Supplementary information

Minimizing defect states through multidentate coordination and morphology regulation for enhancing the performance of inverted perovskite solar cells

Himangshu Baishya[a], Mayur Jagdishbhai Patel[b] Ramkrishna Das Adhikari[a], Deepak Yadav[b], Parameswar Krishnan Iyer*[a,b]

[a]*Centre for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India.*

[b]*Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, Assam, India*

*Email: pki@iitg.ac.in

1. Materials and methods

1.1 Materials

The perovskite precursor material namely formamidinium iodide (FAI) was purchased from Greatcell Solar Materials. Lead iodide (PbI_2), and Cesium iodide (CsI) were purchased from Sigma-Aldrich. Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, >98.0%) was purchased from TCI and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) was purchased from LUMTEC. 4-((trifluoromethyl)thio) benzoic acid was purchased from BLD Pharma, 98%, Fluorine doped tin oxide (FTO) coated glass (7Ω/sq.), chlorobenzene (CB, anhydrous, 99.8%), isopropyl alcohol (IPA, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), N, N-dimethylformamide (DMF, anhydrous, 99.8%), Rhodamine 101 inner salt, silver (Ag) wire molybdenum trioxide (MoO3) was purchased from Sigma-Aldrich. All the chemicals were utilized in their original state.

1.2. Perovskite precursor

The $Cs_{0.1}FA_{0.9}PbI_3$ double-cation perovskite precursor solution was prepared by mixing 1.2M FAI, CsI, and PbI_2 in an anhydrous solvent of DMF: DMSO (7:3 volume ratio, v:v). The resulting solution was stirred at 70°C for 3 hours to ensure thorough mixing and dissolution of the precursors. After that, the precursor was filtered by a 0.2 μm PTFE syringe filter before use.

1.3 Hole transport layer (HTL) precursor

A solution of NiOx hole transporting layer was prepared by dissolving 291 mg of ($Ni(NO_3)_2 \cdot 6H_2O$) salt and 67 μL $C_2H_4(NH_2)_2$ in 1 mL solution of $C_2H_4(OH)_2$. The solution was stirred for one hour and filtered with the 0.45 μm filter.

1.4 Electron transport layer (ETL) precursor

The electron transport layer solution was prepared by dissolving $PC_{61}BM$ in chlorobenzene (12 mg/mL).

1.5 Device fabrication

The FTO glass slides underwent a thorough cleaning process involving sonication in a soap solution, followed by deionized water, acetone, and IPA, each for 15 minutes. After this cleaning regimen, the FTO slides were dried and subjected to treatment with UV-ozone. The NiO_x precursor solution was then spin-coated onto the FTO glass at 4000 rpm for 30 sec and annealed at 300 °C for 1 hour in ambient forming a HTL layer. The perovskite solution was coated on top of the HTL layer after being treated in UV ozonation of the HTL layer in a two-step spin coating process inside the Ar-filled glove box. In the first step, the perovskite precursor was spin-coated at 1000 rpm for 10 sec and 4000 rpm for 30 sec. A 150 µL of CB as antisolvent was dripped continuously after 20 sec of the 2nd step and annealed for 15 min at 100 °C to achieve a perovskite film of ~500 nm thickness. The $PC_{61}BM$ solution was then spin-coated at 1200 rpm for 40 seconds and annealed at 80 °C for 5 min. A thin layer of rhodamine 101 inner salt at a concentration of 0.5 mg/mL in IPA solvent was spin-coated at 4000 rpm for 40 sec. Finally, a shadow mask was used to deposit 100 nm Ag metal as a back electrode through thermal evaporation under high vacuum conditions.

1.6 Material characterization

FTIR spectra were measured on a Jasco FTIR-6100 in a wavelength range of 4000 to 400 cm^{-1}.

The FAI and PbI_2 (100mg/mL) solution prepared by using DMSO anhydrous solvent. First, the characteristic FTIR spectrum of the additive molecule was recorded in its solid state(~2mg). Following this, the shifts in the functional groups were observed by adding a small amount of the FAI and PbI_2 stock solution to the 4-TFTBA powder. To further validate these shifts, we recorded the FTIR spectra of 4-TFTBA both in its powder form and when dissolved in DMSO (50mg/mL). The results show no shifts in the characteristic peaks, confirming that the observed shifts in the FTIR peaks arise from possible interactions between the perovskite components and the functional groups of the 4-TFTBA additive.

