Tuning the Optoelectronic Properties of 2D Hybrid Perovskite Semiconductors with Alkyl Chain Spacers

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Supporting Information

Fitting of the amount of Hartree-Fock exact exchange for the correct prediction of the band gap of 2D layered perovskite, including spin-orbit coupling: C6 monoclinic as test case

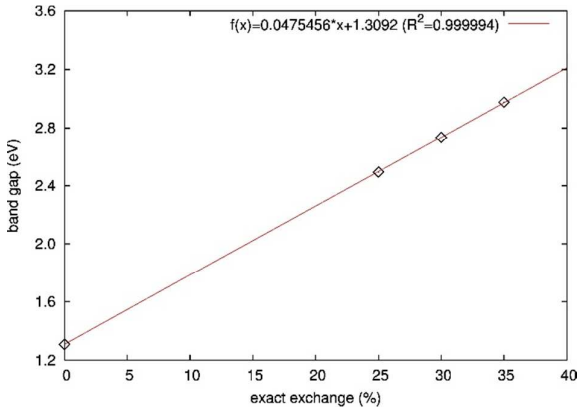

Figure S1. Fit of the amount of the Hartree-Fock exact exchange for PBE0+SOC, in the case of monoclinic phase of C6PbI perovskite. Reference experimental data is 2.7 eV.[1]

Energy of the valence and conduction band edge for the C6 and C12 polymorphs

Table S1. Energy of the valence band edge (VBE) and conduction band edge (CBE) and band gap (Eg), computed for the monoclinic and orthorhombic polymorphs of C6 and C12, using the various computational approaches. All energies are referred to the averaged electrostatic potential of the crystal cell, computed using the various methods. Data in eV.

method	VBE	CBE	Eg	VBE	CBE	Eg
		C6-monoclinic			C6-orthorhomib	
PBE	-0.34	1.70	2.04	-0.47	1.55	2.02
PBE+SOC	-0.39	0.99	1.38	-0.55	0.80	1.35
PBE0	-1.23	2.28	3.51	-1.60	1.82	3.42
PBE CORRECT	-1.28	1.57	2.85	-1.68	1.07	2.75
PBE0+SOC	-1.41	1.32	2.73	-1.41	1.32	2.73
		C12-monoclinic			C12-orthorhombic	
PBE	-0.45	1.72	2.17	-0.23	2.12	2.44
PBE+SOC	-0.50	1.00	1.50	-0.37	1.34	1.71
PBE0	-1.57	2.03	3.60	-1.46	2.43	3.89
PBE CORRECT	-1.68	1.07	2.93	-1.46	1.65	3.11
PBE0+SOC	-1.45	1.42	2.87			

