

Supplementary Information

Compositional Optimization of 2D-3D Heterojunction Interface for 22.6% Efficient and Stable Planar Perovskite Solar Cells

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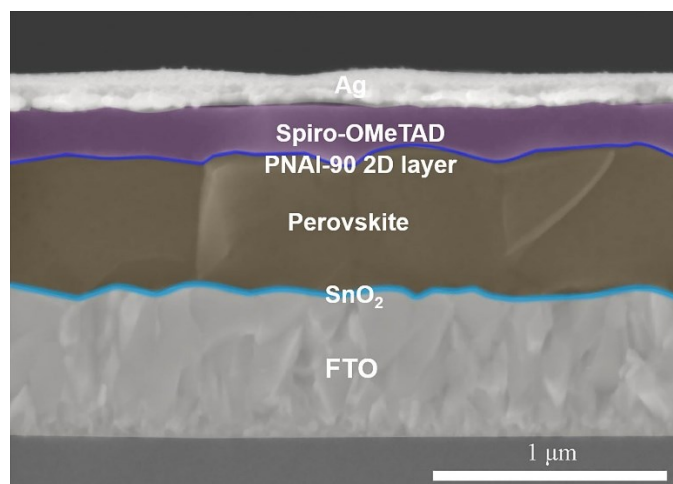


Figure S1 False colored cross-sectional SEM image of PNAI-90 treated perovskite device.

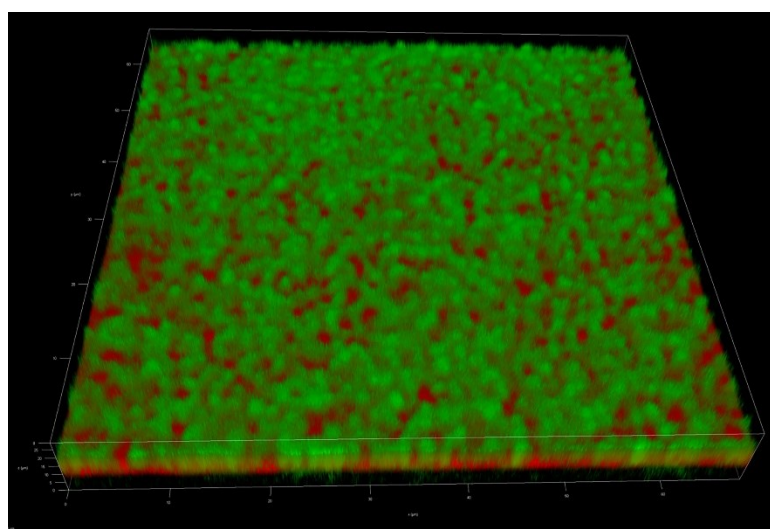


Figure S2 3D CLSM image of PNAI-90 treated perovskite film

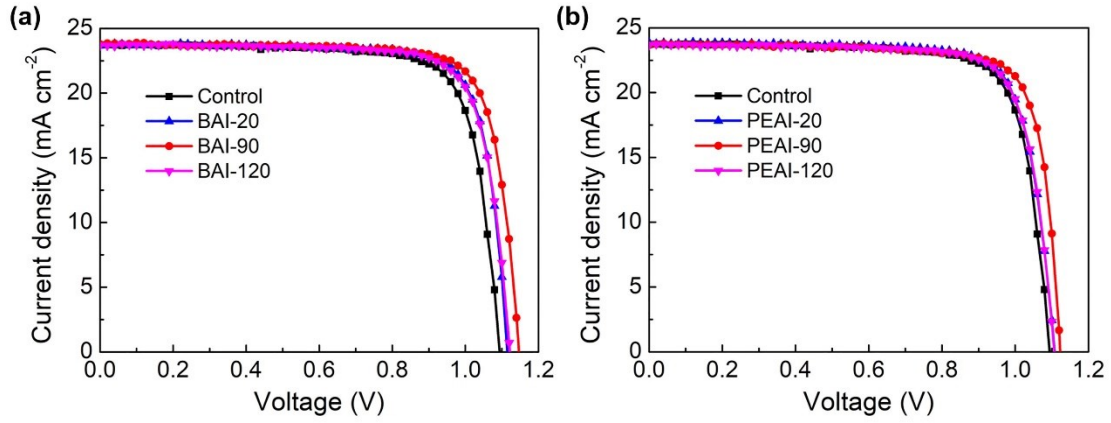


Figure S3 J-V curves of PSCs under different interfacial treatments by BAI (a) and PEAI (b).

