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A New Class of Organic-inorganic Single and Double Hybrid Perovskites with Diammonium-halide-diammonium Spacer Layer

Walter P.D. Wong,[a]† Xinyun Wang,[a]† Rongrong Zhang,[a][b] Kian Ping Loh*[a][b]

[a] Department of Chemistry, National University of Singapore 3 Science Drive 3, Singapore 117543, Singapore

[b] Joint School of National University of Singapore and Tianjin University, International Campus of Tianjin University, Binhai New City, Fuzhou 350207, China

† Both authors contributed equally to this work

*Corresponding author: chmlohkp@nus.edu.sg

Table S1: Summary of key single crystal XRD refinement parameters for $(ED)_4CuBiX_{12}$

Identification code	$(ED)_4CuBiBr_{12}$	$(ED)_4CuBiCl_\alpha Br_{12-\alpha}$	$(ED)_4CuBiCl_4I_8$	$(ED)_4CuBiBr_4I_8$
Empirical formula	$C_8H_{40}BiBr_{12}CuN_8$	$C_8H_{40}BiBr_{10.18}Cl_{1.82}CuN_8$	$C_8H_{40}BiCl_4CuI_8N_8$	$C_8H_{40}BiBr_4CuI_8N_8$
Formula weight	1479.92	1399.00	1678.00	1855.84
Temperature/K	100(5)	100(5)	100(5)	100(5)
Crystal system	Triclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_12_12$	$P2_1/m$
a/Å	9.0208(4)	8.9118(12)	20.749(3)	8.9130(14)
b/Å	9.0364(5)	8.9306(12)	9.0030(9)	22.030(4)
c/Å	11.1463(6)	11.1342(13)	9.8332(12)	9.5776(14)
α/°	108.205(2)	107.767(5)	90	90
β/°	93.991(2)	94.121(5)	90	91.570(5)
γ/°	92.577(2)	92.742(5)	90	90
Volume/Å^3	858.89(8)	839.43(19)	1836.9(4)	1879.9(5)
Z	1	1	2	2
ρ_{calc}g/cm^3	2.861	2.767	3.034	3.279
μ/mm^{-1}	19.706	18.142	12.391	16.075
F(000)	676.0	643.0	1496.0	1640.0
Crystal size/mm^3	0.190 × 0.110 × 0.090	0.14 × 0.078 × 0.062	0.067 × 0.065 × 0.031	0.077 × 0.058 × 0.051
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.694 to 52.748	4.594 to 49.474	4.584 to 49.444	4.932 to 52.744
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 10, 0 ≤ l ≤ 13	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -13 ≤ l ≤ 13	-24 ≤ h ≤ 24, -10 ≤ k ≤ 10, -11 ≤ l ≤ 11	-11 ≤ h ≤ 11, 0 ≤ k ≤ 27, 0 ≤ l ≤ 11
Reflections collected	3457	21039	17363	3909
Independent reflections	3457 [R_{sigma} = 0.0452]	2863 [R_{int} = 0.0953, R_{sigma} = 0.0528]	3148 [R_{int} = 0.0849, R_{sigma} = 0.0535]	3909 [R_{sigma} = 0.0736]
Data/restraints/ parameters	3457/0/160	2863/0/151	3148/43/152	3909/54/150
Goodness-of-fit on F^2	1.045	1.028	1.034	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0310, wR_2 = 0.0732	R_1 = 0.0319, wR_2 = 0.0693	R_1 = 0.0323, wR_2 = 0.0620	R_1 = 0.0600, wR_2 = 0.1299
Final R indexes [all data]	R_1 = 0.0356, wR_2 = 0.0757	R_1 = 0.0436, wR_2 = 0.0752	R_1 = 0.0389, wR_2 = 0.0661	R_1 = 0.0780, wR_2 = 0.1377
Largest diff. peak/hole / e Å^{-3}	1.88/-1.34	1.58/-1.20	0.96/-1.02	3.01/-2.48

Table S2: Summary of key single crystal XRD refinement parameters for $(ED)_4AgBiX_{12}$

Identification code	$(ED)_4AgBiBr_{12}$	$(ED)_4AgBiCl_\alpha Br_{12-\alpha}$	$(ED)_4AgBiCl_\alpha I_{12-\alpha}$	$(ED)_4AgBiBr_\alpha I_{12-\alpha}$
Empirical formula	$C_8H_{40}AgBiBr_{12}N_8$	$C_8H_{40}AgBiBr_{9.47}Cl_{2.53}N_8$	$C_8H_{40}AgBiCl_{2.19}I_{9.81}N_8$	$C_8H_{40}AgBiBr_{3.37}I_{8.63}N_8$
Formula weight	1524.25	1411.76	1887.85	1929.77
Temperature/K	100(5)	100(5)	100(5)	100(5)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.9996(4)	8.8306(5)	9.1764(4)	9.1706(4)
b/Å	9.0011(4)	8.8403(5)	9.1792(4)	9.2051(4)
c/Å	11.2290(5)	11.1883(6)	11.8973(6)	11.8688(4)
α/°	108.040(2)	107.385(2)	94.093(2)	107.4280(10)
β/°	94.137(2)	94.196(2)	107.241(2)	93.9270(10)
γ/°	92.587(2)	92.878(2)	91.825(2)	92.3490(10)
Volume/Å^3	860.46(7)	828.90(8)	953.18(8)	951.69(7)
Z	1	1	1	1
ρ_{calc}g/cm^3	2.942	2.828	3.289	3.367
μ/mm^{-1}	19.621	17.523	13.235	15.682
F(000)	694.0	648.0	831.0	849.0
Crystal size/mm^3	0.181 × 0.095 × 0.088	0.120 × 0.088 × 0.071	0.135 × 0.124 × 0.098	0.089 × 0.087 × 0.068
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.55 to 52.78	5.182 to 52.912	4.958 to 52.772	4.946 to 52.766
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 10, 0 ≤ l ≤ 14	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -13 ≤ l ≤ 14	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -14 ≤ l ≤ 14	-11 ≤ h ≤ 11, -11 ≤ k ≤ 10, 0 ≤ l ≤ 14
Reflections collected	3416	25474	36182	3846
Independent reflections	3416 [R_{sigma} = 0.0547]	3397 [R_{int} = 0.0735, R_{sigma} = 0.0423]	3871 [R_{int} = 0.0497, R_{sigma} = 0.0295]	3846 [R_{sigma} = 0.0381]
Data/restraints/ parameters	3416/30/144	3397/0/149	3871/6/154	3846/0/148
Goodness-of-fit on F^2	1.027	1.036	1.114	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0317, wR_2 = 0.0734	R_1 = 0.0299, wR_2 = 0.0681	R_1 = 0.0190, wR_2 = 0.0407	R_1 = 0.0286, wR_2 = 0.0581
Final R indexes [all data]	R_1 = 0.0376, wR_2 = 0.0781	R_1 = 0.0371, wR_2 = 0.0717	R_1 = 0.0194, wR_2 = 0.0410	R_1 = 0.0306, wR_2 = 0.0593
Largest diff. peak/hole / e Å^{-3}	1.38/-1.36	2.31/-1.46	0.73/-0.93	1.02/-0.85

