

Electronic Supplementary Information

## **Degradation of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite materials by localized charges and its polarity dependency**

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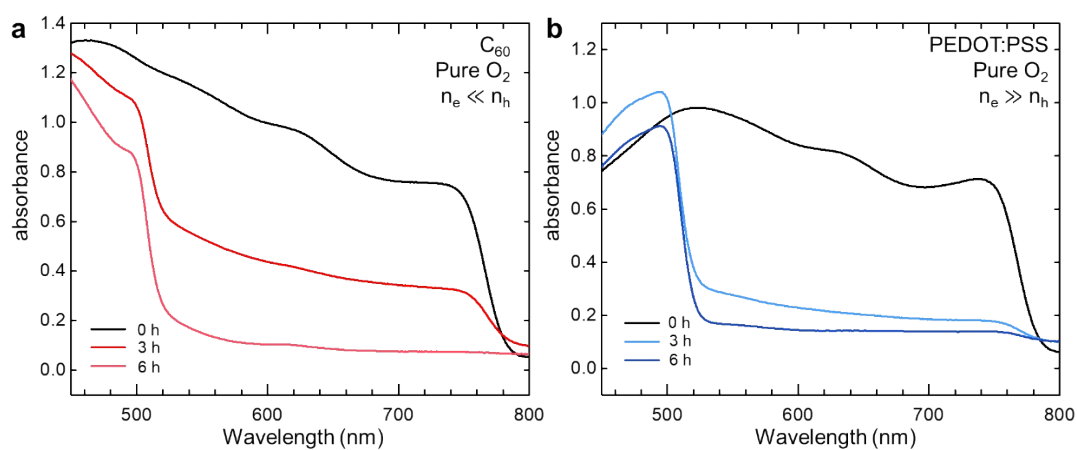
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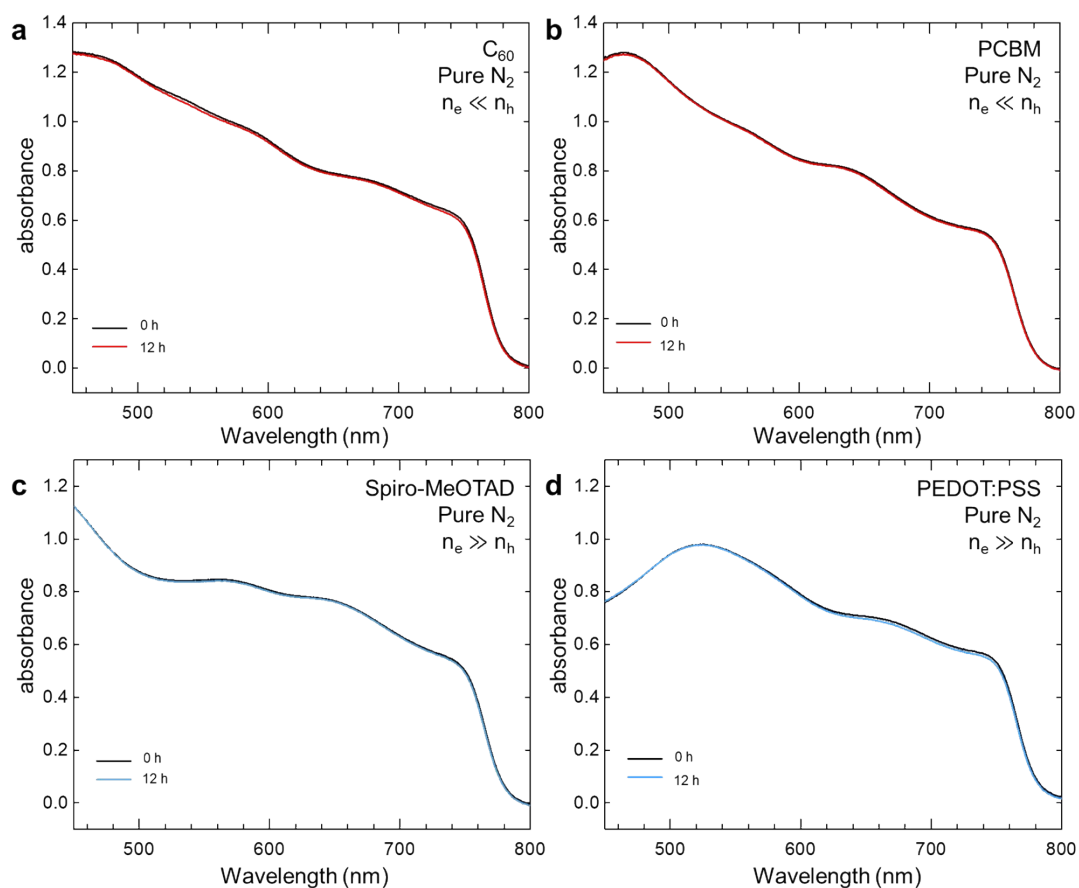
