Supporting Information

for

Stepwise Volatilization Induced by Nature-Sourced Volatile Solid Additives Improving Efficiency and Stability of Perovskite Solar Cells

Jeewon Park^a, Seoyoung Kim^a, Wonjun Kim^a, Zhe Sun^a, Byongkyu Lee^a and Changduk Yang^{a,b*}

a. School of Energy and Chemical Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, South Korea.

b. Graduate School of Carbon Neutrality, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulju-gun, Ulsan 44919, South Korea.

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1. Materials

The SnO₂ (tin(IV) oxide, 15 wt%) colloid precursor was purchased from Alfa Aesar. N,Ndimethylforamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.9%), 2-propanol (IPA, 99.5%), acetonitrile (ACN, 99.9%), octylammonium iodide (OAI), camphor (CP), and camphorquinone (CQ), tert-butylpyridine (t-BP) were all obtained from Sigma-Aldrich. PbI₂ (99.99%) was purchased from Tokyo Chemical Industry UK Ltd. Formamidinium iodide (FAI, 99.99%), Methylammonium iodide (MAI, 99.99%), and Methylammonium chloride (MAI, 99.99%) were all obtained from Greatcell solar. Spiro-OMeTAD was purchased from Xian company.

2. Material characterizations

The density functional theory (DFT) calculations were implemented using the Gaussian 09 package with the nonlocal hybrid Becke three-parameter Lee–Yang–Parr (B3LYP) function and the 6-31G* basis. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted using a differential scanning calorimeter (TA instruments, USA) with a scan rate of 10 °C per minute. For fourier transform infrared (FT-IR) spectroscopy with attenuated Total Reflectance (ATR) mode was utilized using Varian, 670/620 model. Ultraviolet–visible (UV–vis) absorption spectra in solution and thin films were measured using a UV-1800 (SHIMADZU). Static and in-situ photoluminescence (PL) measurements and time-resolved PL (TRPL) were conducted using ELCT-3010 PL mode (Enlitech) and FS5 (Edinburgh instrument). X-ray Photoelectron Spectroscopy (XPS) was performed using K-alpha (ThermoFisher). ²⁰⁷Pb nuclear magnetic resonance (²⁰⁷Pb NMR) spectra of polymers were recorded on a Bruker AVANCE NEO 400 spectrometer using deuterated DMF:DMSO as the solvent. Dynamic light scattering (DLS) measurement was implemented by MALVERN Nano ZS 90 instrument. Liquid chromatograhpy-mass spectroscopy (LC-MS) was measured by Xevo G2 Tof (Waters).

3. Device fabrication

The PSCs were fabricated with a device structure of ITO or FTO/SNO₂/perovskite/OAI/spiro-OMeTAD/Au. The ITO of FTO substrates were cleaned, then irradiated by UV-ozone for 20 min before using. For the ITO substrate (7-8 Ω cm⁻²), a 30 nm of SnO₂ nanoparticle (NP) film (2.67 wt% in ammonium hydroxide) was spin coated on the substrate at 5000 rpm for 30 s and directly annealed at 180 °C for 20 min in ambient condition, then followed by UV-ozone treatment for 20 min. For FTO substrate (Asahi VU glass, 12-13 Ω cm⁻²), chemical bath deposition (CBD) of SnO₂ was carried out, where CBD solution was prepared by mixing SnCl₂ 2H₂O (137.5 mg), urea (625 mg), HCl (625 μ L), thioglycolic acid (12.5 μ L), and SnCl₂ 2H₂O per 50 mL of deionized water. The solution and FTO substrate were loaded to a reaction vessel and reacted at 90 °C for 5 h. Note that the ITO/NPs-SnO₂ substrates were used for most device characterization; the FTO/CBD-SnO₂ based devices were only used for champion efficiency and MPPT stability test. The CP (range from 15 mM to 60 mM) and CQ (range from 1.5 mM to 6 mM) treated Pbl₂ solutions, each additive was previously dissolved in DMF:DMSO mixture solution to ensure homogeneous mixing.