Density of States (DOS) of the C6 and C12 polymorphs

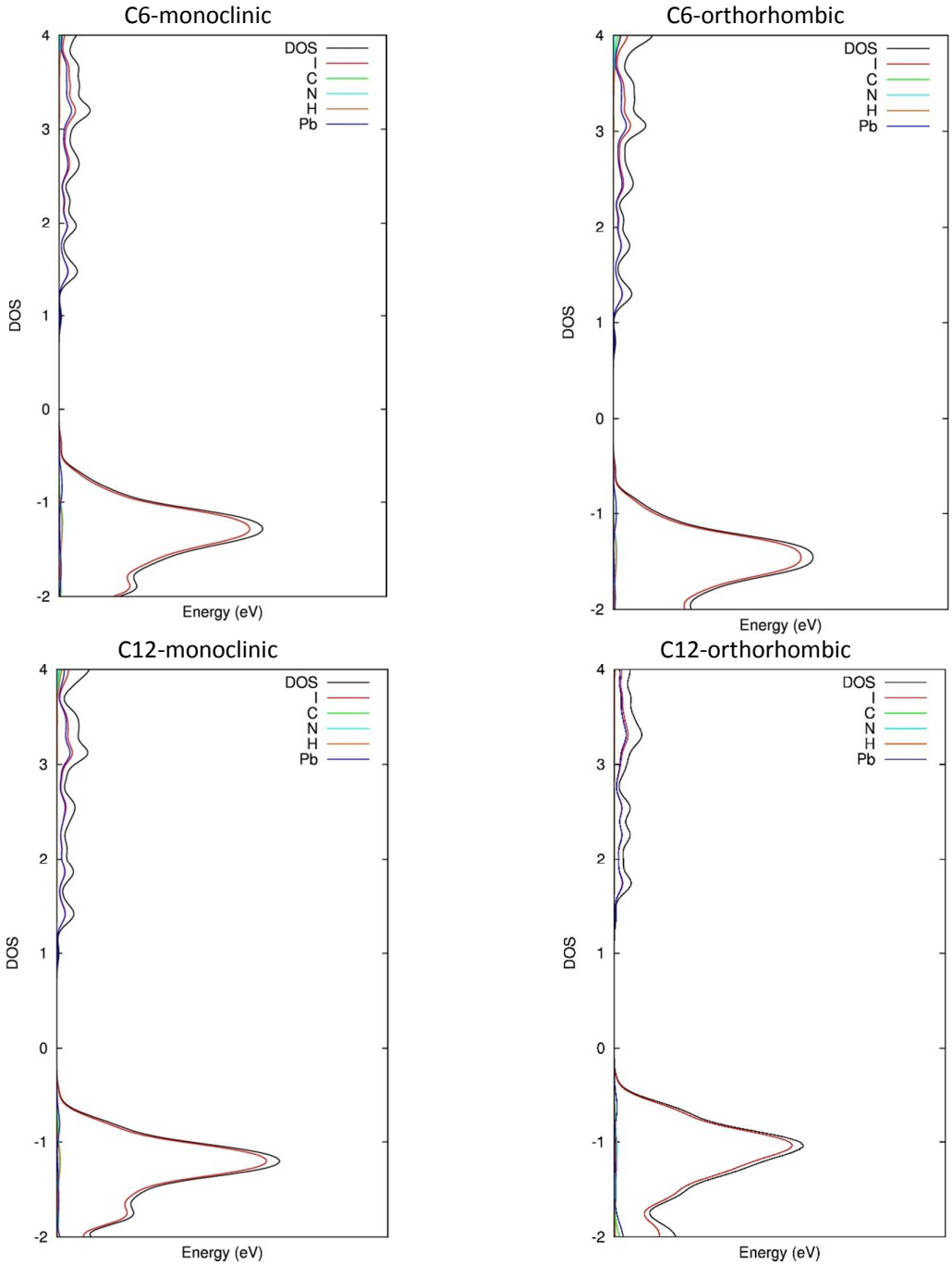

Figure S2. Atomic Density of State of the C6PbI and C12PbI polymorphs. The contribution from the different chemical elements is listed. Electronic structure obtained with the PBE functional for the description of the exchange-correlation interaction, including spin-orbit coupling.