Table S1 Photovoltaic characteristics of the best devices under different interfacial treatments

Devices	PCE(%)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF
Control	20.26	1.08	23.74	78.99
BAI-20	21.17	1.10	23.82	80.80
BAI-90	21.69	1.14	23.89	79.63
BAI-120	20.87	1.12	23.80	78.30
PEAI-20	20.77	1.10	23.88	79.06
PEAI-90	21.30	1.12	23.78	79.97
PEAI-120	20.65	1.10	23.74	79.09

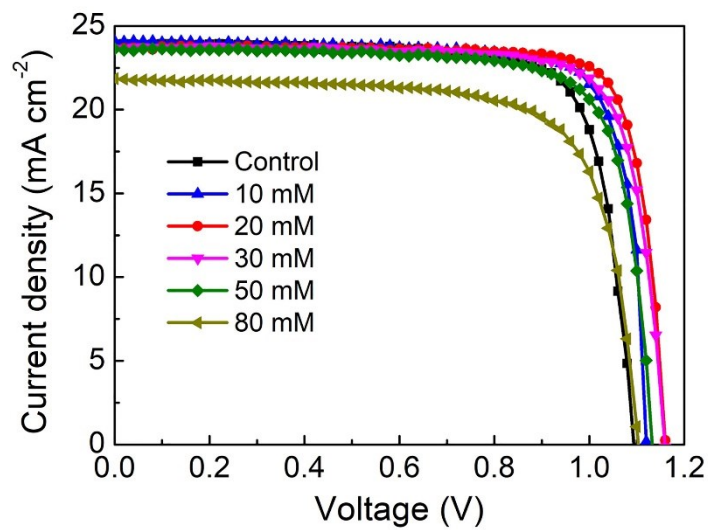


Figure S4 J-V curves of PSCs treated by PNAI-90 at different concentrations.

Table S2 Photovoltaic characteristics of PSCs treated by PNAI-90 at different concentrations.

Devices	PCE(%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF
Control	20.26	1.08	23.74	78.99
10 mM	21.81	1.12	24.09	80.83
20 mM	22.62	1.16	23.82	81.87
30 mM	21.88	1.14	23.79	80.66
50 mM	20.78	1.12	23.64	78.48
80 mM	17.69	1.10	21.85	73.57

Table S3 Photovoltaic characteristics of the devices under different scan directions

Devices	PCE (%)	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF (%)	Hysteresis index
Control	20.26	1.08	23.74	78.99	6.3%
	18.98	1.06	23.68	75.63	
PNAI-90	22.62	1.16	23.82	81.87	2.4%
	22.07	1.16	23.75	80.10	

Table S4 Fitting parameters for the time resolved PL curves of perovskite films.

Samples	T _{avg} (ns)	τ ₁ (ns)	τ ₂ (ns)	τ ₃ (ns)	A1 (%)	A2 (%)	A3 (%)
Control	509.64	7.23	78.37	553.23	34.24	25.24	40.52
PNAI-20	634.42	15.72	87.27	1022.8 0	67.24	27.77	4.98
PNAI-90	1008.3 9	7.04	59.29	1209.5 6	69.47	23.16	7.37
PNAI-120	402.99	16.28	87.47	738.24	62.99	31.86	5.15

$$F(t)=A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3) + \gamma_0$$

where τ₁, τ₂, and τ₃ are fast decay time, intermediate decay time, and slow decay time, A₁, A₂, and A₃ are the coefficient, respectively.

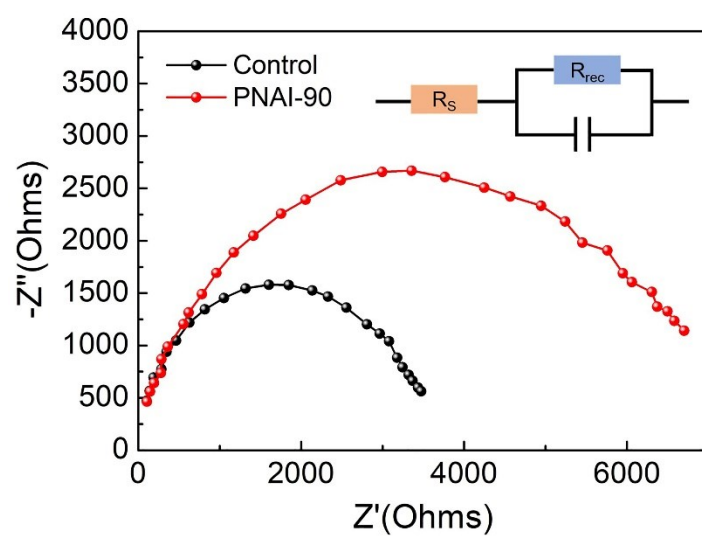


Figure S5 Nyquist plots of control and PNAI-90 treated perovskite solar cells measured in the dark.

