

<Electronic Supplementary Information>

Two-step Growth of $\text{CsPbI}_{3-x}\text{Br}_x$ Films Employing Dynamic CsBr Treatment: Toward All-inorganic Perovskite Photovoltaics with Enhanced Stability

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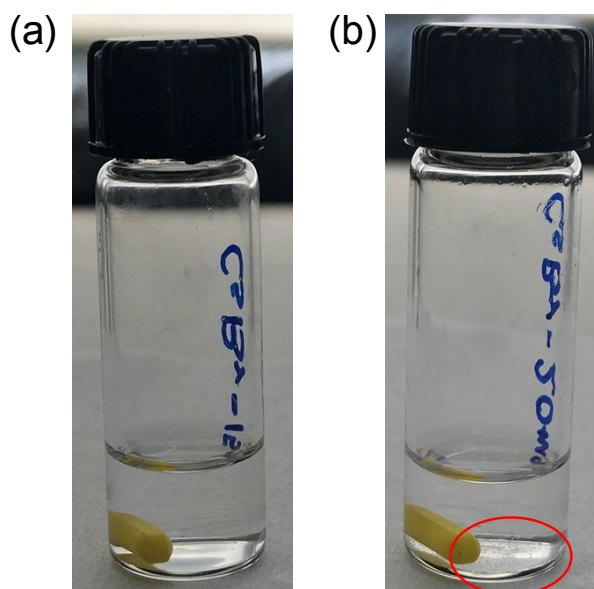


Figure S1. Photographic images showing the solubility of (a) 15 mg and (b) 20 mg CsBr in 1 mL of methanol.

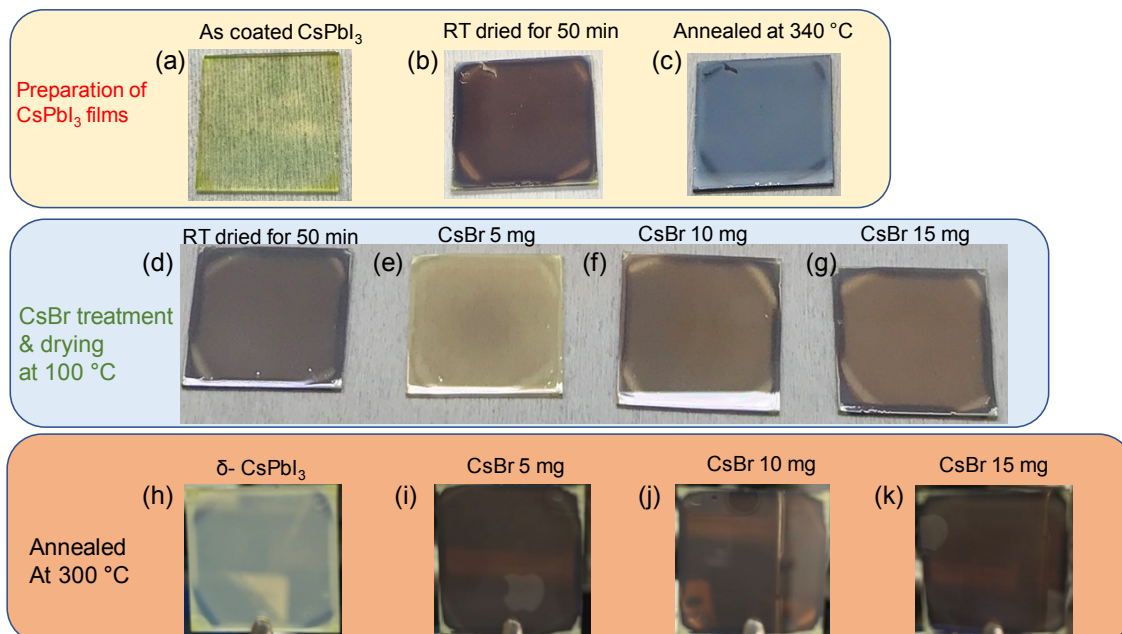


Figure S2. Photographic images of the fabrication process for α -CsPbI_{3-x}Br_x perovskite films (a-c) without and (e-g) with a dynamic coating of various concentrations of CsBr (5–15 mg) and drying at 100 °C and (i-k) annealing at 300 °C. (d) The α -CsPbI₃ film prepared using room temperature (RT) drying that (h) degraded to δ -CsPbI₃ after annealing at 300 °C.

