

Time Resolved Photoemission to Unveil Electronic Coupling Between Absorbing and Transport Layers in a Quantum Dot Based Solar Cell

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1. Effect of the ligand exchange on the absorption spectrum

Figure S 1 shows the infrared spectrum of the native PbS (ie before ligand exchange), we observe three main peaks. A doublet around 2900 cm^{-1} corresponding to the C-H bonds from the alkyl chain, a peak at 1413 cm^{-1} from the O-H bond from the carboxylate function and finally a doublet around 700 cm^{-1} resulting from the unsaturated C=C bond.

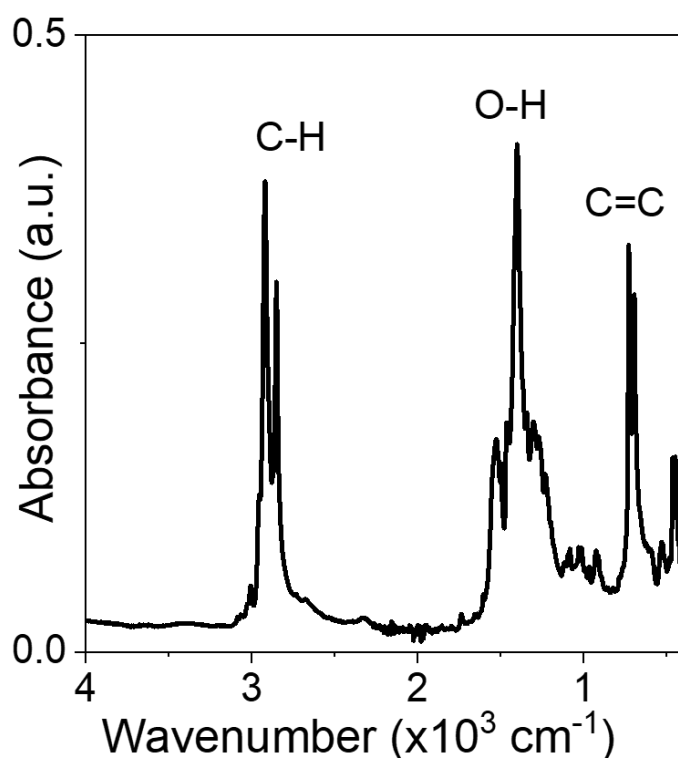


Figure S 1 infrared spectrum of the PbS CQDs capped with oleic acid.

Figure S2 shows the effect of the surface chemistry on the absorption spectrum. As nanocrystals are transferred from solution to film, a clear redshift (from 920 nm to 950 nm is observed). On the other hand, the nature of the ligand has only a marginal effect on the energy of the exciton (20 meV shift)

