

An enthalpy–entropy competition strategy enables moisture-stable and scalable perovskite photovoltaics

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Supplementary Text

Urbach energy

Taking advantage from the reciprocity of the relation between the PL and absorption spectra, the absorption spectra is calculated using generalized Plancks law for a photon current density $dj_e(h\nu)$ per energy interval¹.

$$dj_e(h\nu) \approx A_{BB}(h\nu)(h\nu)^2 \exp\left(-\frac{h\nu}{KT}\right) \quad (1)$$

where $h\nu$ is the photon energy, A_{BB} is the band-to-band absorptance, K is the Boltzmann constant and T is the absolute temperature. Based on the above derivation, the Urbach energy (E_U) can be calculated as follow²:

$$E_U = \left(\frac{d \ln(A_{BB})}{d(E)}\right)^{-1} \quad (2)$$

FF loss

FF loss between the measured FF and the S-Q limit is caused by trap-assisted non-radiative loss and charge transport loss. The non-radiative loss caused maximum FF ($FF_{\max}$) can be calculated according to the following equations^{3,4}:

$$FF_{\max} = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \quad (4)$$

$$v_{oc} = \frac{V_{oc}}{nKT/q} \quad (5)$$

where n , k , T and q are ideality factor, Boltzmann constant, temperature, and elementary electric charge, respectively.

DFT calculation

We have employed the VASP to perform all the spin-polarized density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation. We have chosen the projected augmented

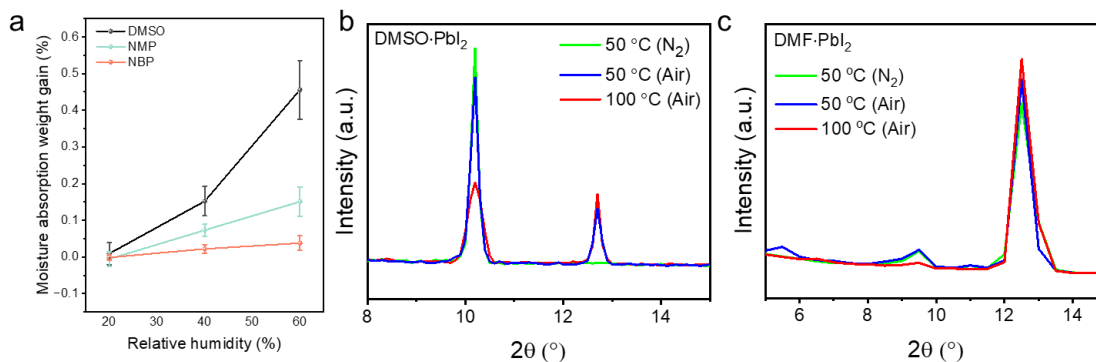
wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 400 eV. Partial occupancies of the Kohn–Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-6} eV. A geometry optimization was considered convergent when the force change was smaller than -0.05 eV/Å². Grimme’s DFT-D3 methodology was used to describe the dispersion interactions among all the atoms. During structural optimizations of the surface models, the $3 \times 3 \times 1$ gamma-point centered k-point grid for Brillouin zone was used.

XPS quantitative analysis

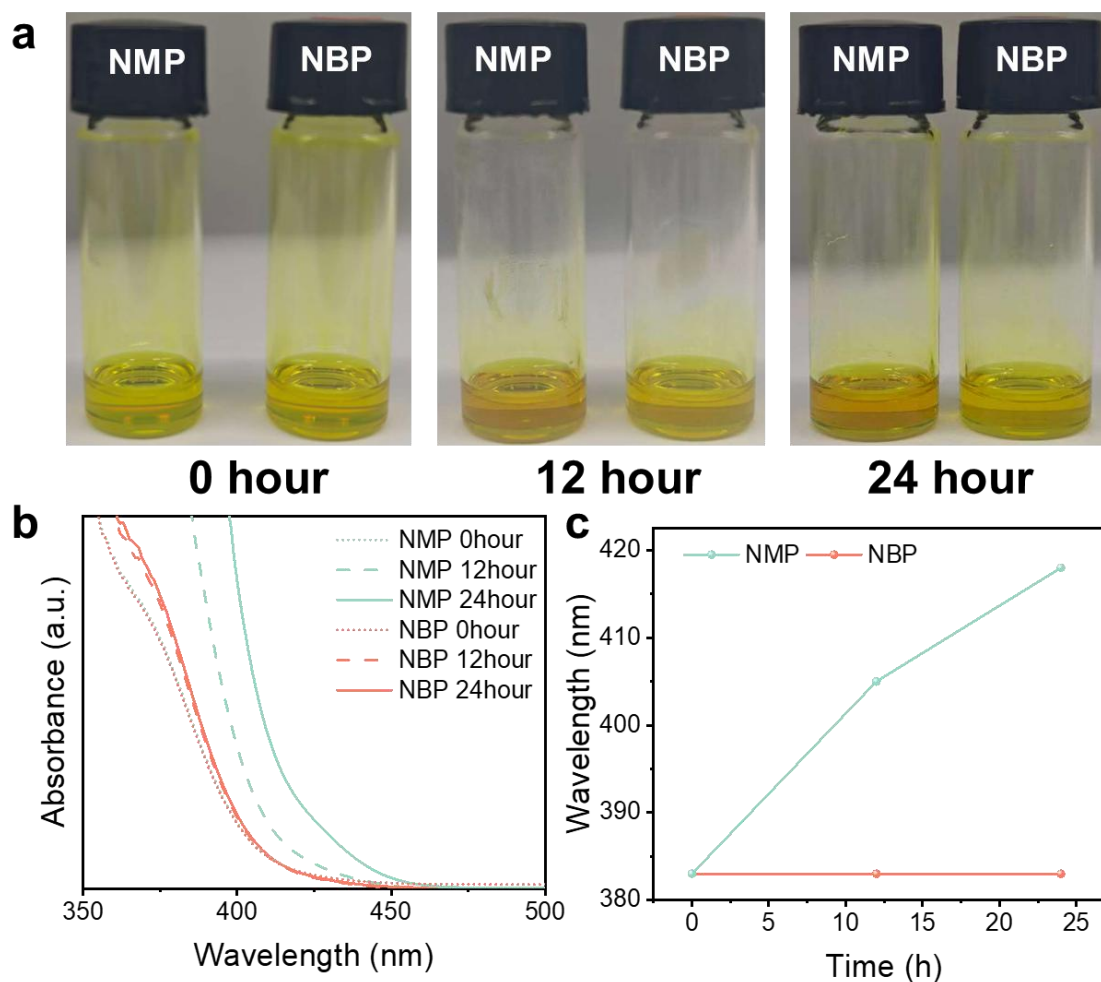
The quantification of the XPS peak was performed by measuring the peak intensity to obtain data. The peak area is automatically corrected for the total dwell time in Advantage (Thermo) according to equation.

$$\text{Normalized peak area} = \text{Peak area} / (\text{SF} \times \text{TXFN} \times \text{ECF}) \quad (6)$$

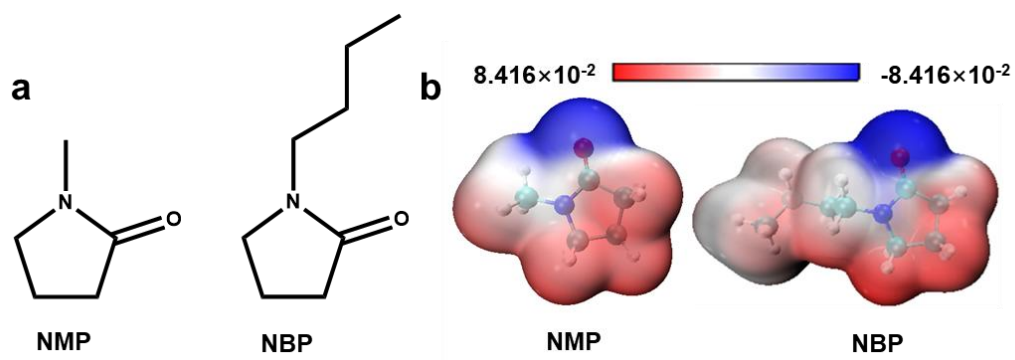
where SF is the sensitivity factor, TXFN is the transmission function, and ECF is the energy compensation factor. In this study, TXFN defaults to 1, the ECF library was chosen as “TPP-2 M”, and the SF pool used the “AISCOF” (I 3d: 19.87, C 1s: 1.0, N 1s: 1.8, Pb 4f: 22.74).



