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Supplemental Materials:

Valence and conduction band engineering in halide perovskites for solar cell applications

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1 Additional computational details

We performed calculations with and without SOC corrections. The effect of SOC corrections to the GGA-PBE band gap (E_g) is, typically, of the order of $0.3-0.4$ and $\sim 0.7-1.3$ eV toward smaller band gaps for Sn and Pb-based perovskites, respectively. SOC corrections do not change the qualitative conclusions of our study: i) both VBM and CBM are important in the tuning of the band gap (Figure S1), ii) the energy of the VBM is mostly affected by the overlap (Figure S2), and iii) that of the CBM mostly by the charge on the B ion (Figure S4). In Reference[1] it is shown that the good agreement between experimental and GGA-PBE computational results for $\mathrm{MAPbI_3}$ is due to a fortuitous cancellation of errors, due to the fact that the underestimation of the band gap in the absence of many-body effects is exactly compensated by the overestimation associated with the lack of SOC corrections.

This compensation is not as efficient in the case of Sn-based perovskites. We also tested the effect of a functional including range-separated exact exchange (HSE[2]). In fact, it might be the exact exchange in the relatively localized VBM and CBM orbitals that lead to the main correction with respect to the GGA results. To test this hypothesis we computed the HSE band gap, E_g^{HSE}, of the $\mathrm{CsSnI_3}$ perovskites (in the cubic, tetragonal and orthorhombic phases), added SOC corrections (described below), and compared computational and experimental results (see Figure S3). SOC corrections are computed from the difference of GGA-PBE results with and without SOC: $\Delta E_g^{\mathrm{SOC}} = E_g^{\mathrm{SOC}} - E_g$. The so computed band gap of orthorhombic $\mathrm{CsSnI_3}$ (1.05-1.14 eV) is in fair agreement with the recent experimental values of 1.2 eV[3],[4]. For this reason in all the figures of this work CBM energies of all Sn containing systems are rigidly shifted so that E_g of the orthorhombic $\mathrm{CsSnI_3}$ is 1.14 eV, i.e. our best DFT estimate of the band gap of this system including exact exchange and SOC effects

2 Correlation between q_{B} and E_{CBM}

In Figure S4, q_{B} vs E_{CBM}. $q_{\mathrm{B}} = \sum_{i \in \mathrm{B}} c_i^2$, values are reported with c_i being the projection coefficient of the CBM state onto B atomic orbitals and q_{B} as a measure of the amount of CBM charge on B atoms. Figure S4 shows a clear correlation between E_{CBM} and q_{B}: the higher is the charge on B the lower is E_{CBM}. As explained in the main text, E_{CBM} grows with the shrinking of q_{B} because part of its charge is moved from the attractive B^{2+} environment to the more repulsive X one. We notice that the trend of E_{CBM} with q_{B} depends on the halide, with an almost rigid shift toward higher E_{CBM} values along the series I→Br →Cl. This is not surprising because along this series the partial negative charge on the halide increases, and so does the electrostatic energy associated to the CBM charge on X. Results with and without SOC present an analogous trend, confirming that the qualitative picture one could gain from pure GGA calculations is correct.

3 Correlation between q_{B} and O_{TVB}

In the main text we explained that bands and band gap tuning strategies can be based on the overlap in the VBM crystal orbital because there is a correlation between this observable, determining the energy of the VBM, and q_{B}, determining

