Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Cation Substitution Effects on the Structural, Electronic and Sun-Light Absorption Features of All-Inorganic Halide Perovskites

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SUPPLEMENTARY MATERIAL

1. ADDITIONAL ELECTRONIC STRUCTURE GRAPHS

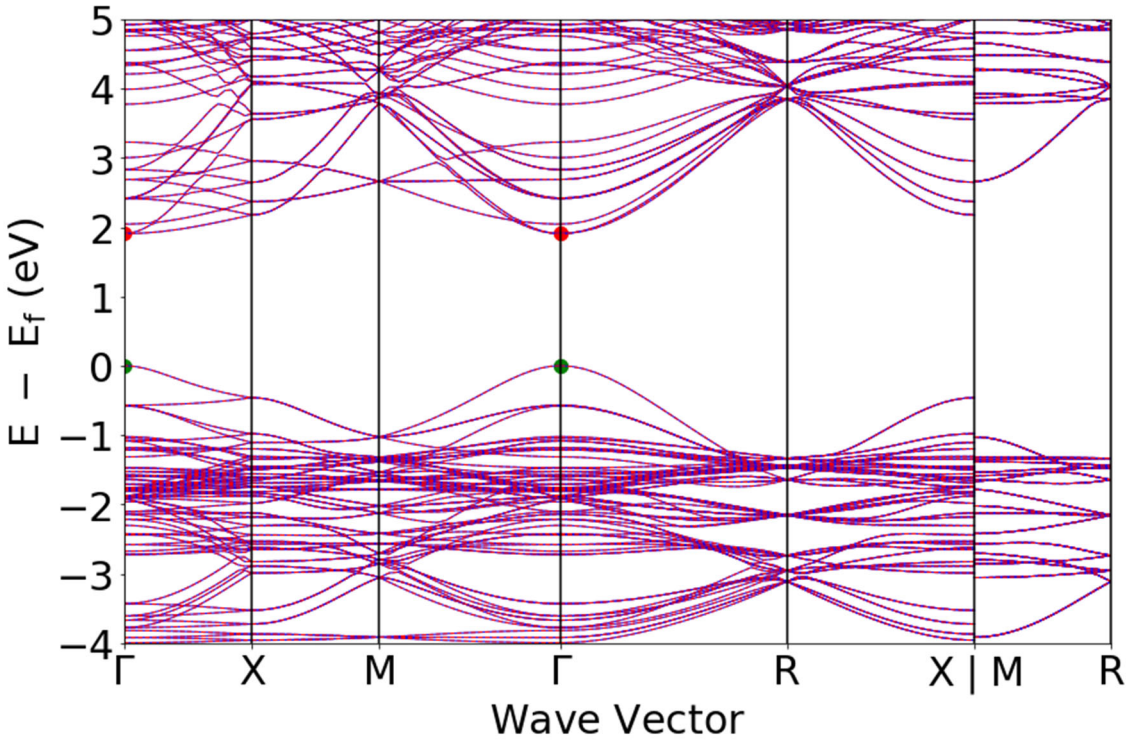

FIGURE S1.1 Band structure of states of $CsPbI_2Br$ with PBE+U (U values of 5.6 eV for *p*-electrons of Pb).

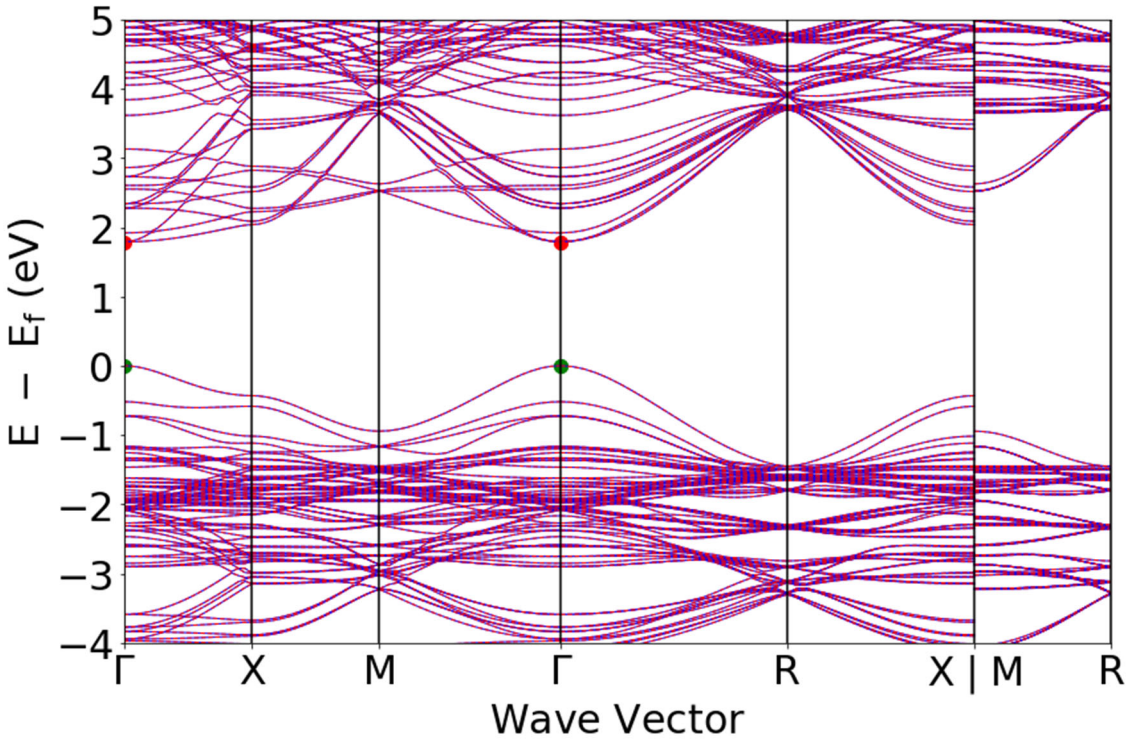

FIGURE S1.2 Band structure of $CsPb_{0.875}Sn_{0.125}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

