

Electronic Supplementary Information

Degradation of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite materials by localized charges and its polarity dependency

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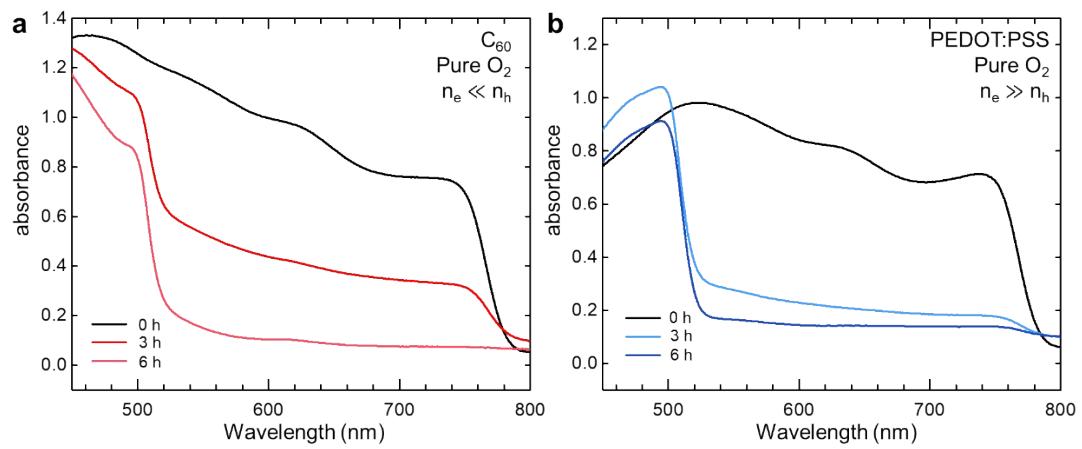
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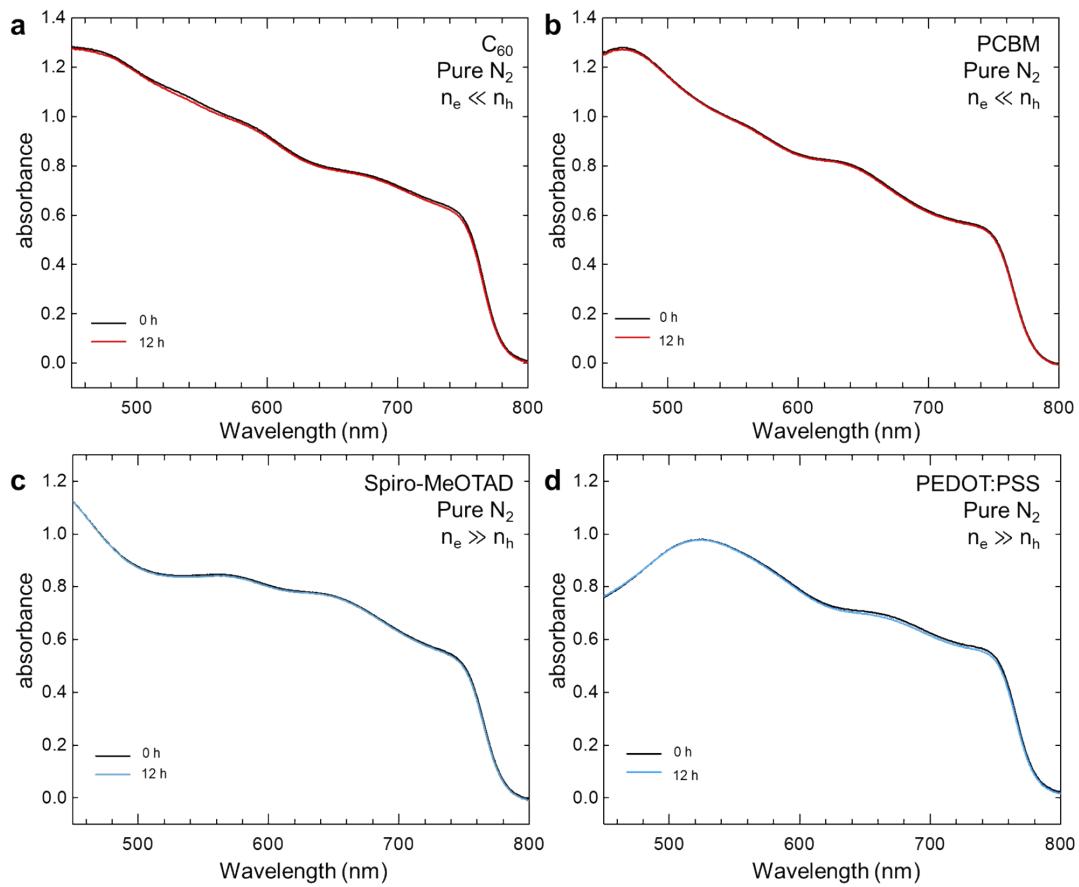
