First Principles Modeling of Mixed Halide Organometal Perovskites for Photovoltaic Applications

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SUPPORTING INFORMATION

1. Starting configurations for structure 1 and 2

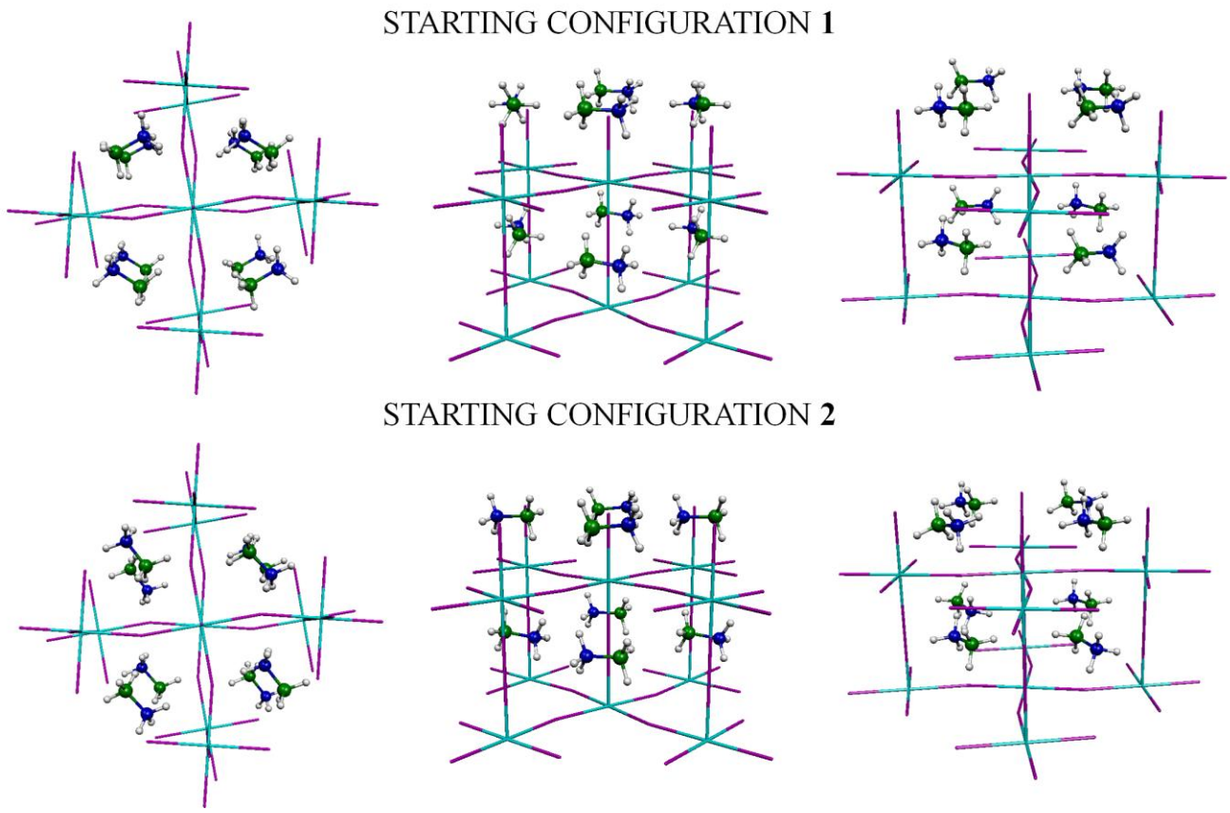

Figure S1. Starting configuration for structure 1 and 2. The X = I case is reported from three different points of view: XY plane, left; YZ plane, center; XZ plane, right.

2. Computational Calibration

To further check the adequacy of the method we tested a more extended Monkhorst–Pack grid of 6x6x6 and 8x8x8 for the species $CH_3NH_3PbI_3$, obtaining converging results in term of relative stability and band gap, see Table S1.

Table S1. Relative stability and optical band gap for $CH_3NH_3PbI_3$ calculated using different Monkhorst–Pack grid at 25/200 Ry as cutoff.

	25/200 Ry	**Relative Energy [eV]**			**Band Gap [eV]**		
	Grid	**4x4x4**	**6x6x6**	**8x8x8**	**4x4x4**	**6x6x6**	**8x8x8**
$CH_3NH_3PbI_3$	**1**	**0.00**	**0.00**	**0.00**	**1.66**	**1.66**	**1.66**
	2	0.06	0.06	0.06	1.63	1.63	1.63

To further validate the accuracy of the employed method, a test using 35-240 Ry as plane-wave basis set cutoffs has been performed on the $CH_3NH_3PbI_2Cl$ system for the structure **1** and **2**. As shown in Table S2, the relative stability and the optical band gap calculated using different plane-wave basis set cutoffs are similar.

Table S2. Relative stability and the optical band gap of $CH_3NH_3PbI_2Cl$ calculated using different plane-wave basis set cutoff with a 4x4x4 k-point grid.

		Relative Energy [eV]		**Band Gap [eV]**	
	Cut off (Ry)	**25-200**	**35-240**	**25-200**	**35-240**
$CH_3NH_3PbI_2Cl$	**1**	0.03	0.03	1.85	1.83
	2	**0.00**	**0.00**	**1.64**	**1.64**

Table S3. Relative stability and the optical band gap calculated using a 6x6x6 Monkhorst–Pack grid at 35/240 Ry cutoff.

