

*Electronic Supplementary Material (ESI)*

**Ab Initio Modeling of 2D and quasi-2D Lead Organohalide Perovskites with Divalent Organic Cations and Tunable Band Gap.**

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### Sketch and coordinates of $k$ -point path.

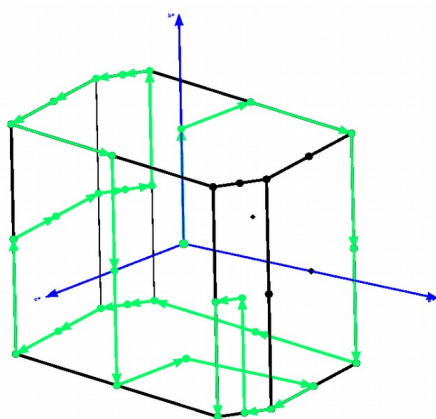


Figure S1. 32  $k$ -point path used for the calculation of band structures.

K_POINT	PATH	COORDINATES		
0.0000000		0.0000000	0.0000000	0.0625000
0.1250000		0.1358683	0.3283072	0.0625000
0.1250000		0.1358683	-0.3283072	0.0625000
0.1250000		0.1358683	-0.1094357	0.0625000
0.1250000		0.4076048	0.1094357	0.0625000
0.1250000		0.4076048	0.3283072	0.0625000
0.1250000		0.4076048	-0.3283072	0.0625000
0.1250000		0.4076048	-0.1094357	0.0625000
0.1250000		-0.4076048	0.1094357	0.0625000
0.1250000		-0.4076048	0.3283072	0.0625000
0.1250000		-0.4076048	-0.3283072	0.0625000
0.1250000		-0.4076048	-0.1094357	0.0625000
0.1250000		-0.1358683	0.1094357	0.0625000
0.1250000		-0.1358683	0.3283072	0.0625000
0.1250000		-0.1358683	-0.3283072	0.0625000
0.1250000		-0.1358683	-0.1094357	0.0625000
0.3750000		0.1358683	0.1094357	0.0625000
0.3750000		0.1358683	0.3283072	0.0625000
0.3750000		0.1358683	-0.3283072	0.0625000
0.3750000		0.1358683	-0.1094357	0.0625000
0.3750000		0.4076048	0.1094357	0.0625000
0.3750000		0.4076048	0.3283072	0.0625000
0.3750000		0.4076048	-0.3283072	0.0625000
0.3750000		0.4076048	-0.1094357	0.0625000
0.3750000		-0.4076048	0.1094357	0.0625000
0.3750000		-0.4076048	0.3283072	0.0625000
0.3750000		-0.4076048	-0.3283072	0.0625000
0.3750000		-0.4076048	-0.1094357	0.0625000
0.3750000		-0.1358683	0.1094357	0.0625000
0.3750000		-0.1358683	0.3283072	0.0625000
0.3750000		-0.1358683	-0.3283072	0.0625000
0.3750000		-0.1358683	-0.1094357	0.0625000