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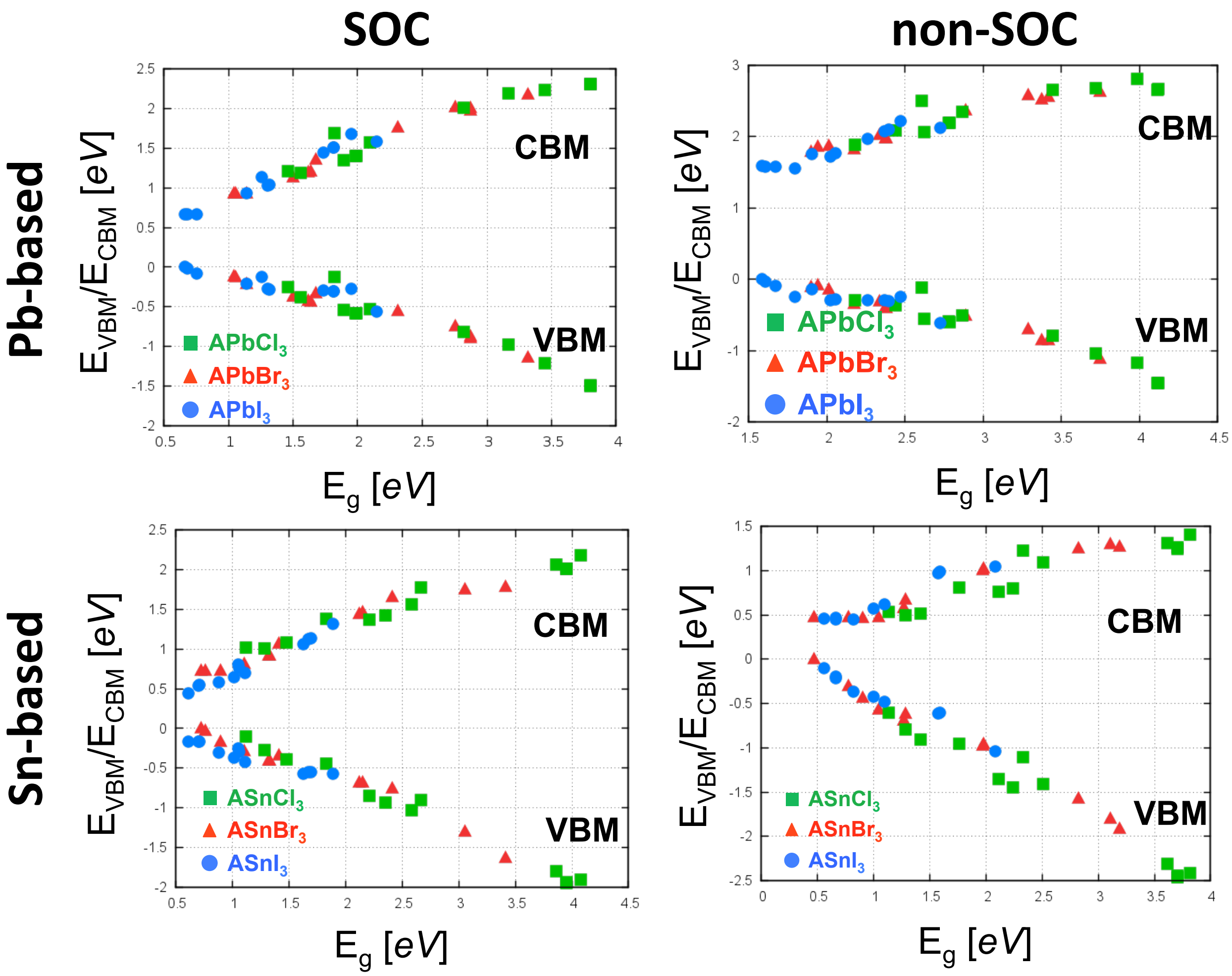

Fig. S1 E_{VBM} and E_{CBM} vs E_g. The top row refers to Pb-based systems, while the bottom row to Sn-based ones. On the left column we report results obtained including SOC, on the right column results obtained without SOC.

