Supplementary Information

Improving the Performance of Lead-Free $Cs_2AgBiBr_6$ Double Perovskite Solar Cells by Passivating Br Vacancies

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Experimental section

Chemicals. Cesium bromide (CsBr, 99.999%), dimethyl sulfoxide (DMSO, anhydrous, ≥ 99.9%), titanium diisopropoxide bis (acetylacetonate) (75 wt.% in isopropanol), hydrochloric acid (37 wt.% in water), hydroiodic acid (57 wt.% in water) and anhydrous ethanol were purchased from Sigma-Aldrich. Isopropanol Alcohol (anhydrous, ≥ 99.5%), hydrobromic acid (48 wt.% in water), and methanol were purchased from aladdin. Silver bromide (AgBr, 99.998%), bismuth (III) bromide ($BiBr_3$, 99%), titanium (IV) chloride ($TiCl_4$, 99.0%) were purchased from Alfa Aesar. Conductive carbon paste was purchased from Shanghai MaterWin New Materials Co., Ltd., China. All reagents were used without further purification.

Device Fabrication. The glass/FTO substrate was cleaned sequentially with glass cleaner, acetone, methanol-ethanol-isopropanol solvent mixture, and anhydrous ethanol for 30 min. And then the cleaned substrate was treated with UV/ozone for 15-25 min.

The compact TiO_2 (c-TiO_2) precursor solution was prepared by mixing titanium diisopropoxide bis (acetylacetone) and anhydrous ethanol at a volume ratio of 1:19. The precursor solution was spin-coated on the substrate at 2500 rpm for 30 s, and then annealed at 120 °C for 3 min. Then it was annealed at 500 °C for 30 min in a muffle furnace to obtain the FTO/c-TiO_2 substrate. The 420 μL $TiCl_4$ was dissolved in 100 mL deionized water to obtain the $TiCl_4$ solution. The FTO/c-TiO_2 substrate was treated with the $TiCl_4$ solution at 70 °C for 30 min and then annealed at 500 °C for 30 min in a muffle furnace.

In the glove box, 1 mmol CsBr, 0.5 mmol AgBr, and 0.5 mmol $BiBr_3$ were mixed in 1 mL DMSO and stirred at 70 °C for 12 h to obtain $Cs_2AgBiBr_6$ perovskite precursor solution. The precursor solution was spin-coated on the FTO/TiO_2 substrate at 1000 rpm for 10 s and 5000 rpm for 30 s, repectively. And then the $Cs_2AgBiBr_6$ precursor film was annealed at 275 °C for 5 min. The FTO/TiO_2/$Cs_2AgBiBr_6$/C device was fabricated by doctor-blading the carbon electrode on the perovskite layer and annealing it at 120 °C for 10 min. Halogenated acid with different volume ratios (1%, 2%, 3%, 4%, 5%) was added to the $Cs_2AgBiBr_6$ perovskite precursor solution. The other processes are the same.

Characterizations. The PCE of the PSC was measured at one sun illumination of AM 1.5G (100 mW cm^{-2}) by a solar simulator (Oriel Sol 3A class) equipped with a Xenon lamp (Newport 91,160) and a Keithley 2400 source meter. The active area of the PSC is 0.09 cm^2. TPC and TPV measurements were performed by using transient surface photovoltage spectroscopy (DSO-X 3104, Agilent). The EQE of the device was measured through the direct current (DC) mode of the spectrum performance testing system (7-SCSpec). An X-ray diffraction instrument (D8-Advance) equipped with Cu K_α radiation (λ = 0.1541 nm) was used to complete the XRD measurement of the perovskite film. The distribution of elements in films was tested by EDX. The elemental composition of the $Cs_2AgBiBr_6$ film was analyzed using XPS (Thermo Fly ESCALAB 250 xi) under an Al $K\alpha$ (1486.6 eV) light source. The Raman spectra of the sample were obtained by excitation of the film at a wavelength of 785 nm on the HORIBA evolutionary Raman spectrometer. The surface and cross-sectional morphologies of films were characterized by SEM (JSM-7900F). TEM was done by using the field-emission source at 200 kV and the microscope (FEI Tecnai F20). The optical absorption properties of $Cs_2AgBiBr_6$ perovskite films were tested by UV-Vis (UV3600-plus, Shimadzu).

Theoretical Calculation. DFT calculations were performed using the Vienna Ab initio simulation package (VASP).[1,2] The exchange-correlation functional is the optimized version of the Perdew-Burke-Ernzerhof formulation for solids (PBEsol).[3] The pydefect package was used for modeling the point defects and analyzing the calculation results.[4] Supercell of 320 atoms was used for the defect calculations. Monkhorst−Pack 2 × 2 × 2 k-point grid was used for the reciprocal space sampling. The residual forces on atoms were reduced to be less than 0.01 eV $Å^{-1}$. Defect formation enthalpies were calculated as:

$$E_f[V^q] = \{E[V^q] + E_{corr}[V^q]\} - E_{Perf} - \sum n_i\mu_i + q(\varepsilon_{VBM} + \Delta\varepsilon_F)$$

where $E[V^q]$ and E_{perf} are the total energies of the supercell with vacancy V in charge state q and the perfect crystal supercell, respectively. $E_{corr}[V^q]$ is the correcting energy for the finite-size error of the defect supercell. n_i is the number of removed i-type atoms, and μ_i refers to its chemical potential depending on the growth condition. ε_{VBM} is the energy level of the VBM in the perfect crystal, and $\Delta\varepsilon_F$ represents the Fermi level with respect to ε_{VBM}. Band structure of supercells are unfolded into the first Brillium Zone of primitive cell using VaspBandUnfolding package.[5]

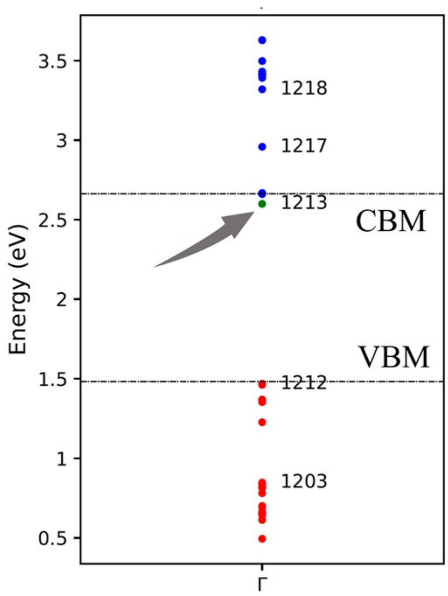

Fig. S1. Identification results for neutral V_{Br} eigenvalues.

