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Predictive Structure–Property Design Rules for Quasi-2D Dion–Jacobson Sn-Based Perovskites Supplementary Information

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1 Calculation Details

First-principles density functional theory (DFT) calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP) [1]. The exchange–correlation potential was described by the minimally empirical, dispersion-corrected meta-GGA functional r^{2}SCAN+rVV10 [2, 3], which has been shown to provide a superior description of both the structural properties of halide perovskites and the delicate non-bonded interactions within organic galleries. The projector-augmented wave (PAW) method [4] was employed to account for the electron–ion interactions. To ensure a high-precision description of the organic-inorganic interface, we employed 'hard' PAW pseudopotentials for the organic components (*C_h*, *N_h*, and *H_h*). Consequently, a high plane-wave cutoff energy of 910 eV was used; this rigorous threshold was strictly necessary to achieve full convergence of the stress tensor and to mitigate potential basis-set errors when describing the density of intermolecular contacts at the hybrid interface..

Structural relaxations of both lattice parameters and internal atomic positions were performed using a conjugate-gradient algorithm until the Hellmann–Feynman forces on each atom were smaller than 1×10^{-5} eV/Å. The Brillouin zone was sampled using Monkhorst–Pack meshes corresponding to a uniform density of $\sim$0.02 k-points/Å^{-1}. For total energy and density of states (DOS) calculations, a Γ-centered mesh was employed in combination with the tetrahedron method including Blöchl corrections.

Finally, molecular dipole moments were calculated for isolated divalent spacer cations in the gas phase. Calculations were performed by solving the restricted Kohn-Sham equations with the ORCA code [5, 6] using the r^{2}SCAN-3C composite method. While this captures the intrinsic polarity of the organic species, we acknowledge that the effective dipole within the perovskite lattice may be modulated by crystal field effects and the local dielectric environment. However, as the focus of this study is on the systematic comparison of molecular architectures, these gas-phase values serve as robust descriptors for identifying relative trends in electronic symmetry breaking across the spacer library.

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2 Supporting Results

Decomposition energies (ΔH_d^g)

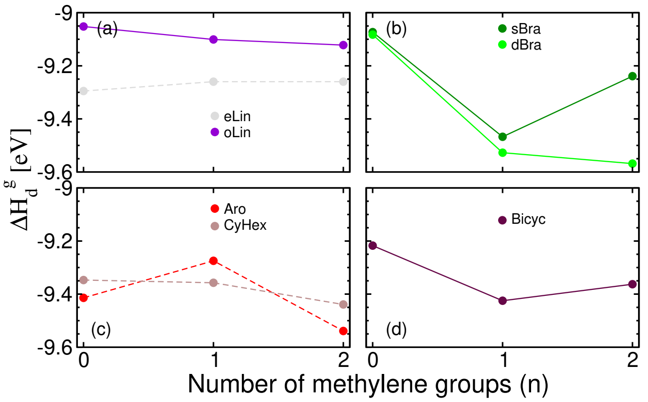
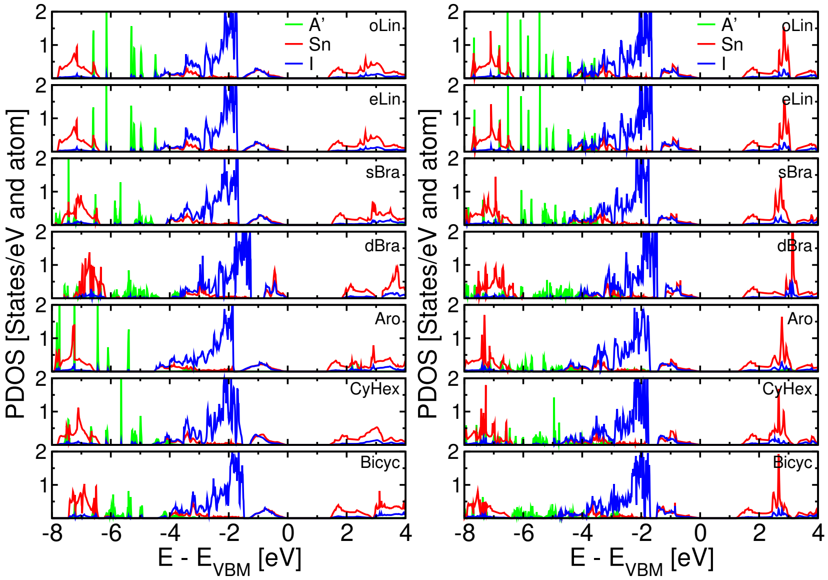


Figure S 1: Decomposition energies ($\Delta H_d^g = E[\mathrm{A'SnI_4}] - (E[\mathrm{SnI_2}] + E[\mathrm{A'}]_{(g)} + E[\mathrm{I_2}]_{(g)})$) for all Q2D perovskite configurations considered, calculated relative to bulk SnI_2 and gas-phase I_2 and A' isolated molecules, as a function of the number of methylene groups n in the aliphatic chain of the spacer. (a) linear cores, (b) branched cores, (c) cyclic (ring) cores (d) Bicyc-core. Dashed and solid lines represent configurations incorporating nonpolar and polar molecules respectively. While absolute values shift to a highly exothermic region (-9.5 to -9.0 eV) compared to the primary metric in ΔH_d, the relative stability trends and the influence of spacer geometry remain consistent.