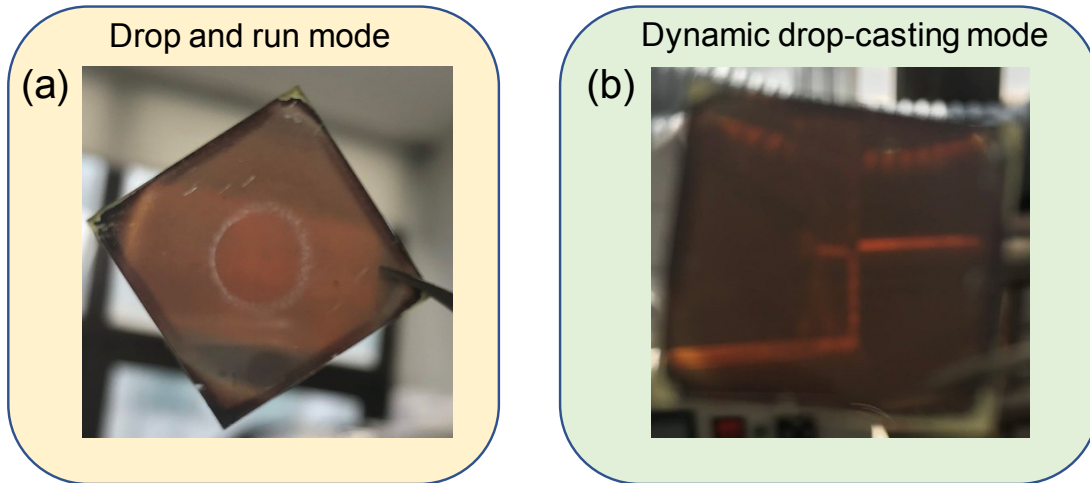


Figure S3. Photographic images of α -CsPbI_{3-x}Br_x perovskite films prepared using the (a) drop and run and (b) dynamic drop-casting of a 15-mg CsBr solution.

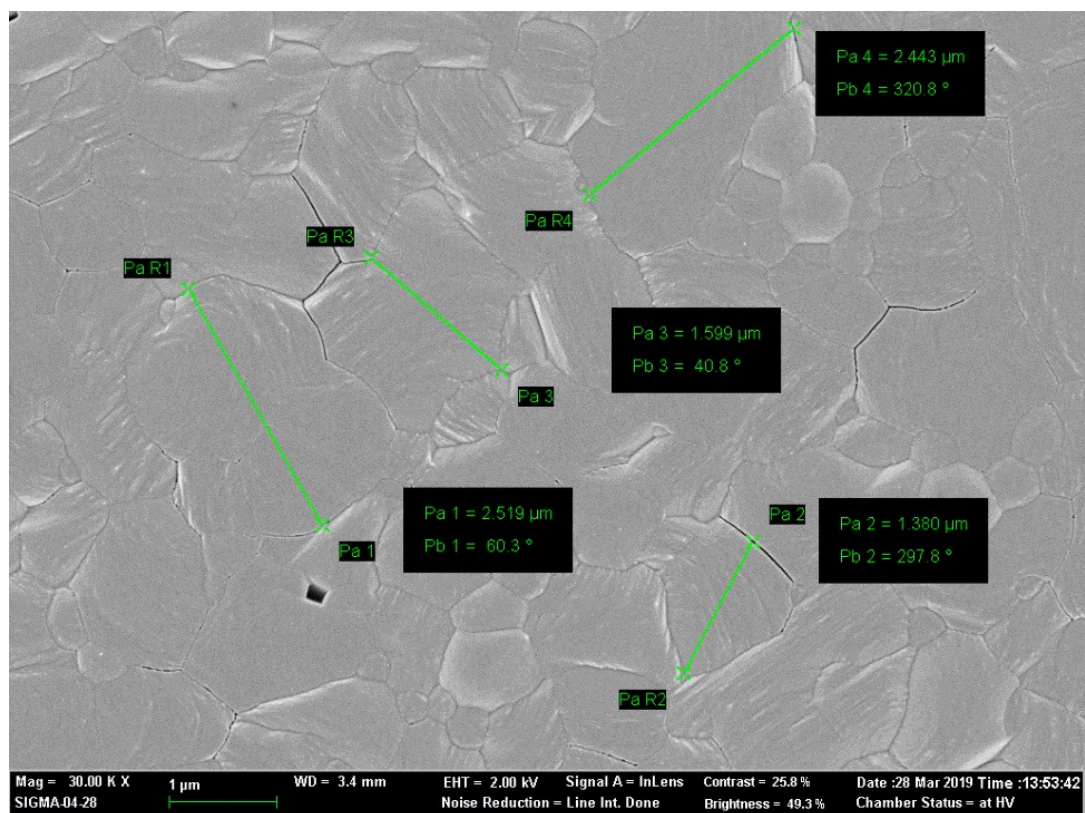


Figure S4. Top-view FE-SEM images of CsBr-15 perovskite film with grain sizes over 2 μm .

