Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information:

Ligand Dependent Oxidation Dictates the Performance Evolution of High Efficiency PbS Quantum Dot Solar Cells

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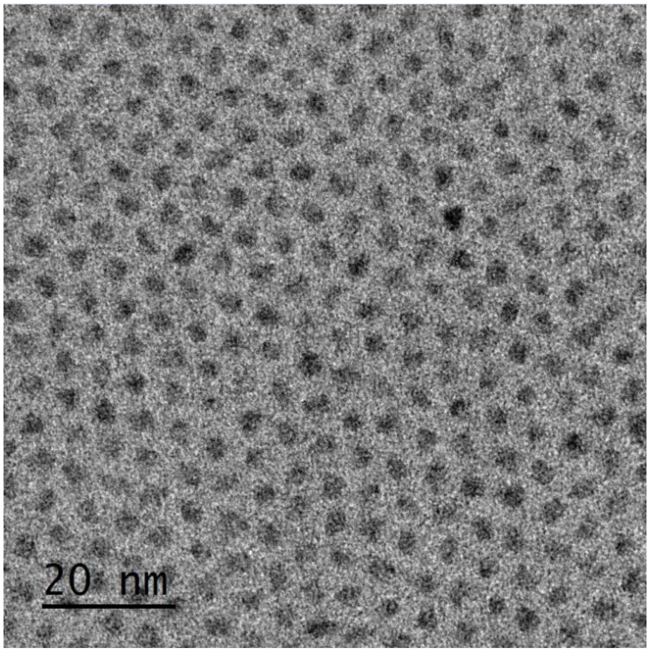

Figure S1. TEM image of PbS QDs: The according first absorption peaks lies at 1050nm and the average dot radius is 3 nm.

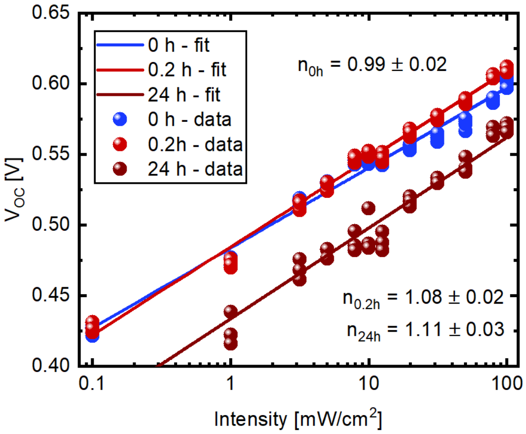

Figure S2. Light intensity dependency measurements of the V_{OC} of a pristine and subsequently degraded devices in 20% oxygen and light. The extracted slopes show a change from the initial value of 0.99 to 1.08 and 1.11 after 0.2 h and 24 h, respectively. This indicates a reduced bimolecular recombination rate[1] very quickly after oxygen exposure during phase I. After longer degradation the recombination order remains largely unchanged since the active layer does not change any further.

