

# Supplementary information to “Fundamentals of tin iodide perovskites: a promising route to highly efficient, lead-free solar cells”

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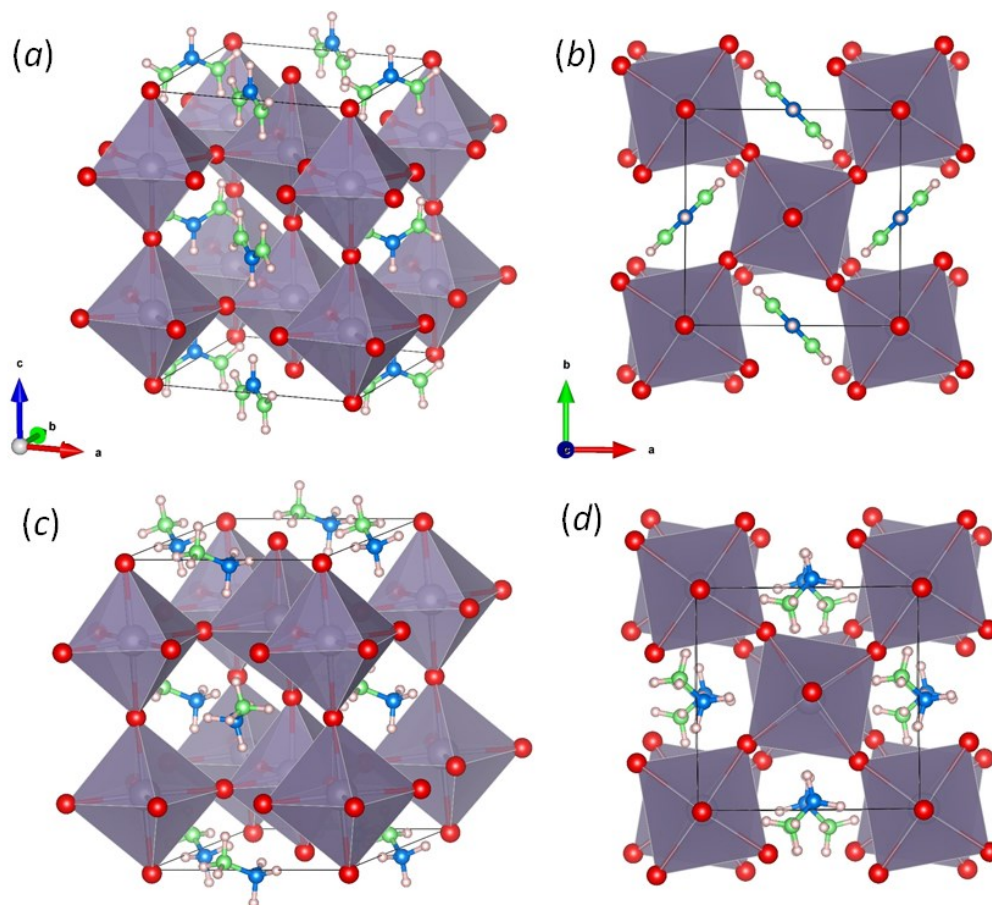
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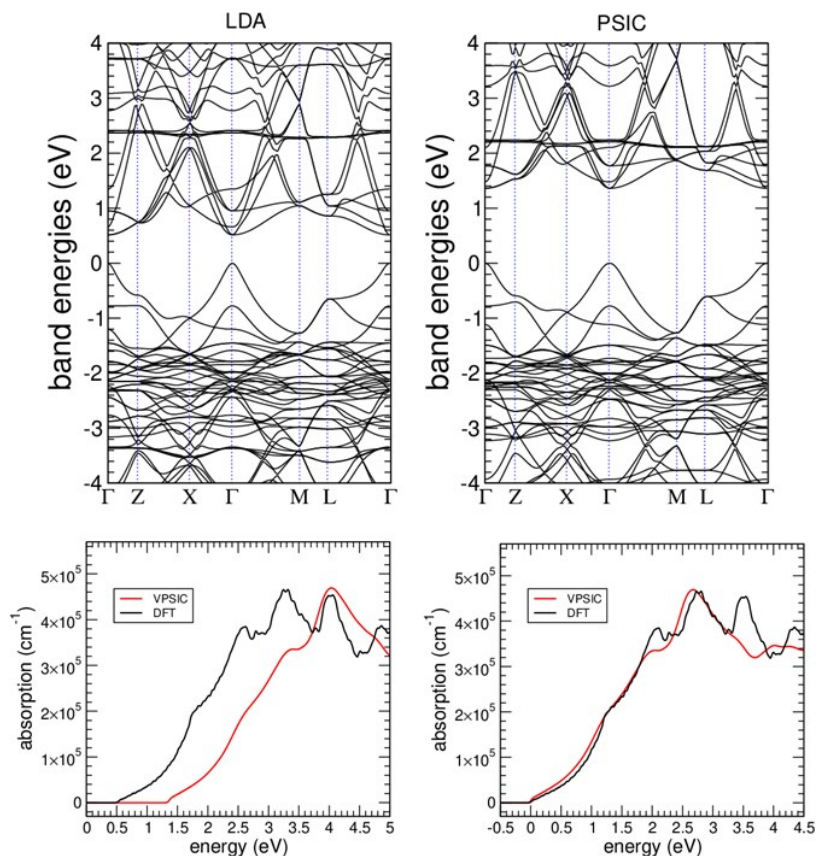
## S1. STRUCTURES



