

Supplementary Information

Materials and Methods

Preparation of perovskite precursor solution

Methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$) and formamidinium iodide ($\text{CH}_2(\text{NH}_2)_2\text{I}$) were purchased from Dyesol. PEDOT:PSS from Pelvis, and all other reagents and materials were procured from Sigma-Aldrich and utilized without any further purification. All perovskite precursor solutions were prepared in 1 molar strength (based on PbI_2) in a DMF/DMSO mixture (4:1, v/v) and stirred for an overnight period at 70 °C. MAPbI_3 precursor solution was prepared by mixing equimolar amounts of lead iodide (PbI_2) and MAI in mixed solvent. For $[\text{An}_2\text{PbI}_4]_x[\text{MAPbI}_3]_{1-x}$ precursor solution, molar ratio between PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$ and $\text{C}_6\text{H}_5\text{NH}_3\text{I}$ were kept to 1:0.8:0.2 respectively. Precursor solution for $[\text{An}_2\text{PbI}_4]_x[\text{FA}_{(0.5)}\text{MA}_{(0.95)}\text{PbI}_3]_{1-x}$ was prepared with a mole ratio of 1:0.8:0.15:0.5 between PbI_2 , $\text{CH}_3\text{NH}_3\text{I}$, $\text{C}_6\text{H}_5\text{NH}_3\text{I}$ and $\text{CH}_2(\text{NH}_2)_2\text{I}$ correspondingly, likewise, for $[\text{An}_2\text{PbI}_4]_x[\text{Cs}_{(0.5)}\text{MA}_{(0.95)}\text{PbI}_3]_{1-x}$ perovskite solution, CsI was used instead of FAI. All perovskite solutions were filtered before use.

Device fabrication

ITO coated glass ($\approx 15 \Omega$ resistance) was cleaned in sequence with detergent, deionized water, ethanol, acetone and then isopropyl alcohol in an ultra-sonic bath for 15 minutes then dried with nitrogen flow and was further treated with UV/ozone for 15 minutes. Afterwards, PEDOT:PSS was spin coated on cleaned ITO coated substrate at 3500 rpm for 15 seconds, and then annealed on a hot plate in air for 15 minute at 150 °C. The devices were then shifted to a nitrogen filled glove box with humidity level less than 0.1%. For perovskite film formation, 40 μL of perovskite precursor solution were spin coated in a single step, at a rotating speed of 4500 rpm for 45 seconds and after 7 seconds, 200 μL of chlorobenzene were poured at once to obtain a smooth film. The films were annealed inside the glove box at 120 °C for 10 minutes.

Subsequently, PCBM was deposited on perovskite film as electron transport layer (ETL). For this, 30 μL of PCBM-61 solution (20 mg/mL in chlorobenzene) were spin coated at 4000 rpm for 30 seconds and then 30 μL of BCP solution (1mg/mL in extra dry ethanol) were rotated for 30 seconds at 5000 rpm. Finally, a 100 nm layer of Ag electrode was deposited in a high vacuum thermal evaporator.

***J-V* Characterization**

Keithley 2420 digital source meter was used to obtain current density-voltage (I-V) curves. The photocurrent was measured under 1 Sun illumination using an Oriel Newport 150W solar simulator (AM 1.5G), calibrated by a Newport Si reference detector (Oriel PN 91150V). The equilibrium quantum efficiency (EQE) of the devices was measured with an Oriel Newport System (Model 66902). All the measurements were carried out at room temperature in ambient air conditions.

UV-Visible and absorbance and photoluminescence characterization

For UV-visible absorbance and photoluminescence measurement, perovskite film in optimized conditions for device fabrication was spin coated on a cleaned quartz glass substrate. Quartz glass substrates were also cleaned by the procedure followed for ITO coated substrates. UV-visible absorbance was noted on a Shimadzu UV 3600, UV-visible NIR instrument. Steady state photoluminescence was recorded on Hitachi F-7000 spectrofluorometer using an excitation wavelength of 450 nm.

GIWAXS Analysis

Grazing incidence wide-angle X-ray scattering (GIWAXS) was recorded using a XEUSS SAXS/WAXS equipment under different conditions. For GIWAXS measurements, perovskite film was fabricated on a Si substrate in optimized conditions as for solar devices.

AFM and KPFM Study.

