Electronic Supplementary Information

Surface recrystallized stable 2D-3D graded perovskite solar cells for efficiency beyond 21%

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Materials: FTO glass substrates (13 Ω sq^{-1}), PbI$_2$ (99.8%), all solvents like DMF (anhydrous, 99.8%), DMSO (anhydrous, 99.8%), Toluene (anhydrous, 99.8%), Chlorobenzene were procured from Sigma-Aldrich. MAI was purchased from Dyesol. Nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) was fobtained from TCI. All other chemicals were used as received.

Synthesis of ABHB: For the synthesis, 1 equivalent of 4-(aminomethyl)benzoic acid was dissolved in ethanol and placed it in ice bath. After that under vigorous stirring condition, hydrogen bromide (1.1 equivalent) was added slowly into the solution. To ensure completion of the reaction, the solution was stirred overnight. Then the solvent was removed from the reaction mixture by rotary evaporator and resulting solid was washed with diethyl ether several times. The white solid was further purified by recrystallization in mixed solvent of methanol and diethyl ether. Finally, the white crystalline solid was filtered and dried under vacuum (yield ~90%). The resulting compound is named as of 4-(aminomethyl)benzoic acid hydrogen bromide (ABHB).

Device Fabrication: NiO$_x$ precursor solution was prepared by dissolving 1M Nickel nitrate hexahydrate and 1M Ethylenediamine in 1ml Ethylene Glycol. Then the NiO$_x$ layer was coated as hole transporting layer on the cleaned FTO. The cleaning process was started with detergent and followed by deionized water, acetone, and isopropyl alcohol for 15 min for each solvent, then dried and treated with UV-ozone for half an hour. NiO$_x$ precursor solution was spin coated onto the FTO substrates @3000 rpm for 40 sec. Afterward the substrates were postannealed at 300 °C for 60 min in ambient air. The MAPbI$_3$ precursor solution was prepared in a glovebox by dissolving MAI and PbI$_2$ (1:1 ratio) in a mixed solvent of gamma-Butyrolactone and DMSO (7:3, v/v) where the concentration of Pb^{2+} was 1.26. The solution was heated overnight and filtered with the 0.45 μm filter prior to spin coating. The filtered precursor solution was spin coated on the NiO$_x$ coated FTO in a two-step spin coating process i.e. 750 rpm for 20 sec and 4000 rpm for 60 sec. In the second step 160 ml anhydrous Toluene was dripped after 20 sec as antisolvent and after that the substrates were annealed @80° C for 10 min. Above the perovskite layer different concentration (1, 2 & 3 mg-mL^{-1}) of ABHB solution (in isopropanol solvent) was spin coated at 4000 rpm for 30 sec. Then the ABHB treated perovskite film was further annealed at 80° C for 5 min. After this, 12 mg/ml PCBM solution was coated @1200 rpm as ETL and again annealed @80° C for 5 min. After that a thin layer of Rhodamine 101 inner salt (0.5 mg/ml) was spin coated @4000 rpm. Finally, Ag was thermally deposited by using a shadow mask to yield an active area of 0.12 cm^2. The area foe the large area device was 2 cm^2.

Device Characterization:
The perovskite blend films were characterized by UV-vis absorption spectroscopy (Perkin Elmer Lambda-35), IR spectroscopy (LabRam HR). The XRD patterns of the samples were

recorded using a Rigaku Micromax-007HF diffractometer equipped with Cu Kα1 irradiation (λ = 1.54184 Å). The morphology of the samples was investigated by scanning electron microscopy (SEM, Hitachi S-4800) and AFM (Oxford, Cypher). The current density−voltage (*J*−*V*) characteristic curves were measured using a Keithley 2400 source meter under argon atmosphere by illuminating the device with a solar simulator (AM 1.5G, 100 mW cm^{-2}, Oriel Sol 3A solar simulator, Newport). The incident external quantum efficiency (EQE) was obtained by using an Oriel IQE-200 instrument under ambient condition. Electrochemical measurements were performed with a CH Instruments 760D. Ultraviolet photoemission spectroscopy (UPS) was measured using a Thermo Fisher Scientific UPS spectrometer (ESCALAB Xi$^+$).

Urbach energy Calculation:
Urbach energy (E_u) can be calculated by using the following equation:

$$\alpha = \alpha_0 exp(\frac{E}{E_u}) \qquad \textbf{S1}$$

where α is the absorption coefficient, α_0 is a constant and E (=hυ) is the energy of photon. From the slope of ln (α) versus photon energy plot E_u can be estimated.