For $FA_{0.92}MA_{0.08}PbI_3$ perovskite layer, The PbI₂ precursor solution (1.5 M PbI₂ in DMF:DMSO (v/v, 9/1) was spin coated onto the ITO/SnO₂ at 1700 rpm for 30 s and 2000 rpm for 5 s, and then immediately annealed at 70 °C for 1 min. After cooling down to room temperature, 100 μ L of the FAI:MAI:MACI (92.4:6.4:9.5 mg mL⁻¹ in IPA) was spin coated onto the PbI₂ precursor film at 2500 rpm for 3 s, 1350 rpm for 15 s, and then 1700 rpm for 12 s.

For $Cs_{0.05}FA_{0.95}PbI_3$ based device, 1.4 M PbI₂ and 0.07 M Cs in DMF:DMSO (v/v, 94/6) was used as a PbI₂ precursor layer. FAI:MACI (80:13 mg mL⁻¹ in IPA) was spin coated onto the PbI₂ precursor film at 2500 rpm for 3 s, 1350 rpm for 15 s, and then 1700 rpm for 12 s.

For $Cs_{0.05}FA_{0.95}Pb(I_{0.95}Br_{0.05})_3$ based device, 1.4 M PbI₂ and 0.07 M Cs in DMF:DMSO (v/v, 94/6) was used as a PbI₂ precursor layer. FAI:MABr:MACI (90:9:9 mg mL⁻¹ in IPA) was spin coated onto the PbI₂ precursor film at 2500 rpm for 3 s, 1350 rpm for 15 s, and then 1700 rpm for 12 s.

When the film color turned from orange to dark brown in glove box, they were immediately transferred to air condition (relative humidity ~ 40 %), followed by thermal annealing at 150

°C for 10 min. For 2D perovskite treatment on the surface layer, OAI solution (3.8 mg/mL in IPA) was spin coated onto the perovskite films. The spiro-OMeTAD solution (85.7 mg/ml in chlorobenzene) was doped with t-BP (25.5 μ L), LiTFSI (15.5 μ L, 520 mg/mL in ACN), and FK209 (12.5 μ L, 368 mg/mL in ACN) and then, spin-coated on the perovskite film at 5000 rpm 30 s. Finally, a 80 nm Au layer were thermally deposited by evaporation under a pressure of 3.0 x 10⁻⁶ Torr. the effective device area with aperture was 0.042 cm² and this area was measured by optical microscopy (Zeiss, Axio scope A1).

4. Solar cell characterization

The current density versus voltage (*J-V*) characteristics were measured using a Keithley 2400 source under AM 1.5G solar illumination with an intensity of 100 mW cm⁻². The *J-V* curves for PSCs were measured in an inert atmosphere with a voltage step size of 0.02 V (Reverse scan: $1.2 \rightarrow -0.2$ V, Forward scan: -0.2 V $\rightarrow 1.2$ V) and a delay time of 20 ms after calibration to standard conditions. The EQE measurement was conducted by Solar Cell Spectral Response Measurement System QE-R3011 (EnliTech.) in ambient condition. Transient Photocurrent (TPC) and Transient Photovoltage (TPV) measurements are performed using the analyzer function of semiconductor parameter test system (McScience T4000) under the illumination with a white light-emitting diode.

5. Morphology characterization

For scanning electron microscopy (SEM), the top-view and cross-sectional SEM measurement was performed by S-4800 (Hitachi). For transmission electon microscopy (TEM), The Pbl₂-CP/CQ nanoparticles were dispersed in CB and then sonicated for 5 min. TEM measurement was conducted by JEM-2100 (JEOL). The surface morphology was analyzed by tapping mode AFM (MultiMode V, Veeco). GIWAXS measurements were conducted using the PLS-II 6D and 9A U-SAXS beamlines at the Pohang Accelerator Laboratory (South Korea). A photon energy of 18.984 keV and an incident angle of 0.13 and 0.1 were used to measure the distribution of the diffracted X-ray intensity.

6. Stability measurement

The maximum power point tracking (MPPT) test were measured using a T3600 (Mcscience) under AM 1.5G (100 mW cm⁻²) LED illumination for the encapsulated devices, which are prepared by glass-to-glass encapsulation with UV curable adhesive (LT-U001, Lumtech) as a selanat. Temperature and humidity were controlled by a chamber with built-in temperature system and humidifier and dehumidifier system.