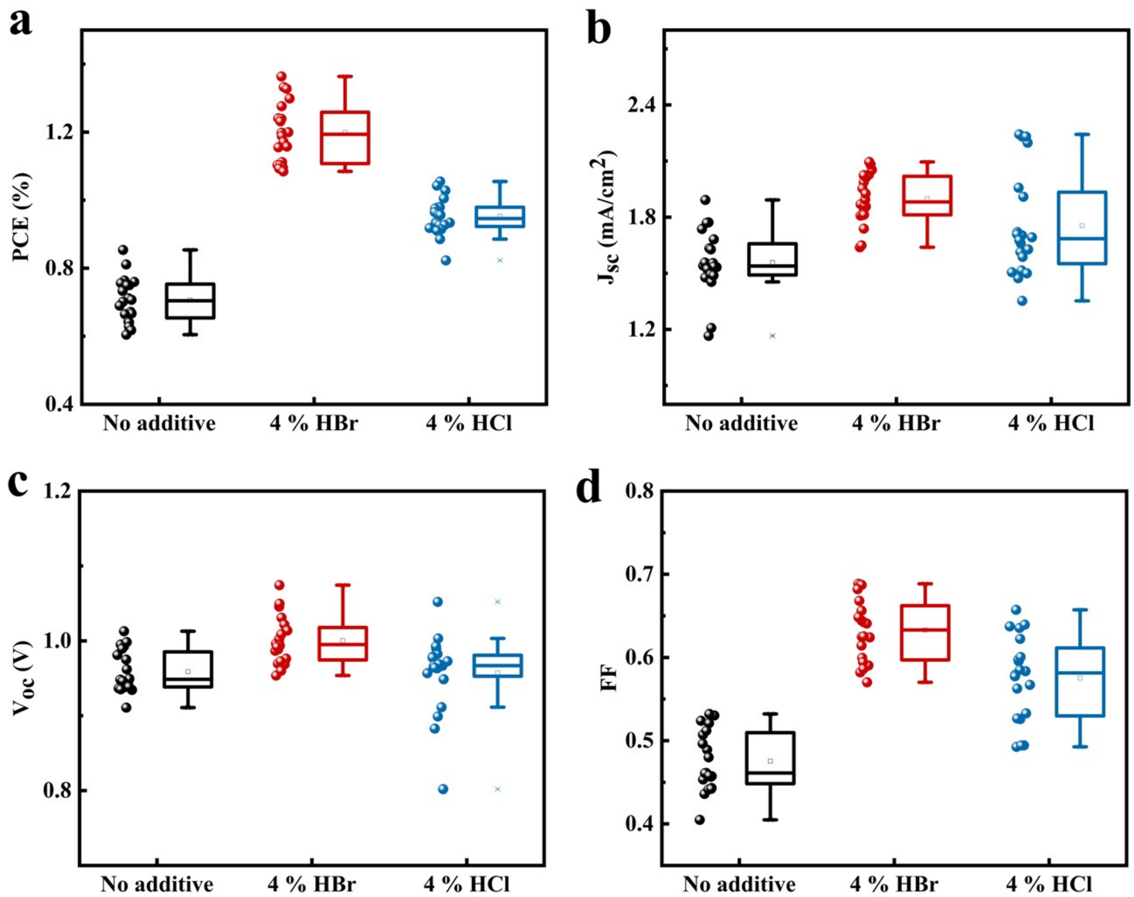

Fig. S2. The distribution of the performance for control, 4 % HCl-$Cs_2AgBiBr_6$, 4 % HBr-$Cs_2AgBiBr_6$ PSCs (a) PCE, (b) J_{sc}, (c) V_{oc}, (d) *FF*.

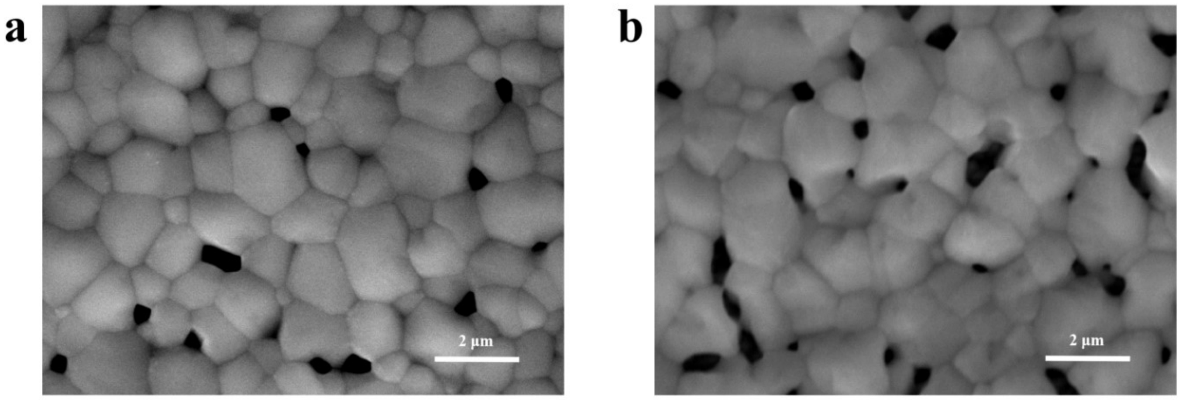

Fig. S3. SEM images of (a) control, (b) 2 % HI-$Cs_2AgBiBr_6$ films.

