

# **Supporting Information**

## **Optoelectronic and Energy Level Exploration of Bismuth and Antimony-Based Materials for Lead-Free Solar Cells**

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## Supporting Tables

**Table S1.** Categorized class of crystal structures evaluated from XRD measurements. (A) without contamination, (B) including a little contamination, (C) including dominant contamination, and (U) crystal structures are unable to be resolved due to the lack of reference or amorphous nature.

Crystal structure	Precursor	Class	reference <sup>a</sup>	Precursor	Class	reference <sup>a</sup>
$A_3M_2X_9$	$Cs_3Bi_2I_9$	A	COD: 8103859	$Cs_3Sb_2I_9$	A	COD: 1537132
	$MA_3Bi_2I_9$	A	COD: 4344961	$MA_3Sb_2I_9$	A	COD: 7237225
	$FA_3Bi_2I_9$	A	COD: 7237621	$FA_3Sb_2I_9$	A	Ref. S2
	$Cs_3Bi_2Br_9$	A	COD: 1531067	$Cs_3Sb_2Br_9$	A	COD: 1537138
	$MA_3Bi_2Br_9$	A	Ref. S1	$MA_3Sb_2Br_9$	A	Ref. S3
	$FA_3Bi_2Br_9$	A	COD: 7701111	$FA_3Sb_2Br_9$	A	-
MSX	$BiSI$	B	COD: 1535800	$SbSI$	A	COD: 1535787
	$BiSBr$	A	COD: 1535795	$SbSBr$	U	COD: 1521208
Layered	$Bi_2S_3$	A	COD: 9003473	$Sb_2S_3$	A	COD: 1011154
	$AgBiI_4$	A	Ref. S4	$AgSbI_4$	U	-
DP	$Cs_2AgBiI_6$	C	-	$Cs_2AgSbI_6$	C	-
	$MA_2AgBiI_6$	C	-	$MA_2AgSbI_6$	C	-
	$FA_2AgBiI_6$	C	-	$FA_2AgSbI_6$	C	-
	$Cs_2AgBiBr_6$	A	COD: 4131244	$Cs_2AgSbBr_6$	B	Ref. S6
	$MA_2AgBiBr_6$	A	Ref. S5	$MA_2AgSbBr_6$	C	-
	$FA_2AgBiBr_6$	U	-	$FA_2AgSbBr_6$	C	-
SAP	$CsBiSI_2$	C	-	$CsSbSI_2$	U	-
	$MABiSI_2$	C	-	$MASbSI_2$	B	Ref. S7
	$FABiSI_2$	C	-	$FASbSI_2$	C	-
	$CsBiSBr_2$	C	-	$CsSbSBr_2$	C	-
	$MABiSBr_2$	C	-	$MASbSBr_2$	C	-
	$FABiSBr_2$	C	-	$FASbSBr_2$	C	-

<sup>a</sup> Crystallography Open Database (COD) number or the reference number in the main text.

**Table S2.** Summary of elemental analysis by EDX on the compositions which showed dominant formation of other crystal phase such as  $A_3M_2X_9$  in Figure S1. Note that MA and FA which is composed of C, N, and H cannot be detected.

Precursor	Elemental ratio	Precursor	Elemental ratio
SbSI (240 °C)	Sb : S : I = 1.0 : 0.89 : 0.89	CsBiSI <sub>2</sub>	Cs : Bi : S : I = 0.92 : 1.0 : 0.72 : 2.4
SbSBr(240°C) )	Sb : S : Br = 1.0 : 0.42 : 1.5	MABiSI <sub>2</sub>	Bi : S : I = 1.0 : 0.46 : 2.2
Cs <sub>2</sub> AgBiI <sub>6</sub>	Cs : Ag : Bi : I = 1.6 : 0.97 : 1.0 : 4.8	FABiSI <sub>2</sub>	Bi : S : I = 1.0 : 0.35 : 2.2
MA <sub>2</sub> AgBiI <sub>6</sub>	Ag : Bi : I = 0.90 : 1.0 : 5.1	CsBiSBr <sub>2</sub>	Cs : Bi : S : Br = 0.84 : 1.0 : 0.77 : 2.8
FA <sub>2</sub> AgBiI <sub>6</sub>	Ag : Bi : I = 0.93 : 1.0 : 5.1	MABiSBr <sub>2</sub>	Bi : S : Br = 1.0 : 0.52 : 2.6
Cs <sub>2</sub> AgSbI <sub>6</sub>	Cs : Ag : Sb : I ]= 2.0 : 0.98 : 1.0 : 5.0	FABiSBr <sub>2</sub>	Bi : S : Br = 1.0 : 0.54 : 2.5
MA <sub>2</sub> AgSbI <sub>6</sub>	Ag : Bi : I = 0.94 : 1.0 : 5.3	MASbSI <sub>2</sub>	Sb : S : I = 1.0 : 1.0 : 1.6
FA <sub>2</sub> AgSbI <sub>6</sub>	Ag : Bi : I = 0.98 : 1.0 : 5.4	FASbSI <sub>2</sub>	Sb : S : I = 1.0 : 0.62 : 1.5
MA <sub>2</sub> AgSbBr <sub>6</sub>	Ag : Bi : Br = 0.83 : 1.0 : 6.3	FASbSBr <sub>2</sub>	Sb : S : Br = 1.0 : 0.77 : 2.7
FA <sub>2</sub> AgSbBr <sub>6</sub>	Ag : Bi : Br = 0.74 : 1.0 : 7.1		

**Table S3.** Summary of calculated Goldschmidt tolerance factors ( $T$ ) of DPs and SAPs. The equation is followed;  $T = (r_A + r_X)/(2^{1/2}(r_B + r_X))$  where  $r_A$ ,  $r_B$ , and  $r_X$  are the effective ionic radii of A site, B site, and X site ion, respectively.

Structure	Bi-based	$T$	Sb-based	$T$
DP	Cs <sub>2</sub> AgBiI <sub>6</sub>	0.876	Cs <sub>2</sub> AgSbI <sub>6</sub>	0.914
	MA <sub>2</sub> AgBiI <sub>6</sub>	0.939	MA <sub>2</sub> AgSbI <sub>6</sub>	0.979
	FA <sub>2</sub> AgBiI <sub>6</sub>	1.02	FA <sub>2</sub> AgSbI <sub>6</sub>	1.06
	Cs <sub>2</sub> AgBiBr <sub>6</sub>	0.890	Cs <sub>2</sub> AgSbBr <sub>6</sub>	0.931
	MA <sub>2</sub> AgBiBr <sub>6</sub>	0.958	MA <sub>2</sub> AgSbBr <sub>6</sub>	1.00
	FA <sub>2</sub> AgBiBr <sub>6</sub>	1.04	FA <sub>2</sub> AgSbBr <sub>6</sub>	1.09
SAP	CsBiSI <sub>2</sub>	0.928	CsSbSI <sub>2</sub>	1.02
	MABiSI <sub>2</sub>	0.994	MASbSI <sub>2</sub>	1.08
	FABiSI <sub>2</sub>	1.08	FASbSI <sub>2</sub>	1.18
	CsBiSBr <sub>2</sub>	0.920	CsSbSBr <sub>2</sub>	1.01
	MABiSBr <sub>2</sub>	0.990	MASbSBr <sub>2</sub>	1.09
	FABiSBr <sub>2</sub>	1.08	FASbSBr <sub>2</sub>	1.18

**Table S4.** Summary of VBM, CBM, and bandgap evaluated by PYS, VBM+bandgap, and Tauc plots of photoabsorption spectra of films (direct transition:  $(ahv)^2$ , indirect transition:  $(ahv)^{0.5}$ ), respectively.

Materials	VBM (eV)	CBM (eV)	Bandgap (eV)
MAPbI <sub>3</sub>	-5.45	-3.83	1.62
TiO <sub>2</sub>	-7.40	-4.20	3.20
PTAA	-5.17	-2.16	3.01
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	-5.83	-3.78	2.05
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	-5.93	-3.71	2.16
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	-6.10	-3.9	2.21
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	-6.30	-3.63	2.67
MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	-6.28	-3.55	2.73
FA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	-5.78	-3.07	2.71
BiSI	-6.20	-4.6	1.60
BiSBr	-5.90	-3.95	1.95
Bi <sub>2</sub> S <sub>3</sub>	-5.50	-4.10	1.40
AgBiI <sub>4</sub>	-6.00	-4.20	1.80
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from Cs <sub>2</sub> AgBiI <sub>6</sub> precursor	-5.83	-3.63	2.20
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MA <sub>2</sub> AgBiI <sub>6</sub> precursor	-5.71	-3.51	2.20
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from FA <sub>2</sub> AgBiI <sub>6</sub> precursor	-5.90	-3.67	2.23
Cs <sub>2</sub> AgBiBr <sub>6</sub>	-5.95	-3.41 (-3.65) <sup>a</sup>	2.54 (2.30) <sup>a</sup>
MA <sub>2</sub> AgBiBr <sub>6</sub>	-5.90	-3.21 (-3.29) <sup>a</sup>	2.69 (2.61) <sup>a</sup>
FA <sub>2</sub> AgBiBr <sub>6</sub>	-5.97	-3.04	2.93
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from CsBiSI <sub>2</sub> precursor	-5.71	-4.01	1.70
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MABiSI <sub>2</sub> precursor	-6.14	-4.38	1.76
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from FABiSI <sub>2</sub> precursor	-6.1	-4.36	1.74
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from CsBiSBr <sub>2</sub> precursor	-6.01	-4.10	1.91
MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from MABiSBr <sub>2</sub> precursor	-6.1	-4.31	1.79
FA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from FABiSBr <sub>2</sub> precursor	-5.94	-4.19	1.75
Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	-5.51	-3.32	2.19
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	-5.56	-3.36	2.20
FA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	-5.76	-3.44	2.32
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub>	-5.81	-3.22	2.59
MA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub>	-6.1	-3.47	2.63
FA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub>	-6.03	-3.30	2.73
SbSI	-5.67	-3.52	2.15
SbSI (240 °C)	-5.84	-4.12	1.72
Sb-S-Br (240 °C)	-5.78	-3.69	2.09
Sb <sub>2</sub> S <sub>3</sub>	-5.62	-3.97	1.68
AgSbI <sub>4</sub>	-5.95	-3.75	2.20

Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from Cs <sub>2</sub> AgSbI <sub>6</sub> precursor	-5.41	-3.14	2.27
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from MA <sub>2</sub> AgSbI <sub>6</sub> precursor	-5.45	-3.07	2.38
FA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from FA <sub>2</sub> AgSbI <sub>6</sub> precursor	-5.92	-3.46	2.46
Cs <sub>2</sub> AgSbBr <sub>6</sub>	-5.64	-3.24 (-3.51) <sup>a</sup>	2.40 (2.13) <sup>a</sup>
MA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from MA <sub>2</sub> AgSbBr <sub>6</sub> precursor	-5.66	-2.92	2.74
FA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from FA <sub>2</sub> AgSbBr <sub>6</sub> precursor	-5.80	-2.93	2.87
CsSbSI <sub>2</sub>	-5.54	-3.56	1.98
MASbSI <sub>2</sub>	-5.55	-3.57	1.98
FA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from FASbSI <sub>2</sub> precursor	-5.68	-3.26	2.42
Cs <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from CsSbSBr <sub>2</sub> precursor	-5.82	-3.38	2.44
MA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from MASbSBr <sub>2</sub> precursor	-5.87	-3.43	2.44
FA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from FASbSBr <sub>2</sub> precursor	-5.77	-3.83	1.94

<sup>a</sup> The values in brackets are indirect transition-based bandgap and CBM. Most of the films show no significant difference in bandgap analyzed by direct and indirect transition.

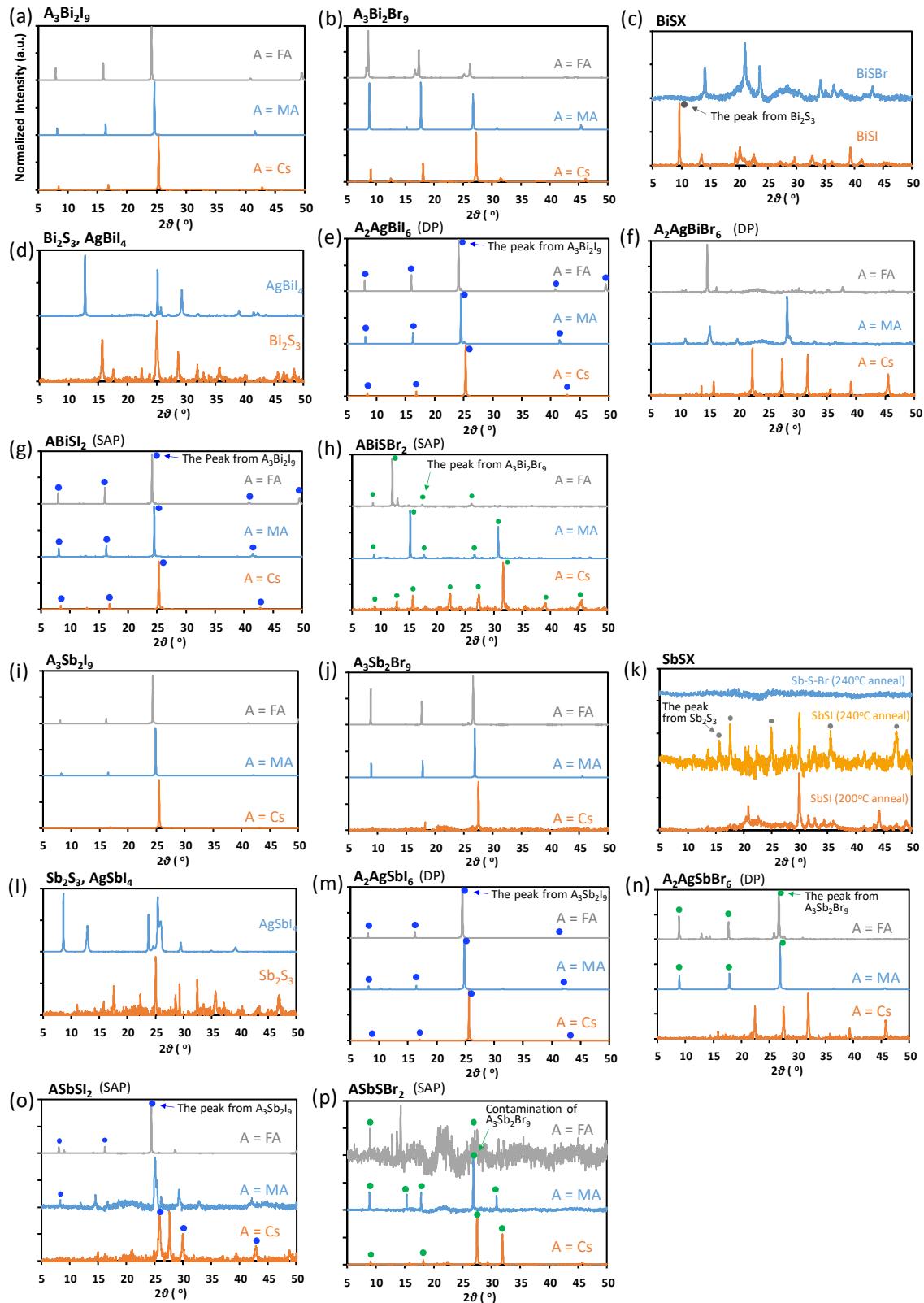
**Table S5.** Summary of solar cell performances.

Materials	HTM: PTAA					HTM: PCPDTBT				
	$J_{SC}$ (mA cm <sup>-2</sup> )	$J_{SC} / J_{SC\_max}^a$	$V_{OC}$ (V)	FF	PCE (%)	$J_{SC}$ (mA cm <sup>-2</sup> )	$J_{SC} / J_{SC\_max}^a$	$V_{OC}$ (V)	FF	PCE (%)
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.082	0.0061	0.29	0.37	8.9×10 <sup>-3</sup>	0.41	0.030	0.48	0.49	0.098
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub>	0.12	0.0097	0.34	0.41	0.016	0.55	0.045	0.38	0.48	0.1
BiSI	0.19	0.0085	0.0024	0.085	4.0×10 <sup>-5</sup>	0.078	0.012	0.032	0.27	6.5×10 <sup>-4</sup>
BiSBr	0	0	0	0	0	0.36	0.037	0.003	0.16	2.0×10 <sup>-4</sup>
Bi <sub>2</sub> S <sub>3</sub>	0	0	0	0	0	0	0	0	0	0
AgBiI <sub>4</sub>	2.4	0.149	0.49	0.55	0.65	2.9	0.18	0.47	0.59	0.78
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from Cs <sub>2</sub> AgBiI <sub>6</sub> precursor	0.073	0.011	0.35	0.42	0.011	0.26	0.056	0.34	0.56	0.05
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MA <sub>2</sub> AgBiI <sub>6</sub> precursor	0.24	0.035	0.48	0.5	0.057	0.48	0.070	0.39	0.65	0.12
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from FA <sub>2</sub> AgBiI <sub>6</sub> precursor	0.028	0.0041	0.13	0.38	1.4×10 <sup>-3</sup>	0.0051	0.0074	0.19	0.35	3.4×10 <sup>-3</sup>
Cs <sub>2</sub> AgBiBr <sub>6</sub>	1.2	0.22	0.95	0.67	0.76	1.1	0.20	0.46	0.59	0.31
Cs <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from CsBiSI <sub>2</sub> precursor	0.078	0.0074	0.032	0.27	6.5×10 <sup>-4</sup>	0.90	0.086	0.23	0.37	0.077
MA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from MABiSI <sub>2</sub> precursor	0.19	0.014	0.036	0.27	1.9×10 <sup>-3</sup>	0.29	0.020	0.012	0.22	7.6×10 <sup>-4</sup>
FA <sub>3</sub> Bi <sub>2</sub> I <sub>9</sub> from FABI <sub>2</sub> precursor	0.017	0.0019	0.11	0.36	7.1×10 <sup>-4</sup>	0.48	0.053	0.22	0.39	0.041
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from CsBiSBr <sub>2</sub> precursor	0.042	0.014	0.012	0.25	1.2×10 <sup>-4</sup>	0.6	0.19	0.062	0.27	0.01