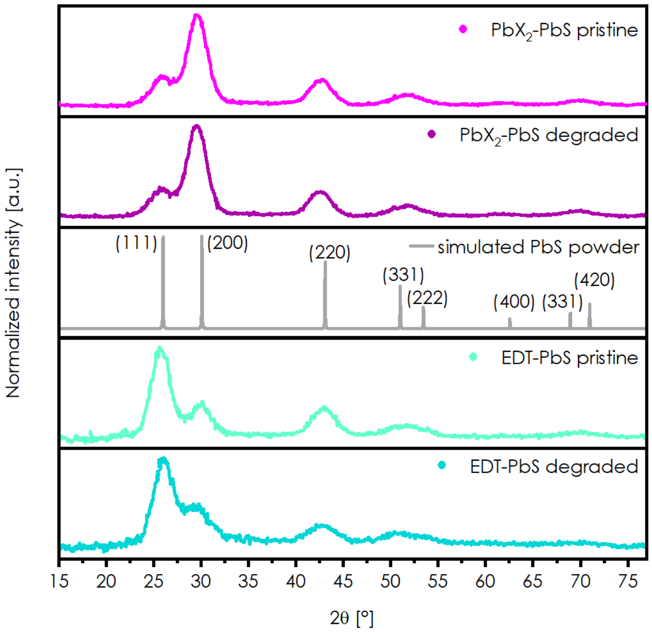

Figure S3. XRD measurements on degraded and pristine QDs films: The two upper diffractograms of PbX_2-PbS (pristine and degraded), the lowest two with EDT-PbS. A pure PbS powder diffractogram has been simulated using the single crystal structure of PbS.[2] PbS as core material can be clearly identified. For the PbX_2-PbS samples no difference can be identified between the pristine and the degraded sample. For EDT-PbS the peak widths get broader in the degraded case (3h in 20% oxygen and light), indicating the presence of byproducts of the reactions and the effective size reduction.