Layered perovskites with exchanged organic spacers

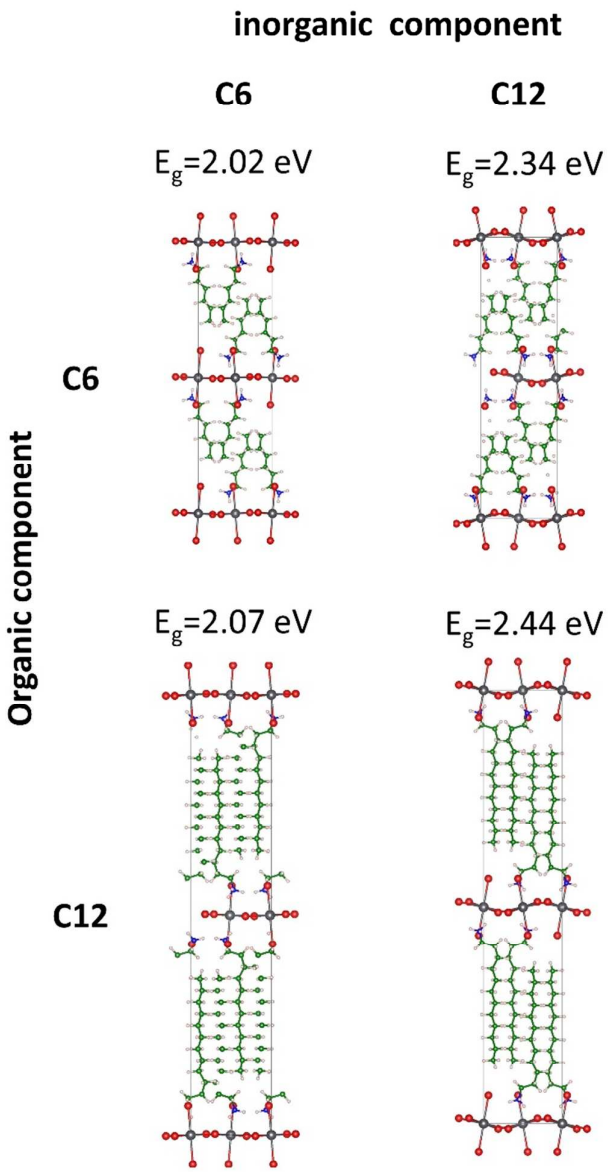

Figure S3. Crystalline models obtained by substituting the organic components of the C6PbI and C12PbI perovskite in the orthorhombic phase. The corresponding band gap obtained at PBE level without SOC are also reported.

Structural analysis of the inorganic structures of C6PbI and C12PbI polymorphs

Table S1. List of the band gap (E_g) and structural parameters (b_1, b_2, b_3, θ and δ) of the inorganic sheet of the monoclinic and orthorhombic polymorphs of C6 and C12 layered perovskites.

phase	E_g		b_1	b_2	b_3	θ	δ
	(PBE0+SOC)	(PBE)					
			C6PbI				
monoclinic	2.73	2.04	3.19	3.18	3.26	152	3.21
orthorhombic	2.70	2.02	3.20	3.19	3.25	154	3.21
			C12PbI				
monoclinic	2.87	2.17	3.22	3.21	3.21	153	0.90
orthorhombic	3.11	2.44	3.23	3.24	3.24	143	6.70

Simplified model to generate the 2D maps describing the band gap dependence on the octahedral tilting

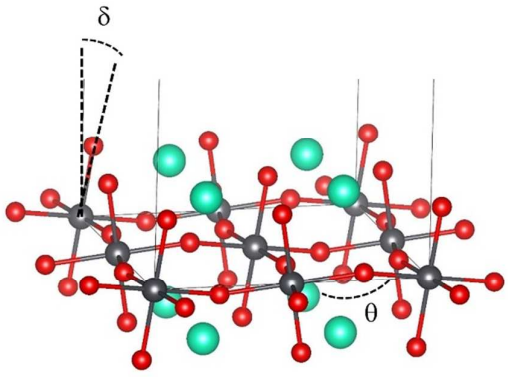

Figure S4. Simplified reference-model used to construct the 2D maps in Figure3. The model contains 4 PbI_4 octahedra in the cell and the organic is substituted by Cesium atoms (cyan). The cell parameters related to the perovskite plane have been changed upon the octahedral rotation (that means, upon deviation of θ and δ angles from 180° and 0°, respectively) to keep the PbI bond length constant.

Comparison of the results for fixed cell and variable cell calculation

Table S3. Comparison of the band gap a (E_g, PBE), and structural parameters (bond lengths , b_1, b_2, b_3, and Pb-I-PB angle θ) for fixed cell and variable cell relaxations.

system		E_g (eV)	b_1 (Å)	b_2 (Å)	b_3 (Å)	θ (°)
			fixed cell			
C6	mono	2.04	3.18	3.19	3.26	152.3
	ortho	2.02	3.20	3.19	3.25	153.8
C12	mono	2.17	3.22	3.21	3.23	153.4
	ortho	2.44	3.24	3.23	3.23	143.4
			variable cell			
C6	mono	1.98	3.09	3.09	3.23	148.8
	ortho	2.04	3.10	3.10	3.23	146.5
C12	mono	2.00	3.07	3.08	3.23	146.3
	ortho	2.33	3.07	3.09	3.22	138.9

Results from TDDFT calculations

Table S4. Results of TDDFT calculation carried out with PBE functional. The energy, transition dipole and the most important components of the TDDFT eigenvectors are listed.

