Supporting Information

for

Intercalation Phenomena in Two-Dimensional Hybrid Perovskites Featuring Discrete Free Volume Elements

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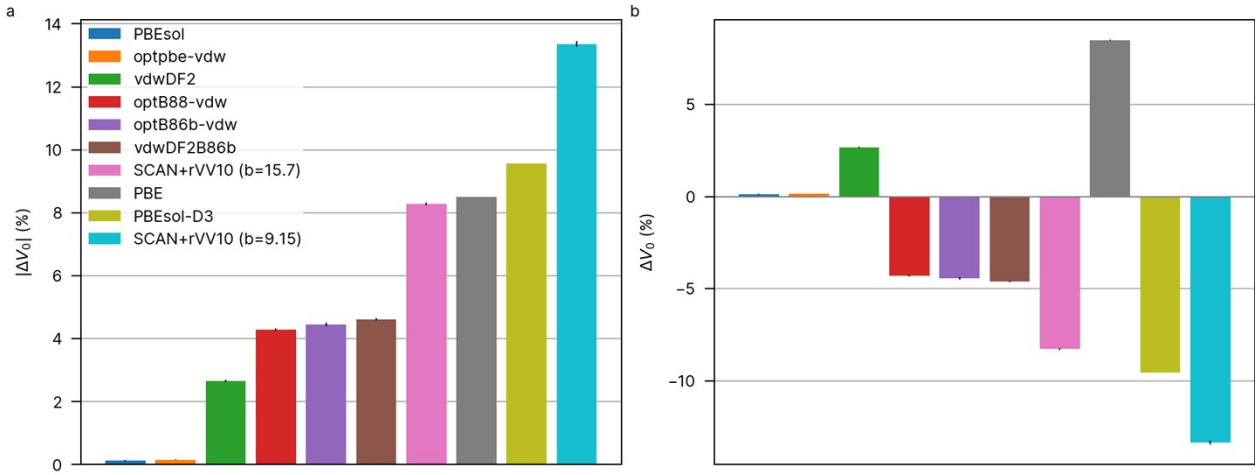

Figure S1. (a) Absolute and (b) relative difference between experimental and relaxed unit cell volume of ((3-(naphthalen-1-yloxy)propan-1-aminium)$_2$PbI$_4$ calculated using different DFT functionals.

