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Electronic Supplementary Information

Fluoroarene Derivative based Passivation of Perovskite Solar Cell Exhibiting Excellent Ambient and Thermo-Stability Achieving Efficiency >20%

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Materials

FTO glass substrates (13 Ω sq^{-1}), PbI_2 (99.8%), all anhydrous solvent e.g. DMF, DMSO, isopropanol (IPA) Toluene, Chlorobenzene, Rhodamine 101 inner salt were purchased from Sigma-Aldrich. Methylammonium iodide (MAI) was obtained from Dyesol. Nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$) was obtained from TCI. All other chemicals were utilized as received.

NiO_x Film Preparation

NiO_x solution was prepared by dissolving Nickel nitrate hexahydrate and Ethylenediamine (in 1:1 molar ratio) in Ethylene Glycol (1ml). Then the NiO_x layer was coated as hole transporting layer (HTL) on the cleaned FTO. The cleaning process of FTOs was started with detergent and followed by deionized (DI) water, acetone, and IPA 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 at 3500 rpm for 45 sec. Afterwards, the substrates were annealed at 300 °C for 60 min under ambient condition.

Device Fabrication

The $MAPbI_3$ precursor solution was prepared in a glovebox by mixing 209 mg of MAI, 581 mg of PbI_2 in a solvent mixture of γ-Butyrolactone and DMSO (7:3, v/v). 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 150 µl anhydrous Toluene was dripped slowly after 20 sec as anti-solvent and after that the substrates were annealed at 80° C for 10 min on a hotplate. For the passivated devices varied concentration of fluorinated aromatic amines (FAAs) solutions in isopropanol (IPA) were coated above perovskite at 4000 rpm for 40 sec and dried at room temperature. After that for both passivated and pristine devices 12 mg/ml $PC_{61}BM$ solution was coated at 1200 rpm as electron transporting layer (ETL) and again annealed at 80° C for 5 min on a hotplate. After that a thin layer of Rhodamine 101 inner salt was spin coated at 4000 rpm from a solution of 0.5 mg/ml in IPA. Finally Ag was thermally deposited by using a shadow mask to obtain the devices with active area of 0.12 cm^2.[1,2]

Device Characterization

The XRD patterns of the perovskite films were studied using a Rigaku Micromax-007HF diffractometer equipped with Cu Kα1 irradiation (λ = 1.54184 Å). The perovskite films were analyzed by UV-vis absorption spectroscopy (Perkin Elmer Lamda-35) and FTIR spectroscopy (LabRam HR) in ATR mode. The film morphology of the samples were investigated by scanning electron microscopy (FESEM, Hitachi S-4800) and AFM (Oxford, Cypher).The current density−voltage (*J*−*V*) characteristic curves were recorded using a Keithley 2400 source meter under inert 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 analyzed using a CH Instruments 760D.

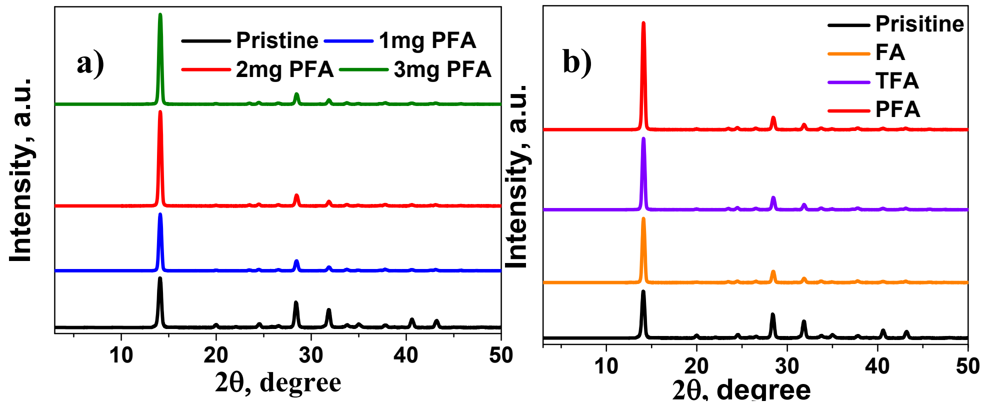

Fig. S1 a) XRD patterns of perovskite film coated with varied concentration of PFA, b) XRD patterns of perovskite films coated with different fluorinated aromatic amines (FAAs).