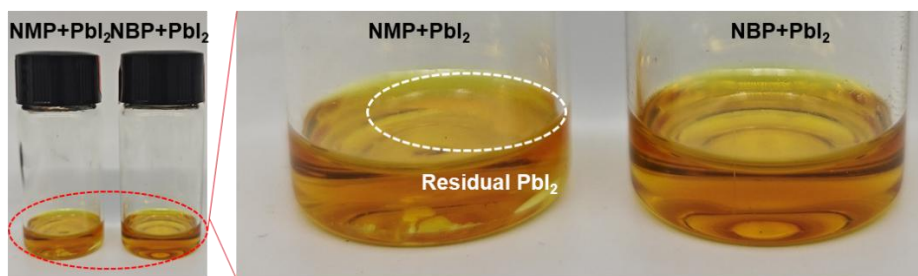
Supplementary Fig. 1. (a) The moisture absorption weight gain of DMSO/NMP/NBP solvents. (b) XRD peak changes in DMSO·PbI₂ at 50 °C and 100 °C. In a N₂ atmosphere, DMSO·PbI₂ can maintain the intermediate phase state. When heated at 50 °C in the environment, the PbI₂ appears. When the annealing temperature is raised to 100 °C, the PbI₂ is enhanced. The extremely strong hygroscopicity of DMSO will destroy the intermediate phase structure. (c) XRD peak changes in DMSO·PbI₂ at 50 °C and 100 °C. Even at 50 °C, a strong PbI₂ peak still appears. The interaction strength between DMF and lead iodide is relatively low, mainly due to its relatively weak Lewis basicity and limited coordination ability, which makes it difficult to effectively compete with the strong Pb–I bonds already present in PbI₂, resulting in insufficient solvation capacity. This characteristic often requires the use of other strong coordinating solvents (such as DMSO) in perovskite preparation to enhance the solubility of precursors and regulate the crystallization process.



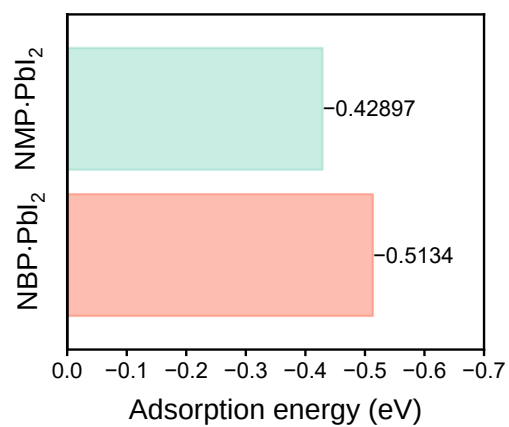
Supplementary Fig. 2. (a) The photo of perovskite ink that was placed at 60% RH for 24 hours. (b) Ultraviolet-visible (UV-Vis) absorption evolutions of aged perovskite ink. (c) The NMP perovskite ink and NBP perovskite ink were aged at 60% RH for 24 hours. The NMP perovskite ink underwent degradation, as evidenced by a darkening of its visual appearance, which correlated with a red shift of the absorption edge from 383 nm to 418 nm. In contrast, the NBP perovskite ink showed no noticeable changes in either appearance or absorption edge characteristics.



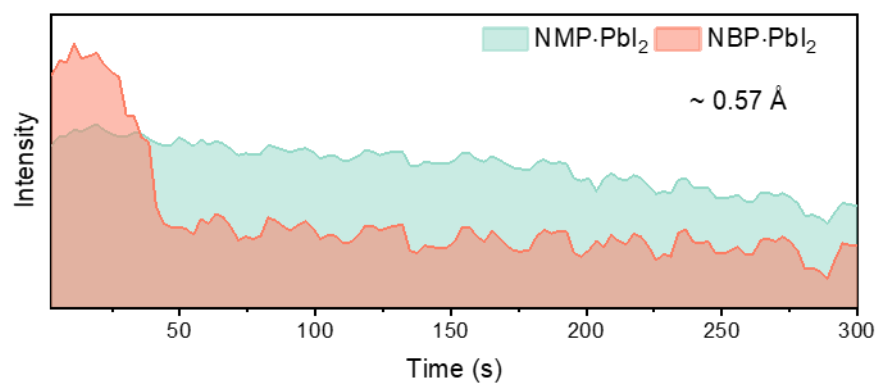
Supplementary Fig. 3. (a) The chemical structural formula of NMP and NBP, (b) Electrostatic potentials of NMP and NBP calculated by the DFT.



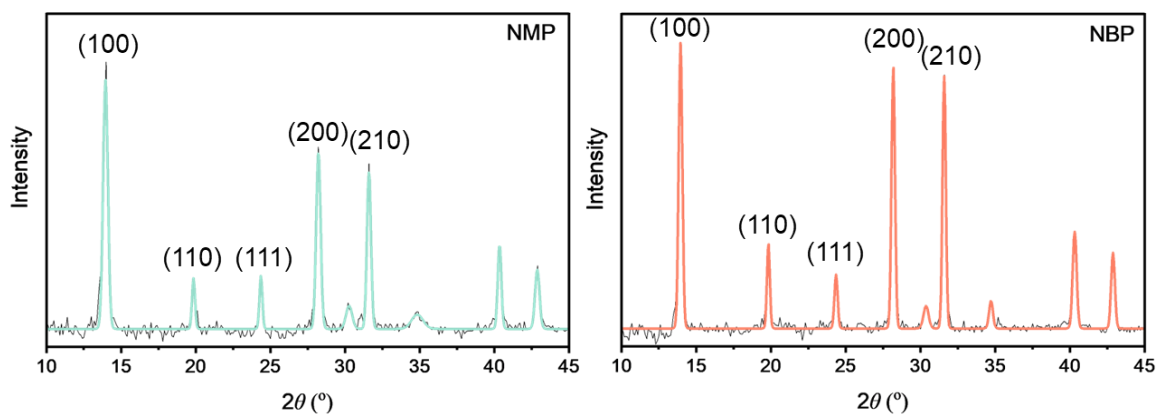
Supplementary Fig. 4. The solubility of PbI_2 in NMP and NBP.



