Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Visualization of 3D to quasi 2D conversion of perovskite thin films via in-situ photoluminescence measurement: a facile route to design graded energy landscape

Jitendra Kumar[a], *Ankur Yadav*[a], *and Monojit Bag*[a,b,]*

[a] Advanced Research in Electrochemical Impedance Spectroscopy Laboratory, Indian Institute of Technology Roorkee, Roorkee 247667, India

[b] Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India

E-mail: monojit.bag@ph.iitr.ac.in

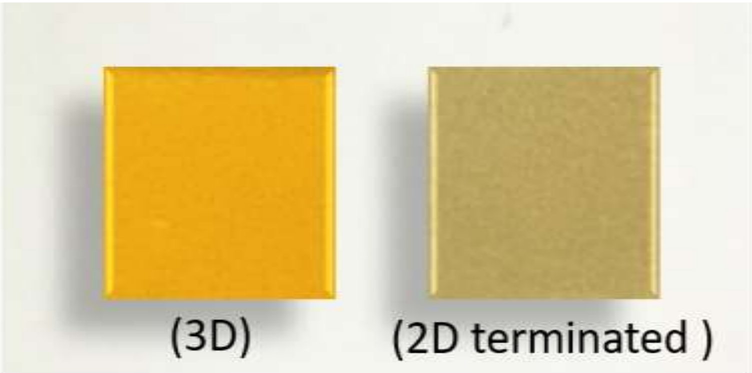

Fig. S1 Photographic image of controlled 3D and post treated 2D terminated perovskite film. Both films show visual difference in colour due to their different spectral absorbance.