Mott-Schottky (M-S) analysis:
Here the depletion layer capacitance (C) can be expressed as a function of the applied bias *V* as

$$\frac{1}{C^2} = \frac{-2}{\varepsilon\varepsilon_0 qA^2 N}(V - V_{bi}) \qquad \textbf{S2}$$

Where ε is the relative dielectric constant, ε_0 is the vacuum permittivity, *A* is the area of the device, *N* is residual charge density and V_{bi} is the built-in potential. *N* can be calculated from the slope of the linearly fitted M-S plot.

Trap density states (t-DOS) analysis:
To calculate the DOS (in electron states/cm^3 V), we have used

$$DOS = (6.24 \times 10^{18})[\frac{C}{d(1-p)}] \qquad \textbf{S3}$$

where *C* is the capacitance/cm^2, *d* is the thickness in cm, p is the porosity assumed to be zero for perovskite, and the conversion factor is the number of electrons per coulomb.

Trap study from hole only device:
The analysis was carried out with the hole-only devices having a device configuration of FTO/NiOx/Perovskite layer/MoO$_3$/Cu. The trap density (N_t) was calculated from the trap-filled limited region with the following equation:

$$N_t = \frac{2V_{TFL}\varepsilon\varepsilon_0}{qL^2} \qquad \textbf{S4}$$

where V_{TFL} is the voltage onset in the trap-filled limited region, ε the relative dielectric constant, ε_0 is the vacuum permittivity, and L is the thickness.
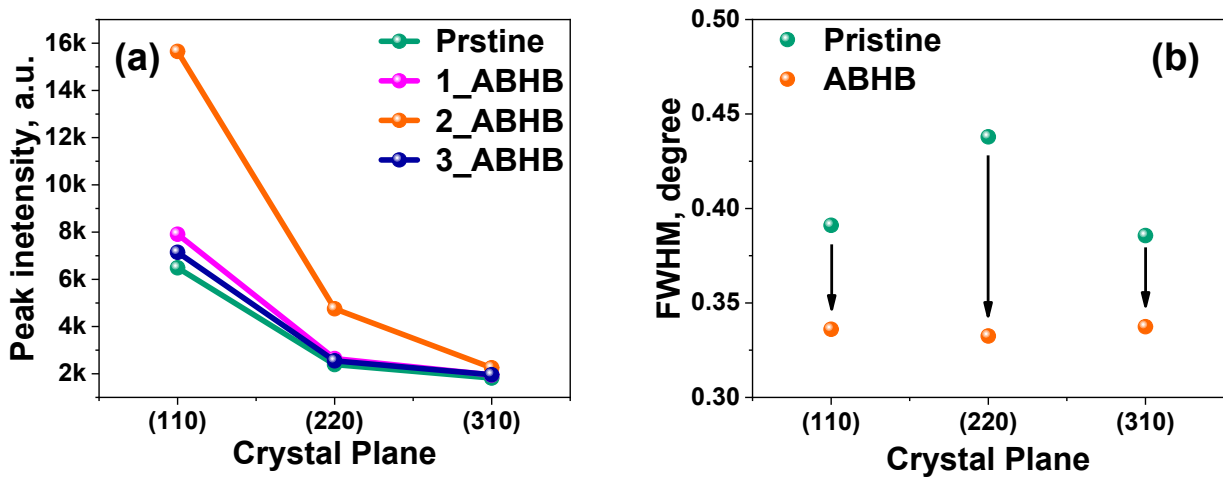
Fig. S1 (a) Peak intensity of the (110), (220), and (310) planes of perovskite films with varied concentrations of ABHB, (b) FWHM for all crystal planes of the perovskite films with and without ABHB.
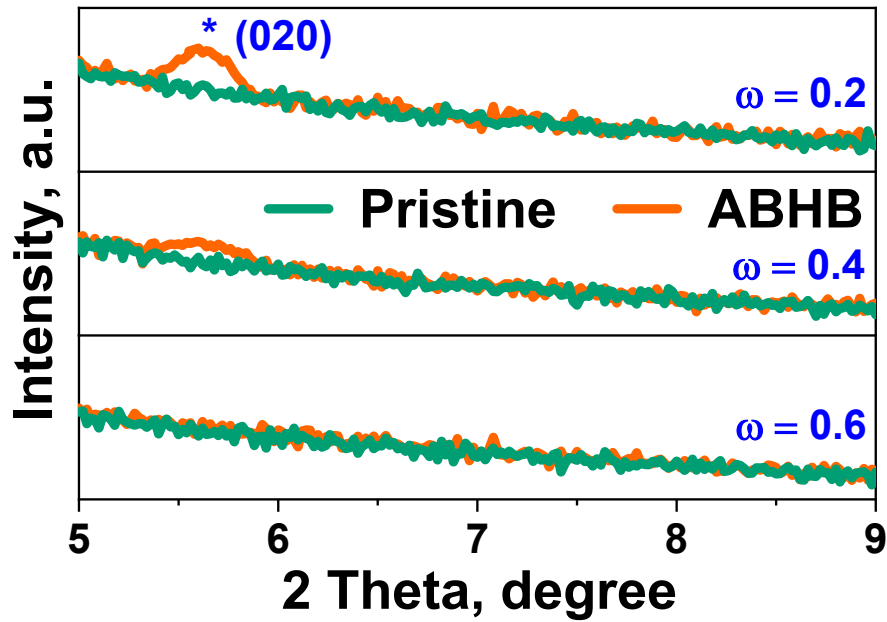

