Electronic Supporting Information

“Mixed Formamidinium-Methylammonium Lead Iodide perovskite from first-principles: Hydrogen-bonding impact in the electronic properties”

Maximiliano Senno[1] and Silvia Tinte[1,2]

[1] Instituto de Física del Litoral, CONICET - Universidad Nacional del Litoral, Güemes 3450 (3000) Santa Fe, Argentina.

[2] Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (3000) Santa Fe, Argentina

Correspondence e-mail: silvia.tinte@santafe-conicet.gov.ar

Total-energy curves as a function of the cation rotation for MA and FA.

Inspection of the total-energy landscape when the inorganic PbI_3-octahedron network is frozen out at their hypothetical high–symmetry structure and only one molecule is rotated around each of the three Cartesian axis keeping its center fixed at the 1a Wyckoff position, whereas the others seven molecules remain pointing along [001].

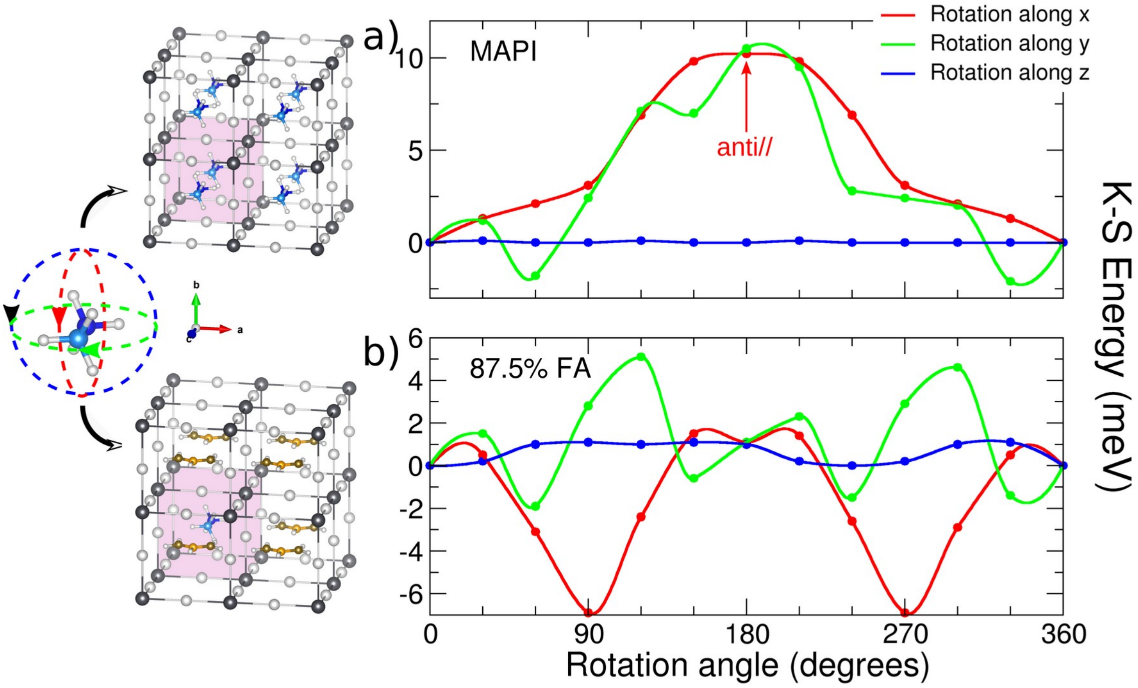

Figure S1: Total-energy surface when one MA cation rotates along the three Cartesian directions (a) in a MA environment (pure MAPI) and (b) in a FA environment (system with x=87.5% of FA content). Rotations of MA cations induce energy changes of a few meV. In pure MAPI the antiferroelectric ordering (maximum at 180°) is completely ruled out in complete agreement with previous reports.[1] In an environment rich in FA (x=87.5 % alloy), MA cations prefer to be oriented perpendicular to the planes of FA cations as indicated by the minimum at 90°.