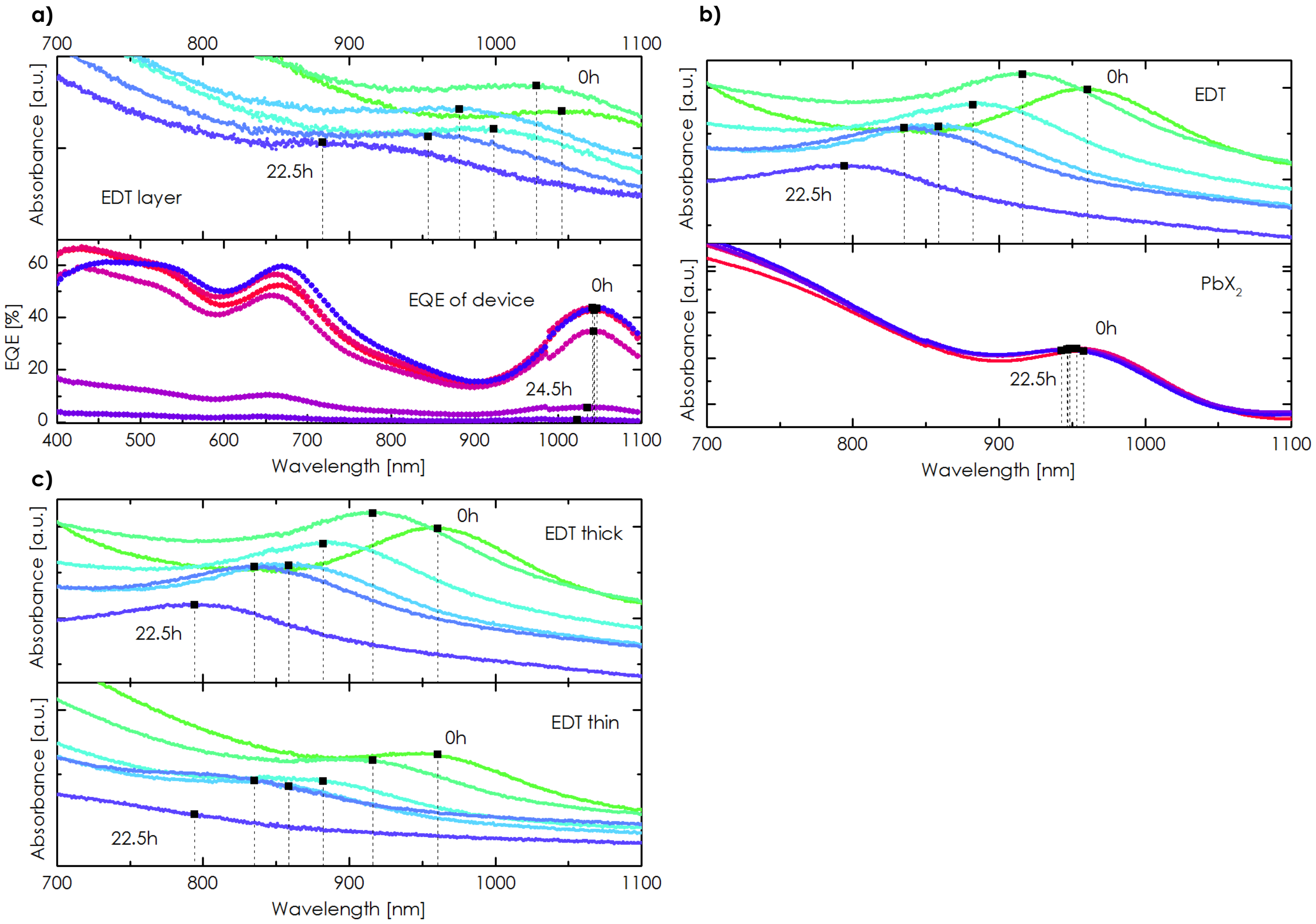

Figure S4. UV-VIS and EQE measurements: from top to bottom, (a) first the absorbance of a EDT-PbS Layer with relatively large dots is shown for an oxygen degradation. Second EQE measurements of a cell also built from relatively large dots, for different time steps in the degradation. The step in the data at around 990nm is caused by a grating change. (b) Following are again two UV-VIS sets for the two different ligands for initially small dots. (c) The last two panels show the same dot sizes, same ligands but different layer thicknesses of 120 nm and 40 nm, respectively.