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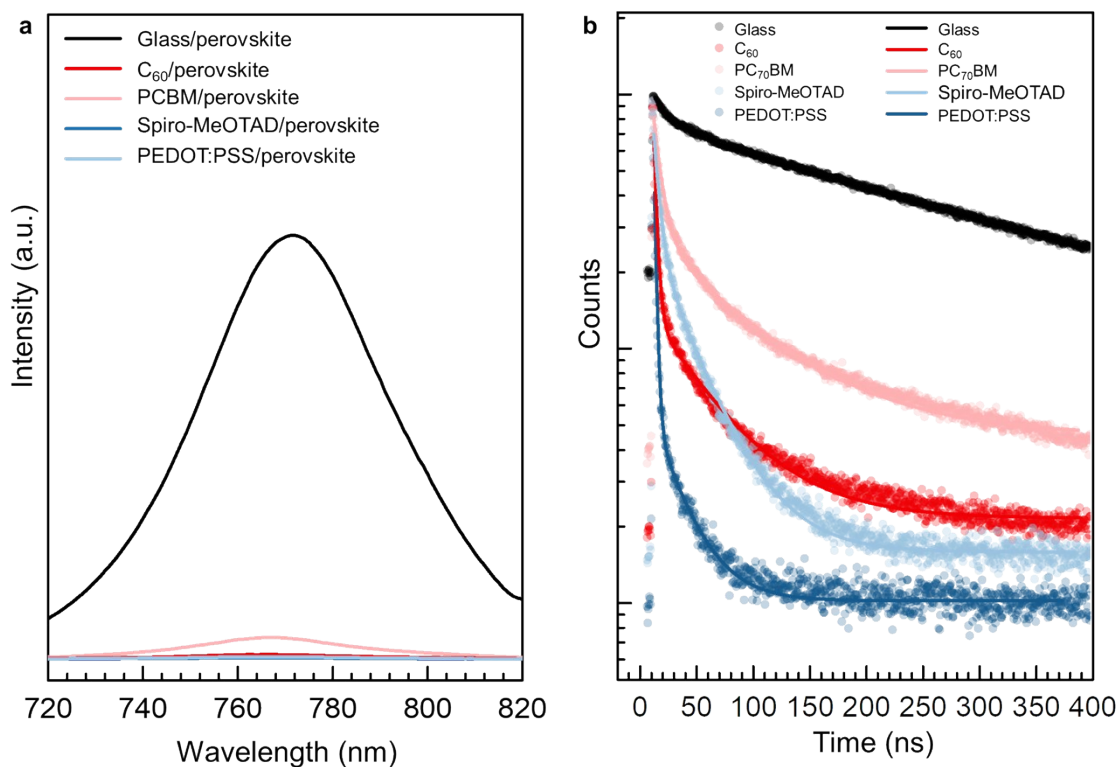
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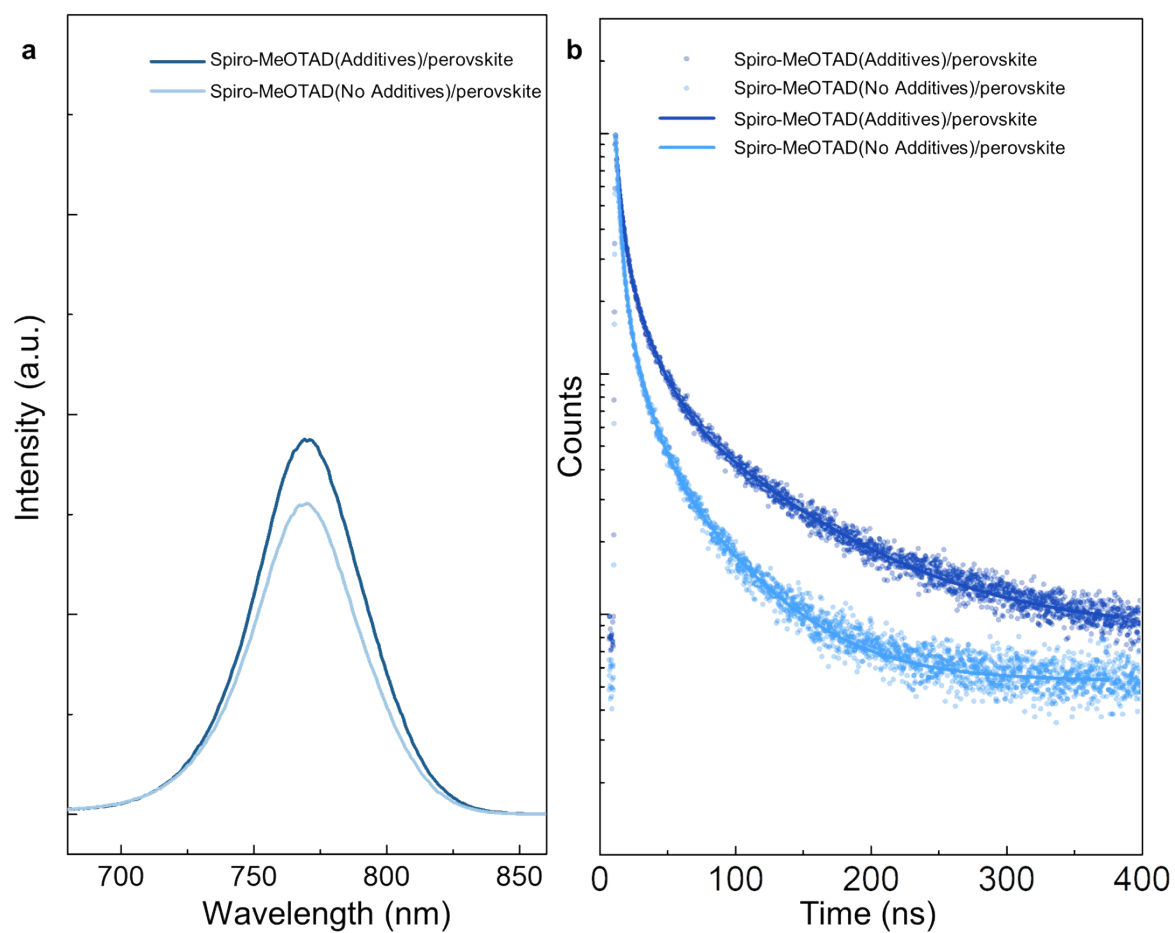
**Supplementary Figure 1.** Time evolution of absorption spectra for (a) the  $C_{60}$ /MAPbI<sub>3</sub> and (b) the PEDOT:PSS/MAPbI<sub>3</sub> half devices in chamber filled with pure  $O_2$  gas before and after light-illumination for 6 h.



