

## Supplementary Information for:

### The Impact of Chemical Composition of the Halide Surface Ligands on the Electronic Structure and Stability of the Lead Sulfide Quantum Dot Materials

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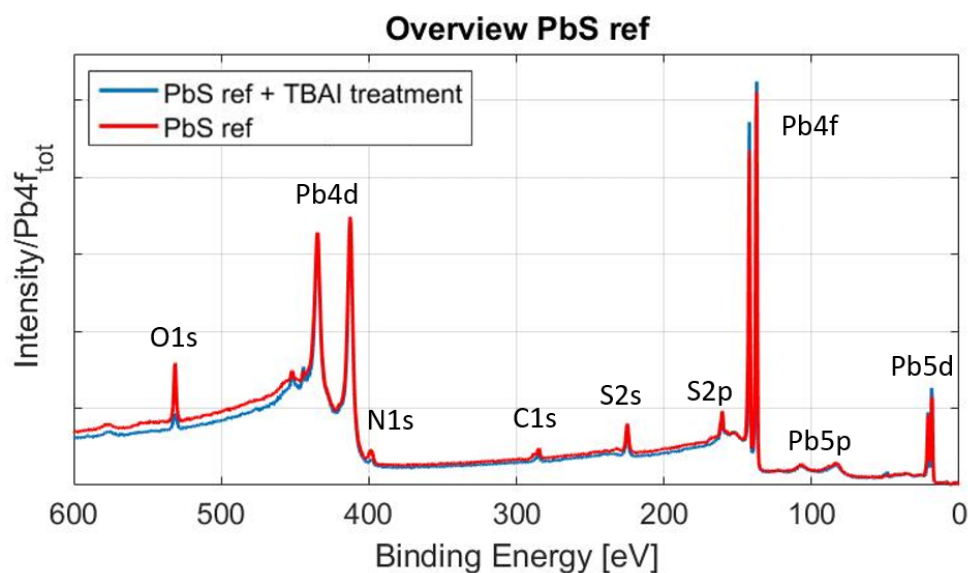


Figure S 1. Overview PES spectra of the PbS reference samples without (red line) and with TBAI surface treatment (blue line), calibrated against Au 4f<sub>7/2</sub> at 84.0 eV measured with a photon energy of 3000 eV.

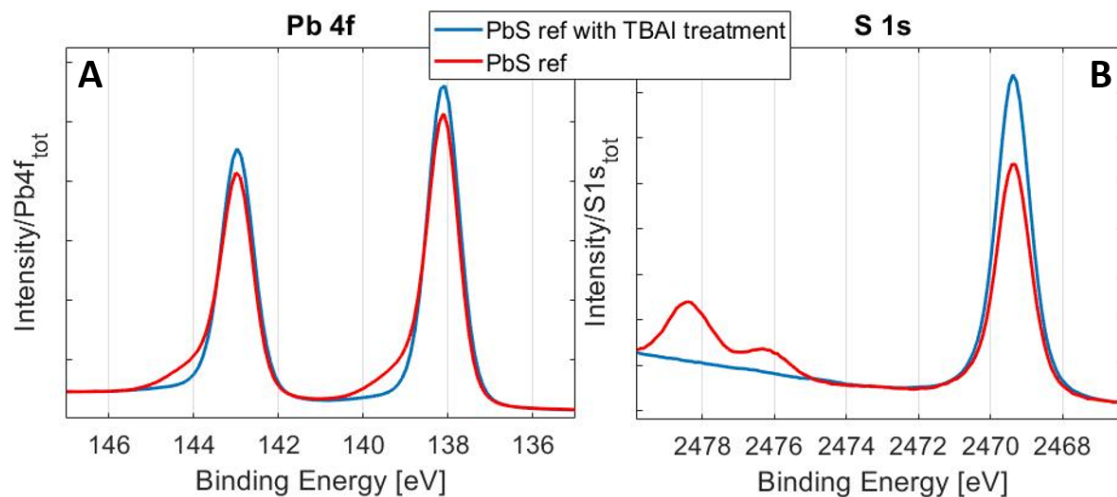


Figure S 2. PES spectra of Pb 4f and S 1s at the surface treated PbS ref (blue line) and initially prepared PbS sample without surface treatment (red line) measured with a photon energy of 3000 eV. The surface treated sample shows no oxidized species of Pb and S. All spectra are internally calibrated to the BE position of S 2p of the PbS (1:1) sample at 160.3 eV.