7. Figures and Tables

Molecule	Dipole moment (Debye)
СР	3.3008
CQ	5.3915

Table S1. Calculated dipole moments of CP and CQ



Figure S1. 2nd running differential scanning calorimetry (DSC) curve of CP and CQ.



Figure S2. Isothermal-temperature TGA plots at 70 $^{\circ}$ C of CP and CQ with calculated vapor pressures as a function of temperature.

Supplementary Note 1

The basis for the calculation is a Langmuir equation¹:

$$\frac{1}{a}\frac{dm}{dt} = p \alpha \sqrt{\frac{M}{2\pi RT}}$$

,where dm/dt is the differential of mass with respect to time [kg s⁻¹] measured at temperature increment, α is the area of the TGA pan [m²], *p* is pressure [Pa], M is the molecular weight of the volatile (kg mol⁻¹), α is an instrumental parameter related to calibration of TGA condition, T is Kelvin temperature [K], R is the gas constant [J K⁻¹ mol⁻¹]. Rearranging the equation,

$$k = \frac{\sqrt{2\pi R}}{\alpha} \qquad \qquad \nu = \frac{1}{a} \frac{dm}{dt} \sqrt{\frac{M}{T}}$$

the simplified expression for calculating vapor pressure is following:

p = k v

Firstly, find slope k using a material for which the relationship between p and v is known. Benzoic acid was used to determine the k constant (Figure S3). The Antonie equation was used to calculate p using A, B, C coefficients of benzoic acid from literature (NIST website, http://webbook.nist.gov/). Then, the v of volatile additive was calculated with mass loss at temperature. With the pressure (p) values according to temperature, the Clapeyron relationship was used to calculate heat of sublimation.

$$\ln p = \frac{\Delta H_{sub}}{RT} + C$$

With obtained heat of sublimation, the vapor pressure could be calculated by extrapolation to the certain temperature. The results are depicted in Figure S4.



Figure S3. Slope k calculation from TGA measurement (10 $^{\circ}$ C/min) of benzoic acid.



Figure S4. The plots of ln(p) as a function of 1/T for CP and CQ.

Table S2. Heat of sublimation and calculated vapor pressure of CP and CQ

	MW [g/mol]	∆H ^{sub} [kJ/mol]	Vapor pressure @70 ℃ [Pa]
СР	152.23	51.73	500.64
cq	166.22	60.47	68.20



Figure S5. FT-IR spectra of PbI₂-CP during first-annealing process (70 $^{\circ}$ C).

Supplementary Note 2

¹H-NMR analysis was performed on the ex-situ taken films at each processing step. The samples were collected at each step, dissolved in DMSO-d₆, and analyzed. Note that we intentionally overused the concentrations (300 mM) of CP and CQ to observe clearer changes. The ¹H-NMR peaks of pristine CP were clearly observed in the CP-PbI₂ film immediately after spin-coating; however, after the first thermal annealing at 70 °C, the CP peaks disappeared, confirming its complete evaporation during the thermal annealing process. In the case of CQ, the ¹H-NMR peaks were detected in both CQ-PbI₂ and CQ-PbI₂-FAI films after the first thermal annealing at 70 °C. On the other hand, after the second thermal annealing step at 150 °C following the FAI spin-coating, the CQ peaks were no longer observed, confirming no residues on perovskite film. These results clearly show that CP and CQ are completely volatilized during the first and second thermal annealing processes, respectively.



Figure S6. Schematic illustration of the confirmation of the presence of CP or CQ using NMR spectroscopy.



Figure S7. ¹H-NMR spectra of *ex situ* taken films at each processing step related to CP.



Figure S8. ¹H-NMR spectra of *ex situ* taken films at each processing step.



Figure S9. Total process of residue analysis of CP and CQ using LC-MS.



Figure S10. Mass spectroscopy of (a) CP and (b) CQ (Top: simulated MS, Bottom: measured MS).



Figure S11. Liquid chromatography of PbI_2 -CP before 1st TA (a) and after 1st TA (b) (The peak area shown in red corresponds to CP. each condition repeated three times).



Figure S12. Liquid chromatography of PbI_2 -CQ before 1st TA (a) and after 1st TA (b) (The peak area shown in red corresponds to CQ. each condition repeated three times).



Figure S13. Liquid chromatography of PVK-CQ after 2nd TA (No CQ peak was detected. each condition repeated three times).