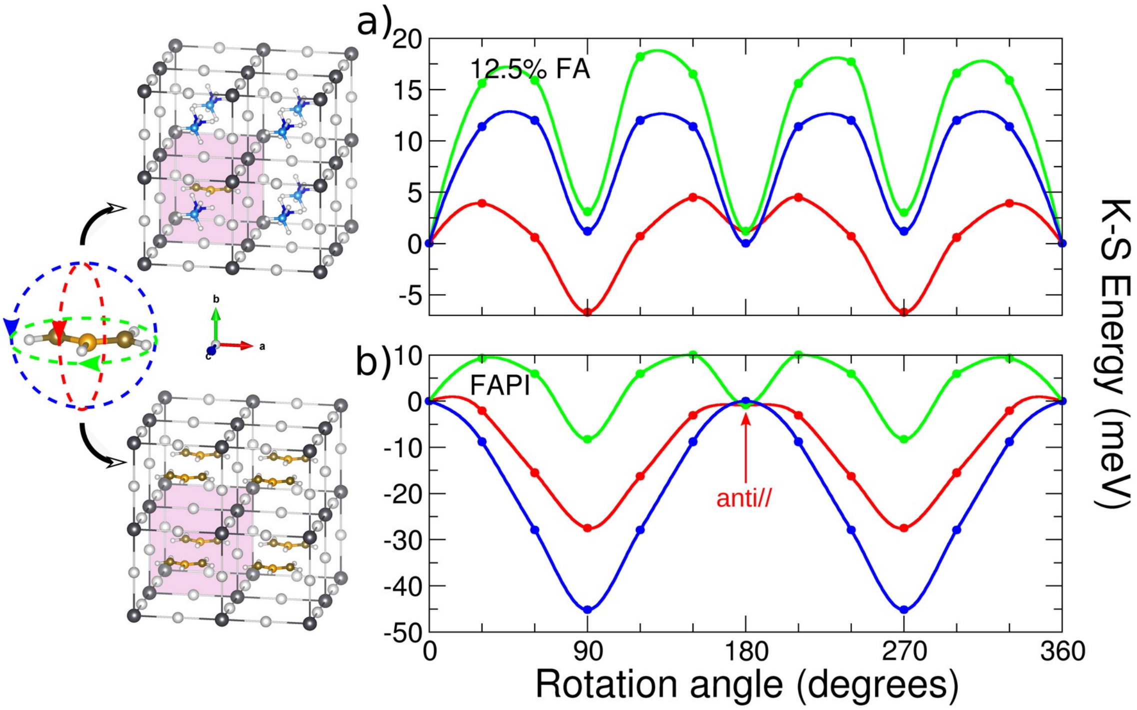

Figure S2: Total-energy surface when one FA cation rotates along the three Cartesian directions (a) in a MA background (system with x=12.5% of FA content) and (b) in a FA background (pure FAPI). Rotations of FA cations induce energy changes around 20-50 meV. Interestingly all configurations of minimum energy correspond to the FA cation oriented 90° with respect to its cationic nearest neighbors. In a MA-rich environment (x=12.5%) FA cations prefer to orient perpendicular to MA dipoles, as already seen by rotating the MA cation in the x=87.5% system.