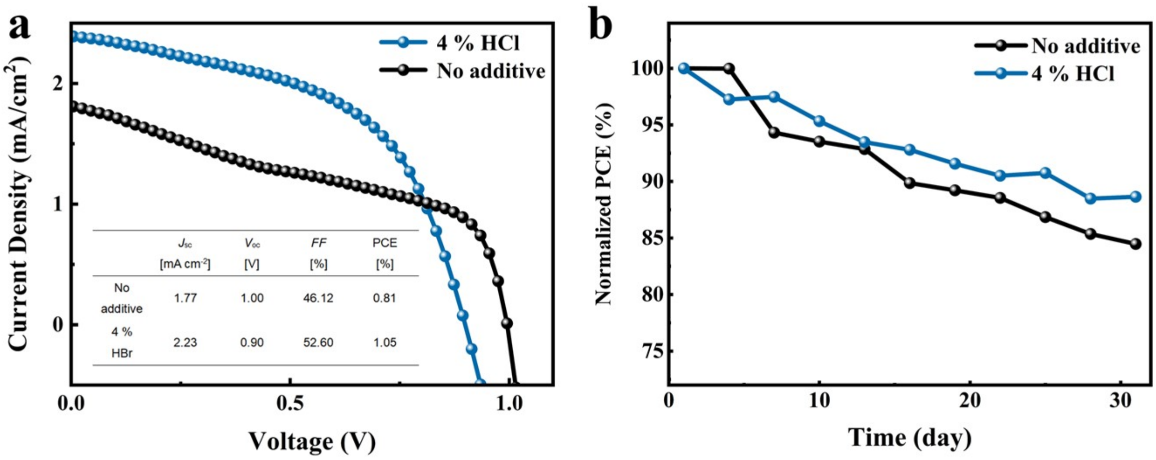

Fig. S4. (a) *J*-*V* curves and (b) stability of control and 4 % HCl-$Cs_2AgBiBr_6$ PSCs (champion).

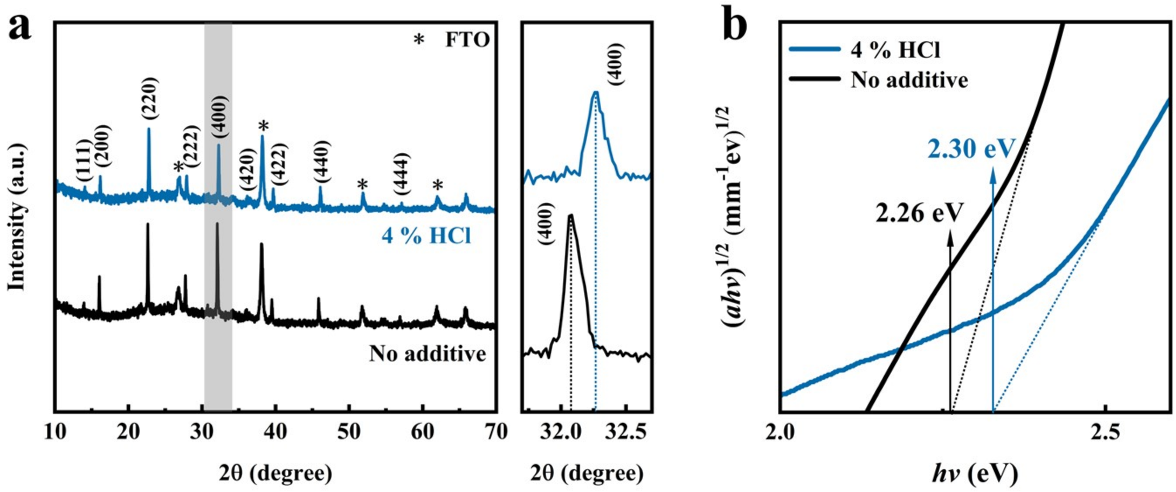

Fig. S5. (a) XRD patterns and the enlargement of (400) of control and 4 % HCl-$Cs_2AgBiBr_6$ films. (b) The Tauc plot of 4 % HCl-$Cs_2AgBiBr_6$ films.

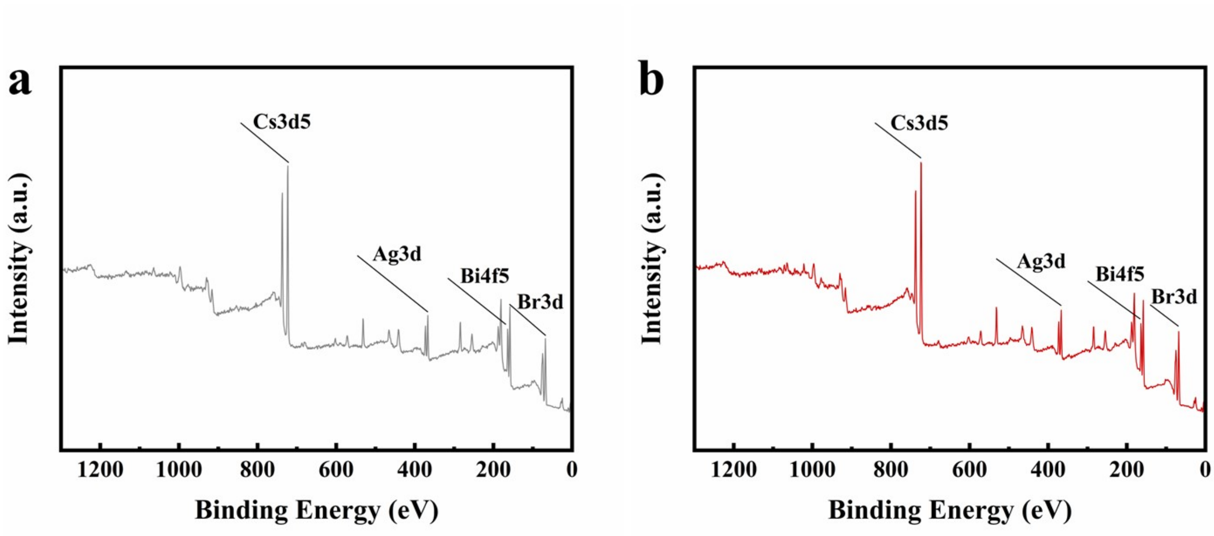

Fig. S6. The XPS full-spectrum of (a) control and (b) 4 % HBr-$Cs_2AgBiBr_6$ films.

