Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPORTING INFORMATION

First-principles analysis of the optical properties of lead halide perovskite solution precursors

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The Systems

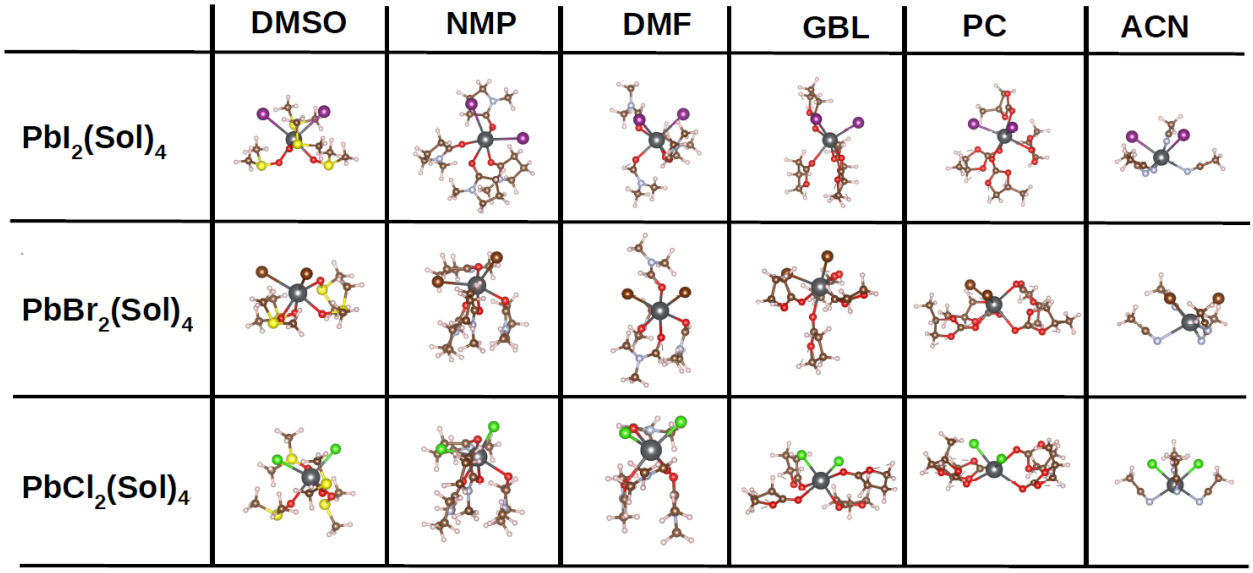

Figure S1: Ball-and-stick representation of the lead halide perovskite solution precursors investigated in this work. The solvent molecules (Sol) chemically bound to the lead halide backbones are labeled in each column. Pb atoms are depicted in grey, I atoms in purple, Br atoms in maroon, Cl atoms in green, C atoms in brown, H atoms in white, N atoms in light blue, and O atoms in red.

Electronic Properties

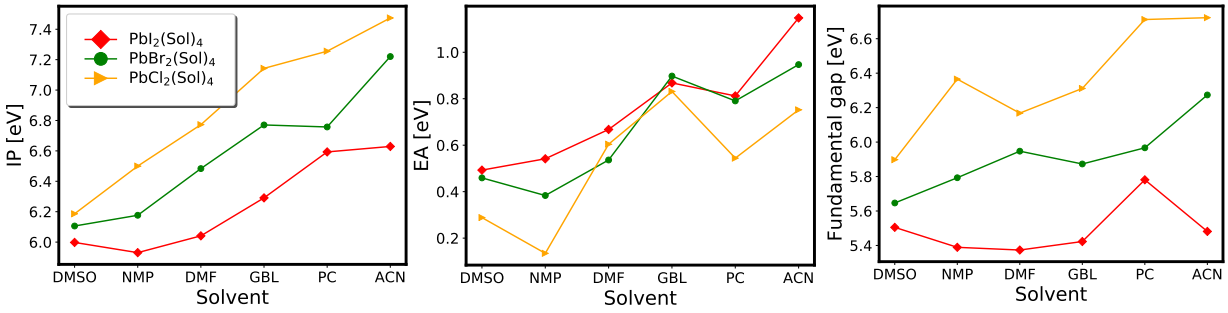

Figure S2: Ionization potential (IP, left panel), electron affinity (EA, middle panel), and fundamental gap calculated as the difference between these two quantities (right panel) for all the 18 systems with chemical formula $PbX_2(Sol)_4$ (X = Cl, Br, I and Sol = DMSO, NMP, DMF, GBL, PC, ACN) considered in this work. IP and EA are calculated in the ΔSCF scheme as the difference of the total energies between the cation and the neutral molecule (IP) as well as the neutral molecule and the anion (EA).