Figure S14. Calibration of standard solutions of (a) CP and (b) CQ for the quantification of *ex*-situ taken films.

Table S3. Quantification of residual CP and CQ amounts in the *ex*-situ taken films during each processing step

	CP residue amount (µg/mL)	CQ residue amount (µg/mL)
Before 1 st TA	154.42	355.03
After 1 st TA	2.94 (negligible)	278.12
After 2 nd TA	-	0

As shown in Table SX, CP was detected at a concentration (154.42 μ g/mL) before first annealing step. However, after the first annealing step, nearly all CP volatilized, with only a negligible amount (2.94 μ g/mL) remaining in the film, indicating effective removal of CP at this stage. In contrast, CQ exhibited only a moderate reduction in concentration following the first annealing, suggesting that a significant portion of CQ remained in the film at this stage. The remaining CQ was completely removed during the second annealing process.

Supplementary Note 3

LC-MS analysis was performed on the ex-situ taken films at each processing step as illustrated in Figure SX. The samples were collected at each step, dissolved in 0.5 mL DMF, and analyzed. Note that we intentionally overused the concentrations (300 mM) of CP and CQ to observe clearer changes. The LC peak of CP was clearly observed in the CP-Pbl₂ film immediately after spin-coating; however, after the first thermal annealing at 70 °C, the CP peak area decreased to negligible level, confirming its complete evaporation during the thermal annealing process. In the case of CQ, the LC peak of CQ was detected in the CQ-Pbl₂ film after the first thermal annealing at 70 °C. On the other hand, after the second thermal annealing step at 150 °C, the CQ peaks were no longer observed, confirming no residues on perovskite film. Residue quantification was further carried out using a calibration curve obtained from standard solutions, based on a linear relationship between LC peak area and solution concentration (Figure SX). The calculated residual amounts of CP and CQ are summarized in Table SX in agreement with the LC-MS results. These results clearly show that the distinct volatilization mechanism of CP and CQ during the first and second thermal annealing processes, respectively.



Figure S15. ¹³C-NMR spectra of CP-mixed PbI₂ precursor solutions with different molar ratios.



Figure S16. ¹³C-NMR spectra of CQ-mixed PbI₂ precursor solutions with different molar ratios.



Figure S17. ¹H-NMR spectra of CP- and CQ in deuterated DMSO solutions.



Figure S18. DOSY spectra of CP-PbI₂ adducts in deuterated DMSO solutions with varying molar ratio of CP and PbI₂.



Figure S19. DOSY spectra of CQ-PbI₂ adducts in deuterated DMSO solutions with varying molar ratio of CQ and PbI₂.

Table S4. Diffusion coefficients of CP- and CQ-mixed PbI₂ in deuterated DMSO solutions

In DOSY NMR measurement, the diffusion coefficient (D) is calculated by Stoke-Einstein equation ($D = kT/6\pi\eta R_H$), where T is the temperature, η is the viscosity, and R_H is the hydrodynamic radius related to the nanostructure size in the mixture.²

	Ratio [mol]	H ₁		H_2	${ m H_3}$	${ m H_4}$	I	I ₅	H ₆
CQ-PbI ₂	1:0	4.40 ×	10-6	4.40×10^{-6}	4.39×10^{-6}	4.39 × 10	4.40	× 10 ⁻⁶	4.34×10^{-6}
	1:5	4.11 ×	10-6	4.12×10^{-6}	4.12×10^{-6}	4.11 × 10	4.11	× 10 ⁻⁶	4.12×10^{-6}
	1:10	3.58 ×	10-6	3.58 × 10 ⁻⁶	3.58 × 10 ⁻⁶	3.58 × 10	⁻⁶ 3.58	× 10 ⁻⁶	3.58×10^{-6}
	1:20	3.09 ×	10-6	3.32×10^{-6}	3.04×10^{-6}	3.00 × 10	3.08	× 10 ⁻⁶	3.29×10^{-6}
	Ratio [mol]	\mathbf{H}_{1}	H_2	${ m H}_3$	${ m H_4}$	H ₅	H ₆	\mathbf{H}_7	H ₈
	1:0	4.43×10^{-6}	4.43 × 10 ⁻⁶	4.46×10^{-6}	4.43 × 10 ⁻⁶	4.43 × 10 ⁻⁶	4.42×10^{-6}	4.42 × 10	4.42×10^{-6}
CP-PbI ₂	1:5	4.11×10^{-6}	4.11×10^{-6}	4.11×10^{-6}	4.11×10^{-6}	4.12×10^{-6}	4.11×10^{-6}	4.11 × 10	4.11×10^{-6}
	1:10	3.82×10^{-6}	3.82×10^{-6}	3.83 × 10	3.83×10^{-6}				
	1:20	3.09 × 10 ⁻⁶	3.08 × 10 ⁻⁶	3.08×10^{-6}	3.08×10^{-6}	3.09×10^{-6}	3.08×10^{-6}	3.08 × 10	3.08×10^{-6}