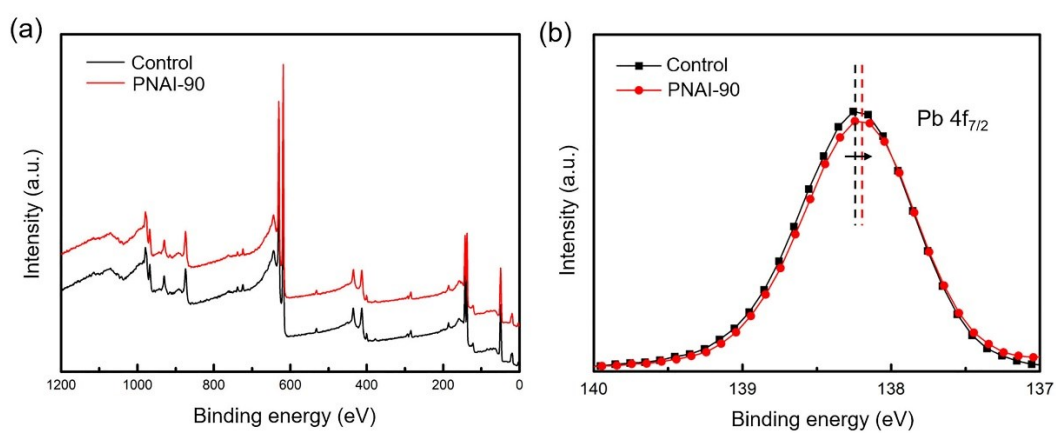


Figure S6 (a) survey scan of XPS spectra of Control and PNAI-90 treated perovskite films. (b) the core level of Pb $4f_{7/2}$ obtained from the narrow scan.

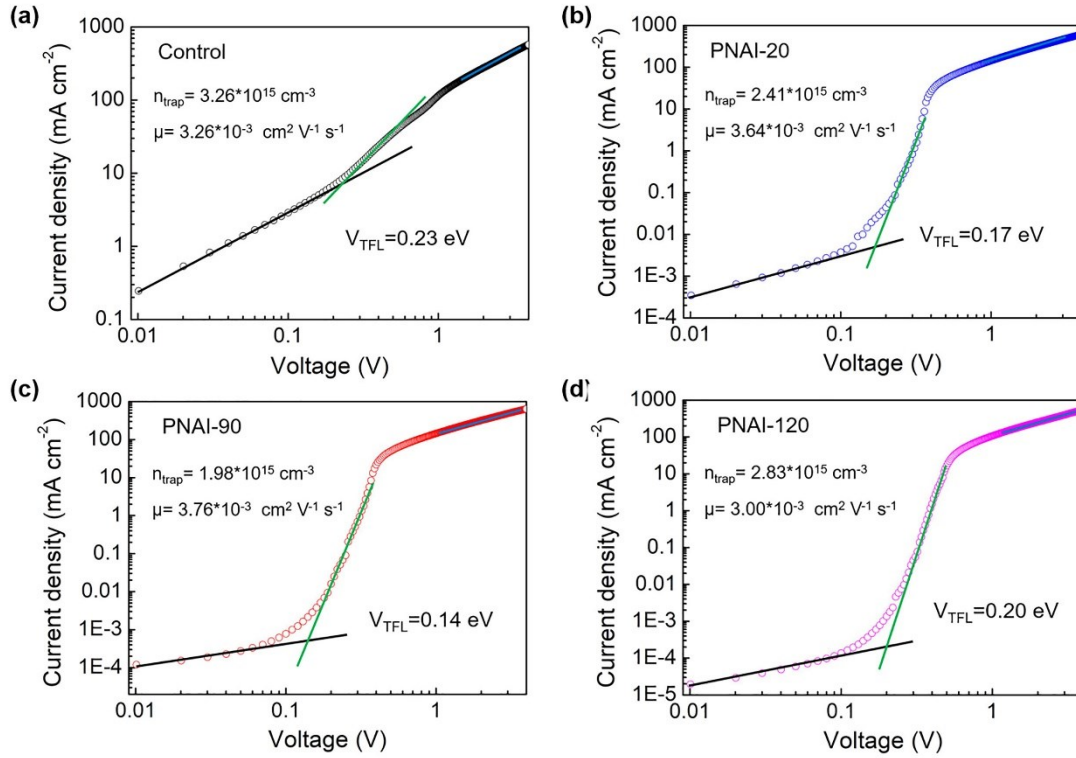


Figure S7 Space charge-limited current (SCLC) of electron-only devices with structure of FTO/SnO₂/Perovskite/with or without interfacial layers/PCBM/Ag under dark conditions.

