Supporting Information of:

Analysis of Energetic Bonding in Metal-Halide Perovskites and Brief Evaluation of Meta-GGA Functionals TPSS and revTPSS

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Basis set convergence: DND vs DNP

Table S1. Energy convergence of the basis sets DND and DNP as a function of the cutt off radii for MAPI only and with a 4x4x3 k-grid.

DND				DNP			
Radii	Energy (Ha)	Energy (eV)	ΔEnergy (eV)	Radii	Energy (Ha)	Energy (eV)	ΔEnergy (eV)
3.100000	-3135.119339	-85310.986389		3.100000	-3135.207582	-85313.387600	
3.300000	-3135.426254	-85319.337963	8.351573	3.300000	-3135.505419	-85321.492150	8.104551
3.500000	-3135.606935	-85324.254543	4.916580	3.500000	-3135.679610	-85326.232150	4.740000
3.700000	-3135.662703	-85325.772079	1.517536	3.700000	-3135.730510	-85327.617194	1.385044
3.900000	-3135.668591	-85325.932308	0.160229	3.900000	-3135.734279	-85327.719757	0.102562
4.100000	-3135.720869	-85327.354866	1.422558	4.100000	-3135.785271	-85329.107326	1.387569
4.300000	-3135.691882	-85326.566067	-0.788799	4.300000	-3135.755018	-85328.284102	-0.823224
4.500000	-3135.712733	-85327.133452	0.567385	4.500000	-3135.776282	-85328.862723	0.578620
4.700000	-3135.707137	-85326.981193	-0.152259	4.700000	-3135.770987	-85328.718627	-0.144095
4.900000	-3135.703988	-85326.895488	-0.085705	4.900000	-3135.766840	-85328.605793	-0.112835
5.100000	-3135.698038	-85326.733589	-0.161900	5.100000	-3135.760707	-85328.438889	-0.166904
5.300000	-3135.722981	-85327.412312	0.678723	5.300000	-3135.786708	-85329.146434	0.707545
5.500000	-3135.671906	-85326.022492	-1.389820	5.500000	-3135.735827	-85327.761872	-1.384562
5.700000	-3135.737932	-85327.819152	1.796660	5.700000	-3135.800677	-85329.526542	1.764670
5.900000	-3135.675298	-85326.114799	-1.704353	5.900000	-3135.737370	-85327.803865	-1.722678
6.100000	-3135.695583	-85326.666774	0.551975	6.100000	-3135.758521	-85328.379421	0.575556
6.300000	-3135.743901	-85327.981574	1.314800	6.300000	-3135.808092	-85329.728301	1.348880
6.500000	-3135.728513	-85327.562867	-0.418707	6.500000	-3135.792846	-85329.313439	-0.414862
6.700000	-3135.729180	-85327.581003	0.018136	6.700000	-3135.793501	-85329.331276	0.017837
6.900000	-3135.728586	-85327.564842	-0.016161	6.900000	-3135.792898	-85329.314867	-0.016408
7.100000	-3135.729625	-85327.593129	0.028286	7.100000	-3135.793932	-85329.342993	0.028126
7.300000	-3135.728665	-85327.567003	-0.026126	7.300000	-3135.792964	-85329.316647	-0.026346
7.500000	-3135.729539	-85327.590767	0.023764	7.500000	-3135.793831	-85329.340258	0.023611
7.700000	-3135.730235	-85327.609719	0.018953	7.700000	-3135.794519	-85329.358972	0.018713
7.900000	-3135.729561	-85327.591379	-0.018340	7.900000	-3135.793835	-85329.340348	-0.018623
8.100000	-3135.730122	-85327.606642	0.015263	8.100000	-3135.794387	-85329.355372	0.015023
8.300000	-3135.731230	-85327.636795	0.030153	8.300000	-3135.795486	-85329.385288	0.029916
8.500000	-3135.731951	-85327.656414	0.019619	8.500000	-3135.796197	-85329.404632	0.019345

k-mesh convergence: MAPI and FAPI

Table S2. Energy convergence as a function of the k-grid for MAPI, having used the DND basis set with a cut off radii of 6.5 Å.

k-mesh	Energy (Ha)	Energy (eV)	ΔEnergy (eV)
1x1x1	-3135.598493	-85324.024827	
2x2x1	-3135.692123	-85326.572641	2.547814
3x3x2	-3135.730366	-85327.613292	1.040651
4x4x3	-3135.728513	-85327.562867	-0.050425
5x5x4	-3135.728783	-85327.570198	0.007331
6x6x4	-3135.728791	-85327.570432	0.000234
7x7x5	-3135.728753	-85327.569378	-0.001053
8x8x5	-3135.728753	-85327.569387	0.000008
8x8x6	-3135.728760	-85327.569566	0.000180
9x9x6	-3135.728760	-85327.569566	0.000000

Table S3. Energy convergence as a function of the k-grid for MAPI, having used the DNP basis set with a cut off radii of 6.5 Å.

k-mesh	Energy (Ha)	Energy (eV)	ΔEnergy (eV)
1x1x1	-3135.663084	-85325.782455	
2x2x1	-3135.756490	-85328.324155	2.541700
3x3x2	-3135.794696	-85329.363780	1.039625
4x4x3	-3135.792846	-85329.313439	-0.050341
5x5x4	-3135.793114	-85329.320753	0.007314
6x6x4	-3135.793123	-85329.320987	0.000234
7x7x5	-3135.793084	-85329.319937	-0.001050
8x8x5	-3135.793085	-85329.319948	0.000011
8x8x6	-3135.793091	-85329.320125	0.000177
9x9x6	-3135.793091	-85329.320125	0.000000

Table S4. Energy convergence as a function of the k-grid for FAPI, having used the DND basis set with a cut off radii of 6.5 Å.

k-mesh	Energy (Ha)	Energy (eV)	ΔEnergy (eV)
1x1x1	-3351.788255	-91206.850930	
2x2x1	-3351.898413	-91209.848478	2.997548
3x3x2	-3351.940740	-91211.000239	1.151761
4x4x3	-3351.938616	-91210.942453	-0.057786
5x5x4	-3351.938978	-91210.952298	0.009845
6x6x4	-3351.938992	-91210.952681	0.000384
7x7x5	-3351.938939	-91210.951239	-0.001442
8x8x5	-3351.938940	-91210.951264	0.000024
8x8x6	-3351.938949	-91210.951525	0.000261
9x9x6	-3351.938949	-91210.951525	0.000000

Cubo-octahedral centers

Table S5. Centers of the four cubo-octahedral cages within the unit-cell of CsPI, due to periodicity it was used the positions of eight Pb atoms.