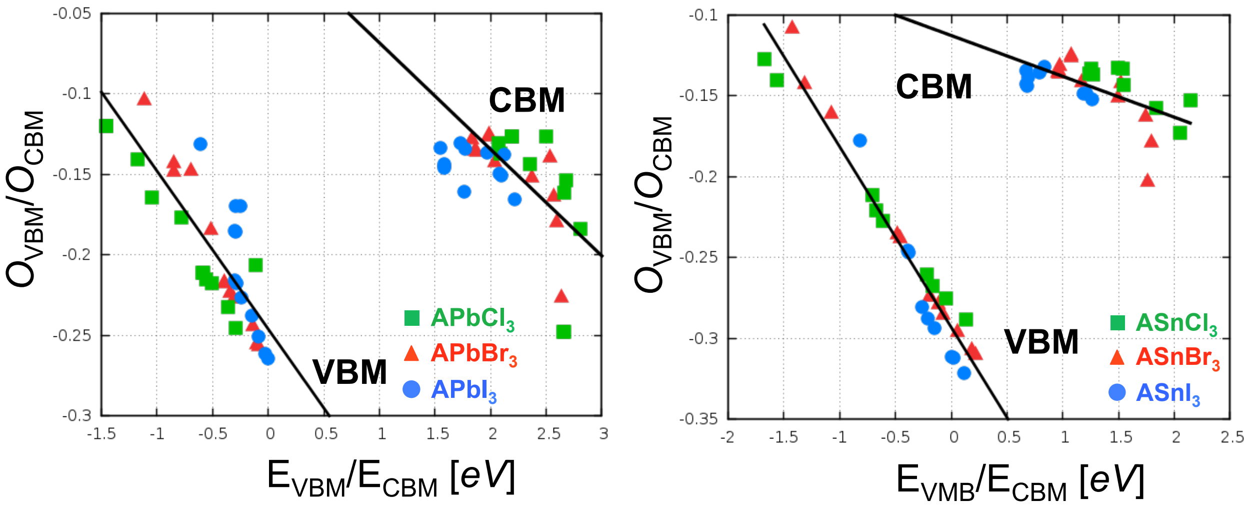

Fig. S2 (see also Figure ??): E_{VBM} (E_{CBM}) vs O_{VBM} (O_{CBM}) without SOC. For Sn-based systems (right), the relation E_{VBM} vs O_{VBM} is linear and its slope is large. E_{CBM} vs O_{CBM}, instead, cannot be satisfactorily fit with a linear relation and presents a smaller negative slope. For the Pb-based systems (right), the linear fitting of both E_{VBM} vs O_{CBM} and E_{CBM} vs O_{CBM} is poor. At variance with the Sn-based perovskites case, here the slope of E_{VBM} vs O_{VBM} and E_{CBM} vs O_{CBM} fitting is comparable.

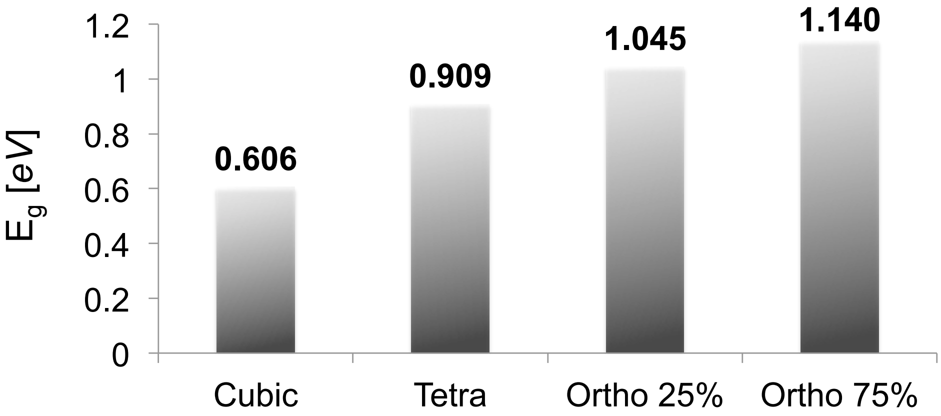

Fig. S3 E_g for the various crystal structures of $CsSnI_3$. Ortho 25% and Ortho 75% refer to the two orthorhombic structures identified by Kanatzidis and coworkers[3]. The fitting of crystallographic data required the adoption of a splitting position model for Cs and I atoms, with occupancy 25 and 75% of the two sites of each atomic species. The band gap reported is obtained from DFT calculations using the HSE exchange and correlation functional[2]. The SOC-corrected HSE E_g (see text above) of the Orthorhombic 75% phase, 1.14 eV, is in nice agreement with the experimental value, 1.3 eV[3],[4].