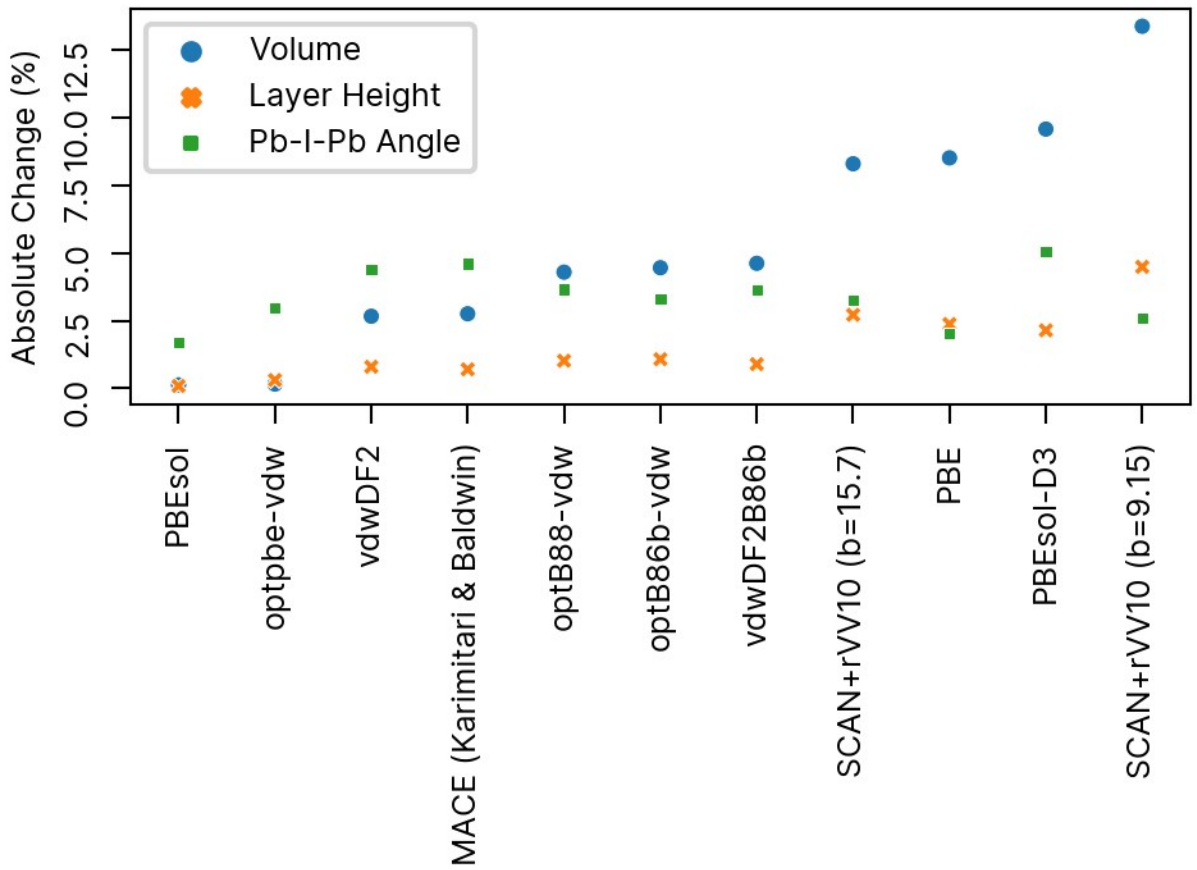

Figure S2. Absolute differences in relaxed unit cell volume, layer height, and Pb-I-Pb angle, relative to experimental data, across different DFT exchange-correlation functions.

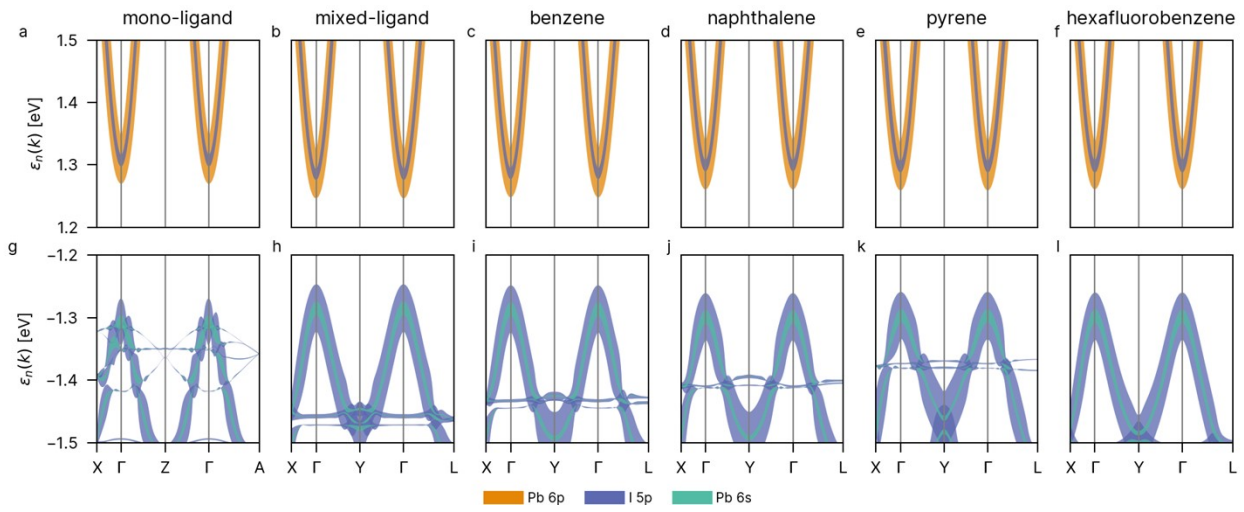

Figure S3. (a–f) Conduction bands and (g–l) valence bands of all structures. (a,g) ((3-(naphthalen-1-yloxy)propan-1-aminium)$_2$PbI$_4$. (b,h) ((3-(naphthalen-1-yloxy)propan-1-aminium)(propan-1-amminium)PbI$_4$ without intercalation and (c,i) with benzene (d,j) with naphthalene (e,k) with pyrene (f,l) with hexafluorobenzene. Only contributions from Pb 6s,p and I 5p are shown. Line thickness is proportional to the contribution from the atomic orbital. The thin lines near the top of the valence band are states on pi systems of the ligands and intercalant molecules.