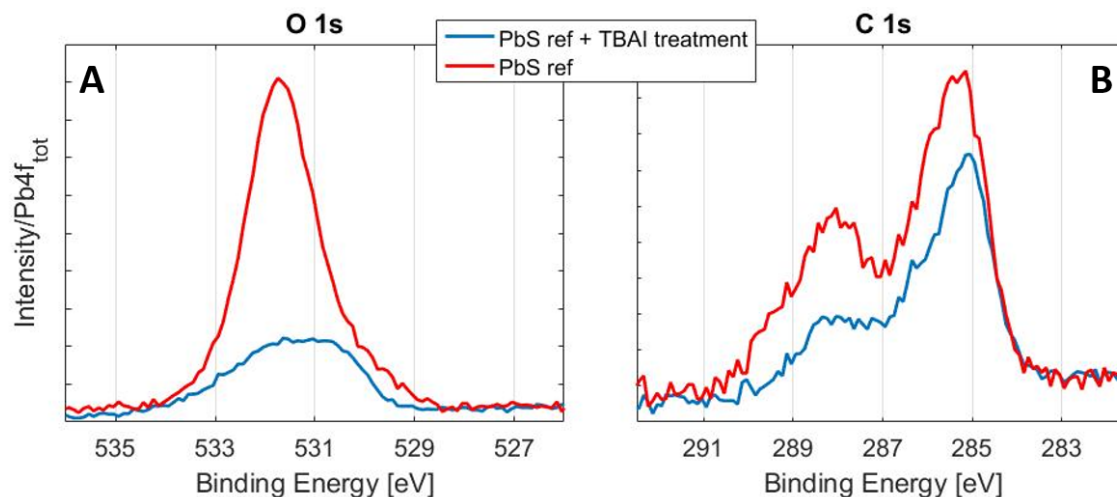


Figure S 3. O 1s and C 1s photoelectron spectra of the PbS ref sample with (in blue) and without surface treatment (in red) at 3000 eV photon energy. The surface treated sample shows significantly less oxygen and carbon compared to the sample without surface treatment. Spectra are internally calibrated to the BE position of S 2p of the PbS (1:1) sample at 160.3 eV.

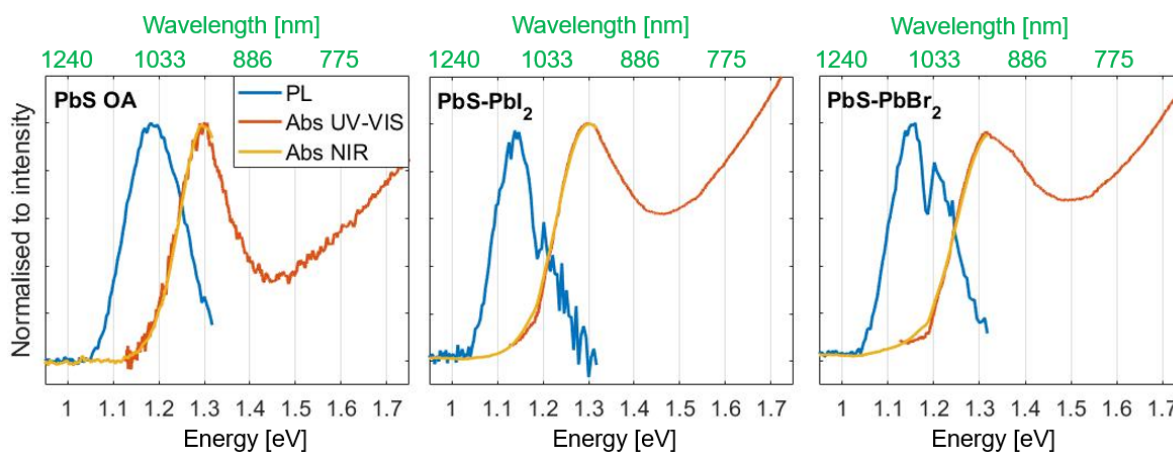


Figure S 4. Absorption and photoluminescence spectra of PbS-OA, PbS-PbI<sub>2</sub> and PbS-PbBr<sub>2</sub> quantum dot solutions with a concentration of 0.25 mg/ml for PbS OA in octane, and 0.2 mg/ml for PbS-PbX<sub>2</sub> in amylamine. Spectra are normalized to maximum intensity.