Inorganic framework response to the ordering of cationic orientations

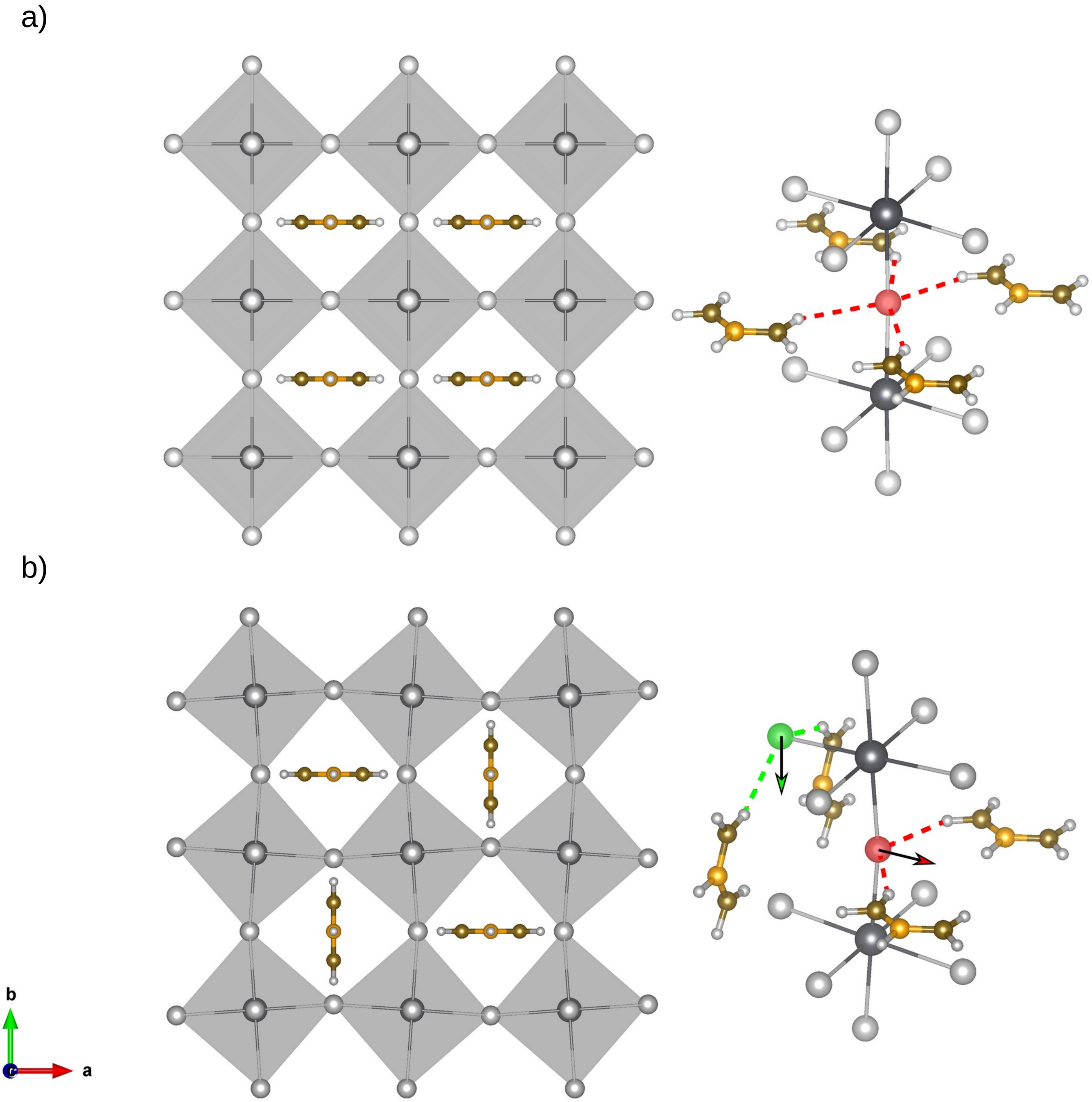

Figure S3: Two completely relaxed configurations of pure FAPI that were initialized with the FA cations: (a) parallel and (b) perpendicular to each other. They show no octahedron tilting and $a^0a^0c^+$ tilt pattern, respectively. The latter is our lowest energy structure. In the structure with all FAs aligned in parallel, iodine anions coplanar to cations FA are pulled equally in all four directions by the respective hydrogen bonds. As a result, there are no iodine net displacements and hence octahedra rotations are inhibited. In our lower energy FAPI structure, iodine anions are unidirectionally dragged towards two FA cations to maintain the $I \cdots H_{N\text{-}FA}$ bond length inducing octahedron rotations.

Effective ionic radius of mixed A-site cation perovskites and tolerance factors.

FA Fraction (%)	0	12.5	25	37.5	50	62.5	75	87.5	100
r_{eff}	2.17	2.22	2.26	2.31	2.35	2.40	2.44	2.49	2.53
t	0.91	0.92	0.93	0.94	0.95	0.96	0.97	0.98	0.99

Table S1: Effective ionic radius of mixed A-site cation perovskites, and its tolerance factors.