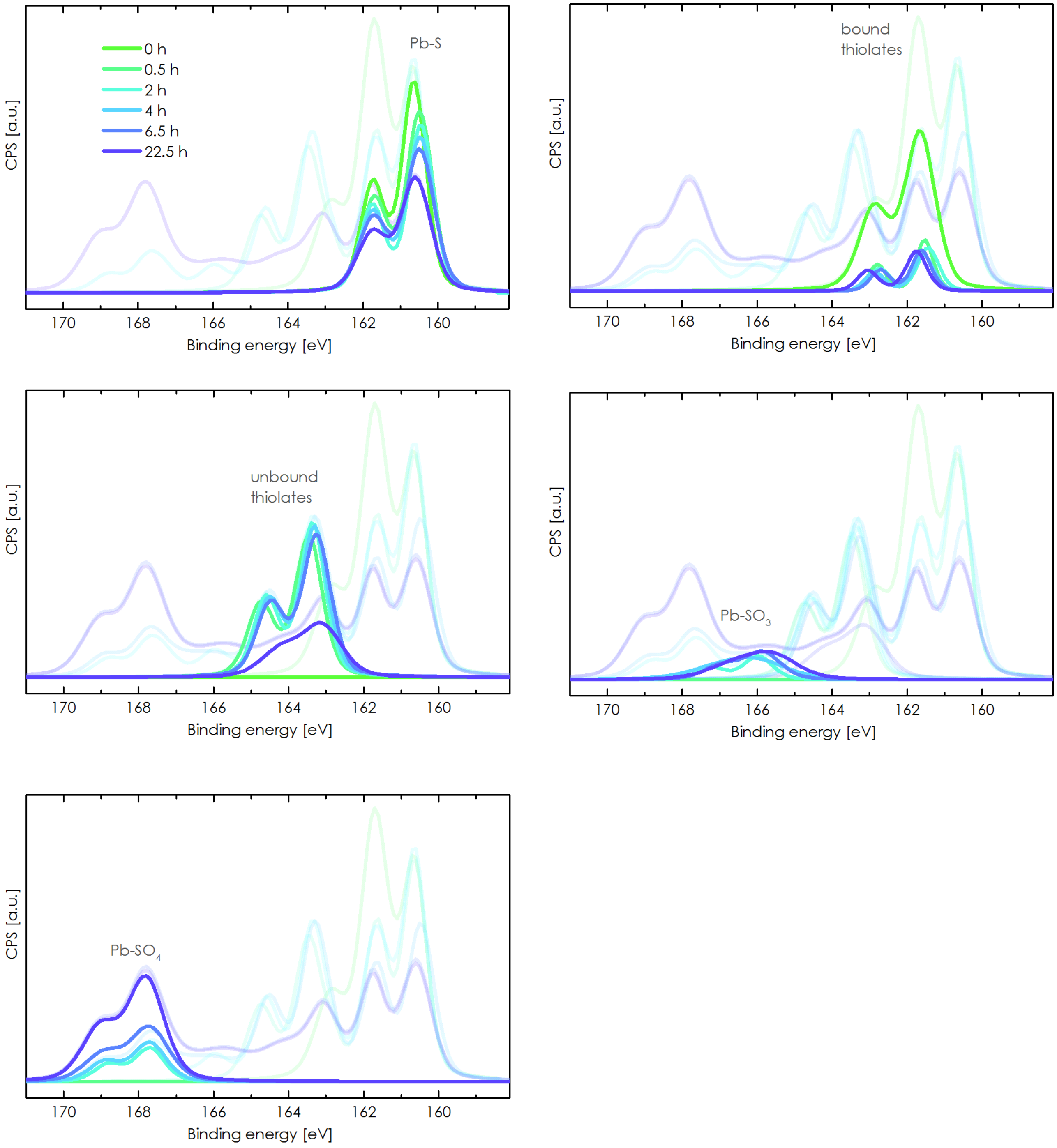

Figure S5. Single species fits for sulfur for EDT degraded in dry air: The different panels show the individual S2p doublets that are associated with different S species.