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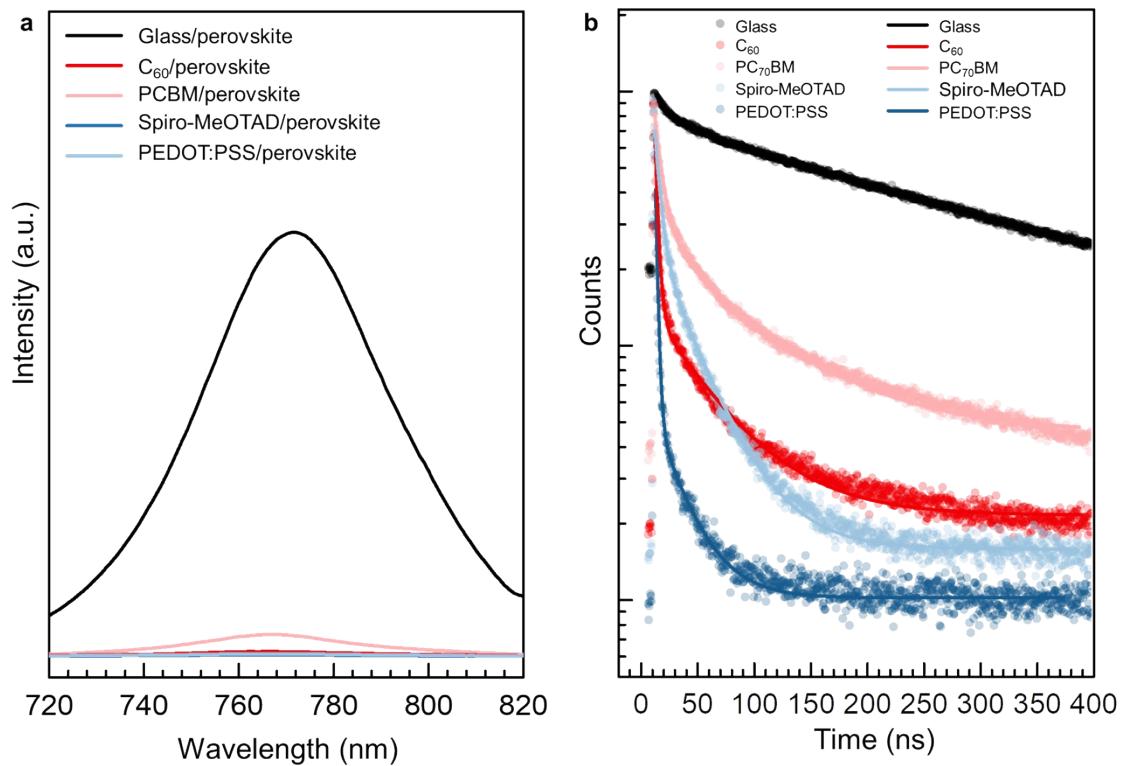
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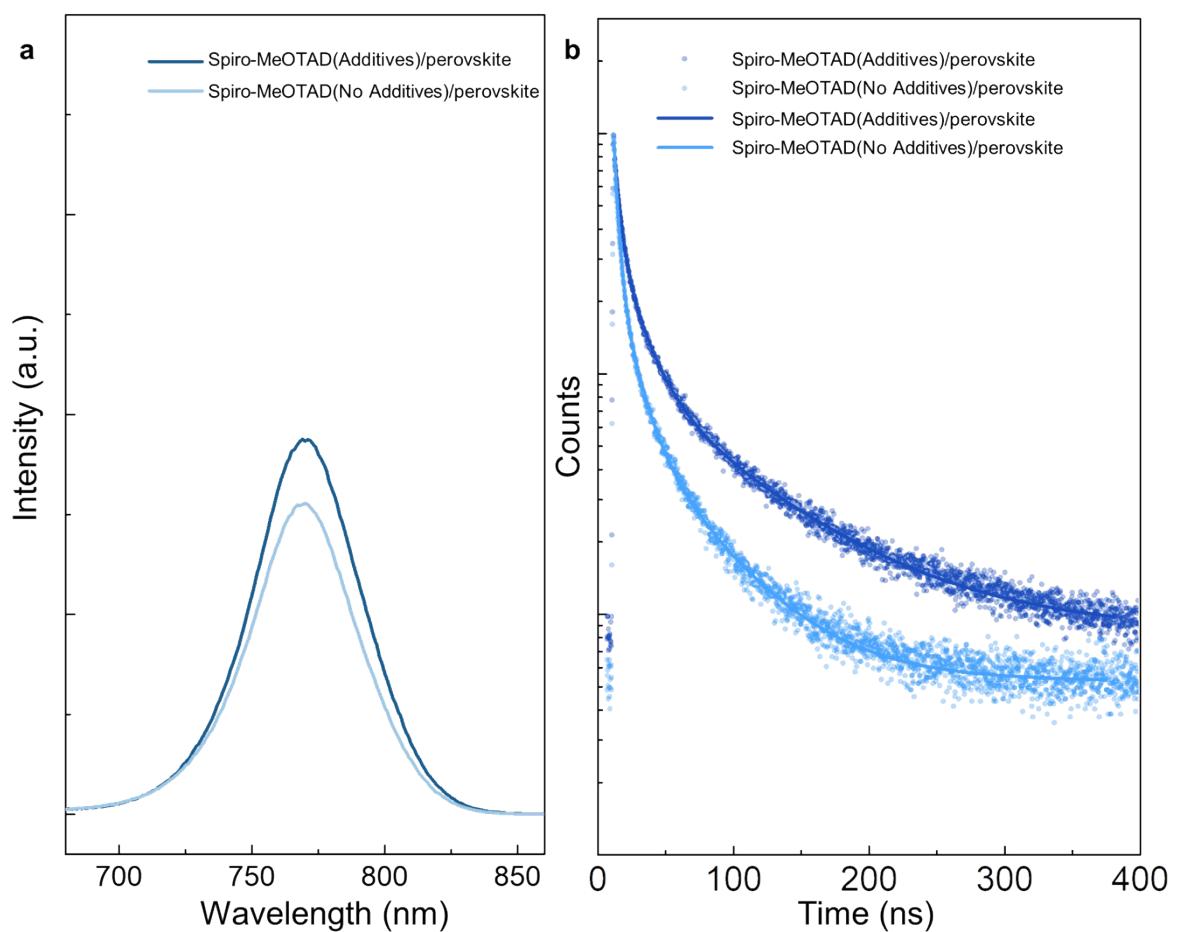
Supplementary Figure 1. Time evolution of absorption spectra for (a) the C₆₀/MAPbI₃ and (b) the PEDOT:PSS/MAPbI₃ half devices in chamber filled with pure O₂ gas before and after light-illumination for 6 h.