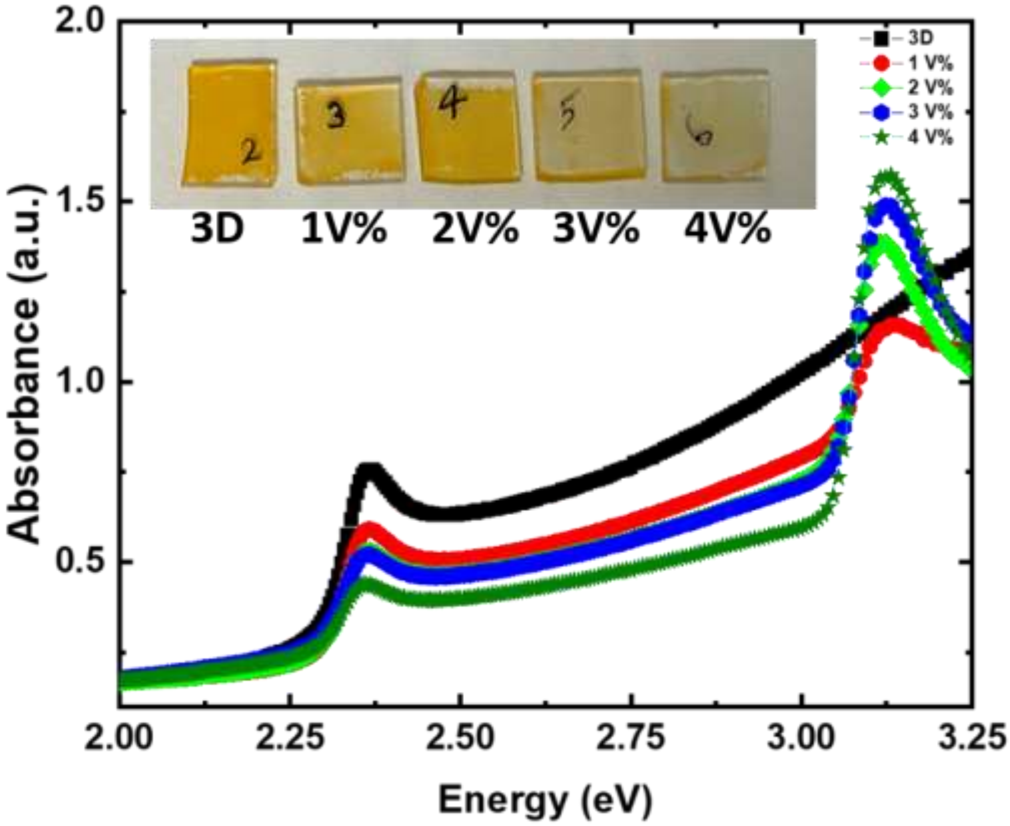

Fig. S2 Absorption spectrum of controlled and post treated films, post treated films are partially redissolved by 1-4 V% solution of Benzylamine in IPA.