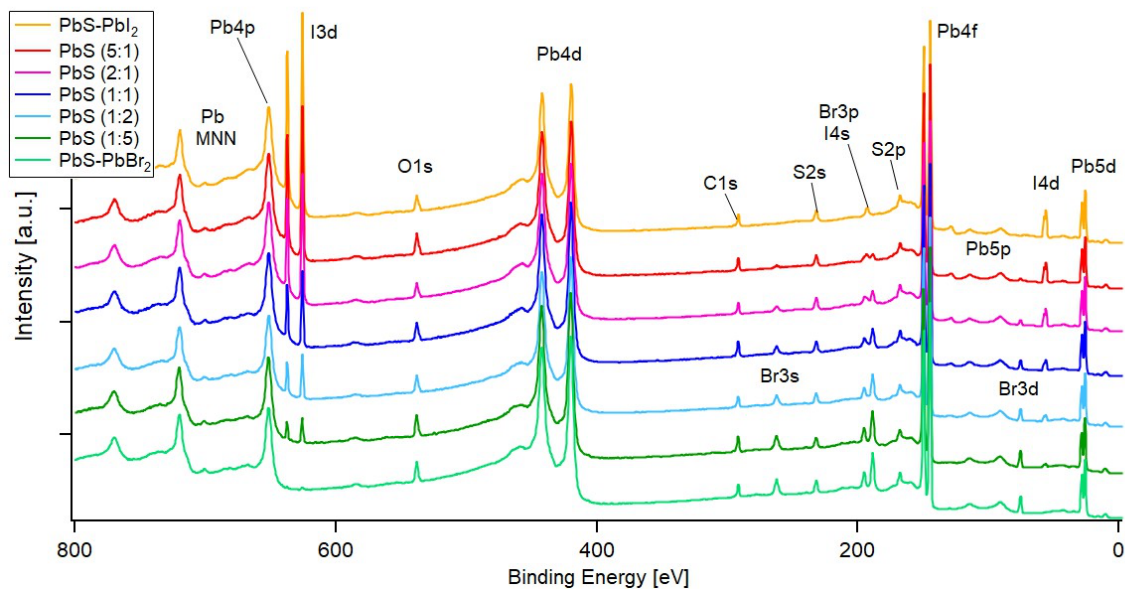


Figure S 5. Overview spectra of all QD samples measured with 3000 eV incident photon energy. Calibrated against Au  $4f_{7/2}$  peak at 84.0 eV. The legend entries correspond to the ligand ratio of  $\text{PbI}_2:\text{PbBr}_2$ .