C6PbI monoclinic

exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.08	6.12	H	L	1.00	-0.013
2	2.17	6.13	H	L+1	-1.00	0.010
3	2.70	0.02	H-1	L	-0.97	0.002
			H-5	L	-0.19	-0.003
4	2.78	0.06	H-2	L	-0.77	0.010
			H-1	L+1	0.58	-0.006
			H-3	L+1	-2.13	-0.001
			H-7	L+1	0.16	-0.002
5	2.82	0.12	H-3	L	-0.91	0.002
			H-2	L+1	-0.39	-0.001
			H-1	L	-0.10	0.002
6	2.84	0.22	H-1	L+1	-0.73	0.008
			H-2	L	-0.50	0.008
			H-3	L+1	-0.35	-0.005
			H-7	L+1	-0.24	0.001
			H-4	L	0.17	-0.001
			H-8	L	0.11	0.002
7	2.84	0.01	H-4	L	-0.96	0.008
			H-6	L+1	-0.21	0.002
			H-1	L+1	-0.13	0.002
8	2.87	0.07	H-2	L+1	0.92	-0.005
			H-3	L	-0.40	0.005
9	2.90	0.00	H-6	L	0.80	-0.007
			H-4	L+1	0.56	-0.003
			H-9	L	-0.18	0.001
10	2.92	0.00	H-5	L	-1.00	0.018
11	2.93	0.65	H-8	L	0.94	-0.004
			H-3	L+1	0.33	-0.002
12	2.95	0.00	H-4	L+1	-0.71	0.008
			H-5	L+1	0.54	-0.004
			H-6	L	0.45	-0.007
13	2.98	0.03	H-7	L	0.95	-0.006
			H-10	L	0.24	-0.002
14	2.99	0.17	H-3	L+1	-0.83	0.014
			H-2	L	0.37	-0.015
			H-8	L	0.32	-0.004
			H-1	L+1	0.22	-0.009
15	3.01	0.00	H-9	L	0.67	-0.006
			H-5	L+1	0.61	-0.004
			H-4	L+1	0.38	-0.006
			H-6	L	-0.18	0.002

C12PbI monoclinic

exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.28	3.64	H	L	-1.00	0.016
2	2.34	3.77	H	L+1	1.00	-0.014
3	2.83	0.01	H-2	L	0.84	-0.003
			H-1	L	-0.48	0.004
			H-3	L+1	0.25	0.003
4	2.86	0.01	H-3	L	-0.79	0.004
			H-2	L+1	-0.56	-0.002
			H-1	L+1	0.26	-0.000
5	2.89	0.03	H-1	L	0.85	-0.015
			H-2	L	0.46	-0.006
			H-9	L	0.23	0.007
6	2.90	0.00	H-4	L	0.92	-0.009
			H-5	L+1	0.33	0.003
			H-7	L+1	0.16	0.005
			H-6	L	-0.15	-0.001
7	2.92	0.36	H-1	L+1	-0.97	0.005
			H-2	L	0.25	-0.005
8	2.94	0.00	H-5	L	0.82	-0.008
			H-4	L+1	0.57	-0.003
9	2.97	0.00	H-6	L	-0.97	0.006
			H-5	L+1	-0.22	0.001
10	2.98	0.19	H-1	L+1	0.95	-0.022
			H-3	L	0.27	-0.007
11	3.01	0.00	H-6	L+1	0.72	-0.002
			H-7	L	-0.50	-0.003
			H-4	L+1	-0.39	0.006
			H-5	L	0.26	-0.005
12	3.02	0.00	H-5	L+1	0.81	-0.009
			H-8	L+1	0.40	0.002
			H-4	L	-0.32	0.009
			H-7	L+1	-0.20	-0.003
			H-6	L	-0.19	0.003
13	3.03	0.17	H-2	L+1	-0.81	0.021
			H-3	L	0.53	-0.018
14	3.06	0.00	H-7	L	0.67	0.002
			H-6	L+1	-0.66	0.007
			H-4	L+1	-0.25	0.006
			H-8	L+1	0.19	0.002
			H-5	L	0.12	-0.004
15	3.11	0.01	H-8	L+1	0.84	0.001
			H-7	L	0.42	-0.005
			H-4	L+1	-0.29	0.010
			H-5	L	0.19	-0.007

Table S5. Results of TDDFT calculation carried out with PBE0 functional, with 15% of exact exchange. The energy, transition dipole and the most important components of the TDDFT eigenvectors are listed.