Fig. S2 Peak intensity variation of (020) plane with incident angle after ABHB treatment.
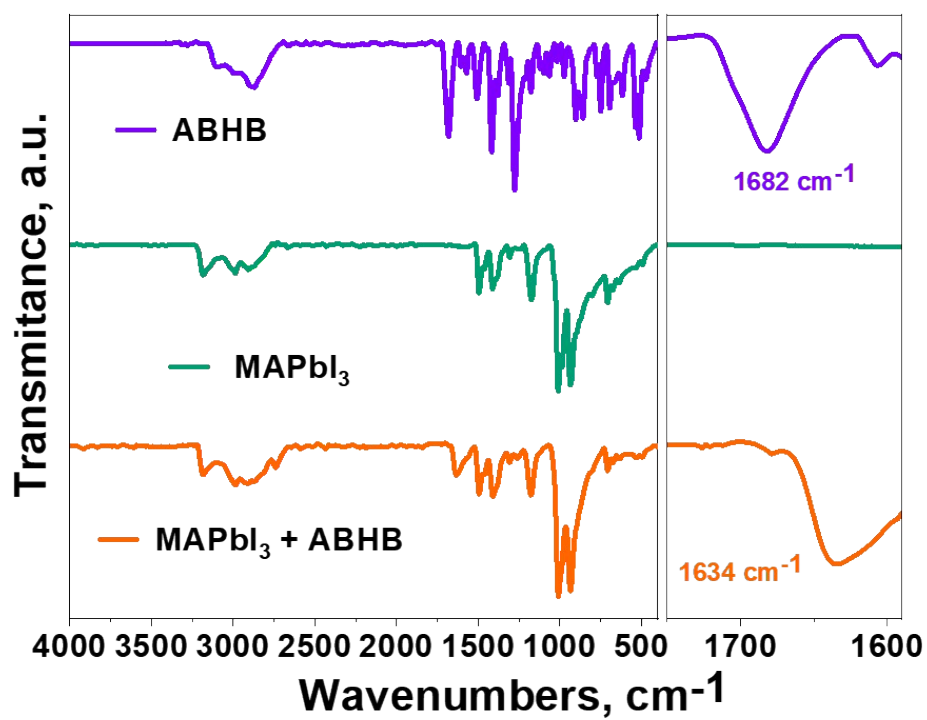
Fig. S3 FTIR spectra of ABHB, MAPbI$_3$, and MAPbI$_3$ + ABHB with its magnification spectra.
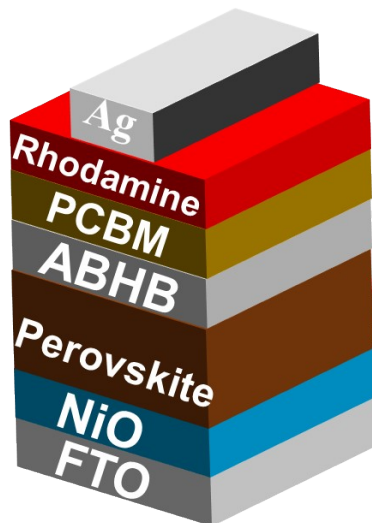

Fig. S4 Schematic illustration of device architecture.

Table S1: Device parameters.

