-X(3)	2.5728(6)	X(2)-Cd(1)-X(3)	105.57(2)
Cd(1)-X(4)	2.5107(8)	X(4)-Cd(1)-X(1)	107.06(3)
		X(4)-Cd(1)-X(2)	111.80(3)
		X(4)-Cd(1)-X(3)	107.24(3)

Table S4. Cd–X (X = Br/Cl) bond lengths (Å) and bond angles (°) for Cl 80% compound.

Bond	Length	Bond	Angle	Bond	Angle
Cd(1)-X(1)	2.6043(15)	X(1)[1]-Cd(1)-X(2)	91.74(4)	X(5)-Cd(2)-X(2)	167.84(5)
Cd(1)-X(1)[1]	2.6282(15)	X(1)[1]-Cd(1)-X(3)	168.12(5)	X(5)-Cd(2)-X(6)[2]	89.53(5)
Cd(1)-X(2)	2.7543(13)	X(1)[1]-Cd(1)-X4)	90.21(4)	X(6)[2]-Cd(2)-X(2)	89.87(5)
Cd(1)-X(3)	2.7048(14)	X(1)[1]-Cd(1)-X(8)	98.47(4)	X(9)-Cd(2)-X(2)	98.16(4)
Cd(1)-X(4)	3.0477(15)	X(1)-Cd(1)-X(1)[1]	86.82(5)	X(9)-Cd(2)-X(3)	96.76(4)
Cd(1)-X(8)	2.6394(11)	X(1)-Cd(1)-X(2)	160.04(5)	X(9)-Cd(2)-X(4)	177.85(4)
Cd(2)-X(2)	2.7959(13)	X(1)-Cd(1)-X(3)	92.49(5)	X(9)-Cd(2)-X(5)	93.93(5)
Cd(2)-X(3)	2.6959(13)	X(1)-Cd(1)-X(4)	83.85(4)	X(9)-Cd(2)-X(6)[2]	87.03(5)
Cd(2)-X(4)	2.6540(14)	X(1)-Cd(1)-X(8)	101.41(4)	X(5)[3]-Cd(3)-X(6)	90.67(5)
Cd(2)-X(5)	2.7097(16)	X(2)-Cd(1)-X(4)	76.24(4)	X(5)[3]-Cd(3)-X(6)[3]	89.33(5)
Cd(2)-X(6)[2]	2.7435(16)	X(3)-Cd(1)-X(2)	84.86(4)	X(5)-Cd(3)-X(5)[3]	180
Cd(2)-X(9)	2.5853(11)	X(3)-Cd(1)-X(4)	77.93(4)	X(5)-Cd(3)-X(6)	89.33(5)
Cd(3)-X(5)	2.6753(15)	X(8)-Cd(1)-X(2)	98.49(4)	X(5)-Cd(3)-X(6)[3]	90.67(5)
Cd(3)-X(5)[3]	2.6753(15)	X(8)-Cd(1)-X(3)	93.29(4)	X(6)[3]-Cd(3)-X(6)	180
Cd(3)-X(6)	2.6840(15)	X(8)-Cd(1)-X(4)	170.04(4)	X(7)[3]-Cd(3)-X(5)	88.52(5)
Cd(3)-X(6)[3]	2.6840(15)	X(3)-Cd(2)-X(2)	84.22(4)	X(7)[3]-Cd(3)-X(5)[3]	91.48(5)
Cd(3)-X(7)	2.5939(15)	X(3)-Cd(2)-X(5)	95.62(5)	X(7)[3]-Cd(3)-X(6)	92.66(5)
Cd(3)-X(7)[3]	2.5939(15)	X(3)-Cd(2)-X(6)[2]	173.37(5)	X(7)[3]-Cd(3)-X(6)[3]	87.34(5)
		X(4)-Cd(2)-X(2)	82.34(4)	X(7)[3]-Cd(3)-X(7)	180
		X(4)-Cd(2)-X(3)	85.37(4)	X(7)-Cd(3)-X(5)	91.48(5)
		X(4)-Cd(2)-X(5)	85.53(5)	X(7)-Cd(3)-X(5)[3]	88.52(5)
		X(4)-Cd(2)-X(6)[2]	90.89(5)	X(7)-Cd(3)-X(6)	87.34(5)
				X(7)-Cd(3)-X(6)[3]	92.66(5)

[1] -*x*+1,-*y*+1,-*z*+1; [2] *x*+1,*y*,*z*; [3] -*x*,-*y*+1,-*z*

Table S5. Cd–Cl bond lengths (Å) and bond angles (°) for pure Cl compound.

Bond	Length	Bond	Angle	Bond	Angle
Cd(1)-Cl(1)	2.5802(12)	Cl(1)^{1}-Cd(1)-Cl(2)	92.50(4)	Cl(5)-Cd(3)-Cl(6)	90.78(4)
Cd(1)-Cl(1)^{1}	2.5912(12)	Cl(1)^{1}-Cd(1)-Cl(3)	167.80(4)	Cl(5)-Cd(3)-Cl(6)^{3}	89.22(4)
Cd(1)-Cl(2)	2.6980(13)	Cl(1)^{1}-Cd(1)-Cl(4)	90.73(4)	Cl(6)^{2}-Cd(2)-Cl(2)	89.67(4)
Cd(1)-Cl(3)	2.6473(12)	Cl(1)-Cd(1)-Cl(1)^{1}	86.11(4)	Cl(6)-Cd(3)-Cl(6)^{3}	180.00(4)
Cd(1)-Cl(4)	2.9718(13)	Cl(1)-Cd(1)-Cl(2)	158.88(4)	Cl(7)^{3}-Cd(3)-Cl(5)	88.31(4)
Cd(1)-Cl(8)	2.5392(13)	Cl(1)-Cd(1)-Cl(3)	92.75(4)	Cl(7)^{3}-Cd(3)-Cl(5)^{3}	91.69(4)
Cd(2)-Cl(2)	2.7325(12)	Cl(1)-Cd(1)-Cl(4)	83.39(4)	Cl(7)^{3}-Cd(3)-Cl(6)	87.42(4)
Cd(2)-Cl(3)	2.6260(12)	Cl(2)-Cd(1)-Cl(4)	75.55(4)	Cl(7)^{3}-Cd(3)-Cl(6)^{3}	92.59(4)
Cd(2)-Cl(4)	2.6085(12)	Cl(3)-Cd(1)-Cl(2)	84.18(4)	Cl(7)-Cd(3)-Cl(5)	91.69(4)
Cd(2)-Cl(5)	2.6866(12)	Cl(3)-Cd(1)-Cl(4)	77.07(4)	Cl(7)-Cd(3)-Cl(5)^{3}	88.31(4)
Cd(2)-Cl(6)^{2}	2.7292(12)	Cl(3)-Cd(2)-Cl(2)	83.91(4)	Cl(7)-Cd(3)-Cl(6)	92.58(4)
Cd(2)-Cl(9)	2.4865(13)	Cl(3)-Cd(2)-Cl(5)	96.40(4)	Cl(7)-Cd(3)-Cl(6)^{3}	87.42(4)
Cd(3)-Cl(5)	2.6631(11)	Cl(3)-Cd(2)-Cl(6)^{2}	172.60(4)	Cl(7)-Cd(3)-Cl(7)^{3}	180
Cd(3)-Cl(5)^{3}	2.6631(11)	Cl(4)-Cd(2)-Cl(2)	81.28(4)	Cl(8)-Cd(1)-Cl(1)	103.17(4)
Cd(3)-Cl(6)	2.6655(11)	Cl(4)-Cd(2)-Cl(3)	84.22(4)	Cl(8)-Cd(1)-Cl(1)^{1}	99.13(4)
Cd(3)-Cl(6)^{3}	2.6655(11)	Cl(4)-Cd(2)-Cl(5)	85.27(4)	Cl(8)-Cd(1)-Cl(2)	97.86(4)
Cd(3)-Cl(7)	2.5538(12)	Cl(4)-Cd(2)-Cl(6)^{2}	91.18(4)	Cl(8)-Cd(1)-Cl(3)	92.97(4)
Cd(3)-Cl(7)^{3}	2.5538(12)	Cl(5)^{3}-Cd(3)-Cl(6)	89.22(4)	Cl(8)-Cd(1)-Cl(4)	168.45(4)
		Cl(5)^{3}-Cd(3)-Cl(6)^{3}	90.78(4)	Cl(9)-Cd(2)-Cl(2)	97.81(4)
		Cl(5)-Cd(2)-Cl(2)	166.45(4)	Cl(9)-Cd(2)-Cl(3)	97.88(4)
		Cl(5)-Cd(2)-Cl(6)^{2}	88.98(4)	Cl(9)-Cd(2)-Cl(4)	177.63(5)
		Cl(5)-Cd(3)-Cl(5)^{3}	180	Cl(9)-Cd(2)-Cl(5)	95.57(4)
				Cl(9)-Cd(2)-Cl(6)^{2}	86.62(4)