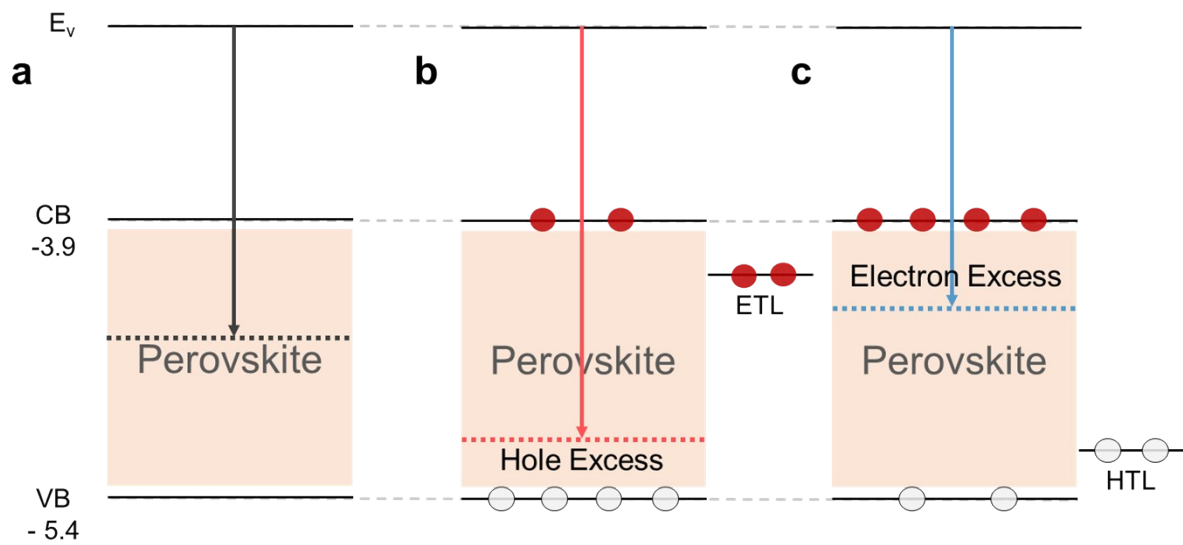
**Supplementary Figure 2.** Absorption spectra of perovskite films deposited on (a) C<sub>60</sub>, (b) PCBM, and perovskite films deposited on (c) Spiro-MeOTAD and (d) PEDOT:PSS in chamber filled with pure N<sub>2</sub> gas before and after light-illumination for 12 h.