C6PbI monoclinic

exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.14	1.87	H	L	-1.00	0.021
2	2.22	1.86	H	L+1	-1.00	0.018
3	2.95	0.01	H-1	L	-0.99	0.011
			H-3	L	0.15	-0.001
4	3.05	0.01	H-2	L	-0.75	0.003
			H-1	L+1	0.63	-0.007
			H-3	L+1	-0.15	-0.002
			H-8	L+1	0.10	0.007
5	3.08	0.08	H-1	L+1	0.76	-0.013
			H-2	L	0.62	-0.007
			H	L+2	0.15	0.006
			H-8	L+1	0.11	0.007
6	3.10	0.02	H-3	L	-0.97	0.004
			H-2	L+1	-0.19	-0.002
			H-1	L	-0.15	0.002
7	3.10	0.00	H-4	L+1	0.98	-0.007
			H-5	L	-0.19	0.002
			H-6	L	0.11	0.005
8	3.14	0.04	H-2	L+1	0.98	-0.005
			H-3	L	-0.19	0.004
9	3.18	0.00	H-5	L	-0.98	0.013
			H-6	L	-0.18	0.001
10	3.18	0.19	H-7	L	0.99	-0.004
11	3.19	0.00	H-4	L+1	-0.80	0.003
			H-6	L	-0.59	0.002
			H-5	L+1	0.12	-0.001
12	3.20	0.00	H-8	L	0.99	-0.013
			H-7	L+1	-0.13	0.000
13	3.20	0.01	H-3	L+1	0.95	-0.007
			H	L+2	-0.26	-0.005
			H-2	L+2	-0.12	0.006
14	3.21	0.00	H-6	L	0.71	-0.008
			H-4	L+1	-0.58	0.006
			H-5	L+1	-0.39	0.000
15	3.28	0.24	H-8	L	0.99	-0.004
			H-7	L+1	0.12	-0.002

C12PbI monoclinic

exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.18	1.40	H	L	1.00	-0.015
2	2.31	1.47	H	L+1	0.99	-0.016
3	2.86	0.00	H-2	L	0.99	-0.007
			H-1	L	0.13	0.002
4	2.99	0.01	H-1	L	0.99	-0.006
			H-3	L	0.15	0.000
5	2.99	0.04	H-3	L	0.99	-0.005
			H-1	L	-0.13	0.003
6	2.99	0.09	H-2	L	0.96	-0.004
			H-3	L+1	0.20	0.004
			H-1	L+1	-0.14	0.002
			H-6	L	-0.10	-0.002
7	2.99	0.00	H-4	L	0.98	-0.010
			H-5	L+1	0.12	0.004
			H-7	L	-0.10	-0.001
8	2.99	0.05	H-2	L+1	-0.99	0.004
9	2.99	0.11	H-3	L+1	0.84	-0.006
			H-6	L	0.52	0.002
			H-2	L	-0.12	0.004
10	2.99	0.00	H-5	L	-0.76	0.006
			H-4	L+1	-0.63	0.004
			H-9	L	-0.16	0.001
11	3.13	0.00	H-7	L	0.98	-0.007
			H-5	L+1	0.17	0.000
12	3.13	0.00	H-7	L+1	0.87	-0.002
			H-4	L+1	-0.39	0.008
			H-5	L	0.30	-0.007
13	3.13	0.23	H-6	L	-0.83	0.011
			H-3	L+1	0.50	-0.012
			H-2	L	-0.19	0.008
			H-8	L+1	0.12	0.000
14	3.13	0.21	H-6	L+1	0.90	-0.003
			H-8	L	-0.42	0.005
15.00	3.13	0.00	H-5	L+1	-0.95	0.009
			H-4	L	0.23	0.006
			H-7	L	0.16	-0.002
			H-10	L	0.15	-0.006

Table S6. Results of TDDFT calculation carried out with PBE0 functional, with 30% of exact exchange. The energy, transition dipole and the most important components of the TDDFT eigenvectors are listed.