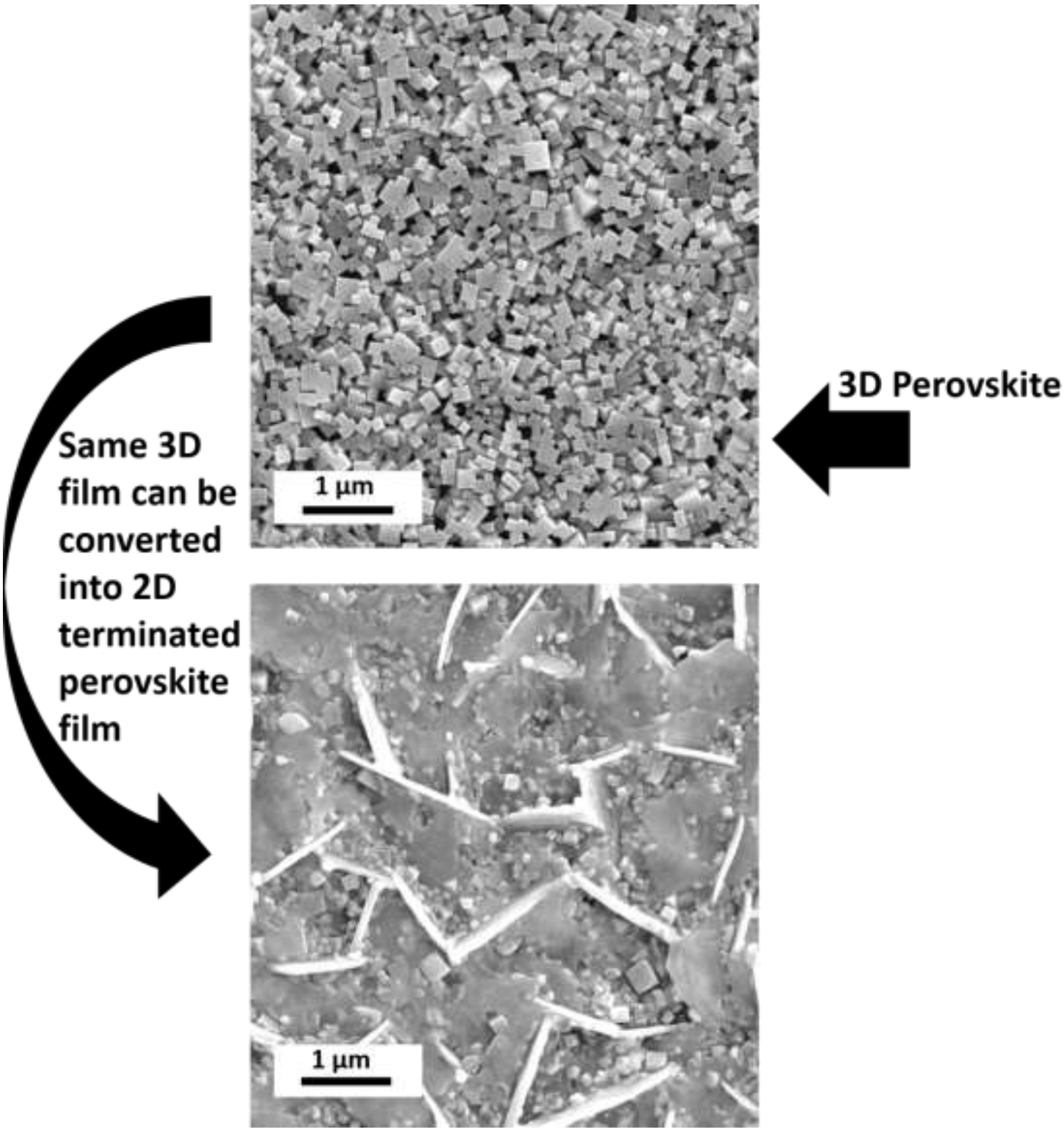

Fig. S3 FESEM image of (a) controlled 3D and (b) partially redissolved 2D terminated perovskite film redissolved with a 2V% solution of benzylamine in IPA. Treated sample presents a typical morphology of a 2D perovskite sample.

After washing with redissolving solvent (IPA mixed with 2V% benzylamine) morphology of 3D samples chenges significantly, now the top part of the film presents flat structures. These structures are generally associated with the formation of 2D perovskite.

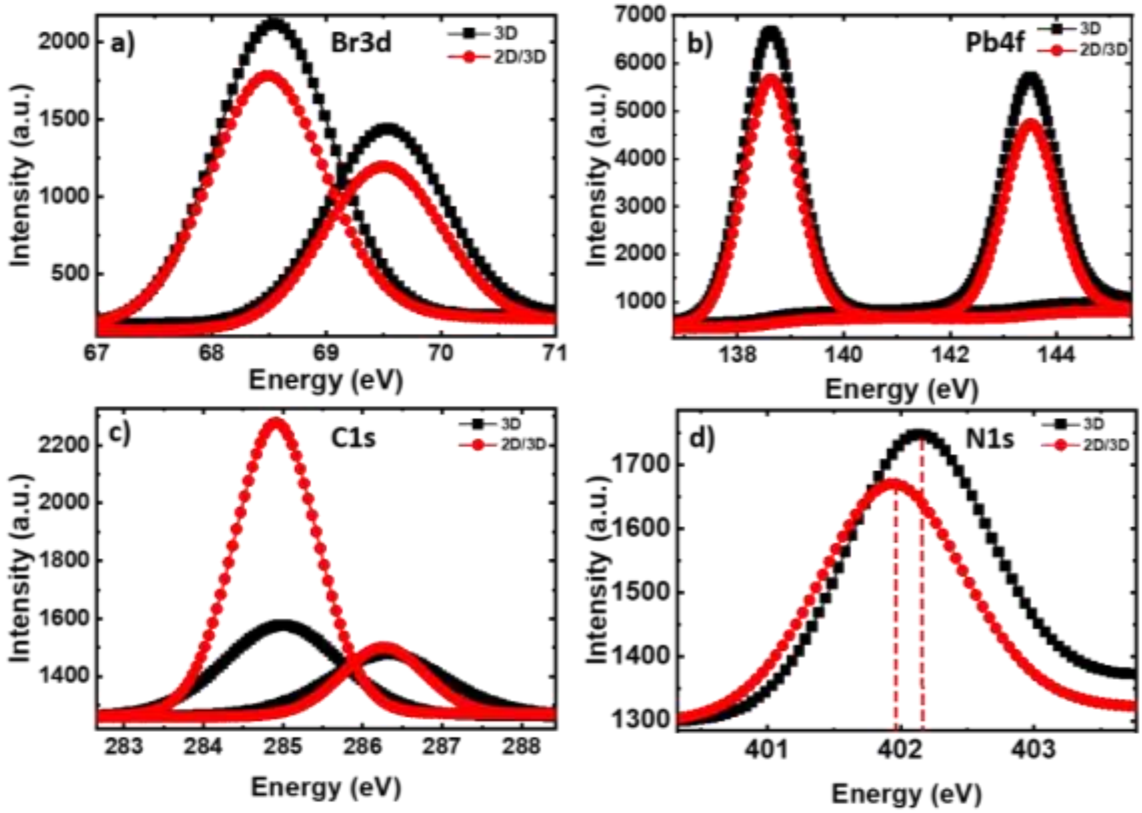

Fig. S4 XPS spectra of controlled 3D and converted 2D/3D perovskite film. C1s1/2 peak show significant rise in intensity, also N1s peak shows a sligth blue shift of ~ 170 meV.