## HOMO and LUMO energies.

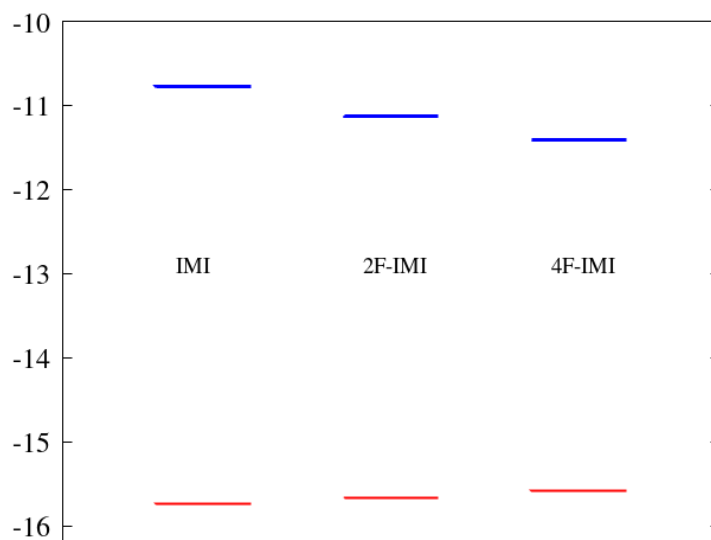
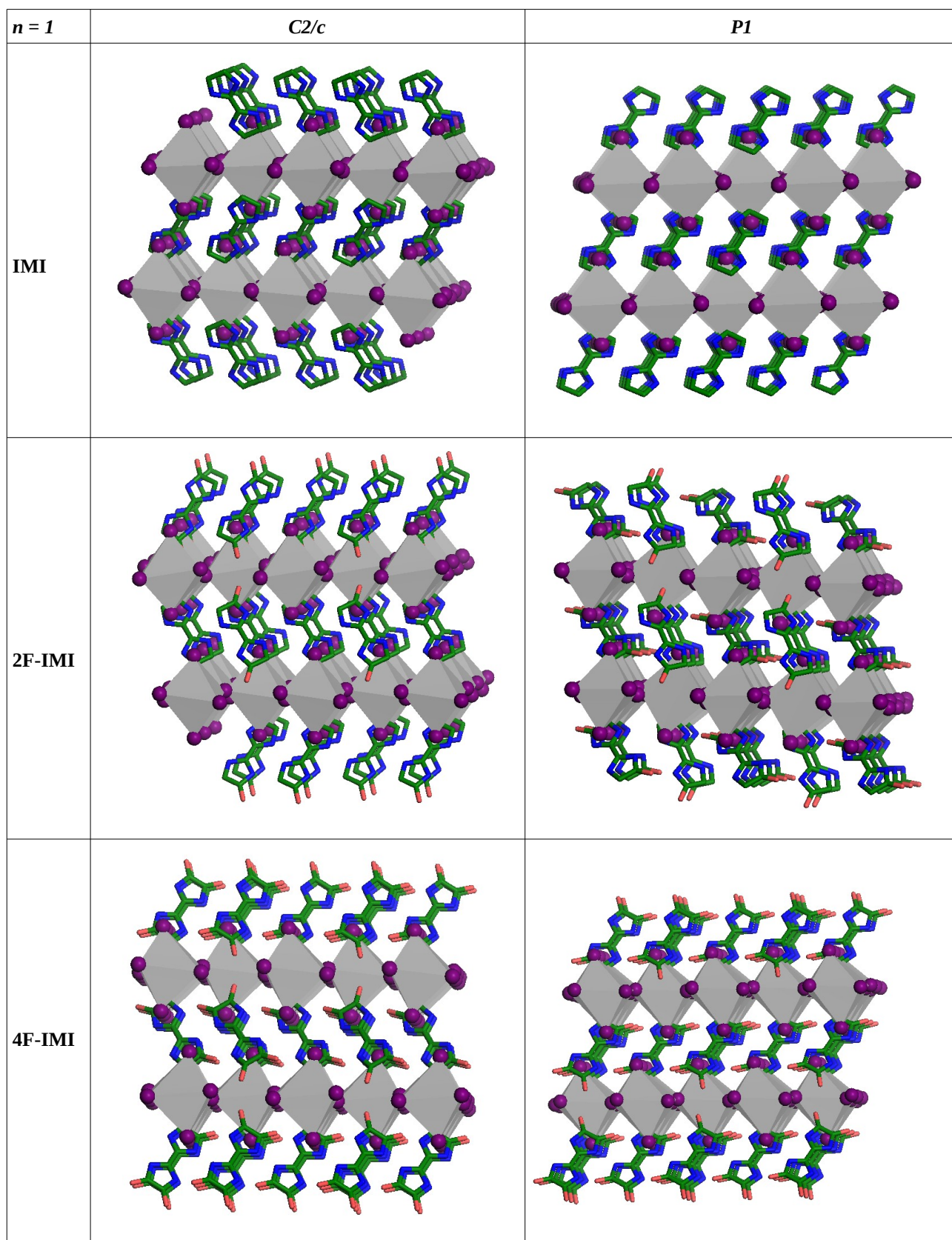
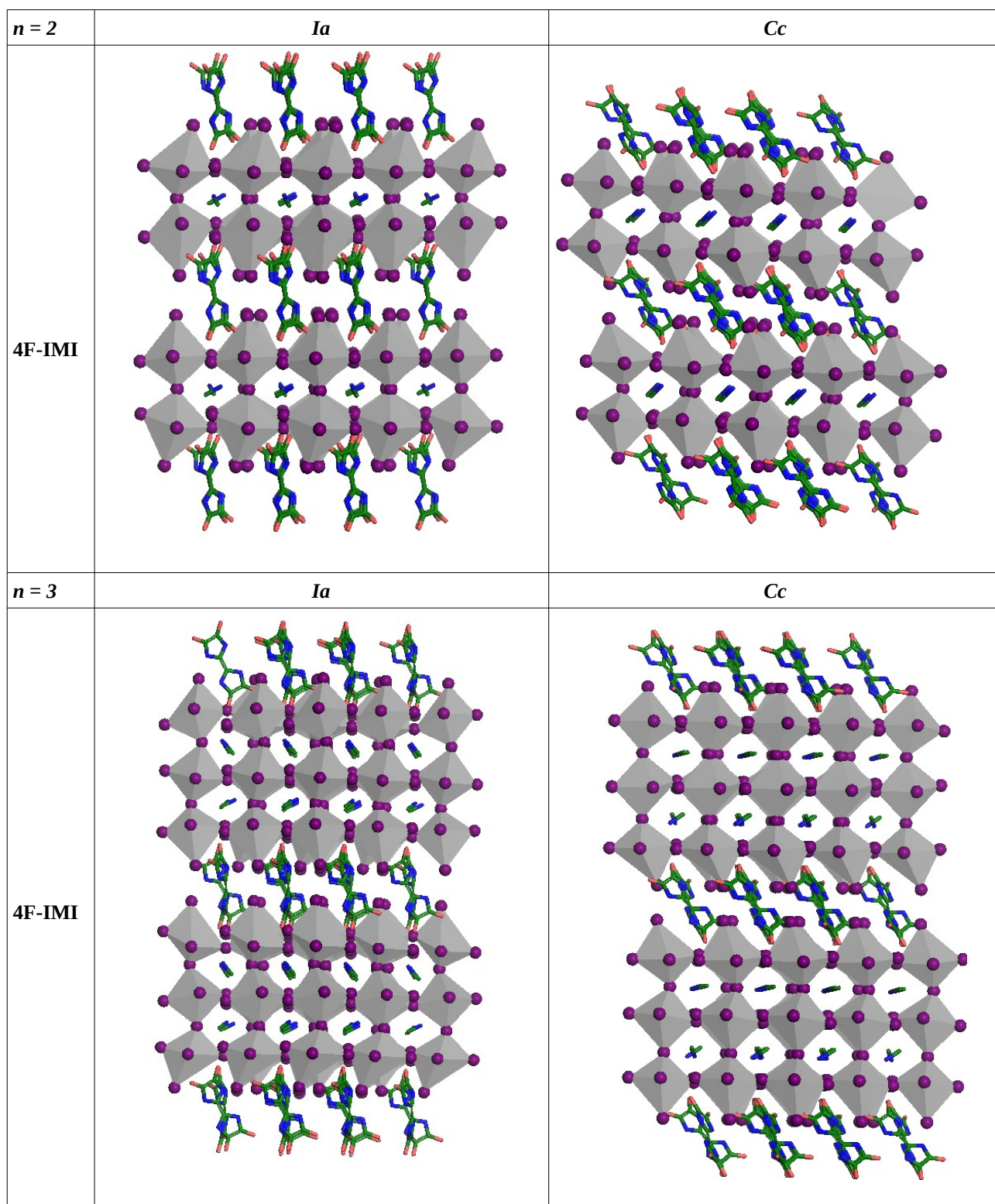