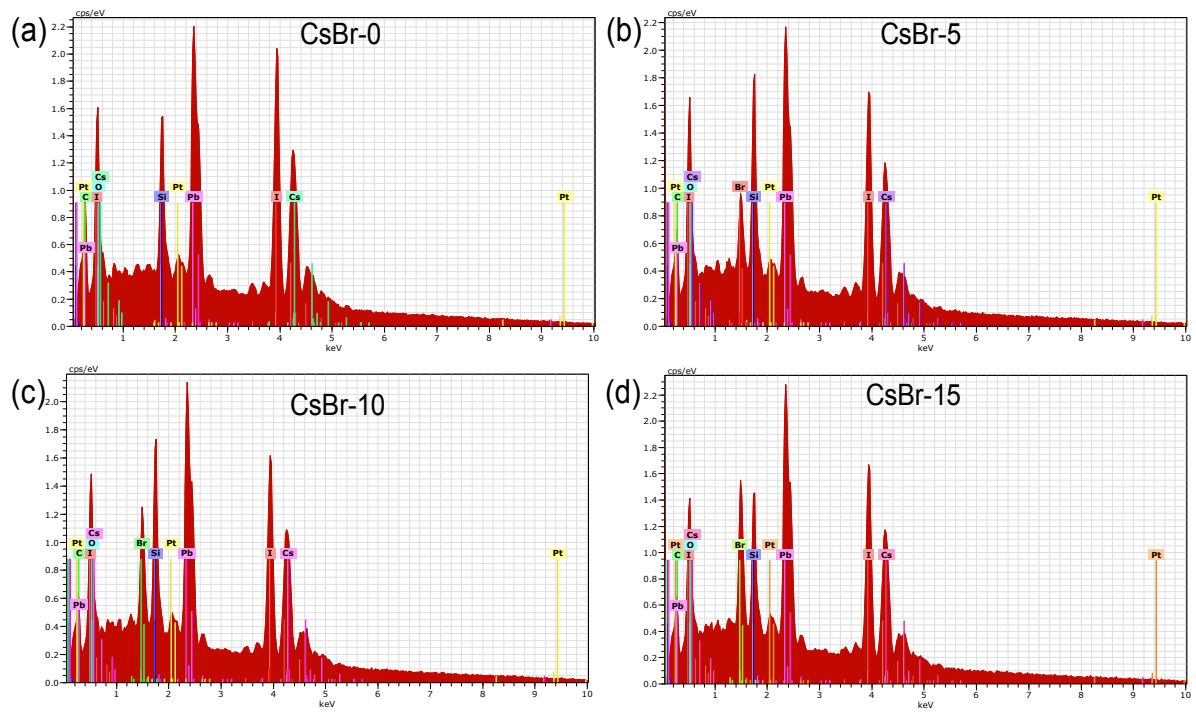


Figure S5. EDX spectra of the (a) CsBr-0, (b) CsBr-5, (c) CsBr-10, and (d) CsBr-15 perovskite films prepared with and without a dynamic CsBr coating.