Mixing energy ΔE of $FA_xMA_{(1-x)}PbI_3$ perovskites

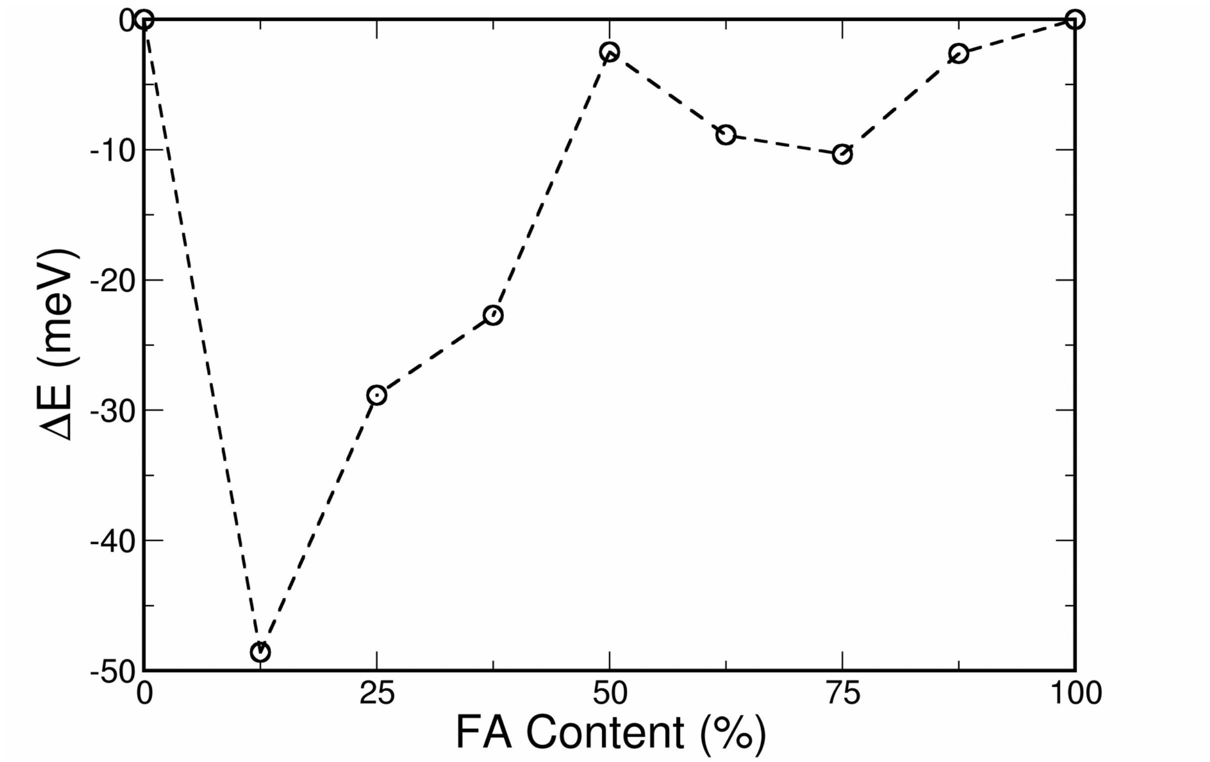

Figure S4: Mixing energy ΔE of every composition. Note that all mixed perovskites have negative ΔE values, which means that are more stable than the pure compounds. The minimum observed at the composition x=12.5% in particular would suggest it as the most stable mixture. However, a precise trend would require analyzing a statistical ensemble for each composition and not just one structure as done here, which is out of the scope of this work.

PBEsol+SOC band structures of mixed halide perovskites near the R(½,½,½) point.