Cubo-octahedral cage 1

Pb	x	y	z
1	4.14082852	-4.51342862	12.79322925
2	-0.00779255	-0.00470997	12.60290321
3	4.14082852	4.58997672	12.32187535
4	8.28215444	0.06681175	12.51705422
5	4.13767834	-4.51645992	6.49218937
6	-0.00746095	-0.00124781	6.30224871
7	4.13767834	4.58694542	6.02083547
8	8.28248604	0.07027390	6.21639973
Center	**4.13830009**	**0.03477018**	**9.40834191**

Cubo-octahedral cage 2

Pb	x	y	z
1	-0.00779255	-0.00470997	12.60290321
2	-4.14911847	4.51845501	12.40772433
3	-0.00779255	9.09869538	12.13154931
4	4.14082852	4.58997672	12.32187535
5	-0.00746095	-0.00124781	6.30224871
6	-4.15226865	4.51542370	6.10668445
7	-0.00746095	9.10215753	5.83089481
8	4.13767834	4.58694542	6.02083547
Center	**-0.00667341**	**4.55071200**	**9.21558946**

Cubo-octahedral cage 3

Pb	x	y	z
1	4.13767834	-4.51645992	6.49218937
2	-0.00746095	-0.00124781	6.30224871
3	4.13767834	4.58694542	6.02083547
4	8.28248604	0.07027390	6.21639973
5	4.14082852	-4.51342862	0.19152925
6	-0.00779255	-0.00470997	0.00120321
7	4.14082852	4.58997672	-0.27982465
8	8.28215444	0.06681175	-0.08464578
Center	**4.13830009**	**0.03477018**	**3.10749191**

Cubo-octahedral cage 4

Pb	x	y	z
1	-0.00746095	-0.00124781	6.30224871
2	-4.15226865	4.51542370	6.10668445
3	-0.00746095	9.10215753	5.83089481
4	4.13767834	4.58694542	6.02083547
5	-0.00779255	-0.00470997	0.00120321
6	-4.14911847	4.51845501	-0.19397567
7	-0.00779255	9.09869538	-0.47015069
8	4.14082852	4.58997672	-0.27982465
Center	**-0.00667341**	**4.55071200**	**2.91473946**

Table S6. Centers of the four cubo-octahedral cages within the unit-cell of MAPI, due to periodicity it was used the positions of eight Pb atoms.

Cubo-octahedral cage 1				Cubo-octahedral cage 2			
Pb	x	y	z	Pb	x	y	z
1	4.45390672	-4.33926380	12.98840640	1	0.03691355	0.13448970	12.98942166
2	0.03691355	0.13448970	12.98942166	2	-4.50569321	4.62024398	12.98349611
3	4.45390672	4.62063537	12.98455946	3	0.03691355	9.09438887	12.98557472
4	8.99651348	0.13488109	12.99048501	4	4.45390672	4.62063537	12.98455946
5	4.44835177	-4.60044511	6.58157134	5	0.02365334	-0.12794633	6.58181725
6	0.02365334	-0.12794633	6.58181725	6	-4.51124816	4.35906267	6.57666105
7	4.44835177	4.35945407	6.57772440	7	0.02365334	8.83195285	6.57797031
8	8.98325327	-0.12755493	6.58288060	8	4.44835177	4.35945407	6.57772440
Center	**4.48060633**	**0.00678126**	**9.78460827**	Center	**0.00080636**	**4.48653515**	**9.78215312**

Cubo-octahedral cage 3				Cubo-octahedral cage 4			
Pb	x	y	z	Pb	x	y	z
1	4.44835177	-4.60044511	6.58157134	1	0.02365334	-0.12794633	6.58181725
2	0.02365334	-0.12794633	6.58181725	2	-4.51124816	4.35906267	6.57666105
3	4.44835177	4.35945407	6.57772440	3	0.02365334	8.83195285	6.57797031
4	8.98325327	-0.12755493	6.58288060	4	4.44835177	4.35945407	6.57772440
5	4.45390672	-4.33926380	0.17220640	5	0.03691355	0.13448970	0.17322166
6	0.03691355	0.13448970	0.17322166	6	-4.50569321	4.62024398	0.16729611
7	4.45390672	4.62063537	0.16835946	7	0.03691355	9.09438887	0.16937472
8	8.99651348	0.13488109	0.17428501	8	4.45390672	4.62063537	0.16835946
Center	**4.48060633**	**0.00678126**	**3.37650827**	Center	**0.00080636**	**4.48653515**	**3.37405312**

Table S7. Centers of the four cubo-octahedral cages within the unit-cell of FAPI, due to periodicity it was used the positions of eight Pb atoms.

Cubo-octahedral cage 1				Cubo-octahedral cage 2			
Pb	x	y	z	Pb	x	y	z
1	4.49286298	-4.54066856	12.81707061	1	-0.02424142	-0.03175931	12.82631652
2	-0.02424142	-0.03175931	12.82631652	2	-4.51881662	4.47769709	12.83432972
3	4.49286298	4.48005844	12.85336105	3	-0.02424142	8.98896769	12.86260696
4	8.98743818	-0.02939796	12.84534785	4	4.49286298	4.48005844	12.85336105
5	4.48502282	-4.52497455	6.40463895	5	-0.00648841	-0.01687046	6.41278142
6	-0.00648841	-0.01687046	6.41278142	6	-4.52665678	4.49339110	6.42189806
7	4.48502282	4.49575245	6.44092939	7	-0.00648841	9.00385654	6.44907186
8	9.00519119	-0.01450910	6.43181275	8	4.48502282	4.49575245	6.44092939
Center	**4.48970889**	**-0.02279613**	**9.62903232**	Center	**-0.01613091**	**4.48638669**	**9.63766187**

Cubo-octahedral cage 3				Cubo-octahedral cage 4			
Pb	x	y	z	Pb	x	y	z
1	4.48502282	-4.52497455	6.40463895	1	-0.00648841	-0.01687046	6.41278142
2	-0.00648841	-0.01687046	6.41278142	2	-4.52665678	4.49339110	6.42189806
3	4.48502282	4.49575245	6.44092939	3	-0.00648841	9.00385654	6.44907186
4	9.00519119	-0.01450910	6.43181275	4	4.48502282	4.49575245	6.44092939
5	4.49286298	-4.54066856	-0.00762939	5	-0.02424142	-0.03175931	0.00161652
6	-0.02424142	-0.03175931	0.00161652	6	-4.51881662	4.47769709	0.00962972
7	4.49286298	4.48005844	0.02866105	7	-0.02424142	8.98896769	0.03790696
8	8.98743818	-0.02939796	0.02064785	8	4.49286298	4.48005844	0.02866105
Center	**4.48970889**	**-0.02279613**	**3.21668232**	Center	**-0.01613091**	**4.48638669**	**3.22531187**

Structural parameters

Table S8. Comparison between the experimental structural parameters (Exp.) and the theoretical ones obtained in this work (identified simple through "Theo."). Extructural information for CsPI, MAPI, and FAPI was extracted from Ref. [1], [2], and [3].