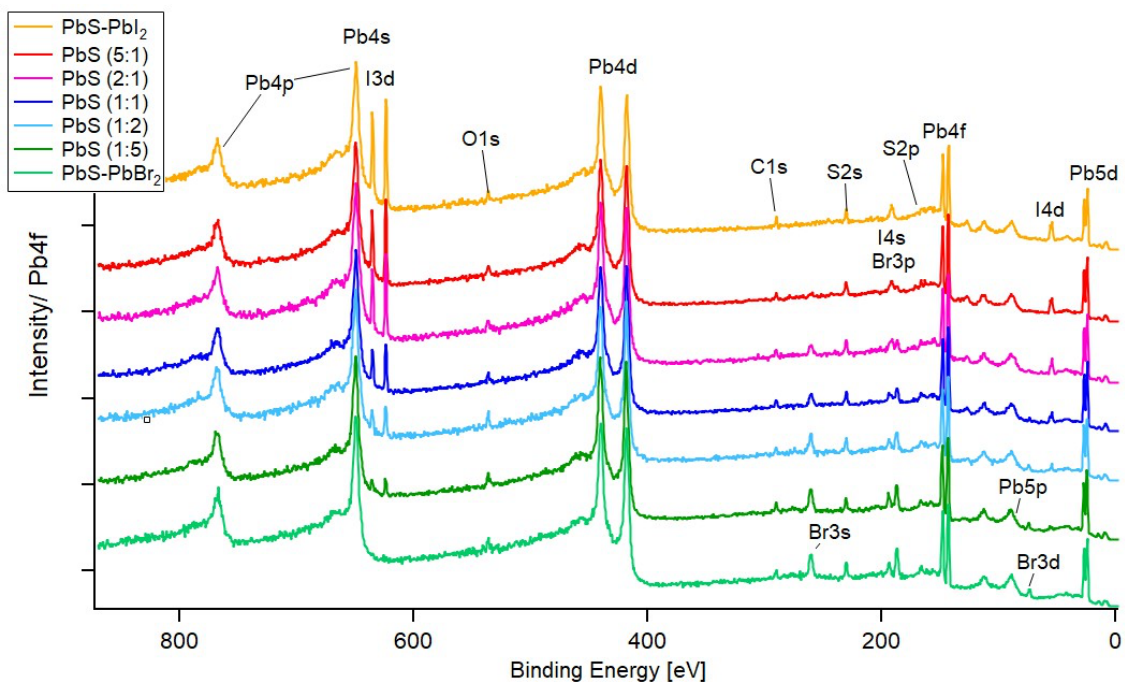


Figure S 6. Overview spectra of all QD samples measured with 6100 eV incident photon energy. Calibrated against Au  $4f_{7/2}$  peak at 84.0 eV. The legend entries correspond to the ligand ratio of  $\text{PbI}_2:\text{PbBr}_2$ .

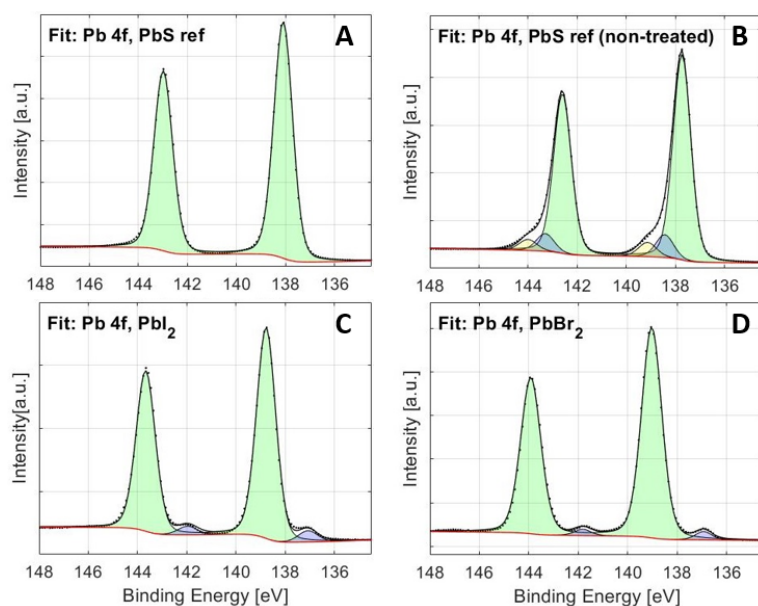


Figure S 7. Curve fits of the PbS ref (A), PbS ref non-treated with TBAI (B), PbI<sub>2</sub> (C) and PbBr<sub>2</sub> (D) reference samples, measured at 3000 eV incident photon energy. The spectra are internally calibrated to the core levels of the PbS (1:1) QD sample (S 2p at 161.3 eV, I 4d at 49.6 eV and Br 3d at 68.9 eV)

Table S 1. Binding energies of main core levels, measured at 3000 eV. PES spectra of the samples are calibrated internally to S 2p, I 4d and Br 3p position of PbS (1:1) sample (S 2p at 161.3 eV, I 4d at 49.6 eV and Br 3d at 68.9 eV)