	35/240 Ry	**Relative Energy [eV]**	
$CH_3NH_3PbI_3$	**Grid**	**6x6x6**	**6x6x6**
	1	**0.00**	**1.65**
	2	0.06	1.63

Table S4. Relative stability and the optical band gap of $CH_3NH_3PbI_2Br$ and $CH_3NH_3PbI_2Cl$ calculated with a 25/200 cutoff and a 4x4x4 k-point grid, comparing experimental lattice parameters with calculated ones.

	Structure	**a**	**b**	**a**	**Erel**	**BG**	**a**	**b**	**b**	**Erel**	**BG**
PbI_2Br	**1**	8.86	8.86	11.83	**0.00**	**1.89**	8.86	8.80	11.80	**0.00**	**1.89**
	2				0.21	1.63	8.78	9.04	11.75	0.16	1.63
PbI_2Cl	1	8.86	8.86	11.24	0.03	1.85	8.92	8.85	11.16	0.09	1.89
	2				**0.00**	**1.64**	8.87	9.01	11.08	**0.00**	**1.63**

3. Density of States for all investigated systems

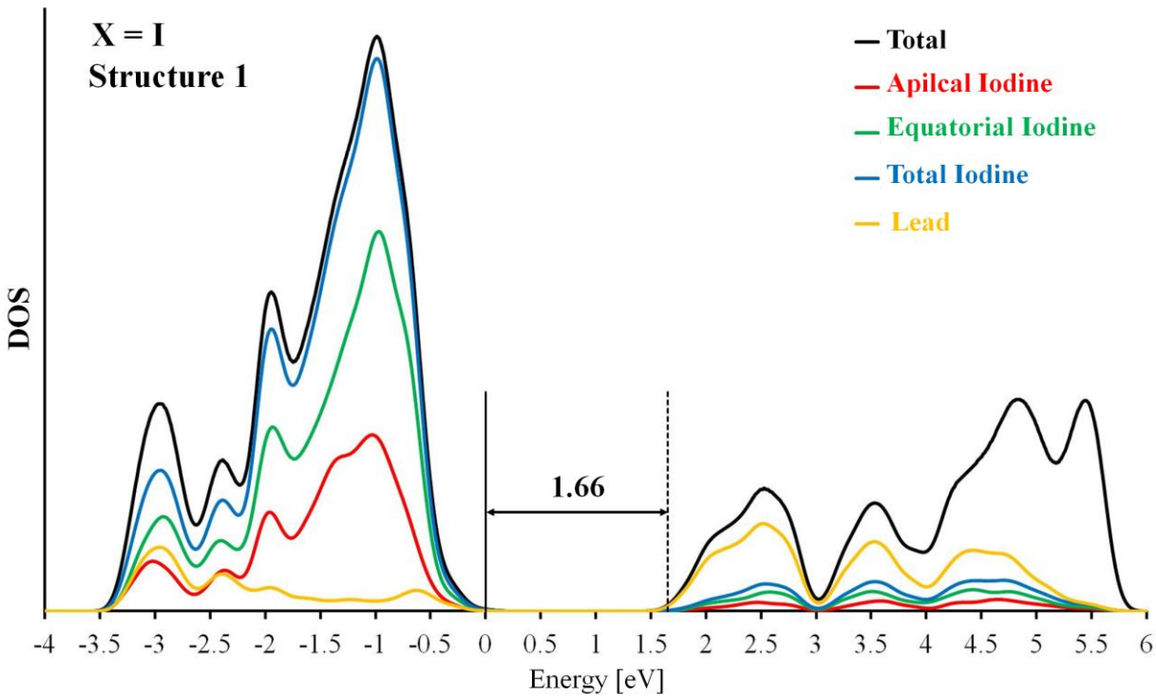

Figure S3. PDOS of the PbI_3 structure 1. Energy values are scaled setting the HOMO level as zero.