Perovskite	a (Å) - Exp.	a (Å) - Theo.	b (Å) - Exp.	b (Å) - Theo.	c (Å) - Exp.	c (Å) - Theo.	α (°) - Theo	β (°) - Theo	γ (°) - Theo	Volume ($Å^3$) - Exp.	Volume ($Å^3$) - Theo.	Pb-I (Å) - Exp.	Pb-I (Å) - Theo.
CsPI	8.74	8.29 **-5.1%**	8.74	9.12 **4.4%**	12.35	12.60 **2.0%**	92.96 **3.3%**	90.59 **0.7%**	89.48 **-0.6%**	942.70	951.01 **0.9%**	3.09	3.17 **2.5%**
MAPI	8.81	8.96 **1.7%**	8.81	8.96 **1.7%**	12.71	12.82 **0.8%**	90.02 **0.0%**	89.99 **0.0%**	90.00 **0.0%**	985.87	1028.84 **4.4%**	3.17	3.22 **1.4%**
FAPI	9.00	9.01 **0.2%**	9.00	9.02 **0.3%**	12.72	12.82 **0.8%**	89.77 **-0.3%**	89.88 **-0.1%**	89.98 **0.0%**	1030.01	1042.54 **1.2%**	3.18	3.23 **1.5%**

Table S9. Structural characterization of the lead-halide bonds.

Pb-I bond length (Å)				
Type of I atom	No. of I atom	CsPI	MAPI	FAPI
Equatorial	1	3.251	3.199	3.259
		3.217	3.203	3.257
	2	3.210	3.248	3.247
		3.241	3.253	3.251
	3	3.240	3.255	3.247
		3.218	3.238	3.252
	4	3.213	3.195	3.260
		3.238	3.202	3.256
	5	3.110	3.194	3.244
		3.103	3.202	3.253
	6	3.084	3.251	3.250
		3.078	3.242	3.262
	7	3.107	3.242	3.263
		3.105	3.247	3.249
	8	3.080	3.196	3.252
		3.081	3.191	3.242
Average		3.16	3.22	3.25
Standard deviation (sample)		0.07	0.03	0.01
Apical	1	3.149	3.210	3.176
		3.175	3.218	3.236
	2	3.159	3.209	3.176
		3.204	3.217	3.235
	3	3.170	3.212	3.176
		3.155	3.217	3.236
	4	3.203	3.216	3.178
		3.159	3.217	3.236
Average		3.17	3.21	3.21
Standard deviation (sample)		0.02	0.00	0.03
Pb-I-Pb angle (°)				
		CsPbI3	MAPbI3	FAPbI3
Equatorial	1	146.681	159.103	156.962
	2	144.064	158.232	156.909
	3	146.325	158.208	156.974
	4	143.678	158.777	156.774
	5	170.065	160.315	157.046
	6	168.986	158.559	157.415
	7	169.897	158.005	157.410
	8	168.999	160.131	156.954
Average		157.34	158.92	157.06
Standard deviation (sample)		13.03	0.88	0.23
Apical	1	170.127	172.650	179.240
	2	164.050	172.836	179.398
	3	169.968	171.838	179.788
	4	164.065	170.891	179.661
Average		167.05	172.05	179.52
Standard deviation (sample)		3.46	0.89	0.25

Table S10. Pb-I bond lengths within each octahedron.				
Octahedron number	Pb-I bond label	CsPI	MAPI	FAPI
1	l 1	3.103	3.202	3.253
	l 2	3.078	3.242	3.262
	l 3	3.105	3.247	3.249
	l 4	3.081	3.191	3.242
	l 5	3.155	3.217	3.236
	l 6	3.149	3.210	3.176
Average		3.11	3.22	3.24
Standard deviation (sample)		0.03	0.02	0.03
2	l 1	3.217	3.203	3.257
	l 2	3.241	3.253	3.251
	l 3	3.218	3.238	3.252
	l 4	3.238	3.202	3.256
	l 5	3.175	3.218	3.236
	l 6	3.170	3.212	3.176
Average		3.21	3.22	3.24
Standard deviation (sample)		0.03	0.02	0.03
3	l 1	3.107	3.242	3.263
	l 2	3.080	3.196	3.252
	l 3	3.110	3.194	3.244
	l 4	3.084	3.251	3.250
	l 5	3.159	3.217	3.236
	l 6	3.159	3.209	3.176
Average		3.12	3.22	3.24
Standard deviation (sample)		0.04	0.02	0.03
4	l 1	3.240	3.255	3.247
	l 2	3.213	3.195	3.260
	l 3	3.251	3.199	3.259
	l 4	3.210	3.248	3.247
	l 5	3.204	3.217	3.235
	l 6	3.203	3.216	3.178
Average		3.22	3.22	3.24
Standard deviation (sample)		0.02	0.02	0.03
Total average		3.16	3.22	3.24
Total standard deviation (sample)		0.06	0.02	0.03

Table S11. I-Pb-I bond angles within each octahedron (Part I).				
Octahedron number	Internal I-Pb-I angle	CsPI	MAPI	FAPI
1	Φ_1	90.641	92.981	89.064
	Φ_2	88.824	91.636	88.835
	Φ_3	89.205	85.690	88.813
	Φ_4	91.152	87.547	89.075
	Φ_5	89.507	95.953	90.569
	Φ_6	91.082	87.992	90.612
	Φ_7	90.647	85.362	91.551
	Φ_8	88.941	92.874	91.477
	Φ_9	84.305	88.843	89.709
	Φ_10	95.488	89.013	89.909
	Φ_11	84.139	91.308	90.169
	Φ_12	96.068	90.815	90.135
Average		90.00	90.00	89.99
Standard deviation (sample)		3.57	3.16	0.95
2	Φ_1	87.000	87.403	89.200
	Φ_2	86.858	85.778	88.865
	Φ_3	93.035	90.977	88.748
	Φ_4	92.856	92.791	88.955
	Φ_5	93.017	92.995	90.752
	Φ_6	93.033	85.574	91.114
	Φ_7	86.948	88.590	91.300
	Φ_8	87.253	95.848	91.065
	Φ_9	84.071	90.502	89.902
	Φ_10	95.751	89.262	90.214
	Φ_11	84.099	89.575	89.821
	Φ_12	96.079	90.619	89.985
Average		90.00	89.99	89.99
Standard deviation (sample)		4.38	3.01	0.92

Table S11. I-Pb-I bond angles within each octahedron (Part II).