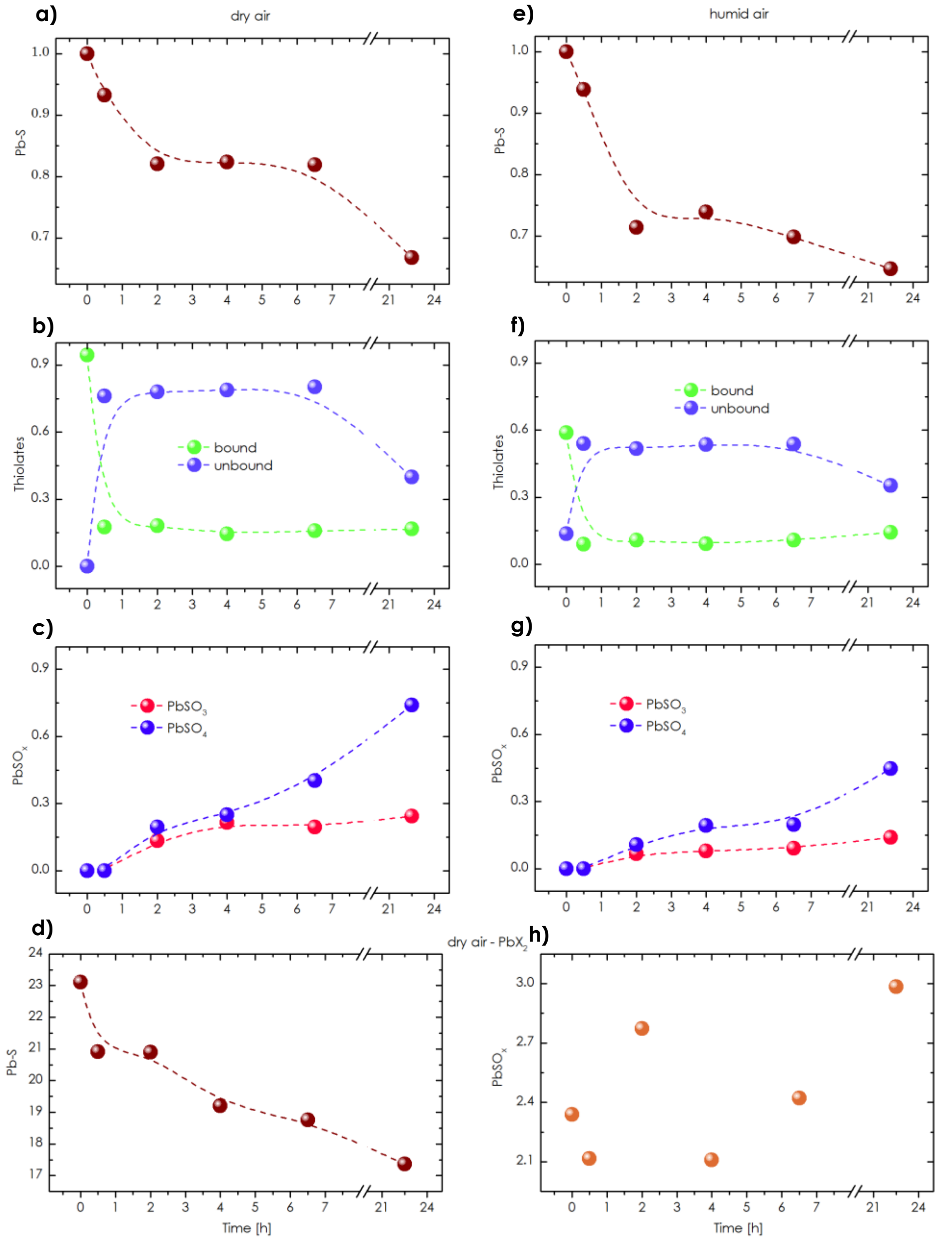

Figure S6. Normalized quantities of the different sulfur species monitored via XPS in EDT-PbS samples as a function of degradation time: the left column (a-c) shows the evolution in dry air, while the right (e-g) shows the same in humid air. The bottom two panels (d, h) show similarly the Pb-S species and PbSO$_x$ for a PbX$_2$–PbS film in dry air.

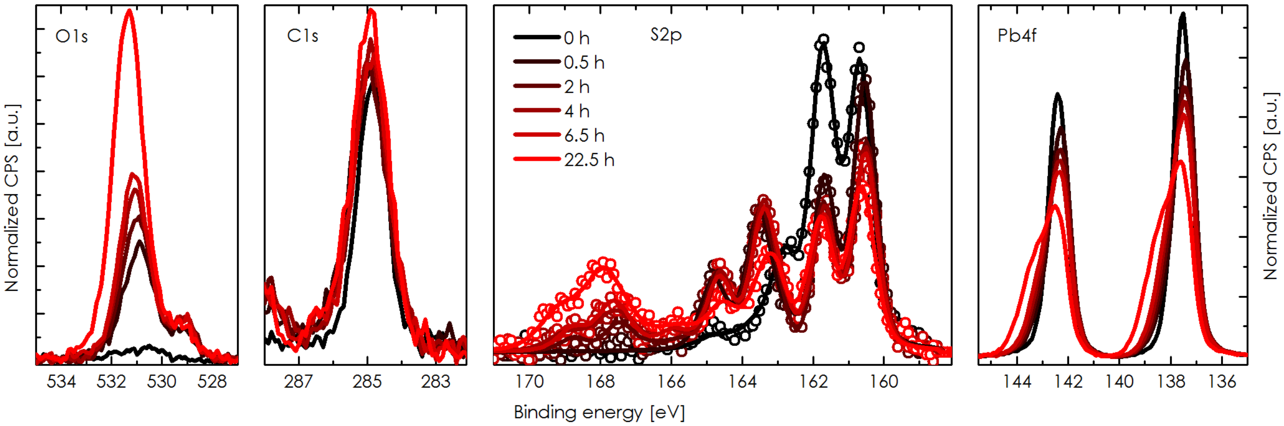

Figure S7. XPS data for EDT-PbS in humid air: oxygen, carbon sulfur and lead XPS data is depicted including the fit for the S *2p*. The single fits follow in Figure 89. The amounts are shown in Figure S6, indicating a slower degradation in humid air.