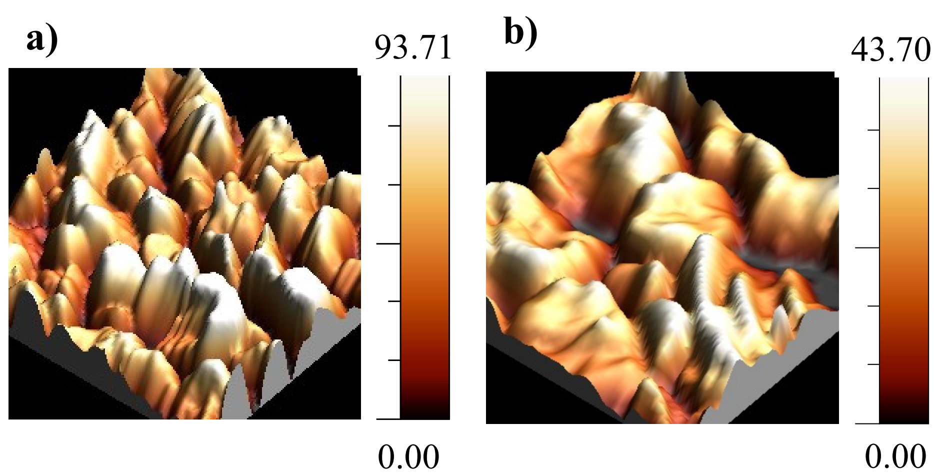

Fig. S2 AFM images (2 µm *2 µm) of a) pristine and b) PFA passivated films.

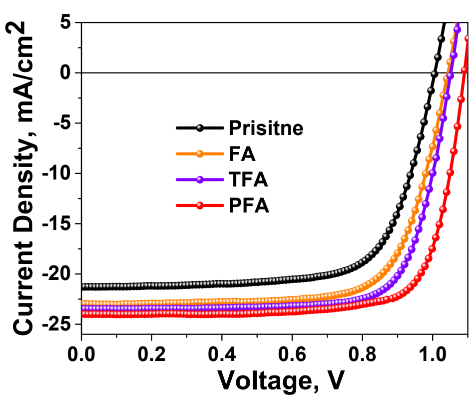

Fig. S3 Current Density versus Voltage (*J*-*V*) plot for PVSCs passivated with different FAAs

Table S1 Photovoltaic parameters for pristine and FAAs passivated PVSCs.

Device	J_{SC}, mA/cm[2]	Voc, V	FF, %	PCE (average)[a], %
Pristine	21.30	1.006	70.4	15.08 (14.33±0.52)
FA	22.98	1.043	71.8	17.22 (16.37±0.65)
TFA	23.46	1.051	75.1	18.54 (17.46±0.67)
PFA	23.99	1.090	76.7	20.05 (19.45±0.38)

[a] Average of 15 devices.