[1] -*x*+1,-*y*+1,-*z*+2; [2] -*x*,-*y*+1,-*z*+1; [3] -*x*+1,-*y*+1,-*z*+1

Table S6. Hydrogen bonding interactions (Å) in pure Br compound.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...Br(2)^{1}	0.86	3.11	3.704(7)	128.5
N(1)-H(1A)...Br(3)^{2}	0.86	2.69	3.406(7)	141.9
N(2)-H(2A)...Br(1)^{3}	0.89	2.84	3.465(7)	128.8
N(2)-H(2A)...Br(1)^{4}	0.89	2.91	3.638(8)	139.7
N(2)-H(2B)...Br(4)	0.89	2.47	3.332(7)	162.1
N(2)-H(2C)...Br(2)^{5}	0.89	2.62	3.396(7)	146.8
N(2)-H(2C)...Br(4)^{5}	0.89	3.12	3.665(8)	121.7

[1] -*x*+2,*y*-1/2,-*z*+1/2; [2] -*x*+2,-*y*+1,-*z*; [3] *x*-1,*y*,*z*; [4] -*x*+1,-*y*+1,-*z*; [5] -*x*+1,-*y*+1,-*z*+1

Table S7. Hydrogen bonding interactions (Å) in Cl 50% compound.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...X(4)[1]	0.86	2.74	3.387(4)	133.7
N(1)-H(1A)...X(3)[2]	0.86	2.69	3.385(4)	138.5
N(2)-H(2A)...X(2)[3]	0.89	2.47	3.344(4)	167.3
N(2)-H(2B)...X(4)	0.89	2.43	3.228(4)	148.7
N(2)-H(2C)...X(2)	0.89	3.04	3.673(4)	129.6
N(2)-H(2C)...X(2)[4]	0.89	2.79	3.498(4)	137.1
N(2)-H(2C)...X(3)[4]	0.89	2.86	3.335(3)	115.2

[1] -*x*+2,-*y*+1,-*z*+1; [2] -*x*+1,-*y*+1,-*z*+1; [3] -*x*+2,-*y*+1,-*z*; [4] -*x*+1,-*y*+1,-*z*

Table S8. Hydrogen bonding interactions (Å) in Cl 80% compound.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...X(6)[5]	0.86	2.55	3.320(9)	150.2
N(2)-H(2A)...X(5)[6]	0.89	2.51	3.319(7)	151.8
N(2)-H(2A)...X(6)[3]	0.89	3.03	3.566(8)	120.8
N(2)-H(2B)...X(7)[2]	0.89	2.59	3.372(7)	146.7
N(2)-H(2C)...X(4)	0.89	2.78	3.285(7)	117.2
N(2)-H(2C)...X(5)	0.89	2.56	3.394(7)	156.3
N(3)-H(3A)...X(8)	0.86	2.4	3.240(7)	166.9
N(4)-H(4A)...X(5)[7]	0.89	2.94	3.536(7)	126.2
N(4)-H(4A)...X(7)[7]	0.89	2.62	3.402(8)	146.5
N(4)-H(4B)...X(1)[7]	0.89	3.11	3.680(7)	124.1
N(4)-H(4B)...X(3)[7]	0.89	2.91	3.479(7)	123.7
N(4)-H(4B)...X(4)[7]	0.89	2.77	3.547(8)	146.9
N(4)-H(4C)...X(2)[8]	0.89	2.55	3.433(7)	173.3

[1] -*x*+1,-*y*+1,-*z*+1; [2] *x*+1,*y*,*z*; [3] -*x*,-*y*+1,-*z*; [4] *x*-1,*y*,*z*; [5] *x*,*y*-1,*z* ; [6] -*x*+1,-*y*+1,-*z*; [7] *x*+1,*y*+1,*z*; [8] *x*,*y*+1,*z*

Table S9. Hydrogen bonding interactions (Å) in pure Cl compound.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...Cl(6)[4]	0.86	2.46	3.264(5)	154.9
N(2)-H(2A)...Cl(5)	0.89	2.92	3.377(5)	113.7
N(2)-H(2A)...Cl(6)	0.89	2.83	3.583(5)	143
N(2)-H(2B)...Cl(5)[2]	0.89	2.86	3.292(5)	111.4
N(2)-H(2B)...Cl(7)[5]	0.89	2.46	3.320(5)	162.4
N(2)-H(2C)...Cl(4)	0.89	2.37	3.244(5)	169.4
N(3)-H(3A)...Cl(8)	0.86	2.28	3.118(5)	165.3
N(4)-H(4A)...Cl(2)[6]	0.89	2.52	3.389(5)	166.5
N(4)-H(4B)...Cl(5)[7]	0.89	2.88	3.528(5)	131.3
N(4)-H(4B)...Cl(7)[7]	0.89	2.63	3.382(5)	143.1
N(4)-H(4C)...Cl(1)[7]	0.89	2.92	3.571(5)	131.2
N(4)-H(4C)...Cl(3)[7]	0.89	2.83	3.445(5)	127
N(4)-H(4C)...Cl(4)[7]	0.89	2.76	3.459(5)	136.8