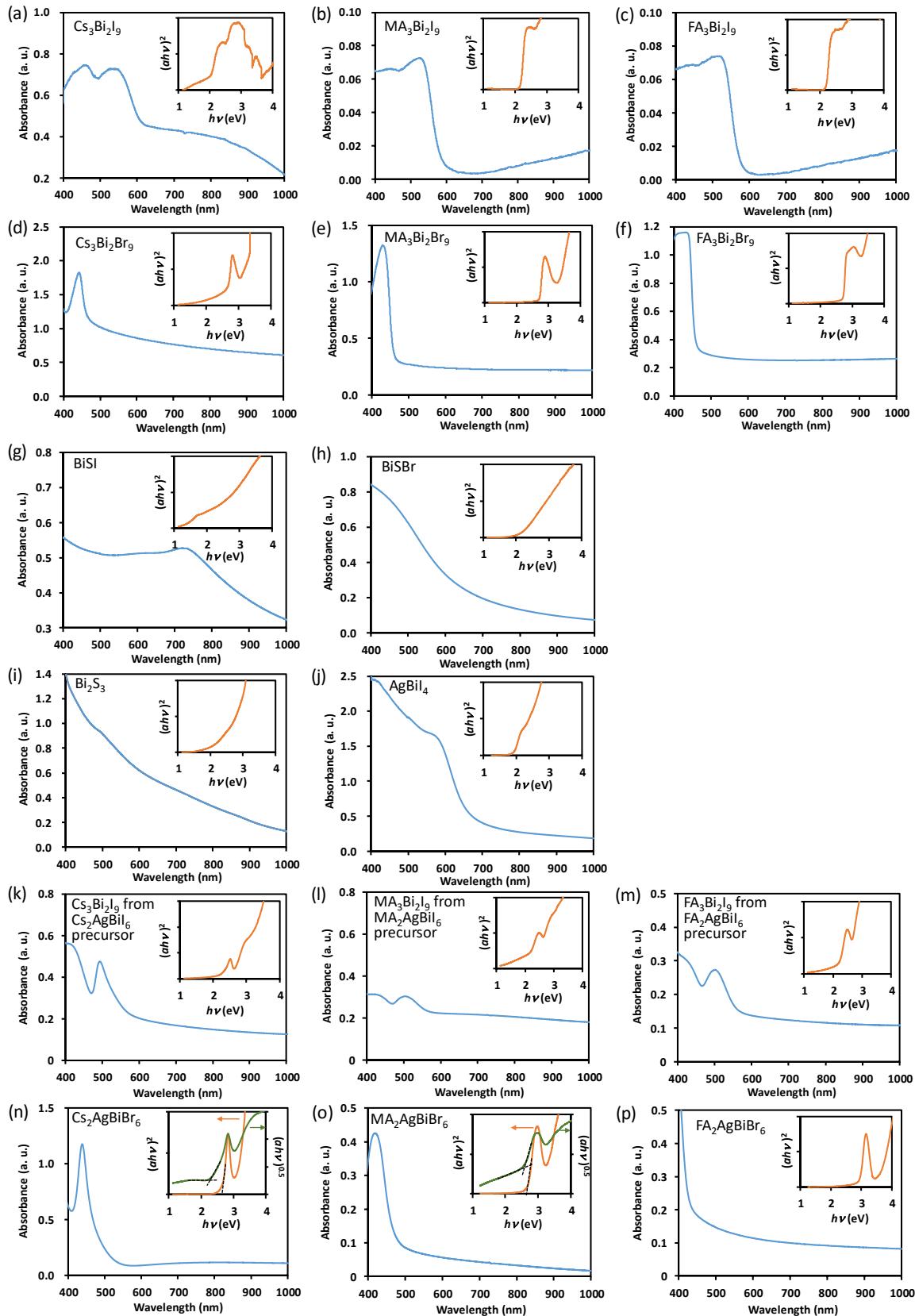
MA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from MABiSBr <sub>2</sub> precursor	0.032	0.0025	0.0059	0.16	3.1×10 <sup>-5</sup>	0.83	0.065	0.017	0.23	3.2×10 <sup>-3</sup>
FA <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub> from FABiSBr <sub>2</sub> precursor	0.41	0.0018	0.14	0.34	0.019	0.022	0.033	0.1	0.36	8.1×10 <sup>-4</sup>
Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	0.14	0.020	0.24	0.6	0.021	0.62	0.086	0.37	0.44	0.1
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub>	0.18	0.039	0.32	0.49	0.028	0.46	0.099	0.29	0.54	0.074
SbSI (200 °C)	0.31	0.028	0.20	0.37	0.023	3.4	0.31	0.31	0.38	0.40
SbSI (240 °C)	0.67	0.051	0.42	0.56	0.16	7.1	0.57	0.37	0.53	1.35
Sb-S-Br (240 °C)	0.33	0.040	0.41	0.56	0.076	5.2	0.62	0.4	0.53	1.1
Sb <sub>2</sub> S <sub>3</sub>	6.1	0.35	0.41	0.39	0.98	9	0.51	0.29	0.44	1.16
AgSbI <sub>4</sub>	0.17	0.092	0.32	0.56	0.031	0.9	0.18	0.33	0.59	0.17
Cs <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from Cs <sub>2</sub> AgSbI <sub>6</sub> precursor	0.15	0.039	0.34	0.46	0.023	0.62	0.16	0.25	0.56	0.087
MA <sub>3</sub> Sb <sub>2</sub> I <sub>9</sub> from MA <sub>2</sub> AgSbI <sub>6</sub> precursor	0.21	0.058	0.39	0.52	0.044	0.31	0.085	0.31	0.59	0.057
Cs <sub>2</sub> AgSbBr <sub>6</sub>	0.29	0.061	0.46	0.5	0.068	0.53	0.11	0.37	0.45	0.088
CsSbSI <sub>2</sub>	1.5	0.022	0.43	0.47	0.31	4.6	0.025	0.38	0.53	0.92
MASbSI <sub>2</sub>	0.8	0.11	0.35	0.46	0.13	2.6	0.34	0.22	0.48	0.27
FA <sub>3</sub> Sb <sub>2</sub> Br <sub>9</sub> from FASbSBr <sub>2</sub> precursor	0.32	0.079	0.31	0.42	0.04	1.24	0.26	0.24	0.44	0.13

<sup>a</sup>  $J_{SC\_max}$  is the maximum  $J_{SC}$  calculated from the transmittance of mpTiO<sub>2</sub>/active layer and sunlight spectrum. See Figure S14.

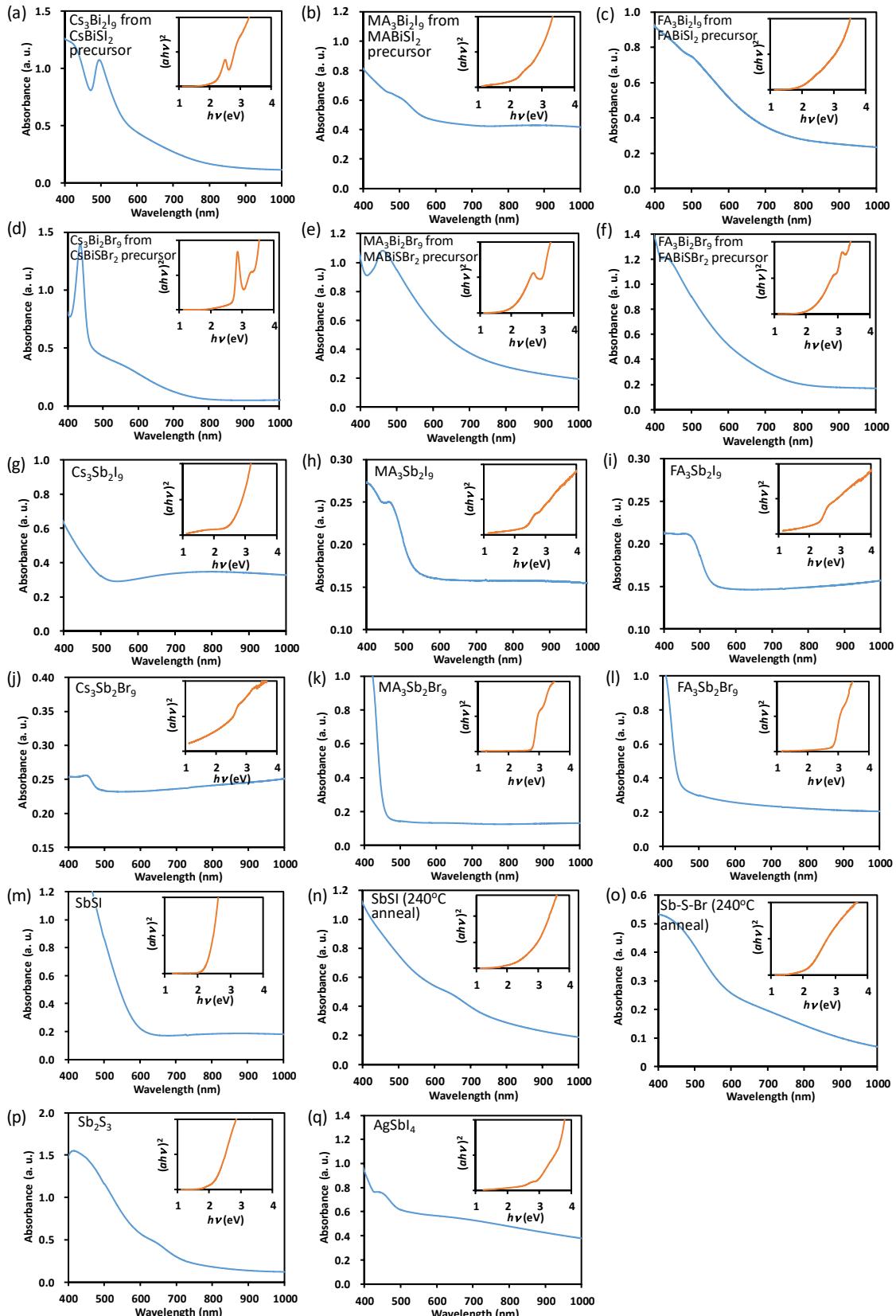
## Supporting Figures.