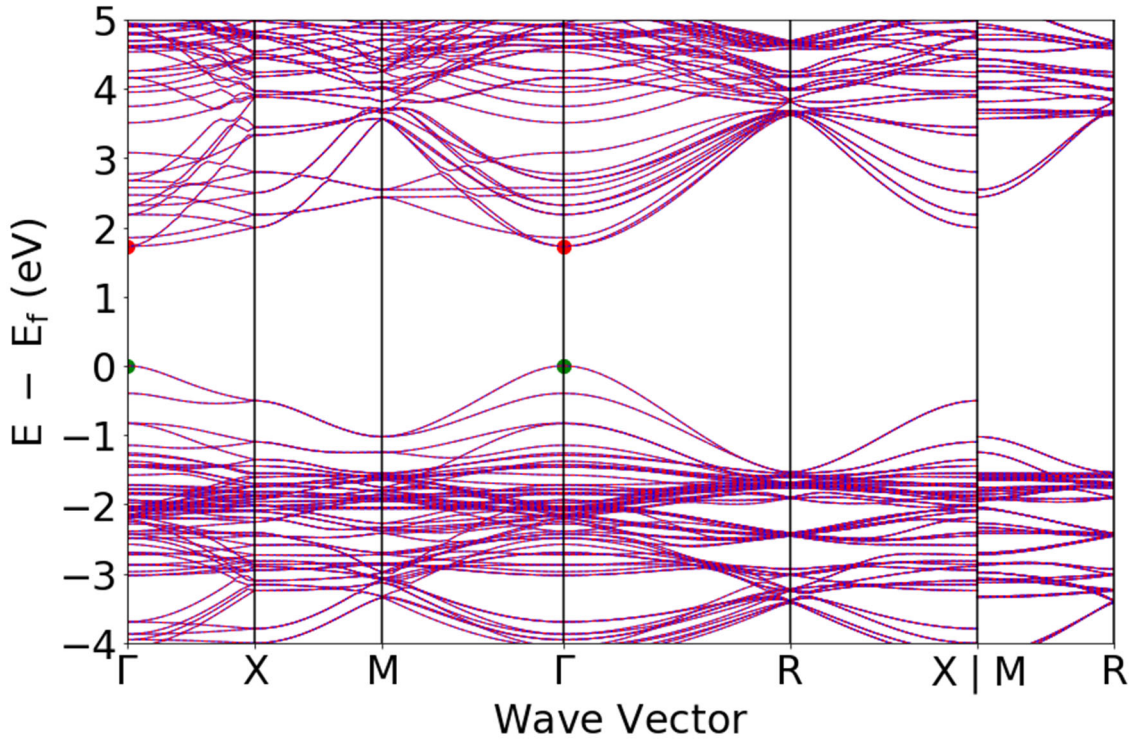

FIGURE S1.3 Band structure of $CsPb_{0.75}Sn_{0.25}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

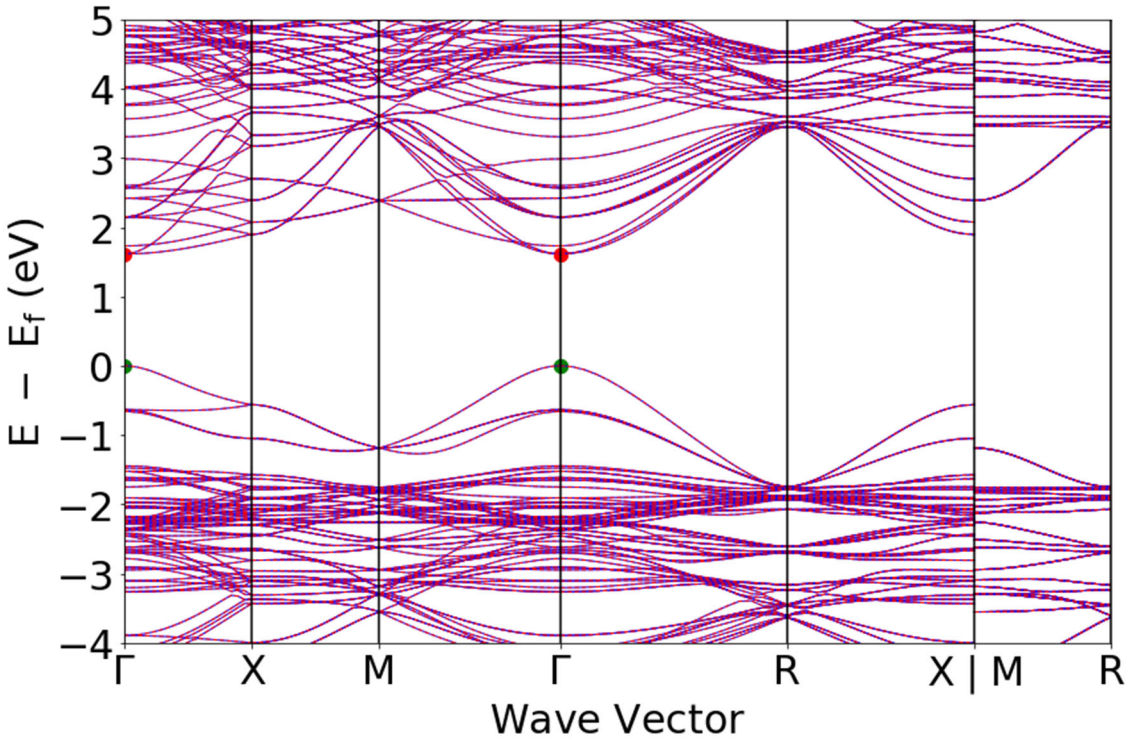

FIGURE S1.4 Band structure of $CsPb_{0.5}Sn_{0.5}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