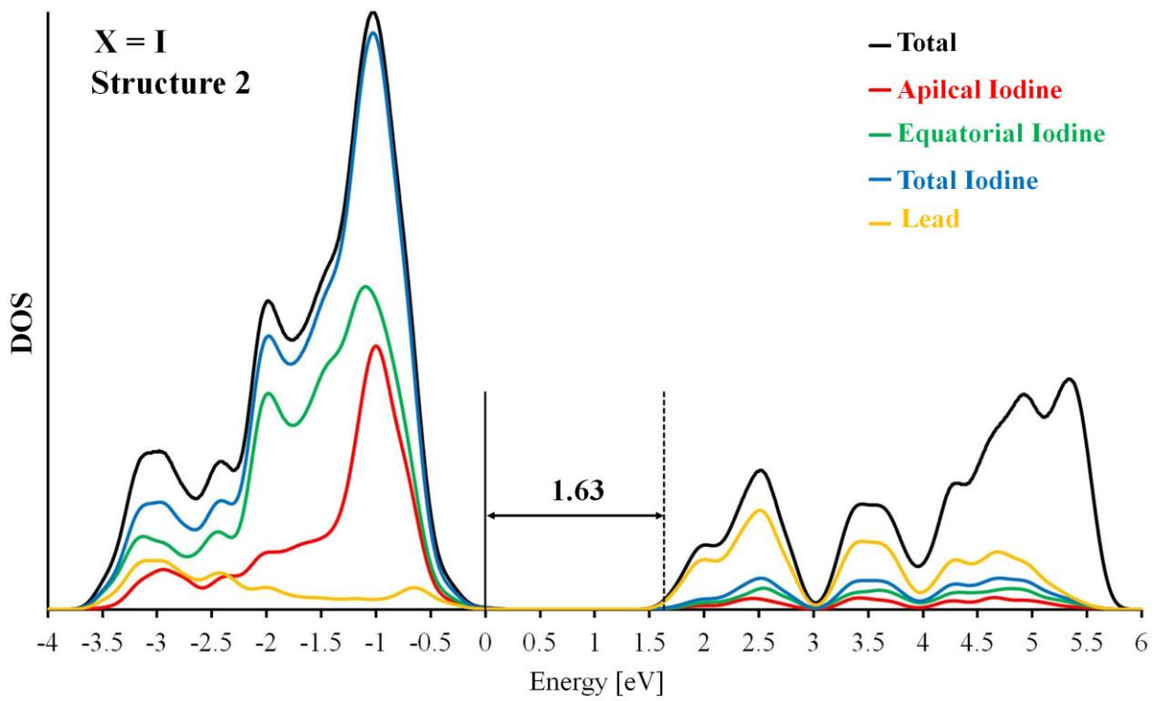

Figure S4. PDOS of the PbI_3 structure 2. Energy values are scaled setting the HOMO level as zero.

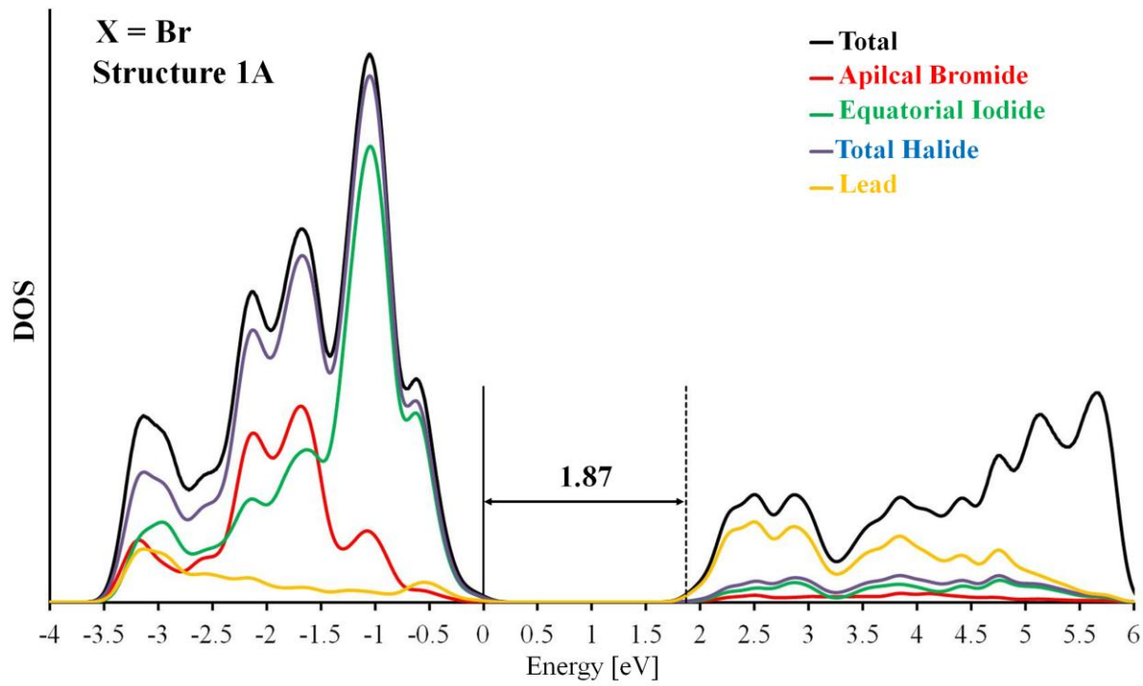

Figure S5. PDOS of the PbI_2Br structure 1A. Energy values are scaled setting the HOMO level as zero.

