Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

TBAB additive for inorganic $CsPbI_{2.4}Br_{0.6}$ perovskite solar cells with efficiency beyond 15%

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Experimental section

1. Materials and precursor solution preparation

SnO_2-colloid precursor (tin(IV) oxide, 15% in H_2O colloidal dispersion), N,N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, >99.8%), Chlorobenzene (CB, 99.9%), Molybdenum(VI) oxide (MoO_3, 99.998%) and silver (Ag, 99.99%) were purchased from Alfa Aesar. Zinc acetate dihydrate (>99%), ethanolamine (99.5%), cesium iodide (CsI, 99.999%) and lead bromide ($PbBr_2$, 99.999%) were purchased from Sigma-Aldrich. Lead iodide (PbI_2, 99.99%) and 2-methoxyethanol (>99.0%) were purchased from TCI. Tetrabutylammonium bromide (TBAB, >99%) was purchased from Acros. Poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) was purchased from Xi'an Polymer Light Technology Corp. Unless otherwise stated, all solvents and chemicals were used without further purification.

2. Precursor solution preparation

The ZnO precursor solution was prepared according to literature [1].

The $CsPbI_{2.4}Br_{0.6}$ precursor solution (0.8 M) was prepared by dissolving CsI (0.8 M), PbI_2 (0.56 M) and $PbBr_2$ (0.24 M) in a mixture of DMF and DMSO (v/v 4:1), then, was stirred at 60 °C overnight in a N_2 glovebox.

A certain amount of TBAB was dissolved in DMF and stirred for 2 h at room temperature. The $CsPbI_{2.4}Br_{0.6}$ -TBAB precursor solution was prepared by adding TBAB DMF solution to the above $CsPbI_{2.4}Br_{0.6}$ precursor solution, and stirred for 2 h.

The PTAA solution was prepared by dissolving PTAA (10 mg) in 1 mL of CB solution.

The $PC_{61}BM$ solution was prepared by dissolving $PC_{61}BM$ (15 mg) in 1 mL of CB solution.

3. Device fabrication

Perovskite solar cells

Perovskite solar cells were fabricated with the structure of ITO/SnO_2/ZnO/PVSK/PTAA/MoO_3/Ag. Patterned ITO substrates with a sheet resistance of 15 Ω sq^{-1} were ultrasonically cleaned by using detergent, deionized water, acetone, isopropanol sequentially, and then treated with UV-ozone for 10min. A thin layer of SnO_2 nanoparticle film was obtained by annealing the substrates at 150 °C for 30 min after spin-coated at 3000 rpm for 30s. Then, the ZnO precursor solution was spin-coated onto substrates (4000 rpm for 30 s). The films were annealed at 200 °C in the air for 20 min. Next, the different perovskite precursor solutions were spin-coated onto ITO/SnO_2/ZnO substrates at 2000 rpm for 40s, respectively. Subsequently, the films were annealed at 320 °C for 10 min. PTAA layer was formed by spin-coating the related precursor onto the perovskite film. Finally, MoO_3 (~6 nm) and Ag (~80 nm) was successively evaporated onto the substrates through a shadow mask (pressure ca. 10^{-4} Pa). The active area for the device is 0.04 cm^2.

Electron-only devices

The structure for electron-only devices is ITO/SnO_2/ZnO/perovskite/$PC_{61}BM$/Ag. SnO_2, ZnO, and perovskite layer were successively spin-coated onto the ITO substrates. The processes are just the same as those of PSCs fabrication. $PC_{61}BM$ layer was formed by spin-coating the related precursor onto the perovskite film (4000 rpm for 30 s). Finally, Ag (~80 nm) was evaporated onto the substrates through a shadow mask (pressure ca. 10^{-4} Pa). *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter in the dark.

4. Characterization

Absorption spectra were measured with a Shimadzu UV-1800 spectrophotometer. Photoluminescence (PL) spectra were recorded on NanoLOG-TCSPC. The 410 nm light was applied as the photon excitation light. X-ray diffraction (XRD) patterns were obtained on

D/MAX-TTRIII (CBO) with Cu Kα radiation (λ = 1.542 Å) operating at 40 kV and 200 mA. Scanning electron microscopy (SEM) was performed on a Hitachi SU8220. The grain size was estimated using Nano Measure software. *J-V* curves were measured by using a computerized Keithley 2400 SourceMeter and a Xenon-lamp-based solar simulator (Enli Tech, AM 1.5G, 100 mW cm^{-2}). The illumination intensity of solar simulator was determined by using a monocrystalline silicon solar cell (Enli SRC2020, 2cm×2cm) calibrated by NIM. The devices were measured in reverse scan (1.3 to -0.20 V, step 0.02 V).The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

References

[1] Sun Y, Seo JH, Takacs CJ et al. Inverted polymer solar cells integrated with a low-temperature-annealed sol-gel-derived ZnO film as an electron transport layer. Adv Mater 2011; 23:1679-1683.