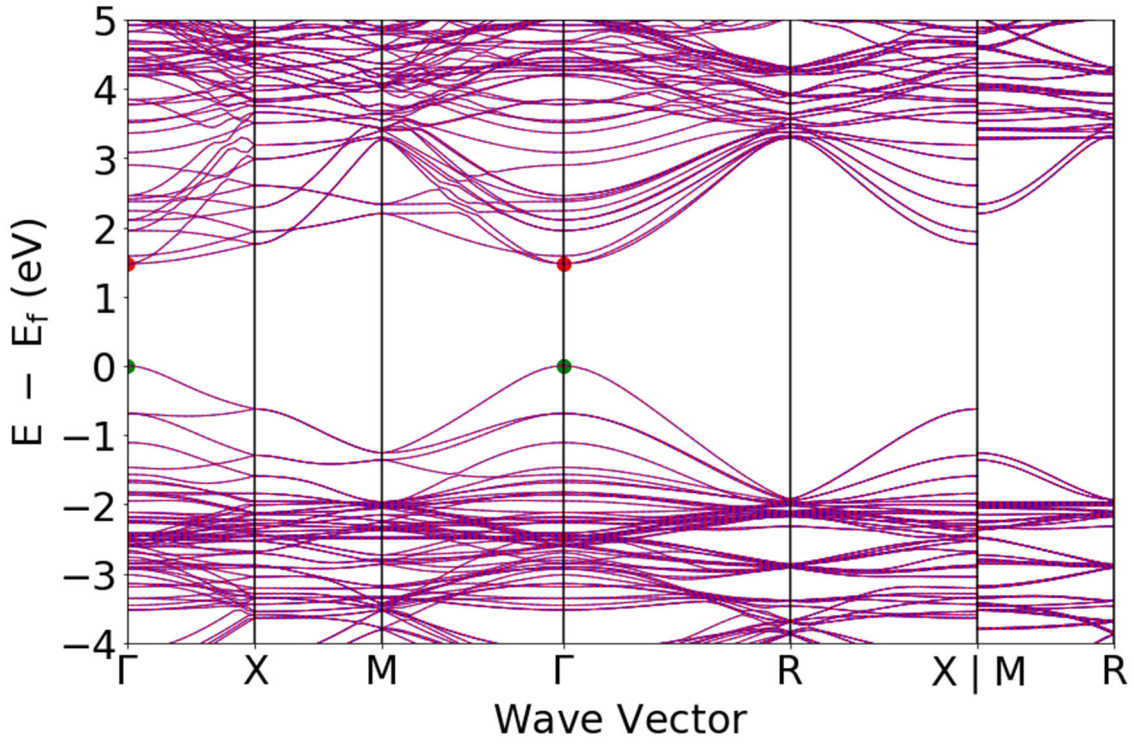

FIGURE S1.5 Band structure of $CsPb_{0.25}Sn_{0.75}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

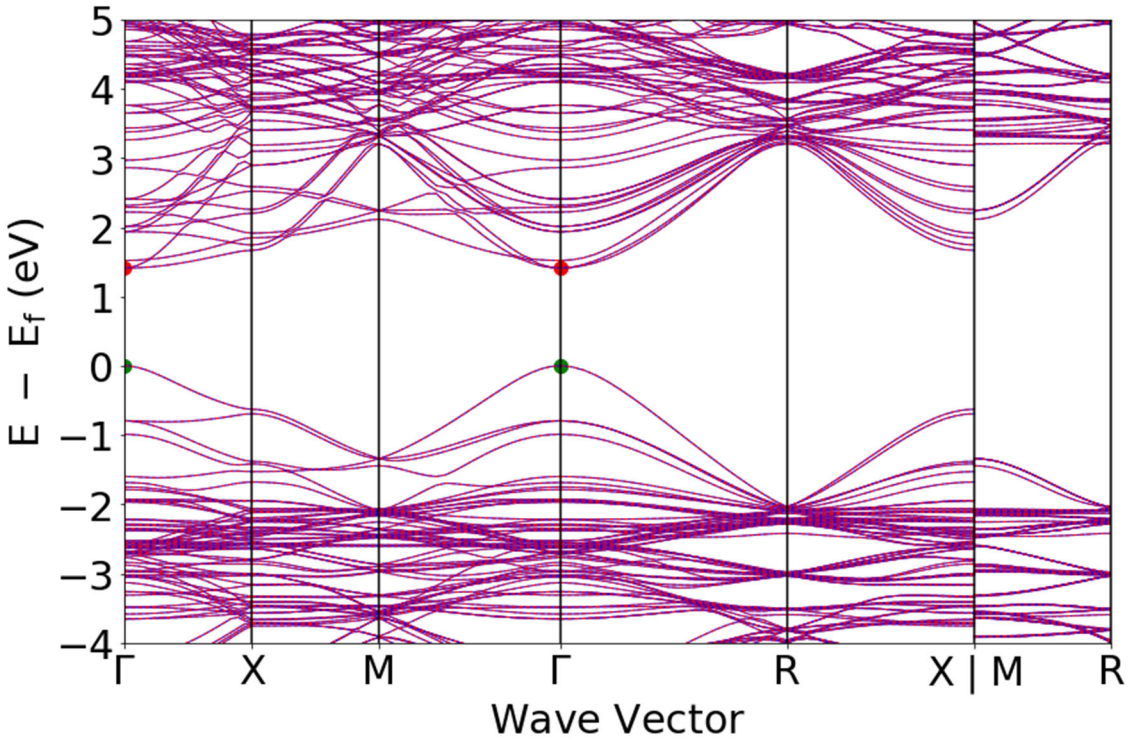

FIGURE S1.6 Band structure of $CsPb_{0.125}Sn_{0.875}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