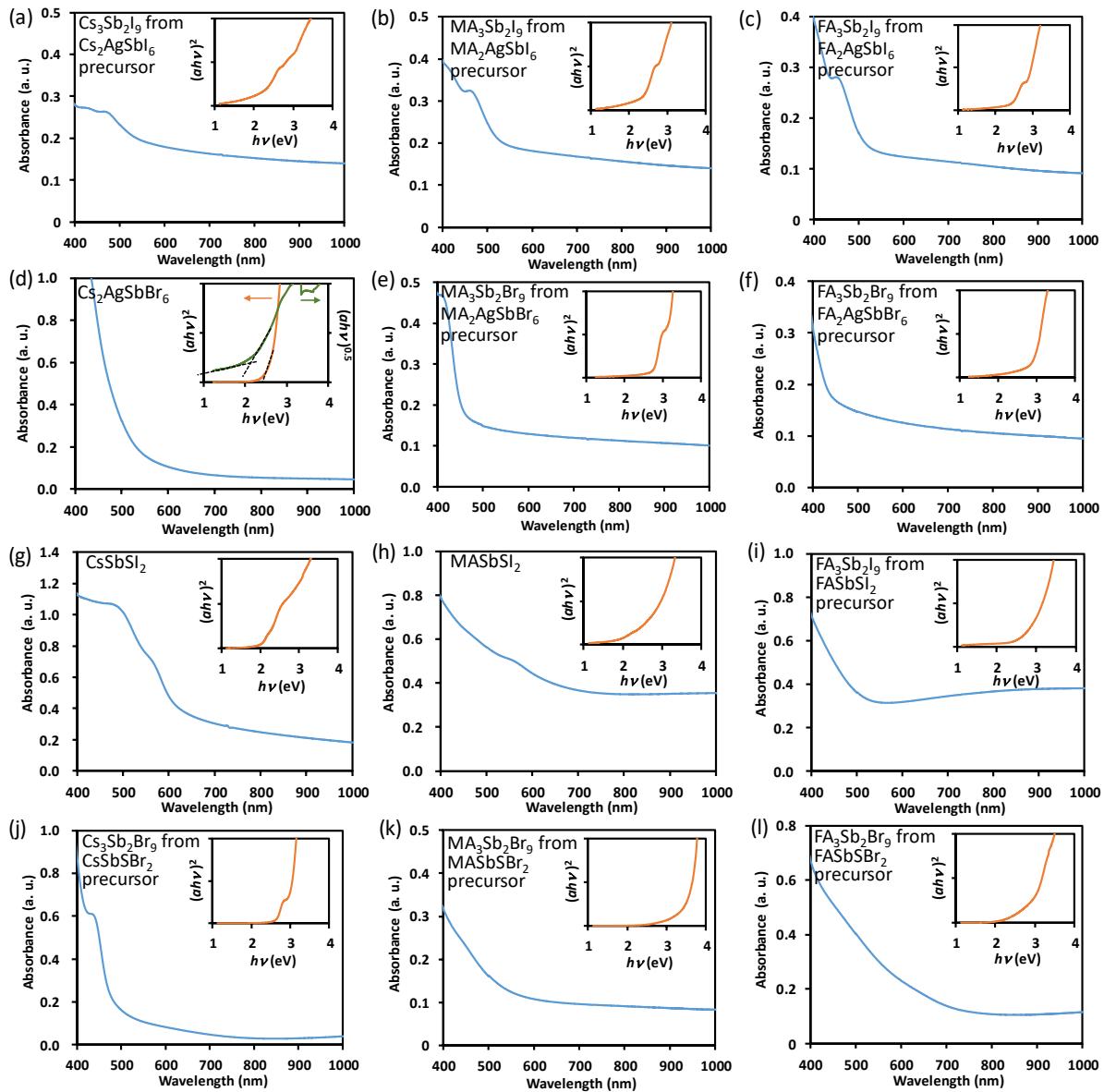
**Figure S1.** XRD patterns. Contamination of other crystal phases such as  $\text{A}_3\text{M}_2\text{X}_9$  is given by the dots.



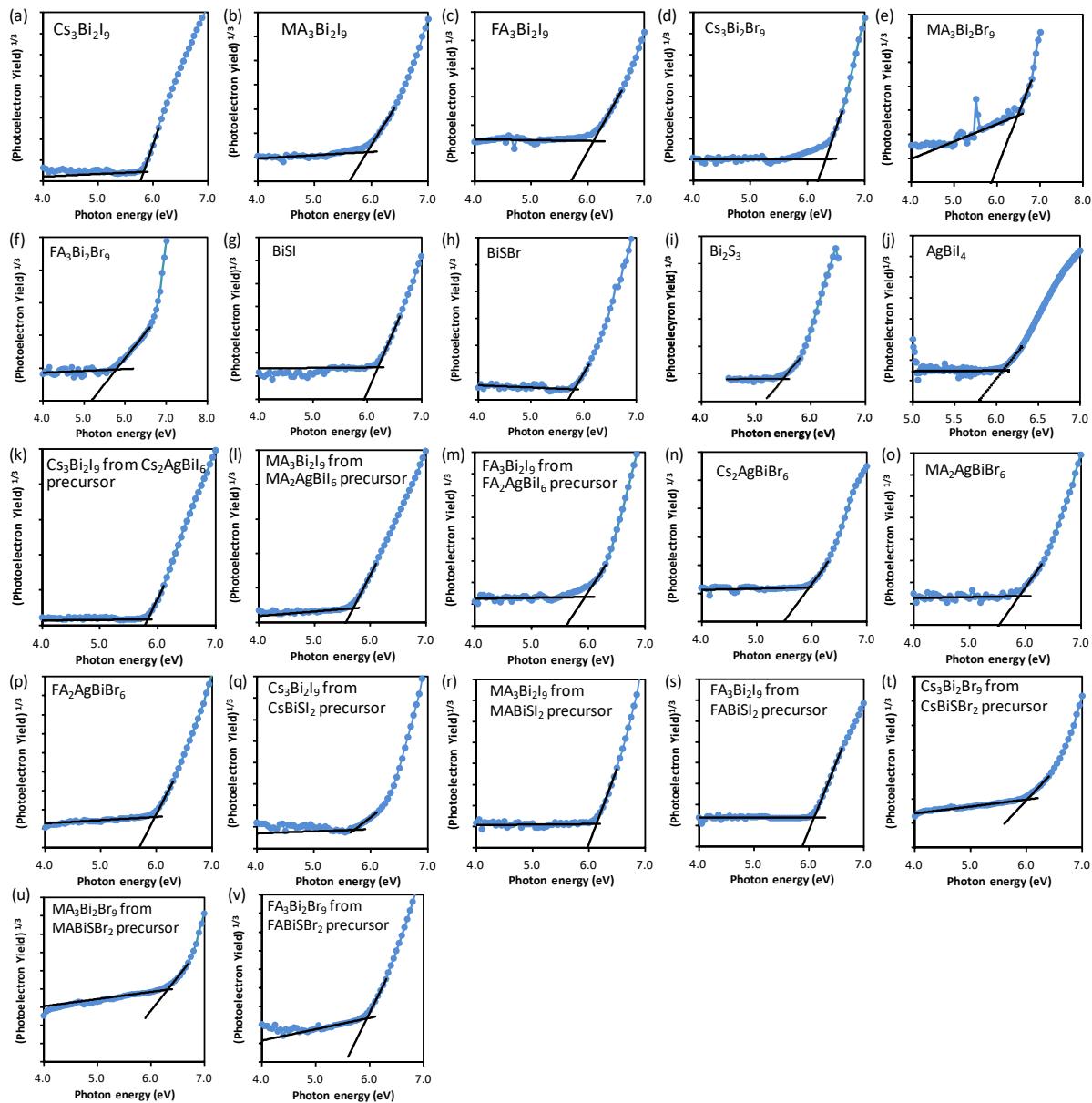
**Figure S2.** UV-vis photoabsorption spectra (blue line). The samples were prepared on quartz substrates. The insets are the Tauc plots (direct transition:  $(\alpha h\nu)^2$  as orange lines, indirect transition:  $(\alpha h\nu)^{0.5}$  as green lines).