Molecular Orbitals

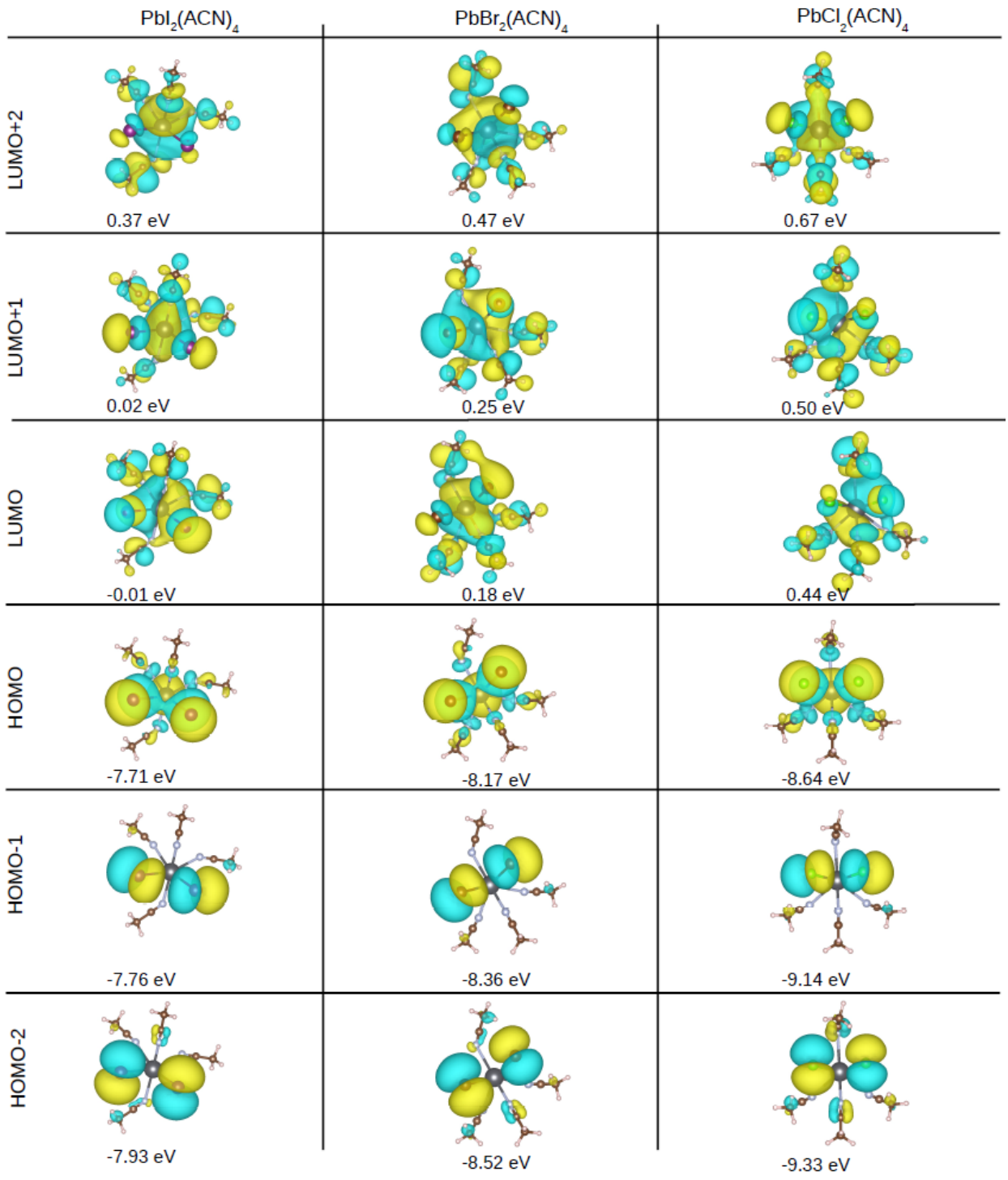

Figure S3: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(ACN)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