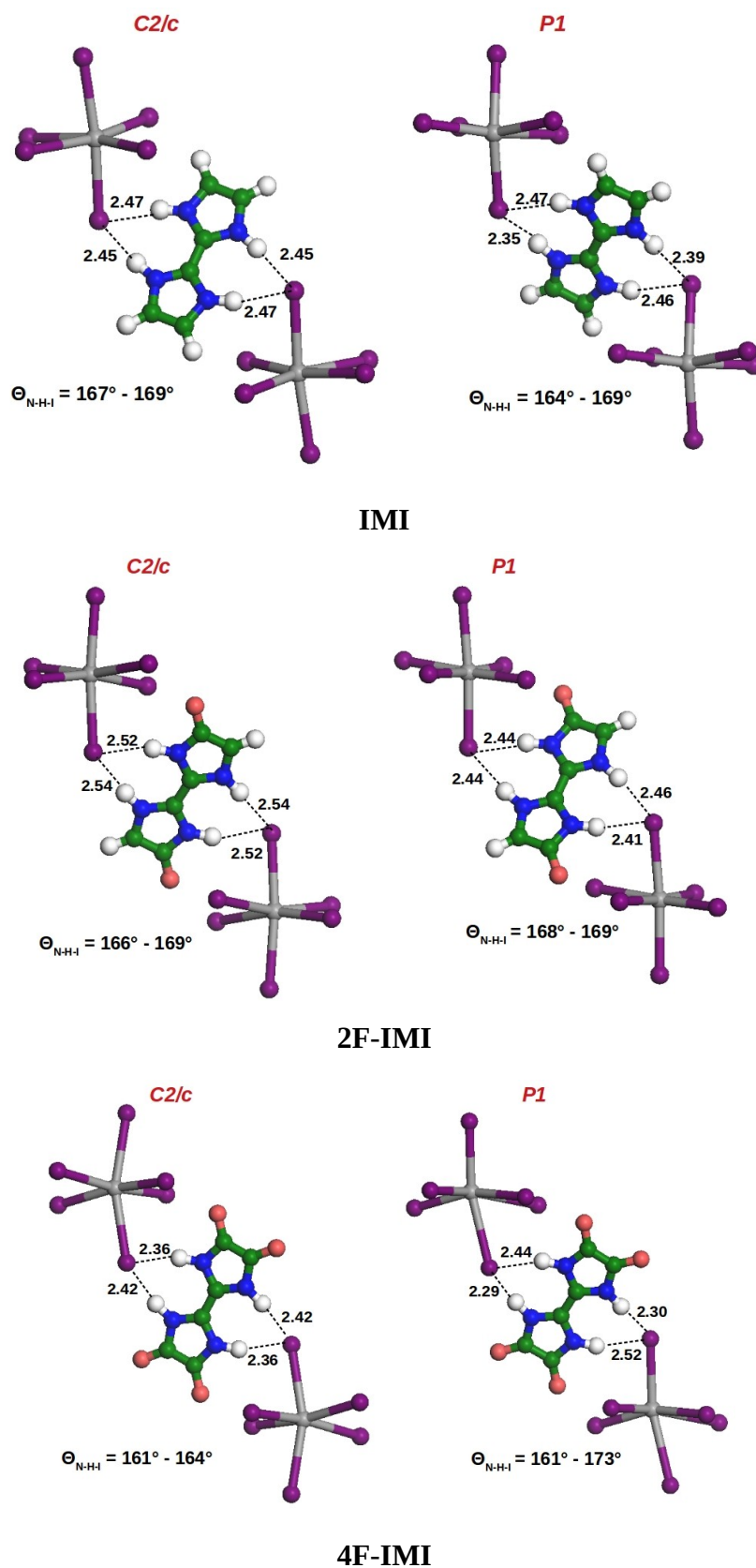
Figure S2. DFT energies (eV) for HOMO (red) and LUMO (blue) orbitals of 2,2'-biimidazolium (IMI), 4,4'-difluoro-2,2'-biimidazolium (2F-IMI) and 4,4',5,5'-tetrafluoro-2,2'-biimidazolium (4F-IMI).



