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Supporting information

High performance ambient-air-stable FAPbI₃ perovskite solar cells with molecule-passivated Ruddlesden-Popper/3D heterostructured film

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Experimental Section

Solution preparation and device fabrication

Materials preparation: Lead iodide (PbI₂, 99.9985%) was purchased from AlfaAesar. Formamidine iodide (FAI), Butylamine iodide (BAI), Butylammonium Bromide (BABr), Butylammonium Chloride (BACl), Lead(II) bromide (PbBr₂, 99.99%) and Lead(II) chloride (PbCl₂, 99.99%) were purchased from p-OLED. N,Ndimethylformamide (DMF, 99.8%), dimethylsulfoxide (DMSO, 99.9%) and γ butyrolactone (GBL, 99%) were purchased from Sigma-Aldrich. ITIC and IDTBR were purchased from One-material. All chemicals were used as received without further purification.

Solution preparation: The precursor solution preparation was conducted under inert atmosphere inside a nitrogen glove box. The FAPbI₃ precursor solution (1.2M) was prepared with equimolar PbI₂ and Formamidine iodide (FAI) dissolved in a mixture of dimethylsulfoxide (DMSO), y-butyrolactone (GBL) and N,N-dimethylformamide (DMF) (volume ratio of 7:7:6) in a glovebox. To form a quasi-2D perovskite solution (1.2M), BAX, FAI, PbX₂ and PbI₂ (X denotes halogen) were mixed with the ratio of 2:60:1:60 and dissolved in the same solvent recipe as FAPbI₃. All solutions were filtered prior to solution-casting. ITIC and IDTBR solutions were resolved in chlorobenzene with the concentration of 0.4 mg/ml. The Spiro-OMeTAD solution prepared by dissolving 90 mg Spiro-OMeTAD, was 22 μL lithium bis(trifluoromethanesulfonyl) imide in acetonitrile and 36 µL 4-tert-butylpyridine in 1 mL chlorobenzene.

Device fabrication: The FTO-coated glass (2.5 cm * 2.5 cm) was cleaned by sequential sonication in acetone, isopropanol and ethanol for 30 min each and then dried under N₂ flow and treated by O₃ plasma for 15 min. The TiO₂ was prepared by chemical bath deposition with the clean substrate immersed in a TiCl₄ (CP, Sinopharm Chemical Reagent Co., Ltd) aqueous solution with the volume ratio of TiCl₄ : H₂O equal to 0.0225 : 1 at 70 °C for 1 hour. The spin-coating was accomplished under inert atmosphere inside a nitrogen glove box. The procedure was performed at 1000 r.p.m. for 10 s followed by 4000 r.p.m. for 40 s. At ca. 25 s before the end of the last spin-coating step, 100 μ L of chlorobenzene solvent or loaded solution was dropped onto the substrate. The substrates were then placed onto a hotplate for 30 min at 150 °C. Subsequently, the HTM were deposited on top of the perovskite by spin coating at 5000 r.p.m. for 30 s followed by evaporation of 100 nm gold electrode on the top of the cell.

Characterization

Optical metrology: UV-Visible absorption spectra were acquired on a PerkinElmer UV-Lambda 950 instrument. Steady-state Photoluminescence (PL) (excitation at 510 nm) was measured with an Edinburgh Instruments Ltd (FLS980 spectrometer).

Electronic microscopy: The surface morphology and structure of the perovskite films were characterized by SEM (FE-SEM; SU-8020, Hitachi) and Atomic force microscopy (AFM, Dimension ICON), respectively.

X-ray diffraction (XRD) measurements were carried out in a θ -2 θ configuration with a scanning interval of 2 θ between 5° and 60° on a Rigaku Smart Lab (X-ray Source: Cu K α ; $\lambda = 1.54$ Å).

Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were performed at D-line at the Cornell High Energy Synchrotron Source (CHESS). The wavelength of the X-rays was 0.972 Å with a bandwidth $\Delta\lambda\lambda$ of 1.5%. The scattering signal was collected by a Pilatus 200K detector, with a pixel size of 172 µm by 172 µm placed 184.0066 mm away from the sample position. The incident angle of the Xray beam was 0.35 degree. Spin-coating experiments were conducted at a custombuilt spin-coating stage with splashing of solvent protected using kapton tape and controlled from a computer outside the hutch. The exposure time was kept at 0.5 s to obtain the detailed information of the process.

UPS measurements: Ultraviolet photoelectron spectroscopy (UPS) was measured with a monochromatic He I light source (21.22 eV) and a VG Scienta R4000 analyzer. *Solar cell characterizations:* The *J-V* performance of the perovskite solar cells was measured using a Keithley 2400 source-meter under ambient condition at room temperature, and the illumination intensity was 100 mW cm⁻² (AM 1.5G Oriel solar simulator). The scan rate was 0.3 V s⁻¹. The delay time was 10 ms; and the scan step was 0.02 V. The power output of the lamp was calibrated by a NREL-traceable KG5-filtered silicon reference cell. The device area of 0.09 cm² was defined by a metal aperture to avoid light scattering from the metal electrode onto the device during the measurement. The EQE was characterized on a QTest Station 2000ADI system

(Crowntech. Inc., USA), and the light source was a 300 W xenon lamp. The monochromatic light intensity for EQE measurements was calibrated with a reference silicon photodiode.

Mobility measurement: Electron-only devices (FTO/c-TiO₂/perovskites/PCBM/Ag) were fabricated to measure the electron mobility of the devices. The dark J-V characteristics of the electron-only devices were measured by a Keithley 2400 sourcemeter. The mobility was extracted by fitting the J-V curves with the Mott-Gurney equation. The trap state density was determined by the trap-filled limit voltage using equation 2.

Electrical impedance spectroscopy (EIS) measurement: Electrical impedance spectroscopy (EIS) measurements were conducted using an electrochemical workstation (IM6ex, Zahner, Germany) with the frequency range from 10 Hz to 4 MHz at open-circuit voltage in the dark.

Contact angle measurements were conducted on a Dataphysics OCA-20 with a drop of ultrapure water (0.05 mL). The photographs were taken 1 second after water dripping.



Fig. S1. (a) Molecular structure of the selected semiconducting molecules with Lewis base functional groups. (b) Schematic diagram of loaded anti-solvent dripping strategy for fabricating RP/3D heterostructured perovskite films.



Fig. S2. (a) Cross-sectional scanning electron microscopy (SEM) image of the control FA film. (b) Atomic force microscopy (AFM) images of the control FA and IDTBR-FABABr films with root-mean-squared (RMS) roughness.



Fig. S3. External quantum efficiency (EQE) and the corresponding integrated current density for the champion control FA and IDTBR-FABABr devices.



Fig. S4. (a-c) Plan-view SEM images for $(FAPbI_3)_n(BAPbI_4)$ RP/3D heterostructured perovskite films with n= 10, 40 and 60. (d) *J-V* curves of champion perovskite devices with different n values.



Fig. S5. *In situ* GIWAXS measurements performed at the end of spin coating for the control FA and RP/3D heterostructured films showing differences in the shape and intensity of scattering patterns.



Fig. S6. (a-b) Plan-view SEM images of FABABr and FABACl films. (c) AFM images of the RP/3D heterostructured perovskite films with root-mean-squared (RMS) roughness.



Fig. S7. Ex situ GIWAXS patterns of the control FA, FABAI and FABACI films.



Fig. S8. Tauc plots of control FA and RP/3D heterostructured films, showing determination of the estimated bandgaps from the intercepts, derived from the UV-Vis spectra.



Fig. S9. Normalized steady-state photoluminescence (PL) spectra for the four films.



