Electronic Supplementary Information

Preferential Crystallographic Orientation via α-CN Stereodirectional Effect for Superior Perovskite Indoor Photodetectors

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Experimental Section

Materials Preparation

The perovskite precursor solution was prepared by mixing methylammonium iodide (MAI) from GreatCell Solar Limited and lead(II) iodide (PbI₂) from TCI in a 1:1 molar ratio to achieve a concentration of 1.4 M. The solvent system consisted of gamma-butyrolactone (GBL) and dimethyl sulfoxide (DMSO) mixed in a 7:3 volume ratio, both purchased from Sigma Aldrich. PEDOT:PSS from Heraeus and PC₇₀BM from Organic Semiconductor Materials were used as the hole and electron transport layers, respectively. All active layer solutions were maintained at 60°C within a glove box environment. 1 v% of α -chloronaphthalene (α -CN) with 99.9% purity was used as an additive to the anti-solvent (chlorobenzene) for treatment during the perovskite film formation process.^{1,2}

Device Fabrication

ITO substrates were sequentially cleaned in ultrasonic baths with detergent, deionized water, acetone, and isopropanol for 30 minutes each, followed by nitrogen drying and heat treatment at 100°C. After UV-ozone treatment for surface modification, PEDOT:PSS was spin-coated at 5000 rpm for 30 seconds to form a 40 nm thick hole transport layer, followed by air annealing. The perovskite layer was deposited using a two-step spin-coating process (1000 rpm for 10 seconds, followed by 5000 rpm for 30 seconds), with chlorobenzene containing 1 v% α -CN being dripped 10 seconds before the end of the second step. The coated film was annealed at 100°C for 10 minutes in a glove box. The electron transport layer was formed by spin-coating PC70BM solution (20 mg/mL in chlorobenzene) at 2000 rpm for 30 seconds. Finally, a 90 nm thick aluminum electrode was deposited by thermal evaporation at 4×10⁻⁶ Torr.

Characterization

Photovoltaic characteristics were measured under AM 1.5G conditions (100 mW/cm²) using a PEC-L01 solar simulator, while low-light measurements were performed in a custom-designed black box equipped with a 6000K white LED. Light intensity was measured using a Samsung SM-G991N illuminance meter. X-ray diffraction (XRD) patterns were recorded using a Rigaku D/MAX-2500 diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å). Crystallite sizes were calculated using the Scherrer equation (1): ³

$$d = \frac{K \times \lambda}{\beta \times \cos \theta} \tag{1}$$

where d is the crystallite size, K is the shape factor (0.9), λ is the X-ray wavelength (0.15406 nm for Cu K α radiation), β is the full width at half maximum (FWHM) in radians, and θ is the Bragg angle.

Device responsivity (R) was calculated as the ratio of photocurrent (I_{ph}) to incident power density (P_o) (2):⁴

$$R = \frac{I_{ph}}{P_o} \tag{2}$$

Shot noise based-detectivity (D*) was determined using (3):5

$$D *= \frac{R}{\sqrt{2qJ_{dark}}} \left[\text{cm Hz}^{1/2} \text{ W}^{-1} \right]$$
(3)

where q is the elementary charge (1.602 \times 10^{-19} C) and J_{dark} is the dark current density.

The linear dynamic range (LDR) was calculated using (4):⁶

$$LDR = 20 \times \log_{10} \left(\frac{J_{photo}}{J_{dark}} \right) [dB]$$
(4)

Ideality factor (n) was extracted from the dark J-V curves using (5):⁷

$$n = \frac{kT}{q} \left(\frac{\partial \ln J}{\partial V}\right)^{-1} \tag{5}$$

where k is the Boltzmann constant, T is the absolute temperature, q is the elementary charge, and $\partial \ln J/\partial V$ is the derivative of the natural logarithm of current density with respect to voltage. Trap-assisted tunneling (TAT) current was analyzed using (6):⁸

$$J_{TAT} \propto \exp\left(-\frac{8\pi\sqrt{2qm_e^*}}{3hE}\phi_{t}^{3/2}\right)$$
(6)

where m_e^* is the effective electron mass, h is Planck's constant, E is the electric field, and ϕ_t is the defect state energy.

Morphological characteristics were analyzed using a Zeiss SIGMA field emission scanning electron microscope (FE-SEM) operated at 5 kV acceleration voltage and a Park Systems NX-10 atomic force microscope (AFM). The root mean square (RMS) roughness was calculated from the AFM height data using (7):⁹

$$R_{q} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (z_{i} - \bar{z})^{2}}$$
(7)

where N is the number of data points, zi is the height at point i, and \overline{z} is the mean height.