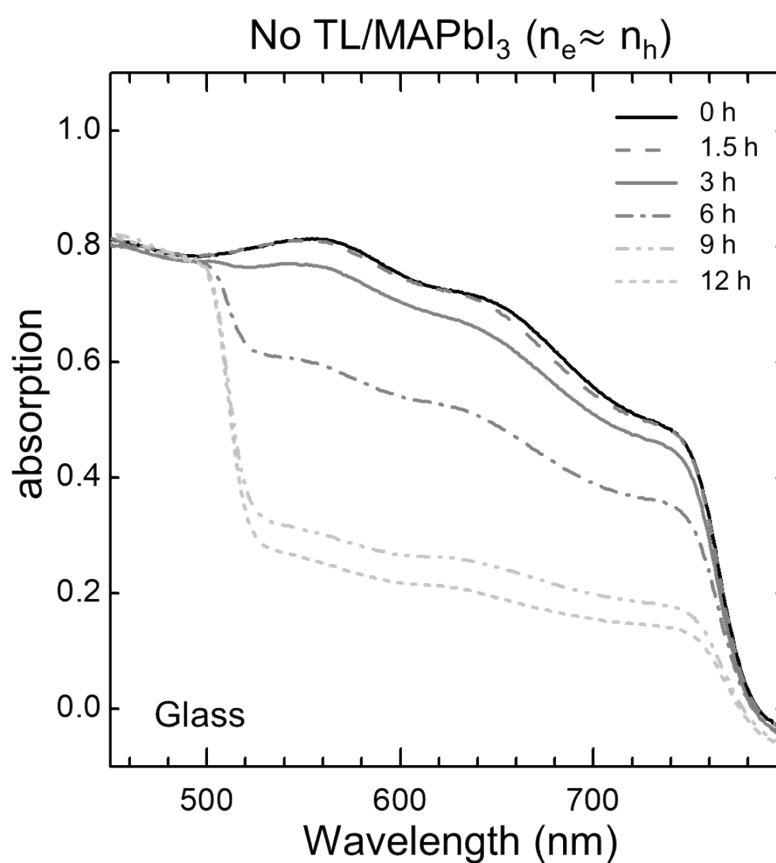
**Supplementary Figure 3.** (a) Steady-state and (b) time-resolved PL spectra obtained for the perovskite films deposited on the glass, PCBM, C<sub>60</sub>, Spiro-MeOTAD, and PEDOT:PSS substrates and fitted with the three-term exponential decay function. Time-resolved PL spectra is plotted as circle, and fitted function is plotted as line.