Sample	Pb 4f	Pb 5d	S 2p	S 2s	S 1s	I 4d	Br 3d
PbS ref	138.1	19.3	161.3	225.7	2469.1	-	-
PbI <sub>2</sub> ref	138.8	19.9	-	-	-	49.6	-
PbBr <sub>2</sub> ref	139.0	20.2	-	-	-	-	68.9
PbS-PbI <sub>2</sub>	138.3	19.5	161.3	225.9	2469.3	49.6	-
PbS (5:1)	138.3	19.5	161.3	225.8	2469.3	49.6	68.9
PbS (2:1)	138.3	19.5	161.3	225.8	2469.3	49.6	68.9
PbS (1:1)	138.3	19.5	161.3	225.8	2469.3	49.6	68.9
PbS (1:2)	138.2	19.5	161.3	225.8	2469.4	49.6	68.8
PbS (1:5)	138.3	19.5	161.3	225.8	2469.4	49.5	68.8
PbS-PbBr <sub>2</sub>	138.3	19.5	161.3	225.9	2469.4	-	68.9

Table S 2. Binding energies of main core levels, measured at 6100 eV. PES spectra of the samples are calibrated internally (S 1s at 2469.3 eV, I 4d at 49.6 eV and Br 3p at 182.3 eV)

Sample	Pb 4f	Pb 5d	S 2s	S 1s	I 4d	Br 3p
PbS ref	138.2	19.3	225.8	2469.3	-	-
PbI <sub>2</sub> ref	138.8	19.9		-	49.6	-
PbBr <sub>2</sub> ref	139.0	20.2		-	-	182.3
PbS-PbI <sub>2</sub>	138.3	19.6	225.9	2469.3	49.5	-
PbS (5:1)	138.3	19.5	226.0	2469.3	49.6	182.3
PbS (2:1)	138.3	19.5	226.0	2469.3	49.5	182.3
PbS (1:1)	138.3	19.6	226.0	2469.3	49.7	182.3
PbS (1:2)	138.3	19.5	225.9	2469.3	49.6	182.4
PbS (1:5)	138.3	19.5	225.9	2469.3	49.6	182.4
PbS-PbBr <sub>2</sub>	138.2	19.4	225.9	2469.2	-	182.3

Table S 3. Probing depth (PD, from which 95% of intensity originates) and percentage of the signal intensity (PSI) coming from the top 3.2 nm (one QD layer) at 3000 and 6100 eV incident photon energy. Calculated using the method introduced by Tanuma et al.<sup>1</sup>

Core Level	Pb 4f	Pb 5d	S 2p	S 2s	S 1s	I 4d	Br 3d	Br 3p
PD [nm] at 3000 eV	14.5	15.0	14.5	14.2	4.0	14.8	14.8	14.3
PD [nm] at 6100 eV	26.6	27.0	26.5	26.3	17.6	26.8	26.8	26.4
PSI [%] at 3000 eV	48	47	49	49	91	47	48	49
PSI [%] at 6100 eV	30	30	30	31	42	30	30	30

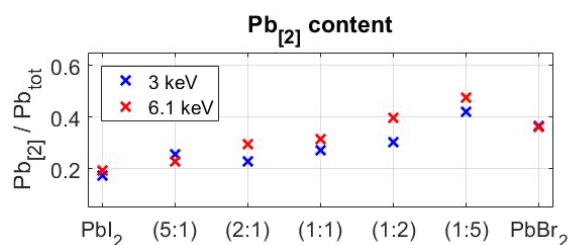


Figure S 8. Ratio of the concentration of the second Pb 4f peak (combination of Pb-O and Pb-Br) and the total concentration of Pb 4f in different PbS QD samples at 3000 eV and 6100 eV incident photon energies.