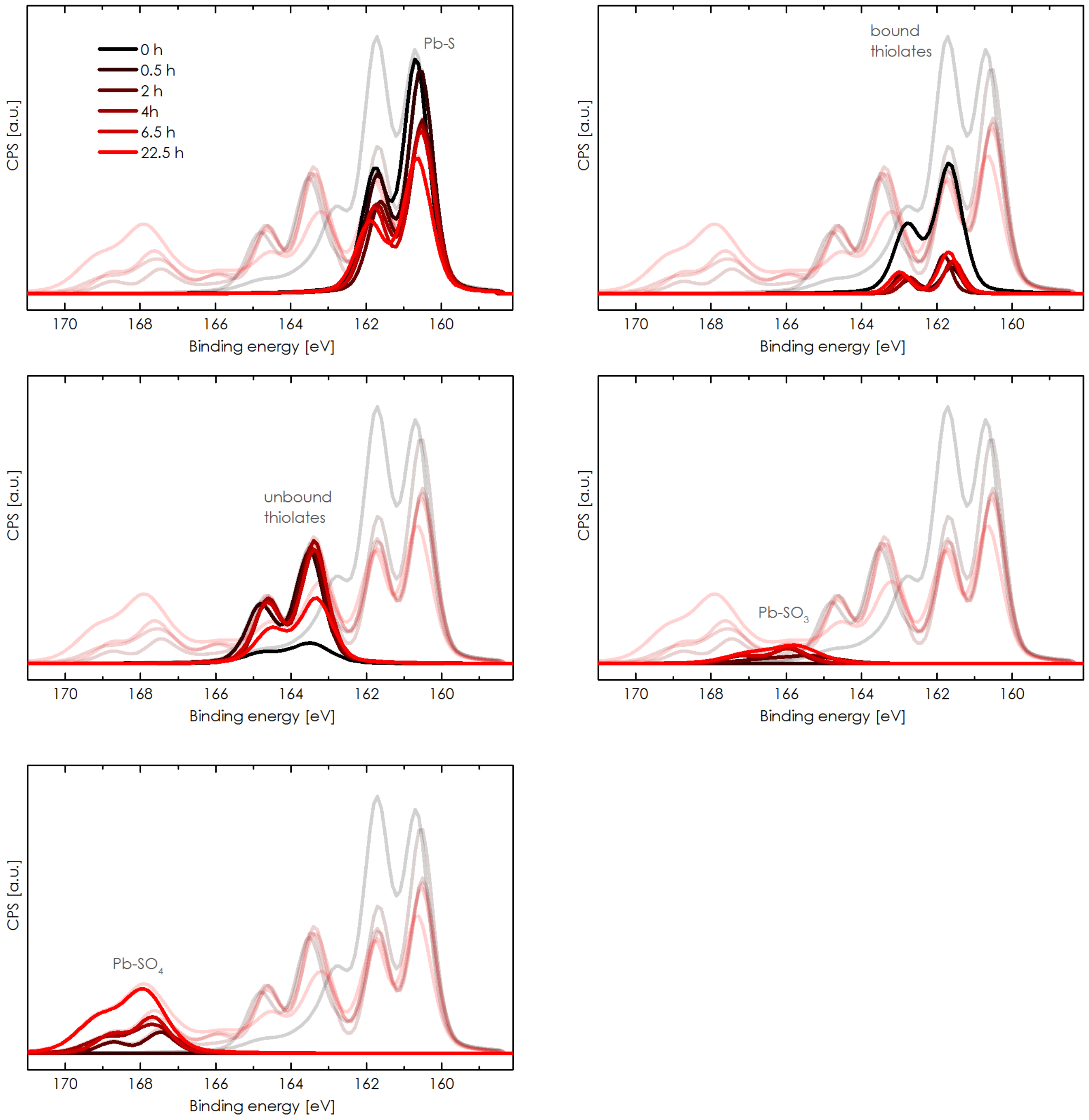

Figure S8. Single species fits for sulfur for EDT degraded in humid air: The different panels show the individual S2p doublets that are associated with different S species. In the background is the sum or envelope curve included, which can be seen in Figure S7.