[1] -*x*+1,-*y*+1,-*z*+2; [2] -*x*,-*y*+1,-*z*+1; [3] -*x*+1,-*y*+1,-*z*+1; [4] *x*+1,*y*,*z* ; [5] -*x*,-*y*,-*z*+1; [6] *x*+1,*y*+1,*z*; [7] *x*,*y*+1,*z*

Table S10. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for pure Cl compound. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	*y*	*z*	*U*(eq)
Cd(1)	0.5494(1)	0.6388(1)	0.9403(1)	0.30(1)
Cd(2)	0.5588(1)	0.6873(1)	0.7134(1)	0.25(1)
Cd(3)	0	0.5	0.5	0.23(1)
Cl(1)	0.2664(2)	0.5004(1)	0.9884(1)	0.29(1)
Cl(2)	0.8253(2)	0.7249(1)	0.8402(1)	0.30(1)
Cl(3)	0.3574(2)	0.7488(1)	0.8385(1)	0.32(1)
Cl(4)	0.4938(2)	0.4828(1)	0.7788(1)	0.32(1)
Cl(5)	0.2855(2)	0.5983(1)	0.6004(1)	0.35(1)
Cl(6)	0.2070(2)	0.3873(1)	0.4004(1)	0.34(1)
Cl(7)	-0.738(2)	0.3298(1)	0.5982(1)	0.35(1)
Cl(8)	0.5952(2)	0.8048(1)	0.10578(1)	0.38(1)
Cl(9)	0.6329(2)	0.8803(1)	0.6488(1)	0.38(1)

Table S11. Atomic coordinates, site occupancy factors and equivalent isotropic displacement parameters ($Å^2$) for Cl 80% compound. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)	Occupancy
Cd(1)	0.5497(1)	0.6378(1)	0.4403(1)	0.41(1)	1
Cd(2)	0.5613(1)	0.6841(1)	0.2131(1)	0.35(1)	1
Cd(3)	0.0	0.5000	0.0	0.33(1)	1
Br(1)	0.2639(2)	0.4994(1)	0.4895(1)	0.38(1)	0.144(6)
Br(2)	0.8328(2)	0.7276(1)	0.3407(1)	0.38(1)	0.267(6)
Br(3)	0.3552(2)	0.7479(1)	0.3391(1)	0.42(1)	0.259(6)
Br(4)	0.4931(2)	0.4772(1)	0.2771(1)	0.41(1)	0.237(6)
Br(5)	0.2851(2)	0.5959(2)	0.1010(1)	0.44(1)	0.035(7)
Br(6)	-0.2054(2)	0.6115(2)	0.996(1)	0.44(1)	0.049(6)
Br(7)	-0.816(2)	0.3276(1)	0.969(1)	0.36(1)	0.021(5)
Br(8)	0.5949(1)	0.8057(1)	0.5637(1)	0.40(1)	0.509(5)
Br(9)	0.6334(2)	0.8824(1)	0.1460(1)	0.41(1)	0.474(4)
Cl(1)	0.2639(2)	0.4994(1)	0.4895(1)	0.38(1)	0.856(6)
Cl(2)	0.8328(2)	0.7276(1)	0.3407(1)	0.38(1)	0.733(6)
Cl(3)	0.3552(2)	0.7479(1)	0.3391(1)	0.42(1)	0.741(6)
Cl(4)	0.4931(2)	0.4772(1)	0.2771(1)	0.41(1)	0.763(6)
Cl(5)	0.2851(2)	0.5959(2)	0.1010(1)	0.44(1)	0.965(7)
Cl(6)	-0.2054(2)	0.6115(2)	0.996(1)	0.44(1)	0.951(6)
Cl(7)	-0.816(2)	0.3276(1)	0.969(1)	0.36(1)	0.979(5)
Cl(8)	0.5949(1)	0.8057(1)	0.5637(1)	0.40(1)	0.491(5)
Cl(9)	0.6334(2)	0.8824(1)	0.1460(1)	0.41(1)	0.526(4)

Table S12. Atomic coordinates, site occupancy factors and equivalent isotropic displacement parameters (Å^2) for Cl 50% compound. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	*y*	*z*	*U*(eq)	Occupancy
Cd(1)	0.4930(1)	0.6878(1)	0.2006(1)	0.39(1)	1
Br(1)	0.5262(1)	0.9154(1)	0.3085(1)	0.58(1)	0.7843(19)
Br(2)	0.6257(1)	0.6780(1)	-0.88(1)	0.61(1)	0.389(4)
Br(3)	0.1050(1)	0.6592(1)	0.1937(1)	0.46(1)	0.587(4)
Br(4)	0.6517(1)	0.4802(1)	0.3251(1)	0.40(1)	0.2157(19)
Cl(1)	0.5262(1)	0.9154(1)	0.3085(1)	0.58(1)	0.2157(19)
Cl(2)	0.6257(1)	0.6780(1)	-0.88(1)	0.61(1)	0.611(4)
Cl(3)	0.1050(1)	0.6592(1)	0.1937(1)	0.46(1)	0.413(4)
Cl(4)	0.6517(1)	0.4802(1)	0.3251(1)	0.40(1)	0.7843(19)

Table S13. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for pure Br compound. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	*y*	*z*	*U*(eq)
Cd(1)	0.7985(1)	0.6162(1)	0.3126(1)	0.45(1)
Br(1)	0.8679(1)	0.5354(1)	0.1294(1)	0.52(1)
Br(2)	0.10244(1)	0.6179(1)	0.5693(1)	0.62(1)
Br(3)	0.8103(1)	0.7215(1)	0.1893(1)	0.50(1)
Br(4)	0.4654(1)	0.5949(1)	0.3647(1)	0.57(1)

Table S14. Br/Cl weight percentages and atomic ratios for (4AEP)$CdBr_{4-x}Cl_x$ and $(4AEP)_4Cd_5Br_{18-x}Cl_x$.

	Weight [%]		4-x	x
	Br	Cl	Br	Cl
(4AEP)$CdBr_{4-x}Cl_x$	37.11	16.46	1.99	2.01

	Weight [%]		18-x	x
	Br	Cl	Br	Cl
$(4AEP)_4Cd_5Br_{18-x}Cl_x$	15.24	28.66	3.44	14.56

Table S15. Distortion values for compounds with Cl ratios of 0%, 50%, 80%, and 100%.

Cl ratio (%)	0	50	80	100
Δd	1.156×10^{-5}	1.017×10^{-4}	3.054×10^{-3} 6.055×10^{-4} 2.343×10^{-4}	2.891×10^{-3} 1.031×10^{-3} 2.095×10^{-4}

Table S16. Elemental analysis (EA) data for pure Br, Cl 50%, Cl 80%, and pure Cl compounds.