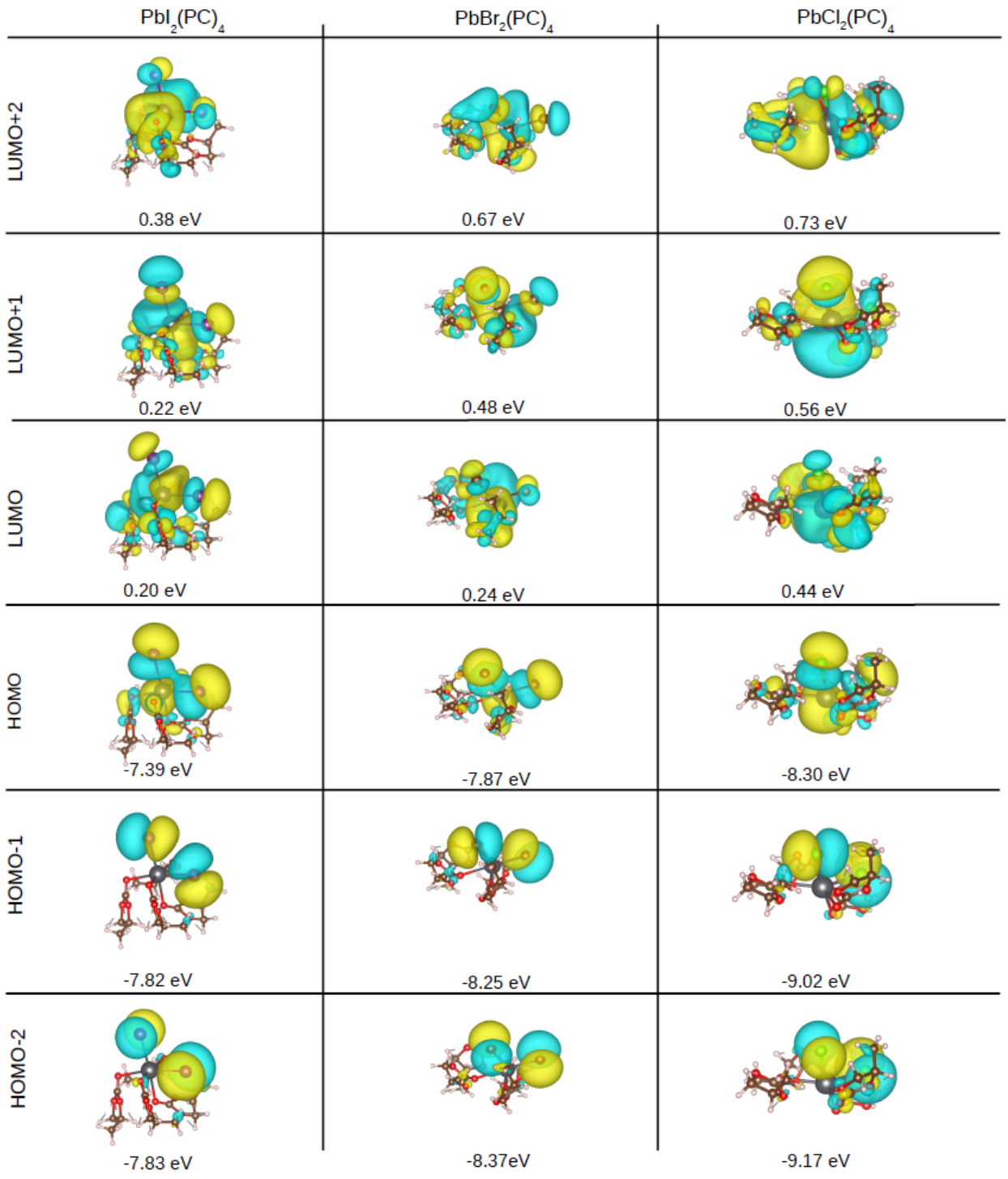

Figure S4: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(PC)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