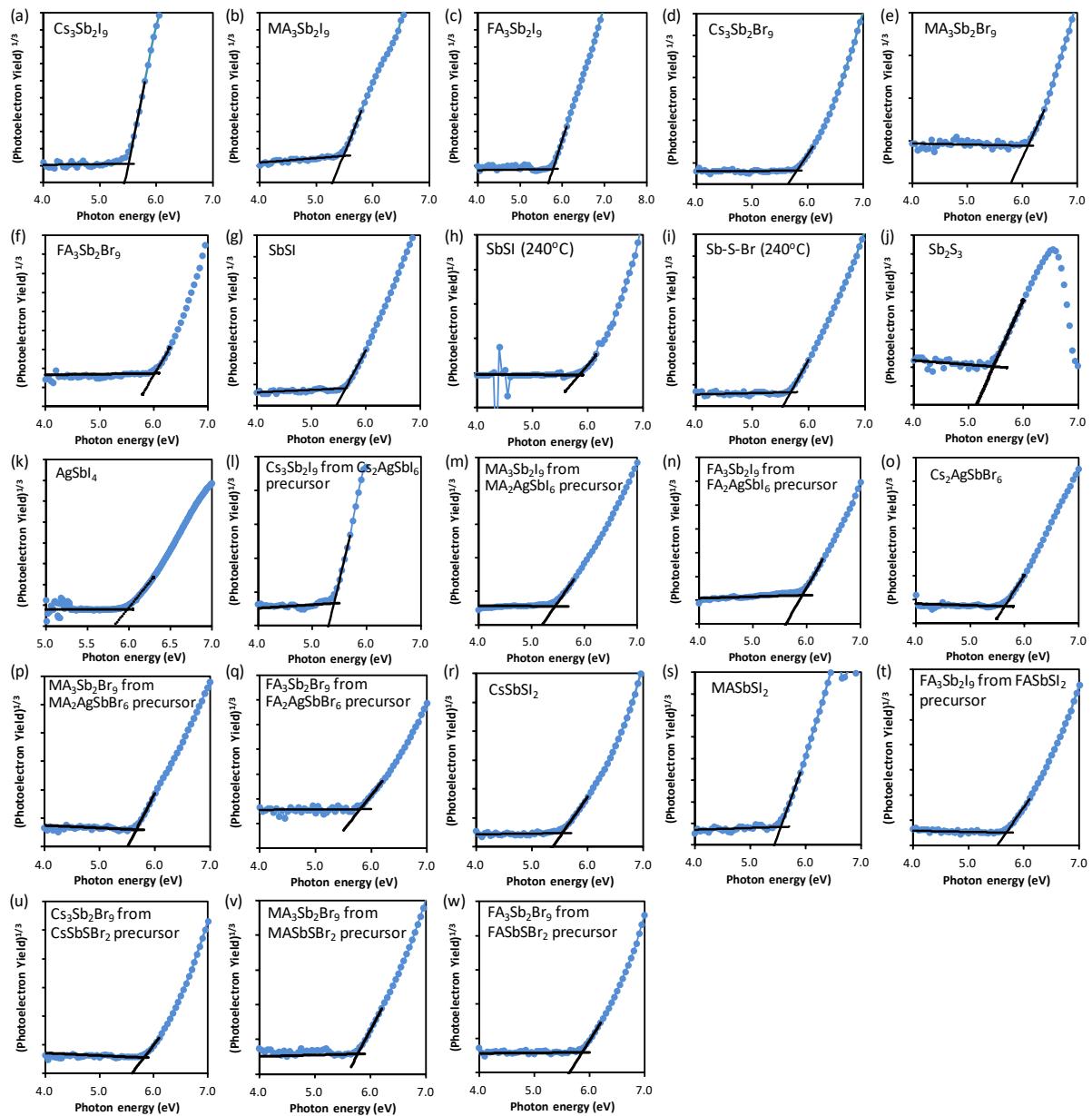
**Figure S3.** UV-vis photoabsorption spectra (blue line). The samples were prepared on quartz substrates. The insets are the Tauc plots (direct transition:  $(\alpha h\nu)^2$  as orange lines, indirect transition:  $(\alpha h\nu)^{0.5}$  as green lines).



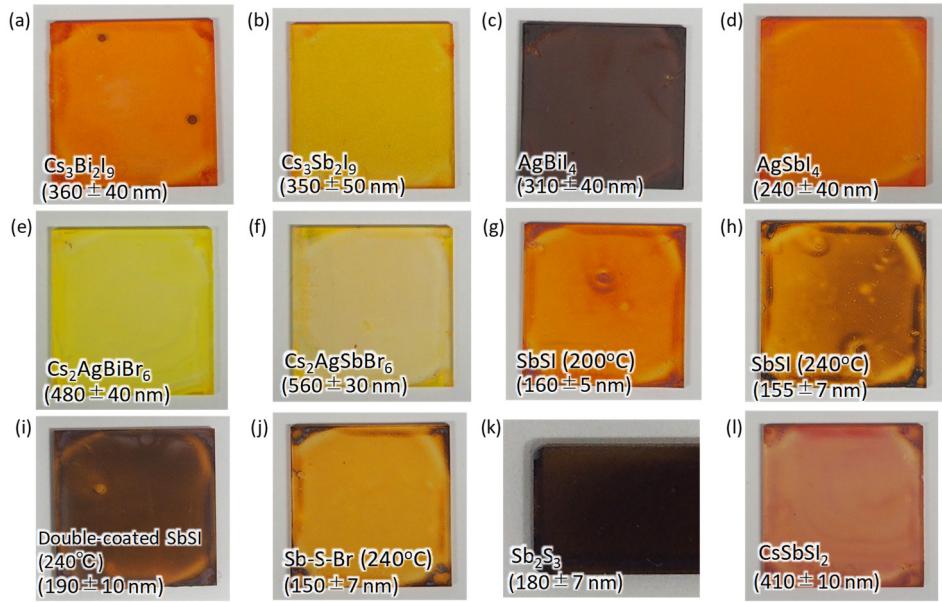
**Figure S4.** UV-vis photoabsorption spectra (blue line). The samples were prepared on quartz substrates. The insets are the Tauc plots (direct transition:  $(\alpha h\nu)^2$  as orange lines, indirect transition:  $(\alpha h\nu)^{0.5}$  as green lines).



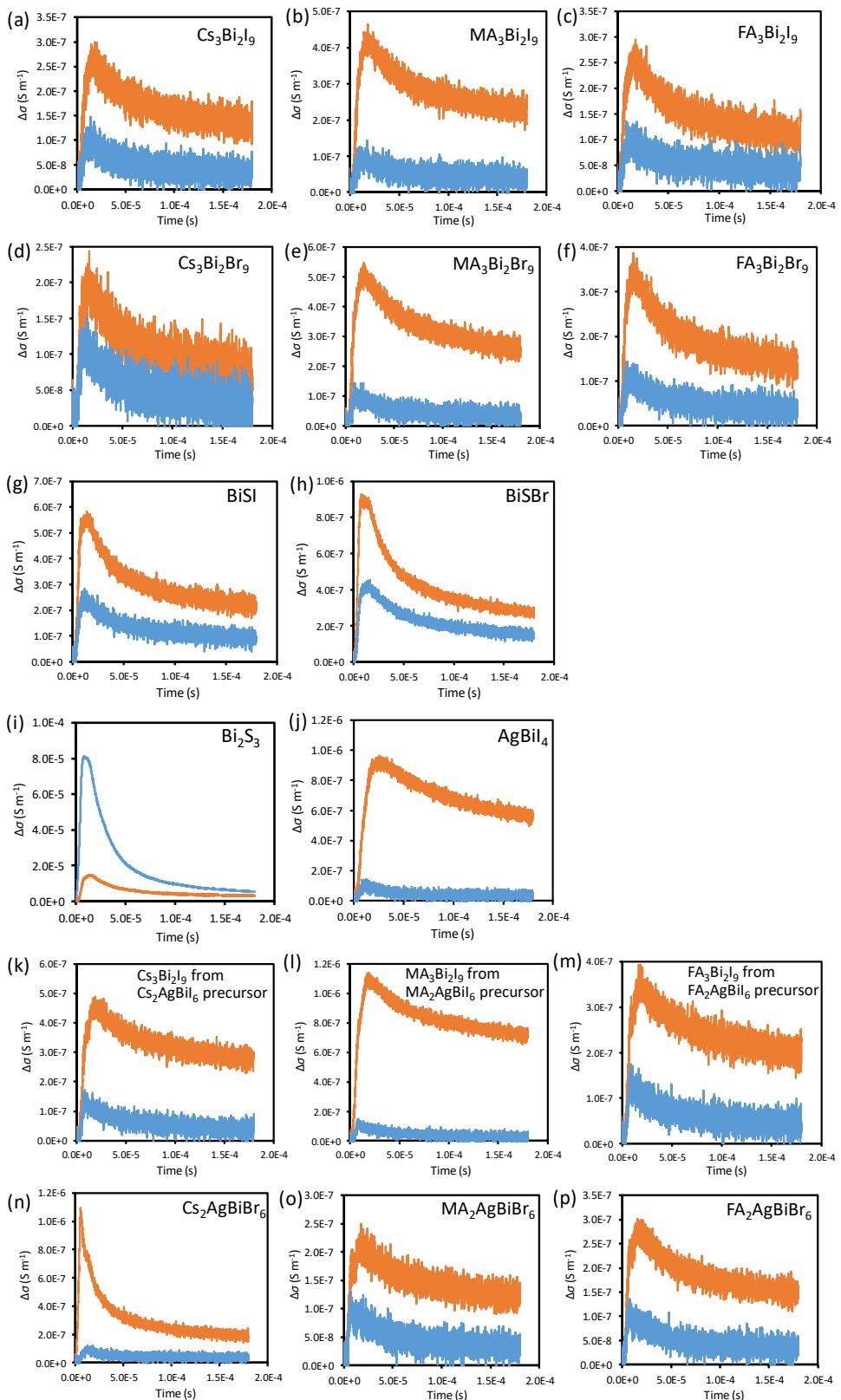
**Figure S5.** PYS spectra. The samples were prepared on FTO substrates.