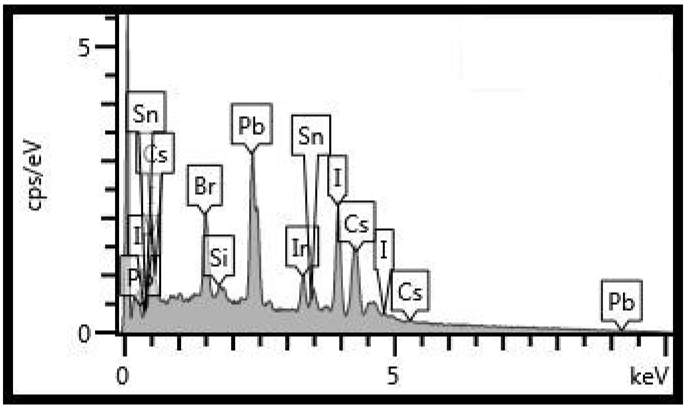

Fig. S1 EDS pattern for the $CsPbI_{2.4}Br_{0.6}$-TBAB film.

Table S1 The element contents for the $CsPbI_{2.4}Br_{0.6}$-TBAB film.

Element	Cs	Pb	I	Br
Content (at%)	18.76	17.05	40.14	10.19

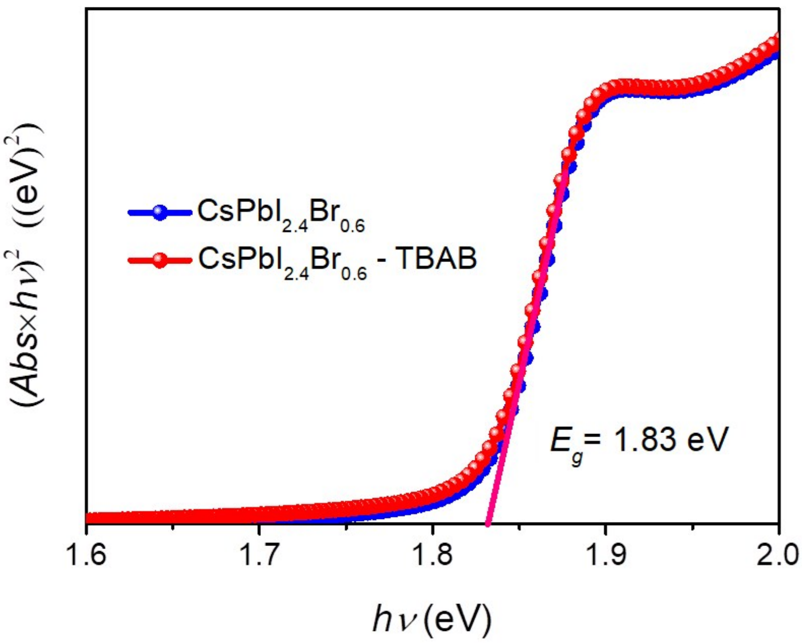

Fig. S2 Tauc plots of $CsPbI_{2.4}Br_{0.6}$ and $CsPbI_{2.4}Br_{0.6}$ - TBAB films possessing a direct bandgap.

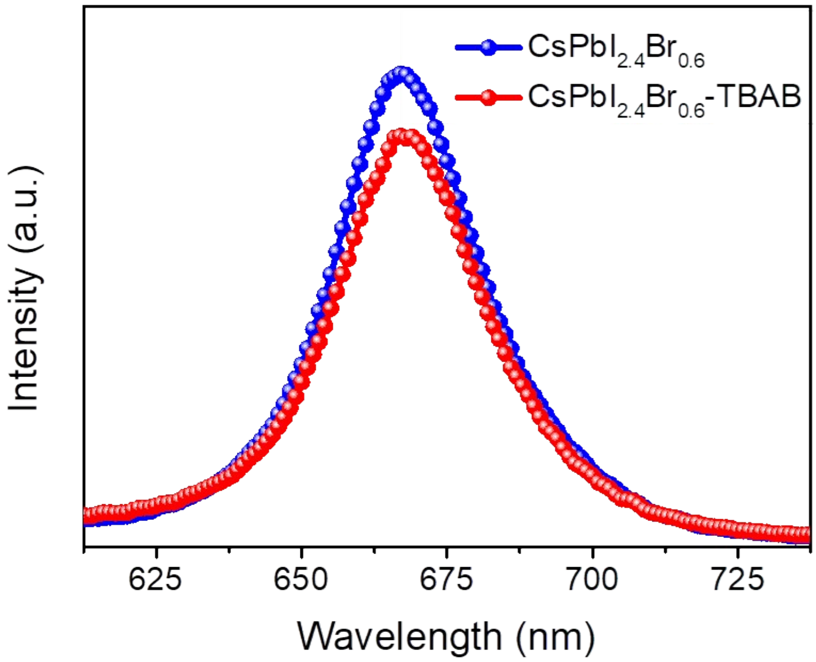

Fig. S3 PL spectra for glass/SnO_2/ZnO/$CsPbI_{2.4}Br_{0.6}$ and glass/SnO_2/ZnO/$CsPbI_{2.4}Br_{0.6}$ - TBAB.