C6PbI monoclinic						
exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.17	0.91	H	L	-0.99	0.015
			H-5	L	-0.11	0.002
2	2.26	0.92	H	L+1	0.99	-0.015
			H-5	L	0.11	-0.002
3	3.16	0.01	H-1	L	-0.96	0.007
			H-8	L	-0.20	0.007
			H-3	L	-0.17	0.001
4	3.27	0.06	H-1	L+1	-0.97	0.008
			H-3	L+1	-0.15	0.002
			H-8	L	-0.13	0.008
5	3.34	0.03	H-2	L	-0.97	0.005
			H	L+2	-0.21	-0.005
6	3.37	0.00	H-3	L	0.90	-0.003
			H-2	L+1	-0.33	0.002
			H-8	L	-0.19	0.002
			H-4	L	-0.14	0.001
			H-1	L	-0.14	0.001
			H-5	L+1	0.10	-0.001
7	3.37	0.00	H-4	L	-0.93	0.006
			H-6	L	0.33	-0.003
			H-3	L	-0.14	0.000
8	3.42	0.00	H-8	L	0.95	-0.008
			H-1	L	-0.23	-0.003
			H-2	L+1	-0.15	0.000
9	3.42	0.03	H-2	L+1	-0.92	0.003
			H-3	L	-0.36	0.000
			H-5	L+1	0.13	0.000
10	3.43	0.00	H-6	L	0.94	-0.007
			H-4	L	0.34	-0.002
11	3.44	0.11	H-5	L	-0.96	0.003
			H	L+2	0.16	0.002
			H-3	L+1	-0.16	0.002
			H	L	0.12	0.000
12	3.46	0.00	H-4	L+1	0.99	-0.006
			H-9	L	-0.11	0.002
13	3.48	0.00	H-3	L+1	0.93	-0.002
			H	L+2	-0.25	-0.002
			H-5	L	-0.21	-0.001
			H-1	L+1	-0.15	0.000
14	3.50	0.00	H-7	L	0.88	-0.007
			H-6	L+1	0.44	0.000
			H-9	L	0.12	-0.004
			H-4	L+1	0.11	-0.002
15	3.55	0.10	H-5	L+1	0.98	-0.004
			H-2	L+1	0.13	-0.001
			H-8	L	0.12	-0.002
			H	L+1	-0.12	0.000

C12PbI monoclinic						
exc. state	energy (eV)	trans dip (a.u.)	from	to	fx	fy
1	2.30	0.71	H	L	-0.98	0.015
			H-2	L	0.13	-0.003
			H-5	L	0.13	-0.002
2	2.37	0.75	H	L+1	0.98	-0.015
			H-2	L+1	-0.14	0.003
			H-5	L+1	-0.12	0.003
3	3.11	0.00	H-1	L	-0.99	0.006
			H-8	L	-0.13	0.007
4	3.19	0.01	H-1	L+1	-0.99	0.006
5	3.22	0.03	H-3	L	0.96	-0.003
			H-2	L+1	-0.24	0.002
			H-5	L+1	0.10	-0.001
6	3.24	0.00	H-4	L	0.98	-0.009
			H-10	L	0.13	-0.001
7	3.25	0.05	H-2	L	-0.98	0.005
			H	L	-0.14	-0.001
8	3.31	0.03	H-2	L+1	-0.95	0.003
			H-3	L	-0.24	0.000
			H-8	L	0.13	-0.002
9	3.33	0.00	H-7	L	-0.99	0.006
			H-6	L+1	-0.10	-0.001
10	3.33	0.02	H-5	L	-0.46	-0.002
			H-3	L+1	0.88	-0.004
11	3.34	0.00	H-6	L	-0.70	0.004
			H-4	L+1	-0.68	0.004
			H-9	L	-0.23	0.001
12	3.36	0.00	H-7	L+1	-0.80	0.002
			H-4	L+1	0.43	-0.009
			H-6	L	-0.36	0.008
			H-9	L	-0.22	0.006
13	3.37	0.10	H-5	L	-0.79	0.009
			H-3	L+1	-0.41	0.009
			H-8	L	-0.41	0.004
			H-8	L+1	0.13	-0.001
14	3.37	0.04	H-8	L	0.74	-0.008
			H-5	L+1	-0.57	0.001
			H-5	L	-0.28	0.003
			H-3	L+1	-0.14	0.003
15	3.42	0.07	H-5	L+1	0.80	-0.004
			H-8	L	0.50	-0.007
			H-5	L	-0.21	0.004
			H-3	L+1	-0.15	0.004