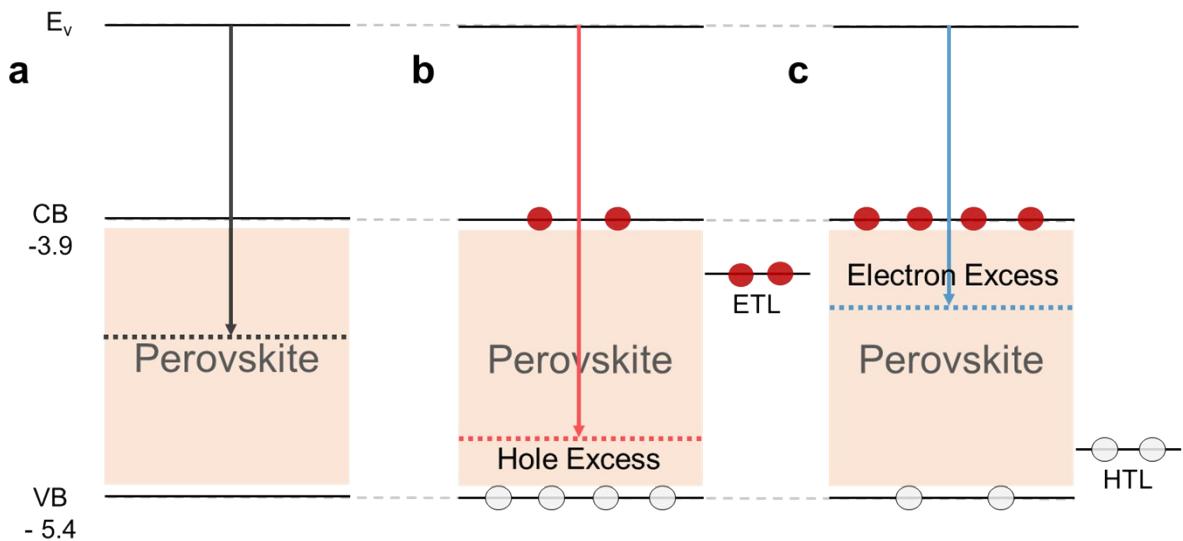
Supplementary Figure 2. Absorption spectra of perovskite films deposited on (a) C₆₀, (b) PCBM, and perovskite films deposited on (c) Spiro-MeOTAD and (d) PEDOT:PSS in chamber filled with pure N₂ gas before and after light-illumination for 12 h.