Table S3: Summary of key single crystal XRD refinement parameters for $(ED)_2PbX_6$ and (R-3AP)$CuBiBr_{12}$

Identification code	$(ED)_2PbBr_2I_4$	$(ED)_2PbCl_2I_4$	$(R\text{-}3AP)_4CuBiBr_{12}$	$(R\text{-}3AP)_4CuBiBr_{12}$
Empirical formula	$C_4H_{20}Br_2I_4N_4Pb$	$C_4H_{20}Cl_2I_4N_4Pb$	$C_{16}H_{48}BiBr_{12}CuN_8$	$C_{16}H_{48}BiBr_{12}CuN_8$
Formula weight	998.85	909.93	1584.06	1584.06
Temperature/K	100(5)	100(5)	100(5)	420(5)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbcn*	*C*2/*m*	$P2_1$	*P*2/*m*
a/Å	8.8705(10)	8.982(3)	9.2700(4)	9.392(9)
b/Å	9.3316(12)	8.648(4)	23.3775(13)	9.449(11)
c/Å	23.161(3)	12.608(6)	9.2708(4)	12.894(14)
α/°	90	90	90	90
β/°	90	104.270(9)	92.320(2)	111.37(2)
γ/°	90	90	90	90
Volume/Å^3	1917.1(4)	949.1(7)	2007.42(17)	1066(2)
Z	4	2	2	1
ρ_{calc}g/cm^3	3.461	3.184	2.621	2.468
μ/mm^{-1}	19.395	15.659	16.872	15.890
F(000)	1744.0	800.0	1464.0	732.0
Crystal size/mm^3	0.160 × 0.144 × 0.020	0.100× 0.048 × 0.021	0.205 × 0.204 × 0.091	0.156× 0.107× 0.068
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.786 to 49.424	6.642 to 49.436	5.228 to 51.436	5.486 to 34.38
Index ranges	$-10 \le h \le 10$, $-10 \le k \le 10$, $-26 \le l \le 27$	$-9 \le h \le 10$, $-10 \le k \le 10$, $-14 \le l \le 14$	$-11 \le h \le 11$, $-28 \le k \le 28$, $-11 \le l \le 11$	$-7 \le h \le 7$, $-7 \le k \le 7$, $-10 \le l \le 10$
Reflections collected	10749	3608	20549	5240
Independent reflections	1959 [R_{int} = 0.1053, R_{sigma} = 0.0611]	872 [R_{int} = 0.0821, R_{sigma} = 0.0661]	7605 [R_{int} = 0.0721, R_{sigma} = 0.0886]	695 [R_{int} = 0.0628, R_{sigma} = 0.0457]
Data/restraints/ parameters	1959/15/71	872/45/65	7605/277/348	695/40/57
Goodness-of-fit on F^2	1.022	1.167	1.016	1.124
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.0985	R_1 = 0.0469, wR_2 = 0.0962	R_1 = 0.0445, wR_2 = 0.0887	R_1 = 0.0731, wR_2 = 0.2095
Final R indexes [all data]	R_1 = 0.0549, wR_2 = 0.110	R_1 = 0.0539, wR_2 = 0.1017	R_1 = 0.0569, wR_2 = 0.0936	R_1 = 0.0868, wR_2 = 0.2337
Largest diff. peak/hole / e Å^{-3}	1.14/-1.47	1.56/-1.70	1.19/-1.41	1.16/-0.55

Table S4: Summary of key single crystal XRD refinement parameters for (R-3AP)$CuBiX_{12}$

Identification code	$(R\text{-}3AP)_4CuBiCl_4I_8$	$(R\text{-}3AP)_4CuBiBr_4I_8$	$(S\text{-}3AP)_4CuBiBr_{12}$	$(3AP)_4CuBiBr_{12}$
Empirical formula	$C_{16}H_{48}BiCl_4CuI_8N_8$	$C_{16}H_{47}BiBr_4CuI_8N_8$	$C_{16}H_{48}BiBr_{12}CuN_8$	$C_{16}H_{38}BiBr_{12}CuN_8$
Formula weight	1782.14	1958.97	1584.06	1573.98
Temperature/K	100(5)	100(5)	100(5)	100(5)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$C2$	$P222_1$	$P2_1$	$P\bar{1}$
a/Å	21.9681(10)	9.5241(7)	9.2586(4)	9.214(3)
b/Å	10.2048(5)	9.5438(6)	23.3644(11)	9.284(3)
c/Å	9.4303(4)	47.395(3)	9.2764(4)	12.255(3)
α/°	90	90	90	105.567(10)
β/°	90.175(2)	90	92.358(2)	96.256(9)
γ/°	90	90	90	92.093(10)
Volume/Å^3	2114.08(17)	4308.0(5)	2004.99(15)	1001.4(5)
Z	2	4	2	1
ρ_{calc}g/cm^3	2.800	3.020	2.624	2.610
μ/mm^{-1}	10.776	14.038	16.893	16.910
F(000)	1608.0	3500.0	1464.0	722.0
Crystal size/mm^3	0.12 × 0.081 × 0.056	0.092 × 0.048 × 0.028	0.148 × 0.121 × 0.105	0.233 × 0.141 × 0.125
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.164 to 52.79	4.296 to 49.446	4.394 to 52.83	5.984 to 49.446
Index ranges	$-26 \le h \le 27$, $-12 \le k \le 12$, $-11 \le l \le 11$	$-11 \le h \le 10$, $-11 \le k \le 11$, $-55 \le l \le 55$	$-11 \le h \le 11$, $-29 \le k \le 29$, $-11 \le l \le 11$	$-10 \le h \le 10$, $-10 \le k \le 10$, $0 \le l \le 14$
Reflections collected	13352	43153	47482	3378
Independent reflections	4154 [R_{int} = 0.0525, R_{sigma} = 0.0704]	7322 [R_{int} = 0.0757, R_{sigma} = 0.0607]	8249 [R_{int} = 0.1030, R_{sigma} = 0.0796]	3378 [R_{sigma} = 0.0923]
Data/restraints/ parameters	4154/79/176	7322/246/376	8249/166/348	3378/78/178
Goodness-of-fit on F^2	1.044	1.050	1.018	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0713	R_1 = 0.0704, wR_2 = 0.1646	R_1 = 0.0447, wR_2 = 0.0829	R_1 = 0.0678, wR_2 = 0.1355
Final R indexes [all data]	R_1 = 0.0515, wR_2 = 0.0765	R_1 = 0.0758, wR_2 = 0.1680	R_1 = 0.0701, wR_2 = 0.0903	R_1 = 0.1074, wR_2 = 0.1575
Largest diff. peak/hole / e Å^{-3}	1.38/-2.35	2.69/-2.14	1.65/-1.06	1.79/-1.60

