Supporting Information

Stability Improvement and Performance Reproducibility Enhancement of Perovskite Solar Cells Following (FA/MA/Cs) $PbI_{3-x}Br_x/(CH_3)_3SPbI_3$ Dimensionality Engineering

Mohamed M. Elsenety,[a] Maria Antoniadou,[a] Nikolaos Balis,[a] Andreas Kaltzoglou,[a] Labrini Sygellou,[b] Anastasios Stergiou,[c] Nikos Tagmatarchis,[c] Polycarpos Falaras[a,]*

[a] National Centre for Scientific Research "Demokritos", Institute of Nanoscience and Nanotechnology, 15341, Agia Paraskevi Attikis, Athens, Greece

[b] Foundation of Research and Technology Hellas, Institute of Chemical Engineering Sciences, Platani GR-26504, Patras, Greece

[c] National Hellenic Research Foundation, Theoretical and Physical Chemistry Institute, 48 Vassileos Constantinou Avenue, 11635, Athens, Greece

AUTHOR INFORMATION

***Corresponding Author**

e-mail address: p.falaras@inn.demokritos.gr; ORCID: 0000-0002-9553-5301

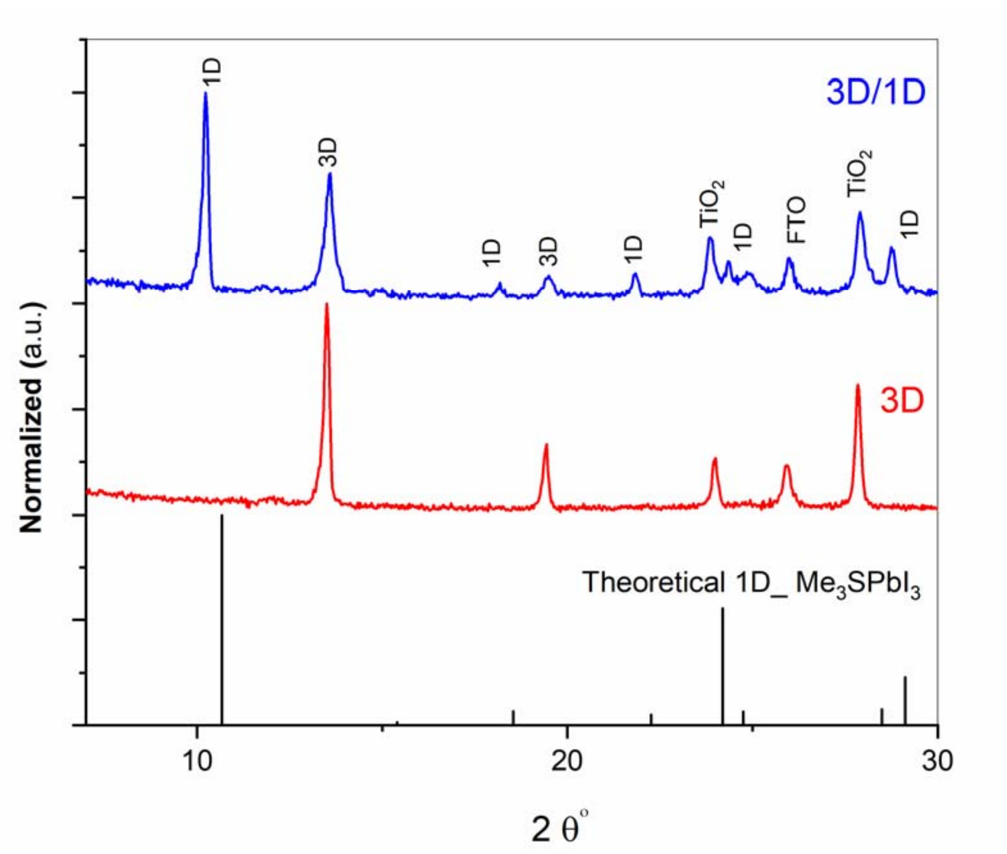

Figure S1. XRPD of TiO_2/(FA/MA/Cs) $PbI_{3-x}Br_x$/$(CH_3)_3SPbI_3$ (3D/1D) and TiO_2/(FA/MA/Cs) $PbI_{3-x}Br_x$ films (3D). The 1D layer consists of 3mg $(CH_3)_3SCl$/ml isopropanol)