	Element	Calculated	Experimental
pure Br	C	15.11	14.82
	N	5.04	4.81
	H	2.17	2.05
	Total	22.32	21.68

	Element	Calculated	Experimental
Cl 50%	C	18.03	17.84
	N	6.01	5.83
	H	2.59	2.59
	Total	26.63	26.26

	Element	Calculated	Experimental
Cl 80%	C	17.96	18.18
	N	5.99	5.98
	H	2.58	2.63
	Total	26.53	26.79

	Element	Calculated	Experimental
pure Cl	C	19.82	19.55
	N	6.61	6.42
	H	2.85	2.84
	Total	29.28	28.81

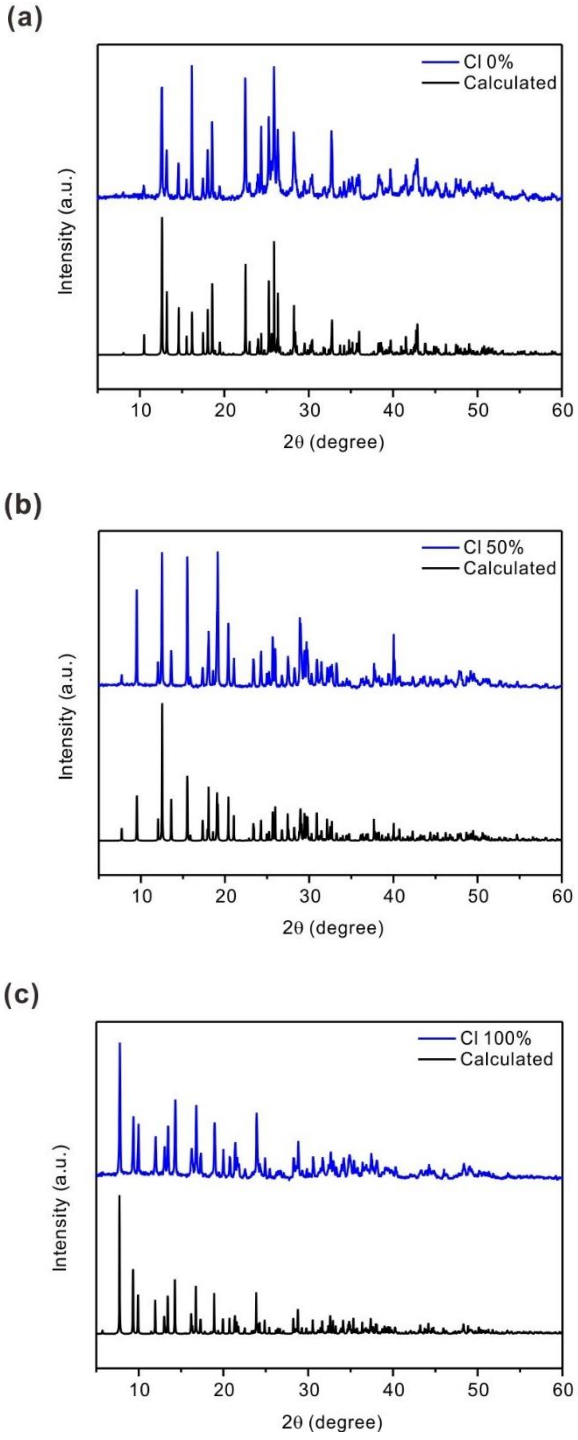

Fig. S1 Experimental and calculated powder X-ray diffraction patterns for compounds with Cl ratios of (a) 0%, (b) 50%, and (c) 100%.

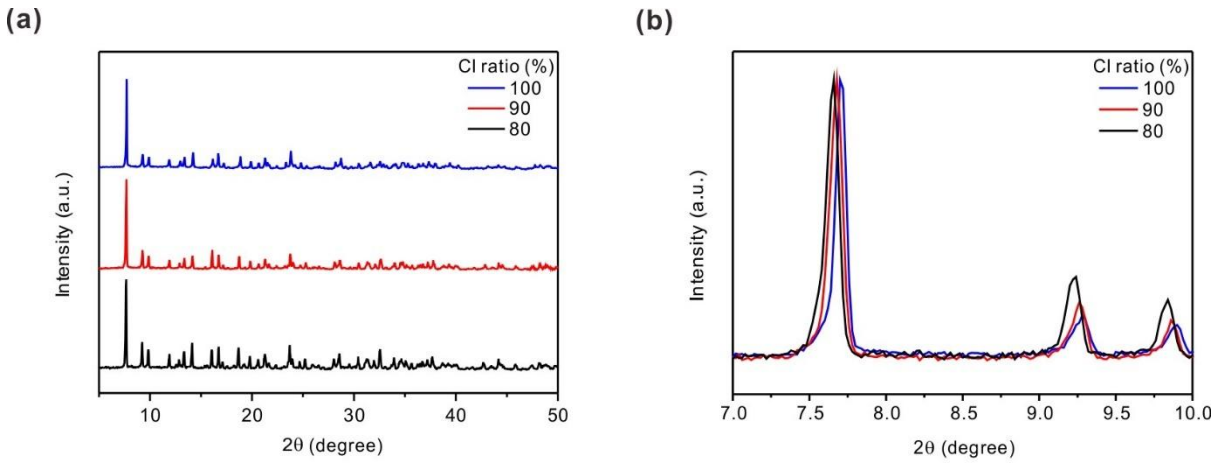

Fig. S2 (a) PXRD patterns of (4AEP)$Cd_5Br_{(18-x)}Cl_x$ with Cl ratios of 100%, 90%, and 80%. (b) Enlarged view of the PXRD patterns in the 2θ range 7.4° to 10.0° for the same samples.

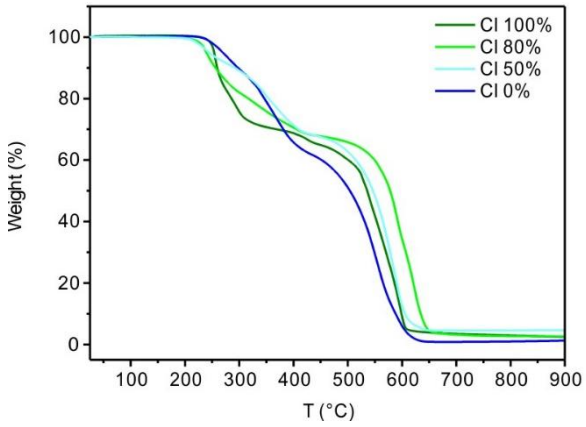

Fig. S3 TGA curves for compounds with Cl ratios of 100%, 80%, 50%, and 0%.