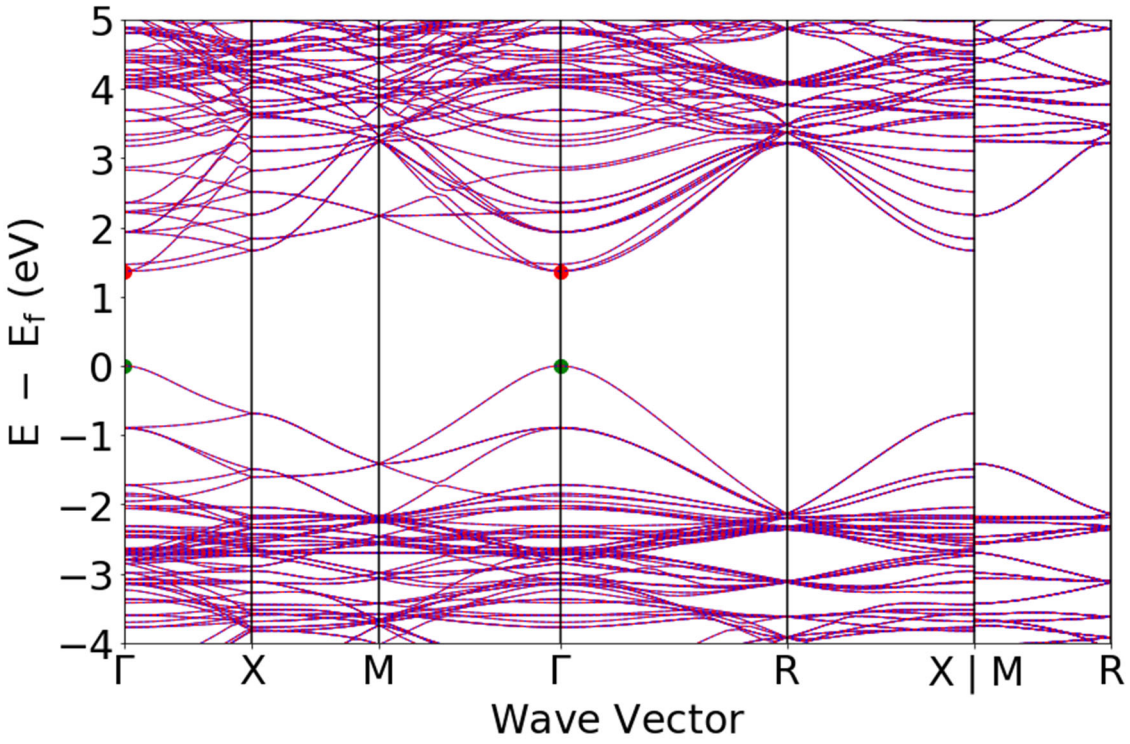

FIGURE S1.7 Band structure of $CsSnI_2Br$ with PBE+U (U values of 11 eV for *p*-electrons of Sn).

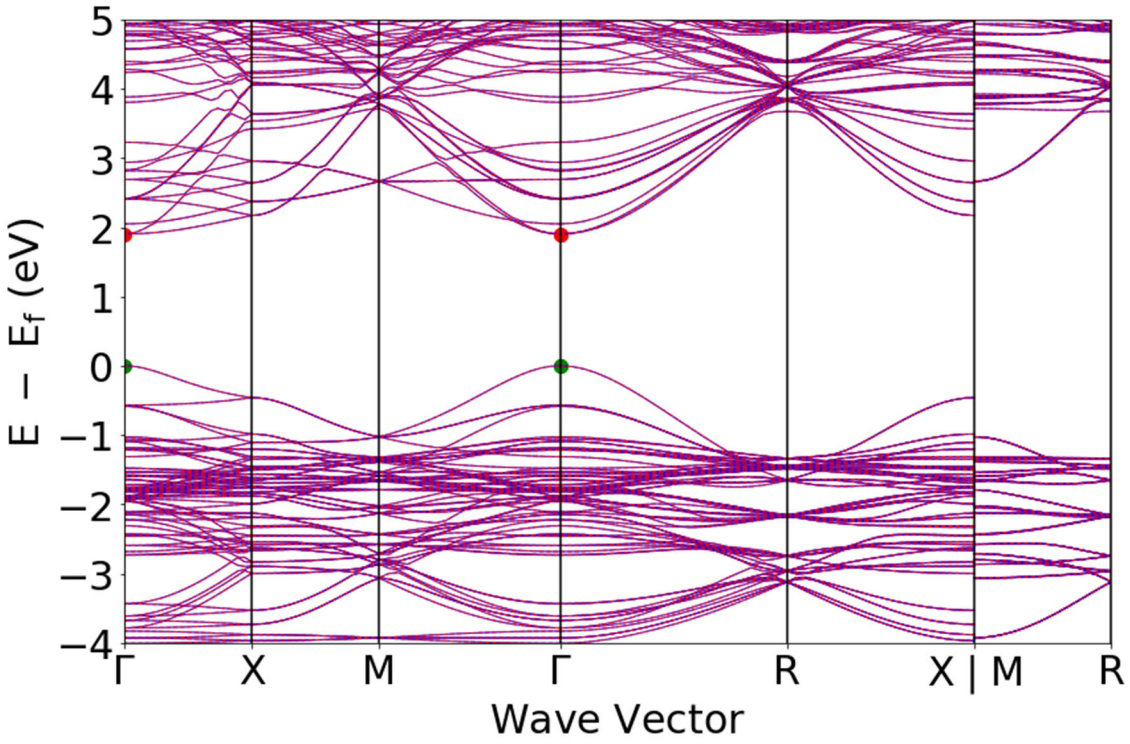

FIGURE S1.8 Band structure of $Rb_{0.125}Cs_{0.875}PbI_2Br$ with PBE+U (U values of 5.6 eV for *p*-electrons of Pb).