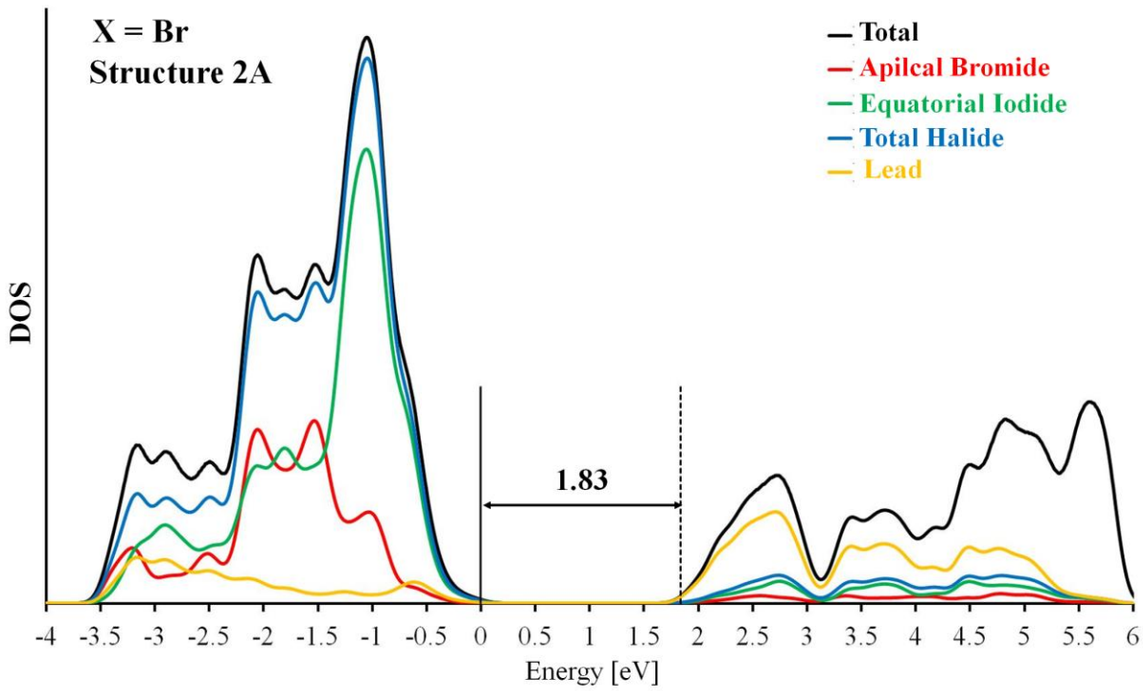

Figure S6. PDOS of the PbI_2Br structure 2A. Energy values are scaled setting the HOMO level as zero.

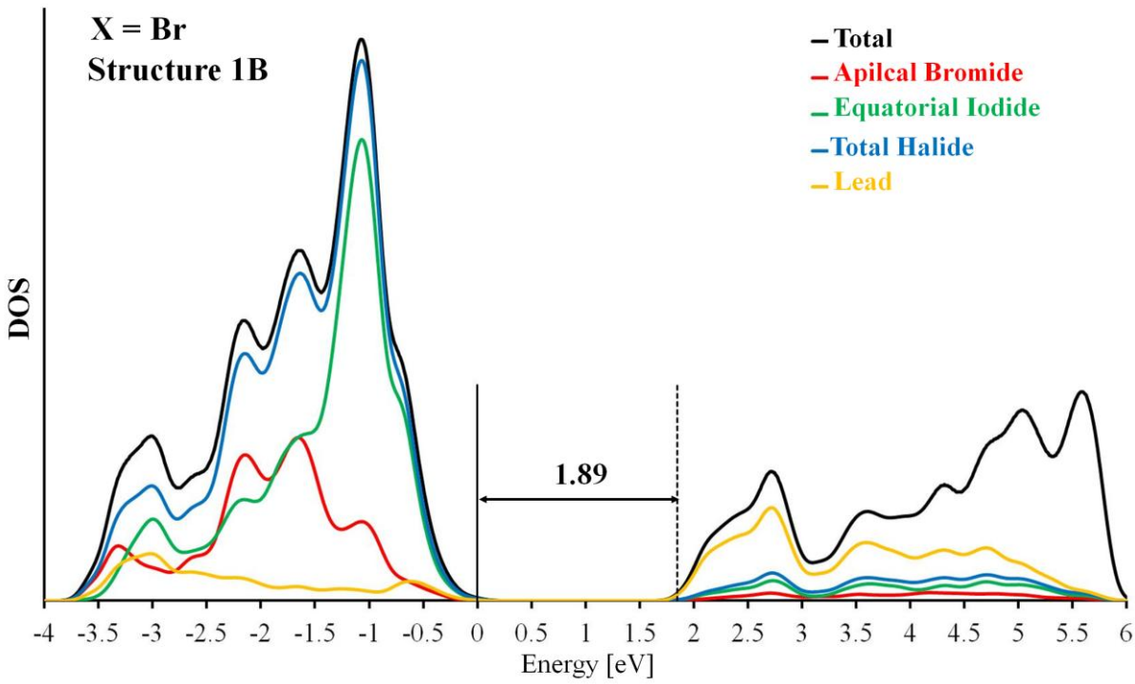

Figure S7. PDOS of the PbI_2Br structure 1B. Energy values are scaled setting the HOMO level as zero.