Figure S20. The UV spectra of Pbl_2 precursor solutions of pristine, Pbl_2 -CP_, and Pbl_2 -CQ.



Figure S21. UV-Vis spectra of pristine CP and CQ.



Figure S22. The UV spectra of Pbl_2 precursor films of pristine, Pbl_2 -CP, and Pbl_2 -CQ.



Figure S23. 2D-GIWAXS Images of pristine, PbI₂-CP, and PbI₂-CQ films.

Pbl ₂ film Cluster	Mean size (nm)	Standard deviation (nm)
Control	99.9	28.9
СР	161.2	38.9
CQ	180.5	54.2

Table S5. The statistical parameters of cluster sizes in the PbI_2 films from the top-view SEM images



Figure S24. Line-cut profiles of PbI₂-CP films under different concentrations (0, 2.5, 5 mg/mL) for (a,b) 0.13° and (c,d) 1.0° incident angles.



Figure S25. Line-cut profiles of PbI_2 -CQ films under different concentrations (0, 0.25, 0.5 mg/mL) for (a,b) 0.13° and (c,d) 1.0° incident angles.



Figure S26. Nanostructure of PbI_2 powders. TEM images of a) PbI_2 , b) PbI_2 -CP, and c) PbI_2 -CQ.



Figure S27. XPS full spectra of control, PbI₂-CP, and PbI₂-CQ films.



Figure S28. Underlying mechanism of the different volatility CP and CQ. (a) PbI₂-CP, which shows high volatility, results in denser PbI₂ structure. (b) PbI₂-CQ, which shows stronger interaction with PbI₂, producing less dense PbI₂ structure.

Perovskite	Mean size Standard de			
grain size	(nm)	(nm)		
Control	602.8	169.4		
СР	858.7	356.3		
CQ	1024.5	456.4		

Table S6. The statistical parameters of grain sizes in the perovskite films from the top-view SEM images



Figure S29. The UV spectra of perovskite films of control, PVK-CP and PVK-CQ.



Figure S30. 2D-GIWAXS Images of pristine, PVK-CP, and PVK-CQ films.

Table S7. The area ratios of the two peaks (90° to 35° & 145°) of perovskite films in GIWAXS pole figure measurements

		Р	eak area				
Incident angle	Film				Area ratio (90°/35°+145°)		
		35°	90°	145°			
				1			
	Control	257	1480	596	1.74		
0.13°	PVK-CP	342	1636	548	1.84		
	PVK-CQ	294	3003	748	2.88		
	Control	1349	2141	1099	0.89		
1 0°	Ρ\/K_C Ρ	1297	3956	1590	1 35		
1.0		1237		1000	1.00		
		E12	10242	1520	0.00		
	РУК-СО	512	16242	1520	8.00		



Figure S31. Effect of additive concentration on morphology of PbI₂ and perovskite films.
(a) SEM images of PbI₂ and perovskite films using CP additive with increasing concentration.
(b) SEM images of PbI₂ and perovskite films using CQ additive with increasing concentration.



Figure S32. Cross-sectional SEM images according to CQ concentration of (a) 3.0 mM and (b) 30 mM.



Figure S33. MPPT stability test on CQ treated PSCs at 3 mM (optimal) and 30 mM (high) concentrations.



Figure S34. The detailed *In-situ* PL spectra of control, PVK-CP, and PVK-CQ as a function of time.