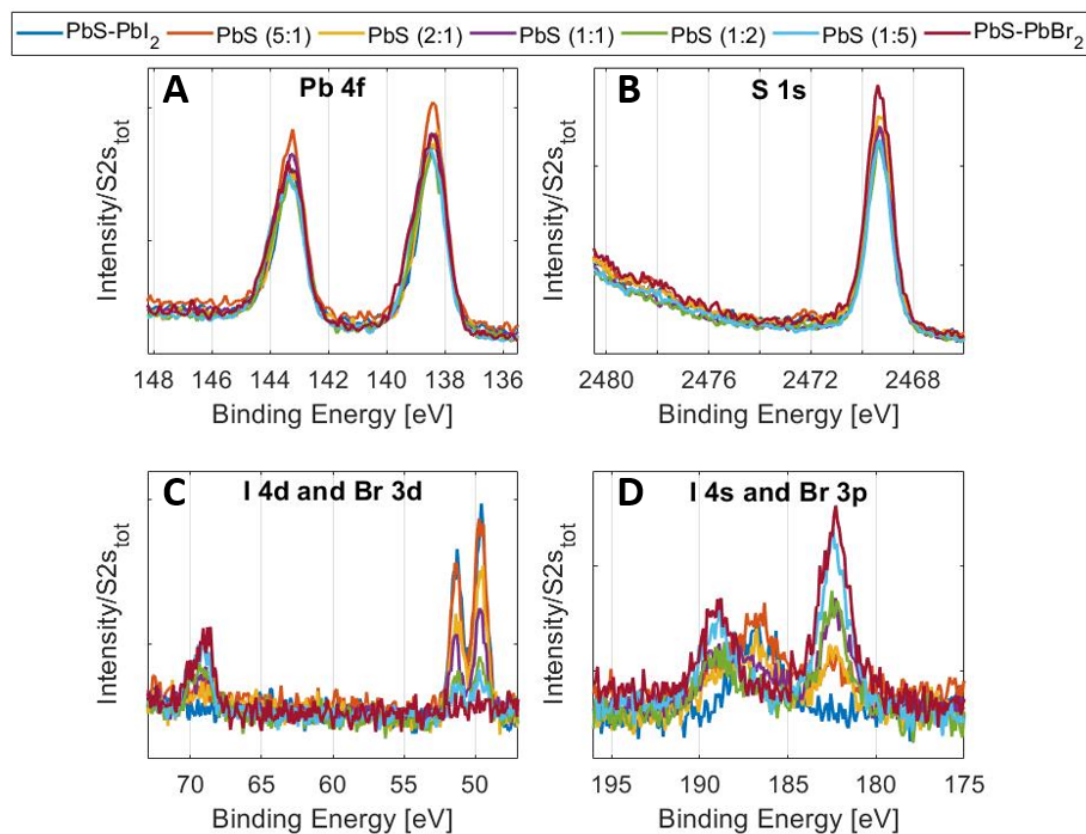


Figure S 9. Pb 4f, S 1s, I 4d, Br 3d, I 4s and Br 3p regions of the PbS QD samples measured at 6100 eV incident photon energy. PES spectra are normalized to total amount of S 2s and energy calibrated internally to the core level of the PbS (1:1) sample (S 1s at 2469.3 eV).



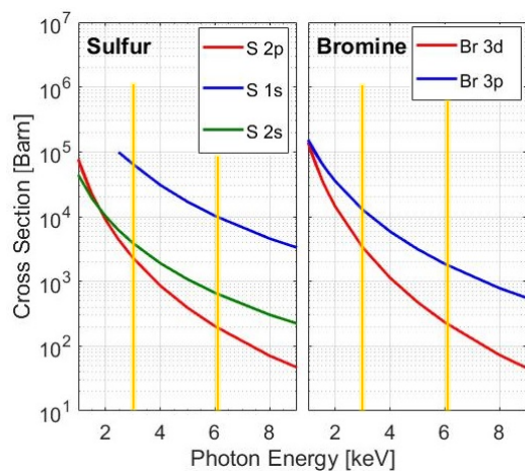


Figure S 10. Ionization cross-sections<sup>1</sup> for S 2p, S 2s, S 1s (left) and Br 3d, Br 3p (right) with highlighted incident photon energies used in this experiment (yellow vertical lines).