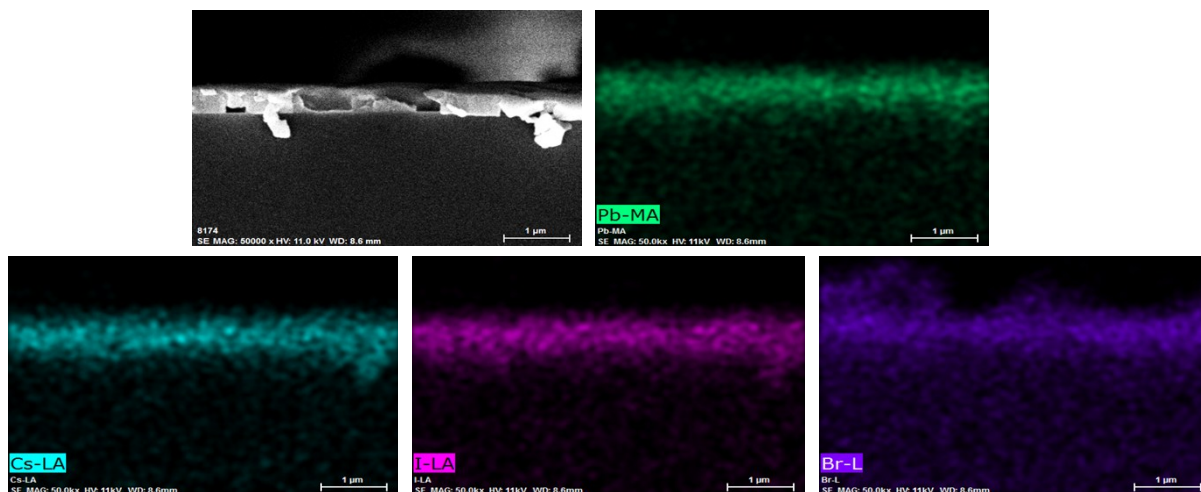


Figure S6. Cross-sectional EDX mapping profile of the CsBr-15 perovskite film.

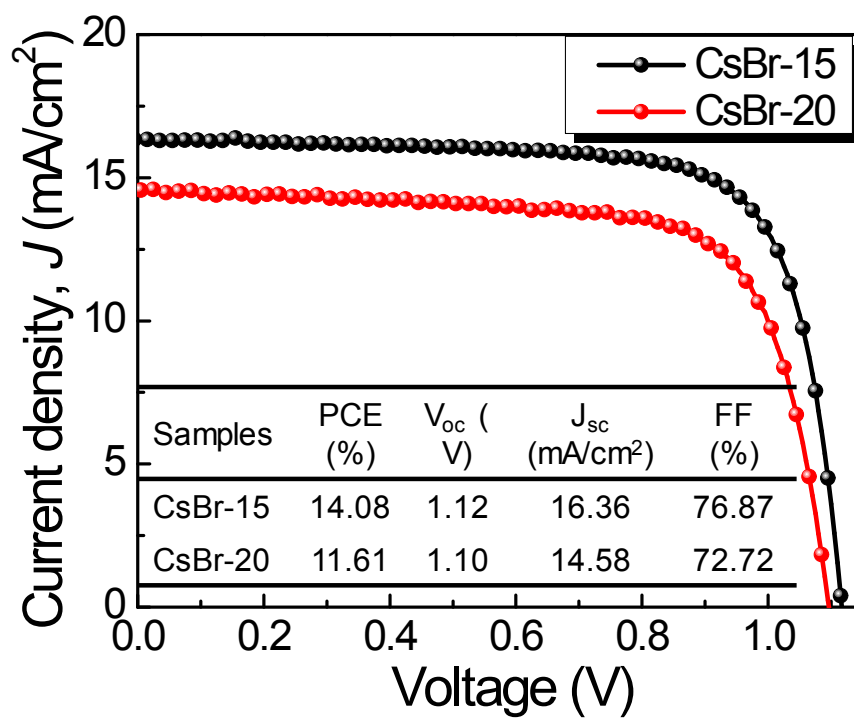


Figure S7. J–V characteristic curves for the CsPbI_{3-x}Br_x inorganic PSCs fabricated with a dynamic CsBr coating using the increased precursor concentration (20 mg/mL, heated at 50 °C) as well as the property of the champion CsBr-15 device (CsBr 15 mg/mL at room temperature).