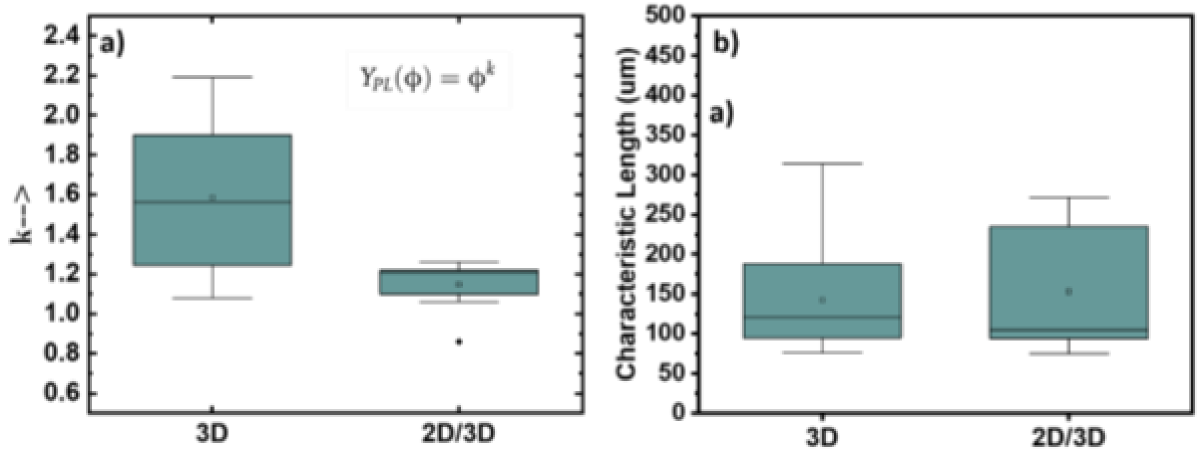

Fig. S5 Excitation intensity dependent PL intensity measurement. PL intensity was found to obey power law, with k closer to 2 in 3D sample wheras k closer to 1 in 2D terminated samples, (b) Position dependent PL intensity variation in 3D and 2D terminated samples shows that the charge carrier diffusion is almost left untouched due to presence of 2D terminated perovskite.

To perform position dependent PL measurement, a 405 nm LASER with 50 mW LASER intensity was utilized, a 1 mm LASER spot was defined with the the help of a circular aperture the sample was directly placed on the aperture, thereafter a long pass filter was directly placed on the sample. PL signal was collected with an optical fibre coupled with the spectrometer(CCS200, Thorlabs). The PL signal was collected with a resolution of 50 µm.