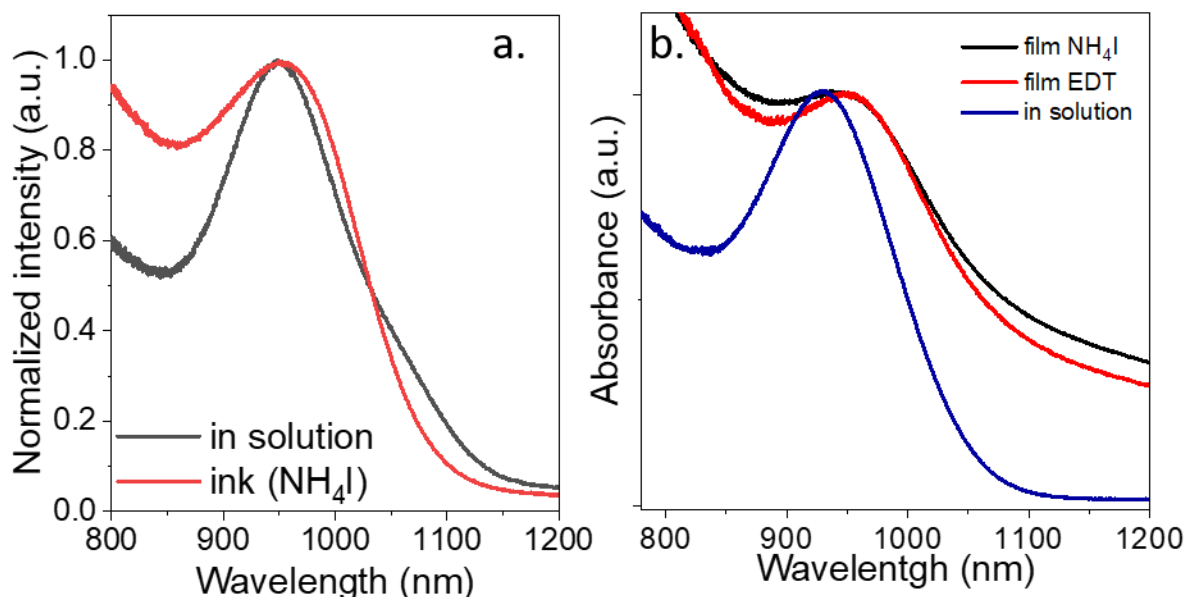


Figure S2 a. absorption spectra of the PbS CQDs in solution and after phase transfer toward DMF thanks to I⁻ capping. b. absorption spectra of the PbS CQDs in solution and on film with two types of surface chemistry.

2. Photoemission for the PbS I⁻ capped sample

Figure S3 shows the photoemission overview spectrum for the PbS CQD film capped with I⁻ as ions. In addition, to the contribution from the Pb and S, we notice a clear peak from the I 4d state at a binding energy of 47 eV. Also, we no longer observe a signature of O 1s state. This confirms that there is no oleate left on the CQD surface.

Part b and c from Figure S3 provide respectively the signal relative to the cut-off of the secondary electrons (work function was measured at 5.1 eV) and the valence band (Fermi level is 0.72 eV above the valence band)