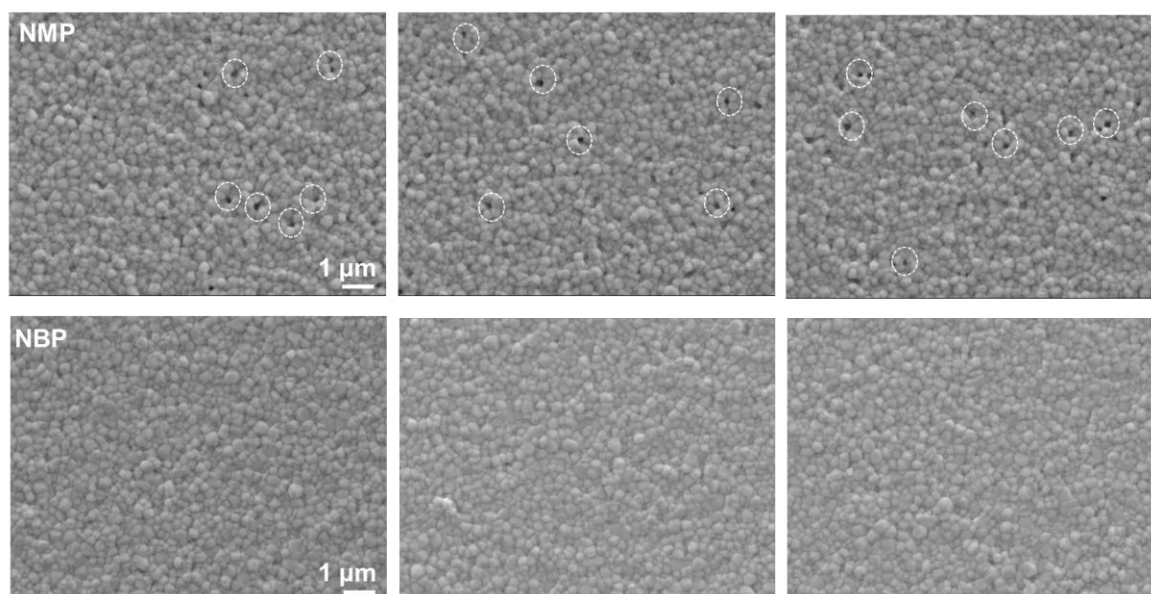
Supplementary Fig. 5. Adsorption energy of NMP·PbI₂ and NBP·PbI₂ calculated by the DFT.



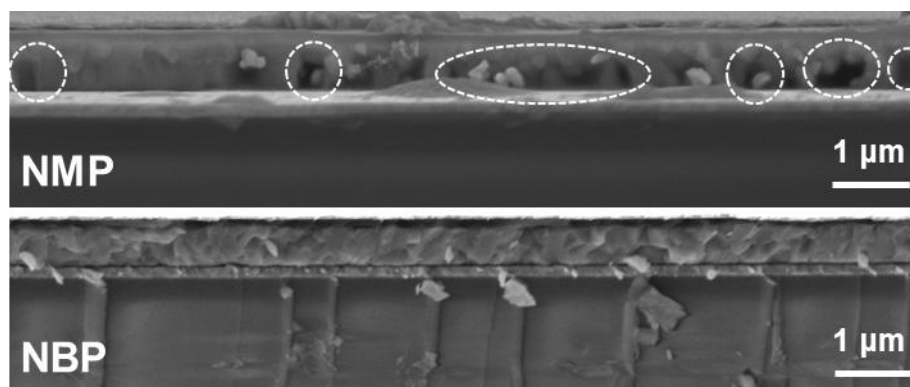
Supplementary Fig. 6. The intensity variation curve of the two-dimensional GIWAXS pattern of NMP·PbI₂ and NBP·PbI₂ ($q = 0.57 \text{ \AA}^{-1}$).



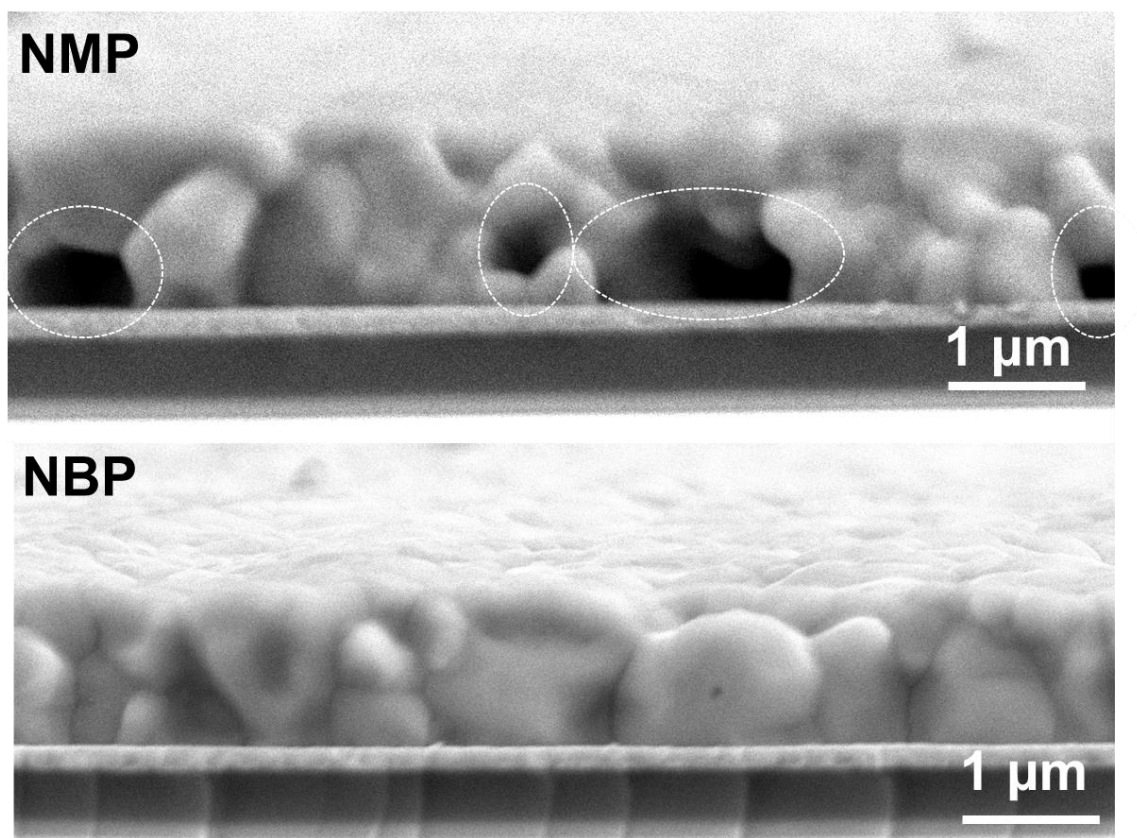
Supplementary Fig. 7. The XRD intensity curve of the NMP and NBP perovskite film. The NBP regulation enhances the (100) diffraction signal due to improved perovskite crystallinity, but reduces the actual (100) facet exposure ratio. For details, please refer to the Supplementary Table 2 and 3.



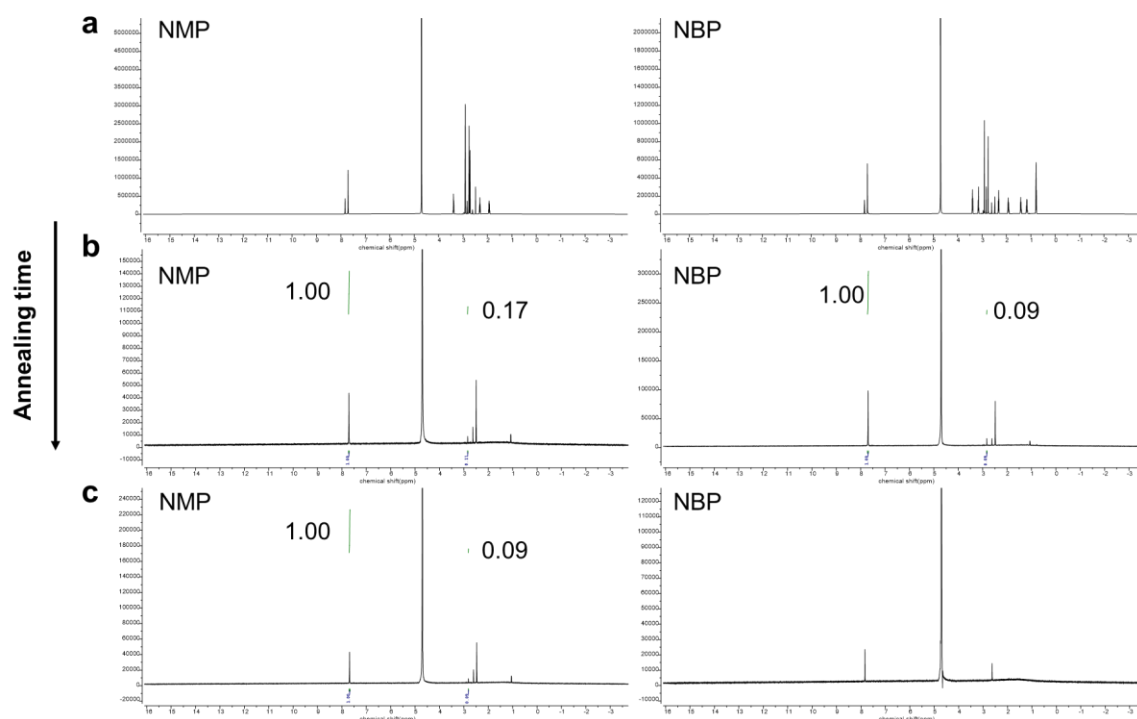
Supplementary Fig. 8. The SEM images of perovskite film from NMP sample and NBP sample. The circled area indicates porosity.



