Electronic supplementary information (ESI) of

Dark electrical bias effect on moisture-induced degradation in inverted lead halide perovskite solar cells measured by advanced chemical probes

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Figure S1. (a) X-ray diffraction spectra of a perovskite solar cell measured through the Ag top electrode before and after bias degradation (1 V, 1 h, 100% RH N_2). (b) XRD spectra measured after bias degradation at two distinct locations, through the degraded cell (humidity + bias) and outside the cell on the perovskite/PCBM/BCP films (humidity, no bias).



Figure S2. Optical microscope images of the perovskite solar cell edge taken during the first 70 s of electrical bias stress. A voltage of 1.2 V was applied to the cell in the dark and the voltage was turned off for capturing the image under illumination. The upper row shows the cell before exposure to humid N_2 whereas the lower row shows the cell after exposure to humid N_2 for 20

min. The orange dashed line represents the edge of the cell, the region on the left-hand side of the edge is not covered by the Ag top electrode.



Figure S3. Hyperspectral cross-sectional secondary electron images at 0-6.0 eV of sample degraded in 40% RH air (1 V for 1 h). (a) After first scan and (b) after a second scan.



Figure S4. Magnified hyperspectral cross-sectional secondary electron image at 0-6.0 eV of degraded grain (bright grain) after a second scan.



Figure S5. Dark current transients with various biasing voltages at 25° C (V_{oc} = 0.85 V). Dark current transients at various voltages were acquired using a Gamry Reference 600 potentiostat. The devices were left at short-circuit for 30 s before a potential step was applied and the dark current recorded until it stabilized (equilibrium reached in less than 30 s).



Figure S6. Chronoamperometry response to 0 - 1 V potential steps for freshly-prepared and 2 days-aged samples.



Figure S7. (a) Current density – voltage curves at 0.8 sun of a fresh perovskite solar cell and after 2 days aging in air. (b) Efficiency drop of the fresh and aged solar cell measured after 1 V bias application in the dark in air. A reference fresh sample that was left in the dark without bias is also shown for comparison.



Figure S8. Current density – voltage curves of MAPbI₃ perovskite devices at 1 sun before and after biasing at 0.5 V, 0.85 V and 1 V under dark conditions for 1 h in 40% RH air.



Figure S9. Current density – voltage curves of $Cs_{0.1}(MA_{0.17}FA_{0.83})_{0.9}Pb(I_{0.83}Br_{0.17})_3$ perovskite devices at 1 sun before (solid blue lines) and after (dashed blue lines) biasing at 1 V for 1 h under dark condition in 40% RH air. Reference cell left in the same environment for the same duration but without bias are also shown for comparison (black lines).