**Figure S1:** Calculated structures for stannates; (a) 3D view of FASI in the low-T tetragonal  $P4bm$  structure; (b) top view of the same FASI structure. (c) 3D view of MASI in the tetragonal  $I4cm$  structure. (d) top view of MASI. Color code: I (red), C (blue), N (green), Sn (gray), H (white)

## S2. VPSIC vs DFT BAND CALCULATIONS

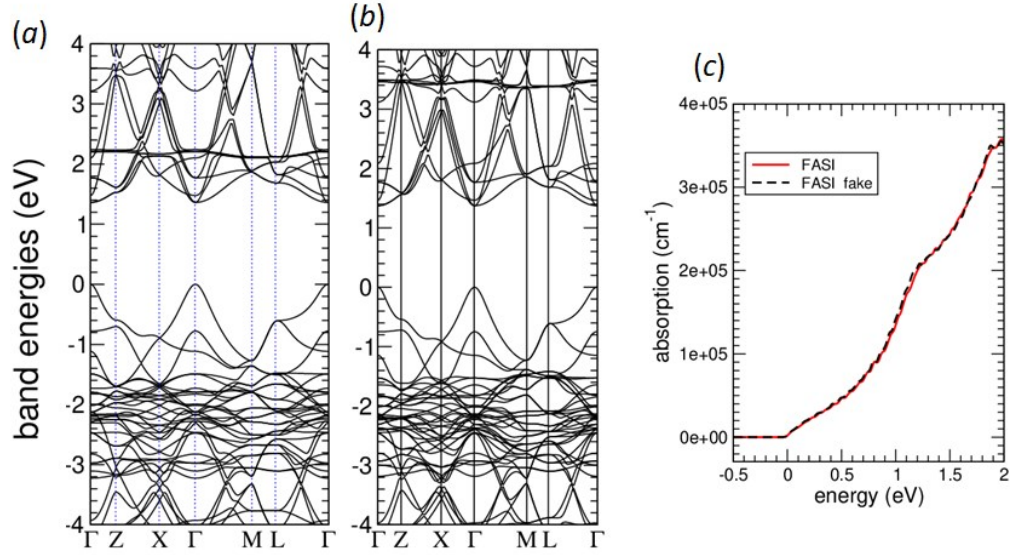
In Fig.S2 it is shown that absorption is not significantly affected by the theoretical approach; in fact, the difference between VPSIC and DFT description largely resides in the band gap, but, when rescaled at the same onset, absorption is very similar.



**Figure S2:** Calculated band energies and absorption spectrum for tetragonal FASI; (a): DFT-GGA calculation; (b): VPSIC calculation; (c) VPSIC vs DFT absorption; (d): same as (c) with the respective band gaps rescaled to zero

### S3. FA CONTRIBUTION TO ABSORPTION

The electronic structure of FASI shows an FA-derived flat band with 2p orbital character located about 0.7 eV above the CBB; the contribution of this state to absorption is arguably small, as a consequence of the small spatial overlap between this state and the Sn 4s orbitals which dominate the VBT; to prove this, in Fig.S3 we compare the FASI absorption with that of a fake electronic system obtained by artificially shifting the localized state much above in the energy; we see that the difference of the two is unnoticed at naked eye.