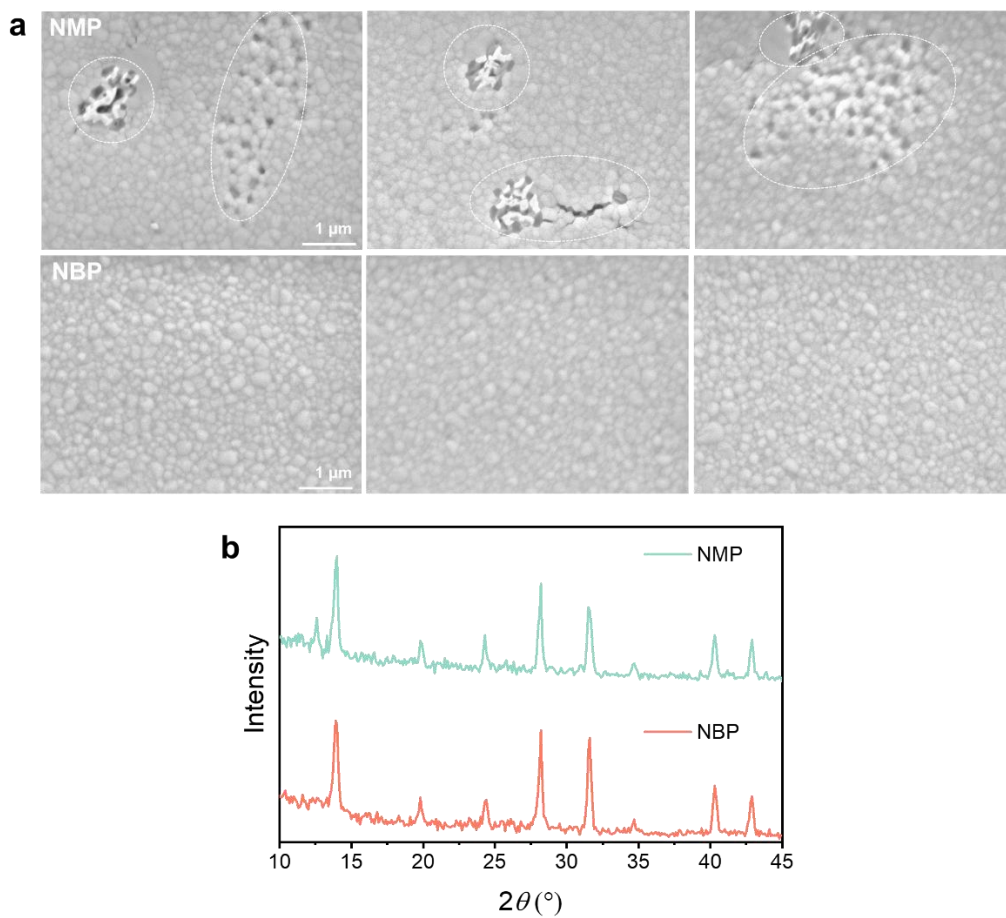
Supplementary Fig. 9. The SEM cross-sectional images of NMP sample and NBP sample. The circled area indicates porosity.



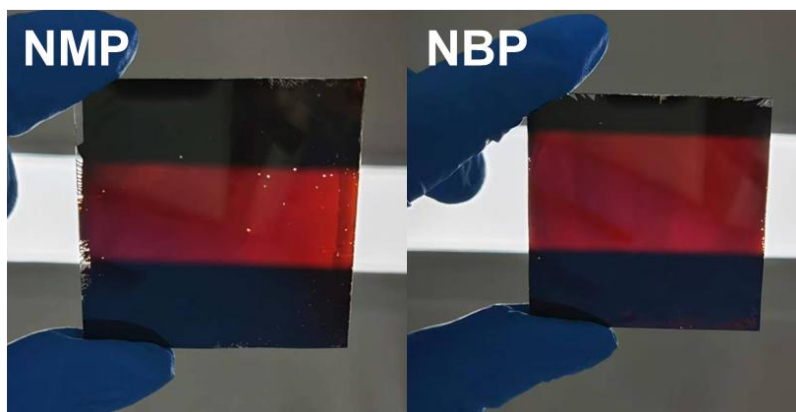
Supplementary Fig. 10. The SEM cross-sectional images of NMP sample and NBP sample. The circled area indicates porosity.



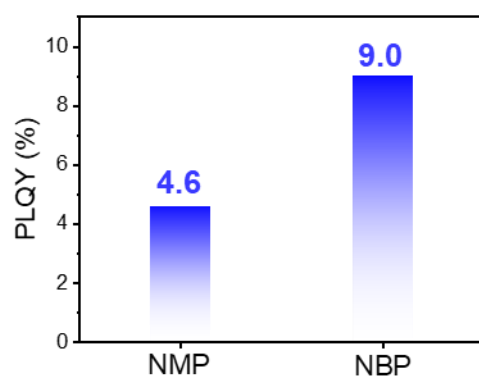
Supplementary Fig. 11. (a) The H-NMR of the NMP and NBP perovskite films annealed for 10 seconds (b) The H-NMR of the NMP and NBP perovskite films annealed for 3 minutes. (c) The H-NMR of the NMP and NBP perovskite films annealed for 10 minutes. The peak of the CHO group of DMF is around 8.0, but it does not appear (b, c) in the H-NMR. Therefore, the interference of DMF can be ruled out. For details, please refer to the Supplementary Table 3 and 4.



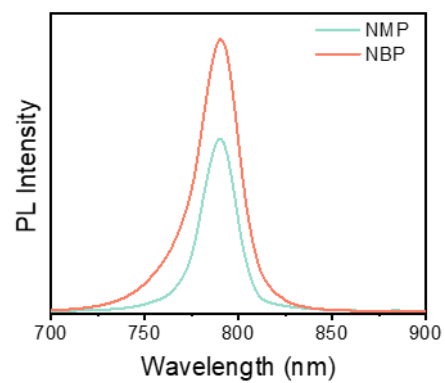
Supplementary Fig. 12. (a) The SEM images of the buried perovskite film from NMP sample and NBP sample. The circled area indicates porosity and the white substance is lead iodide. (b) The XRD ($\theta=0.1$) of NMP and NBP perovskite films buried bottom.