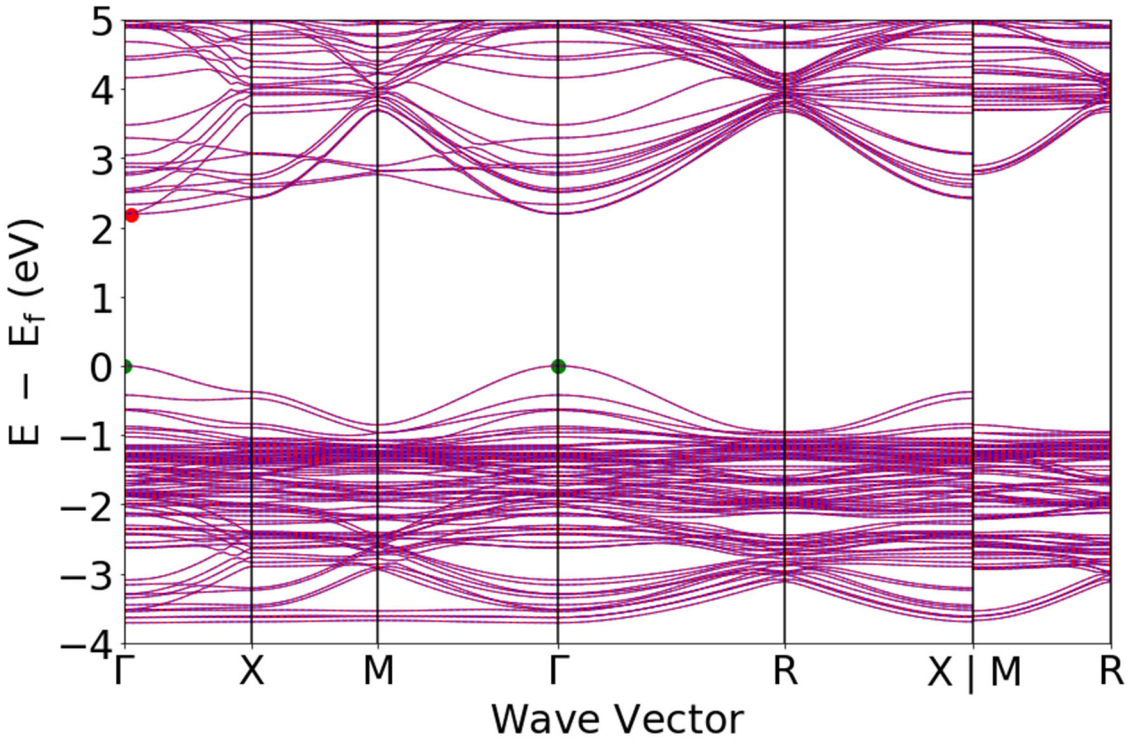

FIGURE S1.9 Band structure of $Rb_{0.125}Cs_{0.875}Pb_{0.875}Sn_{0.125}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

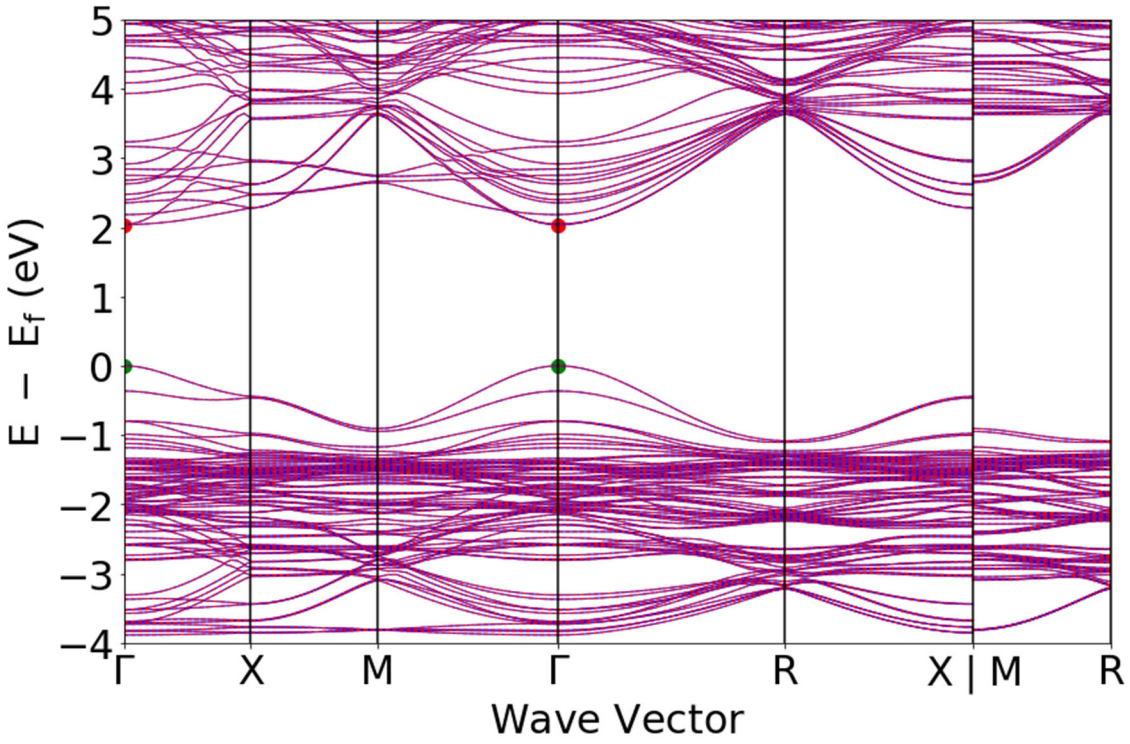

FIGURE S1.10 Band structure of $Rb_{0.125}Cs_{0.875}Pb_{0.75}Sn_{0.25}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