Table S 4. Position of the valence band edge in eV. Determined by finding the intersection of the valence onset on a linear or logarithmic intensity axis, and a baseline of the spectrum. The spectra were calibrated to Pb 5d positions from Table S 1.

Sample	VB edge [eV] (linear)	VB edge [eV] (logarithmic)
PbS bulk	0.57	0.20
PbI <sub>2</sub> ref	1.91	1.51
PbBr <sub>2</sub> ref	2.48	2.13
PbS-PbI <sub>2</sub>	1.14	0.69
PbS (5:1)	1.26	0.81
PbS (1:1)	1.29	0.82
PbS (1:5)	1.12	0.71
PbS-PbBr <sub>2</sub>	1.14	0.69

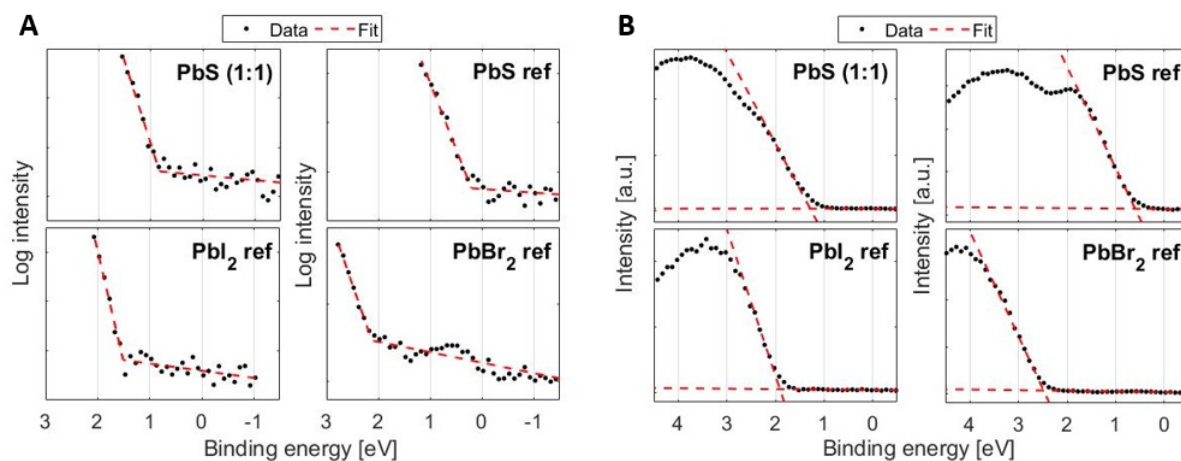


Figure S 11 Logarithmic (A) and linear (B) valence fitting of the quantum dot (PbS (1:1)) and reference samples (PbS ref, PbI<sub>2</sub> ref and PbBr<sub>2</sub> ref). Data shown in the figure is calibrated internally, against Pb 5d positions from Table S 1.

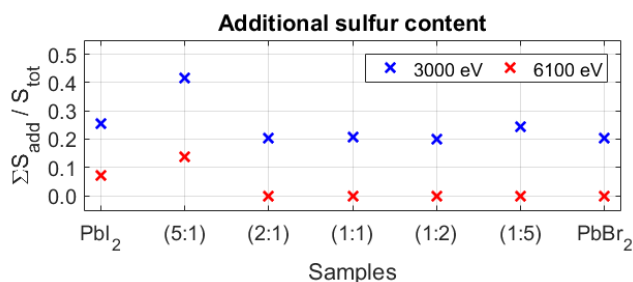


Figure S 12. Content of the additional sulfur species in PbS QD samples with different ligand composition. The content was calculated as a ratio of the sum of the all non-main S 1s species and the total amount of S 1s.