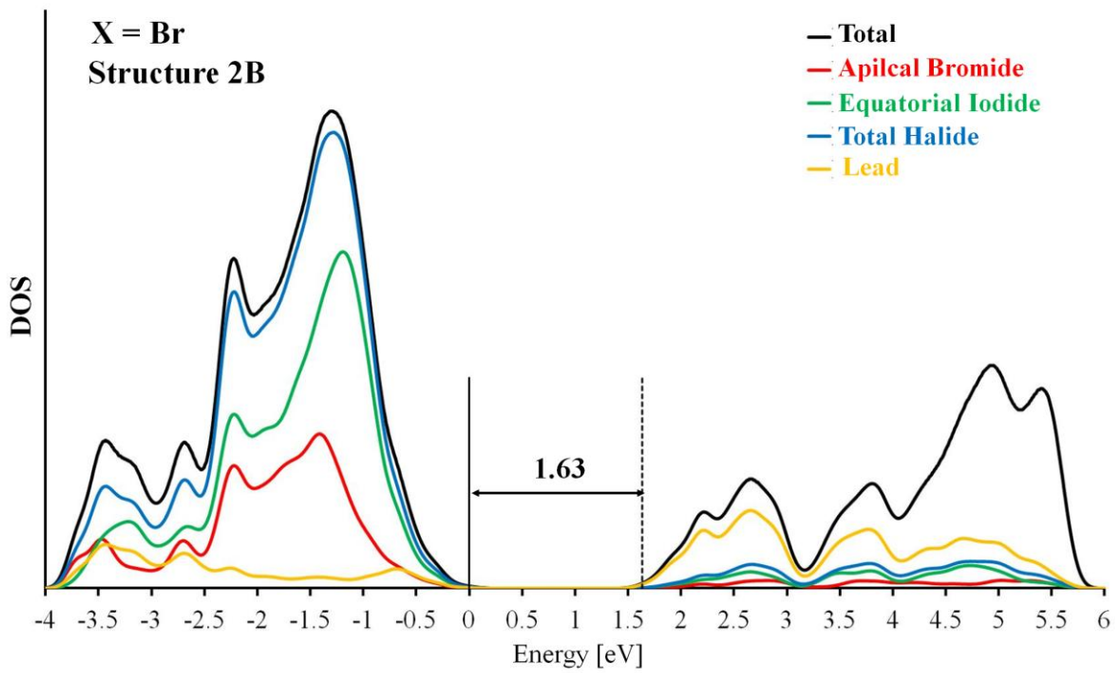

Figure S8. PDOS of the PbI_2Br structure 2B. Energy values are scaled setting the HOMO level as zero.

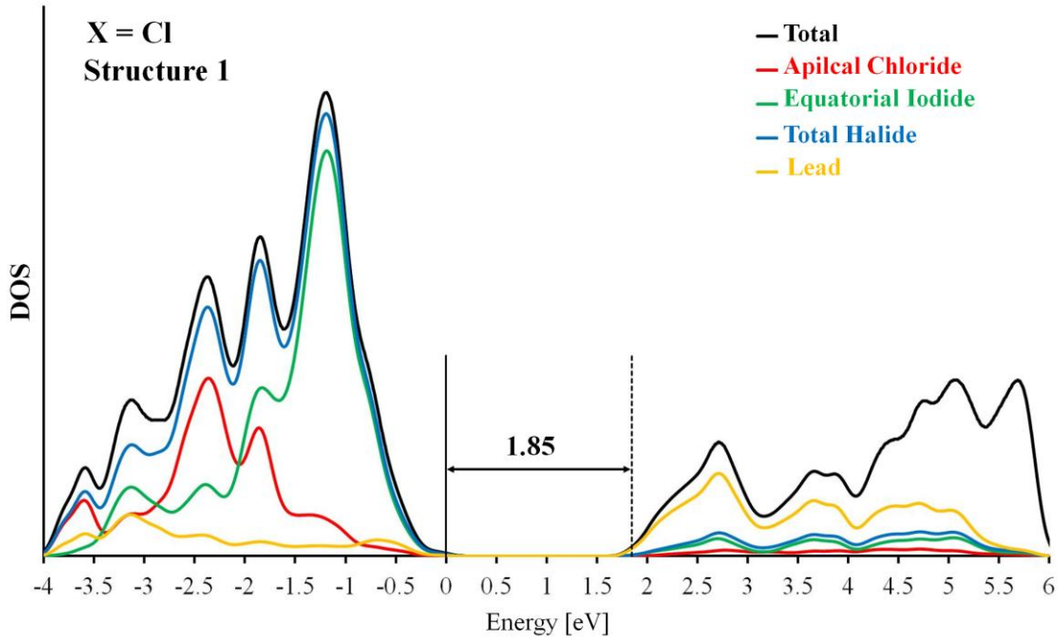

Figure S9. PDOS of the PbI_2Cl structure 1. Energy values are scaled setting the HOMO level as zero.

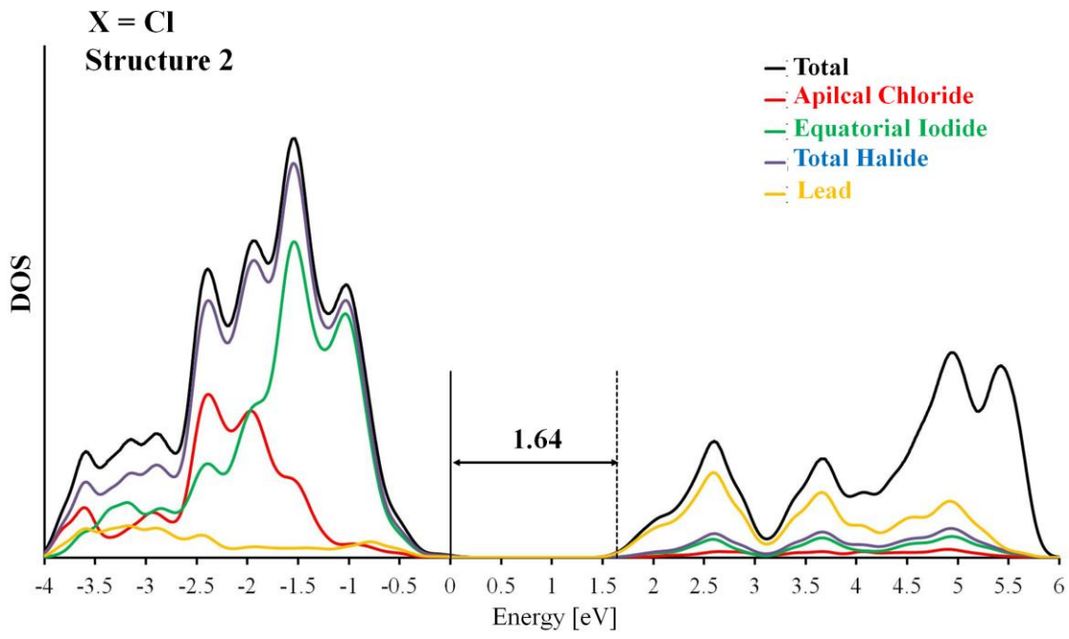

Figure S10. PDOS of the PbI_2Cl structure 2. Energy values are scaled setting the HOMO level as zero.