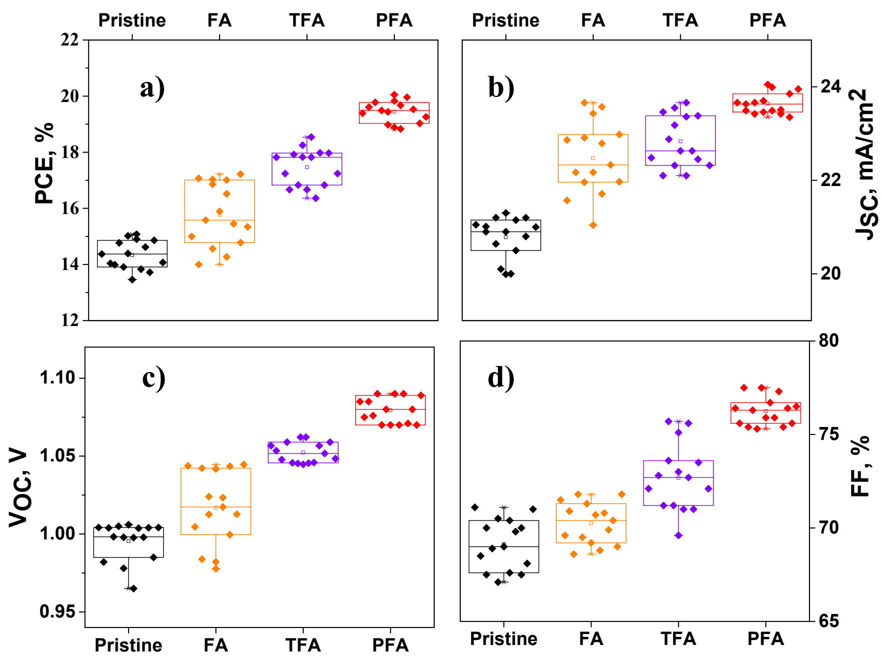

Fig. S4 Box chart of pristine and different FAA modified devices for photovoltaic parameters a) PCE, b) J_{SC}, c) V_{OC}, and d) FF.

Table S2 Device parameters for hysteresis study of pristine and PFA modified device.

Device	J_{SC}, mA/cm[2]	V_{OC}, V	FF, %	PCE, %	HI, %
Pristine_FS	21.30	1.006	70.4	15.08	9.08
Pristine_RS	21.01	1.001	65.2	13.71	
PFA_FS	23.99	1.090	76.7	20.05	0.89
PFA_RS	24.05	1.089	75.9	19.87	

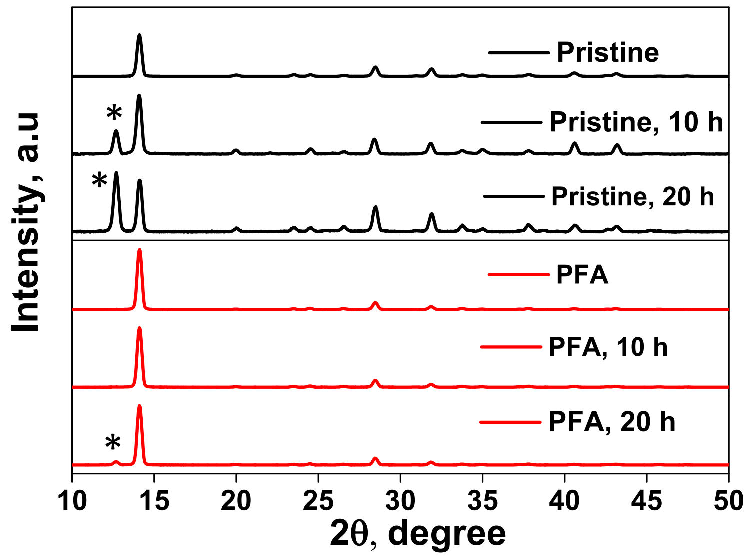

Fig. S5 XRD patterns of perovskite films heated at 100 °C for 20 h (star mark indicates the PbI_2 phase).

Table S3 List of similar research articles highlighting the PVSC performance and stability

No.	Article	Architecture	Passivation Additives	Pristine PCE, %	Champion Cell, %	Thermal Stability (PCE Retention)	Ambient Stability (PCE Retention)
1	J. Mater. Chem. A, **2021**, 9, 4138–4149	FTO/SnO_2/ $FAPbI_3$/Spiro-OMeTAD/MoO_3 /Au	Thiophene based additives	16.91	20.61	NA	90% after 60 days
2	Adv. Energy Mater. **2019**, 9, 1900198	FTO/NiOx/ $MAPbI_3$/$PC_{61}BM$/BCP/Ag	Fluorinated Perylene Diimide (F-PDI)	15.37	18.28	68% after 25 h at 85 ^{0}C	NA
3	*Adv. Sustainable Syst.* ***2020****, 2000078*	FTO/NiOx/ $MAPbI_3$/$PC_{61}BM$/Rhodamine 101/Ag	Chelidamic acid (CA)	13.60	19.06	63% after 60 h at 100 ^{0}C	80% after 1000h.
4	*ACS Appl. Energy Mater.* ***2020****, 3, 2432−2439*	FTO/PEDOT:PSS/ $MAPbI_3$/$PC_{61}BM$/Rhodamine 101/Ag	Oxalic Acid	14.06	17.12	90% after 9 h at100 ^{0}C	NA
5	ACS Appl. Energy Mater. **2021**, 4, 1731−1742	FTO/PEDOT:PSS/ $FA_{0.8}MA_{0.15}Cs_{0.05}Pb_{0.5}Sn_{0.5}I_3$/ C_{60}/BCP/Ag	2-phenylethylazanium iodide	14.61	17.33	NA	85% after 33 h
6	Adv. Funct. Mater. **2020**, 30, 2002861.	FTO/SnO_2/$FA_{0.8}MA_{0.14}Cs_{0.05}$ $PbI_{2.55}Br_{0.45}$/Spiro-OMeTAD /Au	Indacenodithieno [3,2-b]thiophene (IDTT)	18.8%	21.2	71% after 60 h at 85 ^{0}C	80% after, 2000 h
7	ACS Sustainable Chem. Eng. **2020**, 8,	ITO/PTAA/$MAPbI_3$/PCBM/BPhen/Al	Perylene Diimide based small molecule	17.3	20.3	NA	75% after 50 h