Electronic structre



(a) $n = 0$

(b) $n = 2$

Figure S 2: Projected density of states (PDOS) of the DJ perovskites with different diammonium spacers A′ based on the different considered cores incorporating $n = 0$ and $n = 2$ methylene groups in the aliphatic chain.

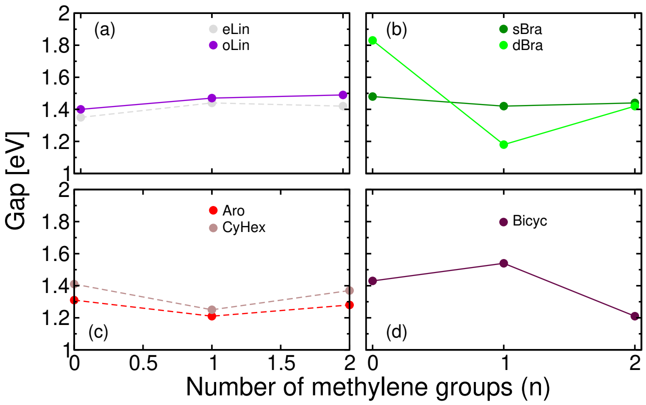
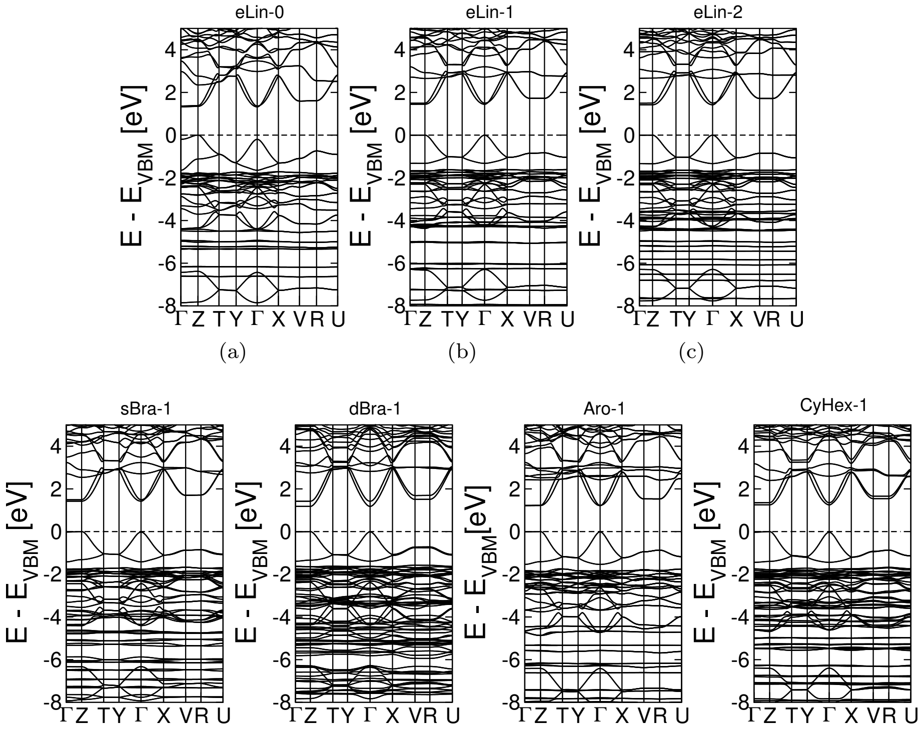


Figure S 3: Electronic band gaps of the DJ perovskites with different diammonium spacers A′ as a function of the number of methylene groups n in the aliphatic chain. (a) linear cores, (b) branched cores, (c) cyclic (ring) cores, and (d) Bicyc-cores. Dashed and solid lines represent nonpolar and polar molecules, respectively.



(a) (b) (c)

(d) (e) (f) (g)

Figure S 4: Electronic Band dispersion for eLin-0, eLin-1, eLin2, sBra-1 dBra-1, Aro-1 and CyHex-1 - based A′SnI$_4$ DJ perovskites.

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