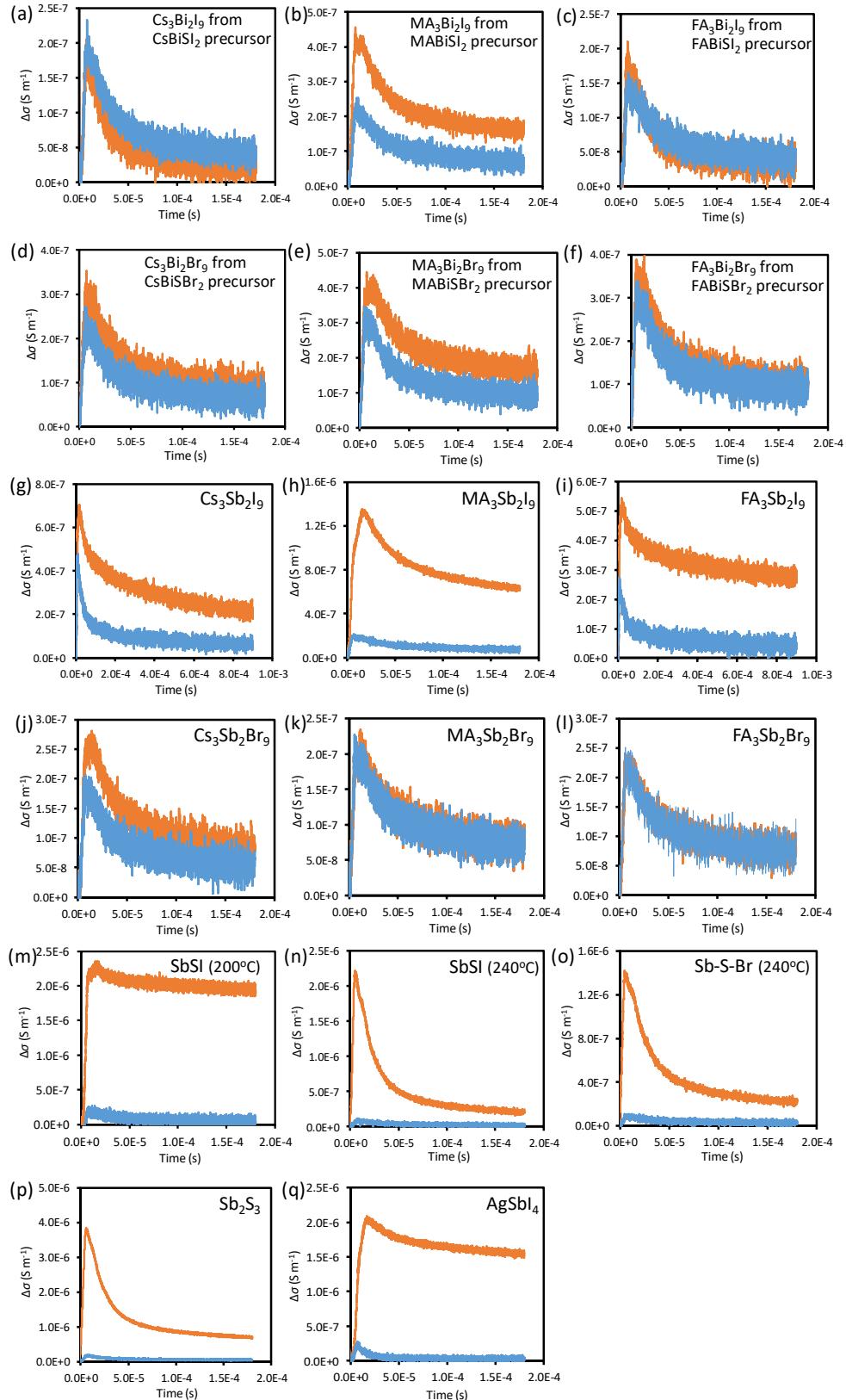
**Figure S6.** PYS spectra. The samples were prepared on FTO substrates.



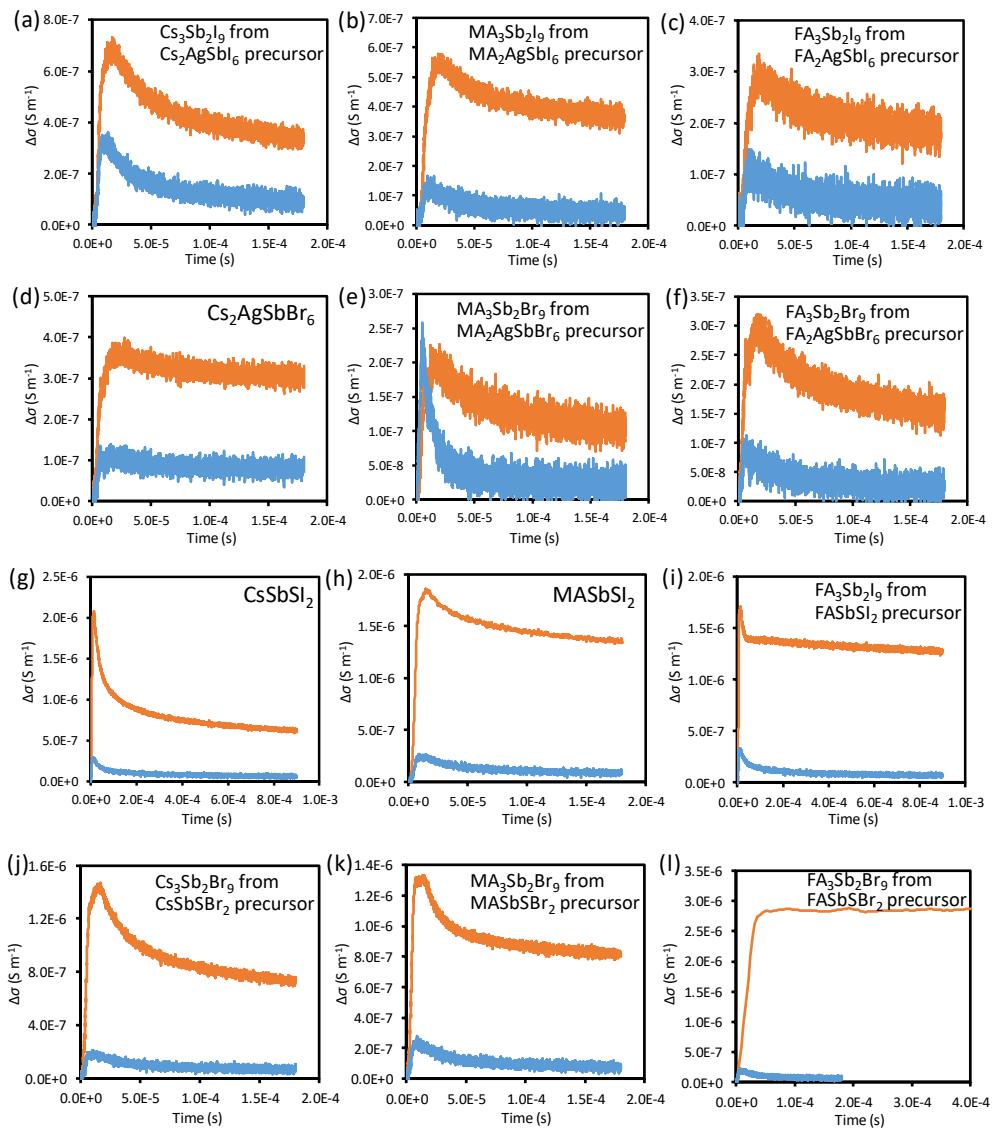
**Figure S7.** Pictures of  $\text{Cs}_3\text{Bi}_2\text{I}_9$ ,  $\text{MA}_3\text{Bi}_2\text{I}_9$ ,  $\text{AgBiI}_4$ ,  $\text{AgSbI}_4$ ,  $\text{Cs}_2\text{AgBiBr}_6$ ,  $\text{Cs}_2\text{AgSbBr}_6$ ,  $\text{SbSI}$  ( $200\text{ }^{\circ}\text{C}$ ),  $\text{Sb}_2\text{S}_3$ -containing  $\text{SbSI}$  ( $240\text{ }^{\circ}\text{C}$ ), double-coated  $\text{SbSI}$ ,  $\text{Sb-S-Br}$  ( $240\text{ }^{\circ}\text{C}$  annealed),  $\text{Sb}_2\text{S}_3$ , and  $\text{CsSbSI}_2$  films. The film thickness of active layer/mp-TiO<sub>2</sub> with a standard deviation is appended in brackets. The thickness of mp-TiO<sub>2</sub> is  $145 \pm 7\text{ nm}$ .