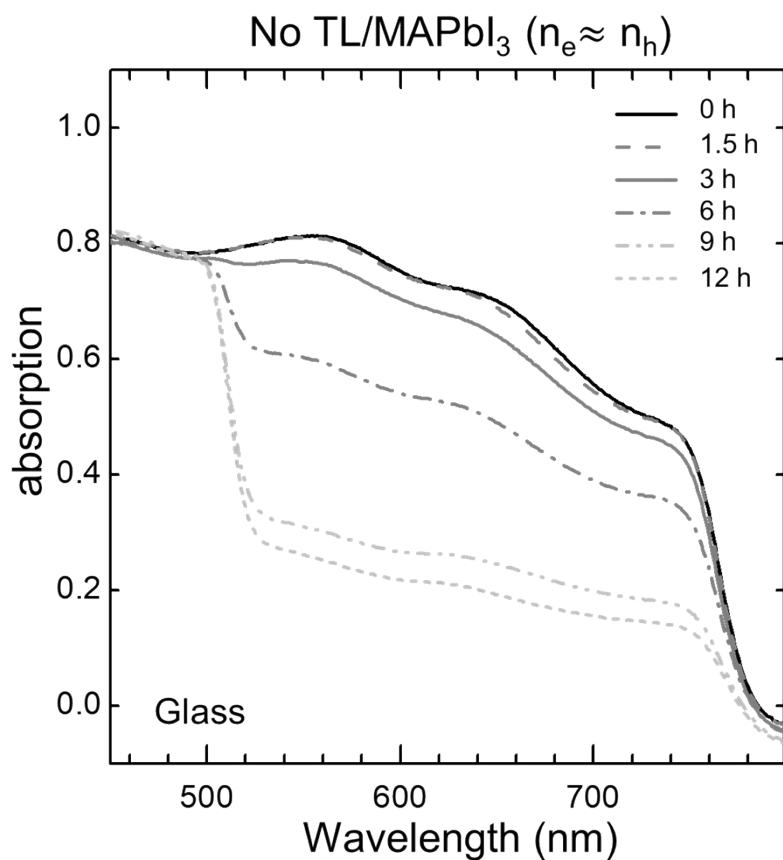
Supplementary Figure 3. (a) Steady-state and (b) time-resolved PL spectra obtained for the perovskite films deposited on the glass, PCBM, C₆₀, Spiro-MeOTAD, and PEDOT:PSS substrates and fitted with the three-term exponential decay function. Time-resolved PL spectra is plotted as circle, and fitted function is plotted as line.