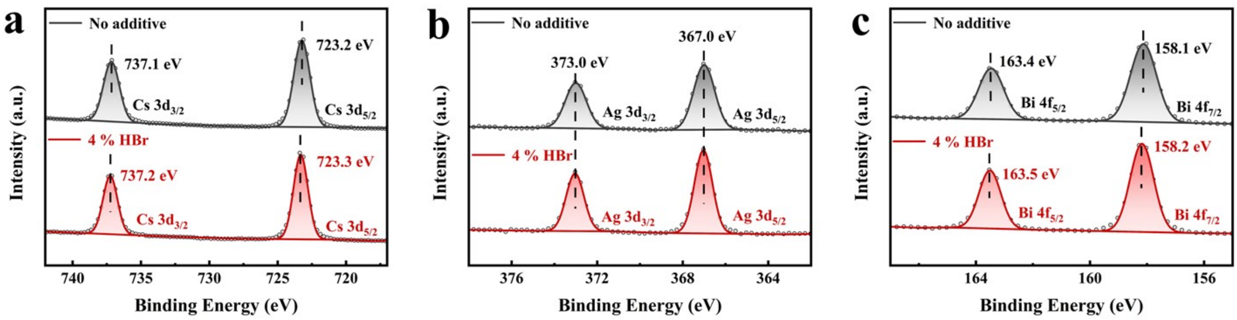

Fig. S7. High-resolution XPS spectra of (a) Cs *3d*, (b) Ag *3d,* and (c) Bi *4f* of control and 4 % HBr-$Cs_2AgBiBr_6$ films.

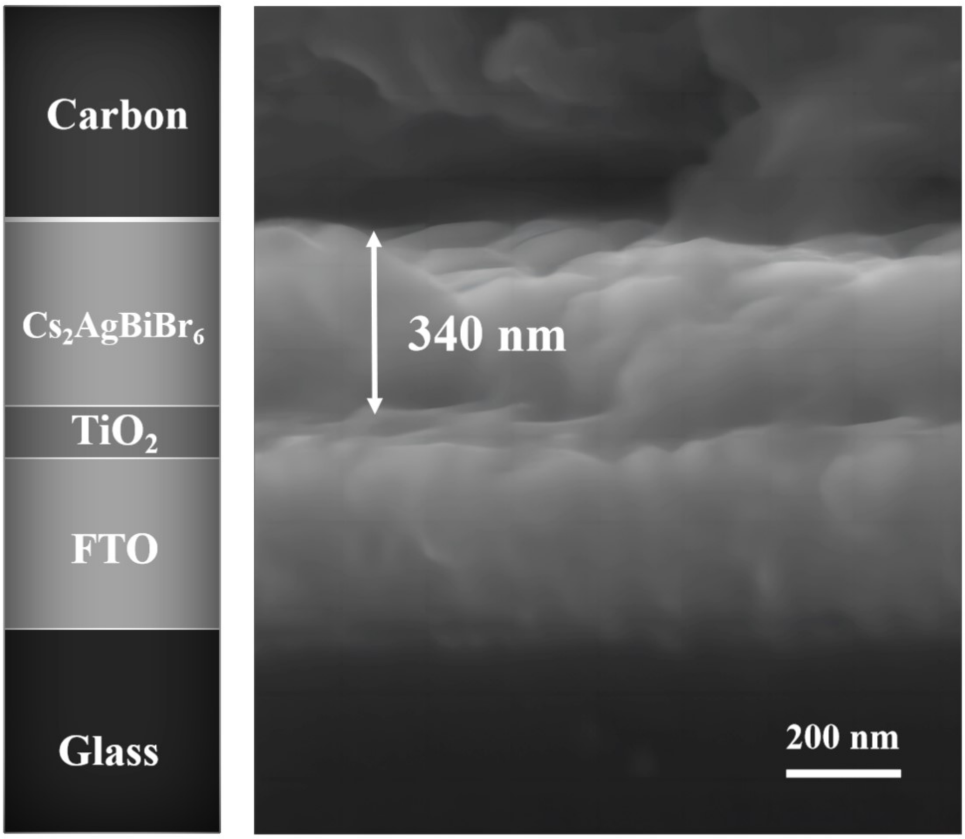

Fig. S8. The cross-section SEM image of PSC.

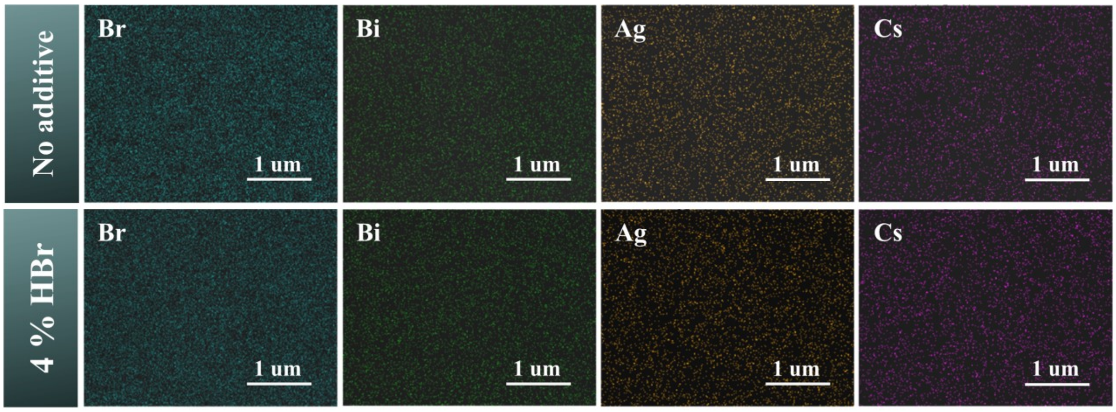

Fig. S9. EDX element mappings of control and 4 % HBr-$Cs_2AgBiBr_6$ films.