Film state	Initial Pbl ₂ filim	FAI coated intermediate film	After 5 min	Final PVK film
Control				
СР				
cQ				

Figure S35. Changes in colors of control, CP-, and CQ-modified films. PbI2 films were deposited by dripping the FAI based solutions, followed by second annealing for final PVK films.



Figure S36. The distribution of the device characteristics of corresponding devices containing 0 (control), 15 mM, 30 mM, and 60 mM of CP.



Figure S37. The distribution of the device characteristics of corresponding devices containing 0 (control), 1.5 mM, 3.0 mM, and 6.0 mM of CQ.



Figure S38. Hysteresis measurement of control, CP-, and CQ-treated devices with a reverse scan (RS) (1.2 V \rightarrow -0.2 V) and forward scan (FS) (-0.2 V \rightarrow 1.2 V).

PCE FF HI	PCE	V _{oc}	J _{sc}	Scan	Dovico
[%] [%] [%]	[%]	[V]	[mA/cm ²]	Direction	Device
22.60 78.81	22.60	1.153	24.86	Reverse	Control
20.50 71.75	20.50	1.147	24.92	Forward	
23.63 80.69	23.63	1.173	24.96	Reverse	
22.18 76.59	22.18	1.153	25.13	Forward	CP
24.19 81.57	24.19	1.187	24.99	Reverse	
4.2 23.15 78.22	23.15	1.172	25.24	Forward	CQ
22.60 78.81 9.2 20.50 71.75 9.2 23.63 80.69 6.1 22.18 76.59 6.1 24.19 81.57 4.2 23.15 78.22 78.22	22.60 20.50 23.63 22.18 24.19 23.15	1.153 1.147 1.173 1.153 1.187 1.172	24.86 24.92 24.96 25.13 24.99 25.24	Reverse Forward Reverse Forward Reverse Forward	Control CP CQ

Table S8. The photovoltaic parameters of control, CP-, and CQ-treated devices under different scan directions



Figure S39. Stabilized power output (SPO) of the control device at the maximum power point at 0.98 V.



Figure S40. Stabilized power output (SPO) of the CQ-treated device at the maximum power point at 1.02 V.



Figure S41. Photovoltaic performance variations for 24 individual devices based on different additives. (a) V_{oc} (b) FF, (c) $J_{sc'}$ (d) PCEs.



Figure S42. Best-performing device performance under forward and reverse scanning. The architecture of PSCs was FTO/CBD-SnO₂/Cs_{0.05}FA_{0.95}PbI₃ perovskite/OAI/Spiro-OMeTAD/Au (Anti-reflecting film was used to enhance current density).

Table S9. Current density-voltage (*J-V*) curves of the champion device measured from forwardscan (FS) and reverse scan (RS).

Device	Scan direction	<i>V</i> _{oc} [V]	J _{SC} [mA/cm ²]	FF [%]	PCE [%]
Control	RS	1.156	25.12	79.93	23.20
	FS	1.159	25.20	77.94	22.77
CQ	RS	1.183	25.95	81.45	25.00
	FS	1.181	25.44	81.72	24.56



Figure S43. EQE spectra and integrated J_{SC} plots of control and CQ-treated best-performing device with architecture of FTO/CBD-SnO₂/Cs_{0.05}FA_{0.95}PbI₃ perovskite/OAI/Spiro-OMeTAD/Au.



Figure S44. Certified PCE at Daegu Technopark Institute (Korea). The certified *J-V* curves give PCE of 24.89% (V_{OC} =1.186 V, I_{SC} =1.082 mA cm⁻², FF=81.48%) under reverse scan (The aperture area was 0.042 cm²).

Table S10. PCE comparison of this work with the reported two-step-based state-of-the-art PSCs for2023-2024.