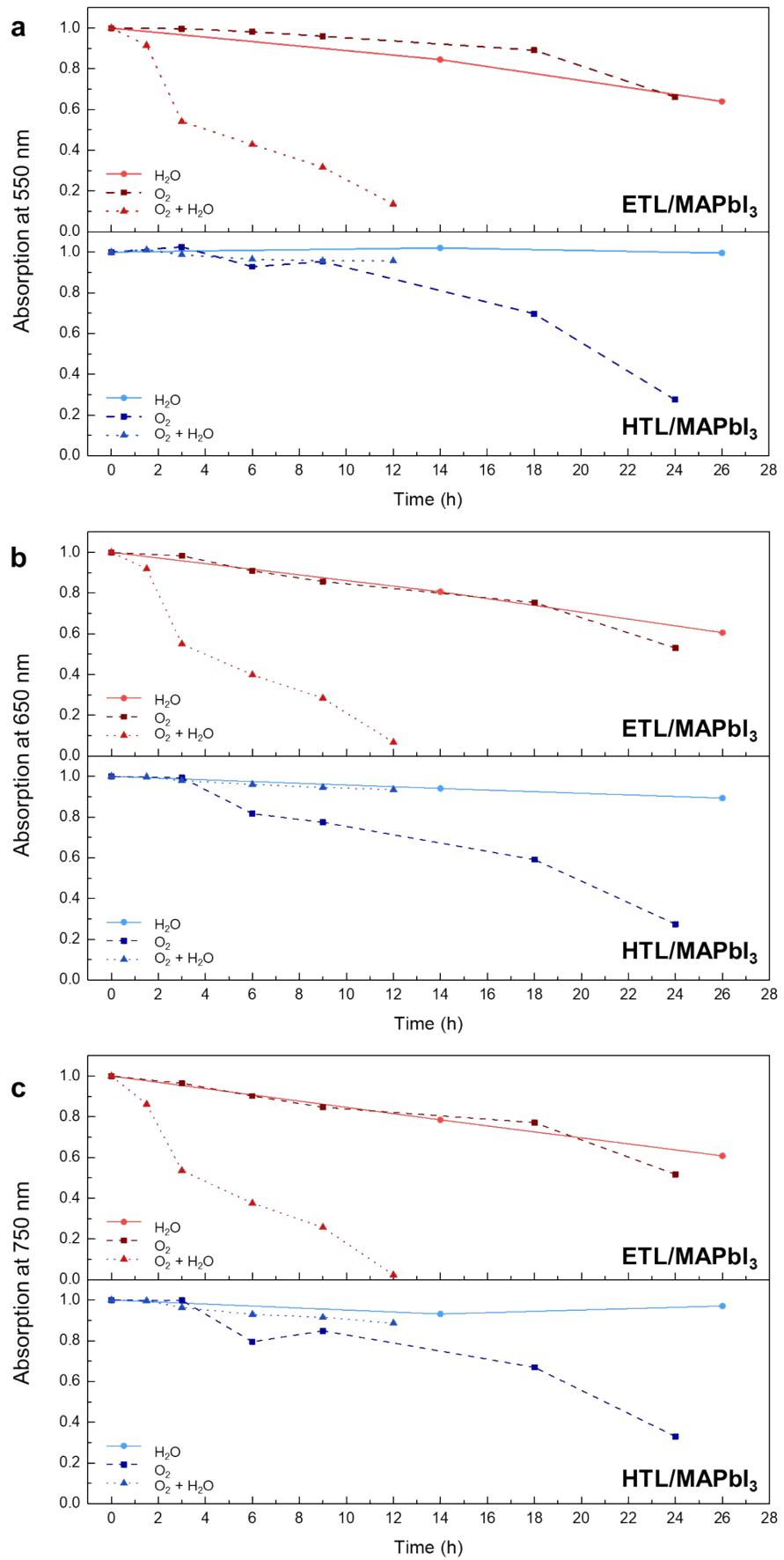
Supplementary Figure 4. (a) Steady-state and (b) time-resolved PL spectra obtained for the perovskite films deposited on the Spiro-MeOTAD with and without additives (such as tBP and Li-TFSI). The data fitted with the three-term exponential decay function.



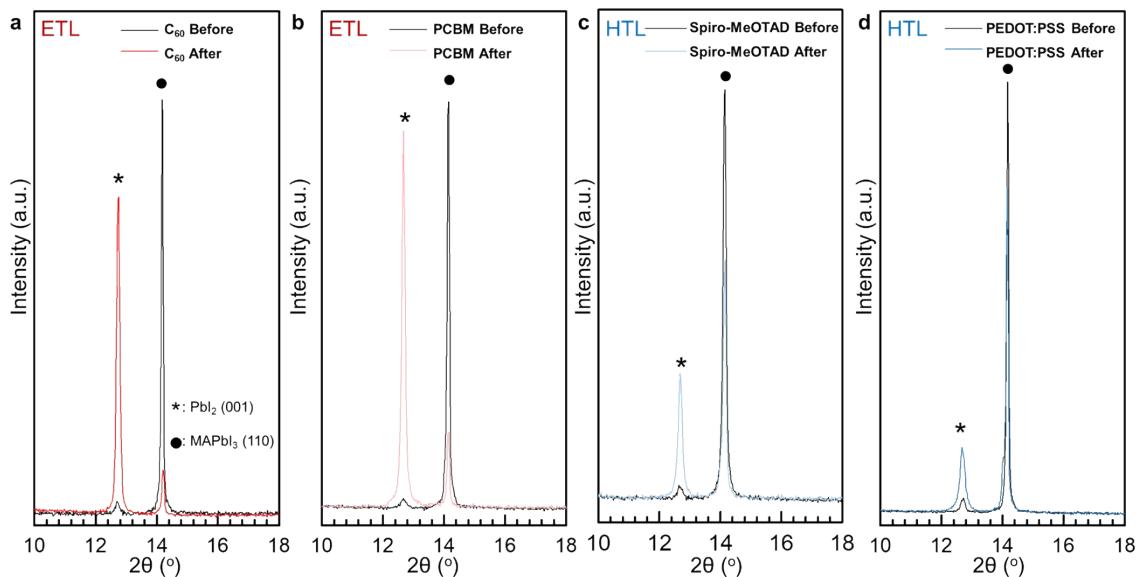
Supplementary Figure 5. Band energy diagram for perovskite films deposited on (a) glass, (b) ETL, and (c) HTL. Quasi fermi level of each films altered due to imbalance of electron-hole carrier concentration. Hole-excess perovskite film deposited on ETL presented lower quasi fermi level, therefore higher surface potential (work function). On the other hands, electron-excess perovskite film on HTL showed lower surface potential.