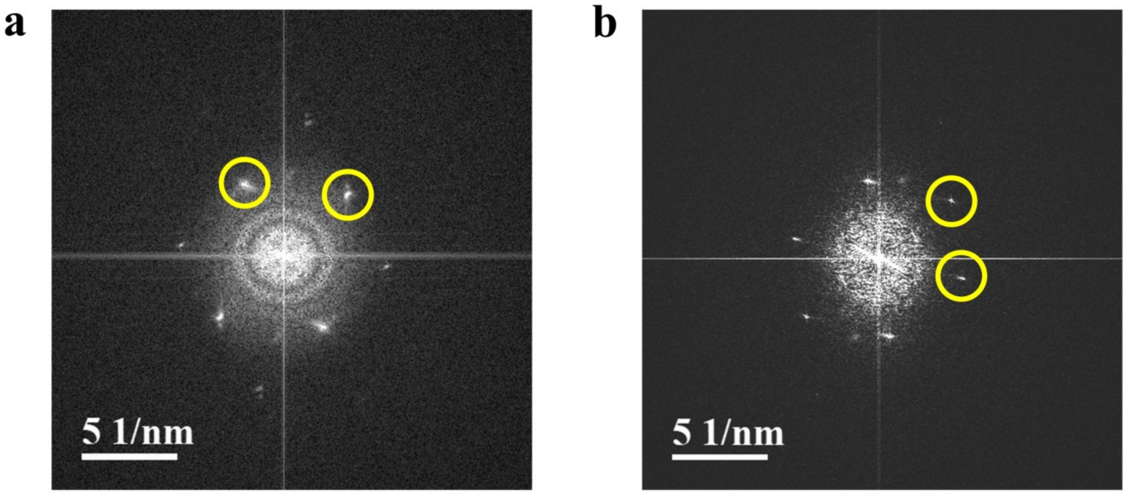

Fig. S10. Diffraction spots in the yellow boxes in the FFT images of (a) control and (b) 4 % HBr-$Cs_2AgBiBr_6$ are used for geometric phase analysis.

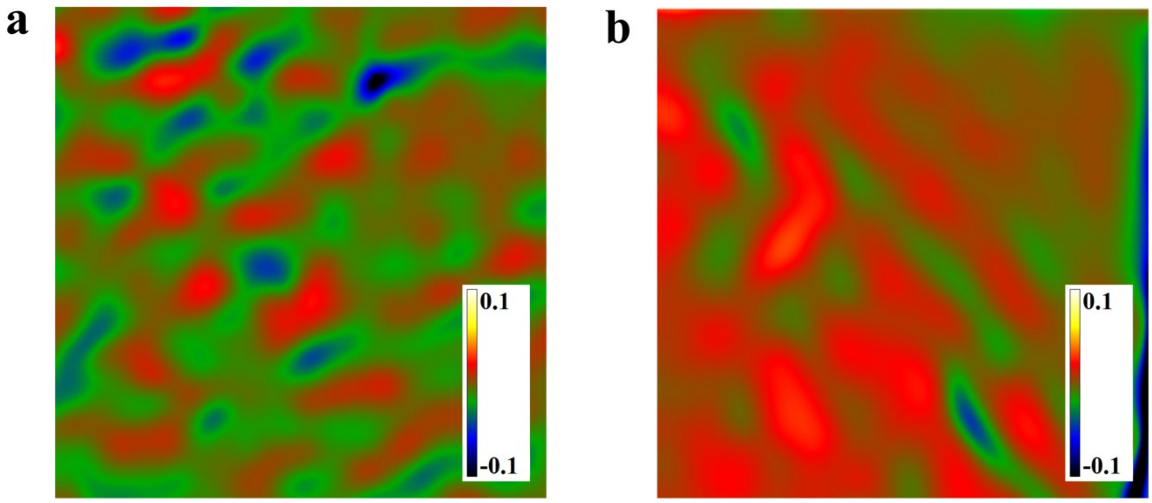

Fig. S11. Mean dilatation (D_{xy}) component of (a) control and (b) 4 % HBr-$Cs_2AgBiBr_6$.

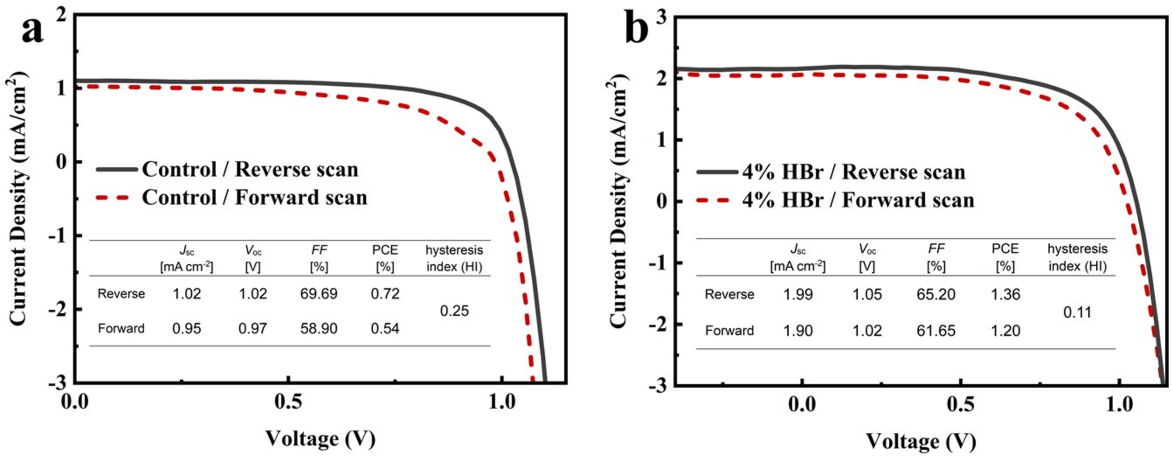

Fig. S12. *J-V* curves of (a) control and (b) 4% HBr-$Cs_2AgBiBr_6$ PSCs measured under reverse scan and forward scan directions. The hysteresis index is defined as $(PCE_{Reverse} - PCE_{Forward})/PCE_{Reverse}$.[6]