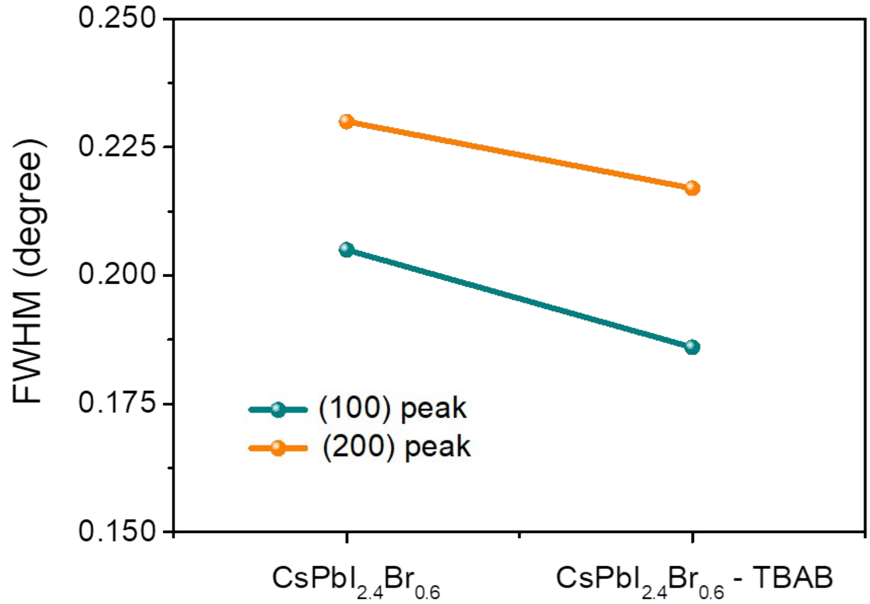

Fig. S4 FWHM of the (100) and (200) peak for $CsPbI_{2.4}Br_{0.6}$ and $CsPbI_{2.4}Br_{0.6}$ - TBAB films.

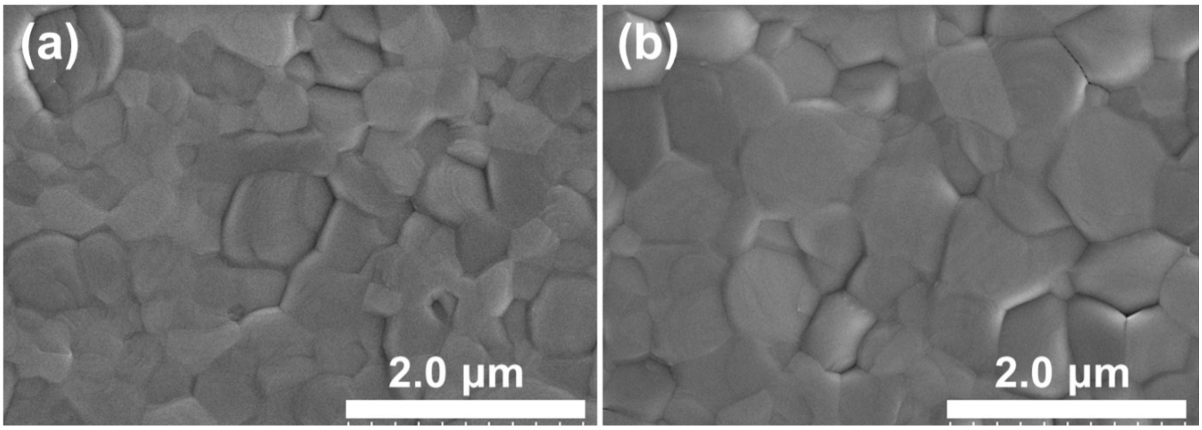

Fig. S5 SEM images for $CsPbI_{2.4}Br_{0.6}$ and $CsPbI_{2.4}Br_{0.6}$ - TBAB films on glass/ITO/SnO_2/ZnO substrates.

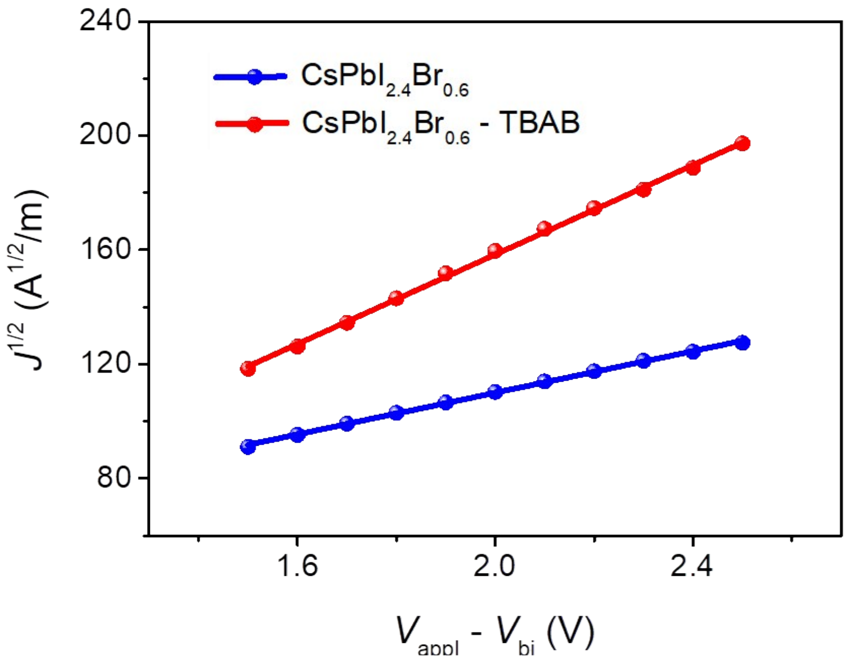

Fig. S6 $J^{1/2}$-V plots for the electron-only devices (in dark).