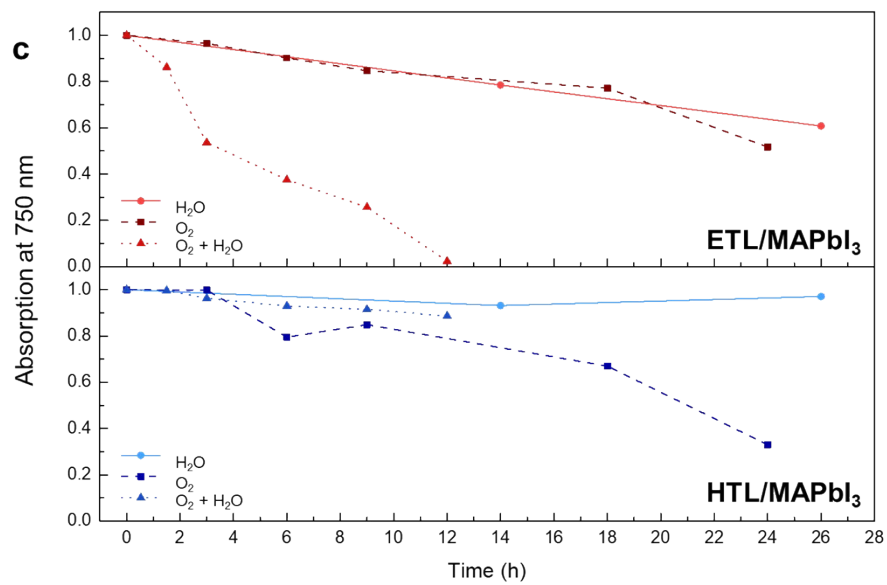
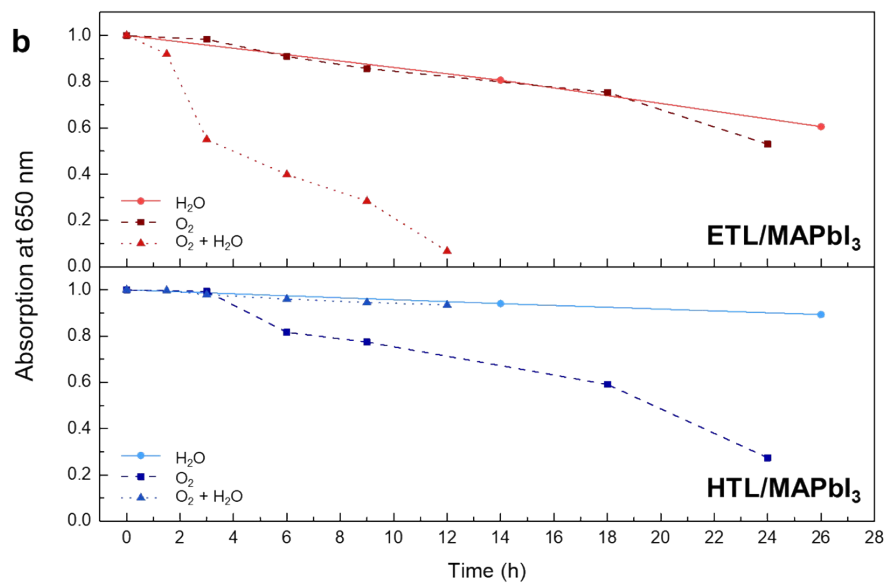
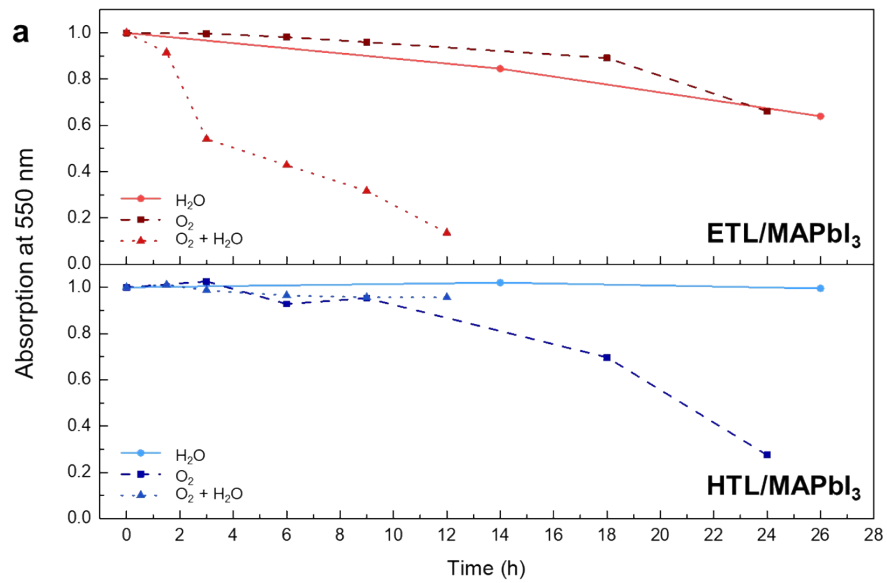
**Supplementary Figure 4.** (a) Steady-state and (b) time-resolved PL spectra obtained for the perovskite films deposited on the Spiro-MeOTAD with and without additives (such as tBP and Li-TFSI). The data fitted with the three-term exponential decay function.



