Electronic Supplementary Information for

Photoinduced degradation of methylammonium lead triiodide perovskite semiconductor

Xiaofeng Tang^{*}, Marco Brandl, Benjamin May, Ievgen Levchuk, Yi Hou, Moses Richter, Haiwei Chen, Shi Chen, Simon Kahmann, Andres Osvet, Florian Maier, Hans-Peter Steinrück, Rainer Hock, Gebhard J. Matt^{*} and Christoph J. Brabec^{*}



Figure S1. Spectrum of white LED.



Figure S2. X-ray photoelectron spectroscopy (XPS) survey spectra (a) and high-resolution Pb 4f spectra (b) for fresh CH₃NH₃PbI₃ film and CH₃NH₃PbI₃ degraded in vacuum/light at 350 K for 24 hours. N 1s spectra (c) for fresh CH₃NH₃PbI₃ film and CH₃NH₃PbI₃ degraded in air/light at 350 K for 24 hours.



Figure S3. Schematic FTO interdigital electrodes with CH₃NH₃PbI₃ on top.



Figure S4. Corresponding Tauc plot of planar FTPS of CH₃NH₃PbI₃ films.

$$PbI_{2} \xrightarrow{light} PbI_{2} + e + h$$

$$h + V_{Pb}^{2+} \xrightarrow{trapped} h (V_{Pb}^{2+})$$

$$2h (V_{Pb}^{2+}) + 2I^{-} \longrightarrow I_{2}$$

$$e + V_{I}^{-} \xrightarrow{trapped} e (V_{I}^{-})$$

$$e (V_{I}^{-}) + Pb^{2+} \longrightarrow Pb^{+} + 2I^{-} + V_{Pb}^{2+}$$

$$2Pb^{+} \longrightarrow Pb^{0} + Pb^{2+}$$

$$PbI_{2} \xrightarrow{vacuum}_{light} Pb + I_{2 (g)}$$

Figure S5. Reported route of photolysis of PbI₂ under vacuum condition.



Figure S6. (a) In-situ XRD of PbI₂ films at 350K under vacuum/light. (b) Integrated intensity calculated from of in-situ XRD patterns of PbI₂ films at 350K under vacuum/light. Selected peaks assigned to PbI₂ (2θ =39.5°) and Pb⁰ (2θ =36.3°).



Figure S7. X-ray diffractogram and photographs of $CH_3NH_3PbI_3$ films that were degraded in N_2 with saturated H_2O for 24 h at 350 K (a). XPS of fresh $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_3$ was degraded in N_2 with saturated H_2O for 24 h at 350 K: C 1s (b) and O 1s (c) binding energy regions.