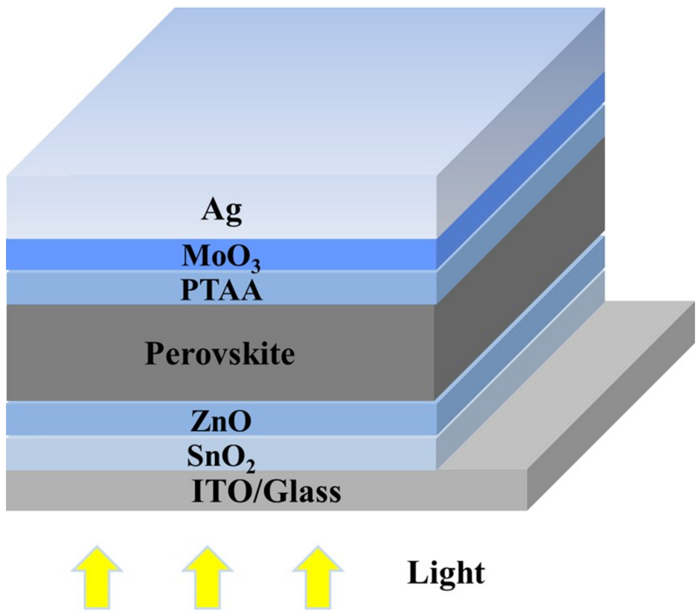

Fig. S7 Structure of perovskite solar cells.

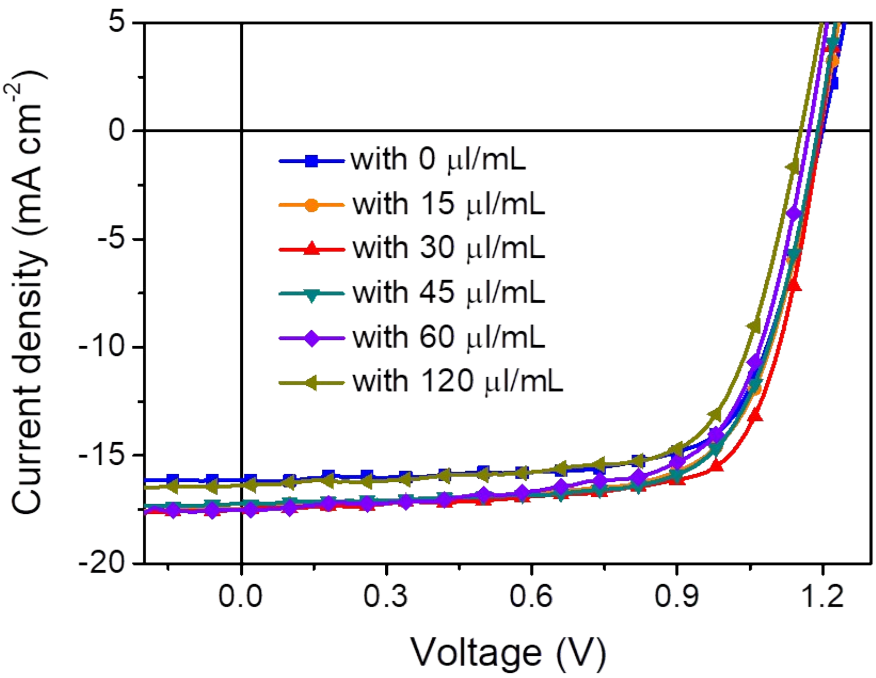

Fig. S8 *J-V* curves for $CsPbI_{2.4}Br_{0.6}$ solar cells made with different additive concentrations (annealing temperature 320 °C, annealing time 10 min).

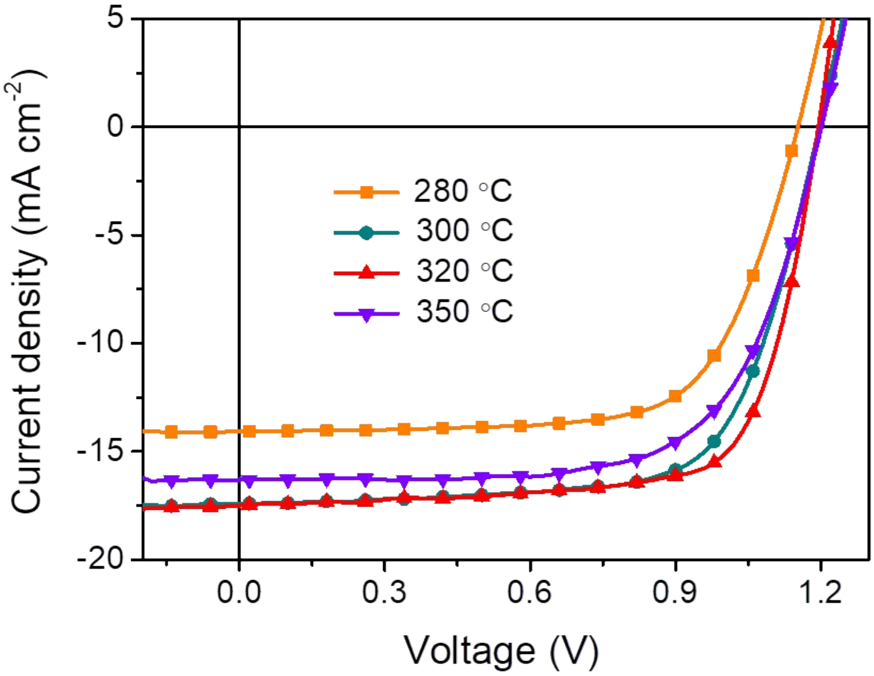

Fig. S9 *J-V* curves for $CsPbI_{2.4}Br_{0.6}$ solar cells with different annealing temperature (30 µl/mL TBAB, annealing time 10 min).