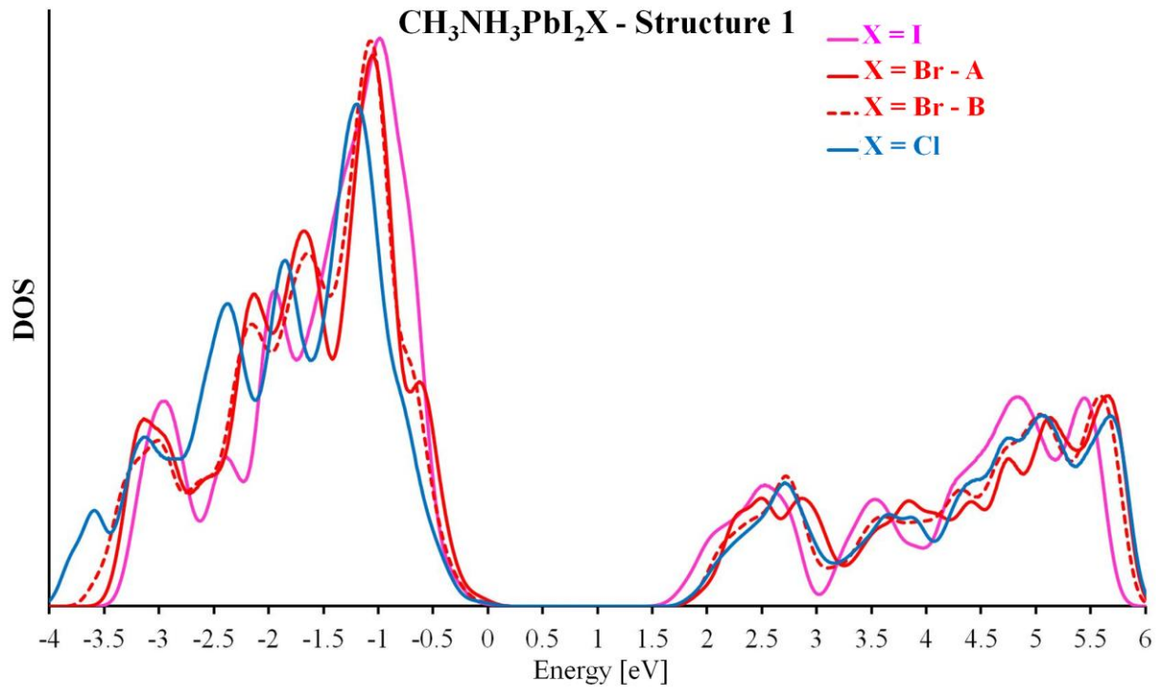

Figure S11. Total DOS for X = I, Br and Cl in structure 1. Energy values are scaled setting the HOMO level as zero.

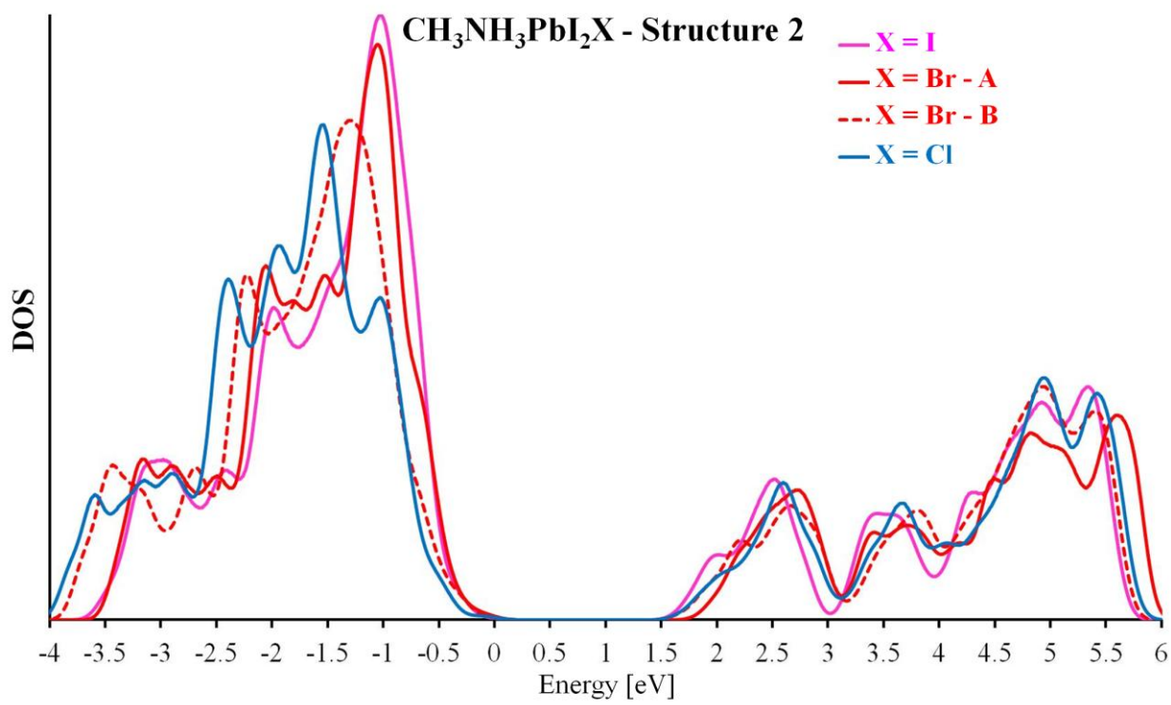

Figure S12. Total DOS for X = I, Br and Cl in structure 2. Energy values are scaled setting the HOMO level as zero.