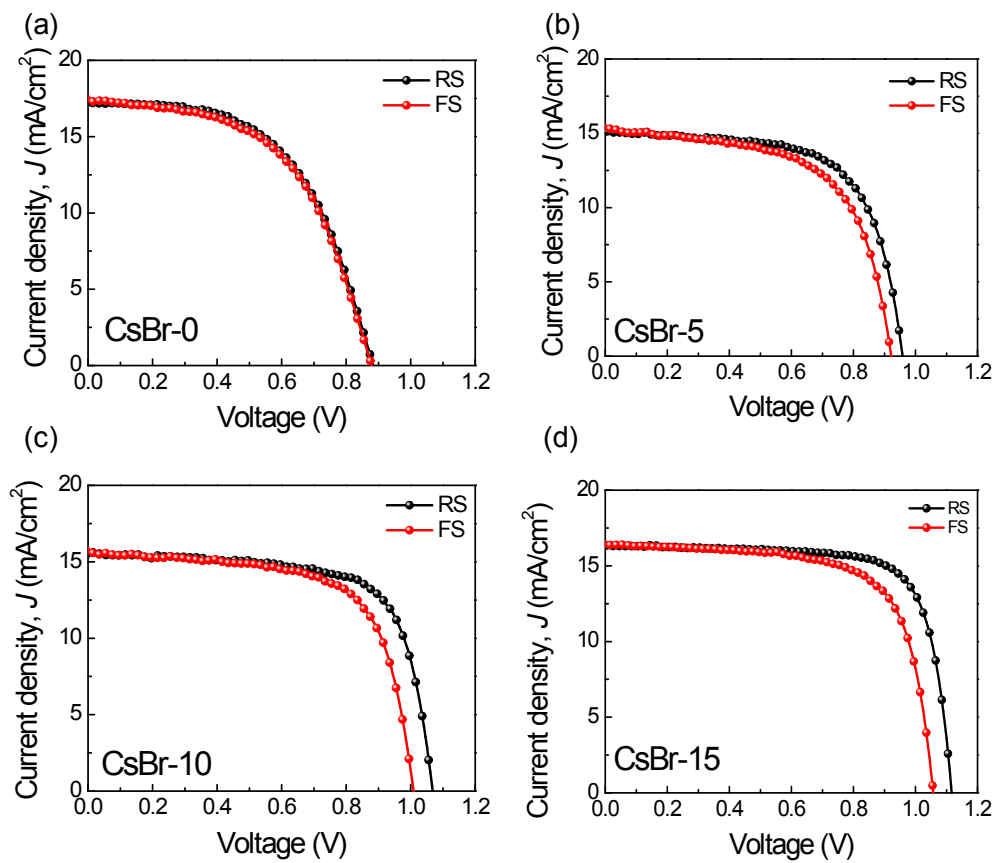


Figure S8. Hysteresis behavior of the CsPbI_{3-x}Br_x PSCs fabricated (a) without CsBr and (b-d) with dynamic CsBr-5, CsBr-10, and CsBr-15 coatings as revealed by reverse and forward scans.

Table S1. Hysteresis behavior of the CsPbI_{3-x}Br_x PSCs fabricated (a) without CsBr and (b-d) with dynamic treatment CsBr-5, CsBr-10, and CsBr-15 coatings as revealed by reverse and forward scans.

Sample	Direction	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
CsBr-0	RS	8.40	0.88	17.20	56.47
	FS	8.33	0.87	17.44	54.69
CsBr-5	RS	9.63	0.96	15.23	66.02
	FS	8.66	0.92	15.58	60.46
CsBr-10	RS	11.81	1.06	15.54	71.33
	FS	10.66	1.01	15.88	66.77
CsBr-15	RS	14.08	1.12	16.36	76.87
	FS	12.18	1.06	16.29	69.90

Table S2. A summary of stability results on recently reported inorganic PSCs.

Ref. No.	Device structure	Temp. (°C)	R.H. (%)	Initial PCE (%)	PCE Decay (%)	Storage Time (h)
N ₂ atmosphere						
R2.1	ITO/ZnO/ Cs _{1.2} PbI ₂ Br _{1.2} /P3HT/Au	70	< 20	9.8	30	500
R2.2	FTO/NiMgLiO/CsPbI ₂ Br /PCBM/BCP/Ag	85	< 20	9.14	10	500
R2.3	FTO/PTAA/CsPbI ₃ /PCBM/BCP/Ag	RT	< 10	13.32	15	720
R2.4	FTO/TiO ₂ /CsPbI ₃ -PTABr/Spiro-OMeTAD/Au	RT	< 10	17.06	9	500
Our work	ITO/TiO ₂ /CsPbI _{3-x} Br _x /P3HT/Au	RT	<10	14.08	30	1200
Air atmosphere						
R2.5	FTO/TiO ₂ /Cs _{0.925} K _{0.075} PbI ₂ Br /Spiro-OMeTAD/Au	RT	20	10.0	20	144
[24]	FTO/TiO ₂ /CsPbI _{2.98} Br _{0.2} /Spiro-OMeTAD/Au	RT	20	10.92	0	192
R2.6	FTO/TiO ₂ /CsPbI ₂ Br ₂ /Spiro-OMeTAD/Au	RT	25	7.31	50	100
[14]	FTO/TiO ₂ /CsPb _{0.96} Bi _{0.04} I ₃ /CuI/Au	RT	55	13.21	32	168
R2.7	FTO/TiO ₂ /CsPbI ₃ QDs/Spiro-OMeTAD/MoO _x /Al	RT	40-60	10.77	74	48
Our work	ITO/TiO ₂ /CsPbI _{3-x} Br _x /P3HT/Au	85	40	14.08	0	48