					Best	-performing		
		Device structure	Perovskite			device		
Year			composition	Strategy	PCE	Certified PCE	Reference	
					(%)	(%)		
2024		FTO/SnO ₂ /PVK/Spiro-OMeTAD/Au	$FA_{0.95}MA_{0.05}PbI_3$	Passivation	25.24		Joule 8, 1105-1119, 2024	
2024		FTO/TiO ₂ /PVK/Spiro-OMeTAD/MoO ₃ /Ag	$Cs_{0.95}FA_{0.95}PbI_3$	ETL modification	25.32	25.32	Adv. Mater. 2024, 36, 2310710	
2024		FTO/SnO ₂ /PVK/Spiro-OMeTAD/Au	$FA_{0.85}MA_{0.15}PbI_3$	Additive	24.04	-	Adv. Mater. 2024, 36, 2313080	
2024		FTO/SnO ₂ /PVK/Spiro-OMeTAD/Au	(FAPbl ₃) _{0.97} (MAPbBr ₃) _{0.03}	ETL modification	24.64	24.37	Joule 8, 817-834, March 20, 2024	
2024		FTO/SnO ₂ /PVK/Spiro-OMeTAD/Au	$FA_{0.95}MA_{0.05}PbI_3$	Water trace	24.58	24.3	Adv. Mater. 2024, 2310237	
2024		ITO/SnO ₂ /PVK/Spiro-OMeTAD/MoO ₃ /Ag	$Cs_{0.05}FA_{0.95}PbI_3$	Additive	25.06	-	Adv. Mater. 2024, 2401476	
2024	N-i-p	ITO/SnO ₂ /PVK/Spiro-OMeTAD/Au	$FA_{0.95}MA_{0.05}PbI_3$	Additive	24.51	-	Adv. Mater. 2024, 36, 2311145	
2023	·	ITO/SnO ₂ /PVK/Spiro-OMeTAD/Au	$Cs_{0.05}FA_{0.95}PbI_3$	Additive	26.07	25.86	Nature 623, 531-537 (2023)	
2023		ITO/SnO ₂ /PVK/Spiro-OMeTAD/Ag	$Cs_{0.05}FA_{0.75}MA_{0.20}Pb(I_{0.96}Br_{0.04})_3$	Passivation	25.43	24.4	Adv. Mater. 2023, 2301624	
2023		ITO/SnO ₂ /PVK/Spiro-OMeTAD/Au	FAPbI ₃	Additive	25.12	24.84	Adv. Mater. 2024, 36, 2307855	
2023		ITO/SnO ₂ /PVK/Spiro-OMeTAD/Au	FA _{0.85} MA _{0.15} PbI ₃	Additive	24.36	24.02	Joule 7, 1033-1050, 2023	
2023		ITO/SnO ₂ /PVK/Spiro-OMeTAD/Ag	$Cs_{0.05}FA_{0.75}MA_{0.20}Pb(I_{0.96}Br_{0.04})_3$	Passivation	24.21	-	Nature. Comm, 2023, 14:3738	
<mark>2024</mark>		FTO/SnO ₂ /PVK/Spiro-OMeTAD/Au	Cs _{0.05} FA _{0.95} Pbl ₃	Additive	<mark>25.00</mark>	<mark>24.89</mark>	This work	



Figure S45. *J-V* curves of CQ-based PSCs using different perovskite composition, a) $Cs_{0.05}FA_{0.95}PbI_3$ and b) $Cs_{0.05}FA_{0.95}Pb(I_{0.95}Br_{0.05})_3$ in the reverse scan direction. The detailed device fabrication procedures are summarized in the Experimental section.

Table S11. Summarized performances of reported studies on preferentially orientedperovskite-based solar cells.