4. Bands structure analysis

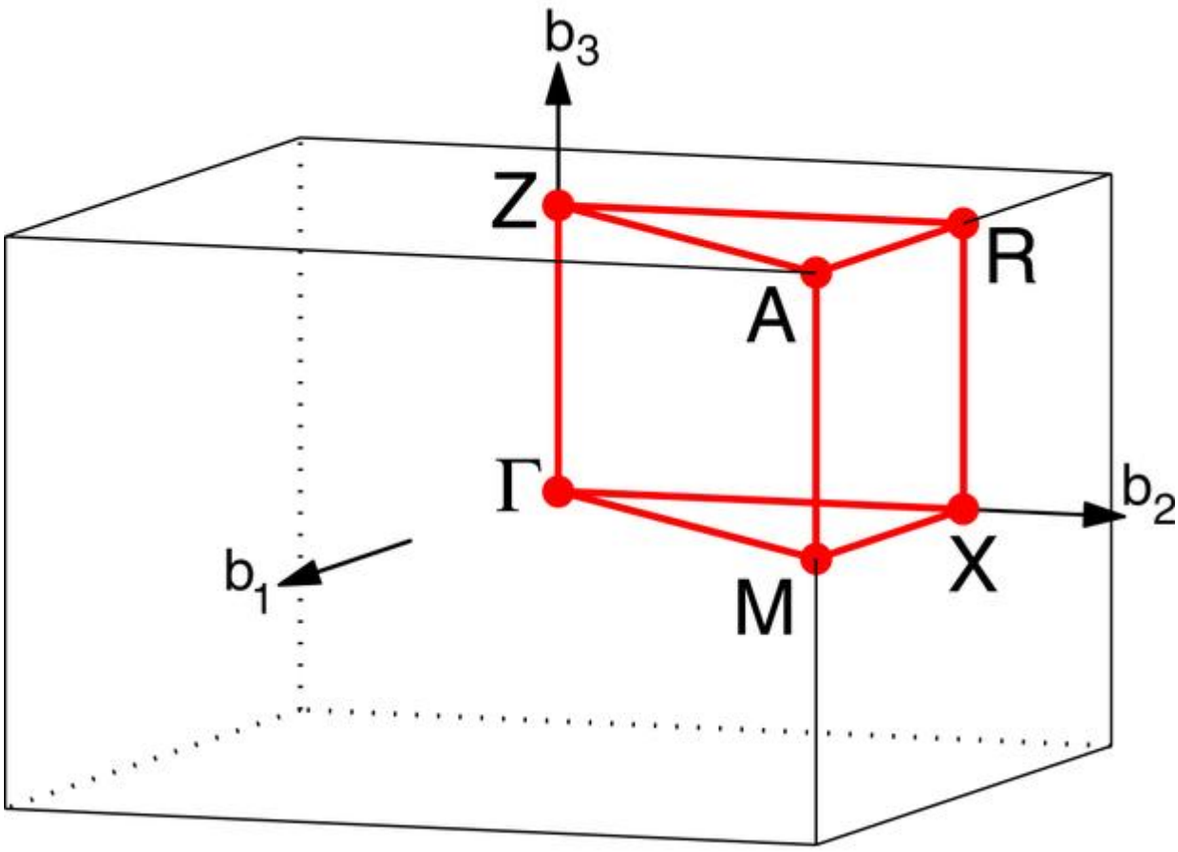

Figure S13. Scheme of the Brillouin Zone for a tetragonal lattice. Adapted from W. Setyawan and S. Curtarolo, Computational Materials Science, 2010, 49, 299.