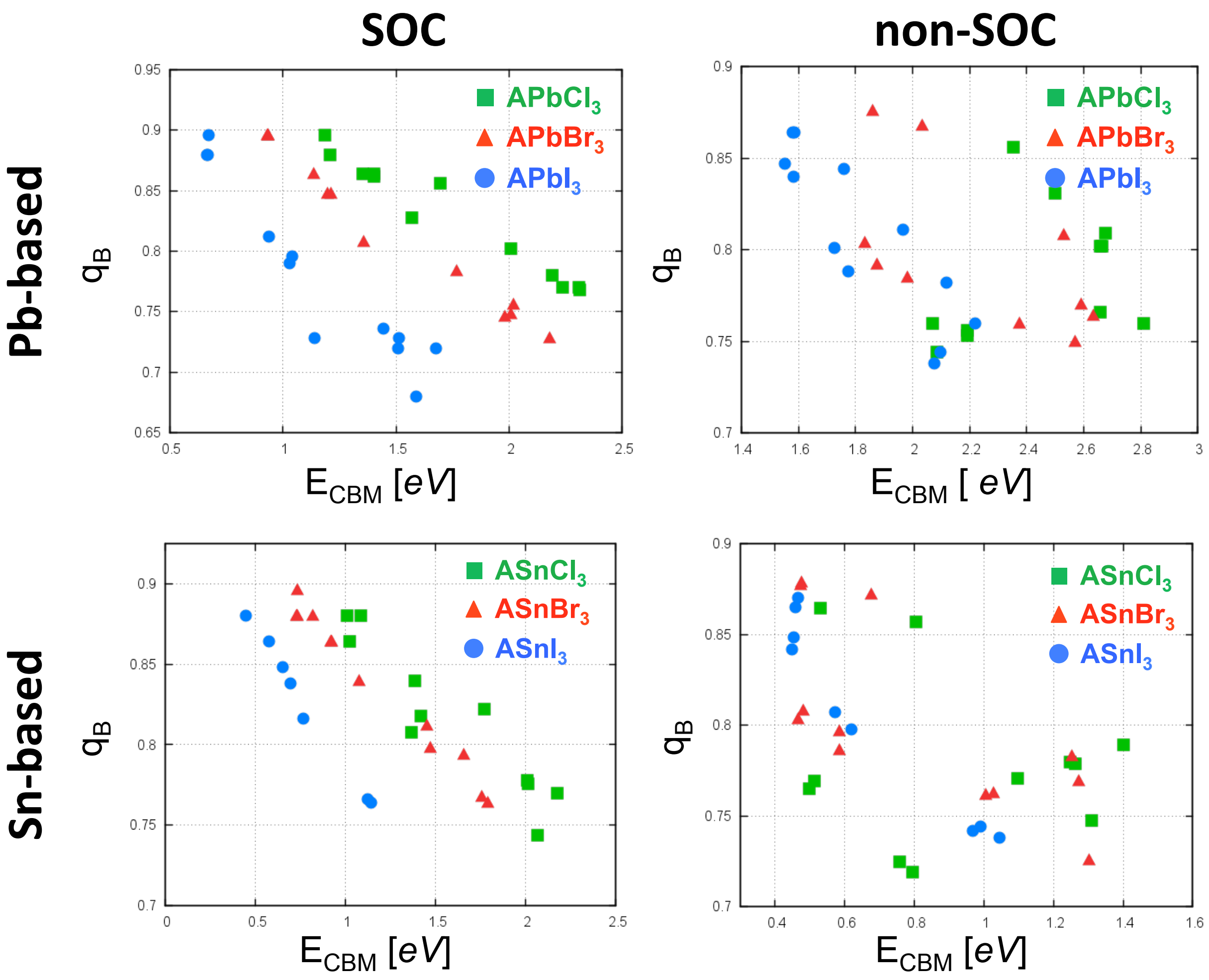

Fig. S4 q_B and E_{CBM}. The top row refers to Sn-based systems, while the bottom row to Pb-based ones. On the left column we report results obtained including SOC, on the right column results obtained without SOC.

the energy of the CBM. This is shown in Figure S5, where we report q_B vs O_{VBM}. We notice that q_B decreases with O_{VBM}, which results in a cooperative action in reducing/increasing the gap: when O_{VBM} changes in the sense of reducing the energy of the VBM, q_B changes in the direction of increasing the energy of the CBM, and vice versa.