Table S5: Summary of key single crystal XRD refinement parameters for (R-3AP)$AgBiX_{12}$

Identification code	$(R\text{-}3AP)_4AgBiBr_{12}$	$(R\text{-}3AP)_4AgBiCl_\alpha Br_{12-\alpha}$	$(R\text{-}3AP)_4AgBiBr_4I_{12}$	$(S\text{-}3AP)_4AgBiBr_{12}$	$(3AP)_4AgBiBr_{12}$
Empirical formula	$C_{16}H_{48}AgBiBr_{12}N_8$	$C_{16}H_{48}AgBiBr_{12}N_8Cl$	$C_{16}H_{48}AgBiBr_4I_8N_8$	$C_{16}H_{48}AgBiBr_{12}N_8$	$C_{16}H_{48}AgBiBr_{12}N_8$
Formula weight	1628.39	1663.84	2004.31	1628.39	1628.39
Temperature/K	100(5)	100(5)	100(5)	100(5)	100(5)
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	$P1$	$P1$	$P2_1$	$P1$	$P\bar{1}$
a/Å	8.9959(4)	8.9634(5)	9.7952(4)	9.0025(10)	9.1349(4)
b/Å	9.3753(3)	9.2927(4)	10.3654(4)	9.3800(9)	9.2332(4)
c/Å	12.1528(5)	12.0715(7)	21.6851(6)	12.1558(14)	12.2348(5)
α/°	96.252(2)	96.259(2)	90	96.258(4)	96.096(2)
β/°	104.273(2)	104.335(2)	90.0580(10)	104.285(4)	104.644(2)
γ/°	91.349(2)	91.315(2)	90	91.315(3)	92.070(2)
Volume/Å^3	986.06(7)	967.07(9)	2201.71(14)	987.49(19)	990.64(7)
Z	1	1	2	1	1
ρ_{calc}g/cm^3	2.742	2.857	3.023	2.738	2.730
μ/mm^{-1}	17.132	17.538	13.696	17.107	17.053
F(000)	750.0	767.0	1788.0	750.0	750.0
Crystal size/mm^3	0.136 × 0.10 × 0.069	0.277 × 0.156 × 0.126	0.226 × 0.173 × 0.117	0.387 × 0.286 × 0.28	0.20 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.908 to 52.776	5.304 to 49.502	3.93 to 52.814	5.26 to 49.462	5.956 to 52.784
Index ranges	$-11 \le h \le 11$, $-11 \le k \le 11$, $-15 \le l \le 15$	$-10 \le h \le 10$, $-10 \le k \le 10$, $-14 \le l \le 14$	$-12 \le h \le 12$, $-12 \le k \le 12$, $-27 \le l \le 27$	$-10 \le h \le 10$, $-11 \le k \le 11$, $-14 \le l \le 14$	$-11 \le h \le 11$, $-11 \le k \le 11$, $-15 \le l \le 15$
Reflections collected	42237	33068	21587	29864	29936
Independent reflections	7978 [R_{int} = 0.0554, R_{sigma} = 0.0442]	6459 [R_{int} = 0.0651, R_{sigma} = 0.0505]	8720 [R_{int} = 0.0556, R_{sigma} = 0.0777]	6506 [R_{int} = 0.0701, R_{sigma} = 0.0615]	4050 [R_{int} = 0.0604, R_{sigma} = 0.0325]
Data/restraints/parameters	7978/3/347	6459/159/331	8720/157/348	6506/48/348	4050/104/178
Goodness-of-fit on F^2	0.948	1.070	1.033	1.017	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.0399	R_1 = 0.0390, wR_2 = 0.1014	R_1 = 0.0345, wR_2 = 0.0761	R_1 = 0.0352, wR_2 = 0.0867	R_1 = 0.0455, wR_2 = 0.1172
Final R indexes [all data]	R_1 = 0.0239, wR_2 = 0.0405	R_1 = 0.0419, wR_2 = 0.1030	R_1 = 0.0354, wR_2 = 0.0767	R_1 = 0.0376, wR_2 = 0.0879	R_1 = 0.0550, wR_2 = 0.1229
Largest diff. peak/hole / e Å^{-3}	0.99/-0.81	3.68/-1.46	1.60/-1.82	2.32/-2.23	2.15/-1.76