^{1}H & ^{19}F NMR spectra of the material were recorded on Bruker 600 MHz (at 298 K) spectrometers. The X-ray photoelectron spectroscopy (XPS) was performed using PHI 5000 Versa Probe III. UV–vis absorption spectra were recorded using a Shimadzu UV2600 spectrophotometer over the 450–900 nm wavelength range. For the photoluminescence (PL) and PL mapping test of the films LabRam HR was used with a 532 nm laser as an excitation light source and for the lifetime of the charge carriers LifeSpec II with 510 nm excitation laser source and time-correlated single photon counting (TCSPC) system was utilized. X-ray diffraction (XRD) patterns were measured by using a Rigaku Micromax-007HF diffractometer equipped with CuKα1 irradiation (λ = 1.54184 Å) at room temperature. The morphological studies of the films were conducted using ZEISS, SIGMA FESEM, and Bruker Innova AFM.

1.7 Device characterization

Current-voltage (J–V) curves of PSCs were measured by a Keithley 2450 source meter measurement system with an AM 1.5G filter at an illumination intensity of 100 mW/cm2 (Oriel Sol 3A solar simulator, Newport). The scan rate corresponding to the curve was 10 mV/step. The external quantum efficiency (EQE) spectra were examined in the air under short-circuit conditions using an Oriel IQE-200 instrument equipped with a 100 W Xe arc lamp. The steady-state current, Mott-Schottky, electrochemical impedance spectroscopy measurements in a

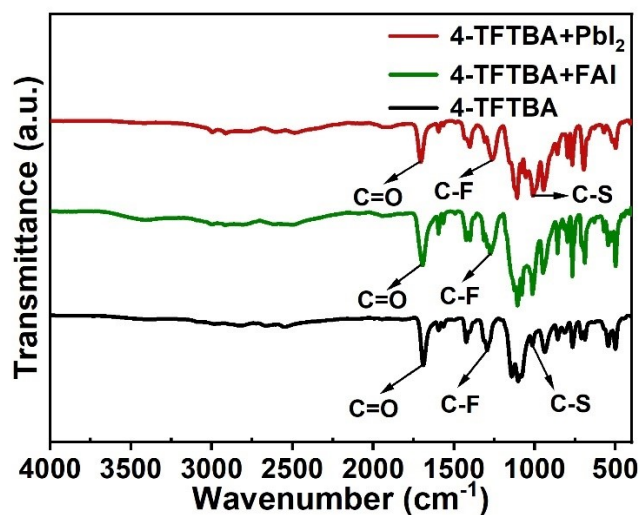frequency range from 1 MHz to 0.1 Hz were performed using an electrochemical workstation (CH-Instruments 680D).

Figure S1. Full-range FTIR spectra of the additive molecule and its mixture with FAI and PbI_2 precursors.
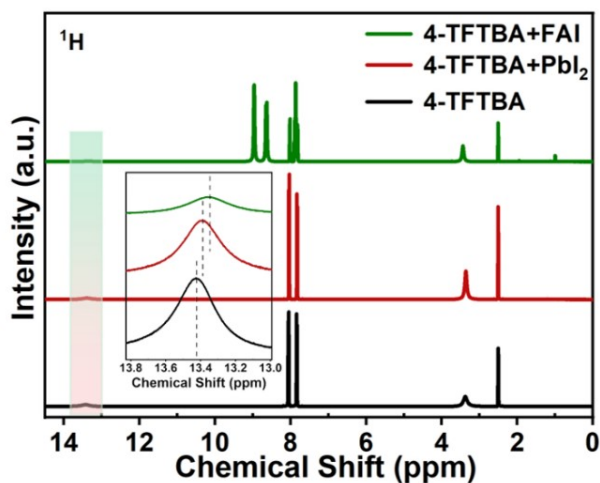