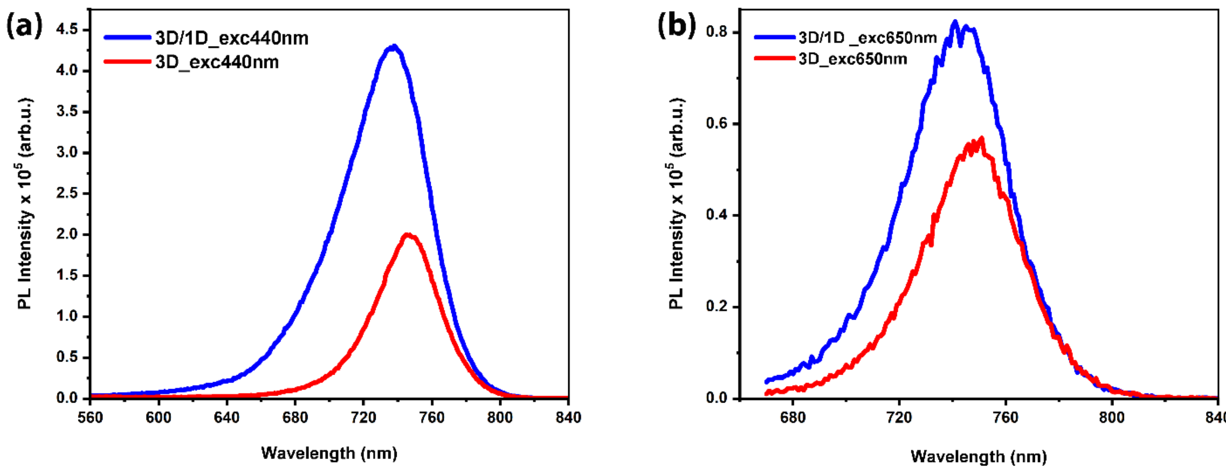

Figure S2. Steady-state PL spectra taken using additional laser excitation beams at 440 (a) and 650 nm (b), respectively.

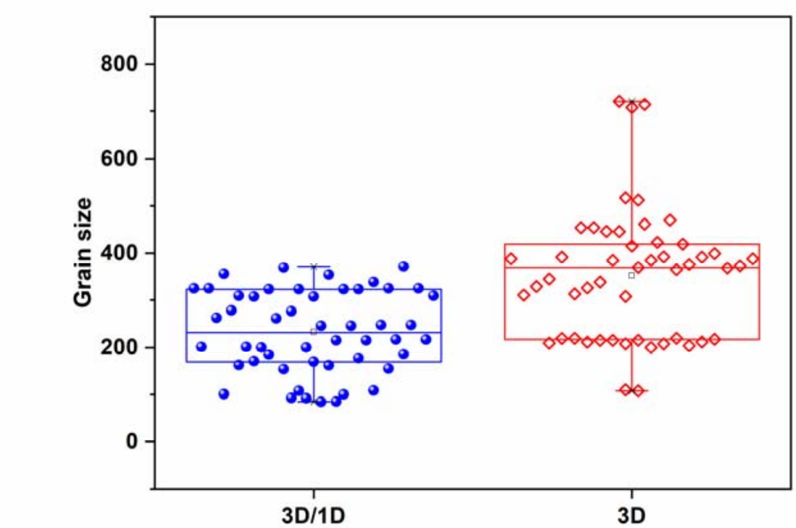

Figure S3. Grain size distribution of TiO_2/(FA/MA/Cs)$PbI_{3-x}Br_x$/$(CH_3)_3SPbI_3$ (3D/1D) and TiO_2/(FA/MA/Cs)$PbI_{3-x}Br_x$ films (3D