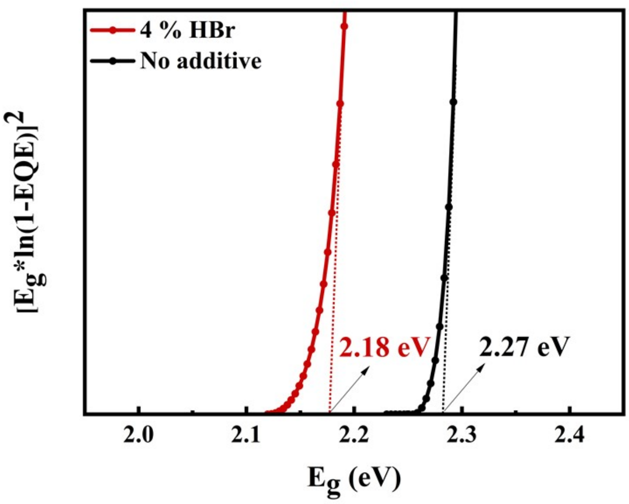

Fig. S13. The bandgap of control and 4 % HBr-$Cs_2AgBiBr_6$ PSCs as calculated by the EQE.

Table S1. Performance parameters of control PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.77	0.99	46.12	0.81	11	1.48	0.94	50.73	0.70
2	1.77	0.99	43.61	0.76	12	1.74	0.98	40.49	0.69
3	1.53	0.93	53.03	0.76	13	1.55	0.95	45.66	0.67
4	1.54	0.94	52.40	0.76	14	1.54	0.95	45.73	0.67
5	1.50	0.94	53.20	0.75	15	1.52	0.95	46.11	0.66
6	1.63	0.94	48.92	0.75	16	1.49	0.98	44.15	0.64
7	1.56	0.95	49.65	0.73	17	1.45	0.96	45.81	0.64
8	1.63	0.91	48.00	0.71	18	1.21	1.00	52.10	0.63
9	1.68	0.95	44.33	0.71	19	1.49	0.94	44.22	0.62
10	1.12	1.03	60.53	0.70	20	1.17	1.01	51.21	0.60

Table S2. Performance parameters of 1 % HCl-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.51	0.96	59.64	0.87	11	1.30	0.96	56.91	0.71
2	1.32	0.99	64.13	0.84	12	1.26	0.97	58.17	0.71
3	1.49	0.95	56.76	0.80	13	1.30	0.97	56.25	0.70
4	1.41	0.97	58.37	0.79	14	1.36	0.95	53.20	0.68
5	1.44	0.94	55.79	0.75	15	1.13	1.01	59.03	0.67
6	1.34	0.93	60.31	0.75	16	1.24	0.93	55.61	0.64
7	1.47	0.94	53.98	0.75	17	1.22	0.95	55.21	0.64
8	1.34	0.93	59.21	0.74	18	1.34	0.93	49.81	0.62
9	1.38	0.96	55.53	0.74	19	1.23	0.92	53.94	0.61
10	1.26	0.99	58.07	0.72	20	1.46	0.91	45.62	0.61

Table S3. Performance parameters of 2 % HCl-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.43	0.94	60.32	0.82	11	1.36	0.96	58.82	0.76
2	1.45	0.95	59.05	0.81	12	1.35	0.96	57.77	0.75
3	1.42	0.94	60.17	0.80	13	1.32	0.97	58.53	0.75
4	1.37	0.96	59.97	0.79	14	1.40	0.95	56.40	0.75
5	1.40	0.95	58.90	0.78	15	1.32	0.96	58.98	0.74
6	1.34	0.97	60.29	0.78	16	1.42	0.95	54.04	0.73
7	1.35	0.96	59.72	0.78	17	1.34	0.97	54.96	0.71
8	1.37	0.96	58.60	0.78	18	1.31	0.97	53.25	0.68
9	1.39	0.95	58.62	0.77	19	1.24	0.97	55.36	0.66
10	1.36	0.96	59.00	0.77	20	1.23	0.92	55.93	0.63

Table S4. Performance parameters of 3 % HCl-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.70	0.97	59.25	0.98	11	1.86	0.91	47.94	0.81
2	2.50	0.94	39.03	0.91	12	2.02	0.96	41.11	0.80
3	2.29	0.93	42.08	0.89	13	2.13	0.84	42.89	0.76
4	2.39	0.92	39.65	0.88	14	1.91	0.98	40.67	0.76
5	2.47	0.92	38.06	0.87	15	2.13	0.84	42.04	0.75
6	2.20	0.86	45.50	0.86	16	2.07	0.85	42.30	0.74
7	2.10	0.88	45.49	0.85	17	1.93	0.97	39.73	0.74
8	2.31	0.92	39.34	0.84	18	1.77	1.00	40.21	0.71
9	2.18	0.69	54.75	0.82	19	1.96	1.04	34.34	0.70
10	2.16	0.69	54.94	0.81	20	2.13	1.02	31.75	0.69