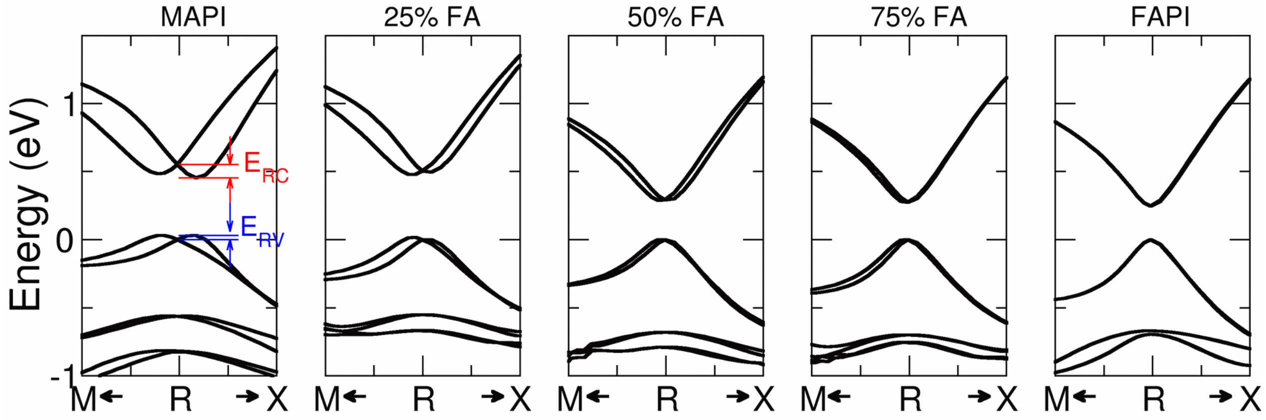

Figure S5: PBEsol+SOC band structures near the R high-symmetry point in the BZ of mixed halide perovskites. MAPI shows large Rashba-type effect, which has been previously related with the parallel alignment of MA cations, resulting in a net displacement of the Pb atoms from the octahedron center[5]. This effect dilutes as the FA content rises. The magnitude of the Rashba-type splitting is measured as the energy difference ERC between the conduction band value at the R-point and the CBM, and as the energy difference ERV between the valence band value at the R-point and the VBM.

DOS and electronic charge density contours for $MA_{0.375}FA_{0.625}PbI_3$.