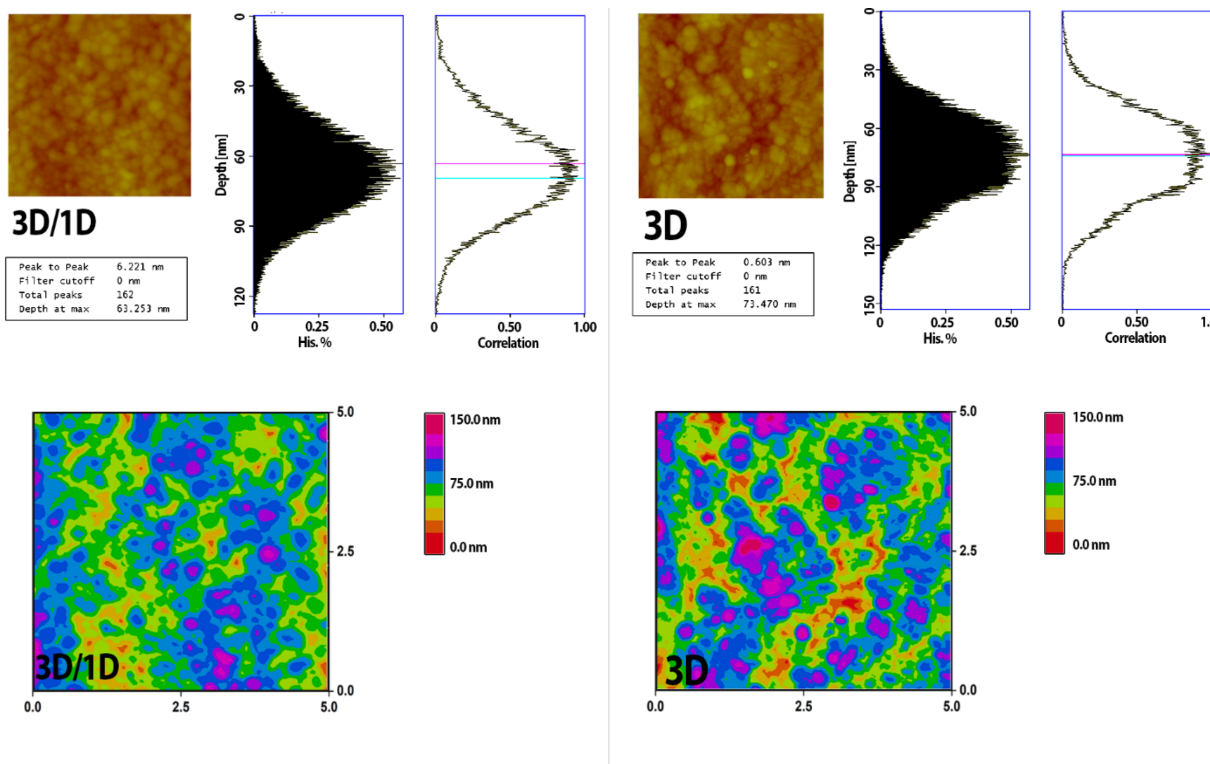

Figure S4. AFM top surface topography with depth histogram of the 3D/1D bilayer (top-left) and the 3D perovskite layer (top-right); AFM Surface topography colored scale for both 3D/1D bilayer (down-left) and the 3D perovskite layer (down-right).

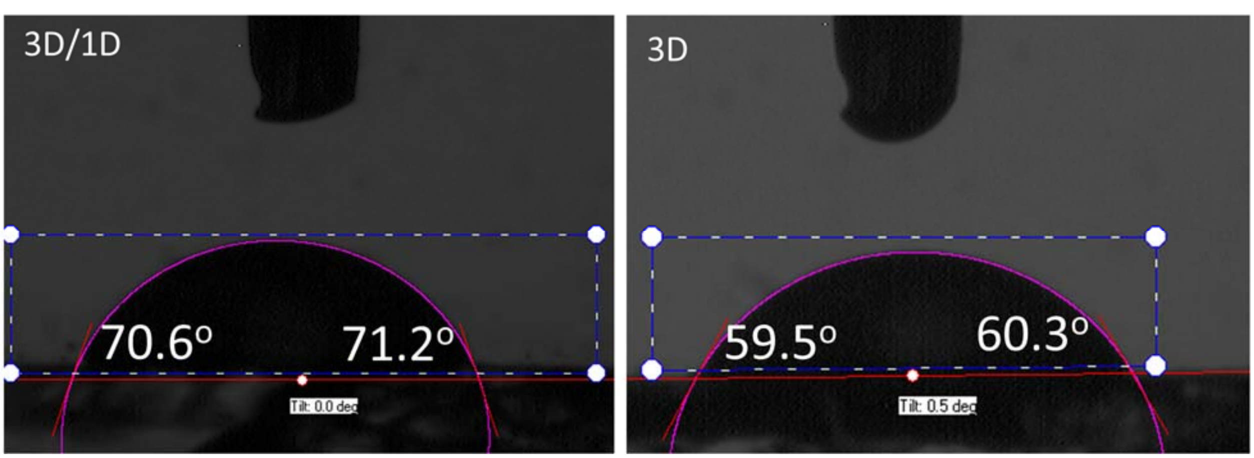

Figure S5. Contact angle measurements of 3D/1D modified film upon Meso-TiO_2 surfaces and the 3D film without modification.