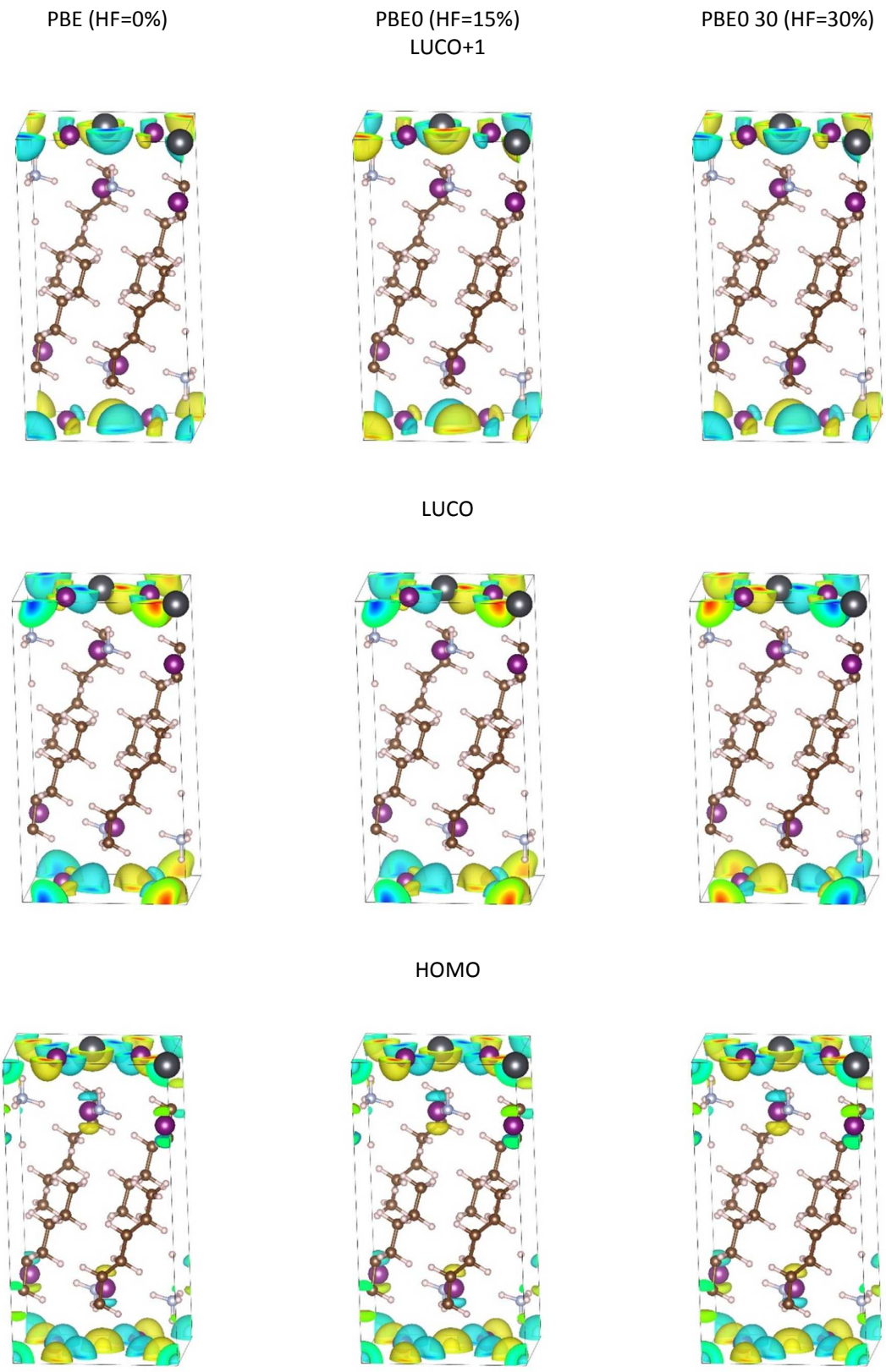

Figure S5. HOCO, LUCO and LUCO+1 molecular orbitals of the monoclinic phase of C6PbI, mainly involved in the two excitonic transitions.