[R2.1] L. A. Frolova, Q. Chang, S. Y. Luchkin, D. Zhao, A. F. Akbulatov, N. N. Dremova, A. V. Ivanov, E. E. M. Chia, K. J. Stevenson and P. A. Troshin, Efficient and stable all-inorganic perovskite solar cells based on nonstoichiometric Cs_xPbI₂Br_x (x > 1) alloys, *J. Mater. Chem. C*, 2019,7, 5314-5323.

[R2.2] S. Zhang, S. Wu, W. Chen, H. Zhu, Z. Xiong, Z. Yang, C. Chen, R. Chen, L. Han and W. Chen, Solvent engineering for efficient inverted perovskite solar cells based on inorganic CsPbI₂Br light absorber, *Materials Today Energy* 2018, 8, 125-133.

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- [R2.5] J.K. Nam, S.U. Chai, W. Cha, Y.J. Choi, W. Kim, M.S. Jung, J. Kwon, D. Kim, J.H. Park, Potassium Incorporation for Enhanced Performance and Stability of Fully Inorganic Cesium Lead Halide Perovskite Solar Cells, *Nano Letters*, 17 (2017) 2028-2033.
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- [R2.7] A. Swarnkar, A.R. Marshall, E.M. Sanhira, B.D. Chernomordik, D.T. Moore, J.A. Christians, T. Chakrabarti, J.M. Luther, Quantum dot–induced phase stabilization of α -CsPbI₃ perovskite for high-efficiency photovoltaics, *Science*, 354 (2016) 92-95.

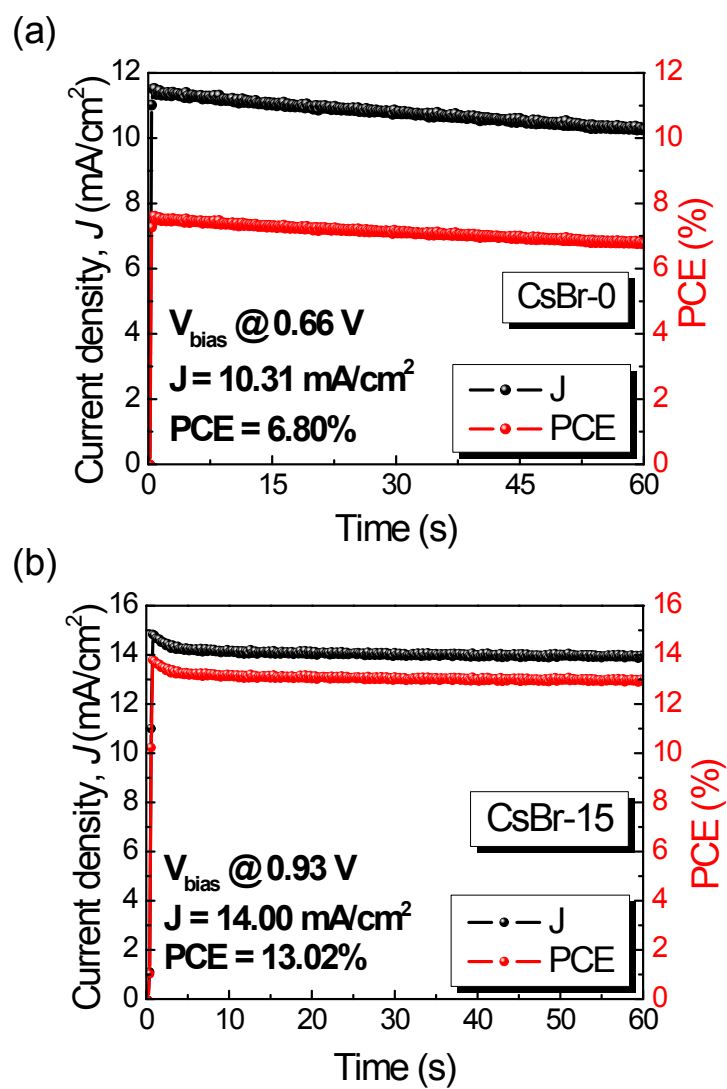


Figure S9. Stabilized photocurrent and PCE of the (a) CsBr-0 and (b) CsBr-15 inorganic PSCs.