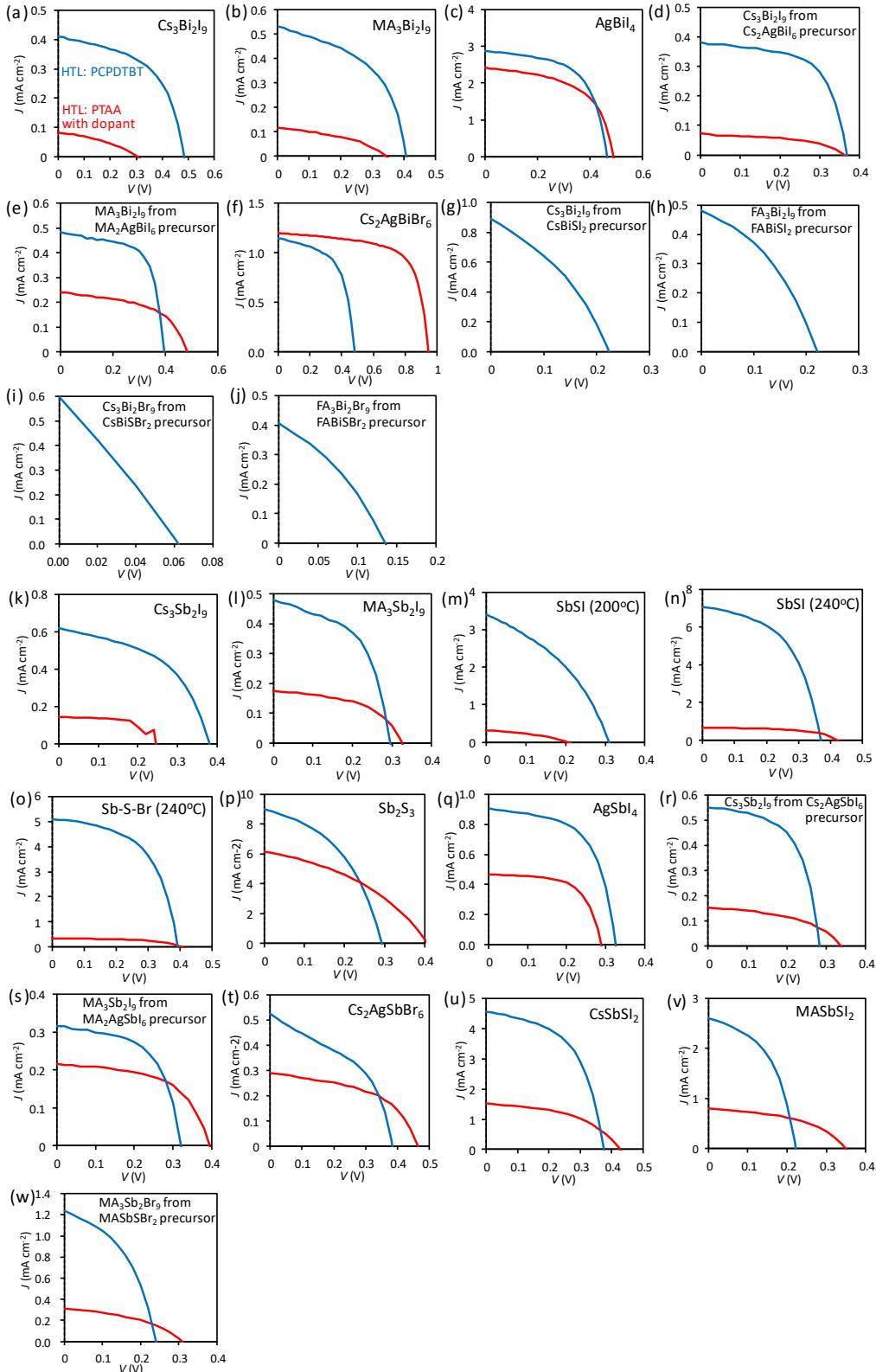
**Figure S8.** Xe-flash TRMC decays of the films on mp-TiO<sub>2</sub>/quartz (orange line) and bare quartz (blue line). All the measurements were conducted in air.



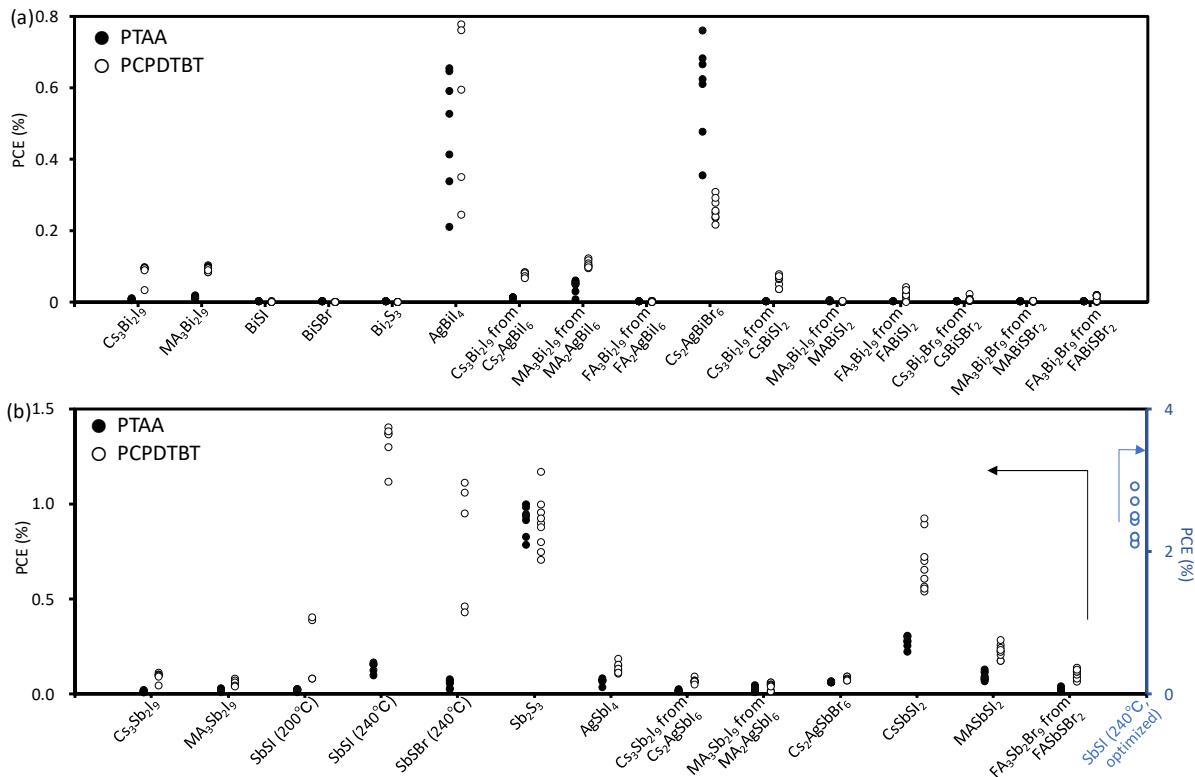
**Figure S9.** Xe-flash TRMC decays of films on mp-TiO<sub>2</sub>/quartz (orange line) and bare quartz (blue line). All the measurements were conducted in air.



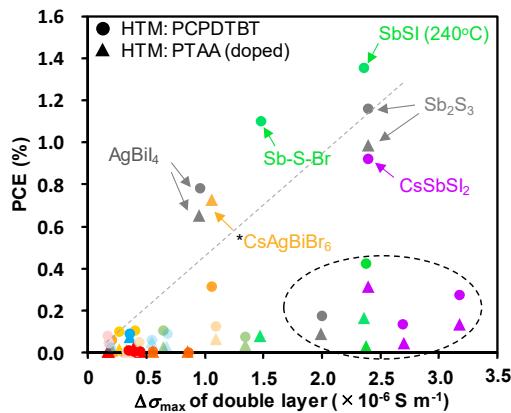
**Figure S10.** Xe-flash TRMC decays of films on mp-TiO<sub>2</sub>/quartz (orange line) and bare quartz (blue line). All the measurements were conducted in air.