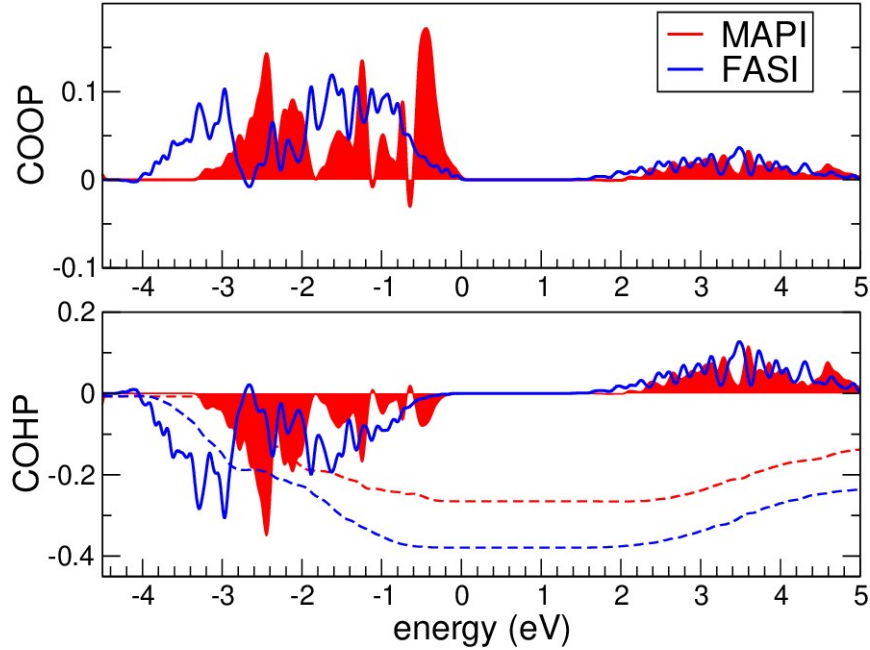


**Figure S3:** Calculated band energies and absorption cross section for FASI. (a) VPSIC calculation (b) fake FASI band energies obtained by adding an artificial upshift to the FA-derived conduction state placed 0.7 eV above the conduction bottom. (c) absorption for FASI and for the fake band structure shown in (b).

#### S4. COOP and COHP ANALYSIS

To analyse the character of Sn-I and Pb-I bonds, which critically determine the electronic properties in the band gap region, we calculate crystal orbital overlap population (COOP) and crystal overlap Hamiltonian population (COHP) for the perovskites under scrutiny. In our plane-wave plus ultrasoft pseudopotential approach, the orbital population matrix is obtained by projecting the Bloch states into an atomic orbital basis, and adding to that an augmented term associated to the core contribution of the ultrasoft atomic orbitals, as is usually done for the calculation of any expected value in the ultrasoft approach. In particular, in Fig. S4 we focus on the most important valence bond, i.e. that formed by Sn 5s and Pb 6s orbitals with I 5p orbital (more exactly  $p_x + p_y + p_z$ ). Red and blue curves are for MAPI and FASI respectively, and the dashed lined of corresponding colours are the integrated (ICOHP) functions. Both materials display a strong bonding character, but the integrated value up to zero energy (corresponding to

the VBT) is much larger for FASI; as described in the main text, the stronger binding energy of stannates should be primarily associated to the smaller octahedral tilting, favouring larger orbital overlap and stronger bonding.