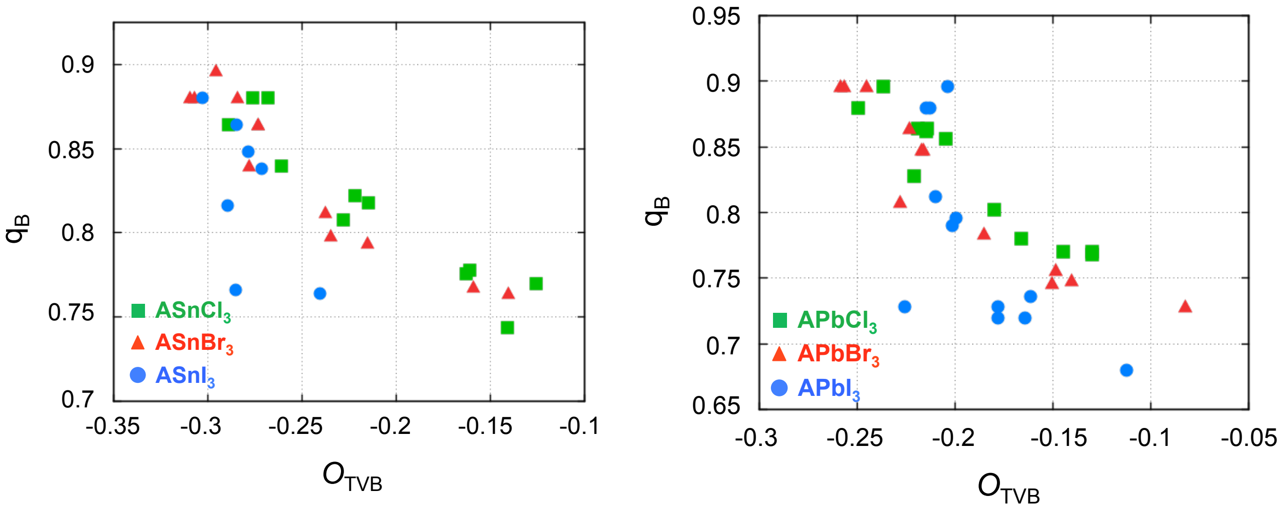

Fig. S5 q_B vs O_{VBM} for Sn-based (left) and Pb-based (right) perovskites

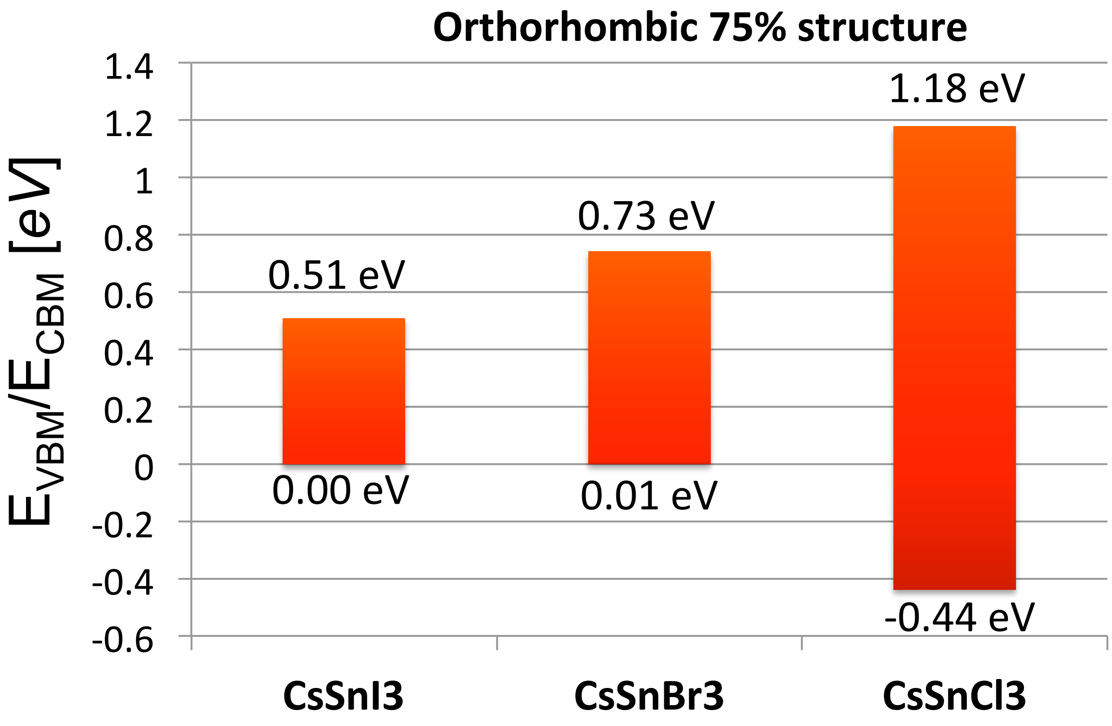

Fig. S6 E_{VBM} and E_{CBM} energies of the orthorhombic structure of $CsSnX_3$ perovskites

4 Calculation of the variation of E_{VBM} and E_{CBM} with stoichiometry and crystal symmetry, and the dependence of E_g on them

Figure S1 shows that the energy of VBM and CBM change by ~ 2 and 1.5 eV, respectively, in the systems investigated. Thus, we must conclude that the change of E_g in the perovskites set is determined by both states. This is only apparently conflicting with the experimental results of Ref.[5]. In fact, considering the systems investigated in this latter work we also observe that the change in the band gap is mostly determined by the change in the CBM (Figure S6).