	8848−8856						
8	Sol. RRL **2020**, 4, 1900529	ITO/PTAA/$MAPBI_3$/PCBM/Al	Isatin-Cl	18.13	20.18	70% after 25 h at 85 ^{0}C	90% after 350 h
9	J. Phys. Chem. Lett. **2020**, 11, 6772−6778	FTO/PTAA/$MAPBI_3$/ $PC_{61}BM$/Al	Polyvinylcarbazole	17.4	18.7	70% after 1500 h at 65 ^{0}C	NA
10	Journal of Energy Chemistry 59, **2021** 755–762756	FTO/SnO_2/ $MAPBI_3$/Spiro-OMeTAD /Au	Indacenodithieno [3,2-b]thiophene (IDTT)	18.32	20.18	NA	95% after 1200 h
11	10.1021/acsami.1c00677 (**ACS AMI 2021**)	FTO/TiO_2/ $MAPbI_3$ NPs/CsFAMA /Spiro-OMETAD	1-hexyl-3-methylimidazolium	17.33	19.44	NA	80% after 6000 h
12	ACS Appl. Energy Mater. **2019**, 2, 6230−6236	FTO/PEDOT:PSS/ $MAPBI_3$/$PC_{61}BM$/BCP/Ag	Fluorinated Aliphatic Amines	12.23	13.76	NA	85% after 240 h
13	J. Mater. Chem. A, **2021**, 9, 5857–5865	ITO/PTAA/$MAPbI_3$/$PC_{61}BM$/ BCP/Ag	Amino acids	17.51	20.49	NA	94.9% after 30 days
14	10.1002/cssc.202002707 (**ChemSusChem 2020**)	FTO/TiO_2/ $FAPBI_3$/Spiro-OMeTAD /Au	2,3,4,5,6-pentafluorobenzyl phosphonic acid	20.19	22.25	NA	90% after 600 h
15	Adv. Funct. Mater. **2021**, 31, 2010603	FTO/TIO_2/ZrO_2/$MAPBI_3$/Carbon	N,1-Fluoroformamidinium Iodide	14.23	17.01	NA	NA
16	Adv. Funct. Mater. **2020**, 30, 2020778	FTO/PEDOT:PSS/ $MAPBI_3$/PC61BM/Rhodamine 101/Ag	Phenylhydrazinium iodide	15.33	18.18	NA	83% after 20 days
17	**This article**	**FTO/NiOx/ $MAPBI_3$/$PC_{61}BM$/Rhodamine 101/Ag**	**Fluorinated aromatic amines**	**15.08**	**20.05**	**82% after 20 h at 100 ^{0}C**	**87% after 1000 h**

References

S1 M. A. Afroz, R. K. Gupta, R. Garai, M. Hossain, S. P. Tripathi, P. K. Iyer *Org. Electron.* 2019, **74**, 172-178.
S2 R. Garai, M. A. Afroz, R. K. Gupta, P. K. Iyer *Adv. Sustainable Syst.* 2020, **4**, 2070016.