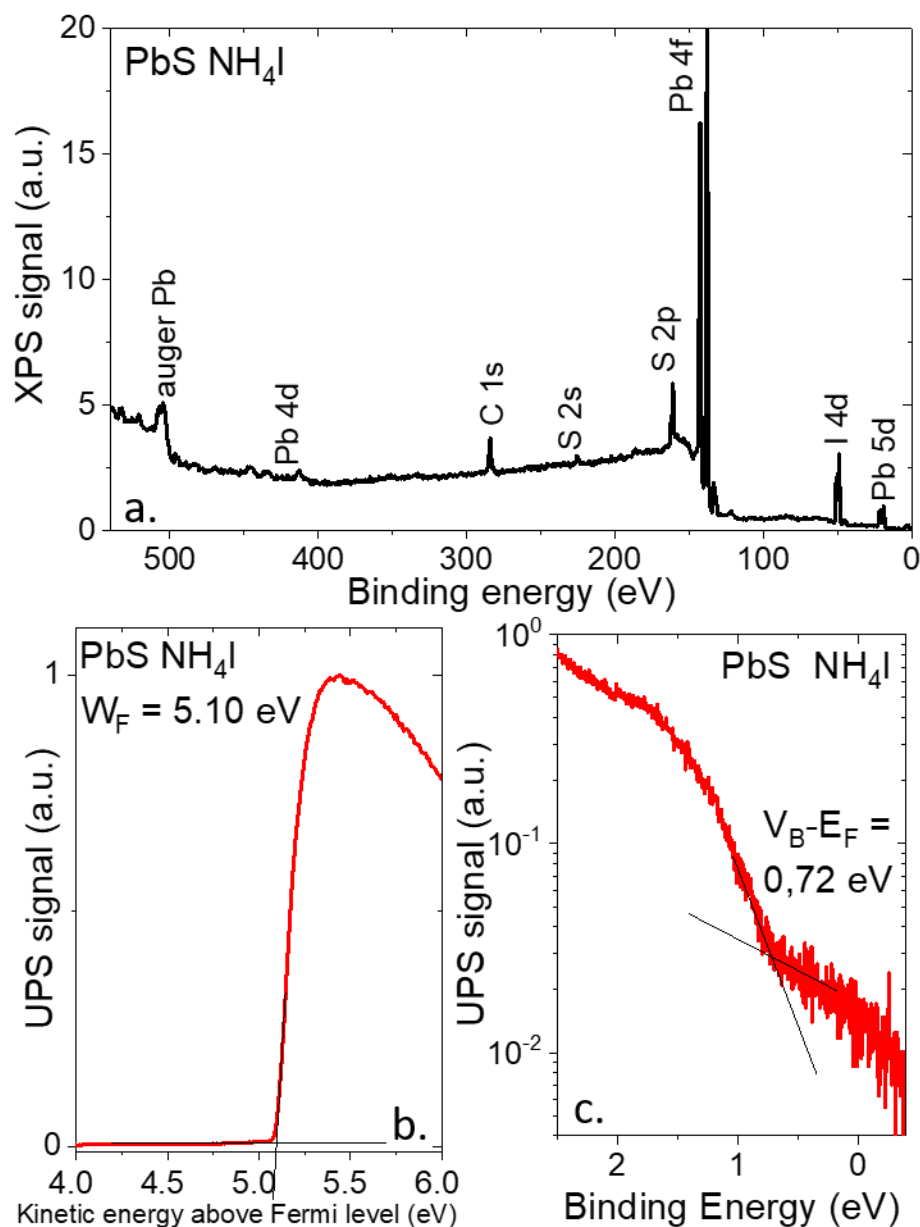


Figure S3 a. X-ray photoemission overview spectrum relative to a thin film of I⁻ capped PbS CQDs. b. Photoemission spectrum relative to the cut-off of the secondary electrons for a thin film made of PbS CQDs capped with I⁻. c. Photoemission spectrum relative to the valence band for a thin film consisting of PbS CQDs capped with I⁻.

3. PbS core level analysis

In Figure S4, we analyze the core level of the Pb 4f state. Independently of the surface chemistry, we observe two components for the lead which are generally attributed to lead coupled to sulfur (main component at binding energy (BE) ≈ 137.8 eV for EDT capped PbS) and the oxidized form of lead resulting from a PbO shell formation.¹ Oxygen being more electronegative than sulfur, the lead gets less electron rich and the binding energy is increased (BE = 138.8 eV for EDT capped PbS). As we compare the effect of surface chemistry, we observe a ≈ 1 eV shift toward higher energies for the I⁻ capped particles with respect to the thiol capped particles. Assuming a rigid shift for the core level and the valence band, this shift is consistent with a stronger *n*-type nature for the I⁻ capped material, see Figure 2e.