5 Bands alignment

Here we report the density of state of a series of test systems, orthorhombic $CsPbI_3$, $LiCsPbI_3$, $CsPbBr_3$, and tetragonal $CsPbI_3$.

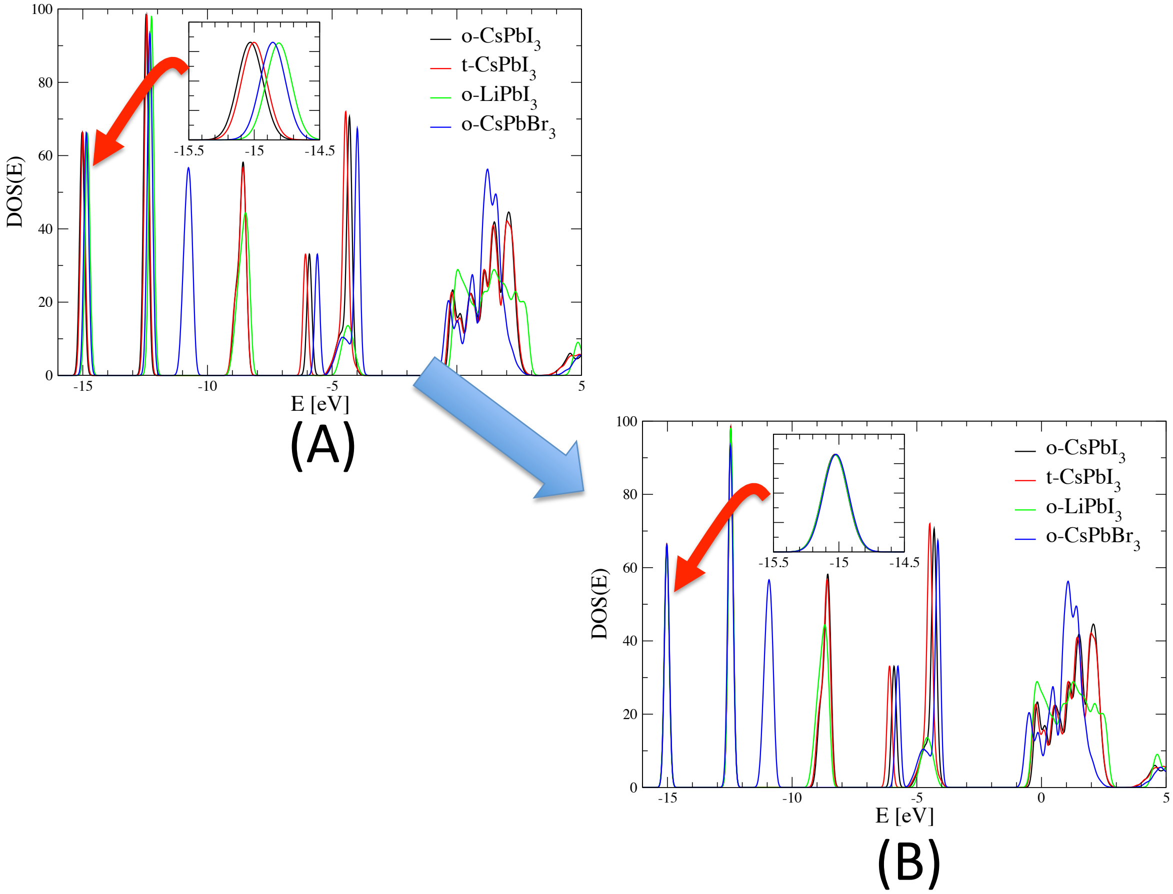

Fig. S7 Density of states (DOS) of orthorhombic $CsPbI_3$, $LiCsPbI_3$, $CsPbBr_3$, and tetragonal $CsPbI_3$ before (A) and after (B) applying the line-up procedure described in Sec. **??**. In the inset is reported the part of the DOS relative to atomic Pb-5d orbitals.

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