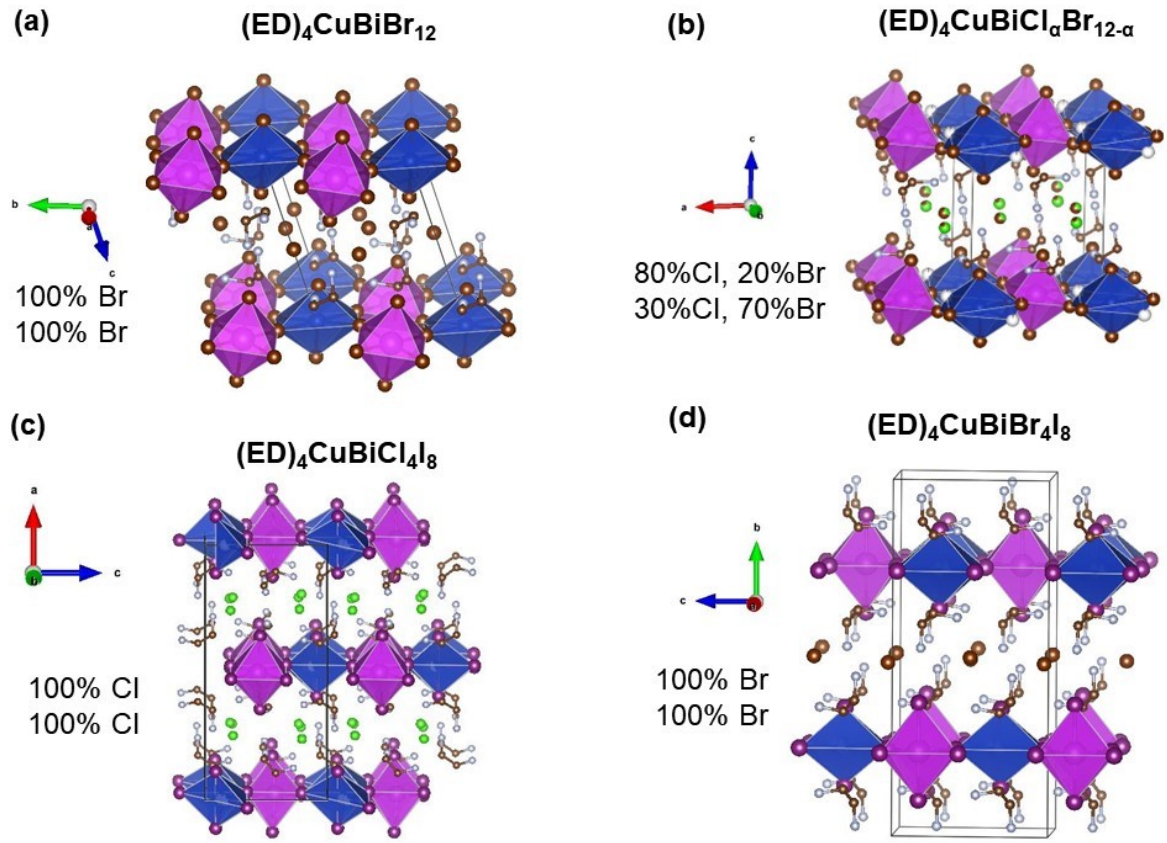

Figure S1: Schematic diagrams of the family of $(ED)_4CuBiX_{12}$.The interlayer halide site occupancy factors are as indicated.

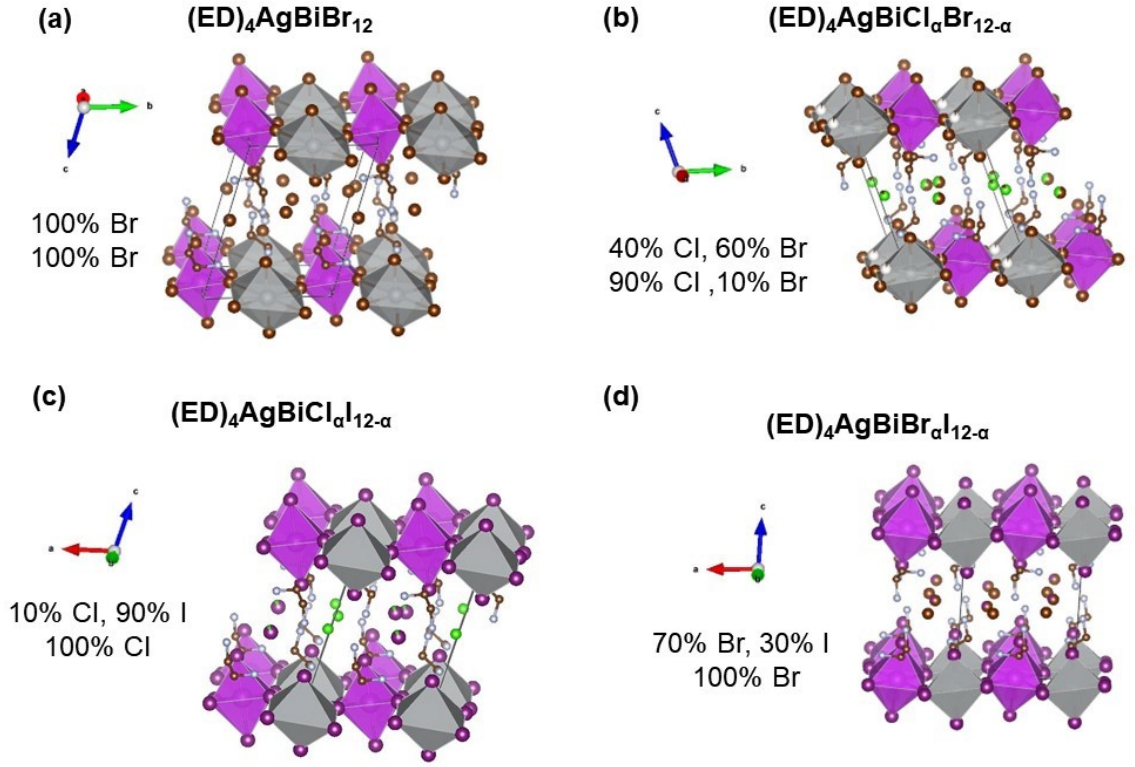

Figure S2: Schematic diagrams of the family of $(ED)_4AgBiX_{12}$.The interlayer halide site occupancy factors are as indicated.

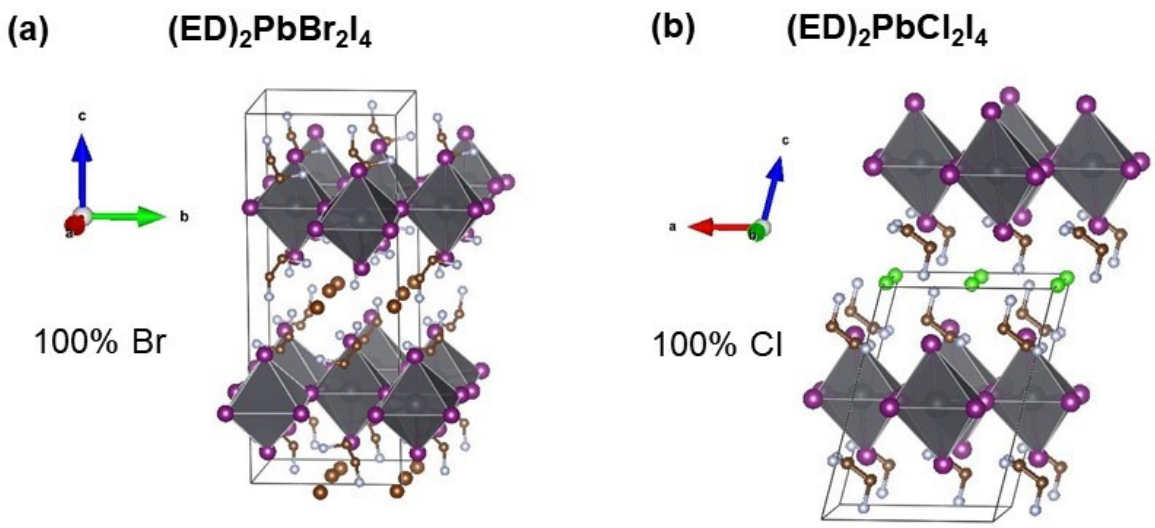

Figure S3: Schematic diagrams of the family of $(ED)_2PbX_6$.The interlayer halide site occupancy factors are as indicated.