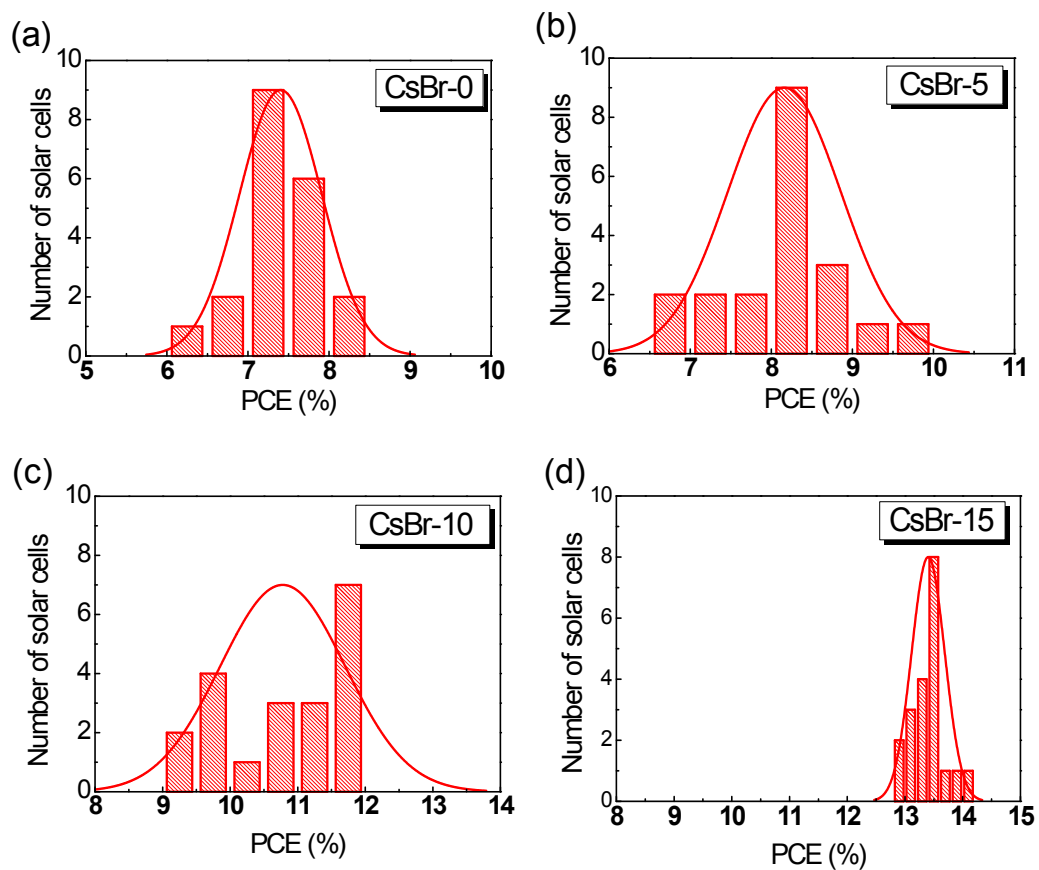


Figure S10. PCE distribution histograms for 20 devices of the $\text{CsPbI}_{3-x}\text{Br}_x$ PSCs fabricated (a) without CsBr (CsBr-0 , CsPbI_3) and (b-d) with dynamic CsBr-5, CsBr-10, and CsBr-15 treatment.