**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.

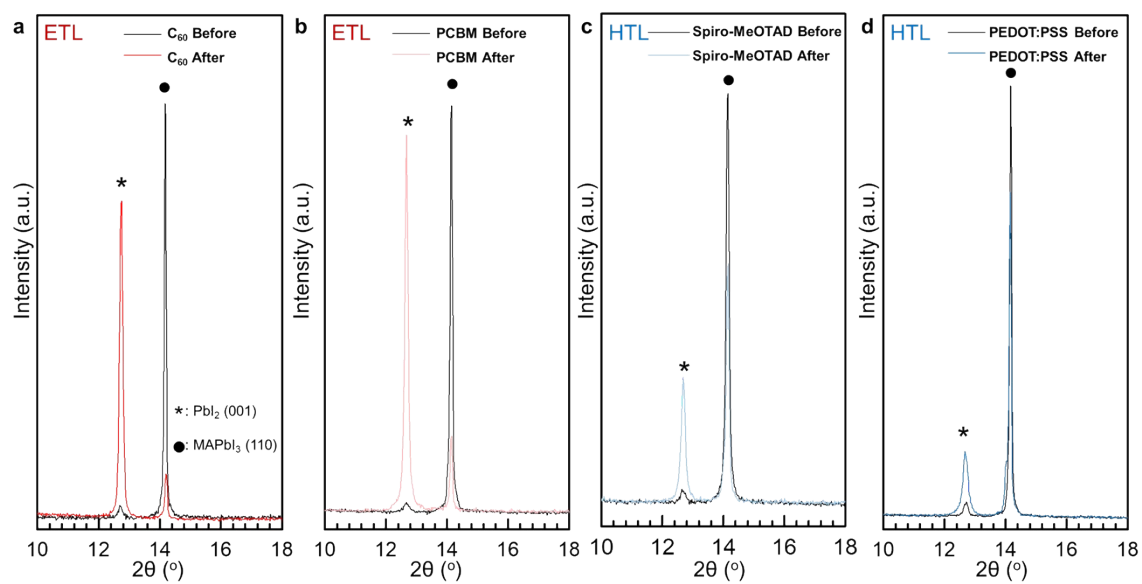


**Supplementary Figure 6.** Time evolution of absorption spectra for glass/MAPbI<sub>3</sub> film in chamber filled with O<sub>2</sub> and H<sub>2</sub>O (~80% R.H.) gas before and after light-illumination for 12 h.