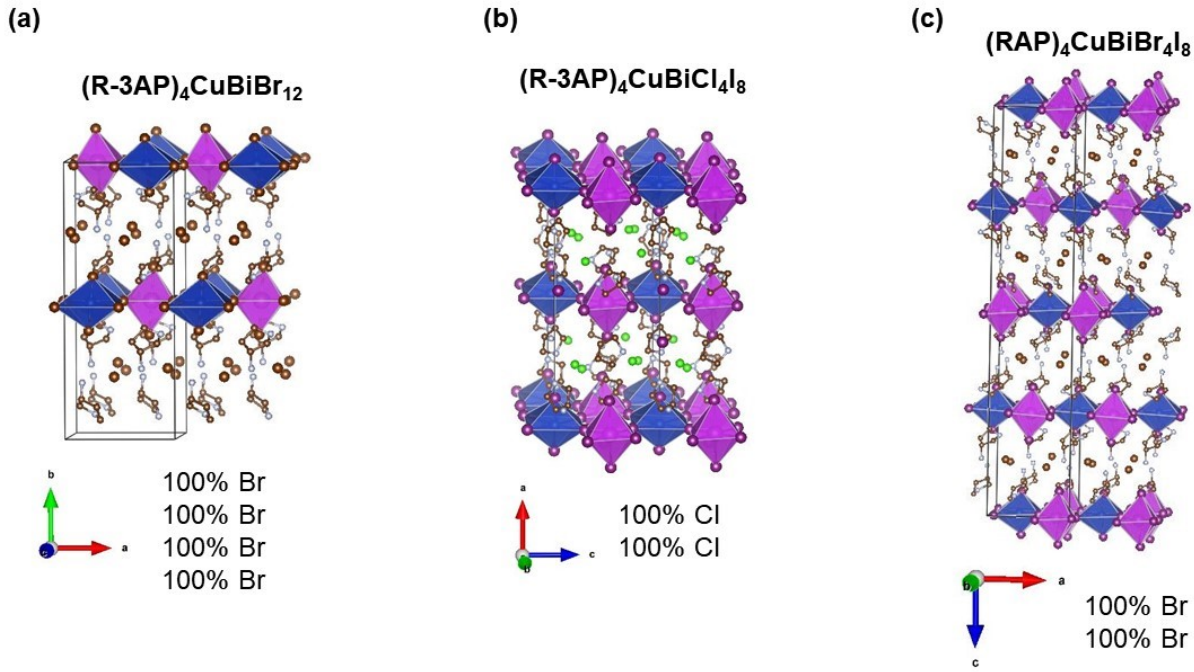

Figure S4: Schematic diagrams of the family of (R-3AP)4CuBiX12. The interlayer halide site occupancy factors are as indicated.

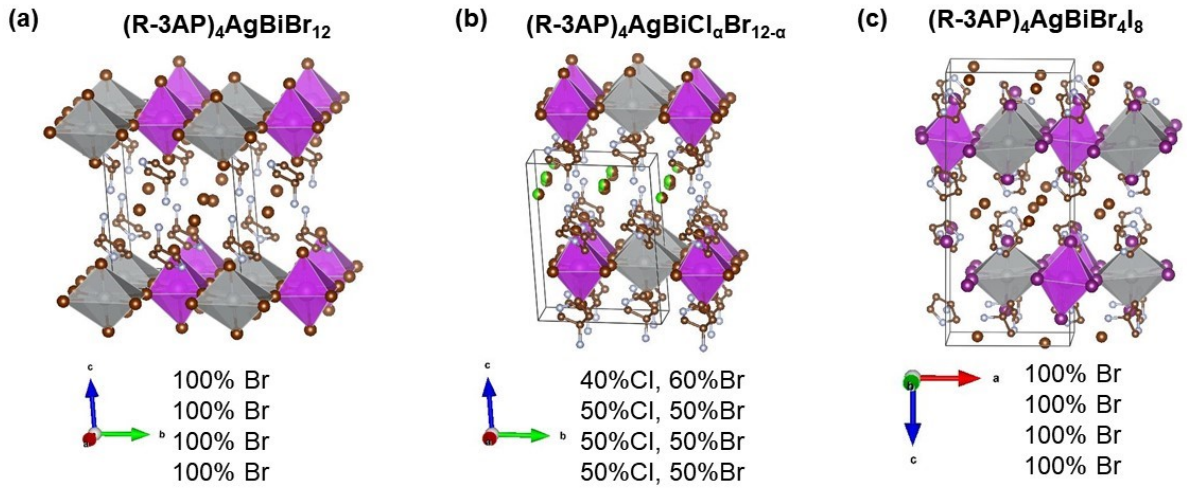

Figure S5: Schematic diagrams of the family of $(R\text{-}3AP)_4AgBiX_{12}$. The interlayer halide site occupancy factors are as indicated.