For topographic analysis and surface potential estimation, using atomic force microscopy, perovskite layer was spin coated on Glass/ITO/PEDOT:PSS as we described earlier. The tapping mode AFM (Asylum Research MFP-3D Infinity) with non-conductive tip (AC240TS-R3) was used to acquire the topographic image. Secondly, KPFM with conductive probe (ASYLEC-01, Tip was coating by Ti/Ir material) was used to map the surface potential [1, 2] of the perovskite films. KPFM mappings were characterized by using two-pass technique: the first pass same as tapping mode was used to explore the topographic image, while the second pass was used to explore the V_{CPD} by keeping the tip at a selected lift height. The V_{CPD} value can be measured by applying VDC and VAC between the tip and sample. Output signal is nullified and F_{ω} reaches to the zero ($F_{\omega}=0$). Because if the F_{ω} reaches minimum, the V_{CPD} can be acquired which shows surface potential of sample [3]. In our study, the conductive probe was kept at a lift height (ΔH) of -20nm to avoid the topographic artefacts.

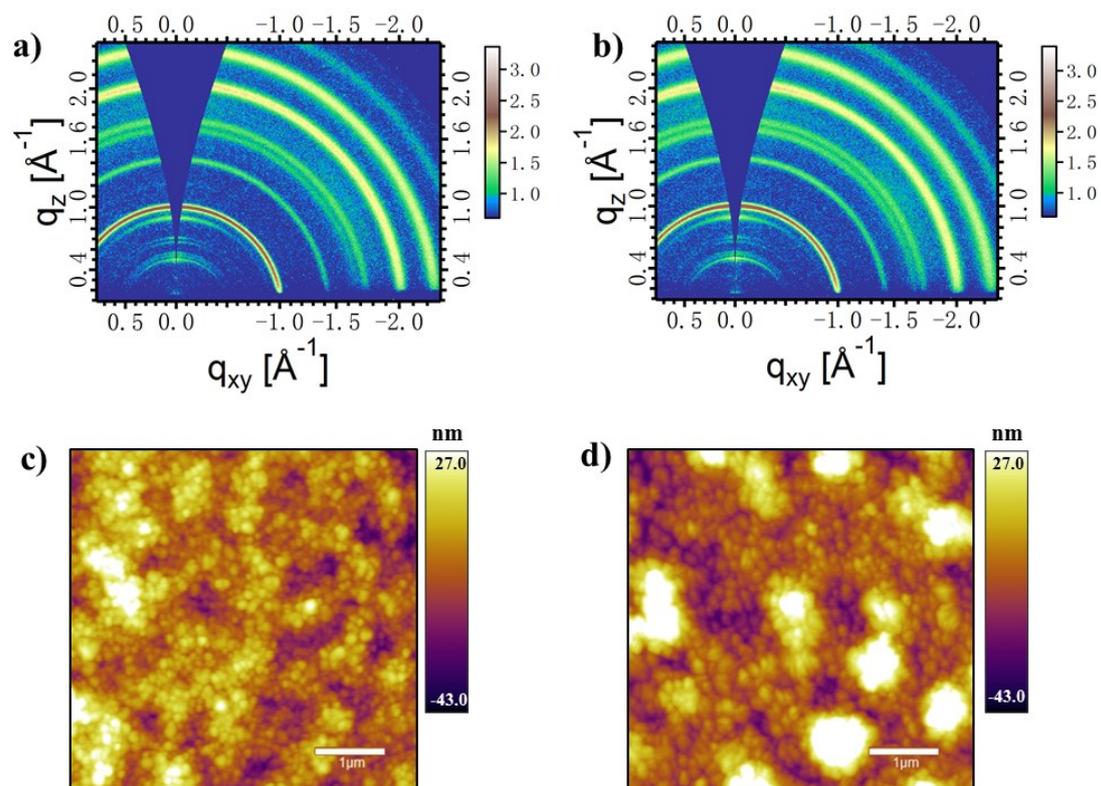


Figure S1: a, b) GIWAXS images of FA and Cs doped 2D/3D perovskite films respectively marked with marked diffraction patterns. c, d) Tapping mode AFM images of same 2D/3D perovskites films fabricated on PEDOT:PSS and annealed at 120 °C for 10 minutes.