Cyclic voltammetry was performed using an Ivium CompactStat instrument (Ivium Technologies, Netherlands) at room temperature. Measurements were conducted in acetonitrile with 0.1 M Bu₄NPF₆ electrolyte at a 50 mV/s scan rate. The setup employed a platinum wire counter electrode and an Ag/Ag⁺ reference electrode.



Figure S1. Step-by-step comparison of perovskite crystallization mechanisms between reference (W/O α -CN, left) and optimized condition (W/ α -CN, right) processes: (1) Initial coordination environment: coordination bond deficiency in reference vs. multi-directional coordination with α -CN as an interface modifier; (2) Nucleation stage: unaligned nucleation in reference vs. directional selective nucleation with α -CN; (3) Crystal growth pattern: nondirectional crystal growth in reference vs. preferential crystal growth along the (110) plane with α -CN; (4) Final grain structure: random grain orientation in reference vs. stereo-directional effect with aligned grains in optimized sample. Both 2D and 3D representations illustrate the dramatic difference in crystallographic alignment resulting from α -CN incorporation.



Figure. S2 Schematic illustration of perovskite film fabrication process via anti-solvent treatment during spin-coating.



Figure S3. Optical Analysis of (a) UV-visible absorbance and (b) steady state photoluminescene comparison for the samples with glass/CH₃NH₃PbI₃ (without or with α -CN).



Figure S4. X-ray diffraction spectroscopy (XRD) spectra of $CH_3NH_3PbI_3$ films at adduct phase and perovskite phase: (220) plane change of (a) without α -CN and (b) with α -CN.



Figure S5. X-ray diffraction spectroscopy (XRD) spectra of $CH_3NH_3PbI_3$ films at adduct phase and perovskite phase: (222) plane change of (a) without α -CN and (b) with α -CN.



Figure S6. Atomic force microscopy (AFM) analysis of CH₃NH₃PbI₃ films (5×5 μ m²) without and with α-CN treatment. (a) 3D topography image of perovskite film without α-CN. (b) Height distribution histogram with Gaussian fit of film without α-CN. (c) 3D topography image of perovskite film with α-CN treatment. (d) Height distribution histogram with Gaussian fit of film with α-CN.



Figure S7. Grain size distribution of $CH_3NH_3PbI_3$ films (a) without α -CN and (b) with α -CN derived from line profile of AFM images.



Figure S8. Cross-sectional FE-SEM images of $CH_3NH_3PbI_3$ based devices (a) without α -CN and (b) with α -CN.



Figure S9. (a) Cyclic voltammetry (CV) measurements showing (a) ITO substrate with work function of -4.75 eV, (b) ITO/PEDOT:PSS/CH₃NH₃PbI₃ without α -CN showing HOMO level at -5.13 eV, (c) ITO/PEDOT:PSS/CH₃NH₃PbI₃ with α -CN showing HOMO level at -5.03 eV, (d) ITO/CH₃NH₃PbI₃ without α -CN showing HOMO level at -5.41 eV, and (e) ITO/PEDOT:PSS/CH₃NH₃PbI₃ with α -CN showing HOMO level at -5.39 eV. Green dotted circles highlight key oxidation features.



Figure S10. (a) Perovskite optoelectronic device and (b) energy band diagram showing electron and hole flow mechanism with α -CN effect.



Figure S11. Statistical graph of (a) dark current density and (b) responsivity for the $CH_3NH_3PbI_3$ -based devices without and with α -CN additive.



Figure S12. Stability measurements of CH₃NH₃PbI₃-based devices with and without α -CN additive. Normalized responsivity (%) over time for devices (a) without α -CN and (b) with α -CN measured at different days (D+0, D+3, D+28, and D+40). Normalized detectivity (%) over time for devices (c) without α -CN and (d) with α -CN measured at the same time intervals. The green dotted line represents the 90% threshold of initial performance.



Figure S13. J-V curves under (a) 1sun, (b) 1200 lux, (c) 917 lux, and (d) 336 lux of $CH_3NH_3PbI_3$ -based devices without or with α -CN.



Figure S14. Performance Comparison (PCE vs. light intensity) for indoor perovskite optoelectronics.



Figure S15. Light dependent linear characteristic parameters: (a) linear dynamic range (LDR), (b) PCE (power conversion efficiency), (c) shot noise based-detectivity (D^{*} at self-powered condition (@ 0V)) of CH₃NH₃PbI₃-based devices without or with α -CN.