The architectures of electron-only devices are FTO/SnO₂/perovskite/with or without interfacial layer/PCBM/Ag, and their dark trap-filled limit voltage (V_{TFL}) values from the I-V curves are 0.23 eV, 0.17 eV, 0.14 eV, 0.20 eV, respectively. The trap density (n_{trap}) can be calculated according to the following formula¹:

$$n_{trap} = \frac{2\varepsilon_0\varepsilon_r V_{TFL}}{eL^2}$$

Where $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ and $\varepsilon_r = 46.9$ are the vacuum permittivity and the relative dielectric constants of FAPbI₃, respectively²; e is the elementary charge of the electron; $L \sim 605 \text{ nm}$ is the thickness of the perovskite film measured by the cross-section SEM image.

Furthermore, the electron mobility (μ) was derived using the Mott–Gurney law:

$$\mu = \frac{8J_D L^3}{9\varepsilon_0\varepsilon_r V^2}$$

where J_D is the current density and V is the applied voltage.

Table S5 Fitting parameters for the time resolved PL curves of perovskite/HTL films.

Samples	τ_{avg} (ns)	τ_1 (ns)	τ_2 (ns)	A1 (%)	A2 (%)
Control	9.29	1.29	10.70	59.42	40.58
PNAI-20	8.91	1.04	10.32	64.03	35.97
PNAI-90	6.24	1.18	8.11	71.84	28.16
PNAI-120	7.30	1.41	10.12	77.42	22.58

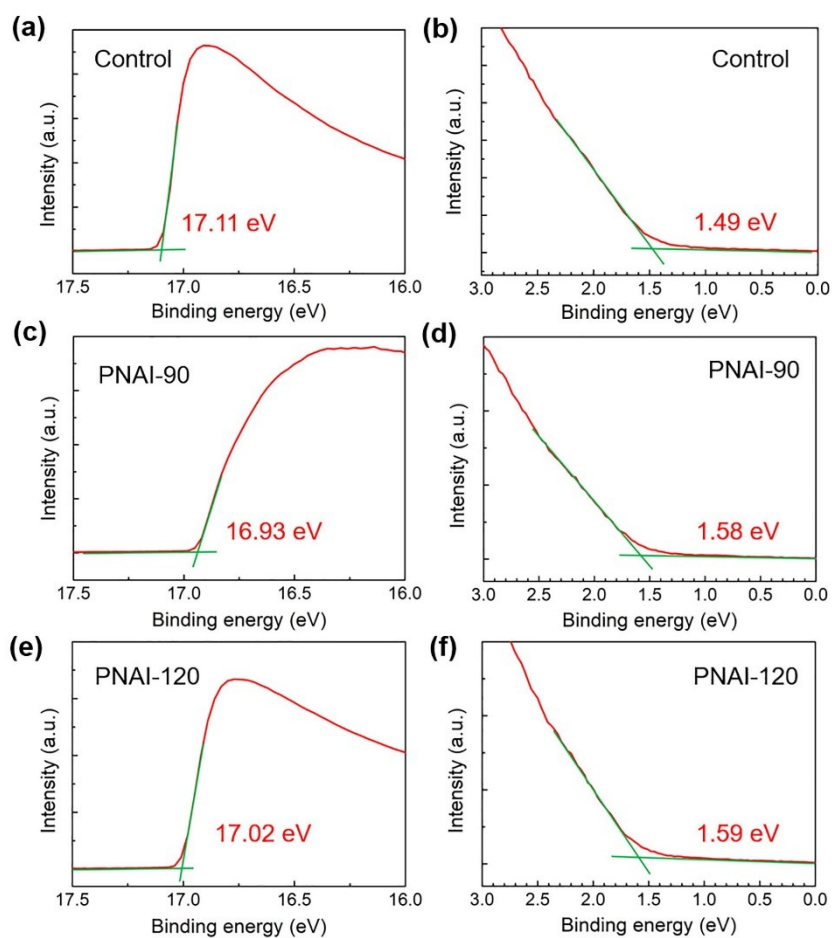


Figure S8 UPS analysis results for work function and valence band of Control, PNAI-90 treated and PNAI-120 treated perovskite film.