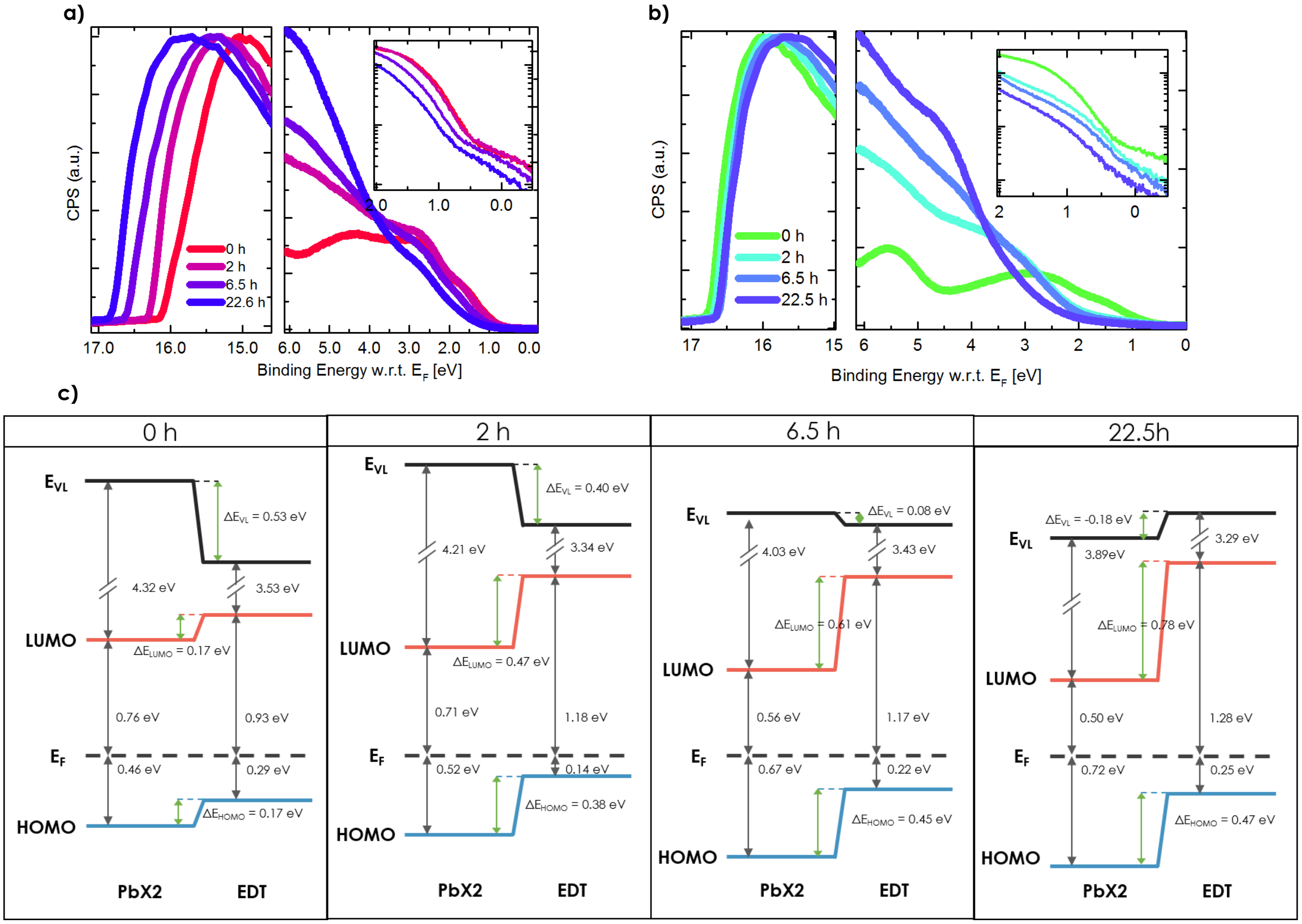

Figure S9. UPS measurements of PbX_2 films (a) and EDT films (b) degraded for 0h, 2h, 6.5h and 22.5 h in 20% oxygen and light. The extracted energy levels are used in (c) to depict the energetic landscape during degradation. The electron blocking barrier increases from 0.17 eV to 0.78 eV.