Fig. S10. Dark *I-V* measurement data of the electron-only devices with the architecture FTO/TiO_2 /perovskite/PCBM/Ag for the four cases displaying V_{TFL} kink point behavior.



Fig. S11. (a) *J-V* curves for champion devices based on RP/3D heterostructured films. (b) EQE and the corresponding integrated current density for the three cases.



Fig. S12. The stabilized power output of the champion devices based on the RP/3D heterostructured films measured at a fixed maximum power point (MPP) voltage as a function of time.



Fig. S13. *J-V* curves recorded in both the reverse and forward scan directions for the RP/3D devices.



Fig. S14. (a) UPS spectrum in the high binding-energy region of post-annealed FABABr film to determine the Ecutoff level. Inset: linear extrapolation in the lowbinding-energy region for the value of E_v - E_f , the Fermi energy (abbreviated as E_f) and the valence band energy (E_v). (b) Energy band diagram of FABABr film calculated from the Tauc plot (Fig. S8) and UPS results. (c) The corresponding energy diagrams in the completed device.^{1, 2}



Fig. S15. (a) Plan-view SEM image of ITIC-FABABr films. (b) AFM image of ITIC-FABABr film with root-mean-squared (RMS) roughness.



Fig. S16. UV spectroscopy measurement for FABABr films with and without ITIC or IDTBR passivation layer on glass.



Fig. S17. (a) The equivalent circuit composed of the series resistance (R_s) , contact resistance (R_{co}) and recombination resistance (R_{rec}) . (b) Nyquist plot of EIS in the high-frequency regime for the FABABr and passivated devices.



Fig. S18. Dark *I-V* measurement of the electron-only devices for the ITIC-FABABr and IDTBR-FABABr cases displaying V_{TFL} kink point behavior.



Fig. S19. Characteristics of devices based on ITIC-FABABr film. (a) *J-V* curves recorded in both the reverse and forward scan directions. (b) The stabilized power output and (c) EQE of the champion device.



Fig. S20. Long term environmental stability characterization. (a) Pictures of the control FA and RP/3D heterostructured perovskite films before and after aging under ambient conditions with 30-40% relative humidity at room temperature. (b) XRD patterns of the four cases before and after aging under ambient conditions with 30-40% relative humidity at room temperature. (c) Contact angle of water on different perovskite films showing increased hydrophobicity of the RP/3D films compared with the control film. (d) Long-term stability measurements of both solar cells without any encapsulation under ambient conditions with 30-40% relative humidity. After 60 d, the RP/3D FABAI, FABABr and FABACl fabricated devices exhibit significantly improved stability against humidity, maintaining 56.1%, 74.2% and 69.4% of their initial PCEs, respectively, in contrast to the control device at only 20.2% of initial PCE.



Fig. S21. (a) Contract angle of water on ITIC-FABABr and IDTBR-FABABr films. (b) Long-term stability measurements for the FABABr and passivated devices. For the ITIC passivated device, 90.1% of the initial PCE value was retained after 60 days, which is better than the value of FABABr at 74.2% and IDTBR passivated one at 87.3%.



Fig. S22. Operational Stability. The evolution of the PCEs for the non-encapsulated control FA, FABABr, ITIC-FABABr and IDTBR-FABABr devices exposed to continuous illumination (100 mW cm⁻²) under open-circuit condition in air (50-60% RH and 50 °C). The ITIC-FABABr and IDTBR-FABABr based devices still maintained 72.6% and 68.9% of the initial values after 130h continuous illumination, respectively, which significantly outperform the control one.

	V _{oc} (V)	J _{SC} (mA cm ⁻²)	FF (%)	PCE (%)	PCE _{max} (%)
Control FA	1.05±0.01	24.1±0.6	74.0±1.9	18.6±0.5	19.15
IDTBR-FABABr	1.07±0.01	24.1±0.5	76.1±1.5	19.5±0.5	20.62

Table S1. Photovoltaic parameters of devices based on the control FA and IDTBR-FABABr films.