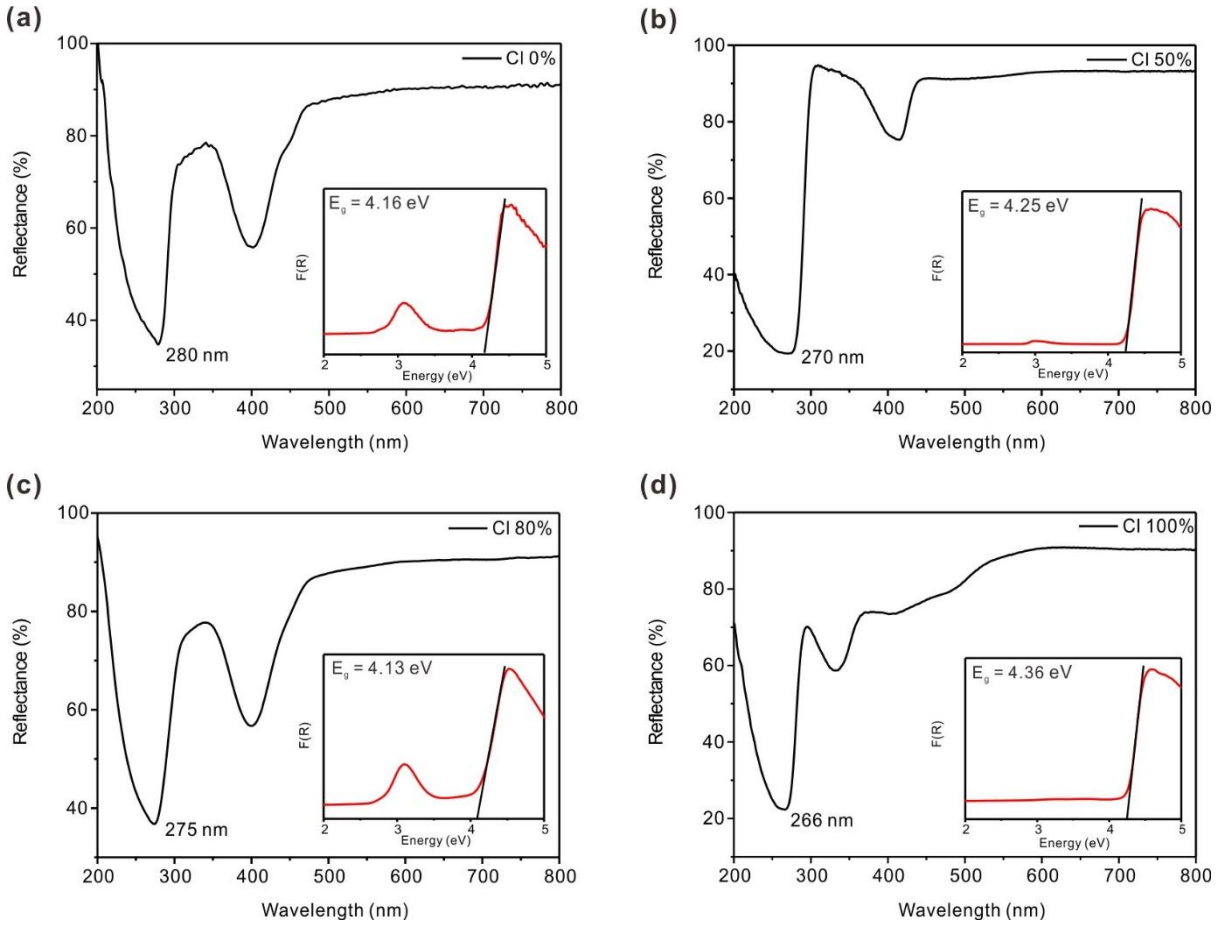

Fig. S4 UV-vis diffuse reflectance spectra and corresponding optical band gaps for compounds with Cl ratios of (a) 0%, (b) 50%, (c) 80%, and (d) 100%.

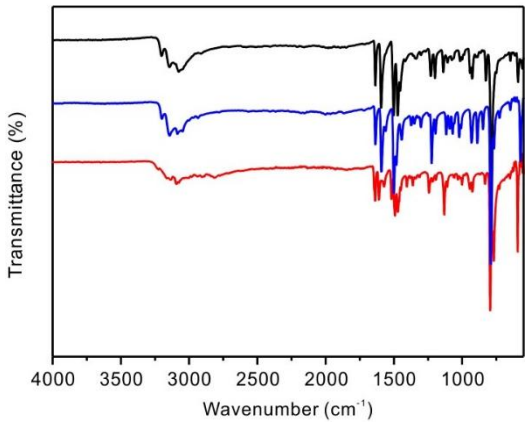

Fig. S5 IR spectra for compounds with Cl ratios of 0%, 50%, and 100%, shown from top to bottom.

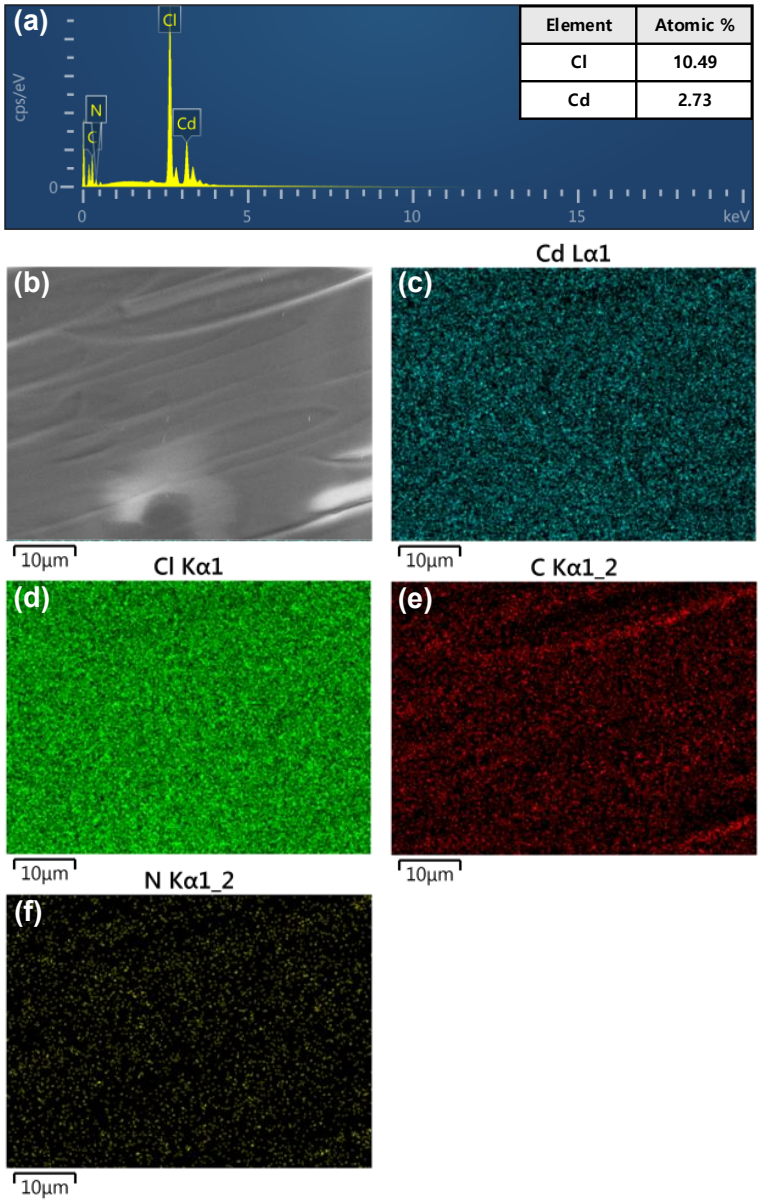

Fig. S6 EDS analysis results for the pure Cl compound. (a) EDS spectrum, (b) SEM image, and (c–f) elemental distribution maps of Cd, Cl, C, and N on the crystal surface.