Pb 4f state

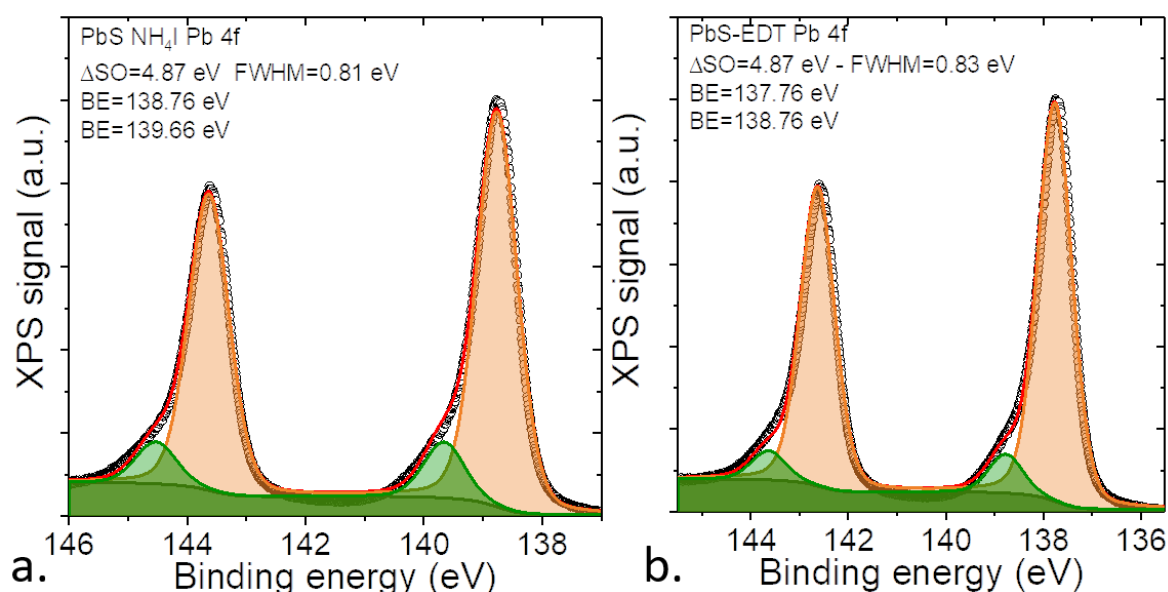


Figure S4 Photoemission spectra relative to the Pb 4f state coming from PbS CQDs with I⁻ (a.) and EDT (b.) as surface chemistry.

S 2p state

In the case of the S 2p state, we observe a single component in the case of I⁻ surface chemistry, see Figure S5a. We can attribute it to the sulfide in the PbS. In the case of thiol surface chemistry, two components can be clearly observed. The main one at BE ≈ 160.9 eV is resulting from the sulfur in the PbS,² while the second one at BE ≈ 162 eV is attributed to the thiol ligand.³⁻⁵