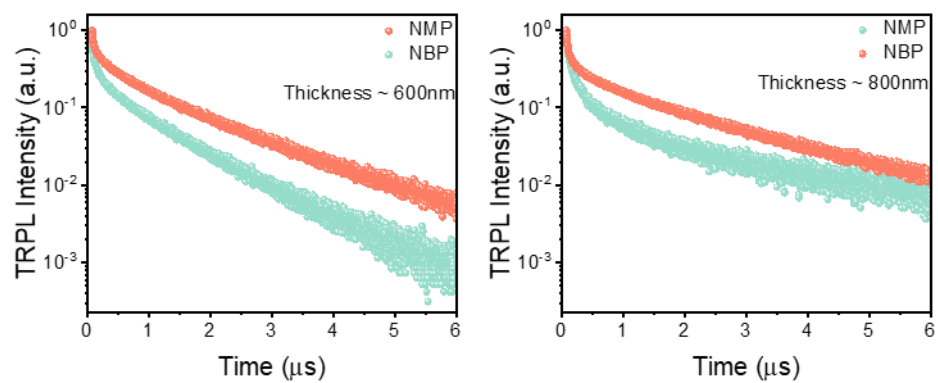
Supplementary Fig. 13. The photo of the perovskite film from NMP sample and NBP sample.



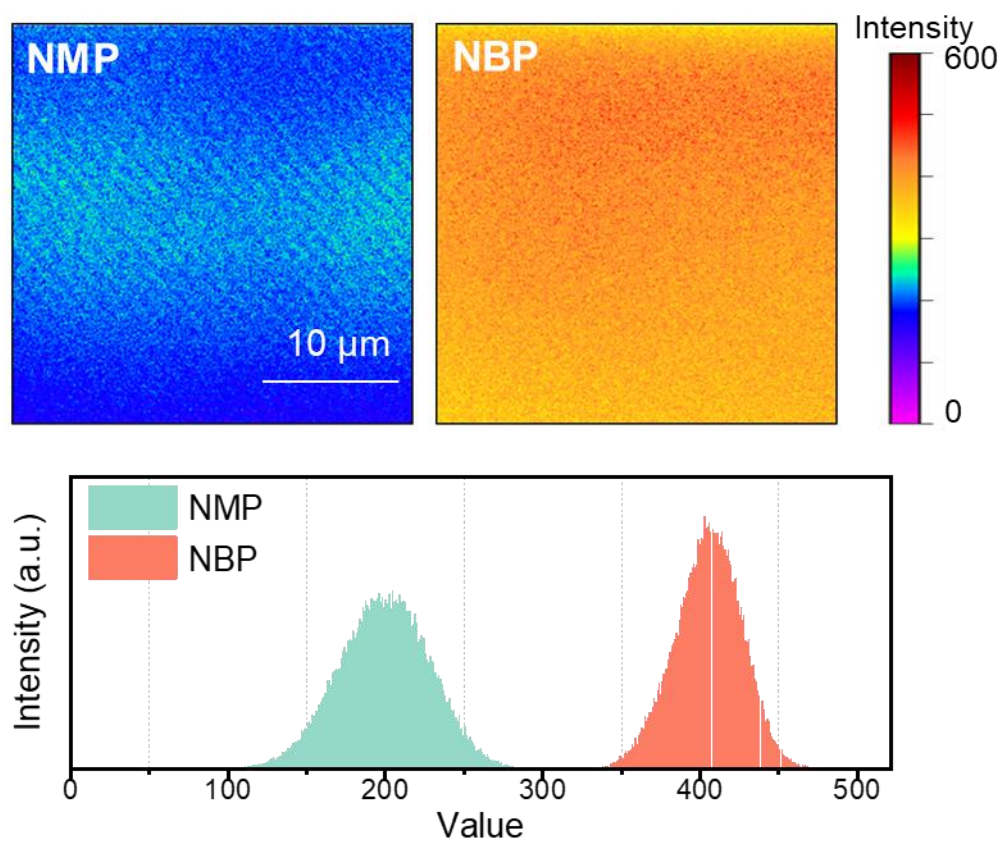
Supplementary Fig. 14. The PLQY of perovskite film from NMP sample and NBP sample.



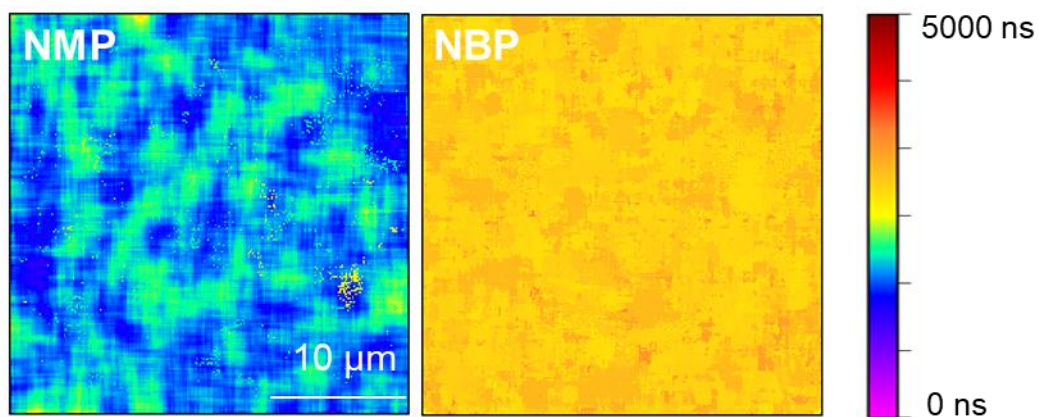
Supplementary Fig. 15. The PL of perovskite film from NMP sample and NBP sample.



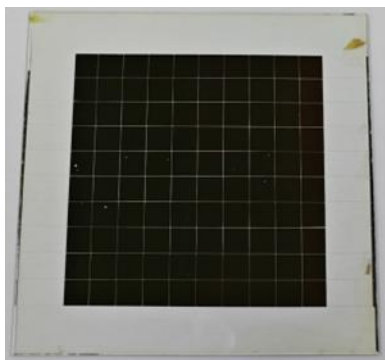
Supplementary Fig. 16. The TRPL of perovskite film from NMP sample and NBP sample.



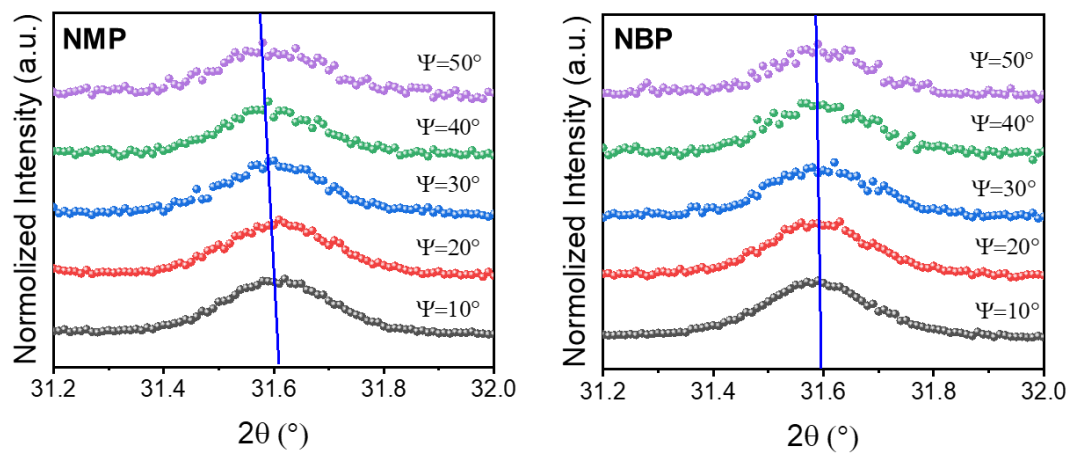
Supplementary Fig. 17. The PL Mapping of perovskite film from NMP sample and NBP sample.