Octahedron number	Internal I-Pb-I angle	CsPI	MAPI	FAPI
3	Φ_1	87.174	91.161	89.039
	Φ_2	89.569	93.519	89.003
	Φ_3	92.805	87.640	88.822
	Φ_4	90.465	85.733	88.889
	Φ_5	93.024	88.383	90.344
	Φ_6	90.224	95.497	90.837
	Φ_7	86.996	92.909	91.795
	Φ_8	89.741	85.237	91.267
	Φ_9	84.150	89.604	89.690
	Φ_10	95.645	88.891	90.244
	Φ_11	83.956	90.499	90.095
	Φ_12	96.249	90.989	89.892
Promedio		90.00	90.01	89.99
DESVEST		4.00	3.08	0.97
4	Φ_1	82.368	85.484	89.209
	Φ_2	88.920	87.410	88.978
	Φ_3	97.718	93.047	88.761
	Φ_4	90.912	91.242	88.865
	Φ_5	97.878	85.148	90.961
	Φ_6	90.876	93.348	90.875
	Φ_7	82.036	96.300	91.069
	Φ_8	89.290	87.953	91.282
	Φ_9	85.279	90.501	89.996
	Φ_10	94.547	90.890	89.811
	Φ_11	85.038	89.361	89.959
	Φ_12	95.136	89.212	90.157
Average		90.00	89.99	89.99
Standard deviation (sample)		5.56	3.28	0.91
Total average		90.00	90.00	89.99
Total standard deviation (sample)		4.30	3.03	0.91

Hydrogen bonds

Table S12. Hydrogen bond lengths within FAPI and MAPI.

No. of cubo-octahedral cage	X—H…I type	FAPI		MAPI	
1	N—H…I	3.164	132.440	2.593	166.430
		3.123	133.469		
		3.002	135.283	2.618	161.068
		3.021	134.288		
	C—H…I	3.144	126.529		
		3.165	125.654		
Average		3.10	131.28	2.61	163.75
Standard deviation (sample)		0.07	4.13	0.02	3.79
2	N—H…I	3.155	132.800	2.611	163.764
		3.135	133.179		
		3.008	134.829	2.602	163.660
		3.012	134.697		
	C—H…I	3.153	126.098		
		3.155	125.966		
Average		3.10	131.26	2.61	163.71
Standard deviation (sample)		0.07	4.13	0.01	0.07
3	N—H…I	3.132	132.682	2.607	164.978
		3.122	133.280		
		3.015	134.827	2.587	164.988
		3.028	134.359		
	C—H…I	3.152	126.573		
		3.159	126.092		
Average		3.10	131.30	2.60	164.98
Standard deviation (sample)		0.06	3.93	0.01	0.01
4	N—H…I	3.151	132.599	2.584	169.353
		3.109	133.550		
		3.013	134.872	2.599	162.902
		3.030	134.299		
	C—H…I	3.151	126.646		
		3.157	126.147		
Average		3.10	131.35	2.59	166.13
Standard deviation (sample)		0.06	3.92	0.01	4.56
Total average		3.10	131.30	2.60	164.64
Total standard deviation (sample)		0.06	3.76	0.01	2.48

COHP analysis for CsPI, MAPI, and FAPI

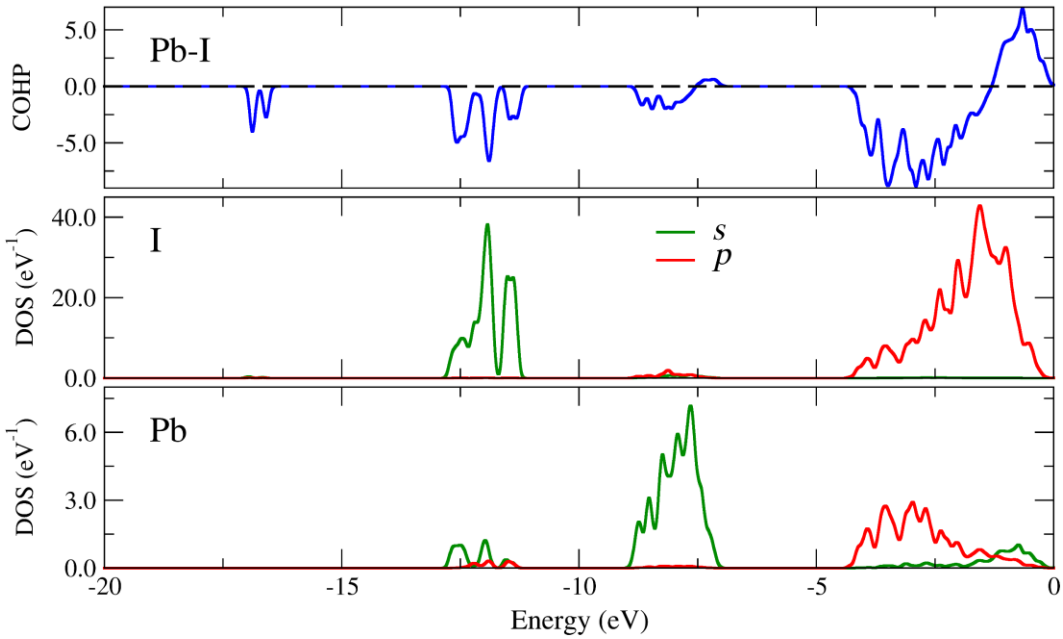

Figure S1. COHP curve of the Pb-I bonds within CsPI perovskite. The density of states from s and p orbitals of both I and Pb species are also shown for comparison. The ICOHP energy value was -16.21 eV.