Table S5. Performance parameters of 4 % HCl-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	2.23	0.90	52.60	1.05	11	1.47	0.97	65.72	0.94
2	2.24	0.88	52.67	1.04	12	1.69	0.97	56.71	0.93
3	2.20	0.80	58.35	1.03	13	1.96	0.97	49.27	0.93
4	2.23	0.91	49.44	1.01	14	1.52	0.96	63.54	0.93
5	1.66	0.99	59.56	0.98	15	1.50	0.97	63.94	0.93
6	1.70	0.98	58.51	0.98	16	1.51	0.96	63.74	0.92
7	1.72	0.98	57.94	0.98	17	1.91	0.97	49.43	0.91
8	1.71	0.98	57.75	0.96	18	1.68	0.96	56.26	0.91
9	1.61	0.99	59.76	0.96	19	1.35	1.05	62.24	0.89
10	1.59	1.00	60.06	0.96	20	1.63	0.95	53.29	0.82

Table S6. Performance parameters of 5 % HCl-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.71	1.03	51.39	0.90	11	1.60	1.01	50.84	0.82
2	1.48	0.95	63.73	0.90	12	1.49	0.92	59.39	0.81
3	1.52	0.95	61.97	0.89	13	1.57	1.00	51.42	0.81
4	1.76	1.02	49.35	0.88	14	1.56	1.01	50.48	0.80
5	1.49	0.94	62.50	0.88	15	1.60	1.01	48.46	0.78
6	1.53	0.92	60.74	0.86	16	1.52	1.01	49.63	0.76
7	1.51	0.93	59.95	0.84	17	1.50	1.01	47.77	0.72
8	1.88	1.01	44.37	0.84	18	1.47	1.05	44.67	0.69
9	1.51	0.93	59.86	0.84	19	2.03	0.91	45.70	0.84
10	1.46	0.93	61.49	0.83	20	2.07	0.90	44.70	0.83

Table S7. Performance parameters of 1 % HBr-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.73	0.93	52.40	0.85	11	1.73	0.89	52.01	0.80
2	1.53	0.89	61.83	0.84	12	1.42	0.90	62.47	0.80
3	2.01	0.92	44.95	0.83	13	1.90	0.93	44.72	0.79
4	1.76	0.91	52.16	0.83	14	1.47	0.89	60.30	0.78
5	1.69	0.93	52.40	0.83	15	1.45	0.89	60.56	0.78
6	1.94	0.93	45.20	0.82	16	1.35	0.91	61.47	0.75
7	1.43	0.88	60.99	0.77	17	1.31	0.90	60.91	0.72
8	1.40	0.90	63.38	0.80	18	1.30	0.89	61.56	0.72
9	1.40	0.90	63.67	0.80	19	1.39	0.91	55.83	0.71
10	1.81	0.94	46.69	0.80	20	1.32	0.89	59.60	0.70

Table S8. Performance parameters of 2 % HBr-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	2.37	0.94	48.98	1.09	11	2.14	0.74	55.90	0.89
2	2.28	0.97	49.30	1.09	12	1.42	0.96	64.32	0.88
3	2.16	0.98	50.13	1.06	13	1.47	0.96	61.54	0.86
4	2.00	1.00	52.13	1.04	14	1.38	0.97	64.63	0.86
5	2.30	0.88	51.03	1.03	15	1.71	0.99	50.86	0.86
6	2.25	0.89	51.69	1.03	16	1.80	0.93	50.33	0.84
7	2.29	0.96	44.24	0.97	17	1.58	1.00	52.60	0.83
8	1.85	1.03	50.79	0.96	18	1.44	0.90	63.48	0.82
9	1.51	0.96	63.55	0.92	19	1.47	1.04	52.92	0.81
10	1.51	0.96	61.91	0.90	20	1.81	0.90	47.76	0.78

Table S9. Performance parameters of 3 % HBr-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	2.00	0.98	62.09	1.22	11	1.98	0.95	59.29	1.12
2	2.02	0.98	61.11	1.21	12	1.92	0.96	59.71	1.10
3	1.82	0.98	65.58	1.17	13	1.85	0.95	62.01	1.09
4	2.04	0.96	59.85	1.17	14	1.87	0.94	61.20	1.08
5	1.98	0.98	59.16	1.15	15	1.61	1.01	65.68	1.07
6	2.03	0.96	58.46	1.14	16	1.89	0.93	60.45	1.06
7	1.89	1.00	60.66	1.14	17	1.95	0.94	56.14	1.03
8	1.96	0.98	59.14	1.13	18	1.85	1.00	53.30	0.99
9	1.98	0.96	59.33	1.13	19	1.73	0.98	53.86	0.91
10	1.89	1.00	58.86	1.12	20	1.64	1.00	54.49	0.89

Table S10. Performance parameters of 4 % HBr-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.99	1.05	65.63	1.36	11	1.81	1.05	62.48	1.19
2	2.01	1.03	64.24	1.33	12	1.86	1.01	62.54	1.17
3	2.03	1.02	64.08	1.33	13	2.10	0.97	57.02	1.16
4	2.05	1.01	62.42	1.30	14	1.87	0.95	64.83	1.16
5	1.84	1.07	64.42	1.28	15	1.87	0.99	59.96	1.11
6	1.81	1.00	68.86	1.24	16	1.64	0.99	68.20	1.10
7	2.02	1.00	61.43	1.24	17	1.95	0.97	58.22	1.10
8	1.81	0.99	68.78	1.23	18	1.89	0.97	59.45	1.10
9	2.08	0.98	59.04	1.20	19	1.65	0.99	66.81	1.09
10	1.74	1.00	68.71	1.20	20	1.93	0.96	58.63	1.08

Table S11. Performance parameters of 5 % HBr-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.74	0.91	51.50	0.82	11	1.82	0.98	40.37	0.72
2	1.77	0.99	46.12	0.81	12	1.51	1.04	45.80	0.72
3	1.79	0.99	44.41	0.79	13	1.37	0.93	56.14	0.71
4	1.77	0.99	43.61	0.76	14	1.37	0.93	56.19	0.71
5	1.35	0.93	59.99	0.75	15	1.40	1.04	48.69	0.71
6	1.43	0.92	55.77	0.74	16	1.10	1.06	60.45	0.70
7	1.40	1.04	50.30	0.73	17	1.47	0.79	55.02	0.64
8	1.42	0.92	55.45	0.73	18	1.37	0.89	51.57	0.63
9	1.33	0.93	58.53	0.73	19	1.21	1.03	49.61	0.61
10	1.77	0.99	41.35	0.72	20	1.38	0.83	52.89	0.60