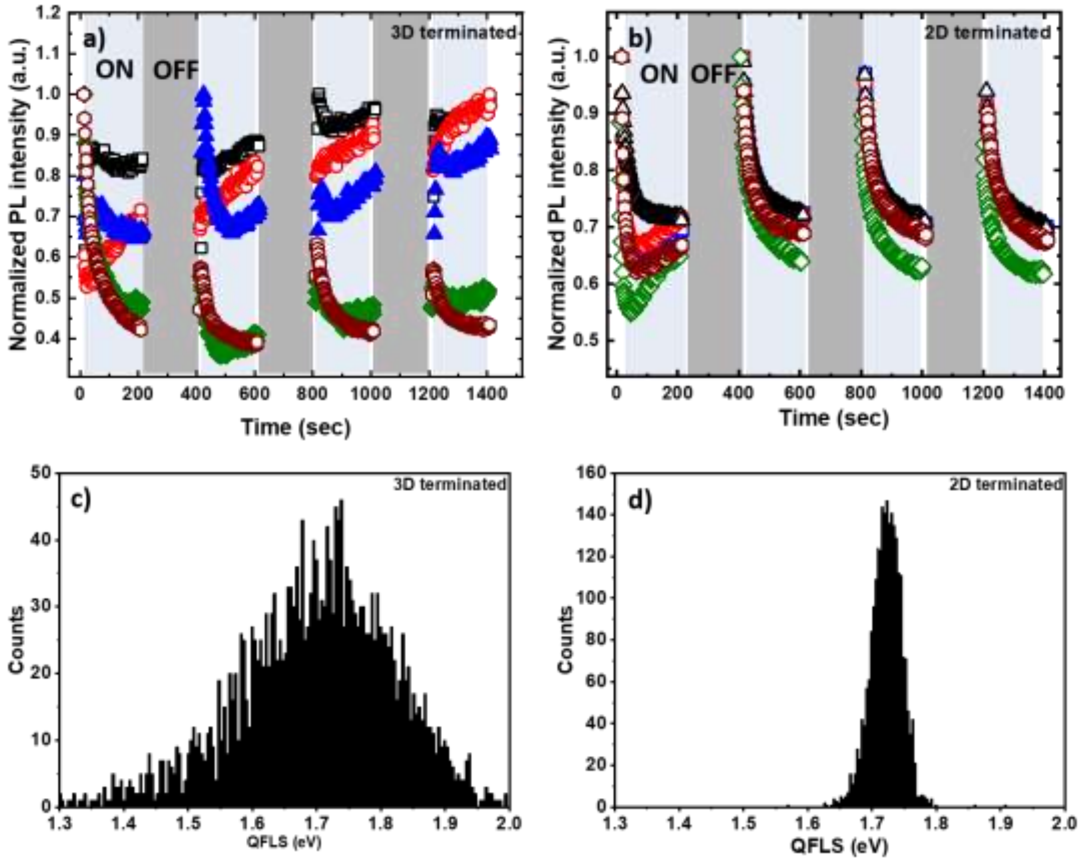

Fig. S6 Light soaking experiment performed with 405 nm (50 mW) LASER in 75% humidity.

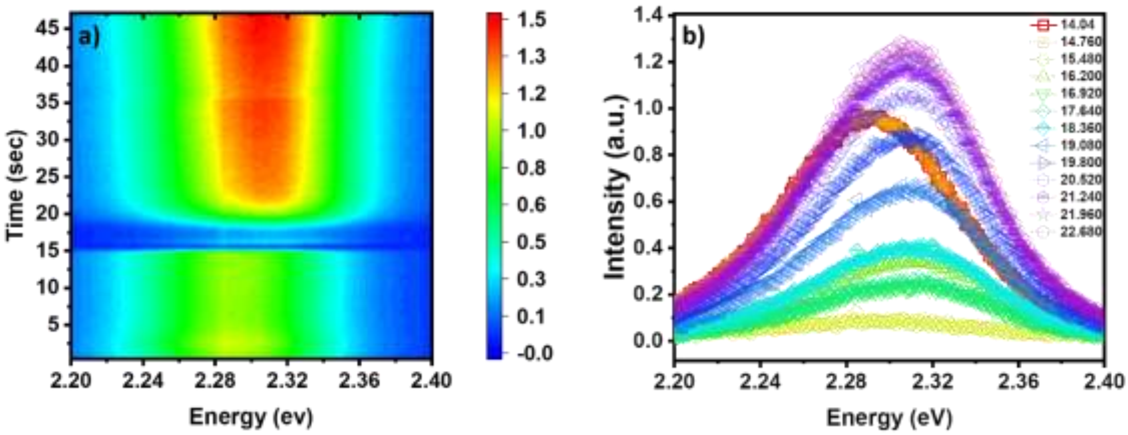

Fig. S7 (a) Real time PL map taken in an situ measurement while conversion of 3D film into 2D/3D film, (b) Variation in PL spectrum close to the convrsion point (~15.480 sec). Legends represent time in seconds.