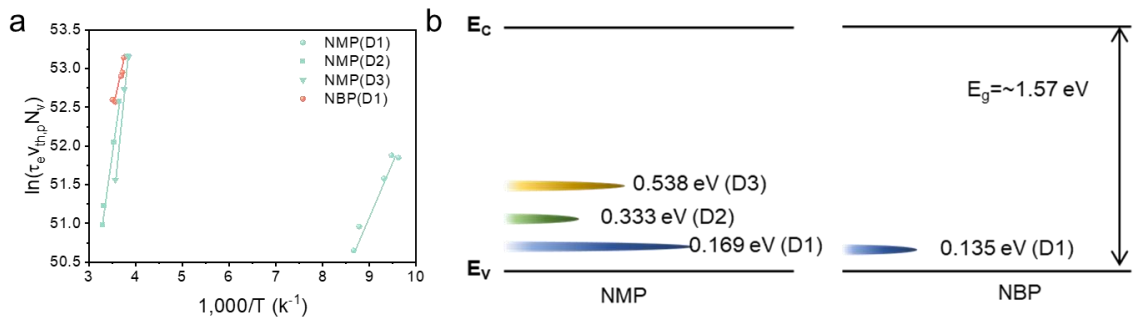
Supplementary Fig. 18. The TRPL Mapping of perovskite film from NMP sample and NBP sample.



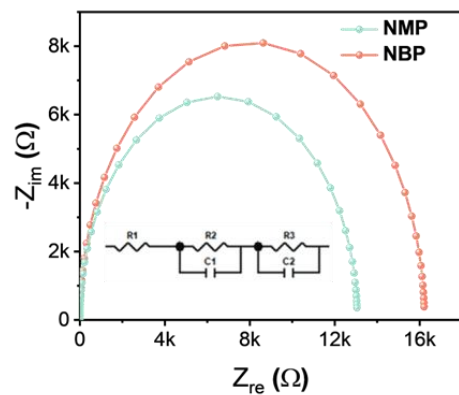
Supplementary Fig. 19. The Photos of perovskite films evenly divided into 100 points.



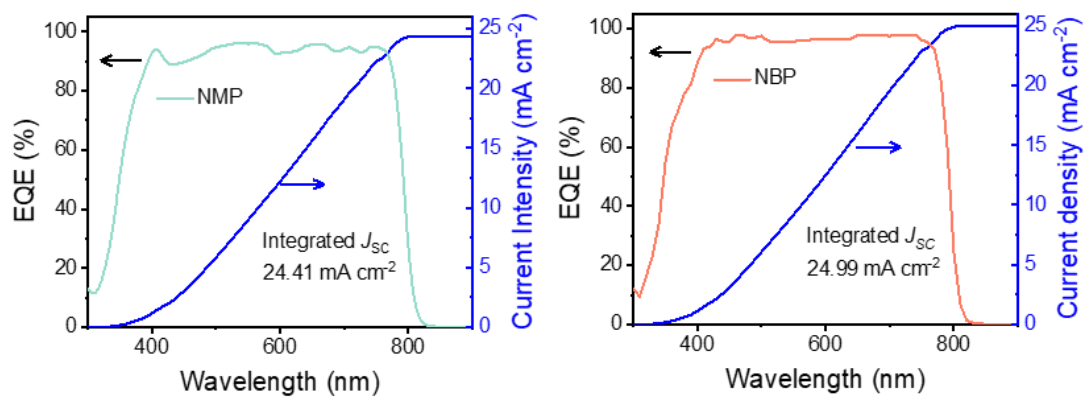
Supplementary Fig. 20. Based on the out-of-plane strain ϵ_{xx} distribution obtained from XRD analysis.



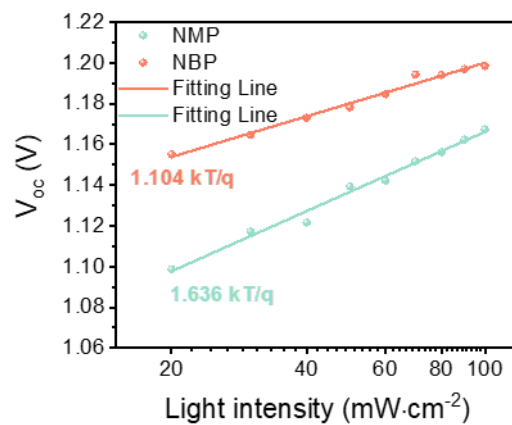
Supplementary Fig. 21. (a) Arrhenius plots to identify traps in perovskite solar cells, (b) Schematic diagram of deep-level traps in the bandgap. The peak location and height correspond to the depth and density of D1, D2 and D3 traps. E_C denotes the conduction band minimum, and E_V denotes the valence band maximum.



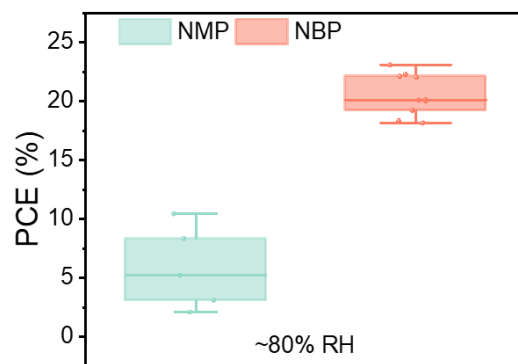
Supplementary Fig. 22. The EIS of PSCs from NMP sample and NBP sample. NBP sample displayed larger impedance semicircles, indicative of reduced trap density and suppressed non-radiative recombination.



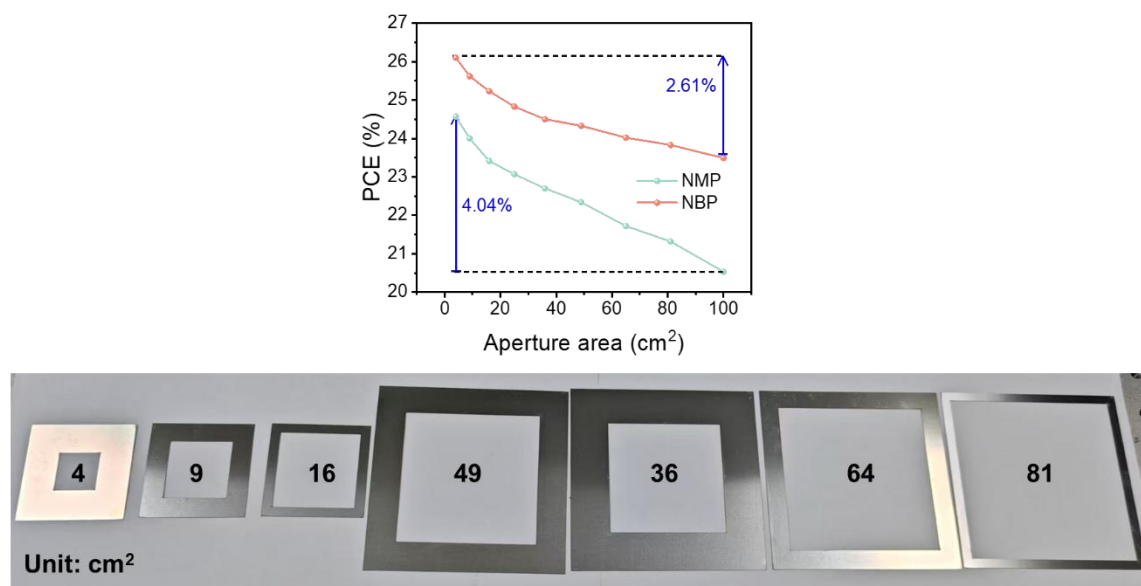
Supplementary Fig. 23. The EQE of PSCs from NMP sample and NBP sample.