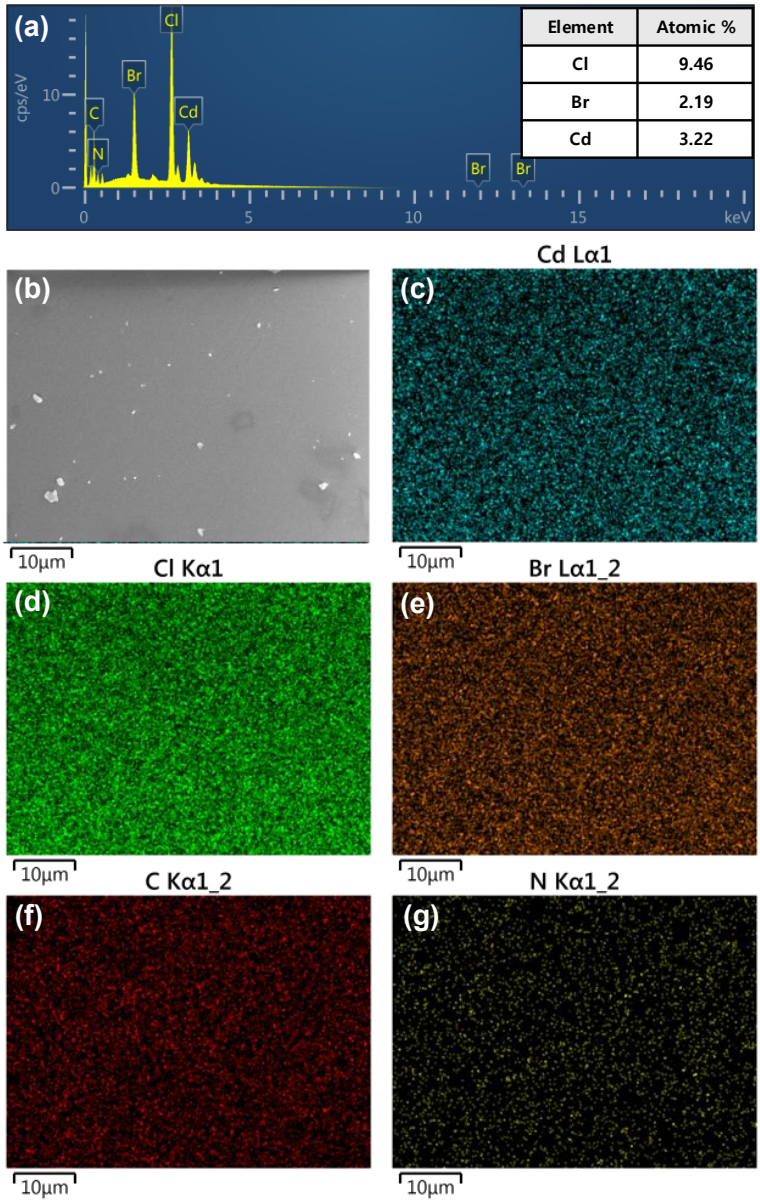

Fig. S7 EDS analysis results for the Cl 80% compound. (a) EDS spectrum, (b) SEM image, and (c–g) elemental distribution maps of Cd, Cl, Br, C, and N on the crystal surface.

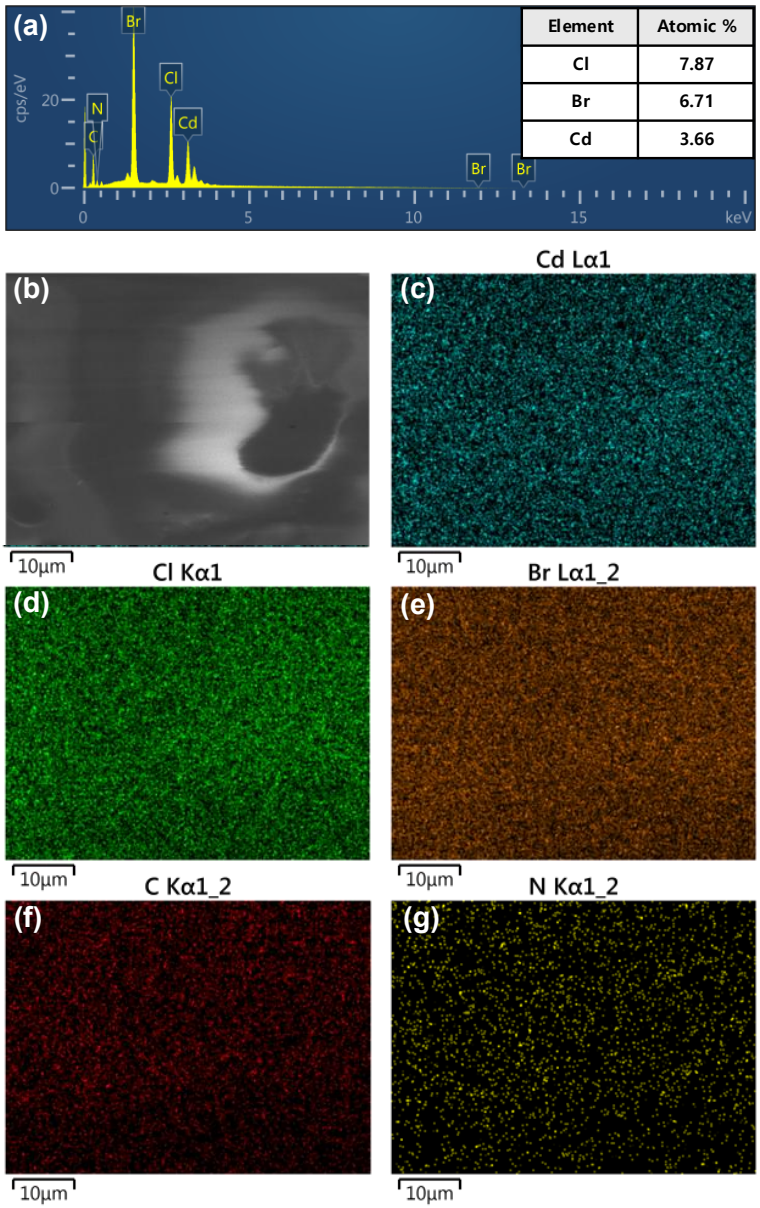

Fig. S8 EDS analysis results for the Cl 50% compound. (a) EDS spectrum, (b) SEM image, and (c–g) elemental distribution maps of Cd, Cl, Br, C, and N on the crystal surface.