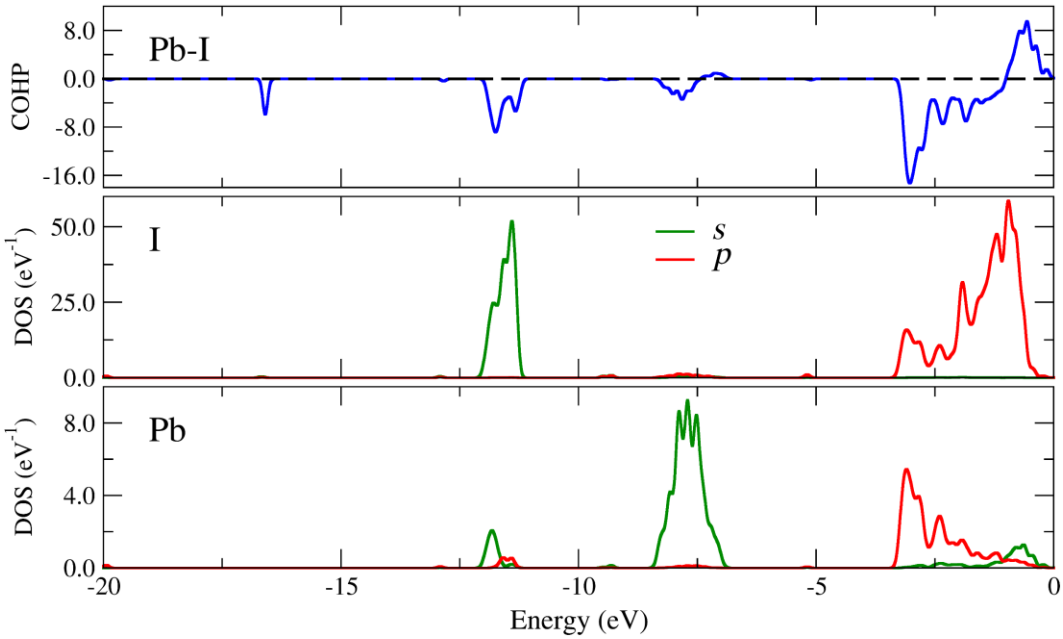

Figure S2. COHP curve of the Pb-I bonds within MAPI perovskite. The density of states from s and p orbitals of both I and Pb species are also shown for comparison. The ICOHP energy value was -15.37 eV.

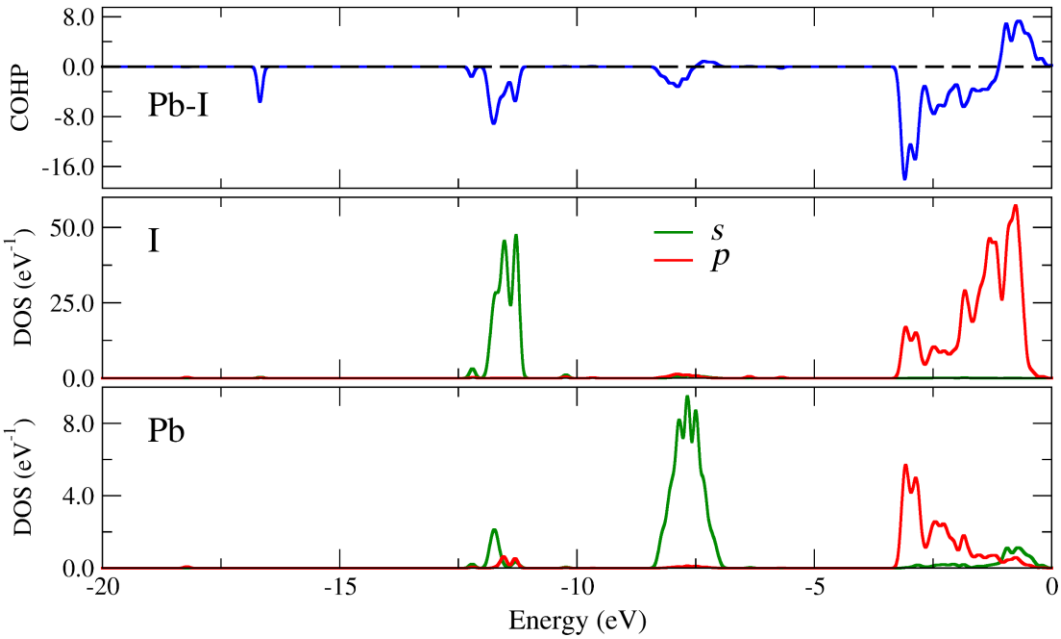

Figure S3. COHP curve of the Pb-I bonds within FAPI perovskite. The density of states from s and p orbitals of both I and Pb species are also shown for comparison. The ICOHP energy value was -15.27 eV.

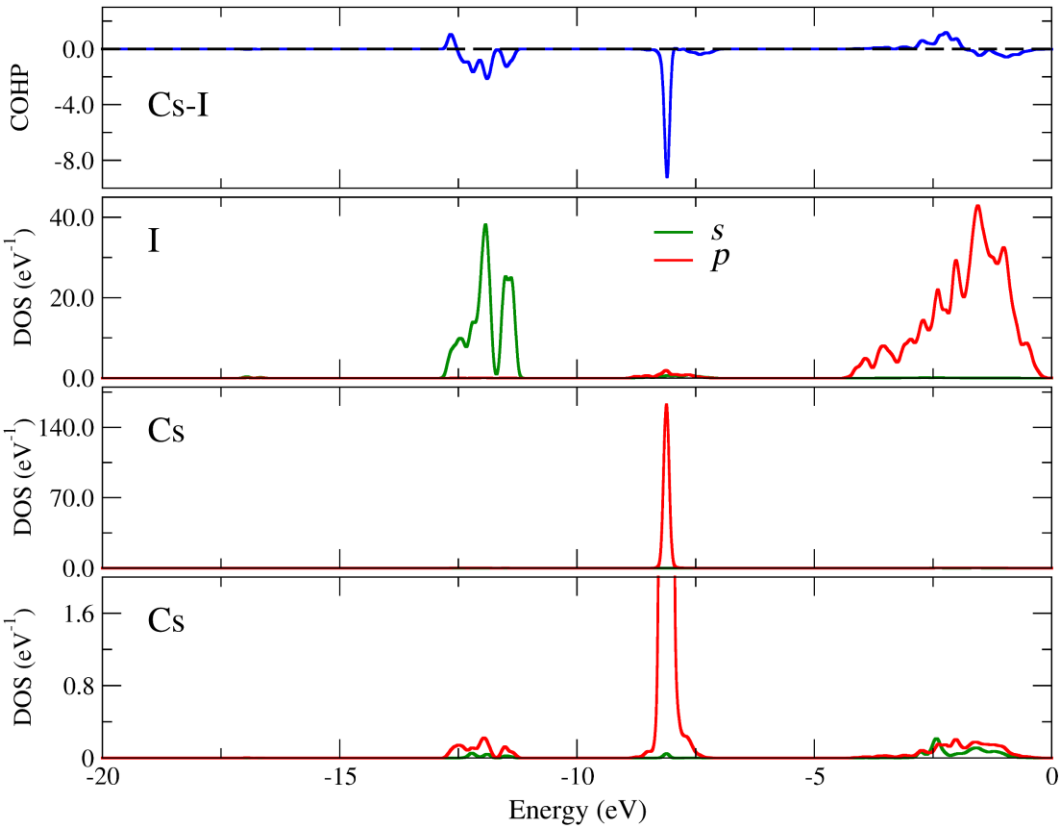

Figure S4. COHP curve of the Cs-I bonds within CsPI perovskite. The density of states from s and p orbitals of both Cs and I species are also shown for comparison. The ICOHP energy value was -2.25 eV.