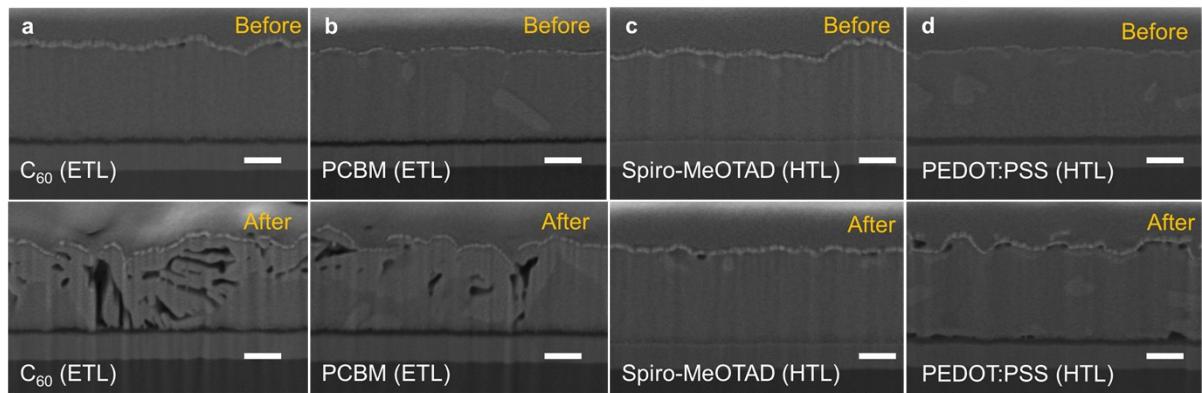
Supplementary Figure 6. Time evolution of absorption spectra for glass/MAPbI₃ film in chamber filled with O₂ and H₂O (~80% R.H.) gas before and after light-illumination for 12 h.



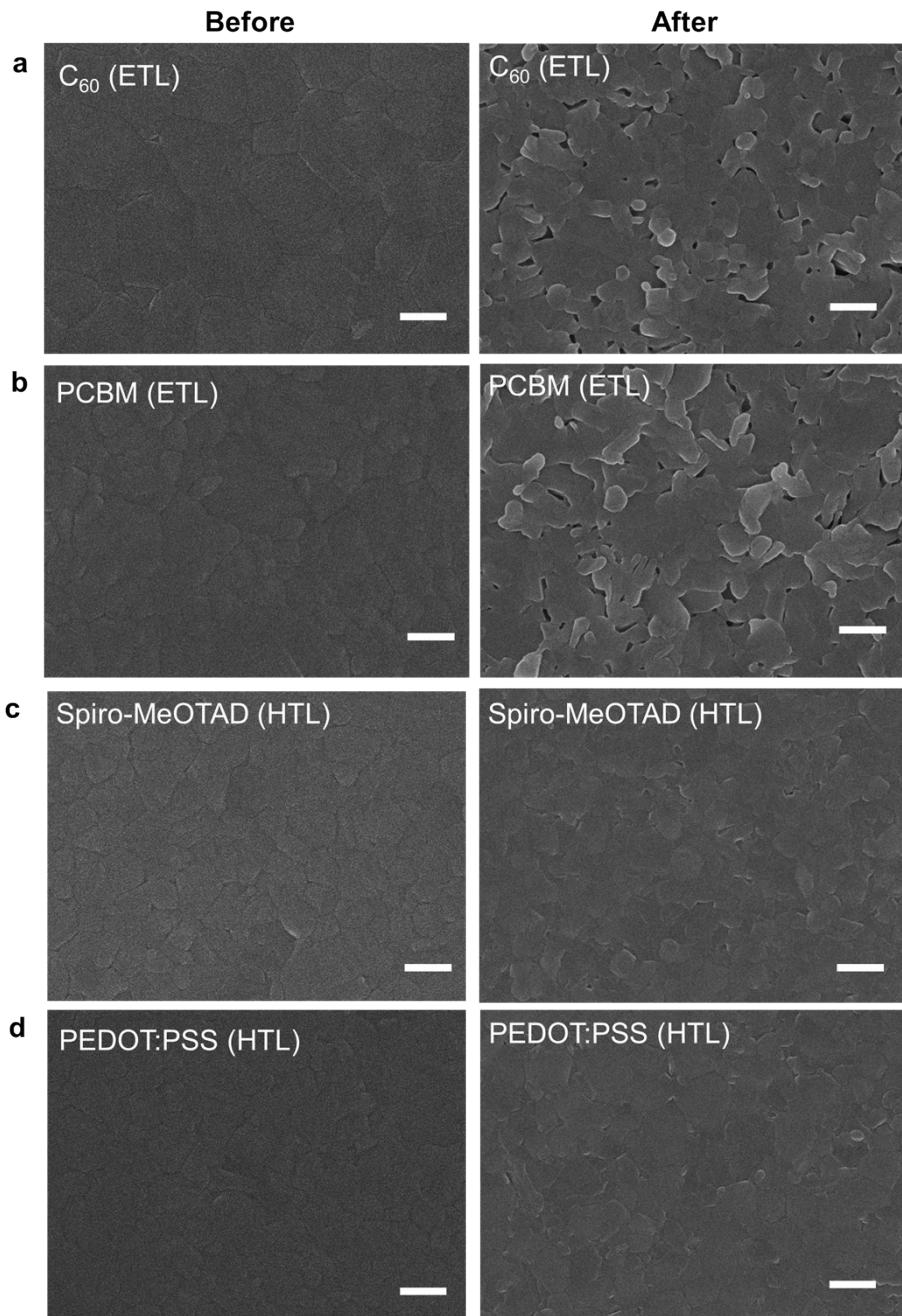
Supplementary Figure 7. Summary of time evolution normalized absorption spectra at (a) 550 nm, (b) 650 nm, and (c) 750 nm wavelength for ETL/MAPbI₃ and HTL/MAPbI₃ under 3 different ambient conditions (the mixture ambient, O₂ (20%) ambient and H₂O (R.H. ~80%) ambient).