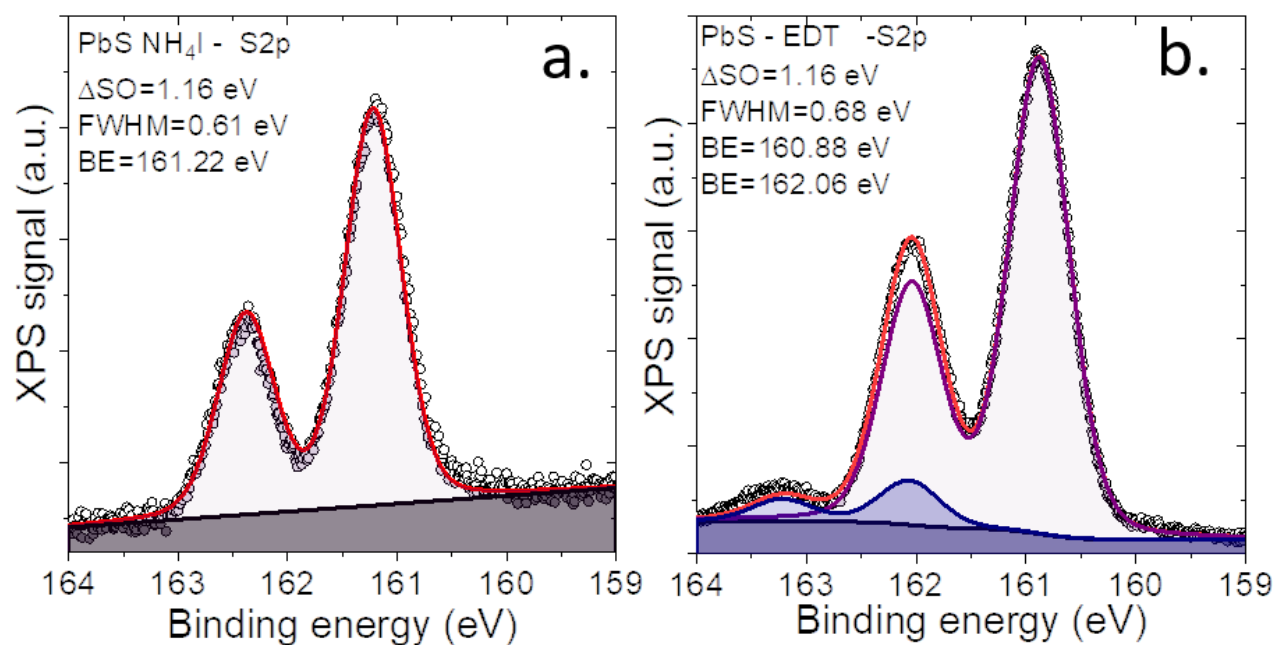


Figure S5 a. Photoemission spectrum relative to the S 2p state coming from PbS CQDs with I⁻ as surface chemistry. b. Photoemission spectrum relative to the S 2p state coming from PbS CQDs with EDT as surface chemistry.

4. MoO₃ core level analysis

In Figure S6a, we show the overview spectrum of the pristine MoO₃ layer. The analysis of the Mo core level shows three contributions for Mo 3d state, which are attributed to +IV, +V and +VI oxidation states of Mo. MoO₃ being thermally evaporated the material appears to be non-stoichiometric

