Supplementary information:

Interface-resolved Photovoltage Generation Dynamics and Band Structure Evolution in a PbS Quantum Dot Solar Cell

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Figure S1. Absorption spectrum of PbS-OA quantum dots dispersed in octane recorded with a Avantes AvaSpec-UV/Vis/NIR dual channel spectrometer and a tungsten halogen lamp (Avantes AvaLight HAL-S-Mini 10 W) as the light source. The position of the exciton peak (1.29 eV) was used to determine the quantum dot diameter according to the sizing equation developed by Moreels et al.¹ to be 3.15 nm.



Figure S2. PES spectra of S 2p, Pb 4f, Br 3d and I 4d core levels of *p-side* samples and cell samples without and with Au on top. The spectra are calibrated to Au $4f_{7/2}$ at 84.0 eV binding energy and normalized to the total Pb 4f intensity. Spectra of the *p-side* samples were recorded with a photon energy of 350 eV, while spectra of the *cell – no Au* and *cell – Au* samples were recorded with 363 eV. The spectra show the typical Pb 4f, S 2p signals of PbS quantum dots, as well as I 4d and Br 3d signals from the ligand shell.



Figure S3. PES spectra of Pb 5d of the *n-side* samples with 50 nm and 250 nm film thicknesses (left) and Pb 4f of the *p-side* samples with 50 nm and 250 nm film thicknesses (right). The spectra are calibrated to Au $4f_{7/2}$ of a reference gold foil at 84.0 eV binding energy and normalized to the total core level intensity.



Figure S4. Pb $4f_{7/2}$ binding energy as a function of pump-probe delay time for *p-side* samples with two different thicknesses and at two different laser intensities determined with a photon energy of 350 eV. Each colour comes from the analysis of the measurement of a fixed laser to X-ray delay, which contains as many data points as the ratio of the X-ray repetition rate to the laser repetition rate (120).



Figure S5. Change in Pb 4f binding energy relative to the longest delay times as a function of pumpprobe delay time for *p-side* samples with two different thicknesses and at two different laser intensities determined with a photon energy of 350 eV. Each colour comes from the analysis of the measurement of a fixed laser to X-ray delay, which contains as many data points as the ratio of the X-ray repetition rate to the laser repetition rate (120).



Figure S6. Kinetic traces of change in binding energy relative to the longest delay times obtained from the delay scans of the p-side samples (ITO/Au/PbS-EDT/PbS-PbX₂) with two different thicknesses (250 and 50 nm) of the PbS-PbX₂ layer, for two different laser pulse energies and a photon energy of 350 eV, with multiexponential fits to the data included.



Figure S7. Pb $5d_{5/2}$ binding energy as a function of pump-probe delay time for *n-side* samples with two different thicknesses and at two different laser intensities determined with a photon energy of 90 eV. Each colour comes from the analysis of the measurement of a fixed laser to X-ray delay, which contains as many data points as the ratio of the X-ray repetition rate to the laser repetition rate (120).



Figure S8. Left / Right: Kinetic traces of averaged absolute Pb $4f_{7/2}$ / Pd $5d_{5/2}$ binding energies obtained from the delay scans recorded with the lower laser power on the *p-side* / *n-side* samples with two different thicknesses (250 and 50 nm) of the PbS-PbX₂ layer and a photon energy of 350 eV. Peak positions determined without laser included as horizontal lines.



Figure S9. Pb $4f_{7/2}$ binding energy (left) and change in Pb $4f_{7/2}$ binding energy relative to the longest delay times (right) as a function of pump-probe delay time for the *cell – no Au* (ITO/MgZnO/PbS-PbX₂/PbS-EDT) sample determined with a photon energy of 363 eV. Each colour comes from the analysis of the measurement of a fixed laser to X-ray delay. The laser intensity was 14.9 nJ per pulse.



Figure S10. Au $4f_{7/2}$ binding energy (left) and change in Au $4f_{7/2}$ binding energy relative to the longest delay times (right) as a function of pump-probe delay time for the *cell* –*Au* (ITO/MgZnO/PbS-PbX₂/PbS-EDT/Au) sample determined with a photon energy of 363 eV. Each colour comes from the analysis of the measurement of a fixed laser to X-ray delay. The laser intensity was 14.9 nJ per pulse.



Figure S11. Kinetic traces of photovoltage determined from the difference in peak position with and without laser for the *cell* - *Au* (ITO/MgZnO/PbS-PbX₂/PbS-EDT/Au) sample through measurement of the Pb 4f and Au 4f core level in different spots on the sample with a laser intensity of 14.9 nJ per pulse.



Figure S12. Au 4f core level spectra including curve fitting of the *cell* – *Au* sample before (top left) and after (top right) time-resolved laser measurements in the same spot and of a reference Au foil (bottom left). The values indicate the fitted Au $4f_{7/2}$ positions, which were calibrated by setting the position of the Au 4f from the reference gold foil to 84.00 eV. The bottom right figure shows a comparison of the Au $4f_{7/2}$ from the three different measurements normalised to the fitted intensity. The results show that the Au 4f peak measured on the *cell* – *Au* sample is in the same position as the peak measured on a gold reference within 0.03 eV. This demonstrates that almost no photovoltage is generated by the X-ray illumination of the solar cell sample.



Figure S13. The photoionization cross sections of Pb 5d, Pb 4f and Au 4f as function of photon energy.² The photon energies used for pump-probe delay scans of the different core levels are indicated by vertical lines.

References

- 1 I. Moreels, K. Lambert, D. Smeets, D. De Muynck, T. Nollet, J. C. Martins, F. Vanhaecke, A. Vantomme, C. Delerue, G. Allan and Z. Hens, *ACS Nano*, 2009, **3**, 3023–3030.
- 2 J. J. Yeh and I. Lindau, At Data Nucl Data Tables, 1985, **32**, 1–155.