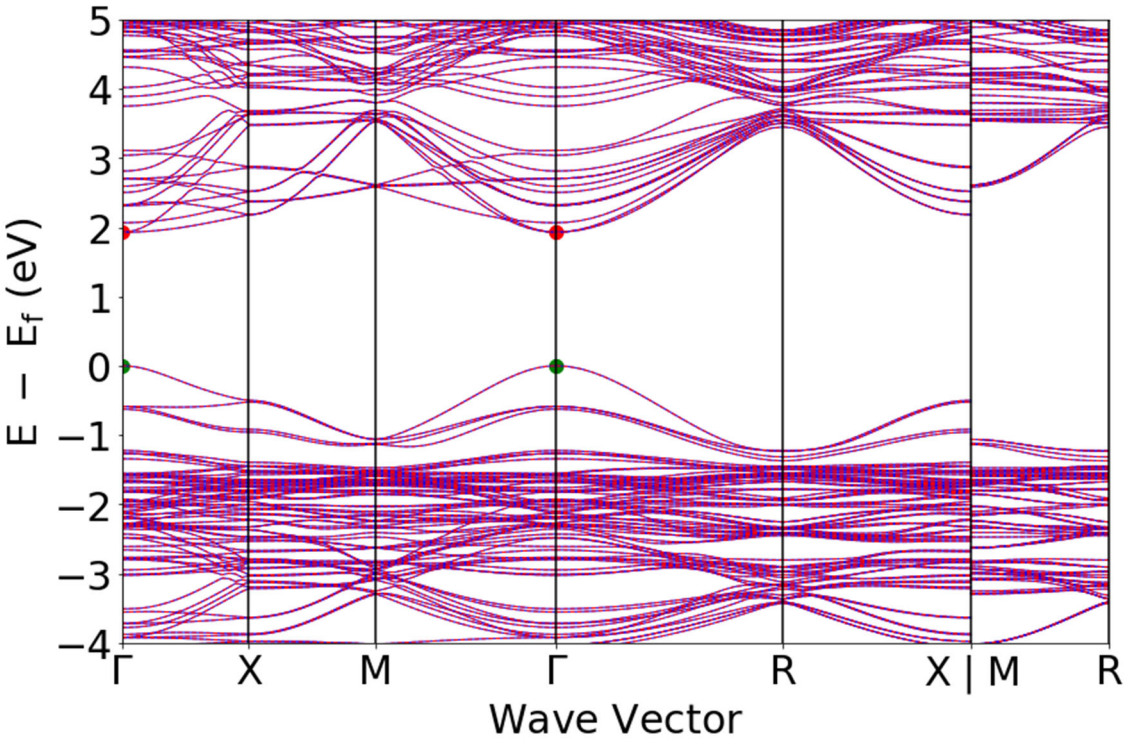

FIGURE S1.11 Band structure of $Rb_{0.125}Cs_{0.875}Pb_{0.5}Sn_{0.5}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

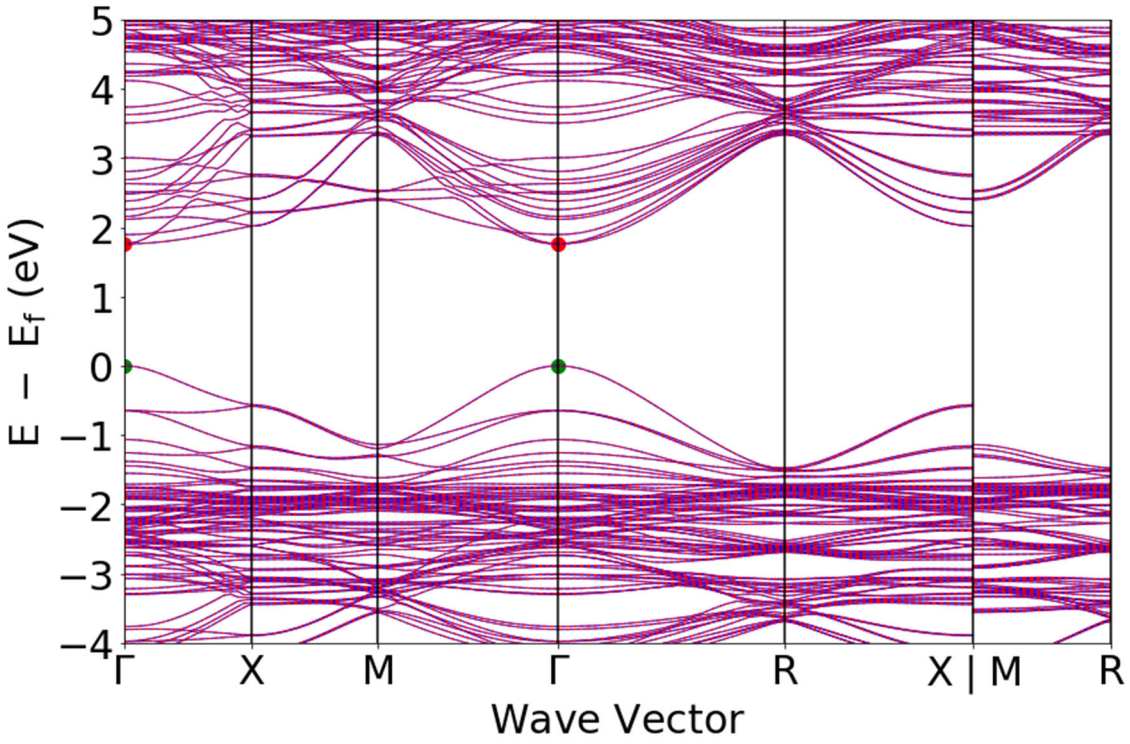

FIGURE S1.12 Band structure of $Rb_{0.125}Cs_{0.875}Pb_{0.25}Sn_{0.75}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