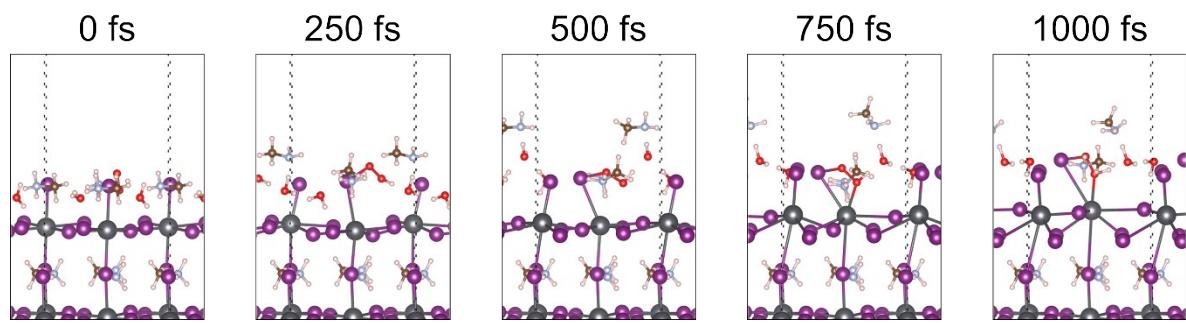
Supplementary Figure 8. XRD reflections of the (a) C₆₀, (b) PCBM, (c) Spiro-MeOTAD, and (d) PEDOT:PSS phases in the 2θ range of 10–18°. PbI₂ species are detected at 12.7°, and MAPbI₃ species are detected at 14.2°.