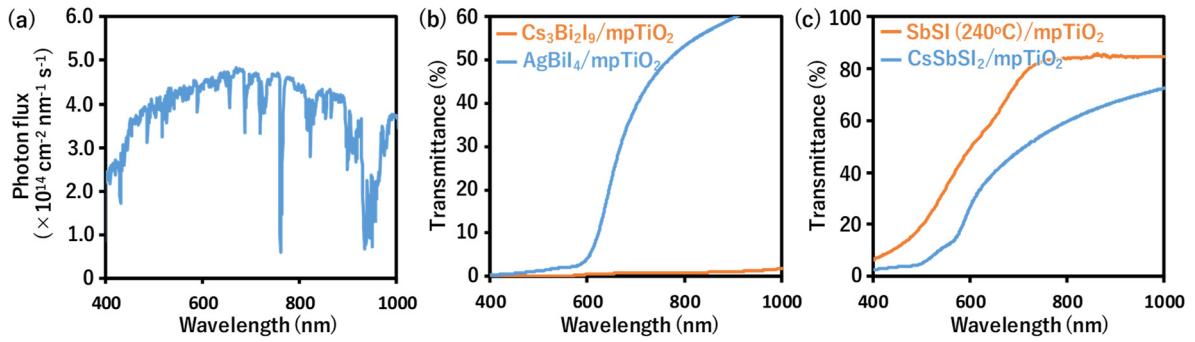
**Figure S11.** The  $JV$  curve of Bi and Sb-based solar cells which showed higher PCE than 0.01%. The colors of  $JV$  curve represent different HTMs, red line: PTAA with dopant, blue line: PCPDTBT. For  $\text{AgBiI}_4$  and  $\text{AgSbI}_4$ , Li-TFSI and tBP was not included into PTAA to avoid dopant-induced degradation. The device structure is shown in Figure S15a.



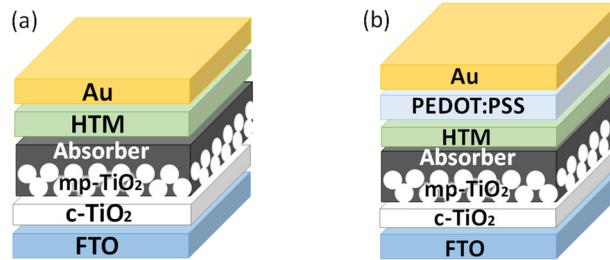
**Figure S12.** Statistics of solar cell performance of (a) Bi- and (b) Sb-based materials, which are corresponding to Table S5. The optimized Sb<sub>2</sub>S<sub>3</sub>-containing SbSI (at 240 °C), prepared by pre-deposition and double spin-coating, are described with blue circles in (b). For each device structure, 5~9 cells were measured.



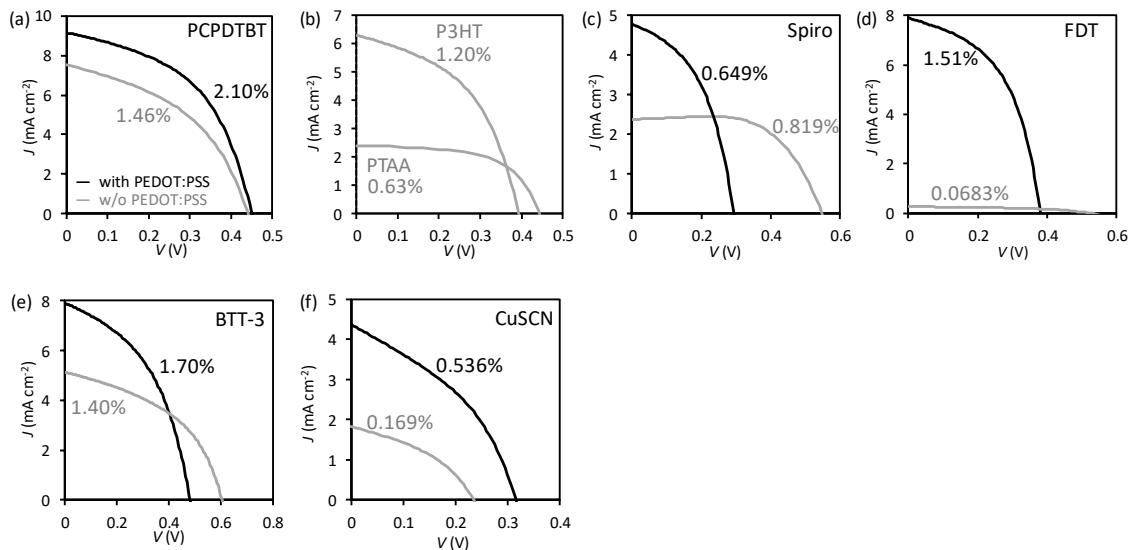
**Figure S13.** PCE vs  $\Delta\sigma_{\max}$  of double layer obtained from Xe-flash TRMC.



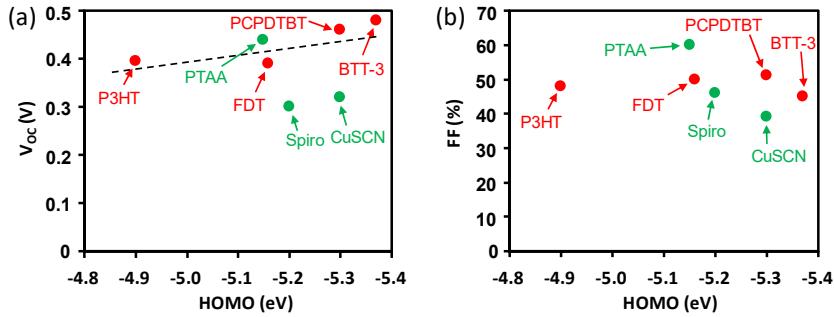
**Figure S14.** (a) Photon flux of AM1.5G sun light obtained from NREL<sup>S8</sup>. (b, c) Transmittance spectra of  $\text{Cs}_3\text{Bi}_2\text{I}_9$ ,  $\text{AgBiI}_4$ ,  $\text{Sb}_2\text{S}_3$ -containing SbSI (240 °C), and  $\text{CsSbSI}_2$  on mp-TiO<sub>2</sub>.



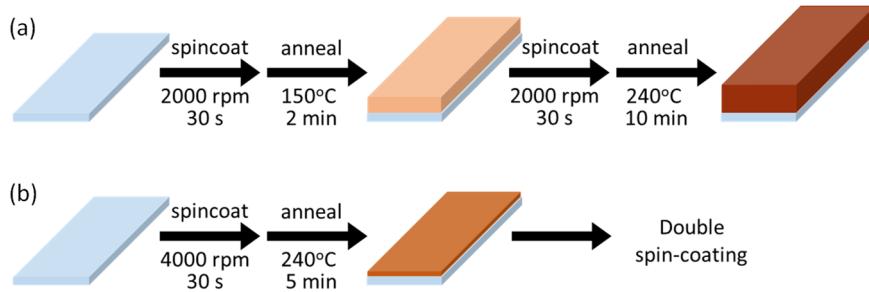
**Figure S15.** (a) Device structure used for the initial screening. (b) Optimized device structure of  $\text{Sb}_2\text{S}_3$ -containing SbSI device.



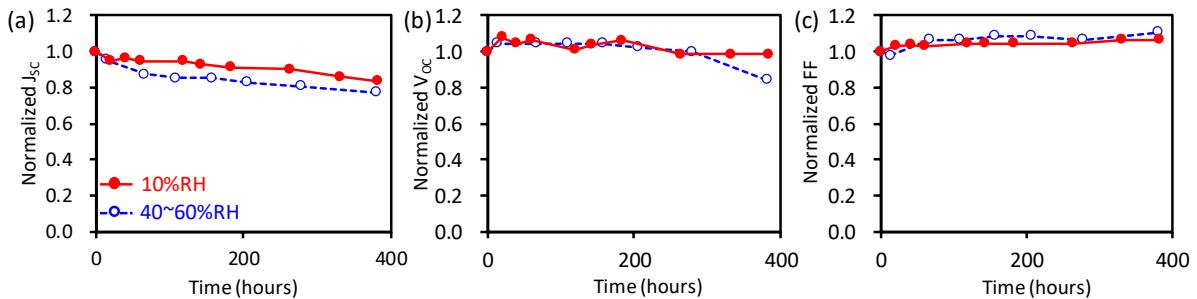
**Figure S16.** The  $JV$  curve of  $\text{Sb}_2\text{S}_3$ -containing SbSI based solar cells with different HTMs. The colors of  $JV$  curve represent inclusion of PEDOT:PSS layer between HTM and Au electrode, black line: with PEDOT:PSS (FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/SbSI/PCPDTBT/PEDOT:PSS/Au), gray line: without PEDOT:PSS (FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/SbSI/PCPDTBT/Au).



**Figure S17.** (a)  $V_{OC}$  and (b) FF vs. HOMO (or VBM) level of each HTM, which is corresponding to Figure 4.



**Figure S18.** Schematic image of (a) double spin-coating and (b) pre-deposition of thin SbSI. The original precursor solution ( $SbI_3$  0.4 M,  $Sb(EtX)_3$  0.3 M) was diluted with DMSO; (a) precursor : DMSO = 1 : 0.5, (b) precursor : DMSO = 1 : 3. The detail is as follows: (a) the diluted solution was spin-coated onto the substrate (2000 rpm, 30 s), followed by annealing (150 °C, 2 min). After cooling the substrate to room temperature, the precursor solution was spin-coated again (2000 rpm, 30 s), and annealed (240 °C, 10 min). (b) The diluted solution was spin-coated (4000 rpm, 30 s) followed by annealing (240 °C, 5 min). Then, SbSI was spin-coated again in the same manner with the process (a).



**Figure S19.** Normalized (a)  $J_{SC}$ , (b)  $V_{OC}$ , and (c) FF as a function of storage time in dried condition (~10%RH) and high humidity (40~60%RH) under room light.

## Supporting Reference

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- (S8) NREL Reference Air Mass 1.5 Spectra <https://www.nrel.gov/grid/solar-resource/spectra-am1.5.html>