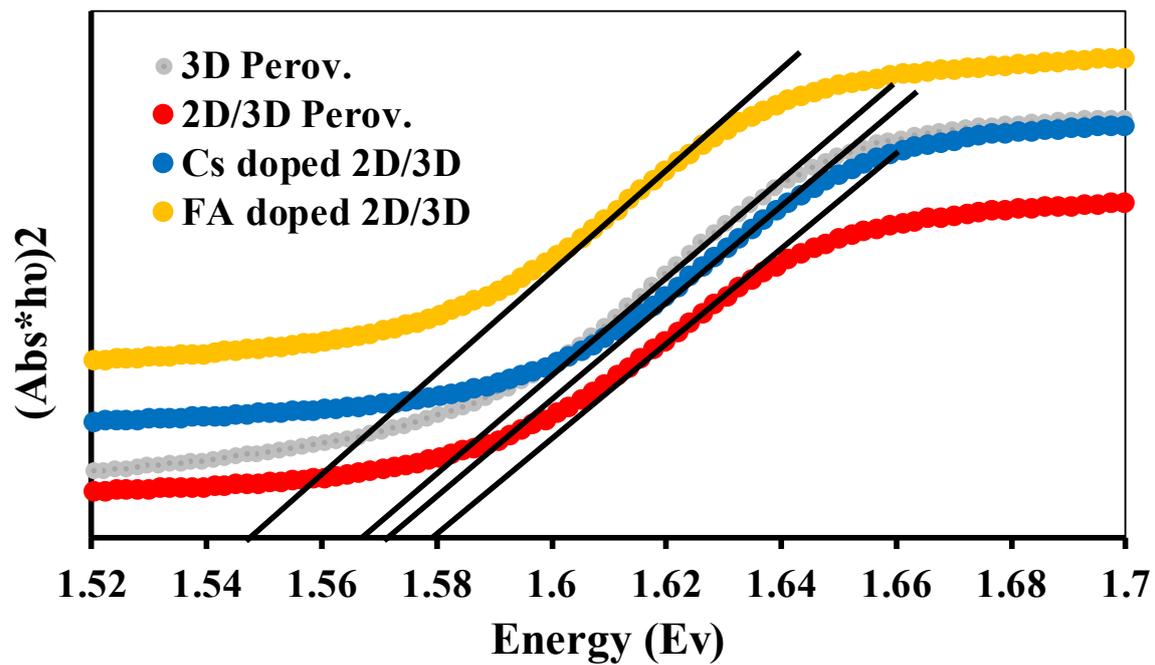


Figure S2: Band gaps measurements of the perovskite films using tauc plot.

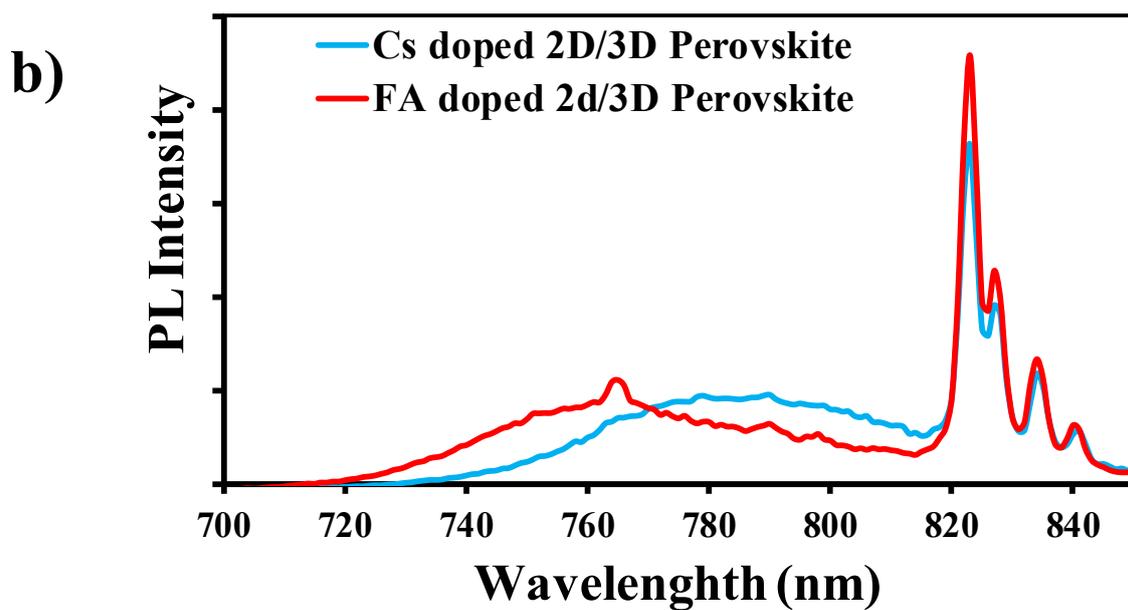
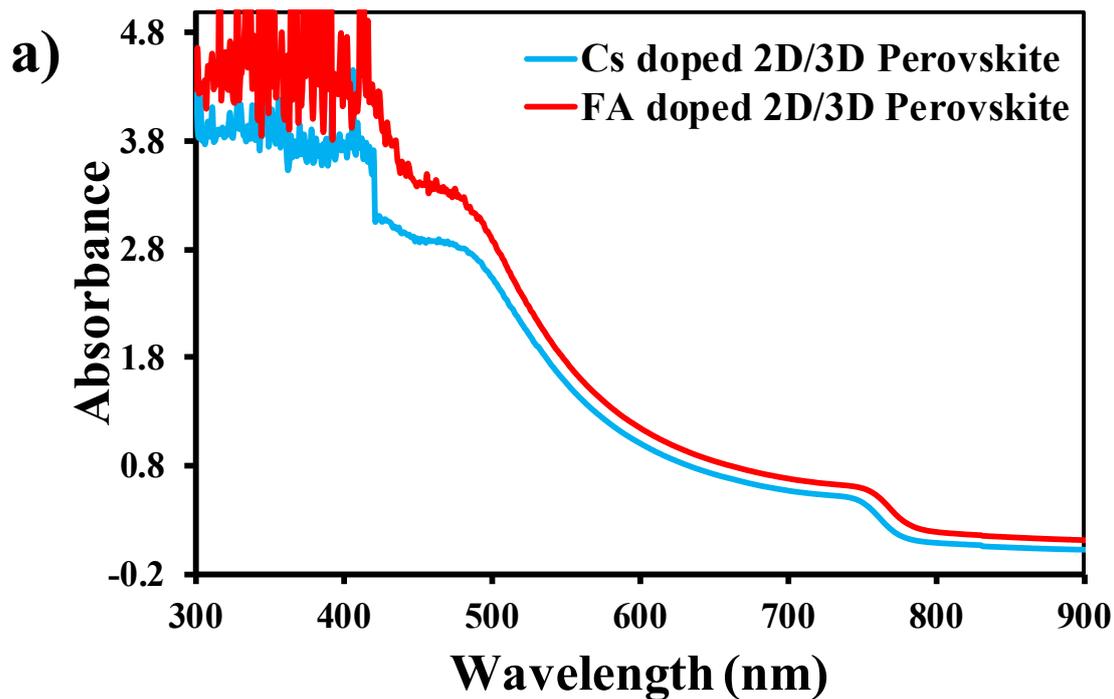