Table S2. The hysteresis parameters of champion devices based on the control FA and IDTBR-FABABr films.

	Scanning	V _{oc}	J _{SC}	FF	PCE	Hysteresis
	mode	(V)	(mA cm ⁻²)	(%)	(%)	Index (%)
Control FA	Reverse	1.06	24.09	74.8	19.15	10.7
	Forward	1.05	22.44	72.7	17.11	10.7
IDTBR-FABABr	Reverse	1.10	24.40	76.9	20.62	2.4
	Forward	1.09	23.89	76.7	19.91	5.4

Table S3. Photovoltaic parameters of champion devices based on the $(FAPbI_3)_n(BAPbI_4)$ films with different n values.

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(FAPbI ₃) _n (BAPbI ₄)	V _{oc} (V)	$J_{\rm SC}$ (mA cm ⁻²)	FF (%)	PCE (%)	$ m R_{S}$ (Ω cm ⁻²)	$ m R_{Sh}$ (Ω cm ⁻²)		
n=10	1.04	21.46	66.2	14.79	97.7	12246		
n=40	1.03	22.80	71.4	16.75	73.7	25655		
n=60	1.06	23.92	74.0	18.84	69.5	50082		

Table S4. Photovoltaic parameters of devices based on the RP/3D heterostructured films.

	V _{oc}	J _{SC}	FF	PCE	PCE _{max}
	(V)	$(mA cm^{-2})$	(%)	(%)	(%)
FABAI	1.05 ± 0.02	23.8±0.3	72.7±2.1	18.2±0.4	18.84
FABABr	1.06 ± 0.02	23.7±0.4	73.1±1.3	18.1±0.4	18.76
FABACl	1.06 ± 0.01	22.9±0.2	70.3±1.4	17.1±0.5	17.66

	Scanning	V _{OC}	J _{SC}	FF	PCE	Hysteresis	
	mode	(V)	(mA cm ⁻²)	(%)	(%)	index (%)	
FABAI	Reverse	1.06	23.92	74.0	18.84	4.2	
	Forward	1.05	23.76	72.3	18.03	4.5	
FABABr	Reverse	1.08	23.77	72.9	18.76	5 3	
	Forward	1.07	23.40	71.2	17.76	5.5	
FABACl	Reverse	1.08	23.02	71.0	17.66	0.7	
	Forward	1.01	22.64	69.5	15.95	9.1	

Table S5. The hysteresis parameters of champion devices based on the RP/3D heterostructured films.

Table S6. Summaries of EIS parameters for different devices.

	R _s	R _{co}	R _{rec}	C _{co}	C _{rec}
	(Ω)	(Ω)	(Ω)	$(F \text{ cm}^{-2})$	$(F \text{ cm}^{-2})$
FABABr	13.7	39.4	349.6	2.4×10-9	9.8×10 ⁻⁸
ITIC-FABABr	8.4	32.5	373.9	7.8×10 ⁻⁹	9.6×10 ⁻⁸
IDTBR-FABABr	9.5	29.5	473.1	6.2×10 ⁻⁸	9.1×10-9

Table S7. Photovoltaic parameters of devices based on the ITIC-FABABr film.

	V _{oc}	J _{SC}	FF	PCE	PCE _{max}
	(V)	$(mA cm^{-2})$	(%)	(%)	(%)
ITIC-FABABr	1.07 ± 0.01	24.0±0.5	75.0±1.3	19.2±0.4	20.10

Table S8. The hysteresis parameters of champion devices based on the ITIC-FABABr films.

	Scanning	V _{oc}	J _{SC}	FF	PCE	Hysteresis
	mode	(V)	(mA cm ⁻²)	(%)	(%)	Index (%)
ITIC-FABABr	Reverse	1.07	23.86	78.6	20.10	4 1
	Forward	1.06	23.48	76.7	19.19	4.1

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