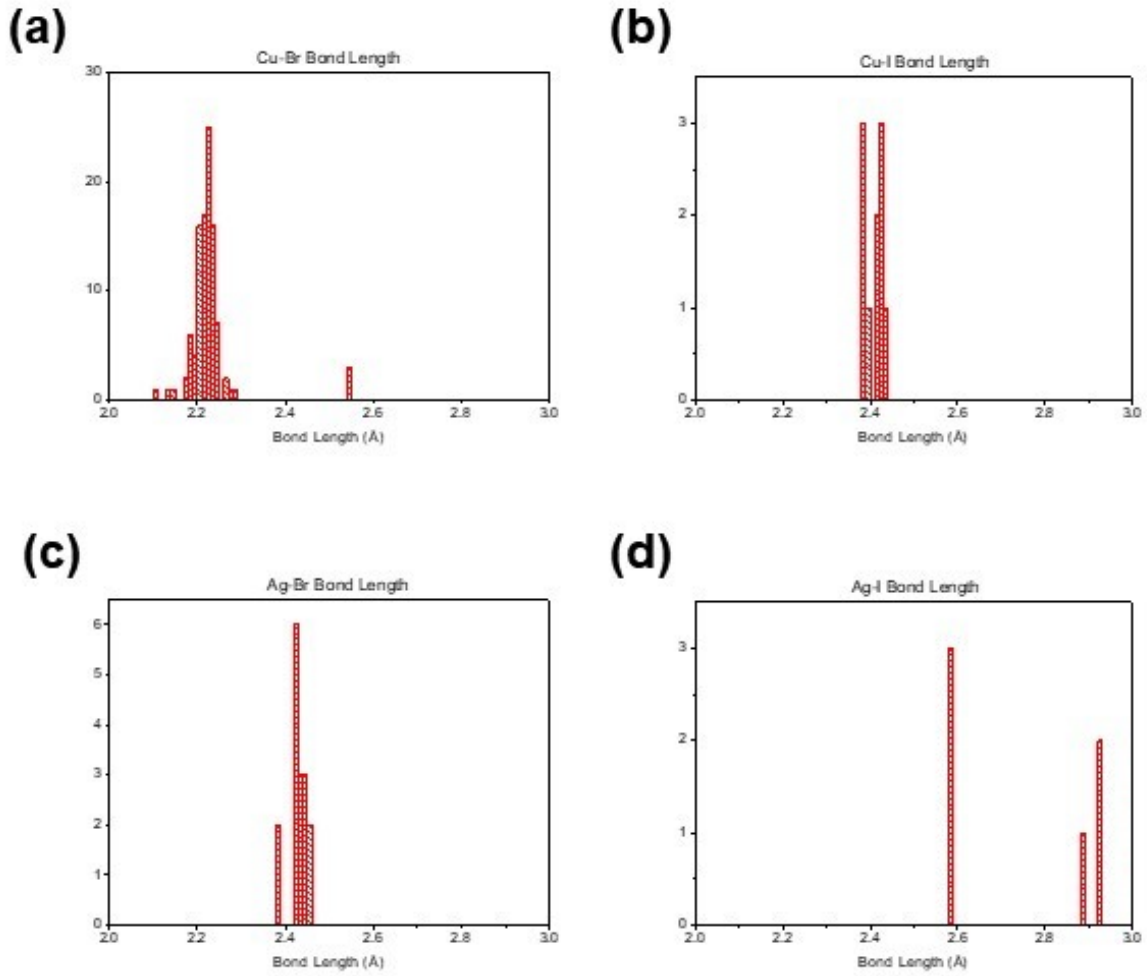

Figure S6: A histogram of the reported bond lengths of (a) Cu-Br, (b) Cu-I, (c) Ag-Br and (d) Ag-I as extracted from the CCDC database.

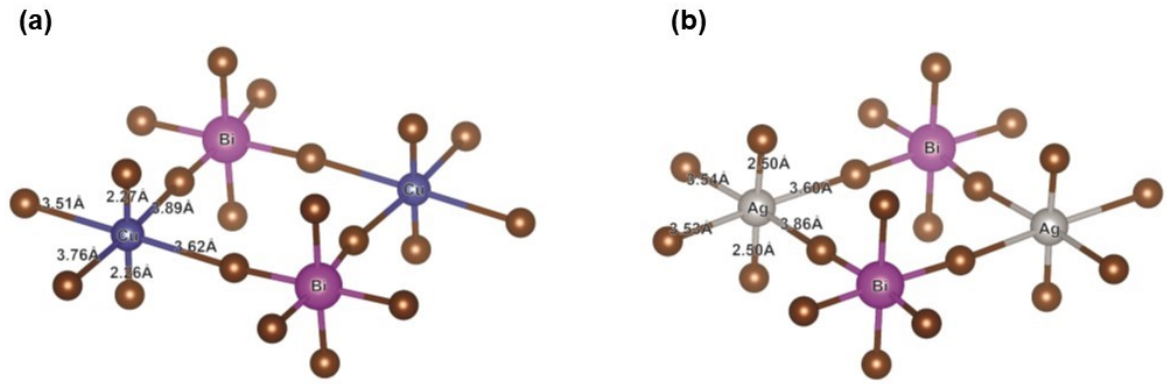

Figure S7: Bond lengths of the axial and equatorial bonds of CuBr and AgBr octahedra. It can be seen clearly that the equatorial bond lengths are all significantly longer than the axial bond lengths and also much larger than those found in other systems that are reported in the CCDC database.

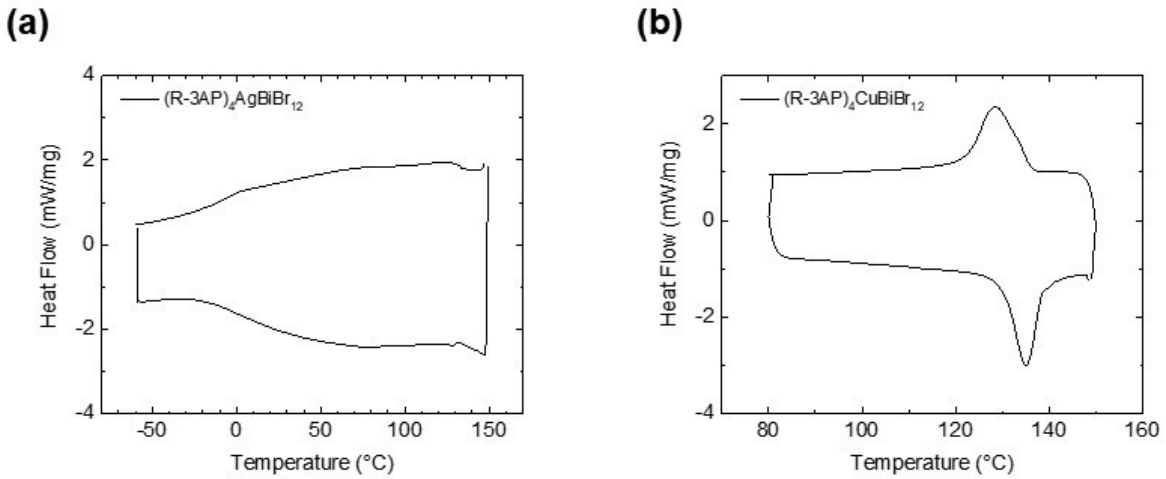

Figure S8: Differential Scanning Calorimetry (DSC) results of (a) $(R\text{-}3AP)_4AgBiBr_{12}$ and (b) $(R\text{-}3AP)_4CuBiBr_{12}$.A clear phase transition can be seen in $(R\text{-}3AP)_4CuBiBr_{12}$ at around 138 °C indicating that a ferroelectric to paraelectric phase transition has taken place.