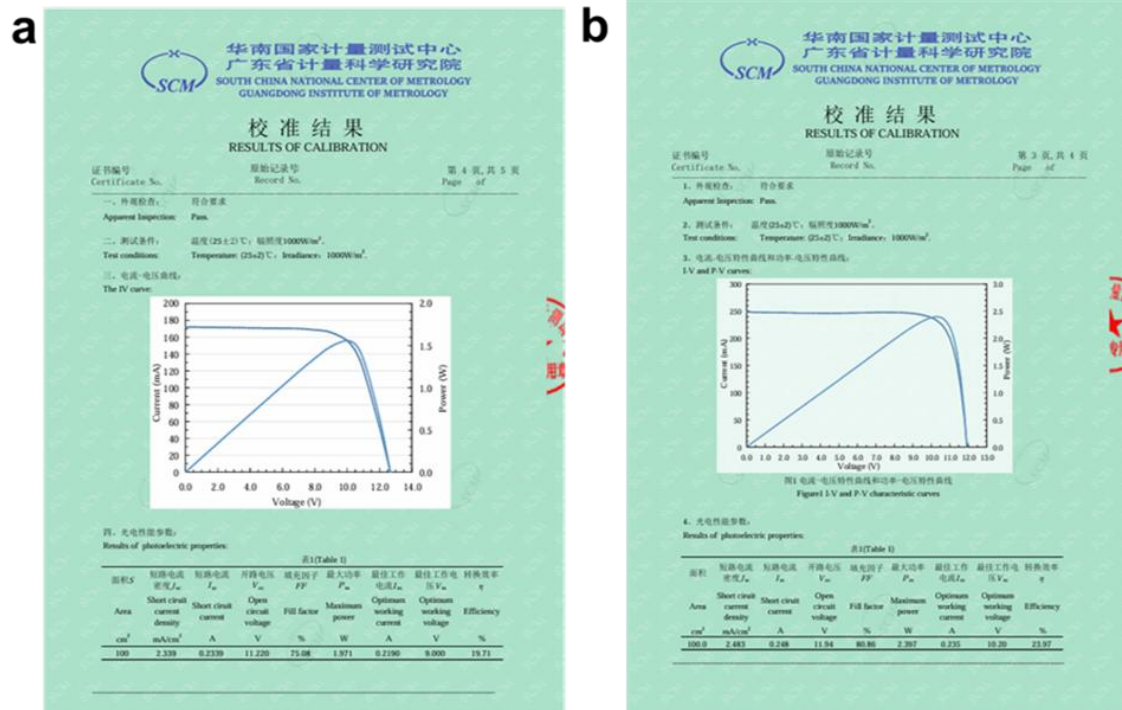
Supplementary Fig. 24. The Light intensity dependence test of PSCs from NMP sample and NBP sample.



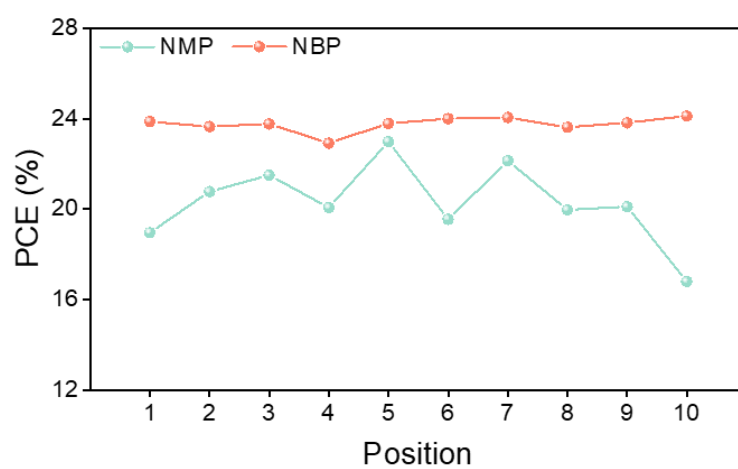
Supplementary Fig. 25. The PCE for NMP and NBP PSCs under 80% RH at 25 °C (10 PSCs for each condition), and five NMP sample exhibiting no photoelectric properties are omitted from the figure. Box plots: box limits = 25th–75th percentiles, central line = median, whiskers = full range (minima to maxima).



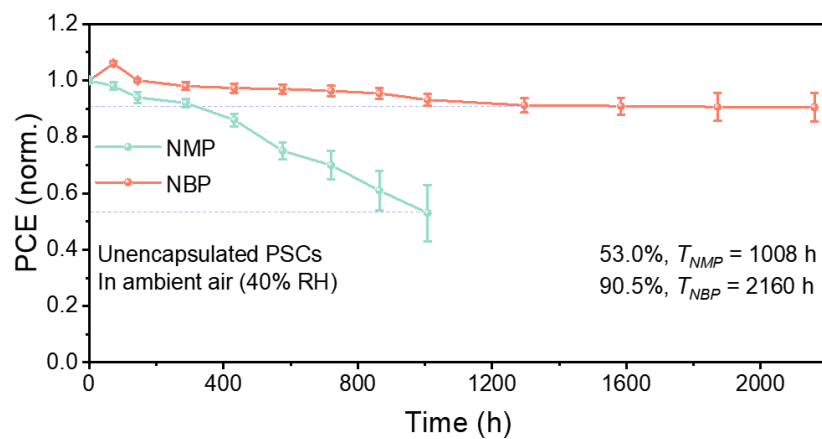
Supplementary Fig. 26. The device with different aperture areas of NMP sample and NBP sample. Standard mask plate dimensions are 25 cm² and 100 cm², which are not specifically illustrated.



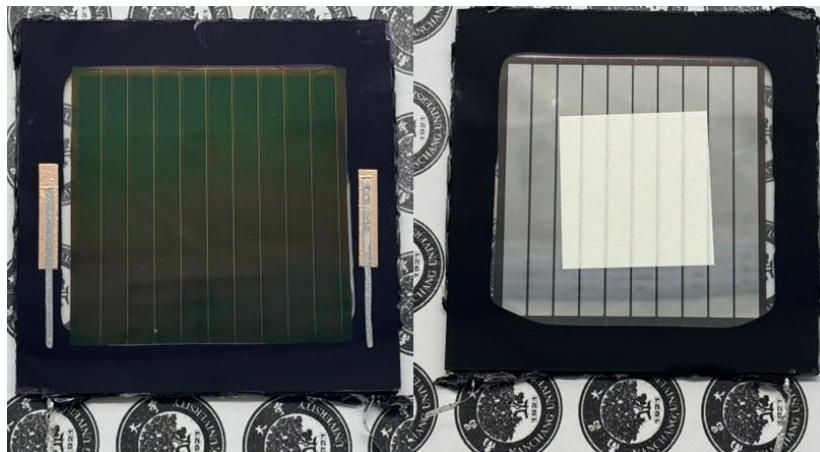
Supplementary Fig. 27. A certification report (J-V characterization) of the (a) flexible and (b) rigid PSM fabricated using NBP in ambient conditions. This report is issued by SCM (South China National Center of Metrology Guangdong Institute of Metrology). The aperture area is measured by SCM to be 100 cm².



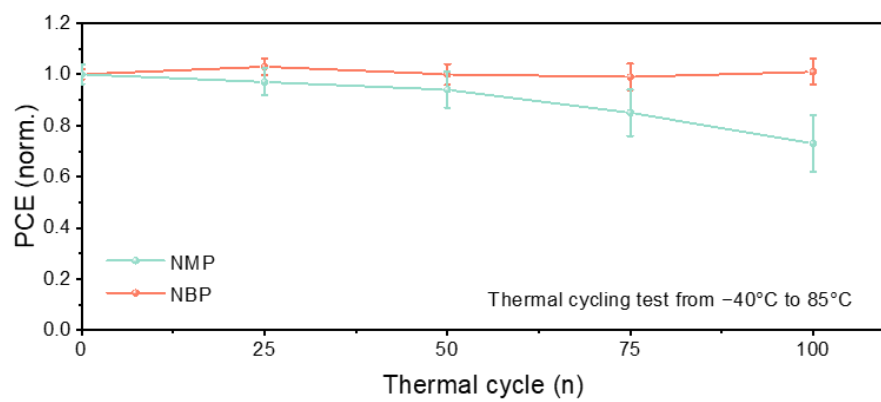
Supplementary Fig. 29. NMP and NBP PSMs single cell PCE distribution.



