

Two-dimensional eclipsed arrangement hybrid perovskites for tunable energy level alignments and photovoltaics

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Supporting Information

Table S1: Lattice parameters of the $2 \times 1 \times 1$ supercells of (AEQT)PbX₄ (X = Cl, Br, I), calculated using the PBE functional with Grimme’s D3 dispersion correction, in comparison with the unit cell in the computational study. a is along the direction perpendicular to the perovskite sheet. Lattice lengths given in Å and lattice angles given in °

Compounds	Functional	a	b	c	α	β	γ
(AEQT)PbCl ₄	PBE-D3	11.192	11.346	39.976	92.5	90.0	90.0
	Ref. 1	11.295	10.949	40.851	91.8	90.0	90.0
(AEQT)PbBr ₄	PBE-D3	11.525	11.824	39.037	91.9	90.0	90.0
	Ref. 1	11.603	11.480	39.950	91.2	90.0	90.0
(AEQT)PbI ₄	PBE-D3	12.107	12.589	38.072	92.2	90.0	90.0
	Ref. 1	12.097	12.225	39.015	91.1	90.0	90.0

Table S2: Average in-plane and out-of-plane Born effective charges (Z^*) over Pb/Sn and Cl/Br/I atoms. Superscripts $\parallel$ and $\perp$ indicate properties parallel (in-plane) and perpendicular (out-of-plane) to the 2D perovskite sheets, respectively

Compounds	Atom	$Z_{\parallel}^*$	$Z_{\perp}^*$
(AEQT)PbCl ₄	Pb	3.651	3.718
	Cl	-1.583	-1.627
(AEQT)PbBr ₄	Pb	3.968	3.434
	Br	-1.544	-1.701
(AEQT)PbI ₄	Pb	4.229	3.024
	I	-1.726	-1.254
(AEQT)SnCl ₄	Sn	3.861	3.937
	Cl	-1.630	-1.697
(AEQT)SnBr ₄	Sn	4.532	3.623
	Br	-1.620	-1.888
(AEQT)SnI ₄	Sn	5.315	3.287
	I	-2.015	-1.293

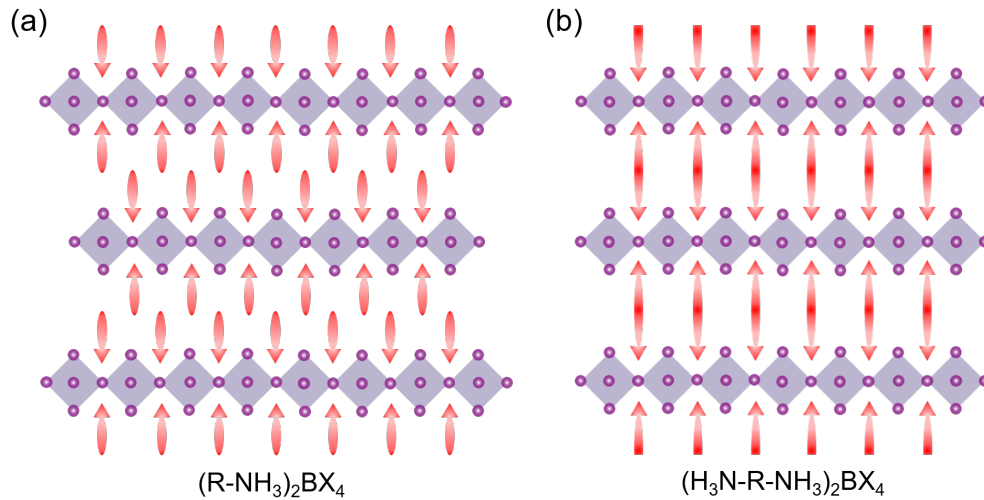


Figure S1: The basic structure of 2D hybrid perovskites: (a) “staggered” ((R–NH₃)₂BX₄) and (b) “eclipsed” arrangement ((H₃N–R–NH₃)₂BX₄).