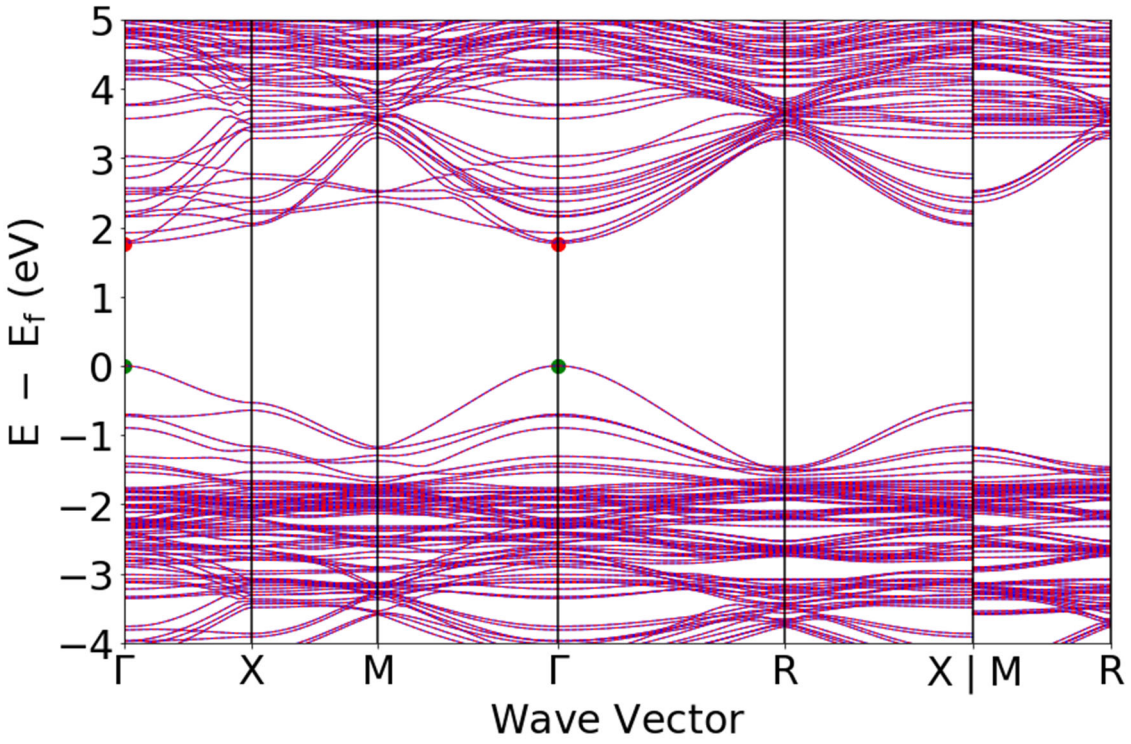

FIGURE S1.13 Band structure of $Rb_{0.125}Cs_{0.875}Pb_{0.125}Sn_{0.875}I_2Br$ with PBE+U (U values of 5.6 and 11 eV for *p*-electrons of Pb and Sn respectively).

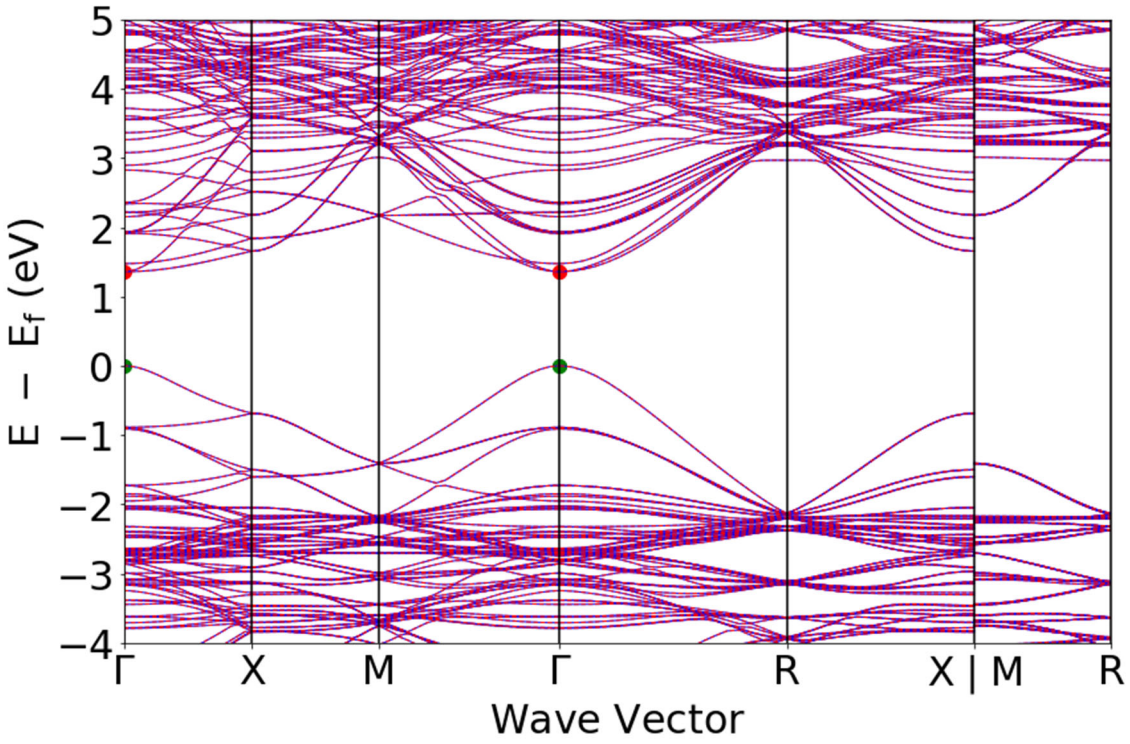

FIGURE S1.14 Band structure of $Rb_{0.125}Cs_{0.875}SnI_2Br$ with PBE+U (U values of 11 eV for *p*-electrons of Sn).