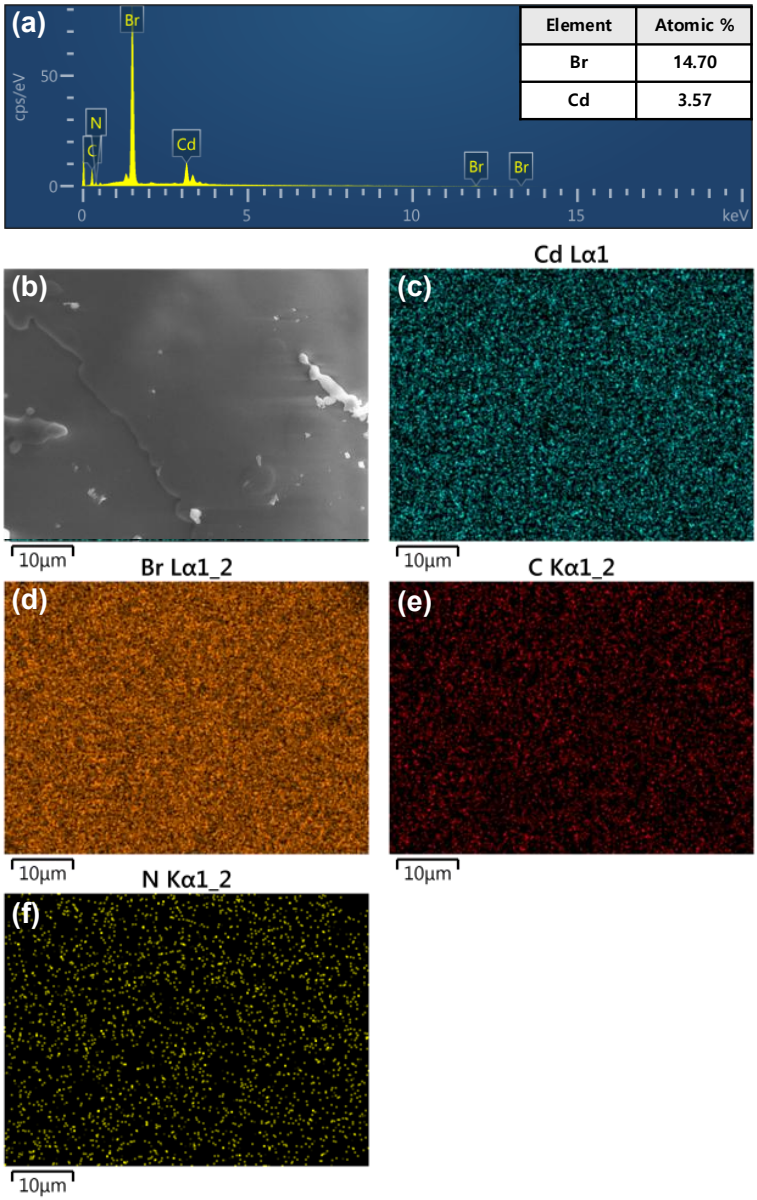

Fig. S9 EDS analysis results for the pure Br compound. (a) EDS spectrum, (b) SEM image, and (c–f) elemental distribution maps of Cd, Br, C, and N on the crystal surface.

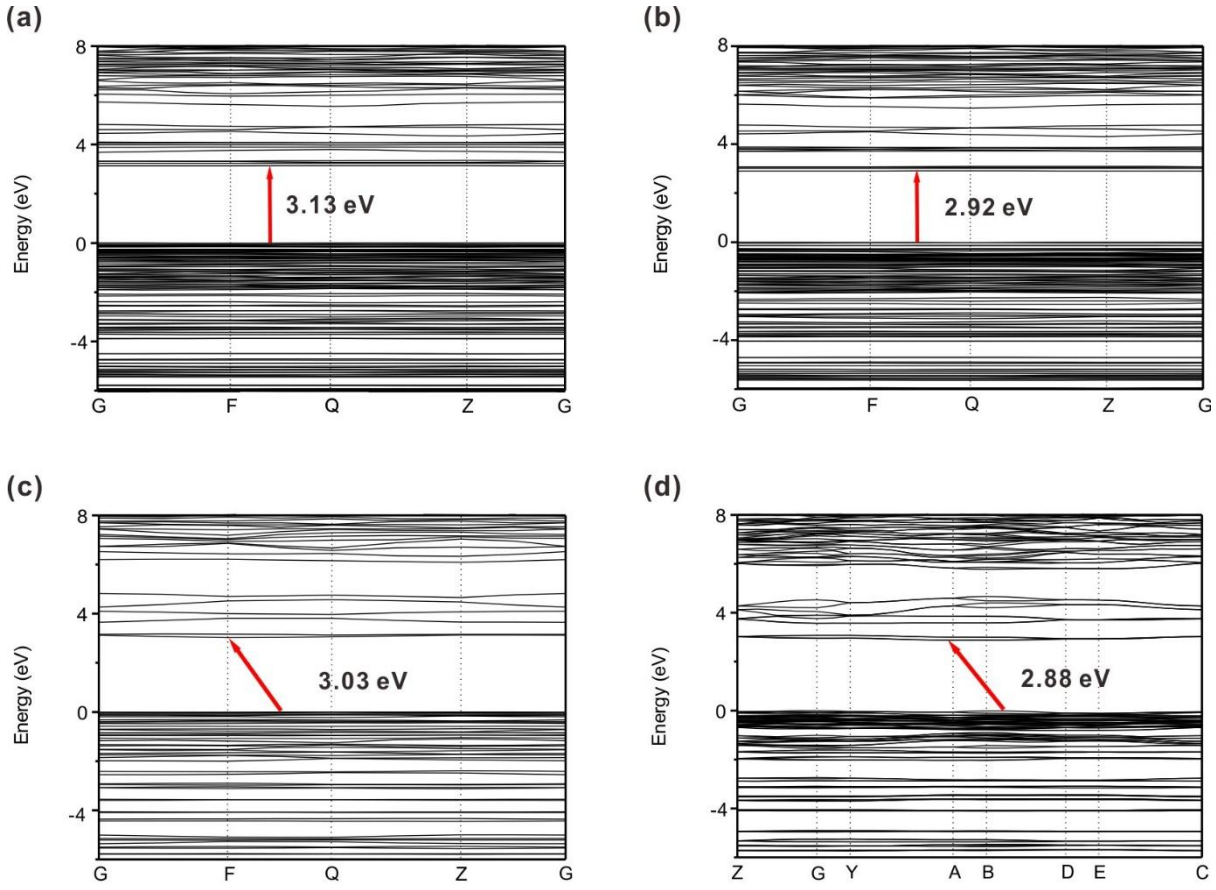

Fig. S10 Band structures of (a) pure Cl, (b) Cl 80%, (c) Cl 50%, and (d) pure Br compounds.