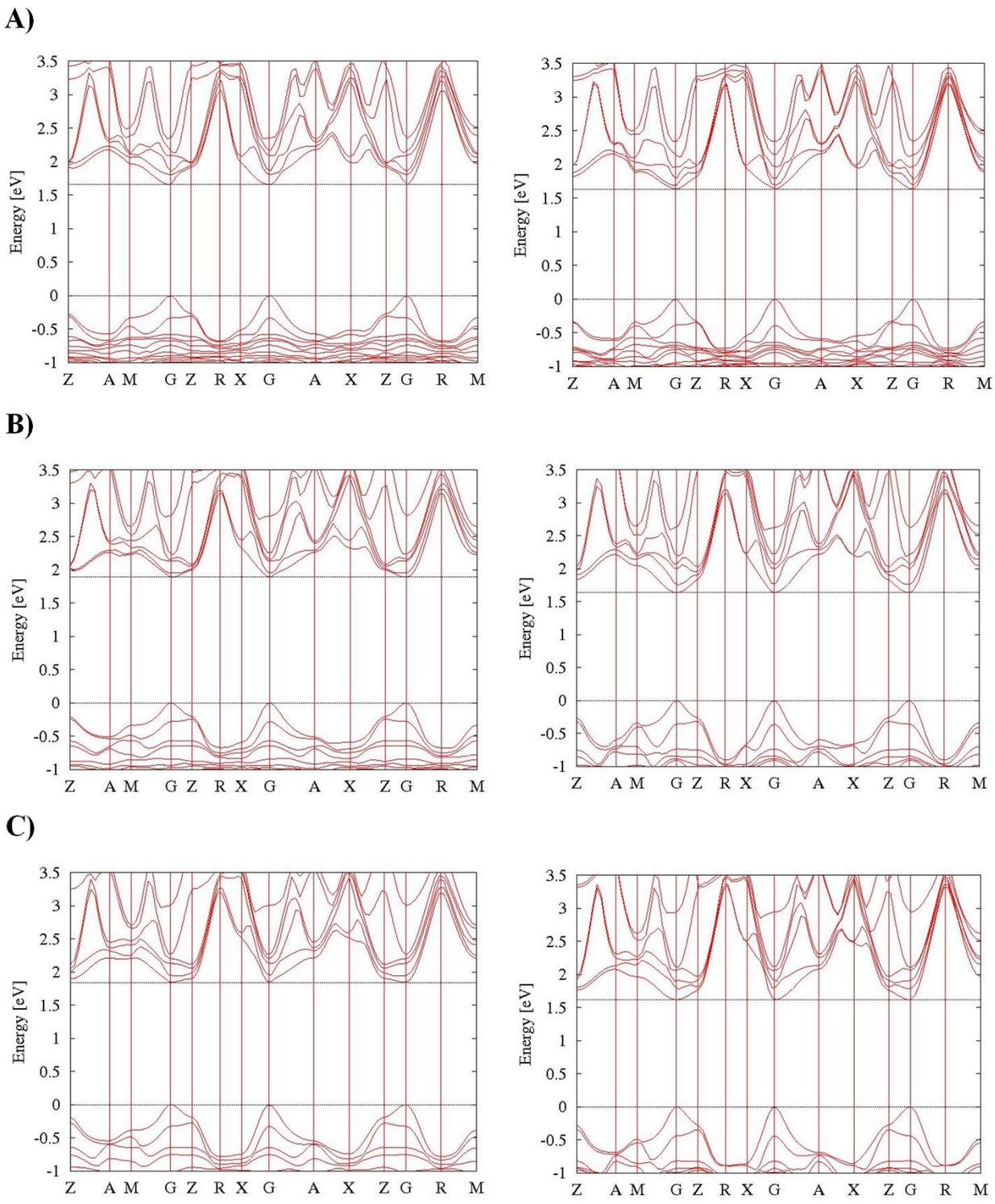

Figure S14. Bands structure of the investigated systems: (A) $CH_3NH_3PbI_3$ for structure 1 (left) and 2 (right); (B) $CH_3NH_3PbI_2Br$ for structure 1B (left) and 2B (right); (C) $CH_3NH_3PbI_2Cl$ for structure 1 (left) and 2 (right). Energy values are scaled setting the HOMO energy as zero.

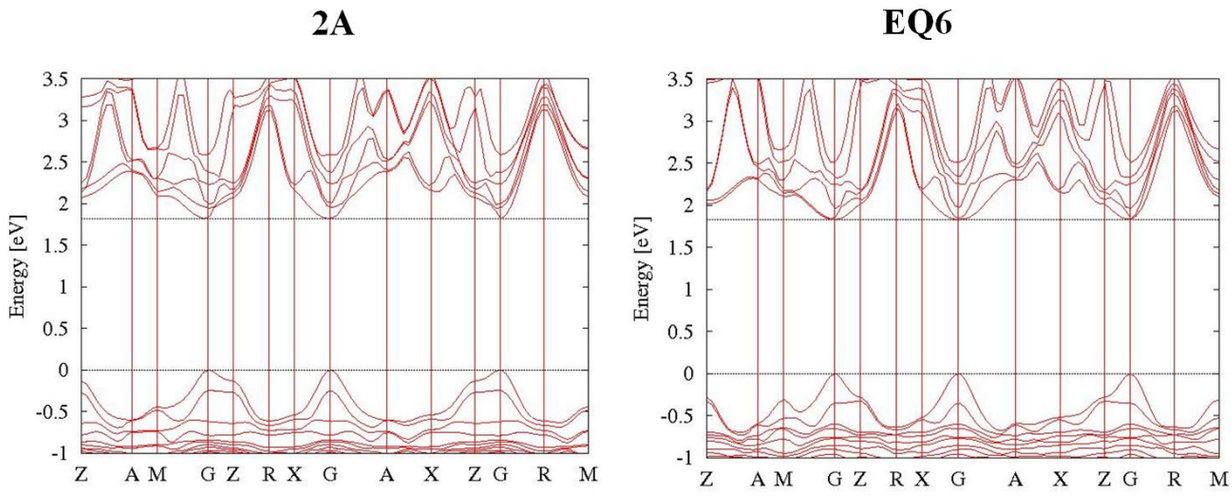

Figure S15. Bands structure of $CH_3NH_3PbI_2Br$ for structure 2A (left) and EQ6 (right) are shown. Energy values are scaled setting the HOMO energy as zero.