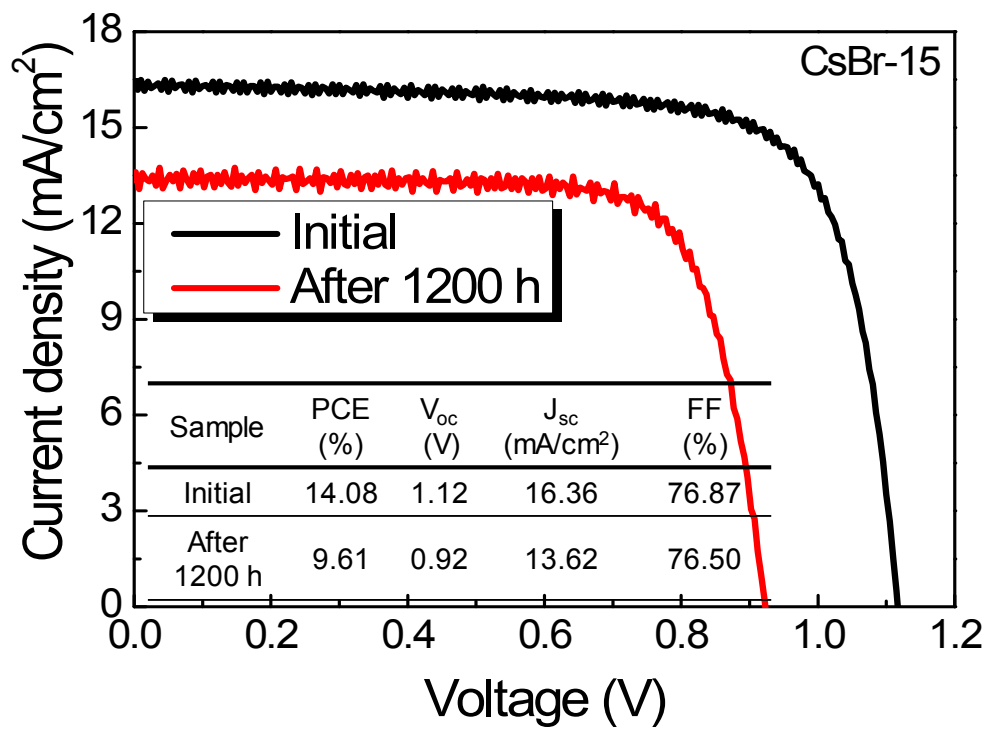


Figure S11. J-V curves (measured in atmospheric air ambient) of the unencapsulated CsBr-15 all-inorganic perovskite solar cells stored in a nitrogen-ambient for over 1200 h. The inset table presents the performance of fresh and stored devices.

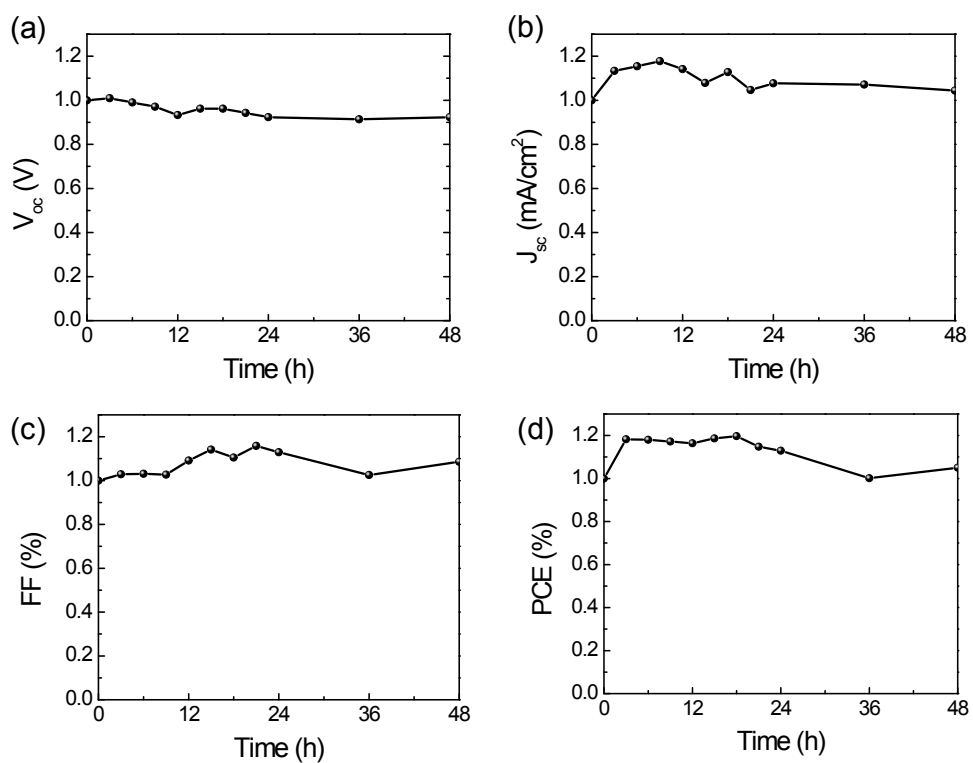


Figure S12. Normalized (a) V_{oc} , (b) J_{sc} (c) FF, and (d) PCE as a function of time for the CsBr-15 PSC without encapsulation, measured under ambient air at the temperature of 85 °C and RH of 40% for 48 h.