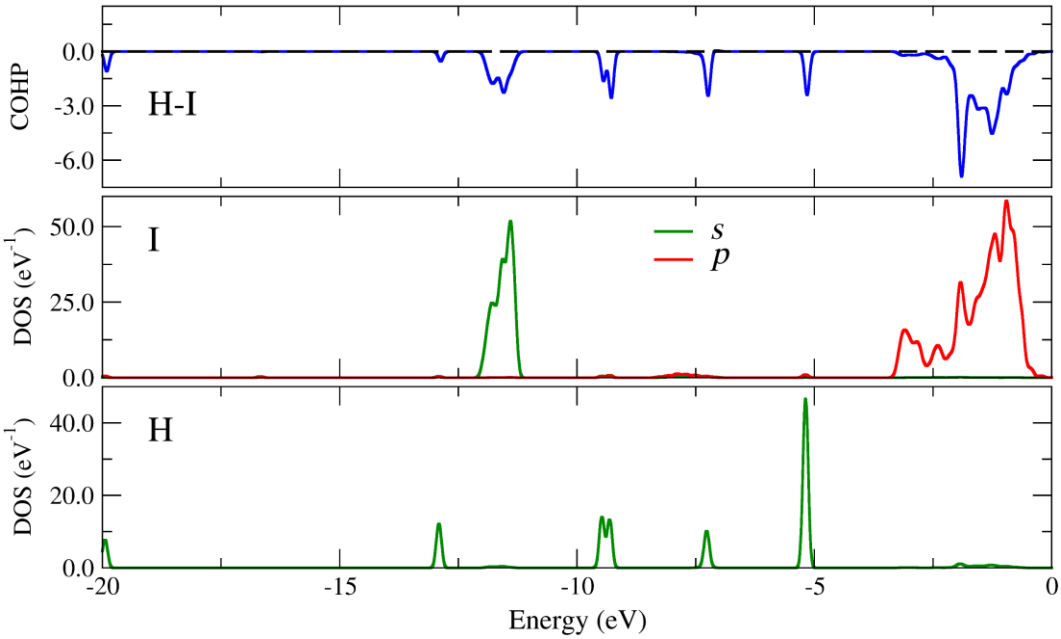

Figure S5. COHP curve of the H-I bonds within MAPI perovskite. The density of states from s and p orbitals of both H and I species are also shown for comparison. The ICOHP energy value was -7.02 eV.

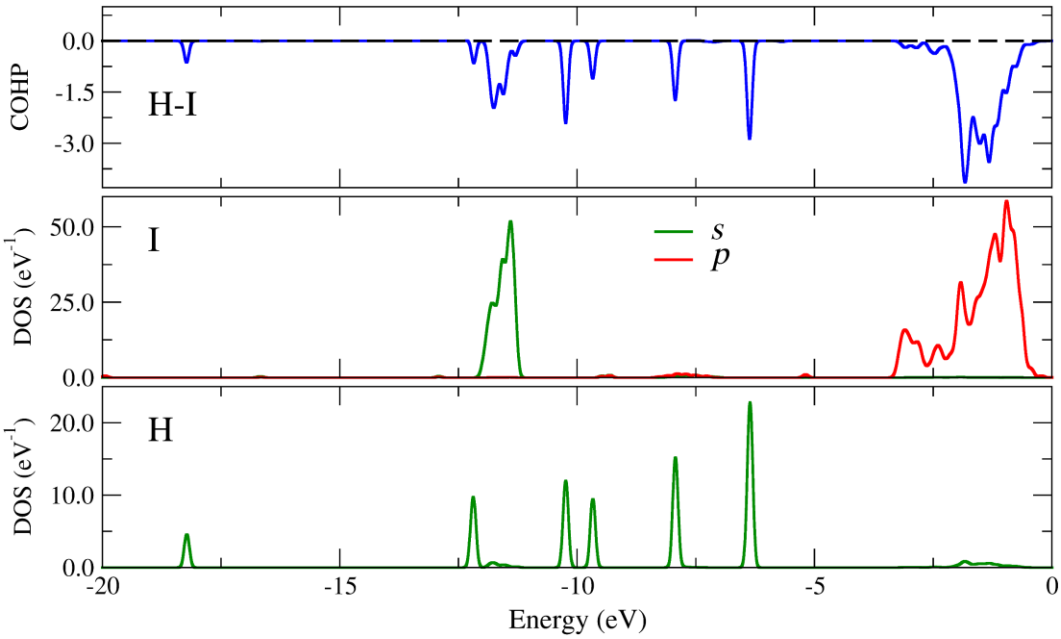

Figure S6. COHP curve of the H-I bonds within FAPI perovskite. The density of states from s and p orbitals of both H and I species are also shown for comparison. The ICOHP energy value was -5.43 eV.

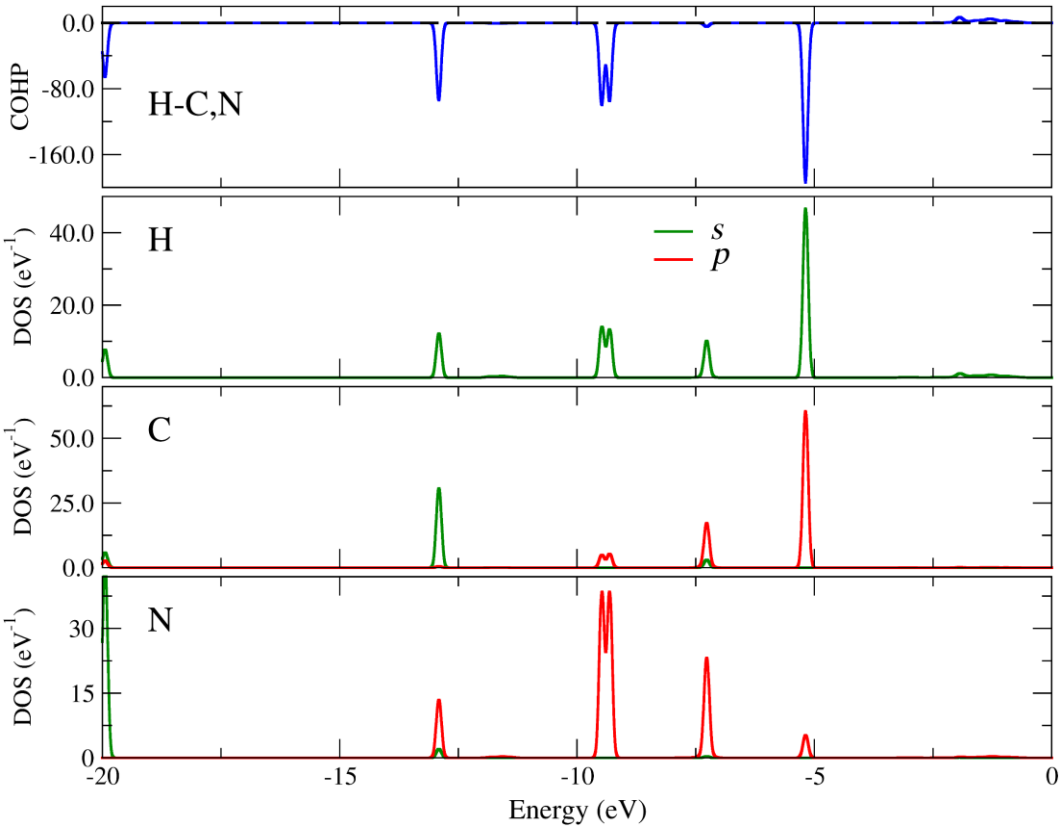

Figure S7. COHP curve of the H-C and H-N bonds (or simply H-C,N) within MAPI perovskite. The density of states from s and p orbitals of H, C, and N species are also shown for comparison. The ICOHP energy value was -65.70 eV.