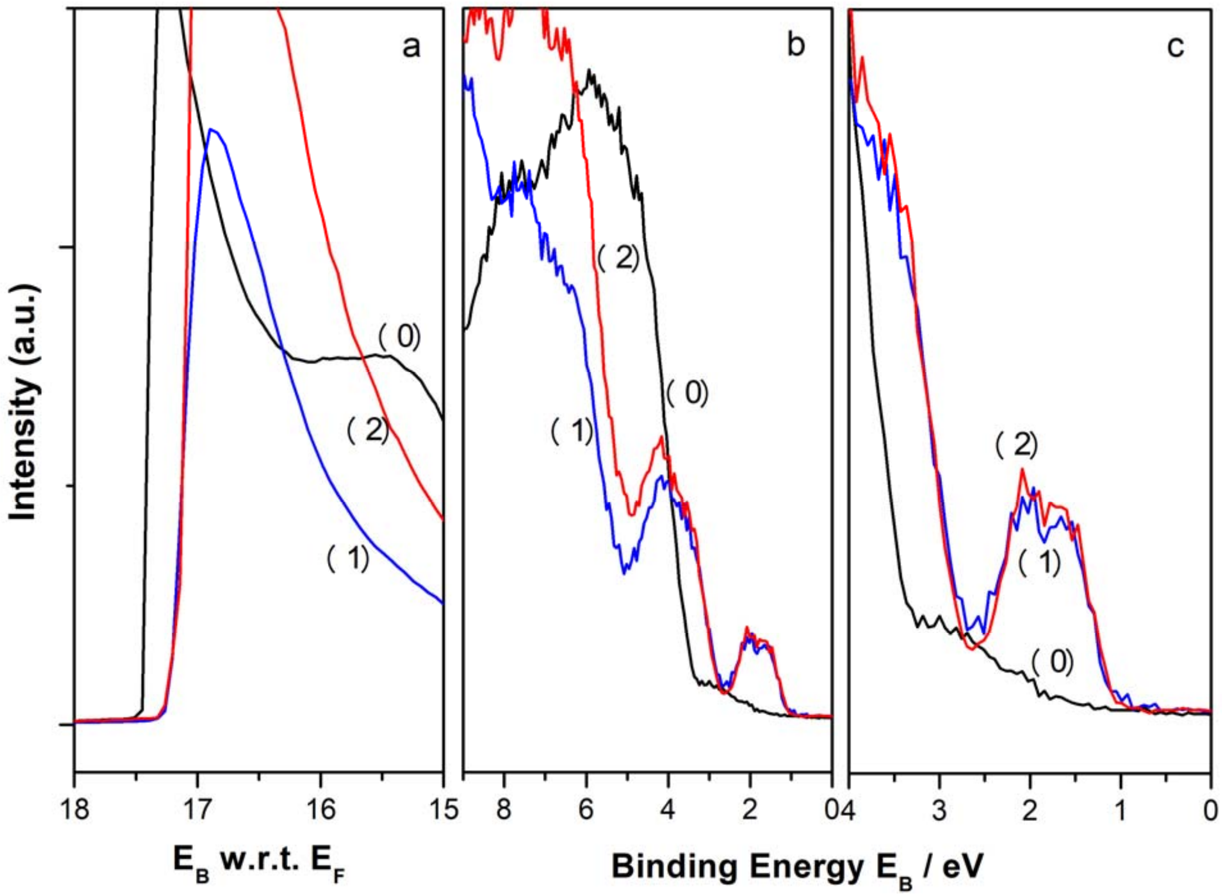

Figure S6. Ultraviolet photoemission spectra (UPS): Secondary electron cutoff (a), valence band region (b) and close-up of valence band region (c) of ITO/TiO_2 (0), ITO/TiO_2/$MAFACsPbI_xBr_{3x}$/Me_3SPbI_3/Spiro-MeOTAD (1) and ITO/TiO_2/$MAFACsPbI_xBr_{3x}$/Spiro-MeOTAD (2). The work function and VBM were determined with a linear extrapolation of the secondary electron cutoff and the leading edge of the valence band, respectively.