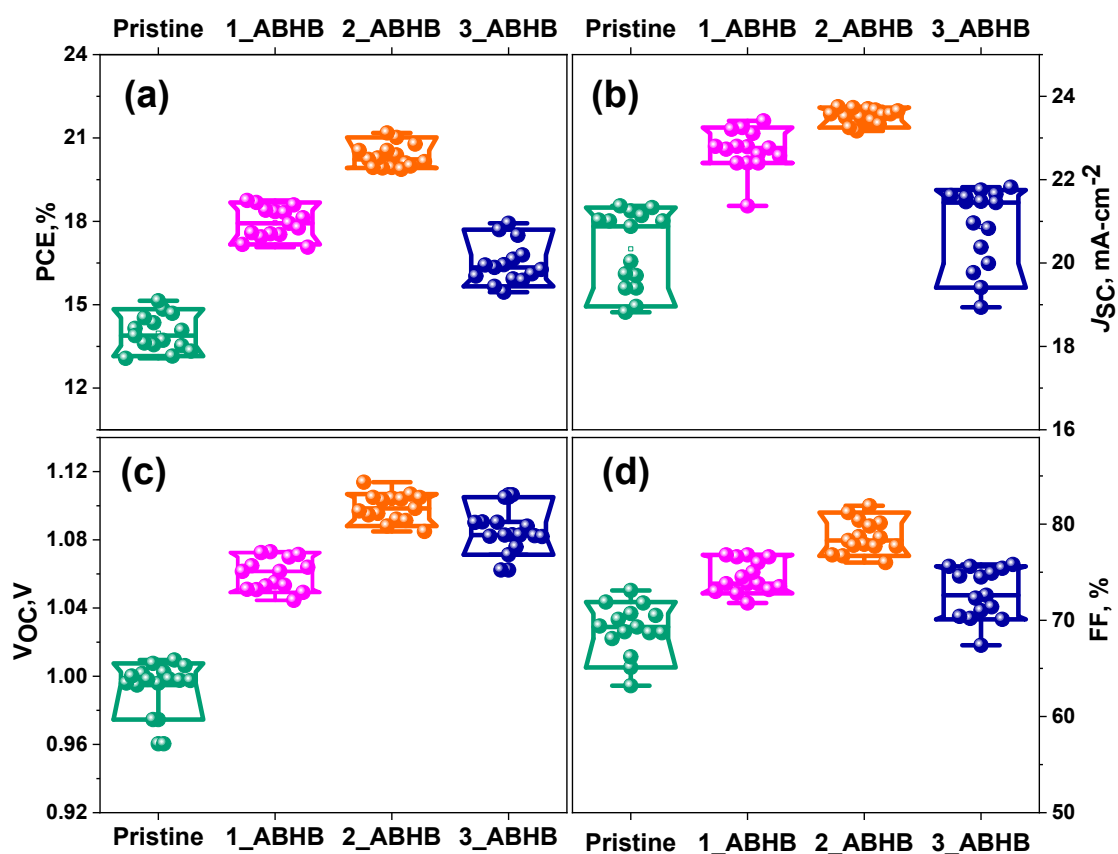| Device	J_{SC}, mA-cm^{-2}	V_{OC}, mV	FF, %	PCE (average)[a], %
Pristine	21.25	1007.5	70.7	15.14 (13.97±0.63)
1_ABHB	22.79	1071.4	76.8	18.75 (17.95±0.55)
2_ABHB	23.42	1104.9	81.9	21.18 (20.32±0.41)
3_ABHB	21.75	1106.4	74.5	17.93 (16.47±0.73)

[a]Average of 15 devices.

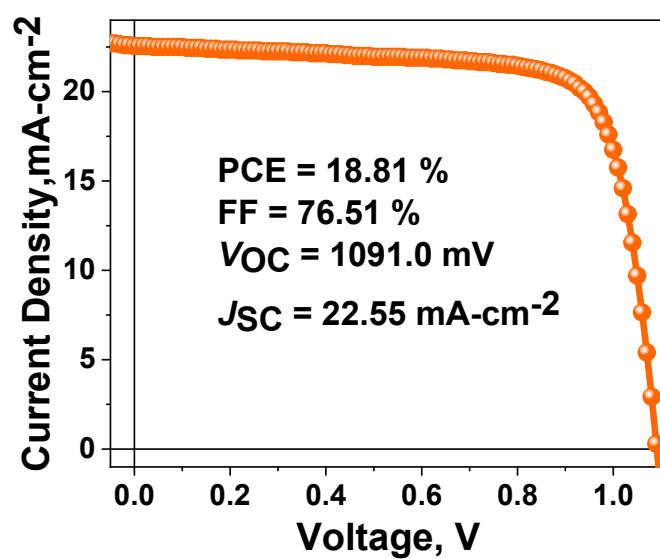**Fig. S5** Box chart of pristine and varying concentration of ABHB treated devices.