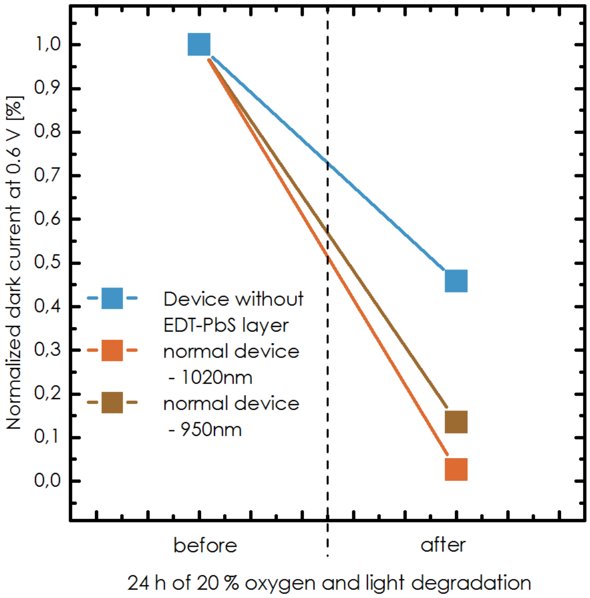

Figure S10. Transport information extracted from dark I-V characteristics: The dark I-V characteristics of different cells were measured and the current at 0.6 V was extracted at the beginning of the degradation in 20% oxygen and light and after 24 h. The values were normalized to the initial value to compare the transport properties through the film. In cells without an EDT-PbS layer the current does not fully collapse compared to the cells with EDT. Indicating that the EDT layer is mostly responsible for the demise of the device. Smaller dots (first absorption peak position 950nm) seem not as broken/insulating as bigger dots. Probably because the volume of the degraded shell in the bigger dots is larger, make it harder to be overcome.

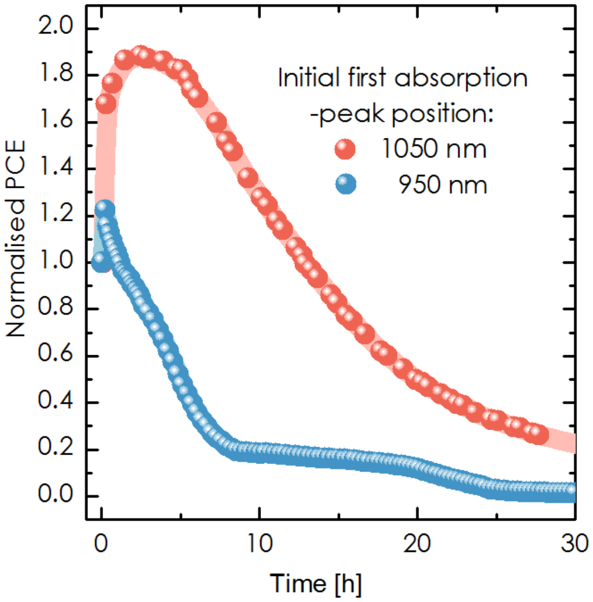

Figure S11. Influence of the initial dot size: PCE monitored while the cells being degraded in 20% oxygen and light. The initial dot size corresponds to a first absorption peak of 950 nm and 1050 nm, respectively.

References:

1. Z. Liu, S. Niu, N. Wang, *J Colloid Interface Sci*, 2018, **509**, 171–7, 10.1016/j.jcis.2017.09.010

2. Y. Noda, S. Ohba, S. Sato, Y. Saito, *Acta Crystallogr. Sect. B.*, 1983, **39,** 312–317, 0.1107/S0108768183002463.