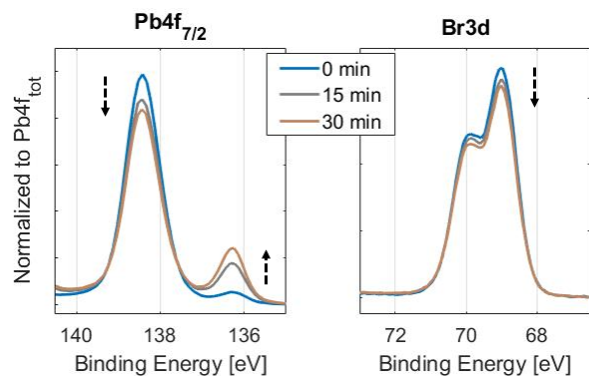


Figure S 13. Evolution of the PES spectra of the Pb 4f and Br 3d core levels over time in PbBr<sub>2</sub> reference sample measured with 3000 eV incident photon energy.

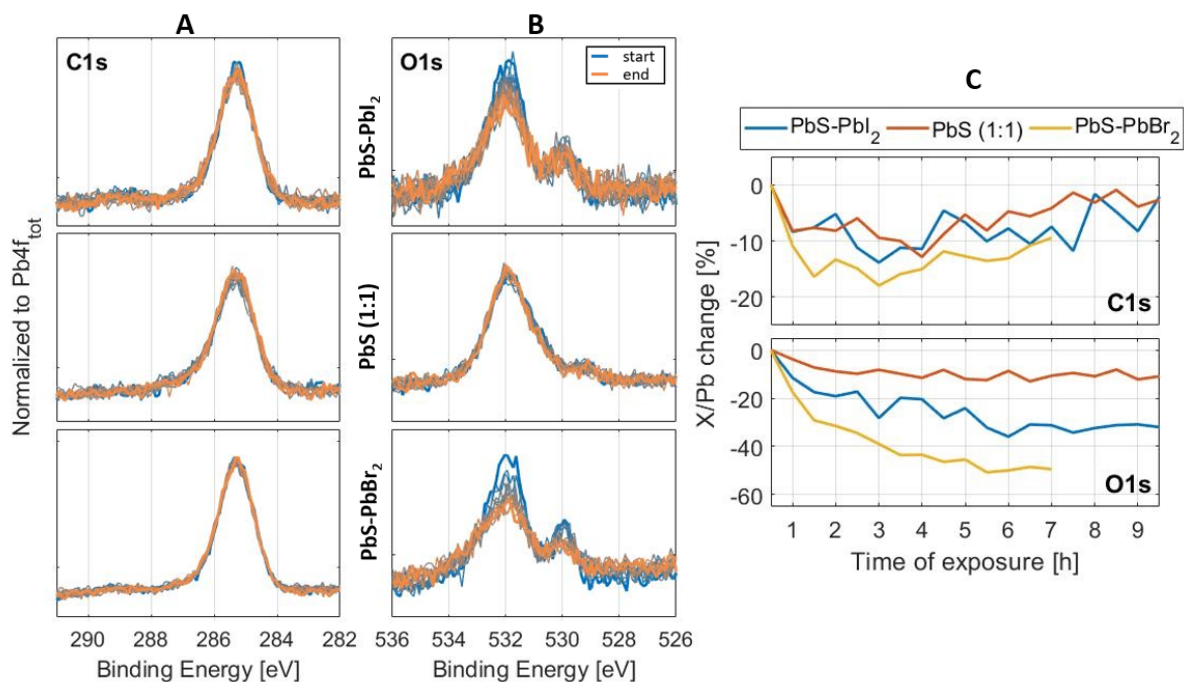


Figure S 14. Stability measurements of samples PbS-Pbl<sub>2</sub>, PbS (1:1) and PbS-PbBr<sub>2</sub> under X-ray illumination with 3000 eV. Panels on the left show the spectral evolution of the C 1s (A column) and O 1s (B column) core levels, whereas the panels on the right (C column) show the evolution of these core levels over time. The X/Pb stands for the ratio of the core level (C 1s, O 1s) to the total amount of lead (Pb 4f). The X/Pb change is normalized to the “time zero” ratio (ratio at the beginning measurement). The measurement took 7-10 h depending on the sample. All spectra are internally energy calibrated (see Figure 3 in main text).

## References

- (1) Tanuma, S.; Powell, C. J.; Penn, D. R. Calculations of Electron Inelastic Mean Free Paths. *Surf. Interface Anal.* **1993**, *21*, 165–176.