Figure S2. ^1H NMR spectra of the additive molecule and its mixture with FAI and PbI_2 in DMSO-d_6 solvent.
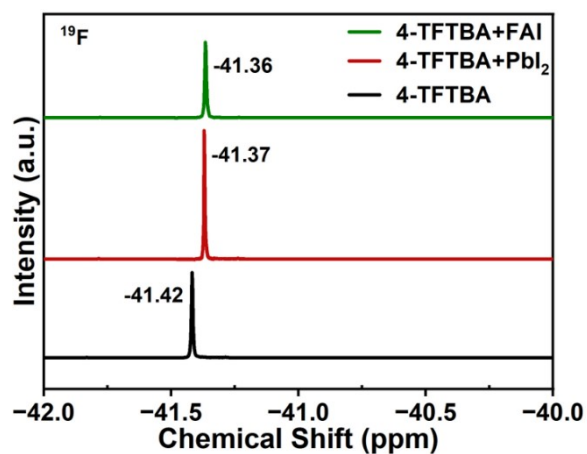
Figure S3. ^{19}F NMR spectra of the additive molecule and its mixture with FAI and PbI_2 in DMSO-d_6 solvent.
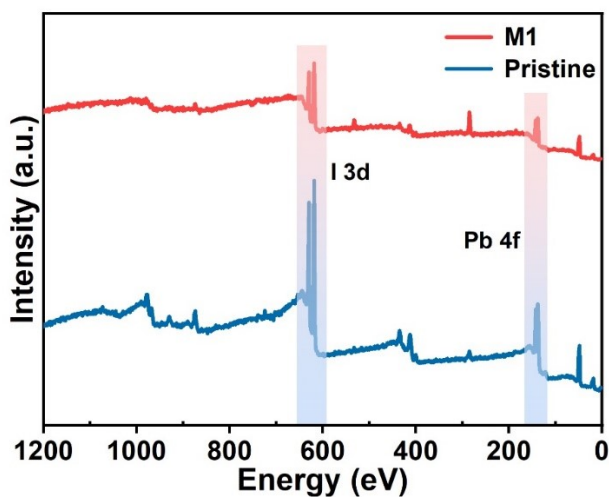

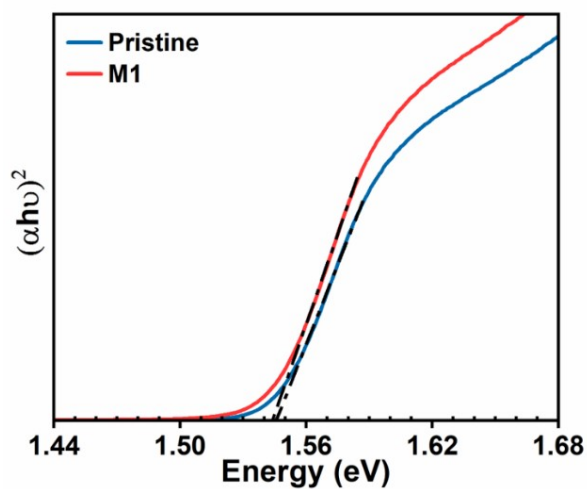**Figure S4.** Survey XPS spectra of pristine and optimized perovskite film.

Figure S5. TauC plot of the pristine and M1 modified perovskite film.
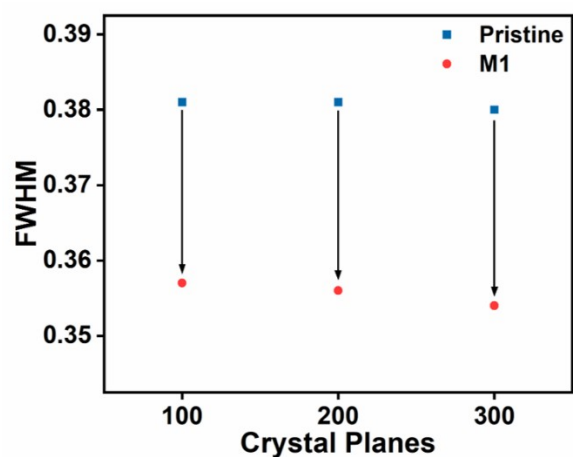
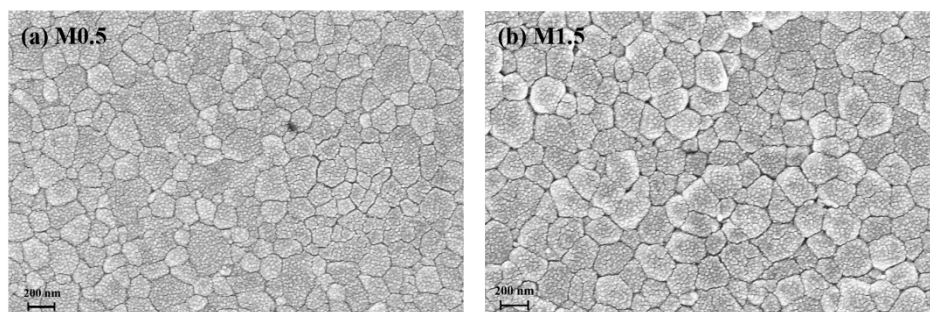**Figure S6.** FWHM value of the pristine and M1 modified perovskite film respectively.