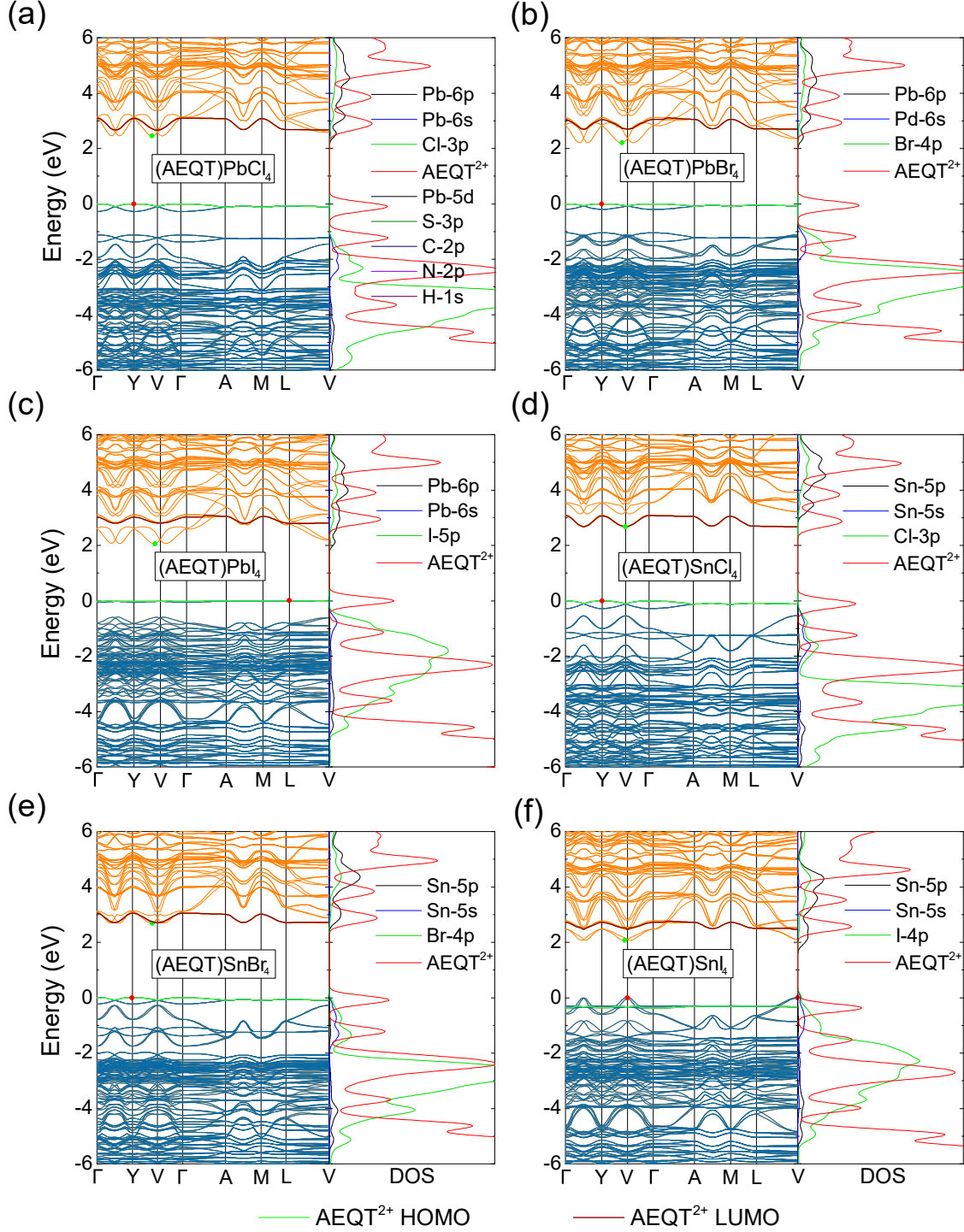


Figure S2: HSE43+SOC calculated band structures and density of states (DOS) for the layered tin hybrid perovskites: (a) (AEQT)PbCl₄, (b) (AEQT)PbBr₄, (c) (AEQT)PbI₄, (d) (AEQT)SnCl₄, (e) (AEQT)SnBr₄ and (f) (AEQT)SnI₄. The valence band maximum is set to 0 eV. Valence and conduction bands except the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of AEQT²⁺ are indicated by blue and orange lines, respectively, while the HOMO and LUMO of AEQT²⁺ are marked in green and brown, respectively. A Green and red circles indicate the position of the valence band maximum and conduction band minimum.