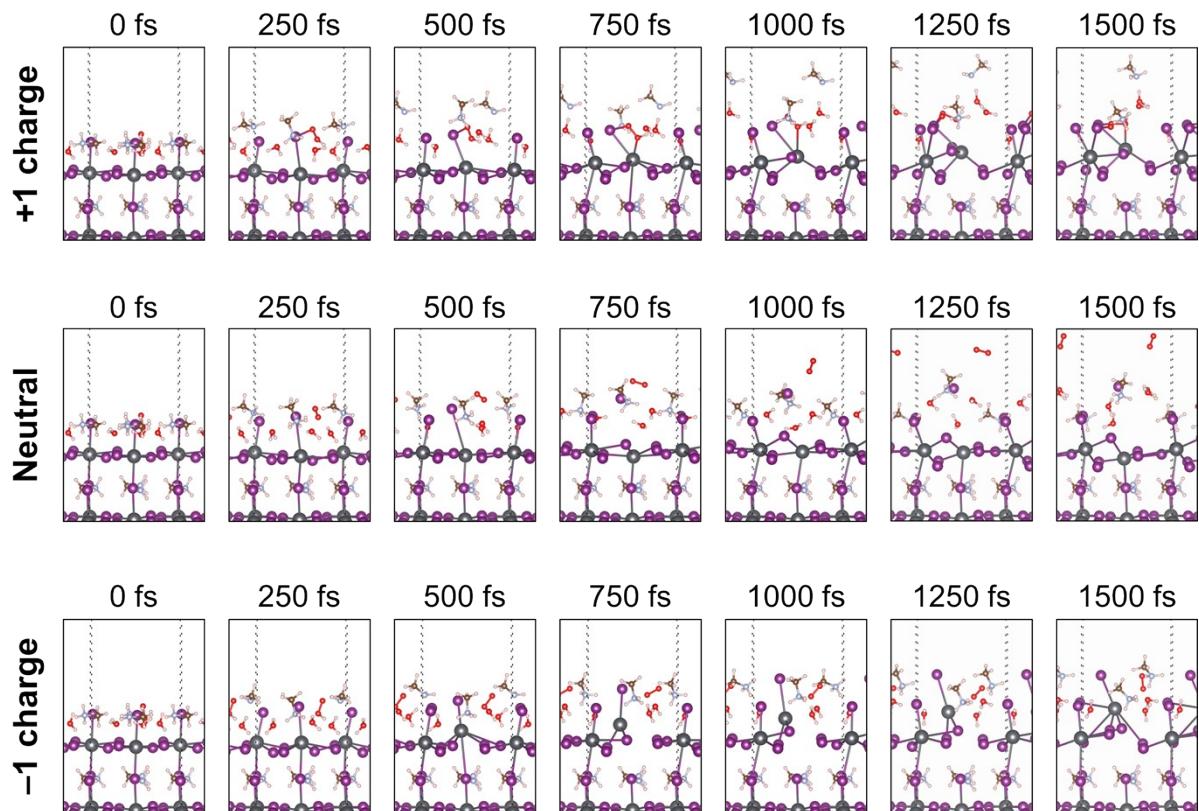
Supplementary Figure 9. The cross-sectional SEM images of the (a) C₆₀, (b) PCBM, (c) Spiro-MeOTAD, and (d) PEDOT:PSS layers obtained by using a focused ion beam before and after light exposure for 3 h. All scale bars are equal to 200 nm.



Supplementary Figure 10. Plane-view SEM images of the perovskite layers deposited on the (a) C_{60} , (b) PCBM, (c) Spiro-MeOTAD, and (d) PEDOT:PSS substrates before and after 6 h of light-soaking. All scale bars are equal to 300 nm.



Supplementary Figure 11. Temporal snapshots of the AIMD simulated atomic geometries of MAPbI_3 crystal with a charge of +1 in the presence of two water and one oxygen molecules.



Supplementary Figure 12. Temporal snapshots of the AIMD simulation of MAPbI_3 crystal in the presence of three water and one oxygen molecules for 1.5 picoseconds.

	A₁(%)	τ₁(ns)	A₂(%)	τ₂(ns)	A₃(%)	τ₃(ns)	Avg. τ
Glass	0.36	7.87	1.64	31.95	98.00	332.89	332.38
C₆₀	13.93	1.99	26.65	22.02	59.42	103.82	96.33
PCBM	6.80	3.86	24.24	28.96	68.96	151.07	143.03
PEDOT:PSS	12.11	3.76	48.01	20.99	48.01	52.69	43.15
Spiro-MeOTAD	25.88	1.47	20.82	5.17	53.30	32.97	30.77

Supplementary Table 1. A summary of the time-resolved PL lifetime parameters obtained for the glass, C₆₀, PCBM, PEDO:PSS, and Spiro-MeOTAD/perovskite systems described in Supplementary

$$\tau_{avg} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$$

Figure 2b. Intensity weighted average lifetime was calculated by

Bottom Layer		PbI ₂ (12.7°)	MAPbI ₃ (14.2°)
C ₆₀ (ETL)	Before	428	7867
	After	6077	1031
	Ratio	18.38	17.0%
PCBM (ETL)	Before	632	9895
	After	9215	2181
	Ratio	14.58	22.0%
Spiro-MeOTAD (HTL)	Before	651	7599
	After	2614	4612
	Ratio	4.02	60.7%
PEDOT:PSS (HTL)	Before	772	13804
	After	2371	10508
	Ratio	3.07	76.1%

Supplementary Table 2. XRD intensities of the PbI₂ (12.7°) and MAPbI₃ (14.2°) peaks obtained for the perovskite layers deposited on the C₆₀, PCBM, Spiro-MeOTAD, and PEDOT:PSS substrates before and after light exposure.

	0 fs	250 fs	500 fs	750 fs	1000 fs
Pb	+1.01	+0.96	+1.00	+1.01	+0.99
I	+0.11	+0.36	+0.44	+0.41	+0.36
O1	-0.29	-0.41	-0.47	-0.50	-0.44
O2	-0.22	-0.62	-0.61	-0.62	-0.66
H1	+0.59	+0.64	0.62	+0.62	+0.64

Supplementary Table 3. Time evolution of Bader charge of Pb, I, O, O, and H atoms