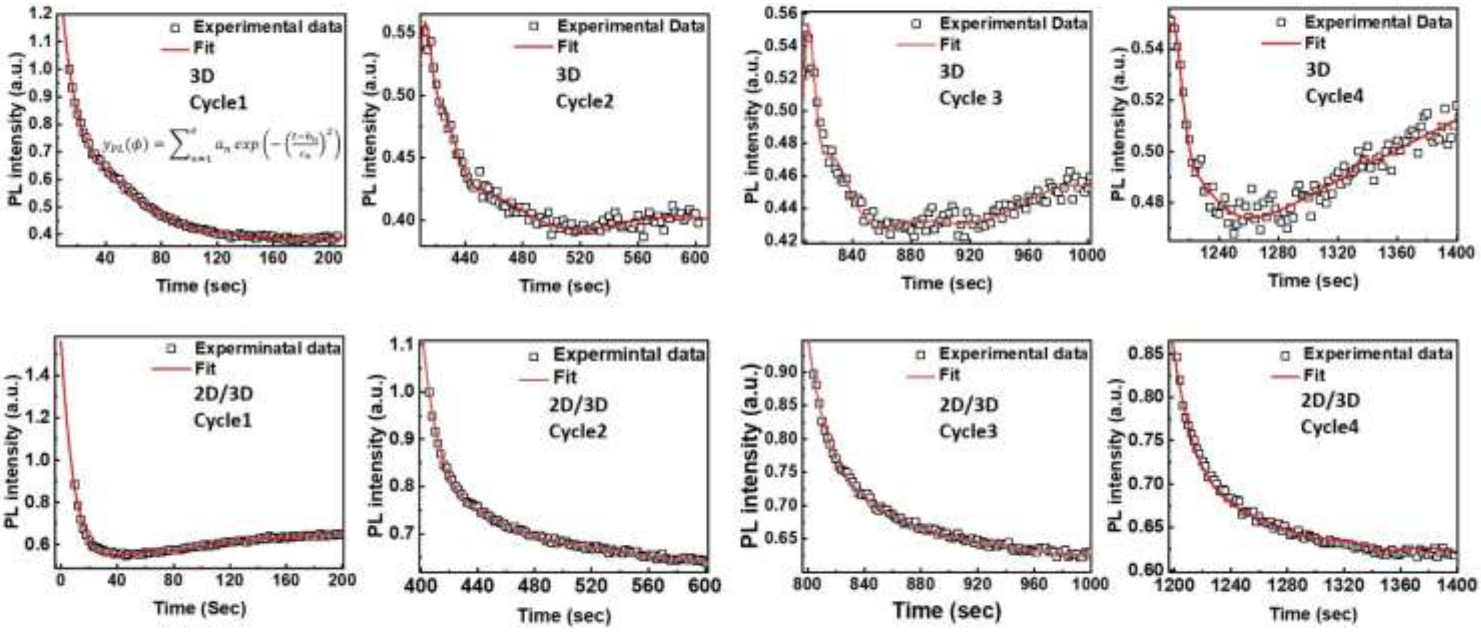

Fig. S8 Fitting of PL intensity traces under light soaking experiment. PL intensity was measured in 4 cycles for both controlled and 2D/3D samples and fitted with a sum of 4 gaussian function. Fitting parameters can be found in table S1.