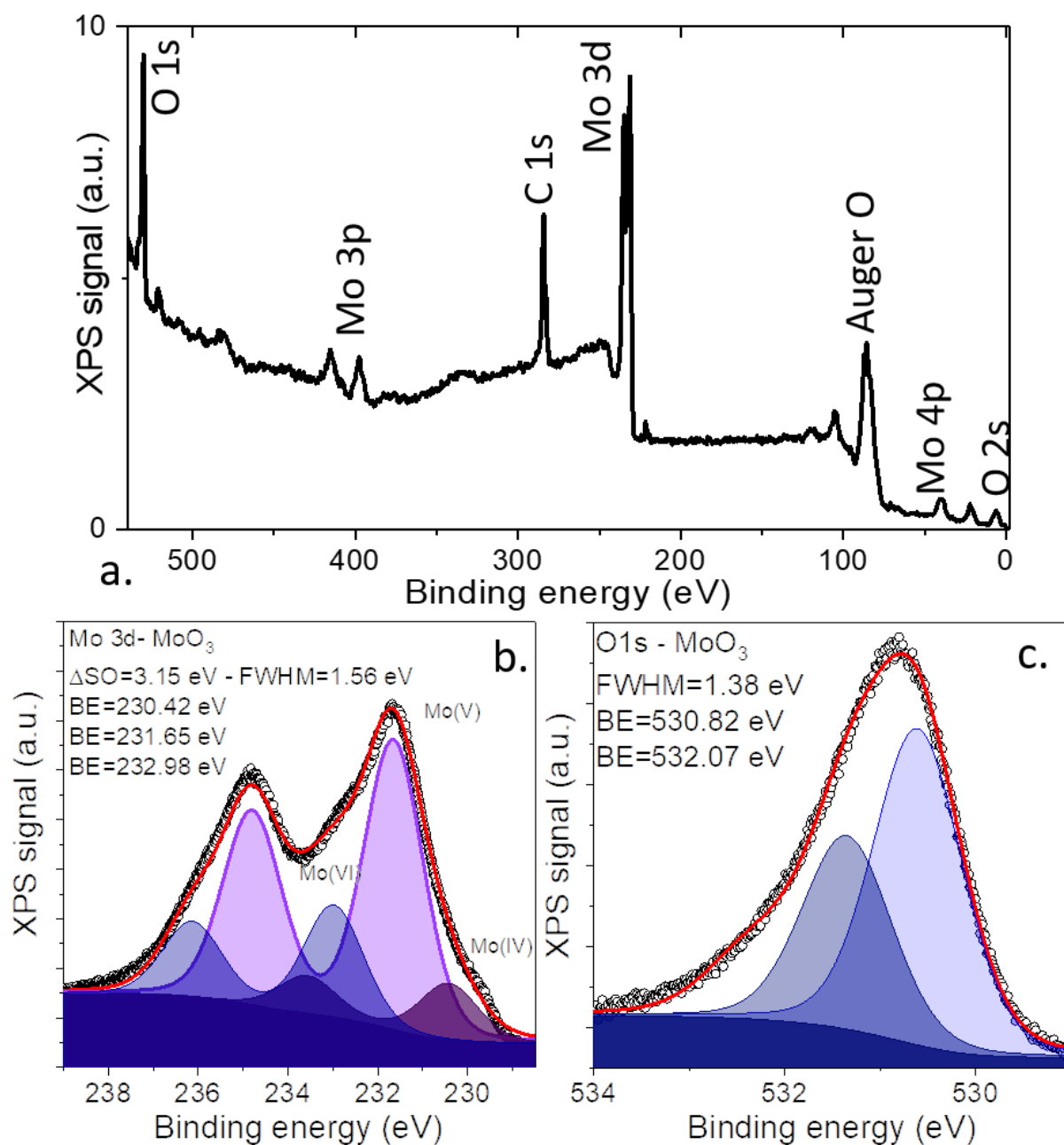


Figure S6 a. Photoemission overview spectrum from a pristine MoO₃ layer. b. Photoemission spectrum relative to Mo 3d state from a pristine MoO₃ layer. c. Photoemission spectrum relative to O 1s state from a pristine MoO₃ layer.

In Figure S7a, we show the overview spectrum of the MoO₃ capped PbS (EDT capped) sample. Despite having still a non stoichiometric material (*i.e.* with the presence of several components), the weight of the high binding energy component in the Mo 3d spectrum is more intense suggesting that the PbS EDT used as substrate is less eager to reduce the MoO₃ than the gold substrate used in Figure S6.