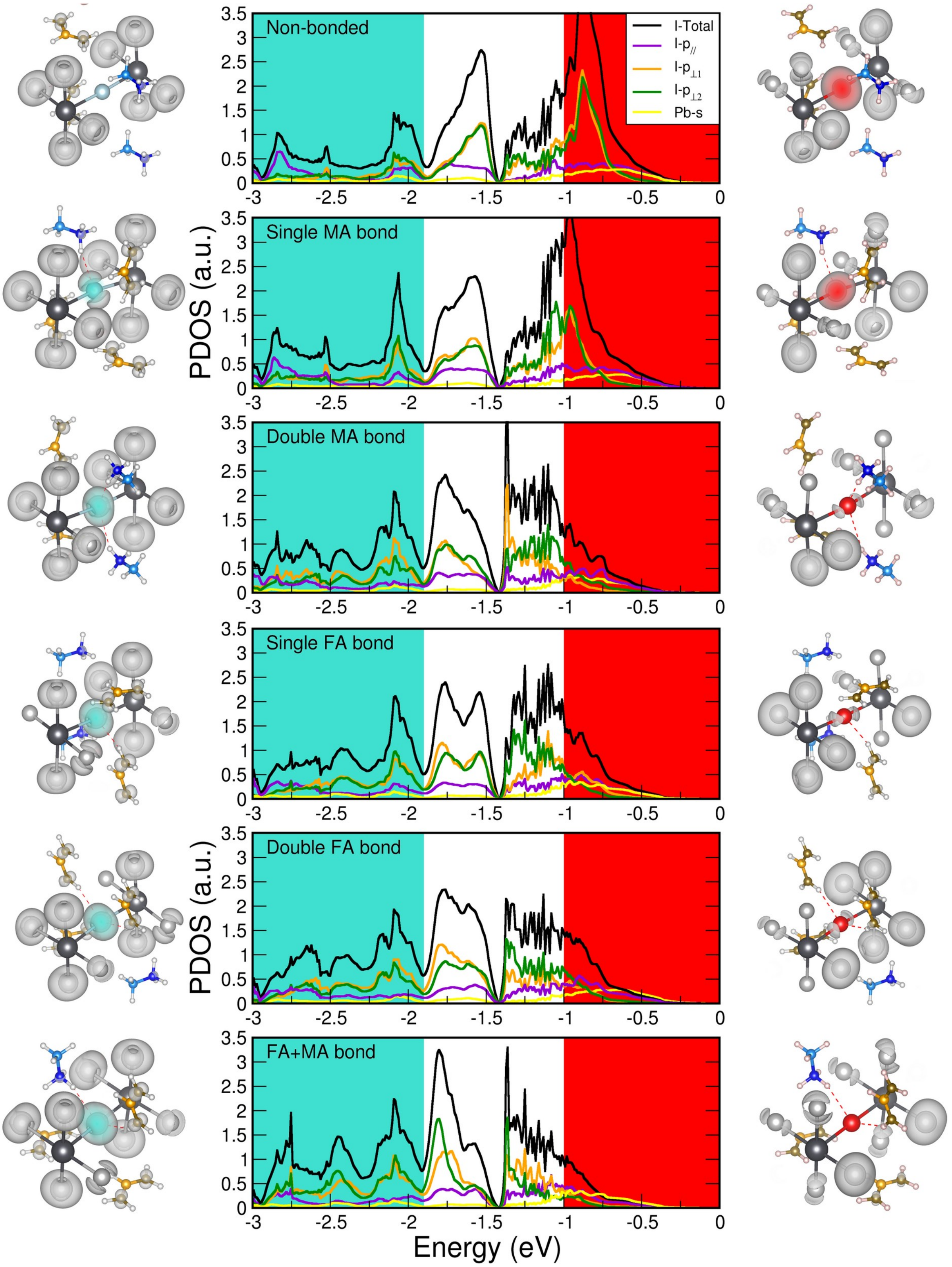

Figure S6: Density of States for six selected I in the $MA_{0.375}FA_{0.625}PbI_3$ solid solution with the Fermi level sets to zero (center). Projected DOS on the I-5p orbitals which are spanned along the parallel

(I-5p$_{//}$) and perpendicular (I-5p$_{\perp}$) direction to the Pb-I-Pb bond axis. From top to bottom: unbonded iodine, I bonded to one and to two MA cations, to one and two FA cations, and to one MA and one FA cations. (Top and bottom figures are also shown in the main text). Electronic charge densities contours corresponding to the shaded energy regions of (-3,-1.8) eV (left) and (-1,0) eV (right) with an isovalue of 0.004, where only the electronic charge around the selected iodine anions are colored. From no bonded to FA+MA bonded iodine anions, a progressive redistribution of I-5p$_{\perp}$ states to lower energies is observed. The peak near 1 eV decreases when the I is bonded to two MA cations, or one and two FA cations.

Accordingly, the electronic charge densities in the same energy region shows an quasi-spherical electronic cloud which contracts perpendicularly to Pb-I-Pb bond axis as the number of H-bonds rises. The opposite trend is verified in the energy region of (-3,-1.8) eV, where the I-5p$_{\perp}$ states distribution increases together with the number of H-bonds, as well as the electronic charge densities do.

Energy distribution of the pDOS curves projected on I-5p$_{//}$ and I-5p$_{\perp}$ orbitals.