Supplementary Fig. 30. The device stability of NMP sample and NBP sample.



Supplementary Fig. 31. The PSM packaging photo. For specific packaging steps and details, please refer to the method mentioned above. The white substance in the figure is a label sticker, which is only adhered to the outer surface of the glass and is used for sample identification and experimental information traceability.



Supplementary Fig. 32. Thermal cycling test from -40°C to 85°C .

Supplementary Table 1. The Full Width at Half Maximum (FWHM) and relative peak area of the (100), (200) and (210) crystal planes of the NMP sample.

Crystal Face	FWHM	Relative Peak Area (%)
100	0.3787	31.52
200	0.3495	20.69
210	0.3184	16.73

Supplementary Table 2. The FWHM and relative peak area of the (100), (200) and (210) crystal planes of the NBP sample.

Crystal Face	FWHM	Relative Peak Area (%)
100	0.2883	25.59
200	0.2714	22.10
210	0.2614	20.49

Supplementary Table 3. Residual ratio of NMP/NBP (**Supplementary Fig. 11b**) in perovskite films prepared using NMP/NBP and DMF as solvents.

Sample	NMP/NBP	FA ⁺	Solvent
	peak area	peak area	residual ratio
NMP	0.17	1.00 (Normalized)	8.5%
NBP	0.09		4.5%

Supplementary Table 4. Residual ratio of NMP/NBP (**Supplementary Fig. 11c**) in perovskite films prepared using NMP/NBP and DMF as solvents.

Sample	NMP/NBP	FA ⁺	Solvent
	peak area	peak area	residual ratio
NMP	0.09	1.00	4.5%
NBP	0	(Normalized)	0%

Supplementary Table 5. The specific performance parameters NMP and NBP PSCs.

Sample	V_{oc}	FF	J_{sc}	PCE
NO.	(V)	(%)	mA cm⁻²	(%)
FS-NMP	1.176	80.60	25.80	24.45
RS-NMP	1.170	80.83	25.66	24.27
FS-NBP	1.197	85.42	25.92	26.50
RS-NBP	1.191	85.38	25.93	26.37

Supplementary Table 6. The specific performance parameters NMP and NBP flexible PSMs.

Sample	V_{OC}	FF	J_{SC}	PCE
NO.	(V)	(%)	mA cm^{-2}	(%)
FS-NMP	11.31	66.81	2.273	17.18
RS-NMP	11.08	66.39	2.251	16.56
FS-NBP	11.71	76.81	2.293	20.62
RS-NBP	11.73	75.52	2.305	20.42

Supplementary Table 7. The specific performance parameters NMP and NBP rigid PSMs.

Sample	V_{oc}	FF	J_{sc}	PCE
NO.	(V)	(%)	mA cm⁻²	(%)
FS-NMP	11.53	74.69	2.399	20.66
RS-NMP	11.50	71.92	2.422	20.03
FS-NBP	11.85	81.42	2.503	24.15
RS-NBP	11.77	81.06	2.510	23.95

Supplementary Table 8. Recent PCE statistics of the mini-module report. ^{ap} = aperture area; ^{ac} = active area. R = Rigid PSM; F = Flexible PSM.

Area (cm ²)	Types of PSMs	Fabrication atmosphere	Methods	Lab PCE (%)	Certified PCE (%)	Ref.
100 ^{ap}	R	40% RH	Slot-die coating	24.15	23.97	This work
100 ^{ap}	F	40% RH	Slot-die coating	20.62	19.71	This work
50 ^{ac}	R	Ambient air	Slot-die coating	23.06	-	Angew.Chem.Int. Ed., 2024. 10.1002/ange.202416390
27.21 ^{ap}	R	30-40% RH	Spin coating	21.91	21.51	Energy Environ. Sci., 2024. 10.1039/D4EE01147C
26.9 ^{ap}	R	20-70% RH	Coating	-	21.78	Science., 2023. 10.1126/science.ade9463
23.2 ^{ap}	R	35% RH	Blade coating	20.0	-	Science., 2024. 10.1126/science.adn9453
25 ^{ap}	R	Ambient air	Blade coating	19.9	-	Nat Sustain., 2025. 10.1038/s41893-025-01529-5
12.25 ^{ap}	R	30%-40% RH	Blade coating	22.2	21.6	Sci. Adv., 2025. 10.1126/sciadv.adu3493
12.6 ^{ac}	R	50% RH	Blade coating	22.4	-	Adv. Energy Mater., 2024. 10.1002/aenm.202400932
12.82 ^{ap}	R	<30% RH	Spin coating	18.38	18.22	Joule., 2024. 10.1016/j.joule.2024.06.026
14 ^{ac}	R	40% RH	Spin coating	20.19	-	JACS., 2024. 10.1021/jacs.4c13866
15.64	R	30-40% RH	Printing	21.04	-	Angew.Chem.Int. Ed., 2025. 10.1002/anie.202509459
17.1/65 ^{ac}	R	15±5% RH	Slot-die printing	20.42/19.54	19.3/-	Science., 2021. 10.1126/science.abh1035
48 ^{ap}	R	Ambient air	Coating	20.76	-	Adv. Funct. Mater., 2025. 10.1002/adfm.202506718
56.5 ^{ap}	R	Air	Slot-die coating	21.5	20.3	Nat. Commun.,2025. 10.1038/s41467-025-57303-w

57.2 ^{ap}	R	Ambient air	Blade coating	22.76	21.6	Joule., 2025. 10.1016/j.joule.2025.101919
25/64/12	R/R/F	Air	Slot-die coating	22.05/20.65/18.86	-/20.33/-	Joule., 2025. 10.1016/j.joule.2025.101850
13.2 ^{ac}	R	Ambient air	Blade coating	22.98	-	Angew.Chem.Int. Ed., 2026. 10.1002/ange.202520159
16.02 ^{ap}	R	-	Spin coating	23.33	-	Nature., 2026. 10.1038/s41586-026-10587-4
25 ^{ap}	R	Ambient air	Spin coating	22.15	-	Nat. Synth., 2026. 10.1038/s44160-026-01070-z
14 ^{ac}	R	Ambient air	Spin coating	22.03	-	Nat. Commun., 2026. 10.1038/s41467-026-72793-y
20.25 ^{ac}	R	30% RH	Spin coating	24.0	23.2	Nat. Energy., 2026. 10.1038/s41560-026-02014-9
32.5 ^{ap}	R	Ambient air	Blade coating	23.0	-	Nat. Mater., 2026 10.1038/s41563-026-02546-1
100 ^{ac}	F	10-20% RH	Blade printing	16.39	15.65	Adv. Funct. Mater., 2025. 10.1002/adfm.202424191
9/21/32 ^{ap}	F	Ambient air	Blade coating	20.1/18.7/17.8	18.99/-/-	Nat. Photonics, 2024. 10.1038/s41566-023-01373-z
117 ^{ac}	F	Ambient air	Blade coating	17.52	15.30	Energy Environ. Sci., 2024. 10.1039/d4ee02925a
100 ^{ac}	R/F	30%-55% RH	slot-die coating	-	23.97/20.67	Science.,2025. 10.1126/science.adx9650

Reference

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2. Ugur, E. *et al.*, *J Phys Chem Lett* **13**, 7702-7711 (2022).
3. Wang, H. *et al.*, *Nature* **634**, 1091–1095 (2024).
4. Green, M. A., *Solar Cells* **7**, 337-340, (1982).