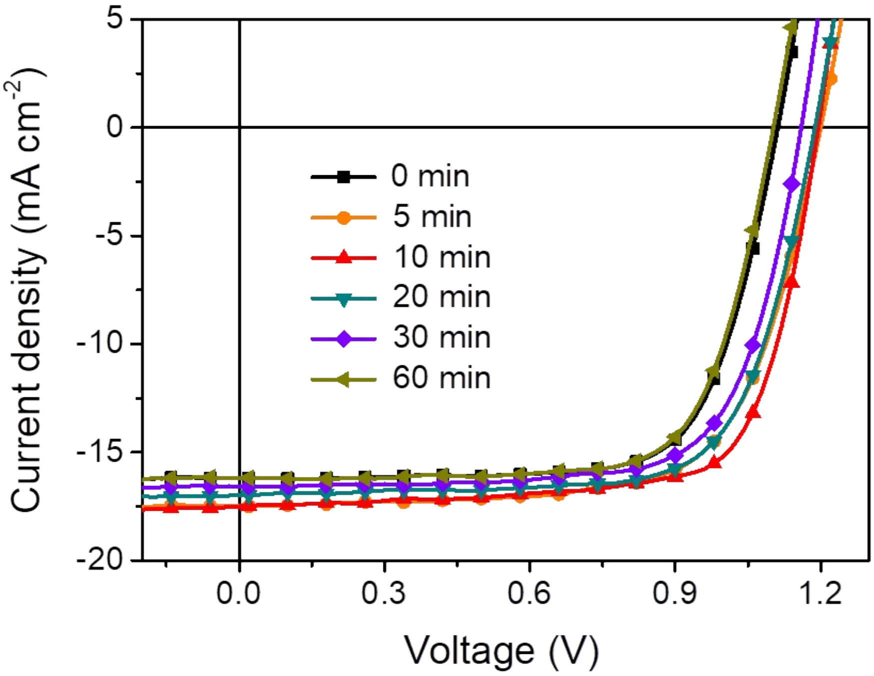

Fig. S10 *J-V* curves for $CsPbI_{2.4}Br_{0.6}$ solar cells with different annealing time (30 µl/mL TBAB, annealing temperature 320 °C).

Table S2 Effect of TBAB content in precursor solution on performance of $CsPbI_{2.4}Br_{0.6}$ solar cells.[a]

TBAB [μL/mL]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0	1.20	16.16	70.94	13.75 (13.60)[b]
15	1.19	17.48	69.00	14.41 (14.22)
30	1.20	17.50	72.75	15.21 (15.05)
45	1.19	17.25	70.71	14.51 (14.35)
60	1.17	17.52	67.79	13.92 (13.62)
120	1.15	16.39	70.33	13.31 (12.97)

[a]Annealing at 320 °C for 10 min;

[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S3 Effect of annealing temperature for $CsPbI_{2.4}Br_{0.6}$ layer on performance of $CsPbI_{2.4}Br_{0.6}$ solar cells.[a]

Annealing temperature [°C]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
280	1.15	14.08	69.00	11.20 (10.71)[b]
300	1.20	17.43	69.28	14.45 (14.08)
320	1.20	17.50	72.75	15.21 (15.05)
350	1.20	16.31	66.90	13.11 (12.96)

[a]30 μL/mL TBAB in precursor solution; annealing for 10 min.

[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S4 Effect of annealing time for $CsPbI_{2.4}Br_{0.6}$ layer on performance of $CsPbI_{2.4}Br_{0.6}$ solar cells.[a]

Annealing time [min]	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]
0	1.11	16.19	72.18	12.99 (12.78)[b]
5	1.20	17.49	68.51	14.38 (14.05)
10	1.20	17.50	72.75	15.21 (15.05)
20	1.19	16.99	71.16	14.37 (14.08)
30	1.16	16.57	71.24	13.69 (13.43)
60	1.10	16.18	72.40	12.92 (12.77)

[a]30 μL/mL TBAB in precursor solution; annealing at 320 °C.

[b]Data in parentheses stand for the average PCEs for 10 cells.

Table S5 A summary of the detail performance parameters of reported inorganic perovskite (PVSK) solar cells.

Perovskite (PVSK)	Device structure	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	Ref.
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Ag	0.66	11.92	52.47	4.13	J. Phys. Chem. Lett. 2016, 7, 3603
$CsPbI_3$	FTO/TiO_2/PVSK/P3HT/MoO_3/Au	0.74	10.48	61	4.68	Sol. Energy Mater. Sol. Cells 2016, 144, 532
$CsPbI_3$	ITO/TiO_2/PVSK/P3HT/Au	1.06	13.8	67.7	10.5	J. Phys. Chem. Lett. 2017, 8, 67
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Au	1.11	14.88	65	10.74	Nat. Commun. 2018, 9, 1076
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/MoO_3/Al	1.23	13.47	65	10.77	Science 2016, 354, 92