Table S1. Calculated total energies and formation energies with guest molecules. Here, the total energy of (NOP)(PA)PbI_4 is given for a unit cell with 2 formula units of PbI_4 , while the total energy of the rest of the compounds is given for a unit cell with 4 formula units of PbI_4.

Material	**Total Energy (eV)**	**Formation Energy (eV)**
(NOP)(PA)PbI_4	–478.47	
(NOP)(PA)PbI_4 benzene	–1025.11	–0.91
(NOP)(PA)PbI_4 hexafluorobenzene	–1013.04	–1.17
(NOP)(PA)PbI_4 naphthalene	–1063.16	–1.15
(NOP)(PA)PbI_4 pyrene	–1116.92	–1.46

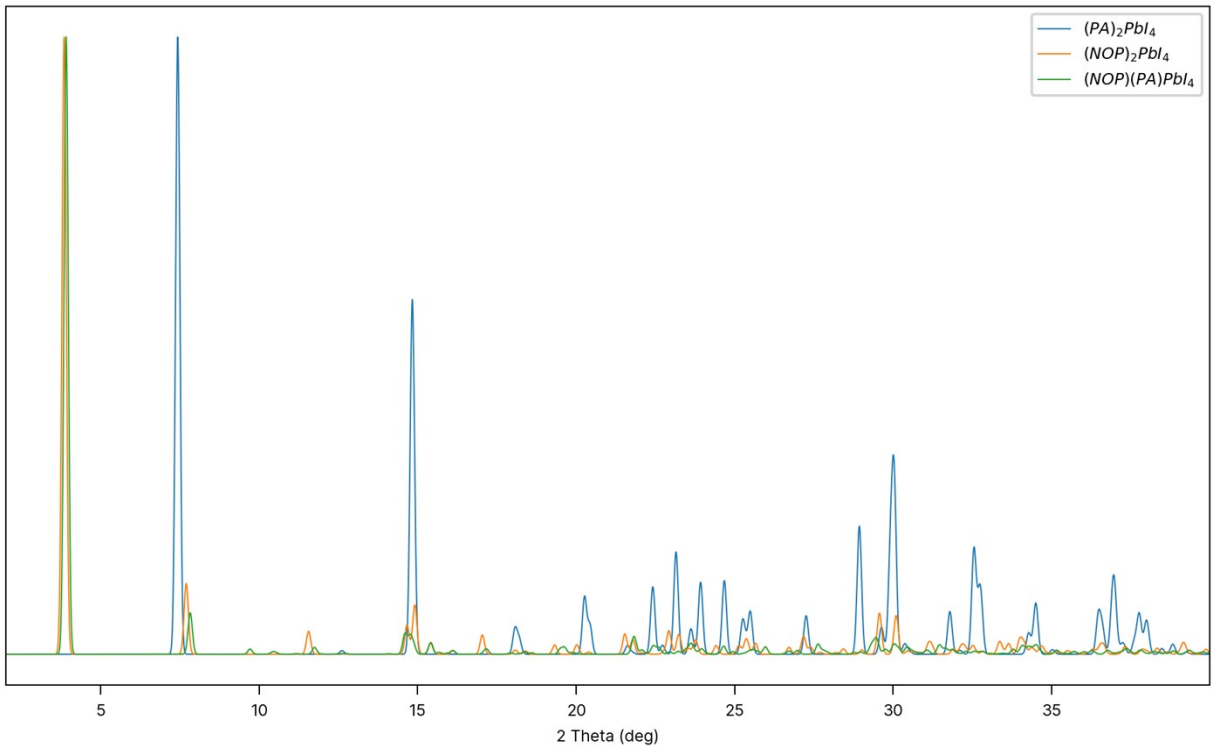

Figure S4. X-ray diffraction calculated using a wavelength of 0.15406 nm (Cu Kα1). Peak broadening was added using the Scherr equation with a grain size of 50 nm. Instrumental broadening was ignored.