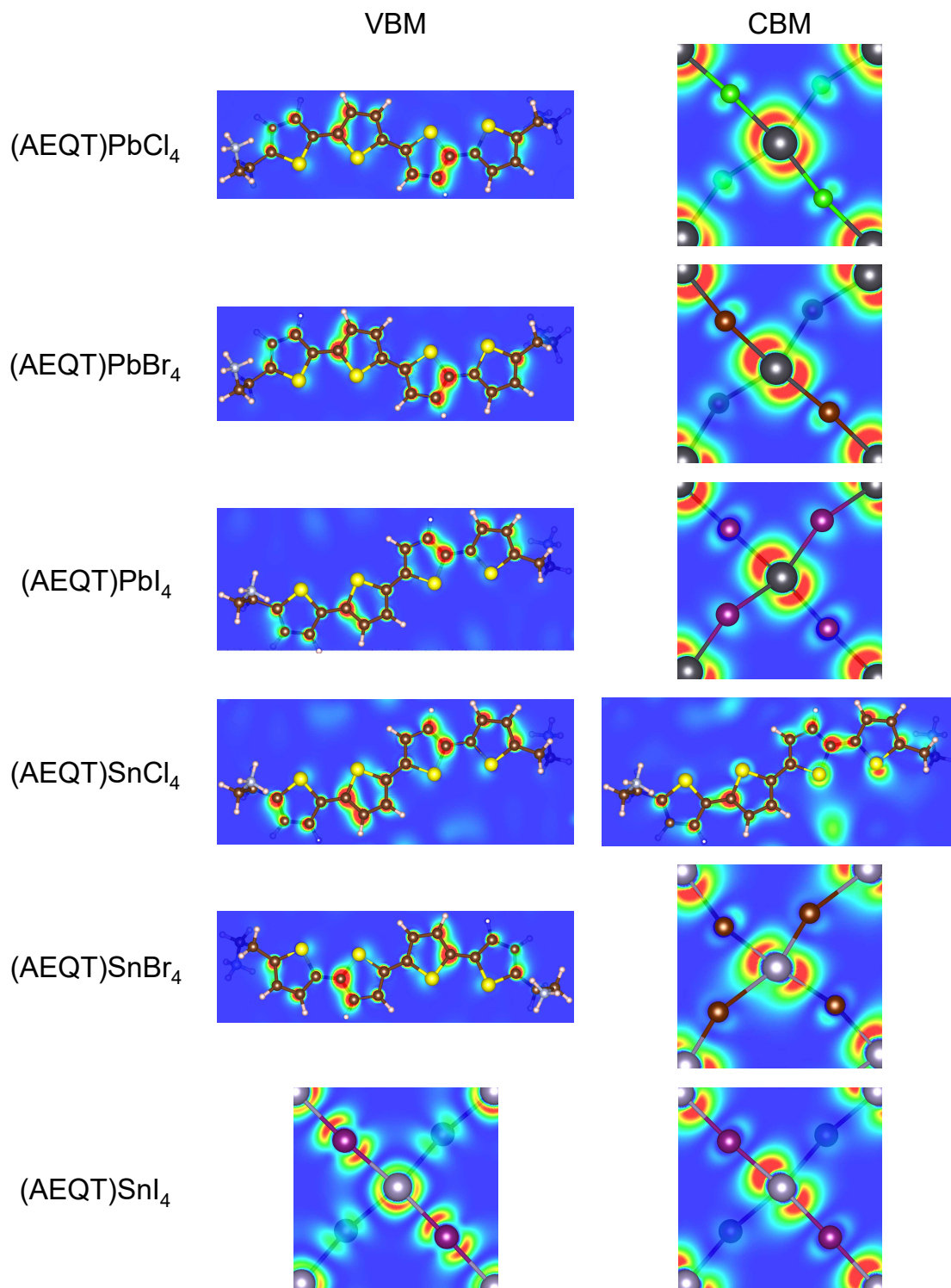


Figure S3: Charge density isosurfaces of the VBM (left) and CBM (right), pictured along the (001) direction, for the layered tin hybrid perovskites: (AEQT)PbCl₄, (AEQT)PbBr₄, (AEQT)PbI₄, (AEQT)SnCl₄, (AEQT)SnBr₄ and (AEQT)SnI₄, where the Pb, Sn and I atoms are shown in black, light grey and purple, respectively. The organic MA cations have been removed for clarity.

References

- (1) Liu, C.; Huhn, W.; Du, K.-Z.; Vazquez-Mayagoitia, A.; Dirkes, D.; You, W.; Kanai, Y.; Mitzi, D. B.; Blum, V. Tunable Semiconductors: Control over Carrier States and Excitations in Layered Hybrid Organic-Inorganic Perovskites. *Phys. Rev. Lett.* **2018**, *121*, 146401.