$CsPbI_3$	FTO/TiO_2/PVSK/P3HT/Au	1.04	16.53	65.7	11.3	J. Am. Chem. Soc. 2018, 140, 11716
$CsPbI_3$	ITO/PTAA/PVSK/PCBM/C_{60}/BCP/Cathode	1.08	14.9	70	11.4	Joule 2017, 1, 371
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Ag	1.15	14.53	71	11.86	Sci. Adv. 2017, 3, e1700841
$CsPbI_3$	ITO/SnO_2/PVSK/Spiro-OMeTAD/Au	1.07	16.59	70	12.4	Joule 2018, 2, 1356
$CsPbI_3$	FTO/TiO_2/PVSK/PTB7/MoO_3/Ag	1.27	12.39	80	12.55	Joule 2018, 2, 2450
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/MoOx/Al	1.20	14.37	78	13.4	Sci. Adv. 2017, 3 , eaao4204
$CsPbI_3$	FTO/TiO_2/PVSK/PTAA/Au	1.06	18.95	74.9	15.07	Nat. Commun. 2018, 9, 4544
$CsPbI_3$	ITO/SnO_2/PVSK/Spiro-OMeTAD/Au	1.08	18.41	79.32	15.71	Nat. Commun. 2018, 9, 2225
$CsPbI_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Ag	1.1	19.15	80.6	17.06	J. Am. Chem. Soc. 2018, 140, 12345
$CsPbI_2Br$	FTO/NiMgLiO/PVSK/PCBM/BCP/Ag	0.98	14.18	66	9.14	Materials Today Energy 2018, 8, 125
$CsPbI_2Br$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Ag	1.11	11.89	75	9.84	Adv. Energy Mater. 2016, 6, 1502458
$CsPbI_2Br$	ITO/SnO_2/PVSK/Carbon	1.19	12.91	66.1	10.13	J. Phys. Chem. Lett. 2019, 10, 194
$CsPbI_2Br$	ITO/NiO_x/PVSK/C_{60}/BCP/Ag	1.05	12.6	78.7	10.4	Adv. Energy Mater. 2018, 1800758
$CsPbI_2Br$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Au	1.23	12	73	10.7	J. Phys. Chem. Lett. 2017, 8, 2936
$CsPbI_2Br$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Ag	1.17	13.98	74	12	Adv. Energy Mater. 2018, 8, 1801050
$CsPbI_2Br$	FTO/TiO_2/PVSK/PTAA/Au	1.19	12.93	80.5	12.39	Adv. Energy Mater. 2018, 8, 1703246
$CsPbI_2Br$	ITO/SnO_2/PVSK/Spiro-OMeTAD/Ag	1.06	15.99	77.12	13.09	ACS Photonics 2018, 5, 4104

$CsPbI_2Br$	FTO/NiO_x/PVSK/ZnO@C_{60}/Ag	1.14	15.2	77	13.3	J. Am. Chem. Soc. 2018, 140, 3825
$CsPbI_2Br$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Au	1.18	14.89	77.23	13.54	Adv. Sci. 2018, 5, 1801117
$CsPbI_2Br$	FTO/NiO_x/PVSK/ZnO@C_{60}/Ag	1.14	15.7	77	13.74	Adv. Energy Mater. 2018, 9, 1803572
$CsPbI_2Br$	FTO/TiO_2/PVSK/FA^+CsPbX_3/FA^+QDs/PTAA/Au	1.22	14.51	79.6	14.12	Adv. Sci. 2018, 5, 1801123
$CsPbI_2Br$	FTO/TiO_2/PVSK/$CsPbI_3$ QDs/PTAA/Au	1.2	15.25	78.7	14.45	Joule 2018, 2, 1500
$CsPbI_2Br$	ITO/SnO_2/ZnO/PVSK/Spiro-OMeTAD/MoO_3/Ag	1.23	15	78.8	14.6	Adv. Mater. 2018, 30, 1802509
$CsPbI_2Br$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Au	1.22	15.33	78.7	14.78	Adv. Funct. Mater. 2018, 28, 1803269
$CsPbI_2Br$	FTO/TiO_2/PVSK/FA^+CsPbX_3/FA^+QDs/PTAA/Au	1.22	15.1	80.3	14.81	Nano Energy 2018, 52, 408
$CsPbI_2Br$	FTO/c-TiO_2/PVSK/Spiro-OMeTAD/Au	1.23	16.79	77.81	16.07	Joule 2018, 3, 191
$CsPbI_2Br$	ITO/SnO_2/PN4N/$CsPbI_2Br$/PDCBT/MoO_3/Ag	1.30	15.3	81.5	16.2	Adv. Mater. 2019, 1901152
$CsPbI_{1.2}Br_{1.8}$	FTO/TiO_2/PVSK/PTAA/Au	1.33	9.7	64	8.2	Adv. Energy Mater. 2018, 8, 1802060
$CsPbI_{1.5}Br_{1.5}$	FTO/TiO_2/PVSK/PTAA/Au	1.28	11	65	9.1	Adv. Energy Mater. 2018, 8, 1802060
$CsPbI_{1.8}Br_{1.2}$	FTO/TiO_2/PVSK/PTAA/Au	1.29	12.3	65	10.3	Adv. Energy Mater. 2018, 8, 1802060
$CsPbIBr_2$	FTO/TiO_2/PVSK/Au	0.96	8.7	56	4.7	Adv. Energy Mater. 2016, 6, 1502202
$CsPbIBr_2$	FTO/NiO_x/PVSK/ZnO/Al	1.01	8.65	63.6	5.57	Nat. Mater. 2018, 17, 261
$CsPbIBr_2$	FTO/TiO_2/PVSK/Carbon	0.96	12.15	53	6.14	Adv. Energy Mater. 2018, 8, 1800504