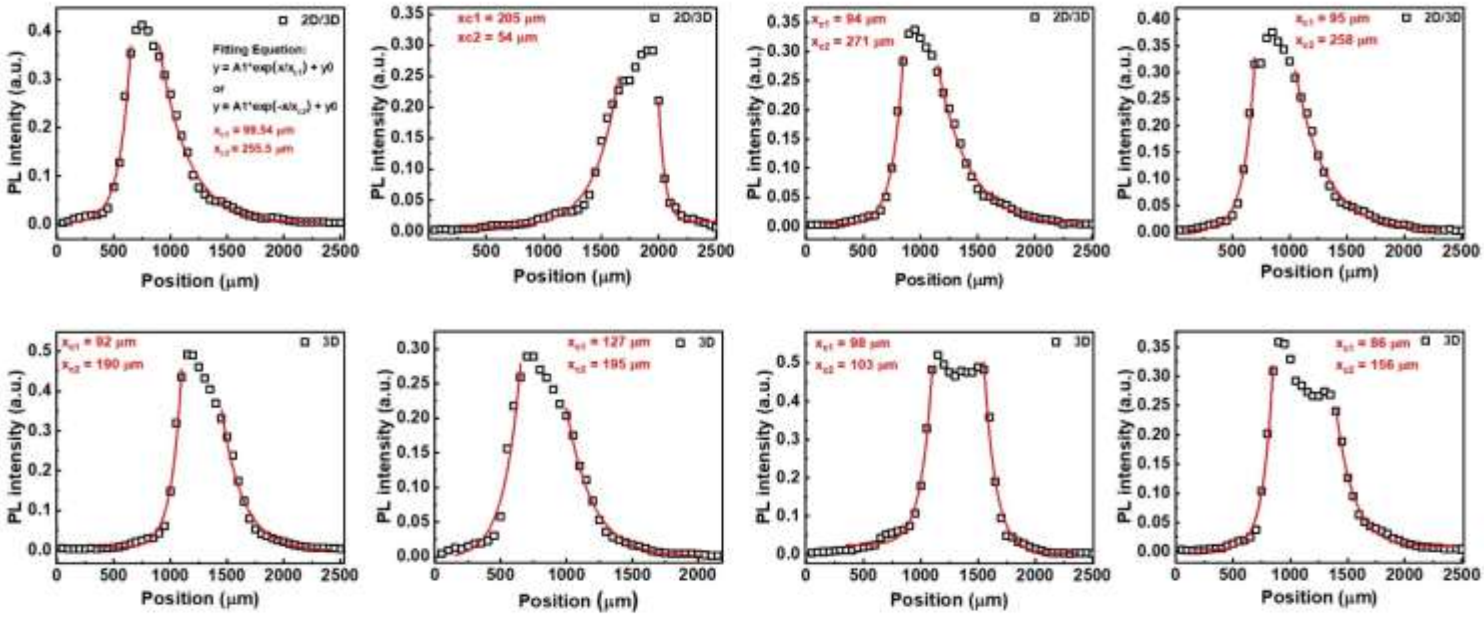

Fig. S9 Fitting of position dependent PL intensity data. $X_{C1/2}$ represent the characteristic distance over which intensity drops by a factor of 1/e.

Table S1. Fitting parameters for the Light Soaking experiment.

3D							
Cycle 1		Cycle 2		Cycle 3		Cycle 4	
a1	4.29e10	a1	0.008	a1	0.035	a1	0.037
a2	0.031	a2	0.031	a2	0.009	a2	0.009
a3	0.017	a3	0.006	a3	0.002	a3	0.021
a4	0.013	a4	0.009	a4	0.006	a4	0.021
b1	-238.6	b1	9.7	b1	229	b1	196
b2	47.84	b2	224.5	b2	10.6	b2	12
b3	180.9	b3	17.1	b3	108.7	b3	24
b4	227.7	b4	19.1	b4	45.6	b4	83
c1	44.05	c1	7.68	c1	296.6	c1	102.8
c2	121.3	c2	313.8	c2	19	c2	15.31
c3	64.26	c3	22.87	c3	28.56	c3	43.17
c4	33.8	c4	72.43	c4	38.92	c4	60.5