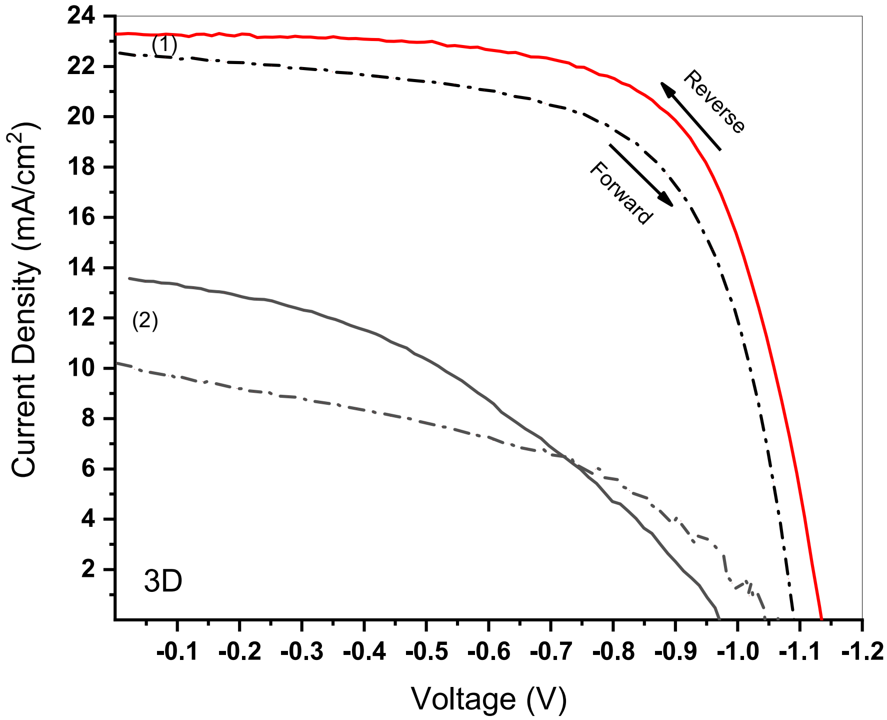

Figure S7. J-V curves (forward and reverse scans) of the best performing solar cells based on the 3D perovskite, as prepared (1) and after one month (2) under storage in dark and ambient conditions.

Table S1. Work function, valence band maximum and ionization potential values resulting from UPS data.

Sample	WF (±0.1) eV	VBM cut off (±0.1)	Ionization Potential or HOMO (±0.1) eV
ITO/TiO_2	3.76	3.2	6.96
ITO/TiO_2/$MAFACsPbI_xBr_{3-x}$	4.22	1.28	5.5
ITO/TiO_2/ $MAFACsPbI_xBr_{3-x}$ /Spiro-MeOTAD	4	1	5
ITO/TiO_2/ $MAFACsPbI_xBr_{3-x}$ /Me_3SPbI_3	4.33	1.26	5.59
ITO/TiO_2/ $MAFACsPbI_xBr_{3-x}$ /Me_3SPbI_3/Spiro-MeOTAD	4	1	5

Table S2. Photovoltaic parameters of reference solar cells (fresh and after storage in ambient and dark conditions for 1 month). V_{oc}: open-circuit voltage; J_{sc}: short-circuit current density; FF: fill factor; PCE: power conversion efficiency; SPCE: Stabilized PCE; HI: Hysteric Index; HF: Hysteresis factor.

Time	Scan directions	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)	SPCE (%)	HI	HF
(Fresh cells)	Reverse	23.52	1.13	0.67	17.97			
	Forward	22.65	1.09	0.65	15.97	17.85	0.07	0.111
	Average	23.09	1.12	0.66	16.97			
(After 1 month)	Reverse	13.70	0.99	0.39	5.32			
	Forward	10.20	1.07	0.43	4.71	5.12	0.27	0.115
	Average	11.95	1.03	0.41	5.02			

Table S3. Photovoltaic parameters with respect to the best performing cell for reference (3D absorber) PSCs. SD: Standard deviation, SE: Standard error, V_{oc}: open-circuit voltage, J_{sc}: short-circuit current density, FF: fill factor, PCE: power conversion efficiency, normalized values in parenthesis.

3D	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
Average	23.48 (0.95)	1.11 (0.98)	0.66 (0.96)	16.85 (0.87)
SD	0.56 (0.02)	0.01 (0.01)	0.02 (0.03)	1.35 (0.07)
SE	0.14 (0.01)	0.003 (0.01)	0.006 (0.01)	0.35 (0.02)

Table S4. Photovoltaic parameters of reference (3D) and modified solar cells (3D/1D) after 4 h of light stress. V_{oc}: open-circuit voltage, J_{sc}: short-circuit current density, FF: fill factor, PCE: power conversion efficiency

3D/1D	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
Fresh cells	20.74	1.08	0.64	14.33
After 4h	17.84	0.78	0.53	7.38

3D	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
Fresh cells	22.54	1.108	0.61	15.34
After 4h	13.22	0.6	0.27	2.5