$CsPbIBr_2$	FTO/c-TiO_2/PVSK/Carbon	1.14	9.11	63	6.55	ACS Appl. Energy Mater. 2018, 1, 4991
$CsPbIBr_2$	ITO/SnO_2/PVSK/Carbon	1.23	8.5	67	7	J. Mater. Chem. A,2019, 7, 1227
$CsPbIBr_2$	ITO/SnO_2/C_{60}/PVSK/Spiro-OMeTAD/Au	1.18	8.32	74.8	7.34	Adv. Energy Mater. 2018, 8, 1800525
$CsPbIBr_2$	FTO/TiO_2/PVSK/Carbon	1.08	12.32	62	8.25	J. Am. Chem. Soc. 2017, 139, 14009
$CsPbIBr_2$	FTO/c-TiO_2/PVSK/Carbon	1.25	10.66	69	9.16	Adv. Energy Mater. 2018, 8, 1802080
$CsPbBr_3$	FTO/TiO_2/PVSK/Carbon	1.29	5.7	68	5	ACS Appl. Mater. Interfaces 2016, 8, 33649
$CsPbBr_3$	FTO/TiO_2/PVSK/Spiro-OMeTAD/Au	1.5	5.6	62	5.4	Nat. Energy 2016, 2, 16194
$CsPbBr_3$	FTO/TiO_2/PVSK/PTAA/Au	1.25	6.7	73	6.2	J. Phys. Chem. Lett. 2016, 7, 167
$CsPbBr_3$	FTO/TiO_2/PVSK/Carbon	1.24	7.4	73	6.7	J. Am. Chem. Soc. 2016, 138, 15829
$CsPbBr_3$	FTO/ZnO/PVSK/Spiro-OMeTAD/Au	1.43	6.17	77.2	6.81	ACS Appl. Mater. Interfaces 2018, 10, 7145
$CsPbBr_3$	ITO/ZnO/PVSK/Spiro-OMeTAD/Au	1.44	7.01	77.11	7.78	Adv. Mater. 2018, 30, 1800855
$CsPbBr_3$	FTO/TiO_2/CQD/PVSK/Spiro-OMeTAD/Ag	1.06	11.34	69	8.29	Adv. Mater. 2017, 29, 1703682
$CsPbBr_3$	FTO/TiO_2/PVSK/Carbon	1.52	7.35	84.3	9.43	Angew.Chem.Int. Ed. 2018, 57,5746
$CsPbBr_3$	FTO/TiO_2/PVSK/Carbon	1.46	8.12	82.1	9.72	Angew. Chem. Int. Ed. 2018, 57, 3787

$CsPb_{0.97}Sm_{0.03}Br_3$	FTO/c-TiO_2/m-TiO_2/PVSK/carbon	1.59	7.48	85.1	10.14	Adv. Energy Mater. 2018, 8, 1802346
$CsPb_{0.97}Tb_{0.03}Br_3$	FTO/c-TiO_2/m-TiO_2/PVSK/SnS:ZnS/NiO_x/carbon	1.57	8.21	79.6	10.26	J. Mater. Chem. A,2018, 6, 24324
$CsPbBr_3$	FTO/SQE36/$CsPbBr_3$/$CsSnBr_3$/carbon	1.61	7.8	84.4	10.6	Sol. RRL 2019, 3, 1800284
$CsPbI_{2.4}Br_{0.6}$	ITO/SnO_2/ZnO/PVSK/PTAA/MoO_3/Ag	1.20	17.50	72.75	15.21	this work