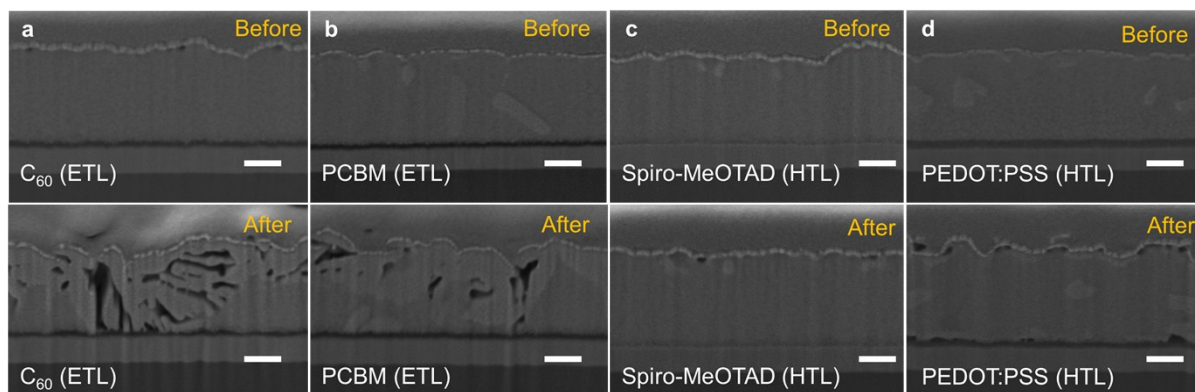




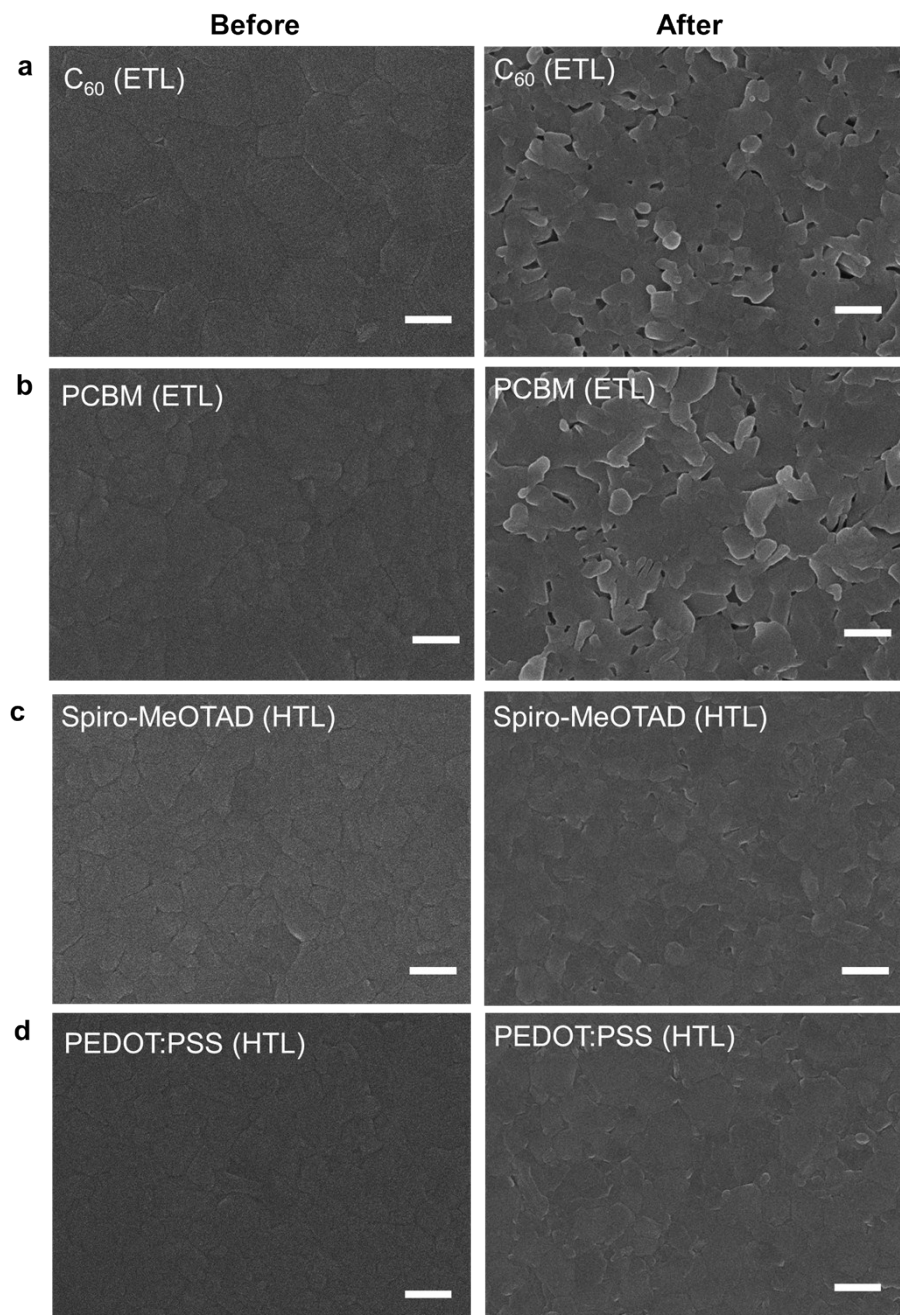
**Supplementary Figure 7.** Summary of time evolution normalized absorption spectra at (a) 550 nm, (b) 650 nm, and (c) 750 nm wavelength for ETL/MAPbI<sub>3</sub> and HTL/MAPbI<sub>3</sub> under 3 different ambient conditions (the mixture ambient, O<sub>2</sub> (20%) ambient and H<sub>2</sub>O (R.H. ~80%) ambient).



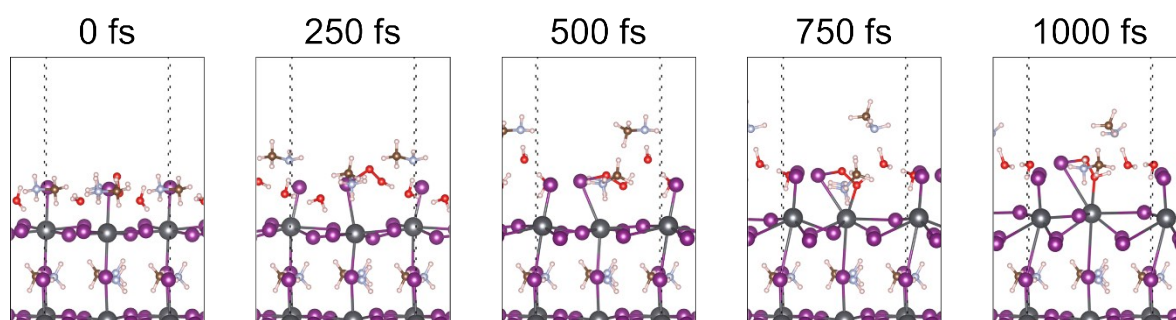
**Supplementary Figure 8.** XRD reflections of the (a) C<sub>60</sub>, (b) PCBM, (c) Spiro-MeOTAD, and (d) PEDOT:PSS phases in the 2θ range of 10–18°. PbI<sub>2</sub> species are detected at 12.7°, and MAPbI<sub>3</sub> species are detected at 14.2°.