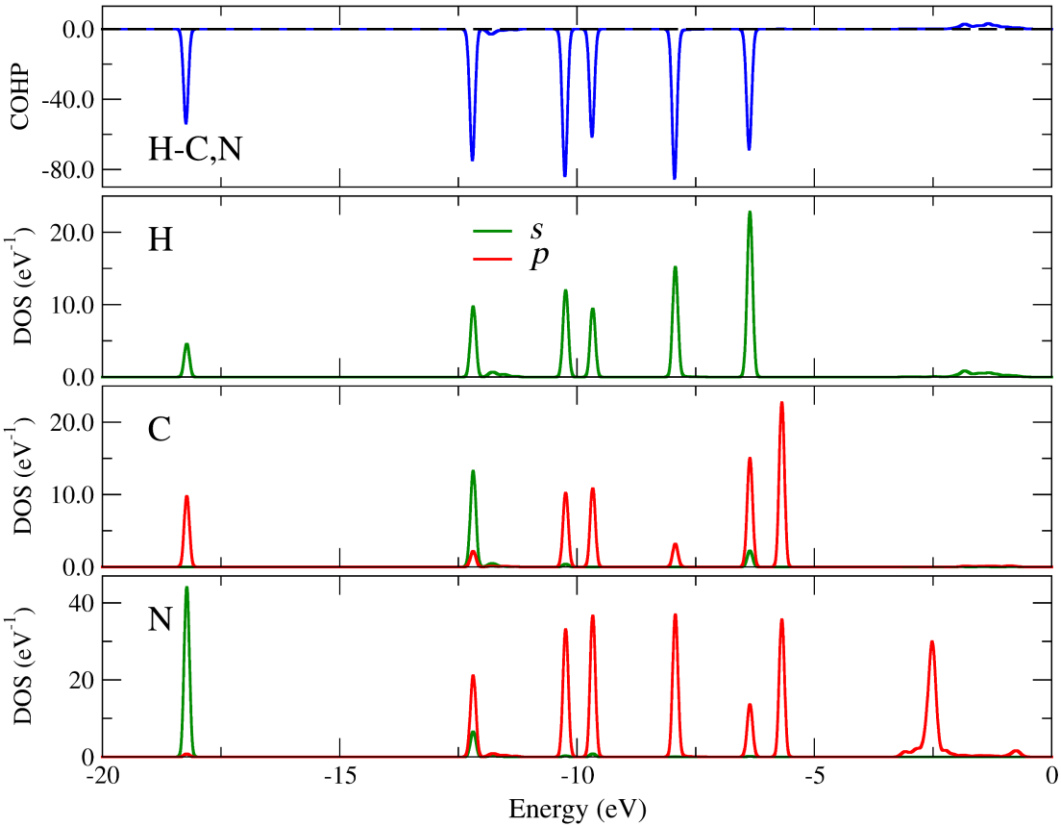

Figure S8. COHP curve of the H-C and H-N bonds (or simply H-C,N) within FAPI perovskite. The density of states from s and p orbitals of H, C, and N species are also shown for comparison. The ICOHP energy value was -55.58 eV.

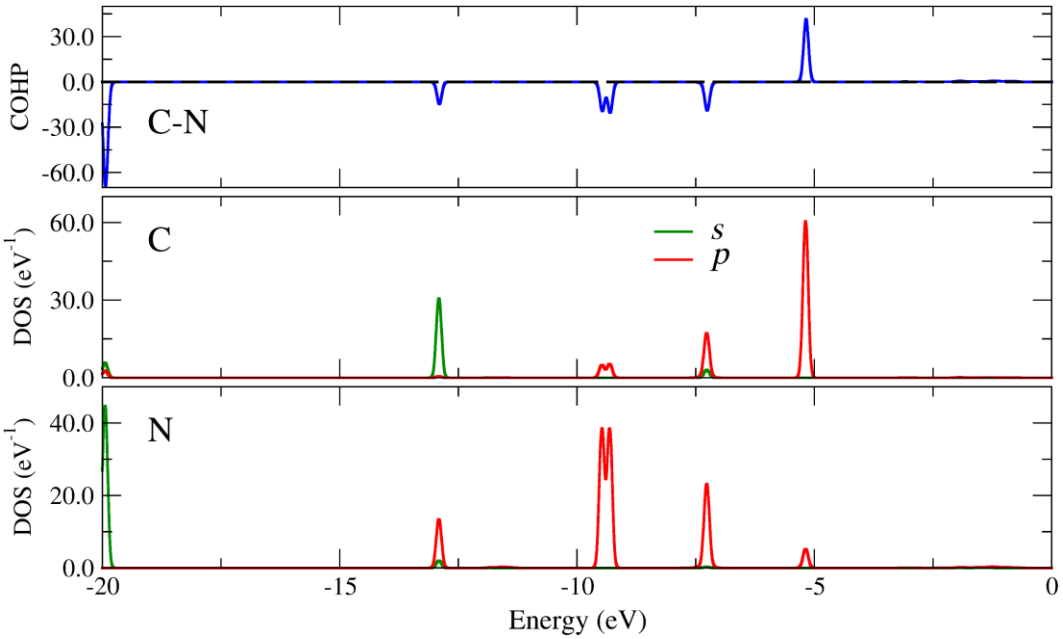

Figure S9. COHP curve of the C-N bonds within MAPI perovskite. The density of states from s and p orbitals of both C and N species are also shown for comparison. The ICOHP energy value was -11.99 eV.