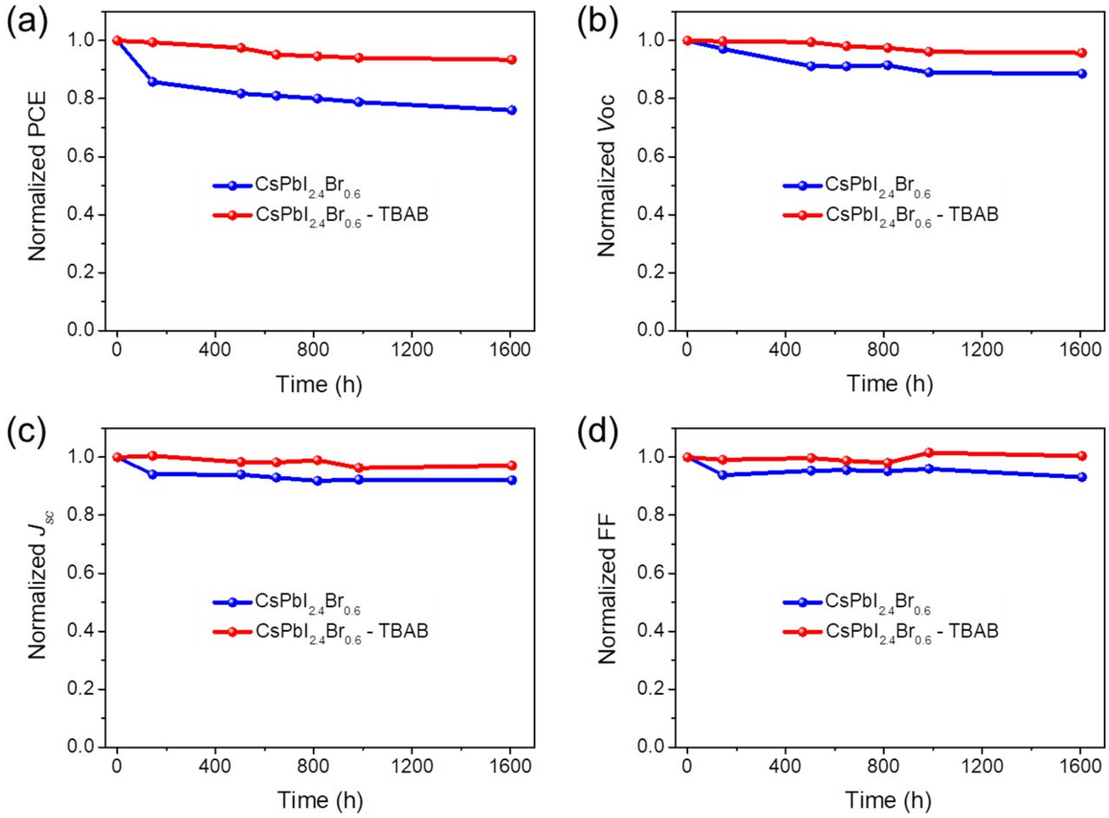

Fig. S11 The normalized (a) PCE, (b) V_{oc}, (c) J_{sc}, and (d) FF for $CsPbI_{2.4}Br_{0.6}$ and $CsPbI_{2.4}Br_{0.6}$ - TBAB based PSCs as a function of storage time in a N_2 glovebox.

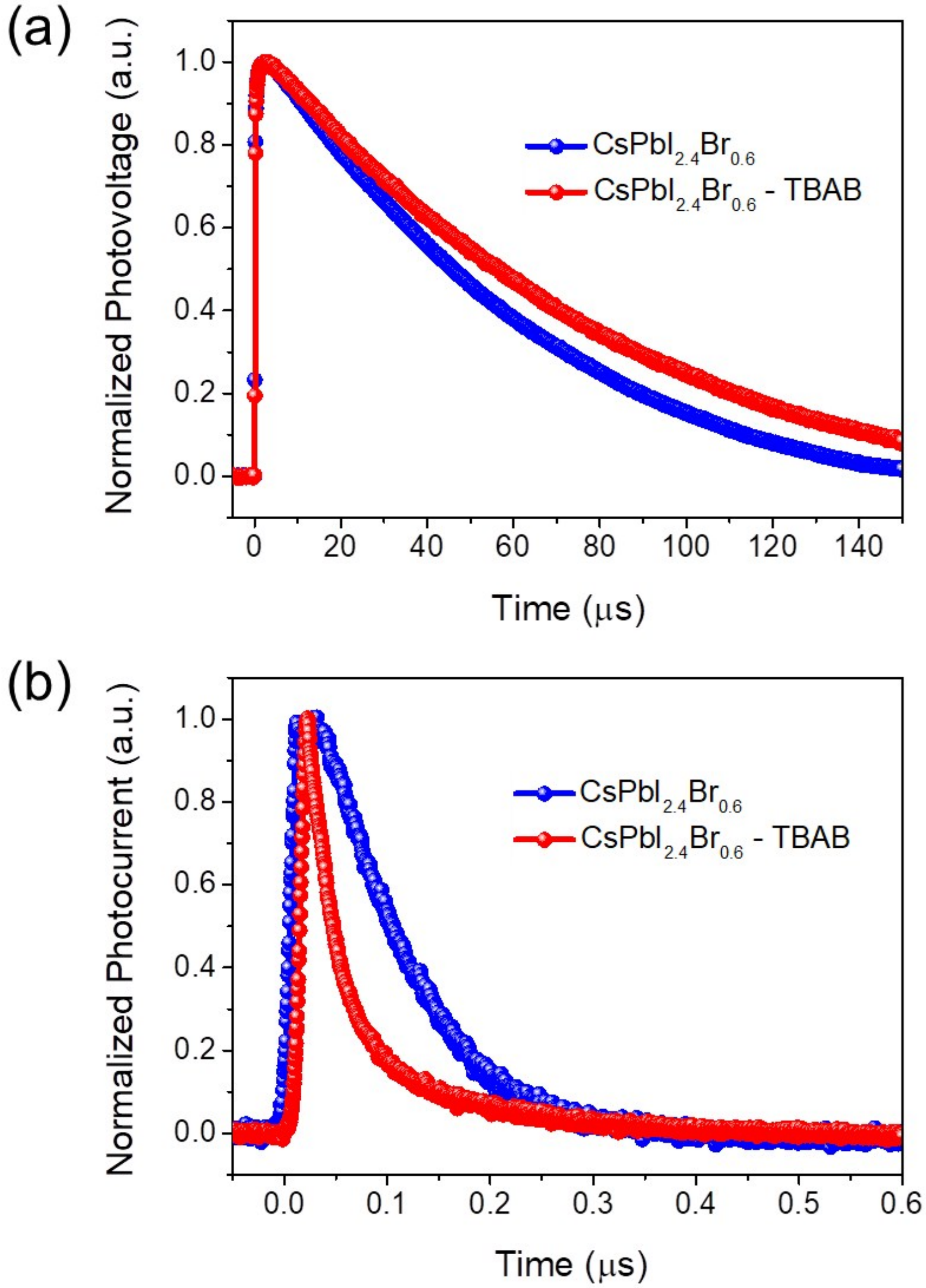

Fig. S12 TPV and TPC for $CsPbI_{2.4}Br_{0.6}$ and $CsPbI_{2.4}Br_{0.6}$ - TBAB based PSCs.