Figure S3: a) UV-visible absorption spectra FA and Cs doped 2D/3D perovskite films spin coated onto quartz glass substrates c) Photoluminescence spectra of the perovskite films,

Table S1: J_{sc} and PCE values measured under 1 Sun illumination and calculated from EQE value.

S. No.	Solution Composition PbI ₂ :MAI:AnI	J_{sc} (mA/cm ²) (Measured)	%PCE	J_{sc} (mA/cm ²) (Integrated)	%PCE (with integrated J_{sc})
1	1:0.8:0.2	25.55	15.96	18.85	11.76
2	1:0.8:0.15:0.05 FAI	28.16	13.25	17.83	8.36
3	1:0.8:0.15:0.05 CsI	19.91	10.73	16.41	8.94
4	1:1:0	23.09	13.38	17.02	9.84

Table S2: Performance of 2D/3D perovskite with different compositions MAI and AnI in precursor solution

Solution Composition PbI ₂ :MAI:AnI	Voc (V)	J_{sc} (mA/cm ²)	%FF	%PCE
1:0.8:0.2	1.04	25.55	60.00	16.0
1:0.9:0.1	0.98	16.83	44.09	7.29
1:0.7:0.3	0.96	18.06	40.09	7.02
1:0.6:0.4	0.91	18.54	35.87	6.06

Table S3: A comparison of photovoltaic performance of different 2D-3D perovskite heterostructures

2D _(n=1) -3D Perovskites	Voc (V)	J _{sc} (mA/cm ²)	%FF	%PCE	Ref.
[An ₂ PbI ₄] _x [MAPbI ₃] _(1-x)	1.04	25.55	60.0	16.0	This Work
[An ₂ PbI ₄] _x [FA _(0.5) MA _(0.95) PbI ₃] _{1-x}	0.90	28.16	52.1	13.3	This Work
[An ₂ PbI ₄] _x [Cs _(0.5) MA _(0.95) PbI ₃] _{1-x}	0.90	19.91	60.5	10.7	This Work
(AVA) ₂ PbI ₄ /MAPbI ₃	1.025	18.8	75.5	14.6	4
PEA ₂ PbI ₄ /MAPbI ₃	1.07	19.9	72.0	15.4	5
(MAPbI ₃) _{1-x} [(PEI) ₂ PbI ₄] _x (x=0.02)	1.08	19.3	72.9	15.2	6
(PEA ₂ PbI ₄) _{0.017} /MAPbI ₃	1.15	22.7	76.3	19.8	7
PEA ₂ SnI ₄ /FASnI ₃	0.61	22.0	70.1	9.4	8
(NAP) ₂ Sn _{0.5} Pb _{0.5} I ₄ /MAPb _{0.5} Sn _{0.5} I _x Cl _{3-x}	0.64	26.5	64.8	10.9	9

References

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