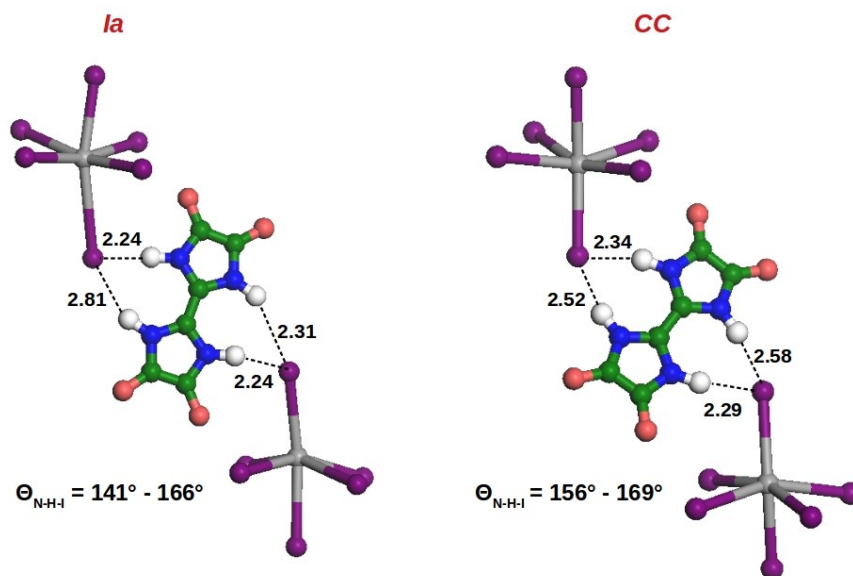
**Figure S3.** Optimized structures for  $n=1$  hybrid perovskites: Pb, gray; I, purple; C, green; N, blue; F, orange; hydrogen atoms not shown for clarity.