Figure S7. (a,b) SEM micrograph of M0.5 and M1.5 modified perovskite film respectively.
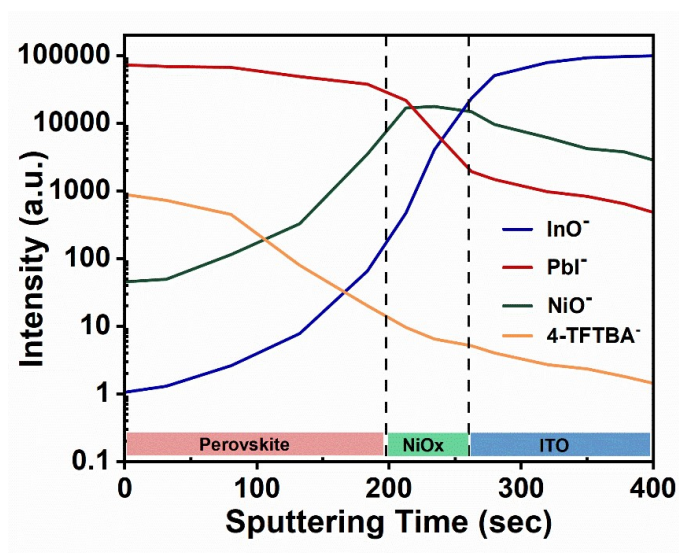

Figure S8. ToF SIMS analysis of the distribution of 4-TFTBA additive within the perovskite layer.
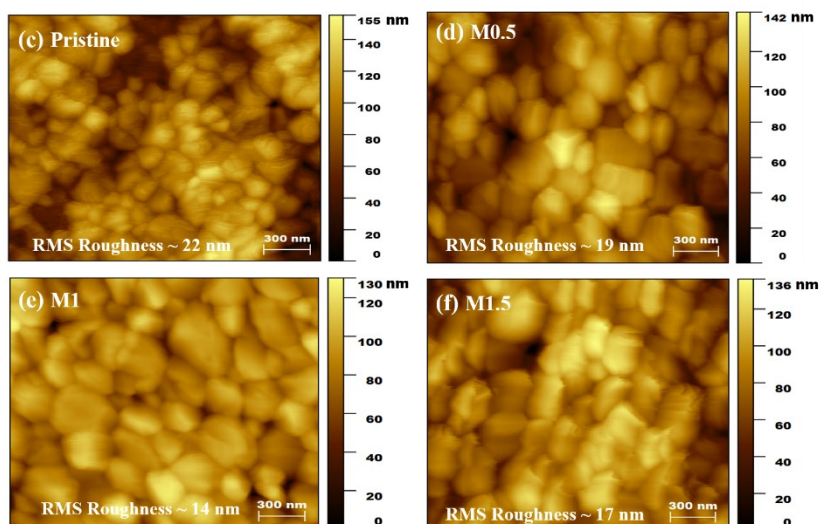
Figure S9. (a-d) AFM images of pristine, and M0.5, M1, and M1.5 modified perovskite film respectively.
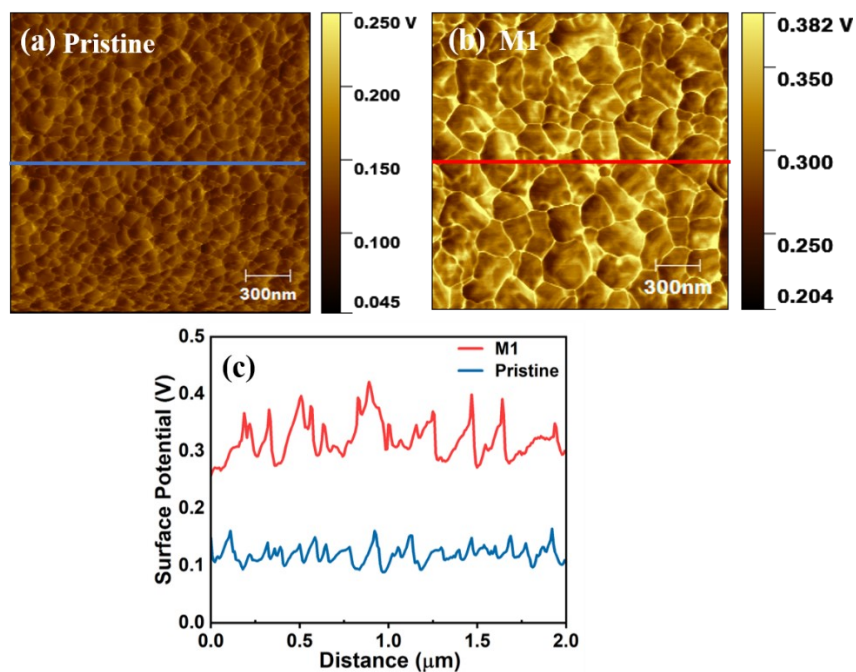

Figure S10. (a-c) KPFM images of pristine and M1 modified film with its surface potential profile respectively.