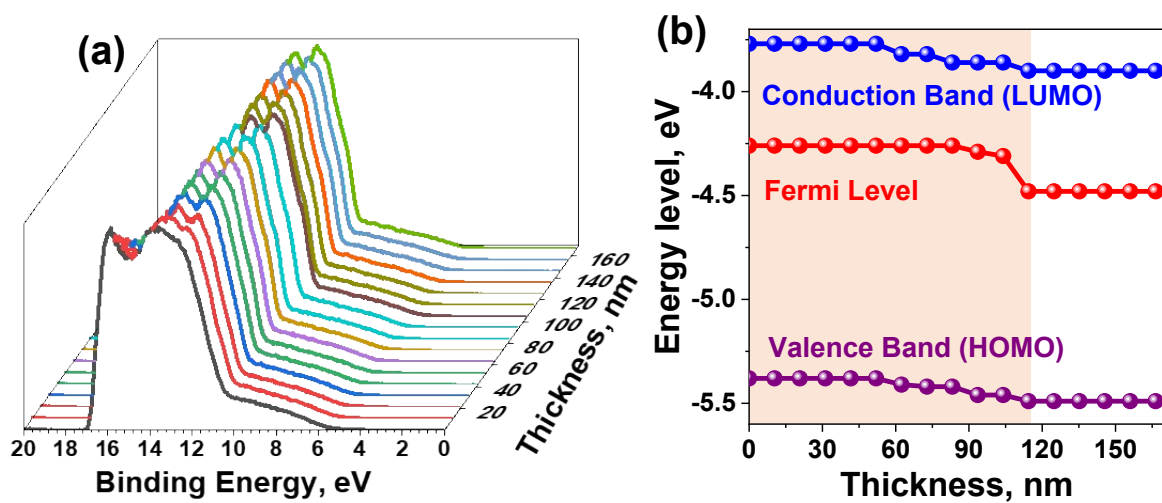**Fig. S6** *J–V* curves for the large area device of ABHB treated devices.

Fig. S7 (a) UPS spectra of the ABHB treated film as a function of depth, and (b) The corresponding energy level diagram extracted from (a).
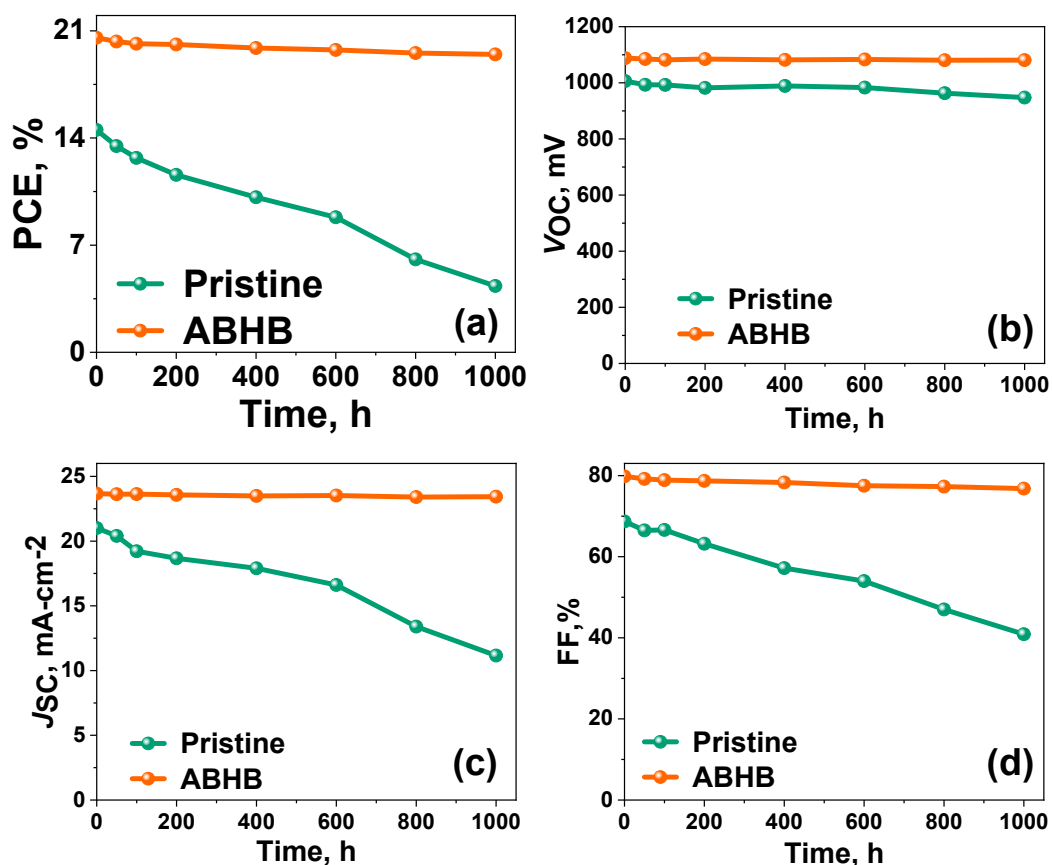
Fig. S8 Efficiency V_{OC}, J_{SC}, and FF variation of pristine and ABHB modified devices aged at room temperature in a relative humidity of 40–50%.