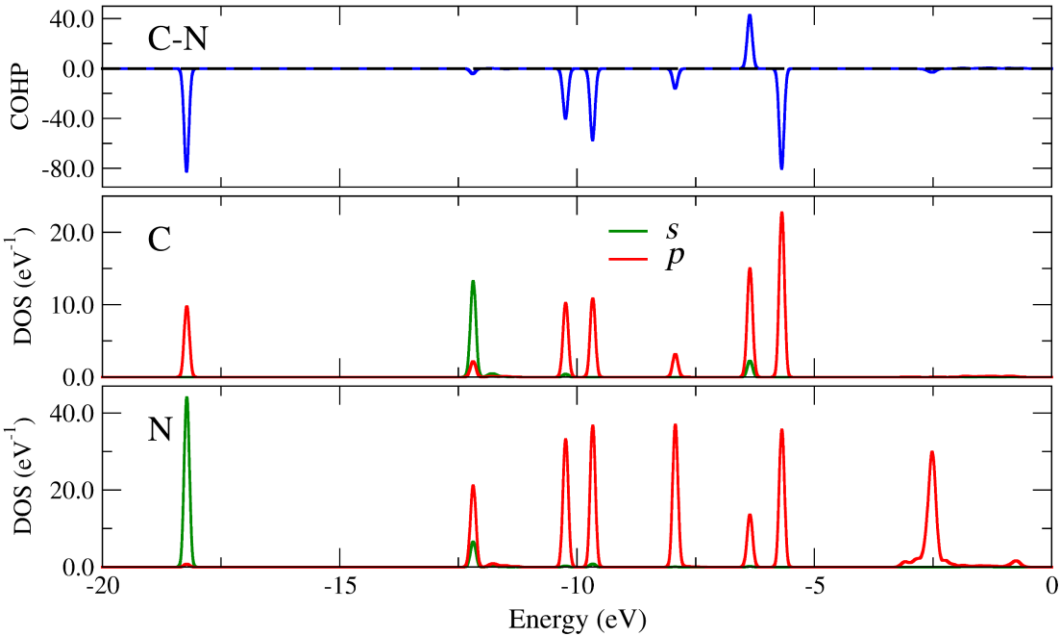

Figure S10. COHP curve of the C-N bonds within FAPI perovskite. The density of states from s and p orbitals of both C and N species are also shown for comparison. The ICOHP energy value was -46.40 eV.

Band structures for the different functionals

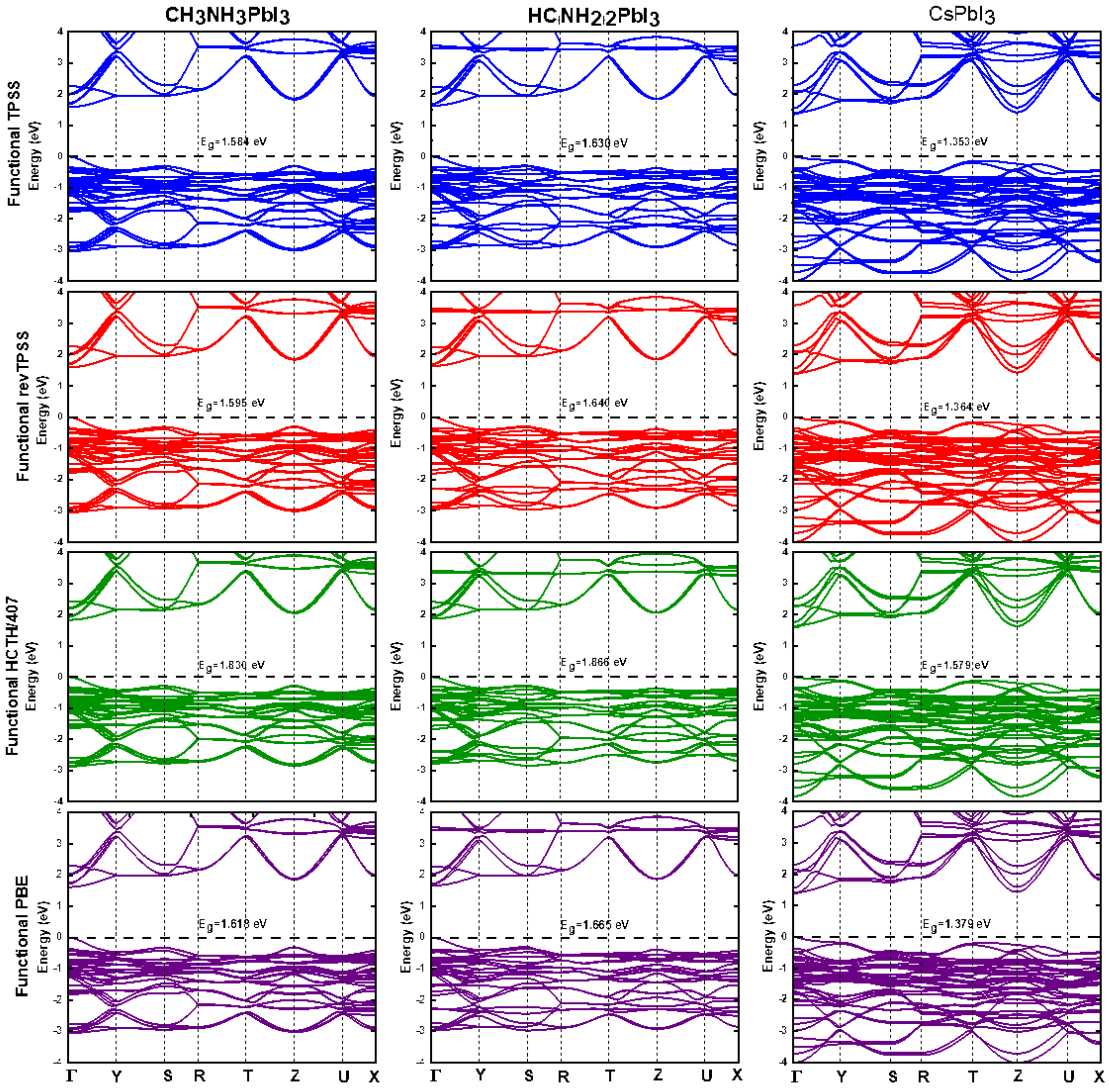

Figure S11. Comparison of the band structures for all three perovskites studied and calculated by means of the TPSS, revTPSS, HCTH/407 and PBE functionals.

References

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[2] M. T. Weller, O. J. Weber, P. F. Henry, A. M. Di Pumpo, and T. C. Hansen. “Complete structure and cation orientation in the perovskite photovoltaic methylammonium lead iodide between 100 and 352 K”. Chemical Communications, 51(20), 4180-4183 (2015).

[3] M. T. Weller, O. J. Weber, J. M. Frost, and A. Walsh. “Cubic perovskite structure of black formamidinium lead iodide, α-[$HC(NH_2)_2$]PbI_3, at 298 K”. The Journal of Physical Chemistry Letters, 6(16), 3209-3212 (2015).