Table S1. TRPL parameters of perovskite films fitted from Fig. 4g.

Device	τ_1 (ns)	τ_2 (ns)	A_1 (%)	A_2 (%)	τ_{avg} (ns)
Pristine	3.84	131	255.09	105.52	122.58
M1 modified	16.05	167.4	110.06	283.08	162

Equation S1. $I(t) = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

where A_1 and A_2 are the corresponding decay amplitudes, and τ_1, τ_2 is the fast decay lifetime ascribe to the trap assisted recombination of photogenerated charge carrier and slow decay lifetime due to radiative recombination.

The average lifetime (τ_{ave}) of the charge carriers is calculated by the equation $\tau_{avg} = \dfrac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$

Equation S2. $HI = |PCE_{FS} - PCE_{RS}/PCE_{FS}|$

Equation S3. $\dfrac{1}{C^2} = \dfrac{2(V_{bi} - V)}{A^2 e \varepsilon_0 \varepsilon N_d}$

Here, ε_0, ε, A, N_d presents vacuum dielectric constant, dielectric constant of perovskite materials, working area, and doping density, respectively.

Equation S4. $n = (q/kT)\dfrac{dV_{OC}}{d\ln(\varphi)}$

Here, q, k, T, and φ represent the elementary charge, Boltzmann constant, absolute temperature, and light intensity respectively.

Equation S5. $\eta_{trap} = 2\varepsilon\varepsilon_0 V_{TFL}/eL^2$

where L is the thickness of the perovskite layer, e is the elementary charge and ε, ε_0 are the dielectric constants of the perovskite and vacuum respectively.

Table S2. Fitting parameters of EIS plot of pristine and optimized device

Device	R_S (Ohm)	R_{rec} (Ohm)

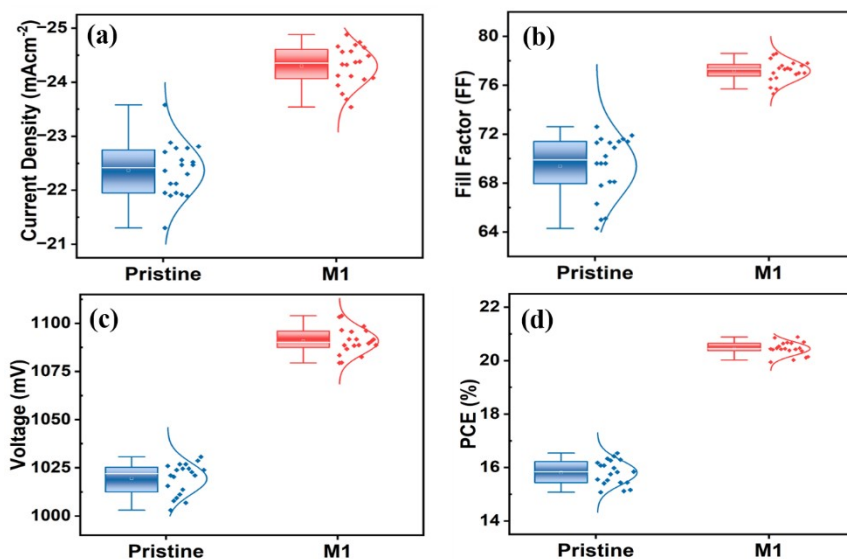|		
Pristine	7.04	2568
M1 modified	5.99	4515

Figure S11. (a-d) Statistical distribution of J_{SC}, FF, V_{OC}, and PCE respectively for a batch of 20 pristine and M1 modified devices.

Table S3. XRD stability analysis data of fresh and aged pristine and optimized perovskite film.

Perovskite film	Fresh (PbI_2/(100))	20 days aged (PbI_2/(100))	40 days aged (PbI_2/(100))
Pristine	0.128	0.175	0.361
M1 modified	0.021	0.135	0.150