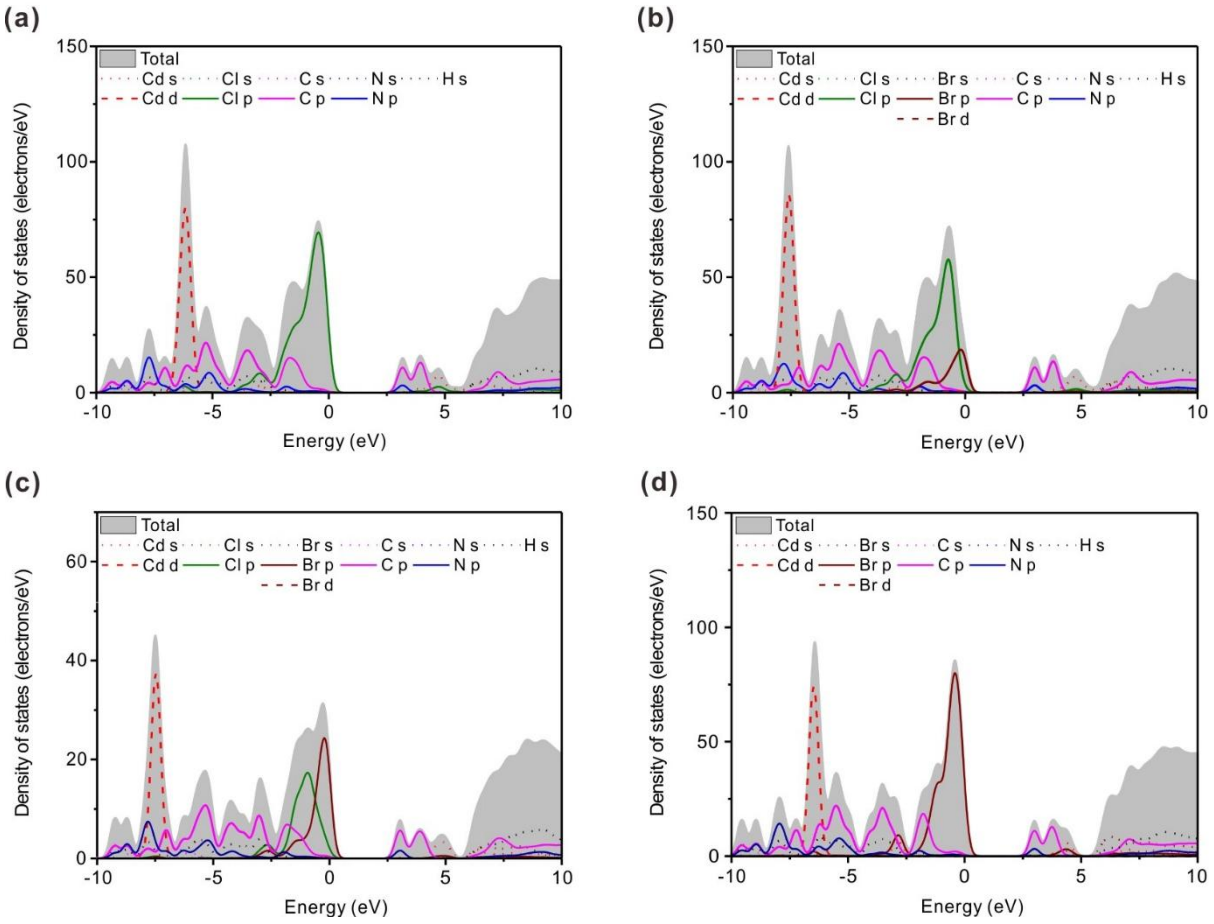

Fig. S11 Density of states (DOS) for (a) pure Cl, (b) Cl 80%, (c) Cl 50%, and (d) pure Br compounds.

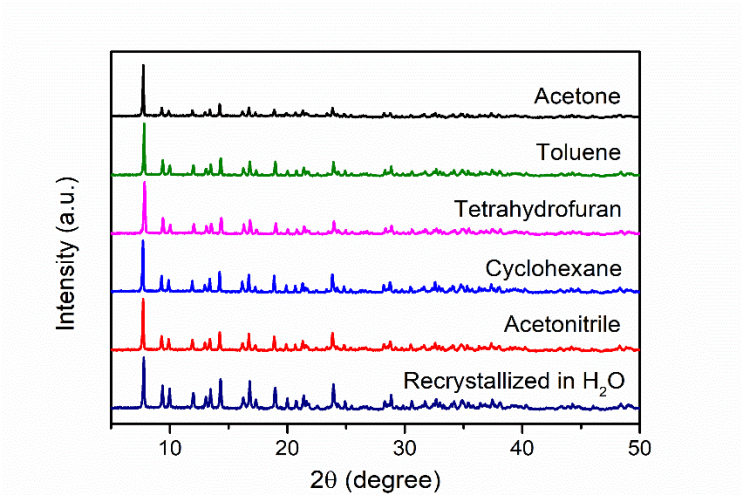

Fig. S12 PXRD patterns of the Cl-rich compound after stability tests in various organic solvents and water.

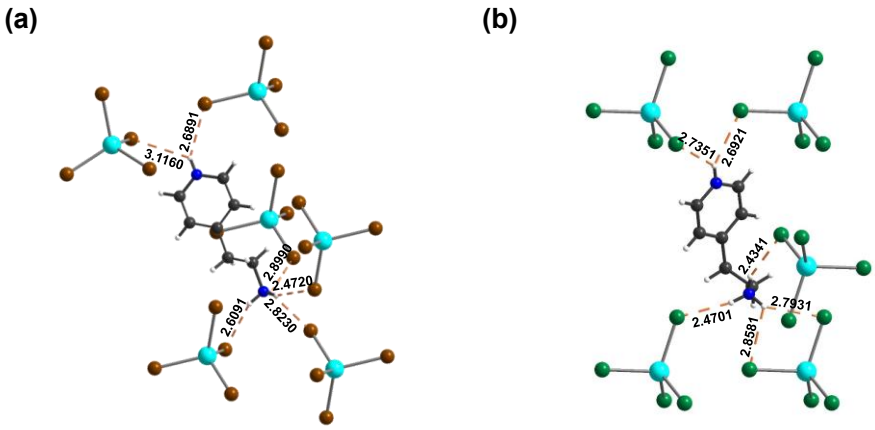

Fig. S13 Hydrogen bonding interactions between $(4AEP)^{2+}$ and the surrounding CdX_4 (X = Br or Cl) tetrahedra in (a) pure Br and (b) Cl 50% compounds.

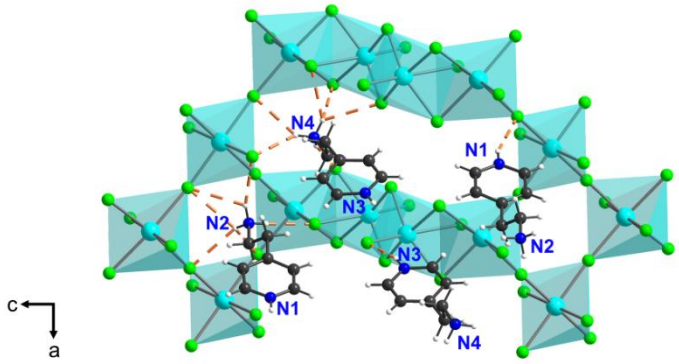

Fig. S14 Hydrogen bonding interactions between $(4AEP)^{2+}$ and the inorganic layer in Cl-rich compounds (80%-100%).