2. REPORTED DATA

		b concentration of Sn						
		0.0	0.125	0.25	0.5	0.75	0.875	1.0
Lattice constant (Å)	w/o Rb	6.26	6.24	6.23	6.20	6.17	6.16	6.14
	with Rb	6.26	6.21	6.20	6.18	6.16	6.15	6.15
Shape ratio	w/o Rb	0.94	0.94	0.94	0.93	0.93	0.93	0.93
	with Rb	0.93	0.92	0.92	0.92	0.92	0.92	0.93
Pb-I (Å)	w/o Rb	3.13	3.12	3.12	3.13	3.12	3.11	
	with Rb	3.13	3.16	3.16	3.16	3.15	3.16	
Pb-Br (Å)	w/o Rb	2.93	2.93	2.93	2.93	2.92	2.91	
	with Rb	2.92	2.98	2.96	2.97	2.95	2.97	
Pb-X (Å)	w/o Rb	3.06	3.06	3.06	3.06	3.05	3.04	
	with Rb	3.06	3.10	3.09	3.09	3.08	3.09	
Sn-I (Å)	w/o Rb		3.09	3.08	3.07	3.08	3.08	3.07
	with Rb		3.12	3.11	3.10	3.10	3.11	3.07
Sn-Br (Å)	w/o Rb		2.89	2.88	2.86	2.87	2.87	2.87
	with Rb		2.93	2.91	2.90	2.90	2.91	2.86
Sn-X (Å)	w/o Rb		3.02	3.01	3.00	3.01	3.01	3.00
	with Rb		3.05	3.04	3.03	3.03	3.04	3.00
B-X (Å)	w/o Rb	3.06	3.05	3.05	3.03	3.02	3.01	3.00
	with Rb	3.06	3.10	3.08	3.06	3.05	3.05	3.00
Cs-I (Å)	w/o Rb	4.28	4.27	4.26	4.24	4.22	4.21	4.20
	with Rb	4.28	4.32	4.29	4.27	4.25	4.27	4.20
Rb-I (Å)	-	4.28	3.81	3.85	3.86	3.86	3.84	4.18
Cs-Br (Å)	w/o Rb	4.42	4.41	4.40	4.38	4.37	4.36	4.34
	with Rb	4.43	4.34	4.31	4.30	4.29	4.29	4.35
Rb-Br (Å)	-	4.43	5.20	5.14	5.11	5.04	5.05	4.35
Cs-X (Å)	w/o Rb	4.33	4.32	4.31	4.29	4.27	4.26	4.25
	with Rb	4.33	4.33	4.30	4.28	4.26	4.28	4.25
Rb-X (Å)	-	4.33	4.28	4.28	4.27	4.25	4.24	4.24
I-Pb-I (º) straight angles	w/o Rb	180.00	180.00	180.00	180.00	180.00	180.00	
	with Rb	179.92	177.16	178.34	178.59	177.95	176.50	
I-Pb-I (º) right angles	w/o Rb	90.00	90.00	90.00	90.00	90.00	90.00	
	with Rb	90.00	89.99	89.99	90.00	89.99	89.96	
Br-Pb-Br (º)	w/o Rb	180.00	180.00	180.00	180.00	180.00	180.00	
	with Rb	179.99	178.76	179.44	179.51	179.47	178.54	
Br-Pb-I (º)	w/o Rb	90.00	90.00	90.00	90.00	90.00	90.00	
	with Rb	90.00	89.99	90.00	90.00	90.00	90.01	
I-Sn-I (º) straight angles	w/o Rb		180.00	180.00	180.00	180.00	180.00	180.00
	with Rb		178.38	178.93	178.74	178.76	178.07	179.70
I-Sn-I (º) right angles	w/o Rb		90.00	90.00	90.00	90.00	90.00	90.00
	with Rb		89.99	90.00	90.00	90.00	89.99	90.00
Br-Sn-Br (º)	w/o Rb		180.00	180.00	180.00	180.00	180.00	180.00
	with Rb		179.96	179.72	179.27	179.49	176.37	179.96

Br-Sn-I (º)	w/o Rb		90.00	90.00	90.00	90.00	90.00	90.00
	with Rb		90.00	90.00	90.00	90.00	89.98	90.00
I-B-I (º) straight angles	w/o Rb	180.00	180.00	180.00	180.00	180.00	180.00	180.00
	with Rb	179.92	177.31	178.49	178.66	178.56	177.88	179.70
I-B-I (º) right angles	w/o Rb	90.00	90.00	90.00	90.00	90.00	90.00	90.00
	with Rb	90.00	89.99	90.00	90.00	90.00	89.99	90.00
Br-B-Br (º)	w/o Rb	180.00	180.00	180.00	180.00	180.00	180.00	180.00
	with Rb	179.99	178.91	179.51	179.39	179.49	176.64	179.96
Br-B-I (º)	w/o Rb	90.00	90.00	90.00	90.00	90.00	90.00	90.00
	with Rb	90.00	89.99	90.00	90.00	90.00	89.99	90.00
All straight angles (º)	w/o Rb	180.00	180.00	180.00	180.00	180.00	180.00	180.00
	with Rb	179.94	177.85	178.83	178.91	178.87	177.46	179.79
All right angles (º)	w/o Rb	90.00	90.00	90.00	90.00	90.00	90.00	90.00
	with Rb	90.00	89.99	90.00	90.00	90.00	89.99	90.00
Goldschmidt's parameter	w/o Rb	0.855	0.858	0.862	0.870	0.878	0.883	0.887
	with Rb	0.850	0.854	0.858	0.866	0.874	0.878	0.882
ΔH_f (eV/atom)	w/o Rb	-1.135	-1.126	-1.119	-1.104	-1.089	-1.082	-1.075
	with Rb	-1.127	-1.134	-1.124	-1.107	-1.090	-1.083	-1.068
ΔH_d (meV/atom)	w/o Rb	6.12	1.64	-3.03	-13.25	-23.59	-28.85	-34.32
	with Rb	11.69	-7.71	-10.24	-18.22	-26.33	-32.12	-29.30
Bandgaps (eV)	w/o Rb	1.906	1.789	1.725	1.615	1.473	1.411	1.364
	12.5% Rb	1.902	2.192	2.033	1.927	1.756	1.770	1.358
	6.25% Rb	1.903	1.786	1.723	1.617	1.468	1.406	1.361