Table S12. Performance parameters of 1 % HI-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.80	0.76	34.80	0.48	11	1.39	0.47	46.09	0.30
2	1.40	0.54	48.11	0.36	12	1.40	0.47	42.25	0.28
3	1.52	0.52	44.57	0.35	13	1.66	0.75	22.05	0.28
4	1.03	0.89	38.28	0.35	14	1.52	0.61	29.83	0.28
5	1.48	0.48	47.52	0.34	15	1.41	0.58	32.99	0.27
6	1.50	0.51	44.35	0.34	16	1.41	0.46	40.18	0.26
7	1.34	0.48	51.23	0.33	17	1.69	0.42	30.77	0.22
8	1.55	0.62	32.94	0.31	18	1.66	0.44	29.90	0.22
9	1.17	0.79	33.89	0.31	19	1.08	0.58	31.95	0.20
10	1.52	0.66	30.43	0.31	20	1.03	0.65	26.43	0.18

Table S13. Performance parameters of 2 % HI-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	2.08	0.84	44.44	0.78	11	1.53	0.82	39.69	0.50
2	1.99	0.83	44.07	0.73	12	1.50	0.81	39.39	0.48
3	1.97	0.82	42.87	0.70	13	1.49	0.80	39.19	0.47
4	1.96	0.82	41.81	0.67	14	1.49	0.81	38.25	0.46
5	1.93	0.80	39.84	0.62	15	1.03	0.93	37.80	0.36
6	1.93	0.85	37.56	0.62	16	1.03	0.87	39.68	0.36
7	1.72	0.83	38.21	0.55	17	1.09	0.82	36.79	0.33
8	1.55	0.83	42.48	0.54	18	1.13	0.77	35.13	0.31
9	1.56	0.84	41.68	0.54	19	0.93	0.85	36.34	0.29
10	1.66	0.83	38.42	0.53	20	1.07	0.78	32.53	0.27

Table S14. Performance parameters of 3 % HI-$Cs_2AgBiBr_6$ PSCs.

No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	No.	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.40	0.97	44.51	0.61	11	1.81	0.72	34.89	0.46
2	1.40	0.97	44.74	0.60	12	1.66	0.72	37.00	0.44
3	1.89	0.79	38.68	0.58	13	1.76	0.70	35.36	0.44
4	1.68	0.83	39.51	0.55	14	1.05	0.86	37.22	0.34
5	1.89	0.77	37.35	0.54	15	0.87	0.86	39.69	0.30
6	1.76	0.79	38.58	0.53	16	1.19	0.58	36.04	0.25
7	1.30	0.92	43.70	0.52	17	1.20	0.58	35.35	0.25
8	1.28	0.91	44.36	0.52	18	1.25	0.60	29.31	0.22
9	1.25	0.95	43.53	0.52	19	1.09	0.41	31.54	0.14
10	1.88	0.73	36.04	0.49	20	1.47	0.30	30.26	0.13

Table S15. The average photovoltaic parameters of Control, 4 % HCl-$Cs_2AgBiBr_6$, 4 % HBr-$Cs_2AgBiBr_6$ and 2 % HI-$Cs_2AgBiBr_6$ PSCs.

	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
Control	1.54 ± 0.23	0.96 ± 0.05	47.65 ± 5.55	0.70 ± 0.11
4% HCl	1.76 ± 0.36	0.96 ± 0.07	57.54 ± 8.11	0.95 ± 0.13
4% HBr	1.90 ± 0.25	1.00 ± 0.04	63.16 ± 4.95	1.20 ± 0.16
2% HI	1.53 ± 0.60	0.83 ± 0.05	39.31 ± 5.13	0.50 ± 0.28

Table S16. Performance parameters of 0.77% H_2O-$Cs_2AgBiBr_6$ and 3.10% H_2O-$Cs_2AgBiBr_6$ PSCs.

0.77% H_2O	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]	3.10% H_2O	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF* [%]	PCE [%]
1	1.90	0.93	44.72	0.79	1	1.29	0.94	53.25	0.65
2	1.81	0.94	46.69	0.79	2	1.26	0.98	51.15	0.64
3	1.94	0.92	43.35	0.77	3	1.76	0.99	36.10	0.63
4	1.90	0.92	43.68	0.77	4	0.93	1.06	61.79	0.61
5	1.83	0.93	45.06	0.77	5	1.29	0.94	48.78	0.59
6	1.15	1.03	60.53	0.70	6	1.19	1.04	44.77	0.55
7	1.11	1.04	58.82	0.68	7	0.94	0.99	57.95	0.54
8	1.29	0.94	53.25	0.65	8	1.28	0.99	40.83	0.52
9	1.26	0.98	51.15	0.64	9	0.84	1.00	60.40	0.51
10	1.29	0.94	48.78	0.59	10	0.85	1.04	53.96	0.48

Table S17. Five groups of pH values of 4% HBr-$Cs_2AgBiBr_6$ and 4% HCl-$Cs_2AgBiBr_6$ tested by pH meter.

	1	2	3	4	5	Average
4% HBr-$Cs_2AgBiBr_6$	1.83	1.85	1.84	1.83	1.80	1.83
4% HCl-$Cs_2AgBiBr_6$	1.85	1.84	1.84	1.81	1.86	1.84

Table S18. Atomic ratios of Control and 4 % HBr-$Cs_2AgBiBr_6$ films measured by XPS.

Atomic [%]	C	O	Cs	Ag	Bi	Br
Control	44.26	17.11	9.15	3.77	2.44	23.27
4 % HBr	35.20	20.79	9.26	4.18	2.70	25.49

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