Structure	Device	J _{sc} [mA/cm²]	V _{oc} [V]	FF [%]	PCE [%]	Ref	
	Control	24.7	1.127	80.2	22.3	[3]	
	Target	24.8	1.177	84.3	24.6	[5]	
ETO/Spo /EA MA Dh /L Dr) /spiro OMoTAD/Au	Control	24.46	1.143	80.38	22.48		
FTO/SHO ₂ /FA _{0.95} IVIA _{0.05} PD (1 _{0.95} Br _{0.05}) ₃ /Spiro-OWIETAD/Au	Target	24.43	1.182	83.45	24.10		
FTO/Spo /Co FA MA Dh/L Dr) /spire OMaTAD/Au	Control	23.95	1.157	76.78	21.27	-	
F10/51102/CS _{0.05} FA _{0.85} IVIA _{0.10} PD(1 _{0.97} B1 _{0.03})3/Spiro-OivieTAD/Au	Target	24.11	1.196	80.77	23.29	[4]	
	Control	23.01	1.031	79.06	18.75		
FTO/PTAA/FA _{0.95} MIA _{0.05} Pb(1 _{0.95} Br _{0.05}) ₃ /PC ₆₁ BMI/C ₆₀ /BCP/Ag	Target	23.22	1.126	82.09	21.46		
	Control	23.48	1.094	79.88	20.51	-	
FTO/PTAA/CS _{0.05} FA _{0.80} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ /PC ₆₁ BM/C ₆₀ /BCP/Ag	Target	23.74	1.138	81.54	22.03	-	
FTO/(PTAA or FTAP)/Cs _{0.05} FA _{0.80} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ /PC ₆₁ BM/	Control	23.39	1.081	78.89	19.95		
C ₆₀ /BCP/Au	Target	23.93	1.156	81.27	22.48		
	Control	24.98	1.09	77.80	21.18	[[]]	
FTO/PTAA/Cs _{0.05} FA _{0.80} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ /PC ₆₁ BM/C ₆₀ /BCP/Ag Targ FTO/(PTAA or FTAP)/Cs _{0.05} FA _{0.80} MA _{0.15} Pb(I _{0.85} Br _{0.15}) ₃ /PC ₆₁ BM/ Cont C ₆₀ /BCP/Au Targ FTO/c-ZnTiO ₃ -ZnS/TiO ₂ / (FA·NMP)PbI ₃ /spiro-OMeTAD/Au Cont Cont Cont	Target	25.48	1.15	82.24	24.10	[5]	
ITO/SnO-/FA MA, PhI-/spiro-OMeTAD/Ag	Control	25,39	1.13	77.13	22.13	[6]	
	Target	25.58	1.19	79.83	24.28	[0]	
FTO/c-TiOa/SpOa/FAPhla/spiro-OMATAD/Au	Control	25.78	1.171	78.71	23.77	[7]	
		26.00	1.175	83.81	25.60	[/]	
	Control	25.12	1.156	79.93	23.20	This	
FTO/SnO ₂ /Cs _{0.05} FA _{0.95} Pbl ₃ /OAI/Spiro-OMeTAD/Au	Target	25.96	1.183	81.45	25.00	work	

Perovskite composition	PSC	<i>V</i> _{oc} [V]	$J_{\rm SC}$ [mA/cm ²]	FF [%]	PCE [%]
FA _{0.92} MA _{0.08} PbI ₃	Control	1.153	24.86	78.81	22.60
	CQ	1.187	24.99	81.57	24.19
Cs _{0.05} FA _{0.95} PbI ₃	Control	1.128	25.26	79.75	22.72
	CQ	1.170	25.64	81.19	24.36
Cs _{0.05} FA _{0.95} Pb(I _{0.95} Br _{0.05}) ₃	Control	1.169	24.56	74.99	21.53
	CQ	1.195	24.67	78.18	23.05

Table S12. Device performance of various perovskite composition systems (reverse scan)



Figure S46. Light intensity versus J_{sc} of control, CP-, and CQ-treated devices.

Table S13. The summary of V_{TFL} and N_{t} values for control, CP-, and CQ-based electron-only devices in the dark



		(x 10 ¹⁶ cm ⁻³)
Control	2.09	1.25
СР	1.53	0.92
CQ	1.40	0.84
CQ	1.40	0.8

Table S14. The summary of V_{TFL} and N_{t} values for control, CP-, and CQ-based hole-only devices in the dark

PSC	V _{TFL} (V)	N _t (x 10 ¹⁴ cm ⁻³)
Control	0.41	2.45
СР	0.20	1.20
CQ	0.15	0.90



Figure 47. J-V curves of control and CQ-treated devices after MPPT aging (0, 100, 300, 500, 1000 h).

Table S15. MPPT aging time-dependent photovoltaic parameters of control and CQ-treated devices.

Device	Time [hour]	V _{oc} [V]	J _{SC} [mA/cm²]	FF [%]	PCE [%]
Control	0 (Initial)	1.152	24.59	77.54	21.97
	100	1.143	24.12	72.44	19.97
	300	1.135	24.55	67.94	18.93
	500	1.105	23.79	66.92	17.59
CQ	0 (Initial)	1.182	24.56	81.62	23.69
	100	1.174	24.72	81.01	23.52
	300	1.169	25.05	78.98	23.15
	500	1.155	24.94	78.62	22.65
	1000	1.154	24.52	76.14	21.58

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