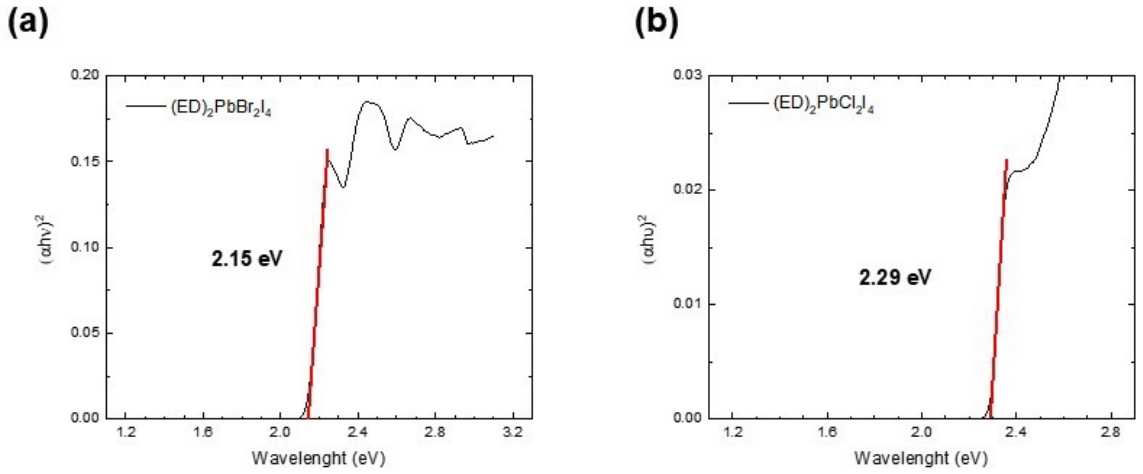

Figure S9: Tauc plot of (a) $(ED)_2PbBr_2I_4$ and (b) $(ED)_2PbCl_2I_4$.

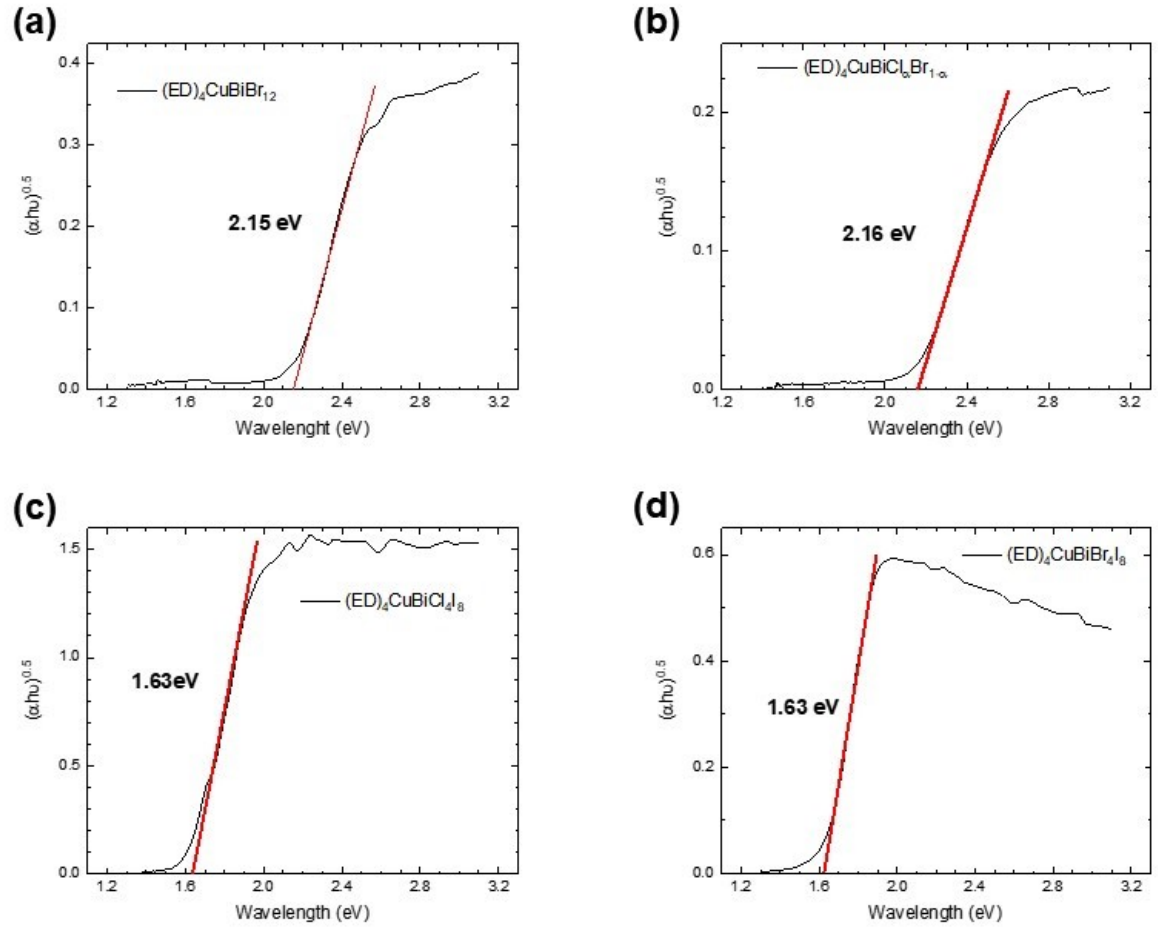

Figure S10: Tauc plot of the $(ED)_4CuBiX_{12}$ family.