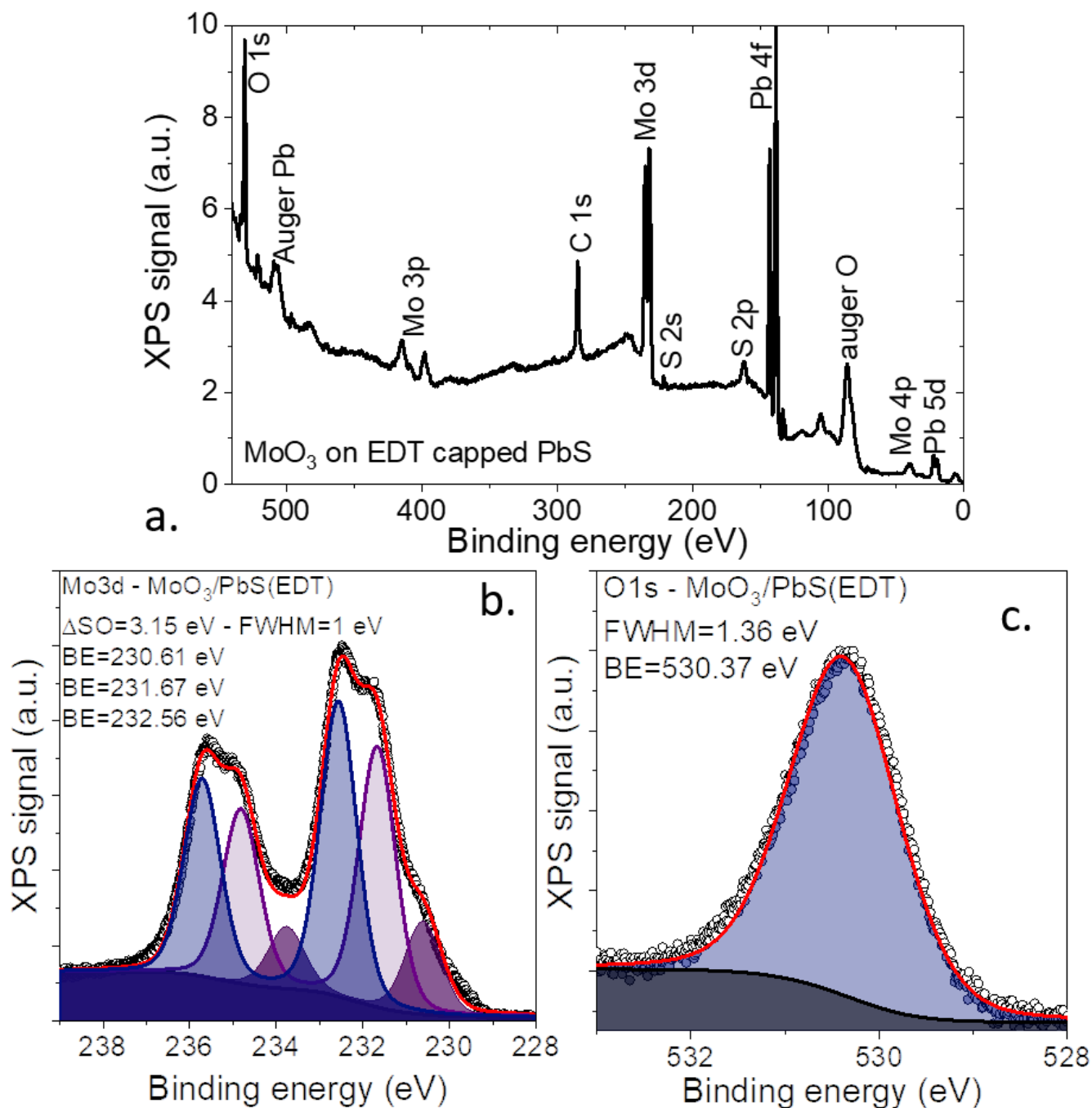


Figure S7 a. Photoemission overview spectrum for an MoO₃ layer covering an EDT capped PbS CQD layer. b. Photoemission spectrum relative to Mo 3d state for an MoO₃ layer covering an EDT capped PbS CQD layer. c. Photoemission spectrum relative to O 1s state for an MoO₃ layer covering an EDT capped PbS CQD layer.

5. TRXPS signal for the PbS/MoO₃ interface

In Figure S8, we compare the light induced shift of the Pb 4f state coming from PbS (EDT capped) and the one from Mo 3d state from the MoO₃ layer.

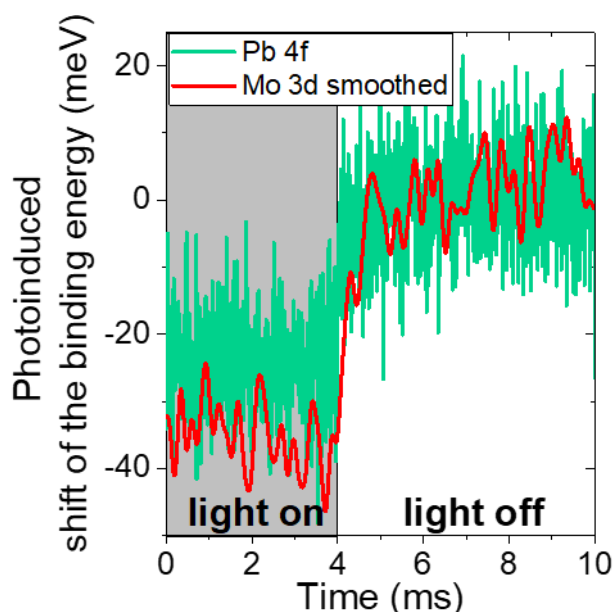


Figure S8 Temporal evolution of the photoemission signal coming from Pb 4f and Mo 3d when the pump light is turned on and off in the case of a PbS(EDT)/MoO₃ interface.

6. REFERENCES

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