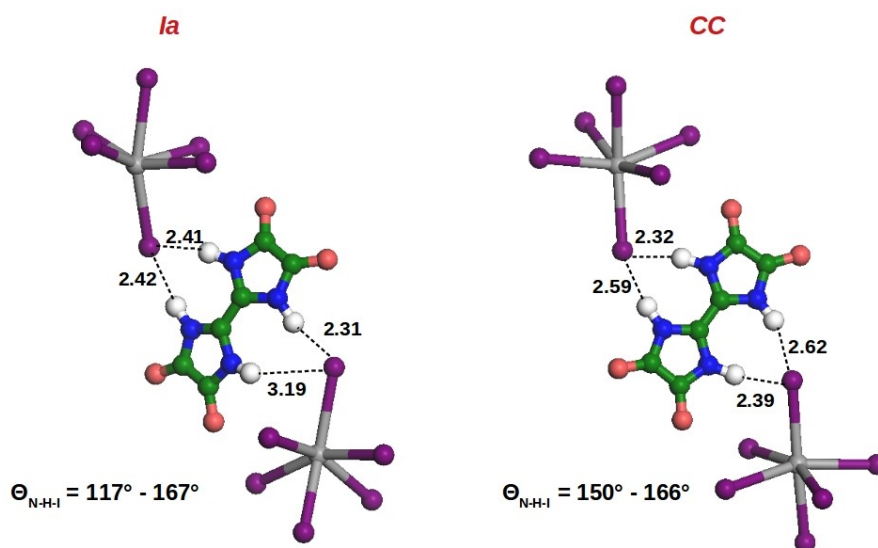
**Figure S4.** Optimized structures for  $n=2, 3$  hybrid perovskites: Pb, gray; I, purple; C, green; N, blue; F, orange; hydrogen atoms not shown for clarity.