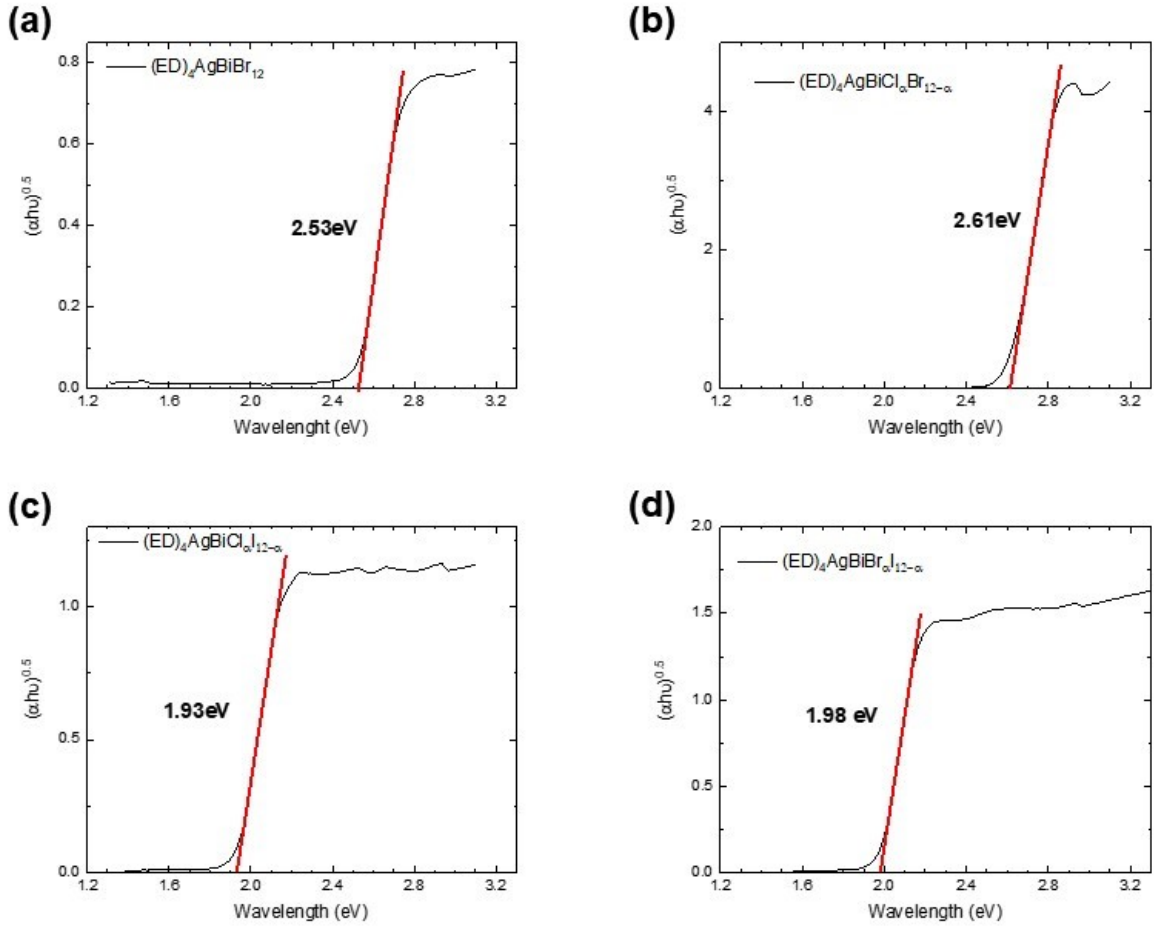

Figure S11: Tauc plot of the $(ED)_4AgBiX_{12}$ family.

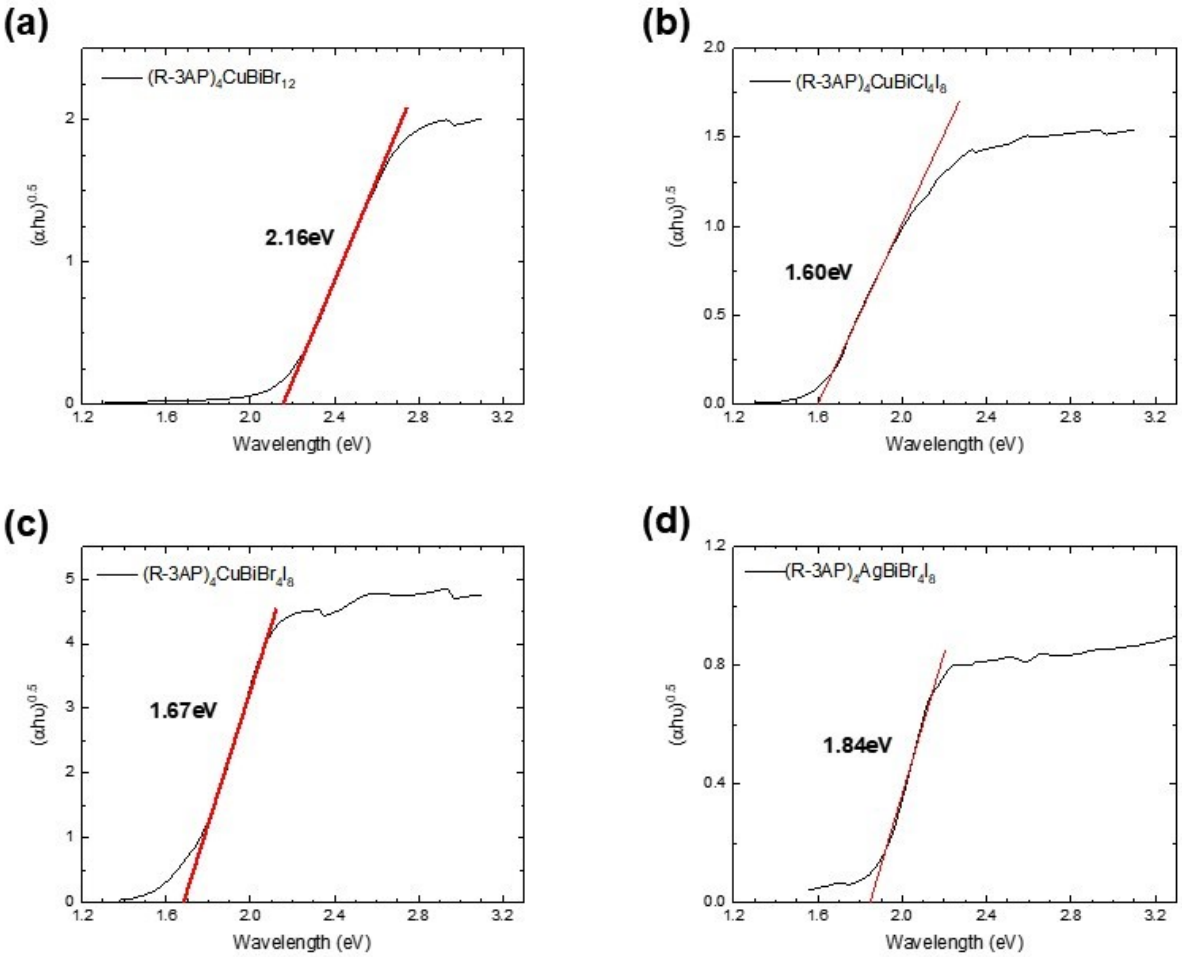

Figure S12: Tauc plot of the $(R\text{-}3AP)_4CuBiX_{12}$ family and $(R\text{-}3AP)_4AgBiBr_4I_6$.