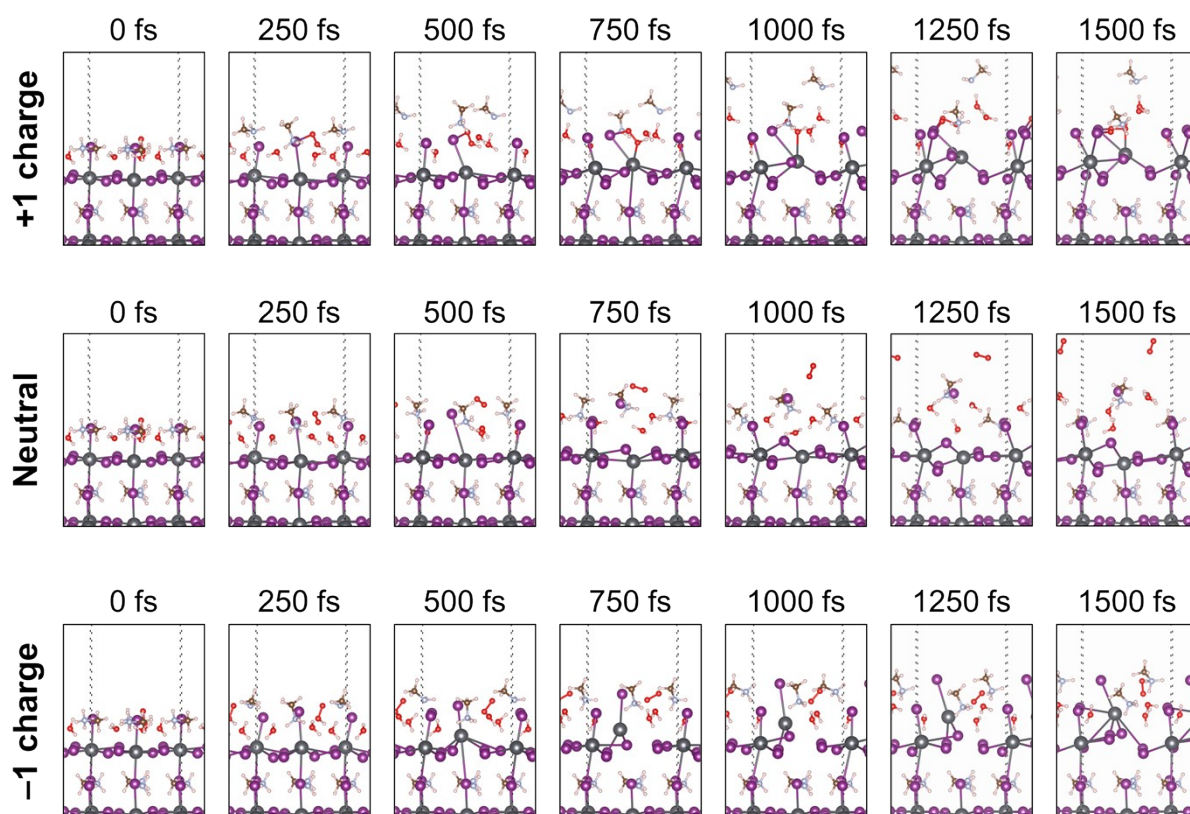
**Supplementary Figure 9.** The cross-sectional SEM images of the (a) C<sub>60</sub>, (b) PCBM, (c) Spiro-MeOTAD, and (d) PEDOT:PSS layers obtained by using a focused ion beam before and after light exposure for 3 h. All scale bars are equal to 200 nm.



**Supplementary Figure 10.** Plane-view SEM images of the perovskite layers deposited on the (a) C<sub>60</sub>, (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<sub>3</sub> 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<sub>3</sub> crystal in the presence of three water and one oxygen molecules for 1.5 picoseconds.

	<b>A<sub>1</sub>(%)</b>	<b>τ<sub>1</sub> (ns)</b>	<b>A<sub>2</sub>(%)</b>	<b>τ<sub>2</sub> (ns)</b>	<b>A<sub>3</sub>(%)</b>	<b>τ<sub>3</sub> (ns)</b>	<b>Avg. τ</b>
<b>Glass</b>	0.36	7.87	1.64	31.95	98.00	332.89	332.38
<b>C<sub>60</sub></b>	13.93	1.99	26.65	22.02	59.42	103.82	96.33
<b>PCBM</b>	6.80	3.86	24.24	28.96	68.96	151.07	143.03
<b>PEDOT:PSS</b>	12.11	3.76	48.01	20.99	48.01	52.69	43.15
<b>Spiro-MeOTAD</b>	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, C<sub>60</sub>, PCBM, PEDOT: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

<b>Bottom Layer</b>		<b>PbI<sub>2</sub></b> (12.7°)	<b>MAPbI<sub>3</sub></b> (14.2°)
C <sub>60</sub> (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 PbI<sub>2</sub> (12.7°) and MAPbI<sub>3</sub> (14.2°) peaks obtained for the perovskite layers deposited on the C<sub>60</sub>, 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