**Figure S5.** H-bonding parameters in  $n=1$  structures.

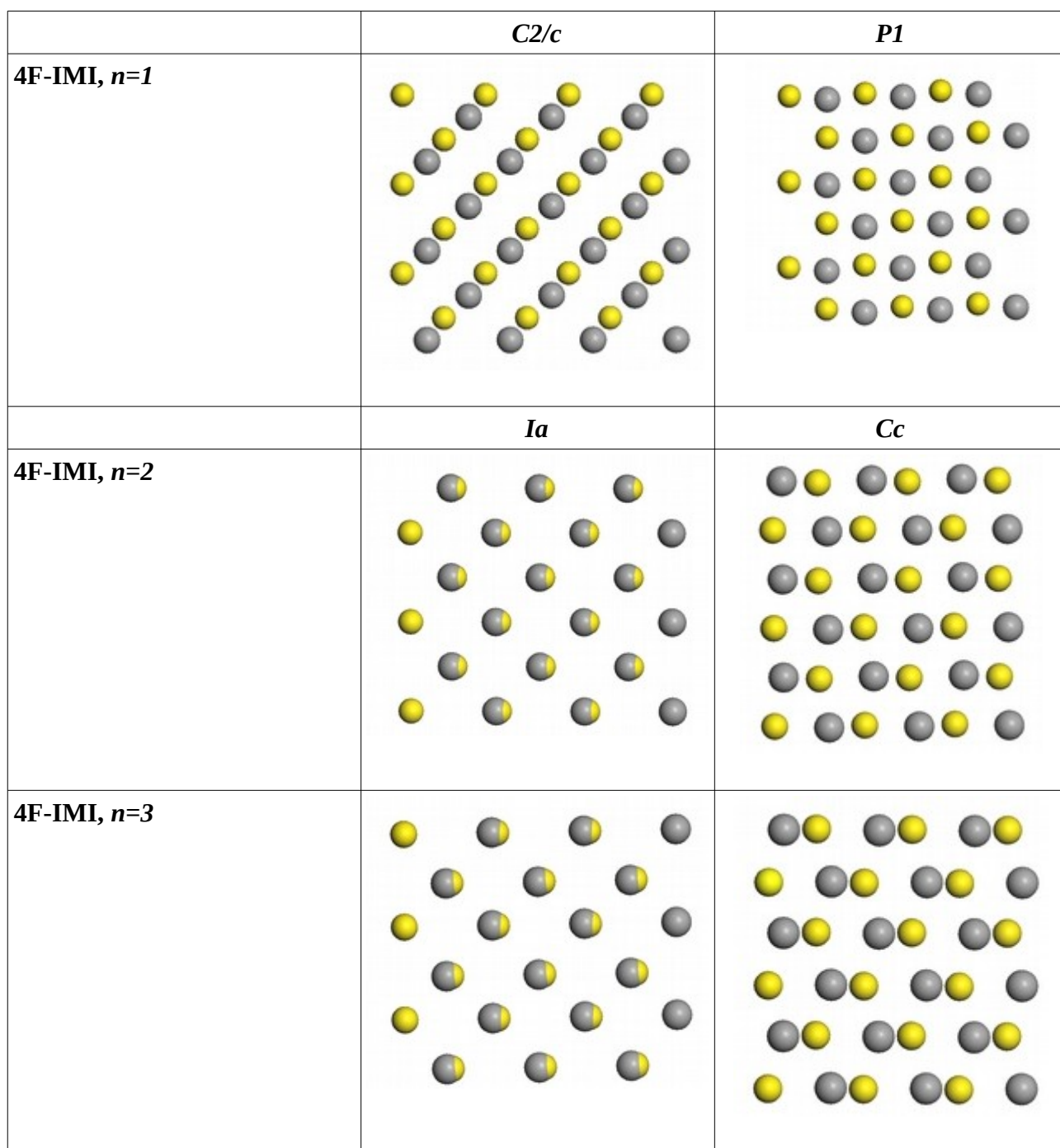


**$n = 2, 4\text{F-IMI}$**



**$n = 3, 4\text{F-IMI}$**

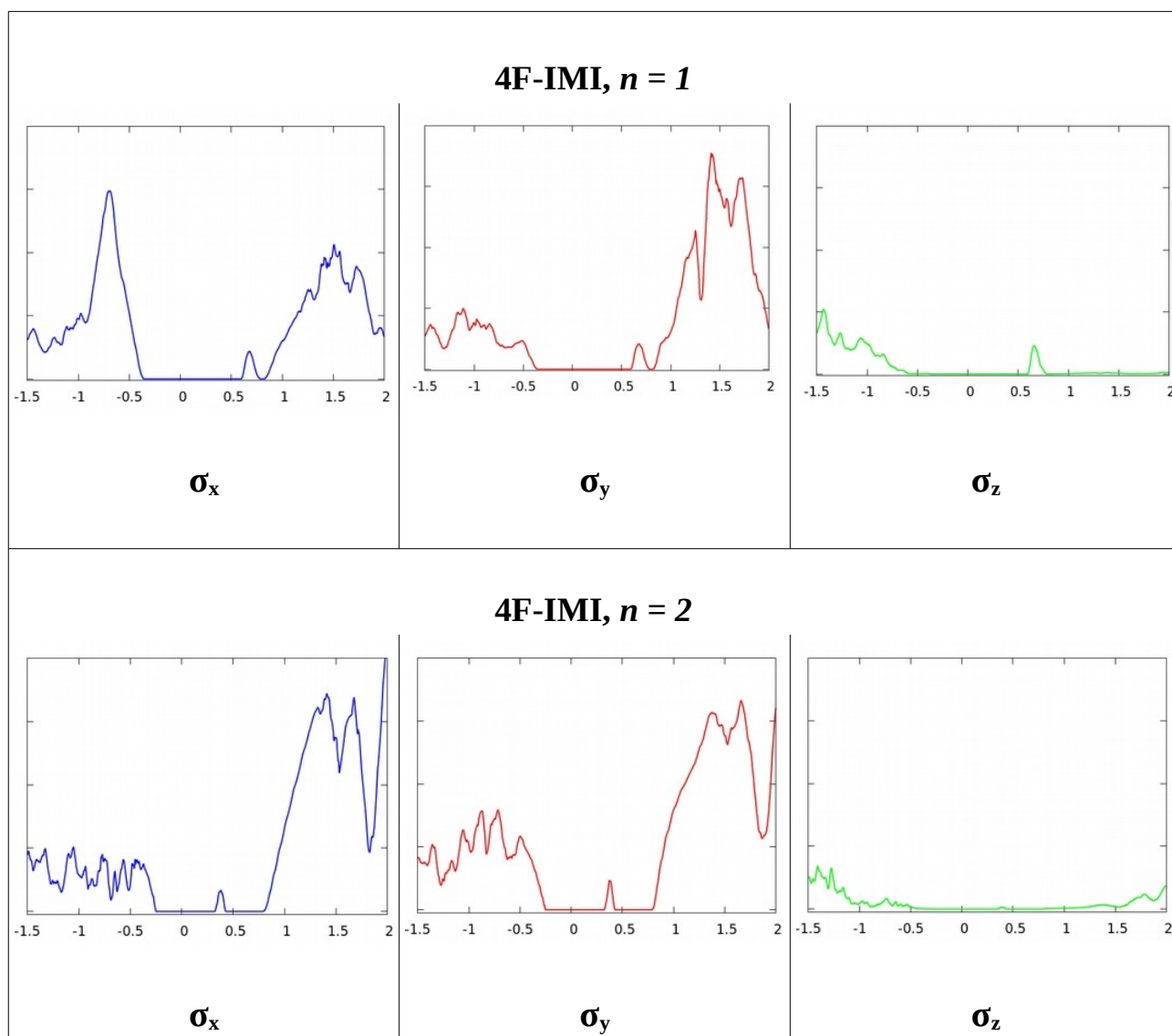
**Figure S6.** H-bonding parameters in  $n=2, 3$  structures.



**Figure S7.** Pb atom positions in a layer (grey) along with the orthogonal projections of Pb atoms from the overhead layer (yellow).



### Charge conductivity in three directions.



**Figure S8.** Diagonal elements of the conductivity tensor for the RP tetra-fluorinated compounds with  $n=1,2$ .

One can see the effect of the strong directionality of the charge carrier mobility, confined in the (x,y) plane of the inorganic sheets. This feature is common to holes (below -0.4 eV wrt Fermi level), inorganic (above 0.9 eV) and organic electrons (ca. 0.7 eV for  $n=1$  and 0.4 eV for  $n=2$ ).

Interestingly, when the inorganic layer is thinner ( $n=1$ ) organic electron conductivity has a component along z also, with intensity comparable to the other directions, which disappears almost completely in the  $n=2$  material. This contribution is clearly due to the charge carriers “jumping” from one layer to the next one, similarly to the mechanism of the conduction modeled in the (x,y) planes for the same organic electrons. When the distance between the organic layers becomes larger,

e. g. for  $n=2$ , the carrier mobility along  $z$  due to this mechanism vanishes, while in  $(x,y)$  it remains almost unaltered.