Table S2. Comparative table with recent literature of MAPbI$_3$ based 2D-3D graded perovskite.

Device configuration	2D Passivation Molecule	Modified PCE [%]	Ambient Stability	Reference
ITO/NiOx/ CH$_3$NH$_3$PbI$_3$/PCBM/BCP/Ag	Benzylammonium chloride	19.80	90% stable after 30 days (R.H. 45%)	Mater. Chem. Front., 2021,5, 3378-3387
FTO/NiOx/Perovskite/PCBM/PEI/Ag	2-thiophene ethylammonium chloride	18.84	80% stable after 400 hours (glove box)	ACS Appl. Energy Mater. 2019, 2, 4821−4832
ITO/SnO$_2$/MAPbI$_3$/spiro-OMeTAD/Ag	Phenylethylammonium iodide and Phenylethylammonium bromide	20.07	88% stable after 80 days (R.H. 38%)	ACS Appl. Mater. Interfaces 2018, 10,

Device configuration	2D Passivation Molecule	Modified PCE [%]	Ambient Stability	Reference
				31755−31764
ITO/SnO$_2$/MAPbI$_3$/spiro-OMeTAD/Ag	N,N′-dimethylethylene-1,2-diammonium iodide	20.18	74% stable after 30 days (R.H. 60-80%)	ACS Appl. Mater. Interfaces 2020, 12, 1159−1168
ITO/SnO$_2$/MAPbI$_3$/spiro-OMeTAD/Ag	5-aminovaleric acid iodide	18.0	72% stable after 20 days (R.H. 40%)	Adv. Funct. Mater. 2018, 28, 1801654.
TO/NiO$_x$/ MAPbI$_3$/PCBM (PN4N)/Ag.	Phenylethylammonium iodide	19.89	60% stable after 30 days (R.H. 20-30%)	Adv. Energy Mater. 2017, 7, 1701038
FTO/SnO2/MAPbI$_3$/Spiro-OMeTAD/Au	1-(ammonium acetyl)pyrene	14.7	No degradation 400 hours (R.H. 60%)	Adv. Funct. Mater. 2018, 28, 1804856.
FTO/TiO$_2$/MAPbI$_3$/Spiro-OMeTAD/Ag	Phenylethylammonium iodide	19.1	NA	Adv. Mater. 2018, 30, 1801401.
FTO/ c-TiO$_2$/SnO$_2$/MAPbI$_3$/Spiro-OMeTAD/Ag	Phenyltrimethylammonium iodide	21.16	95% stable after 1000 hours (R.H. 20-30%)	Angew. Chem. 2020, 132, 1485– 1489.
FTO/SnO$_2$/MAPbI$_3$/Spiro-OMeTAD/Au	Butylamine vapor	19.48	92% stable after 600 hours (R.H. 30-40%)	Nano Lett. 2020, 20, 1296−1304
ITO/NiOx/MAPbI$_3$/PCBM/ZrAcac/Ag	Isobutyl amine	18.29	75% stable after 35 days (R.H. 40-60%)	ACS Appl. Energy Mater. 2020, 3, 2975−2982
FTO/NiOx/Perovskite/ PCBM/Rhodamine 101/Ag	**4-(aminomethyl) benzoic acid hydrogen bromide (ABHB)**	**21.18**	**95% stable after 1000 hours (R.H. 40-50%)**	**This work**