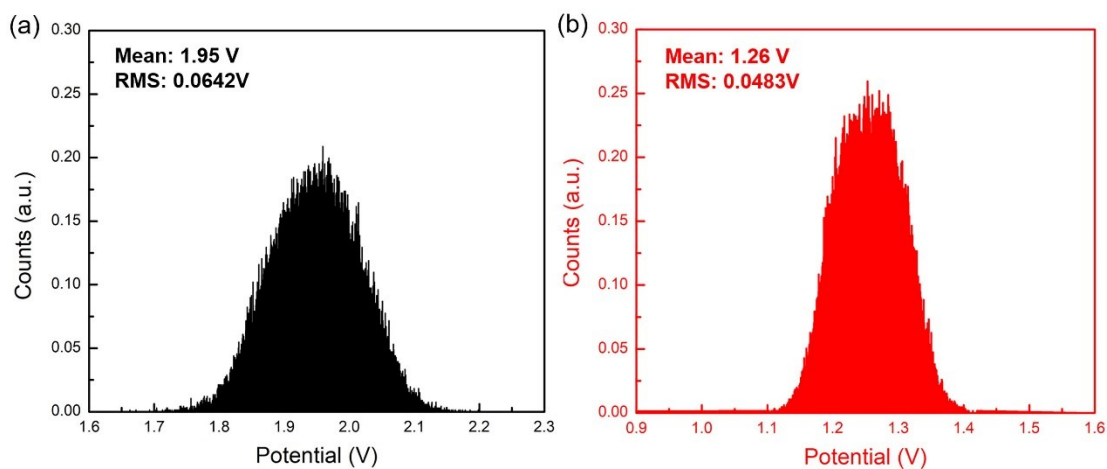


Figure S9 The surface potential distribution charts of (a) control perovskite and (b) PNAI-90 treated perovskite film.

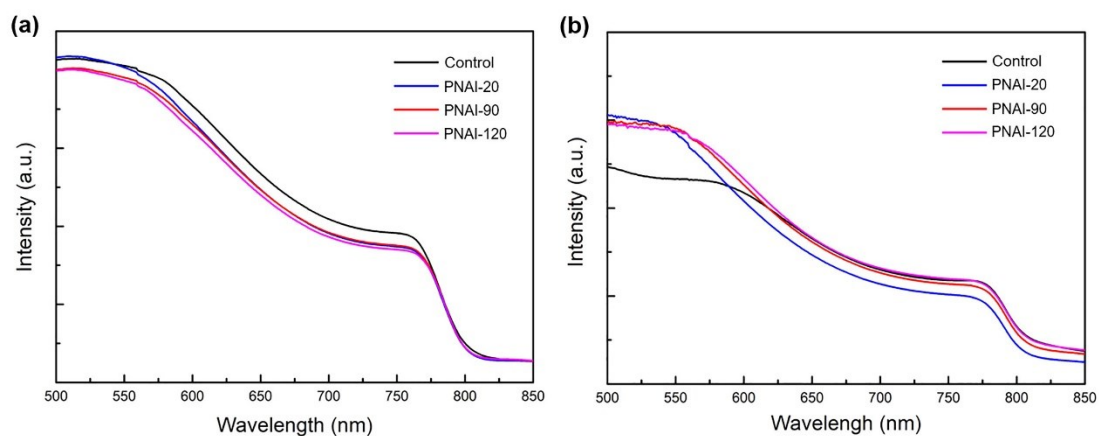


Figure S10 Absorption spectra of the perovskite film under different interfacial treatments before (a) and after (b) stored in high humidity ($70\pm 10\%$ RH) for 150 days.

1. T. Niu, J. Lu, M.-C. Tang, D. Barrit, D.-M. Smilgies, Z. Yang, J. Li, Y. Fan, T. Luo and I. McCulloch, *Energy & Environmental Science*, 2018, **11**, 3358-3366.
2. W. Luo, C. Wu, D. Wang, Y. Zhang, Z. Zhang, X. Qi, N. Zhu, X. Guo, B. Qu and L. Xiao, *ACS applied materials & interfaces*, 2019, **11**, 9149-9155.