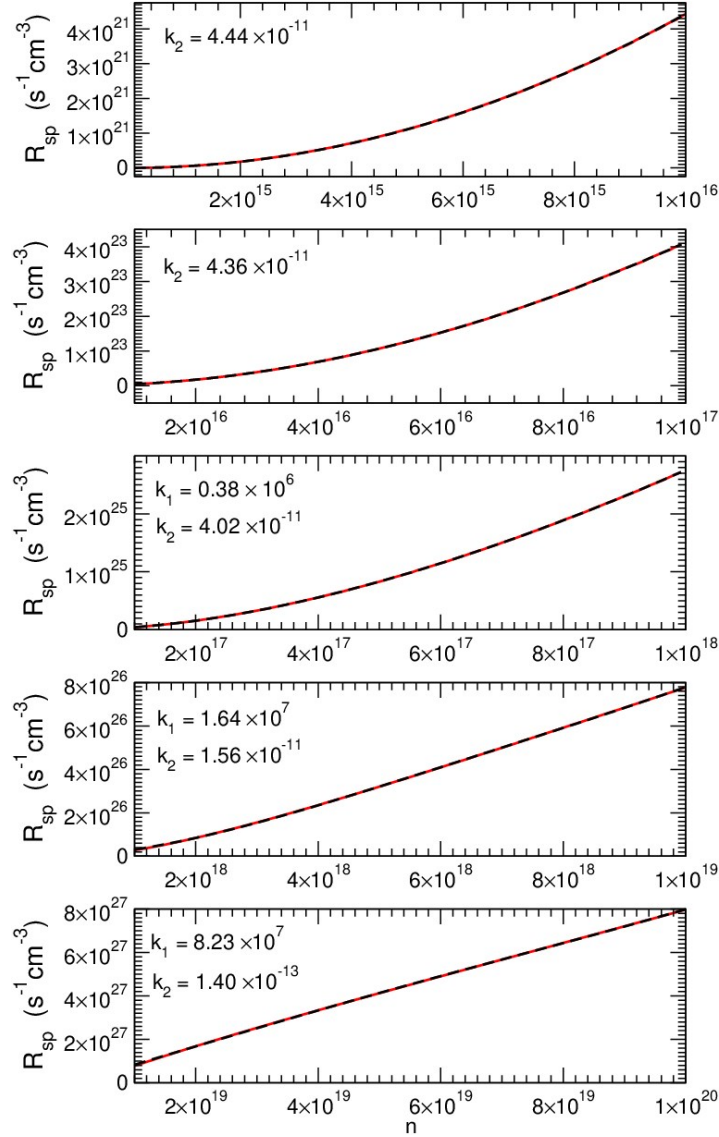


**Figure S4:** Calculated Crystal Orbital Overlap population (upper panel) and Crystal Orbital Hamiltonian population for Sn 5s - I 5p and Pb 6s - I 5p bonds of FASI and MAPI, respectively; dashed lines are the integrated COHP for the perovskite of corresponding colour. Zero energy is set to the valence band top of the two materials.

## S5. RADIATIVE RECOMBINATION RATE ANALYSIS

The  $R$  vs injected charge density ( $n$ ) analysis gives important insights on the mechanisms which govern the recombination process. To the aim, it is customary in literature to fit  $R(n)$  in a  $O(3)$  polynomial to extract coefficients for quadratic recombination, non-radiative linear trapping and cubic Auger effect. However, this procedure may not be extremely accurate, insofar as band-to-band recombination itself may deviate from a purely quadratic behavior; in particular this happens if the fit is operated in a large charge density interval; a more accurate way is first considering radiative recombination alone, and fitting  $R$  in small  $n$  intervals. In Fig.S5 the

recombination rate for FASI is broken apart and separately analyzed in different density ranges, reported in different panels.



**Figure S5:** Radiative recombination rate of tetragonal FASI calculated in different intervals of injected charge  $n$  ; red line: calculations according to VRS approach; black dashed line: quadratic interpolation, whose coefficients are reported in the figure;  $k_1$  and  $k_2$  are linear and quadratic terms, respectively.

We see that up to  $n \sim 10^{17} \text{ cm}^{-3}$ ,  $R$  can be fitted well with a single quadratic term,  $k_2 = 4.4 \cdot 10^{-11} \text{ s}^{-1} \text{ cm}^{-3}$  so in this charge region the radiative recombination is purely bimolecular; between  $10^{17} \text{ cm}^{-3}$  and  $10^{18} \text{ cm}^{-3}$  a linear contribution starts to set in, with  $k_2$  substantially unchanged; this is a

transition region between quadratic and linear regime. Above  $n \sim 10^{18} \text{ cm}^{-3}$  the linear term becomes increasingly important, and becomes dominant above  $n \sim 10^{19} \text{ cm}^{-3}$ . In this high density regime, the radiative lifetime is  $\tau_{\text{rad}} = 1/k_1 \sim 12 \text{ ns}$ . It should be noticed that these values refer to the assumption of a moderate Urbach energy  $U = 15 \text{ meV}$  at the absorption onset. For the larger  $U = 32 \text{ meV}$  measured for FASI,  $\tau_{\text{rad}}$  may be an order of magnitude smaller (see main text).