Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Does the Rashba splitting in $CH_3NH_3PbBr_3$ arise from 2 $\times$ 2 surface reconstruction?

Electronic Supplementary Information

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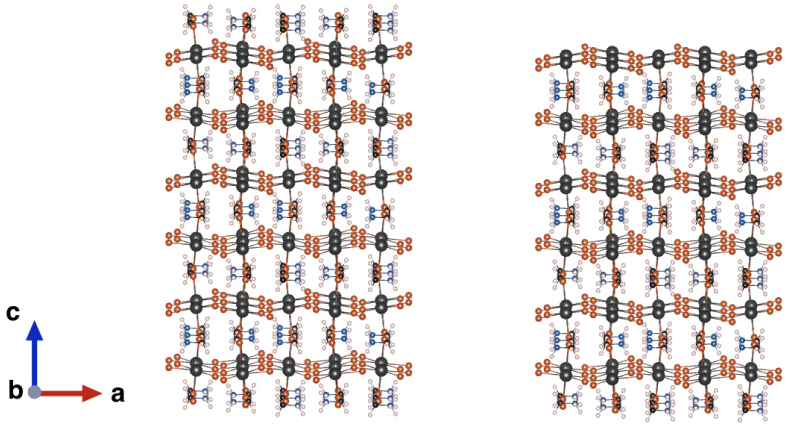

Fig. S1 (001) slabs terminated with MA-Br (left) and Pb-Br (right). The most stable surface is found to be the MA-Br terminated one [Komesu *et al.*, *J. Phys. Chem. C* **2016**, *120*, 21710].

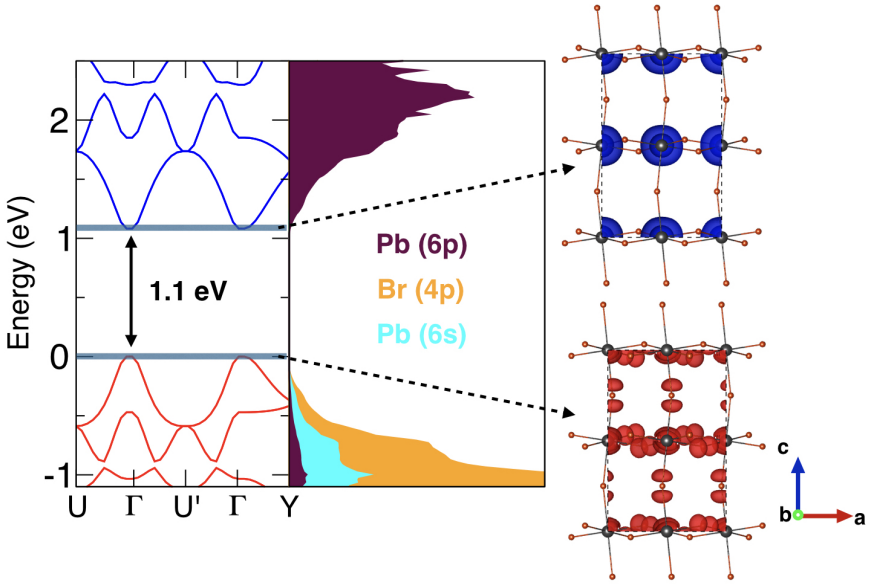

Fig. S2 Electronic properties of bulk $MAPbBr_3$. (left panel) Electronic dispersion evidencing a direct band gap (1.1 eV) at the center of the Brillouin Zone (Γ) computed with SOC. (middle panel) Projected densities of states. (right panel) LDOS illustrating the major contribution of Br(4p) and Pb(6s) in VBM and Pb(6p) in CBM.

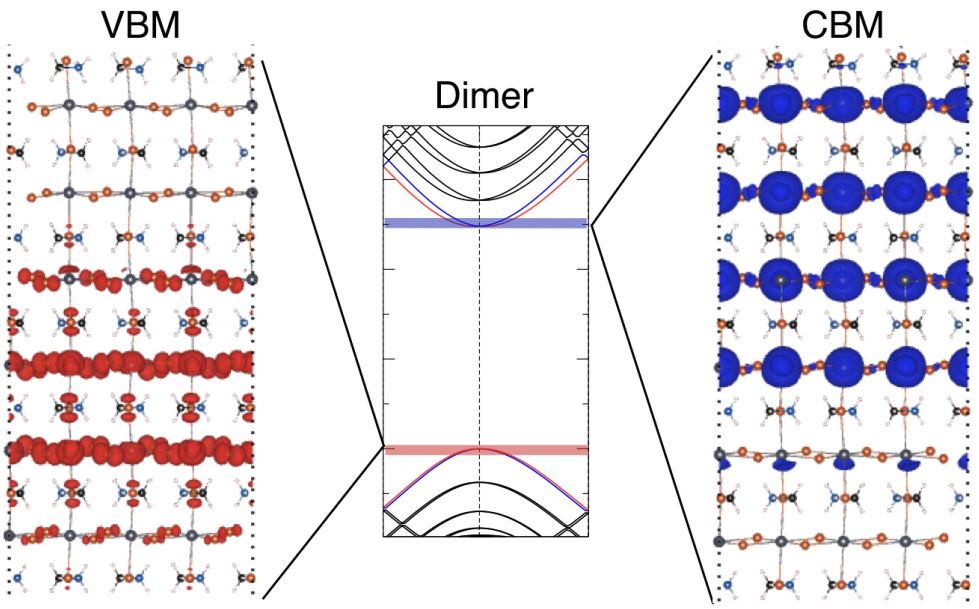

Fig. S3 LDOS of VBM and CBM of the relaxed slab in its dimer configuration, to be compared to those obtained for the zigzag configuration reported in Figure 4c, revealing similar features.

Table S1 The layer by layer vertical Pb-Pb distances, in-plane and out-of-plane Pb-Br distances and tilting angles β and δ (Figure 2d) in the two reconstructed surfaces. The values are averaged over each layer.

Structures	Layer numbers	Vertical distance Pb-Pb (Å)	distance Pb-Br (Å)		Angles tilting (°)	
			in-plane	out-of-plane	β	δ
Experimental bulk	-	5.92	2.98	2.98	9.3	5.8
Relaxed bulk	-	5.90	2.98	2.98	11.5	8.0
Zigzag	1	5.90	2.98	2.98	11.5	8.0
	2	5.91	3.00	2.98	12.2	7.7
	3	5.92	2.99	2.98	12.3	7.3
	4	5.92	3.00	2.99	12.3	7.2
	5	6.00	3.00	2.99	12.5	6.3
	6	-	2.99	3.04	13.5	5.5
Dimer	1	5.90	2.98	2.98	11.5	8.0
	2	5.91	3.00	2.97	12.2	7.5
	3	5.91	3.00	2.98	12.3	6.9
	4	5.93	3.00	2.98	12.3	6.8
	5	5.98	3.00	2.98	12.5	6.1
	6	-	3.00	3.03	11.7	5.9