Table S1. Chemical structures and properties of chlorobenzene (CB) and chloronaphthalene $(\alpha$ -CN) as perovskite anti-solvent materials.

	Materials	Chemical Formula	Boiling Point	Density (at 25 °C)
Pristine Anti-solvent	Chlorobenzene (CB)	C ₆ H ₅ Cl	132 °C	1.106 g/ml
Additive	Chloronaphthalene (α-CN)	C ₁₀ H ₇ Cl	263 °C	1.194 g/ml

Table S2. Rate of change of peak intensity, full width at half maximum (FWHM) values, and crystallite size derived from (220) plane of XRD spectra (from adduct to perovskite phase) shown in **Figure 2**.

(220)	Δ Intensity	Δ FWHM	Δ Crystallite Size	
(220)	(%)	(%)	(%)	
W/O α-CN	+ 188.49	- 29.54	+ 141.95	
W/ a-CN	+147.31	- 36.59	+ 157.69	

Table S3. Rate of change of peak intensity, full width at half maximum (FWHM) values, and crystallite size derived from (222) plane of XRD spectra (from adduct to perovskite phase) shown in **Figure 2**.

(222)	Δ Intensity	Δ FWHM	Δ Crystallite Size	
(222)	(%)	(%)	(%)	
W/O α-CN	+ 194.45	- 23.60	+ 130.90	
W/ a-CN	+ 245.87	- 46.11	+ 185.49	

Table S4. Device performance parameters: values of Voc, Jsc, FF, and PCE of $CH_3NH_3PbI_3$ based devices without or with α -CN under various light condition (1sun, 1200 lux, 917 lux, and 336 lux).

AM 1.5G		V _{oc} (V)	J _{sc} (mA/cm²)	FF (%)	РСЕ (%)
1 sun	W/O α- CN	0.932	20.12	72	13.53
	W/ α-CN	0.915	20.90	76	14.59
WLED, 6000K		V _{oc} (V)	J _{sc} (μA/cm ²)	FF (%)	PCE (%)
@ 1200	W/O α-CN	0.752	110	60	28.04
lux	W/ α-CN	0.735	112	69	32.23
@ 917 lux	W/O α-CN	0.732	81	57	24.97
	W/ α-CN	0.721	81	68	29.58
@336 lux	W/O a-CN	0.671	33	48	21.93
	W/ α-CN	0.677	30	61	25.06

 Table. S5 Performance comparison of various Perovskite optoelectronic device structures

 under different indoor light conditions

Structure [Reference]	Light Condition	PCE (%)
ITO/ALD-TiO ₂ /meso-TiO ₂ /MAPbI _{3-x} Clx/spiro- MeOTAD/Au [Nano Res., 2017, 10, 2130-2145.] ¹⁰	LED @400 lux	23.8
ITO/SnO ₂ /MgO/MAPbI ₃ /Spiro-MeOTAD/Au [Nano Energy, 2018, 49, 290-299.]	LED @400 lux	26.9
ITO/SnO ₂ /CsPbI ₂ Br (MAI 10 w%)/Spiro- OMeTAD/Au [ACS Appl. Mater. Interfaces, 2020, 12, 36228- 36236.] ¹¹	LED, 6500K @1000 lux	23.51
FTO/SnO ₂ /FAPbI ₃ /spiro-OMeTAD/MoO ₃ /Ag	LED, 2956K @1062 lux	31.85
[Adv. Mater., 2022, 34.16, 2200320.] ¹²	LED, 2956K @106 lux	29.89
ITO/MeO-2PACz/Triple-cation perovskite with Al ₂ O ₃ passivation/C ₆₀ /SnO ₂ /Cu [ACS Appl. Mater. Interfaces 2024, 16, 45, 62195– 62202] ¹³	LED, warm white @870 lux	34.00
ITO/DEDOT.DSS/MADDIa with DTAA	LED, 4000K @1000lux	~10.50
interlayer/PCBM/BCP/Ag [ACS Appl. Energy Mater. 2024, 7, 15, 6096–	LED, 4000K @500lux	11.91
6104.] ¹⁴	LED, 4000K @250lux	18.37
	LED, 6000K @1200 lux	32.23
ITO/PEDOT:PSS/MAPbI ₃ (α-CN)/PC ₇₀ BM/Al [This Work]	LED, 6000K @917 lux	29.58
	LED, 6000K @336 lux	25.06

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