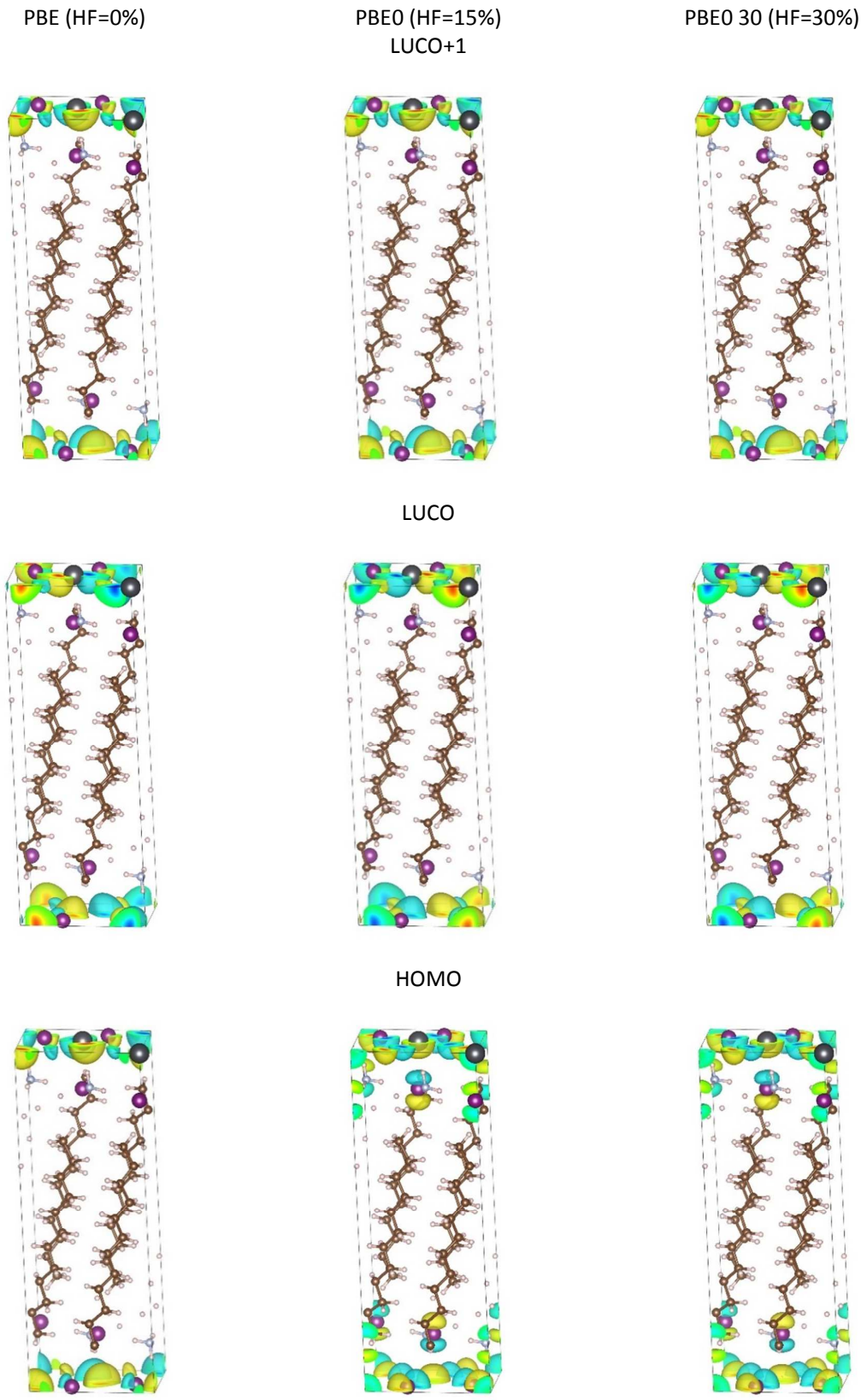

Figure S6. HOCO, LUCO and LUCO+1 molecular orbitals of the monoclinic phase of C12PbI, mainly involved in the two excitonic transitions.

References

(1) Tanaka, K.; Takahashi, T.; Kondo, T.; Umebayashi, T.; Asai, K.; Ema, K. Image Charge Effect on Two-Dimensional Excitons in an Inorganic-Organic Quantum-Well Crystal. *Phys. Rev. B* **2005,** *71*, 045312/1-6.