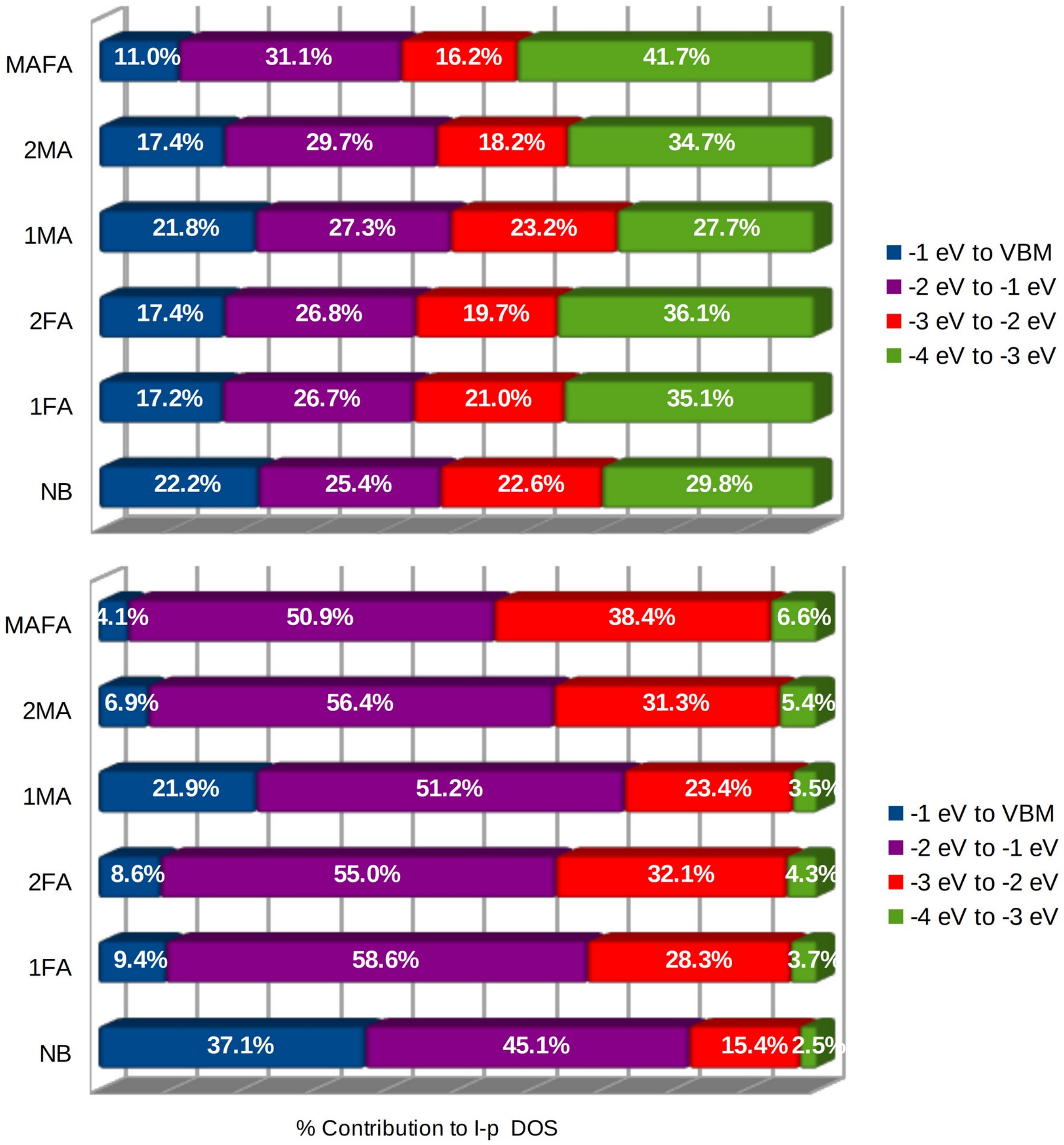

Figure S7: Integrals in blocks of 1 eV of the pDOS curves on the I-5p$_{//}$ (top graphic) and average of I-5p$_{\perp}$ (bottom graphic) plotted in Figure S4, presented as percentage of the total I-5p orbital for each I. I-5p$_{//}$ areas barely change with the increase of H-bonds, although the first region slightly decreases from 22% to 17% or even 11% in MA+FA case. Instead, the areas of the I-5$p_\perp$ orbitals are dramatically affected with the number of H-bonds, a severe drop from 37% to below 10% is observed in the energy interval of (-1,0) eV, whereas the areas in the region of (-3,-2) eV increase from 15% to ~ 30%. These results show how the sensitiveness of the I-5$p_\perp$ to H-bonds notably affects the redistribution of electronic states.

References

1 A. Mattoni, A. Filippetti, M. I. Saba, and P. Delugas, *J. Phys. Chem. C* 2015, 119, 17421–17428.

2 V. C. A. Taylor, D. Tiwari, M. Duchi, P. M. Donaldson, I. P. Clark, D. J. Fermin, and T. A. A. Oliver, *J. Phys. Chem. Lett.* 2018, 9, 895–901.

3 A. Sher, M. van Schilfgaarde, A.-B. Chen and W. Chen. *Phys. Rev. B: Condens. Matter Mater. Phys.* 1987, 36, 4279.

4 F. Brivio, C. Caetano and A. Walsh. *J. Phys. Chem. Lett.* 2016, 7, 6, 1083–1087

5 L. Leppert, S. E. Reyes-Lillo, and J. B. Neaton, *J. Phys. Chem. Lett.,* 2016, 7, 3683–3689.