2D/3D							
a1	2.47e11	a1	57.87	a1	12.31	a1	238
a2	0.09	a2	0.10	a2	0.10	a2	0.09
a3	0.003	a3	0.018	a3	0.025	a3	0.014
a4	0.012	a4	0.033	a4	0.024	a4	0.038
b1	-667.9	b1	-244.8	b1	-172.5	b1	-394.8
b2	199	b2	34.5	b2	15.2	b2	53
b3	96.45	b3	160.1	b3	174.6	b3	144
b4	36.05	b4	216.6	b4	220	b4	202
c1	123.5	c1	87.7	c1	66.7	c1	130.2
c2	304.2	c2	213.6	c2	220.2	c2	173.3
c3	25.64	c3	50.68	c3	63.41	c3	40.31
c4	39.31	c4	39.65	c4	35.81	c4	40.77

Table S2. Input parameters for simulation of 3D and 2D/3D perovskite-based electron injection layer free devices (all the position dependent grading is considered to be linear).

Parameters	PEDOT:PSS	Perovskite (3D)	Graded Perovskite (2D)	
			Left Side	Right Side
Thickness (μm)	0.020	0.300	0.100	
Bandgap (eV)	2.2	2.280	2.280	3.02
Electron affinity (eV)	2.95[1]	3.4[2]	3.1[3]	3.1
Dielectric permittivity (relative)	3	28.5	28.5	38.0
CB effective density of states ($1/cm^3$)	2.2×10^{16}	5×10^{18}	5×10^{18}	5×10^{18}
VB effective density of states ($1/cm^3$)	4×10^{18}	5×10^{19}	5×10^{19}	2×10^{19}
Electron mobility (cm^2/Vs)	2×10^{-2}	34	34	1.7
Hole mobility (cm^2/Vs)	2	34	34	10
Shallow uniform donor density ND ($1/cm^3$)	1×10^{15}	1×10^{15}	1×10^{15}	1×10^{16}
Shallow uniform acceptor density NA ($1/cm^3$)	8.17×10^{18}	1.8×10^{15}	1.8×10^{15}	1.8×10^{14}
Radiative recombination coefficient (cm^3/s)	0	5×10^{-10}	5×10^{-10}	5×10^{-9}
Nt total ($1/cm^3$)	1×10^{15}	1×10^{14}	1×10^{14}	1×10^{15}
Left contact work function for ITO (eV)		4.7		
Right contact work function for Al (eV)		4.3		

Table S3. Simulated device parameters for $CH_3NH_3PbBr_3$ based perovskite solr cell

Device configuration	Voc (eV)	Jsc (mA/cm^2)	Fill factor (FF)	PCE(%)
ITO/PEDOT:PSS/HOIP(3D300)/Al	0.93	4.33	70.36	2.83

ITO/PEDOT:PSS/HOIP(3D20)/HOIP(2D280D)/Al	1.19	2.52	78.22	2.34
ITO/PEDOT:PSS/HOIP(3D100)/HOIP(200)/Al	1.18	3.16	77.00	2.87
ITO/PEDOT:PSS/HOIP(3D150)/HOIP(150)/Al	1.18	3.51	76.98	3.18
ITO/PEDOT:PSS/HOIP(3D200)/HOIP(100)/Al	1.17	3.84	77.38	3.48
ITO/PEDOT:PSS/HOIP(3D280)/HOIP(0)/Al	1.17	4.29	80.18	4.02

References

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[2] M. Pegu, L. Caliò, M. Ahmadpour, H. G. Rubahn, S. Kazim, M. Madsen, S. Ahmad, *Emergent Mater.* **2020**, *3*, 109.

[3] S. Silver, J. Yin, H. Li, J. L. Brédas, A. Kahn, *Adv. Energy Mater.* **2018**, *8*, 1.