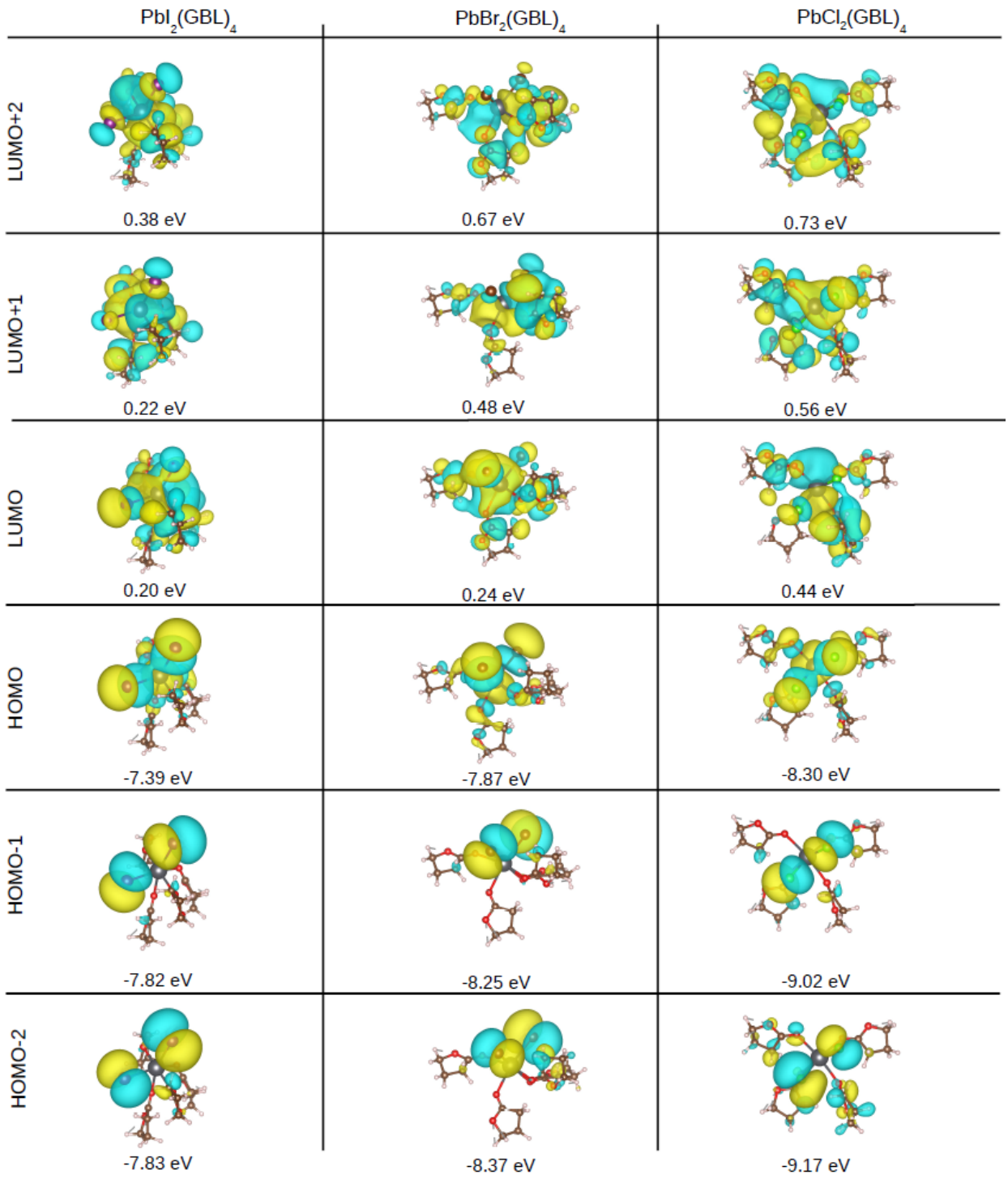

Figure S5: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(GBL)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

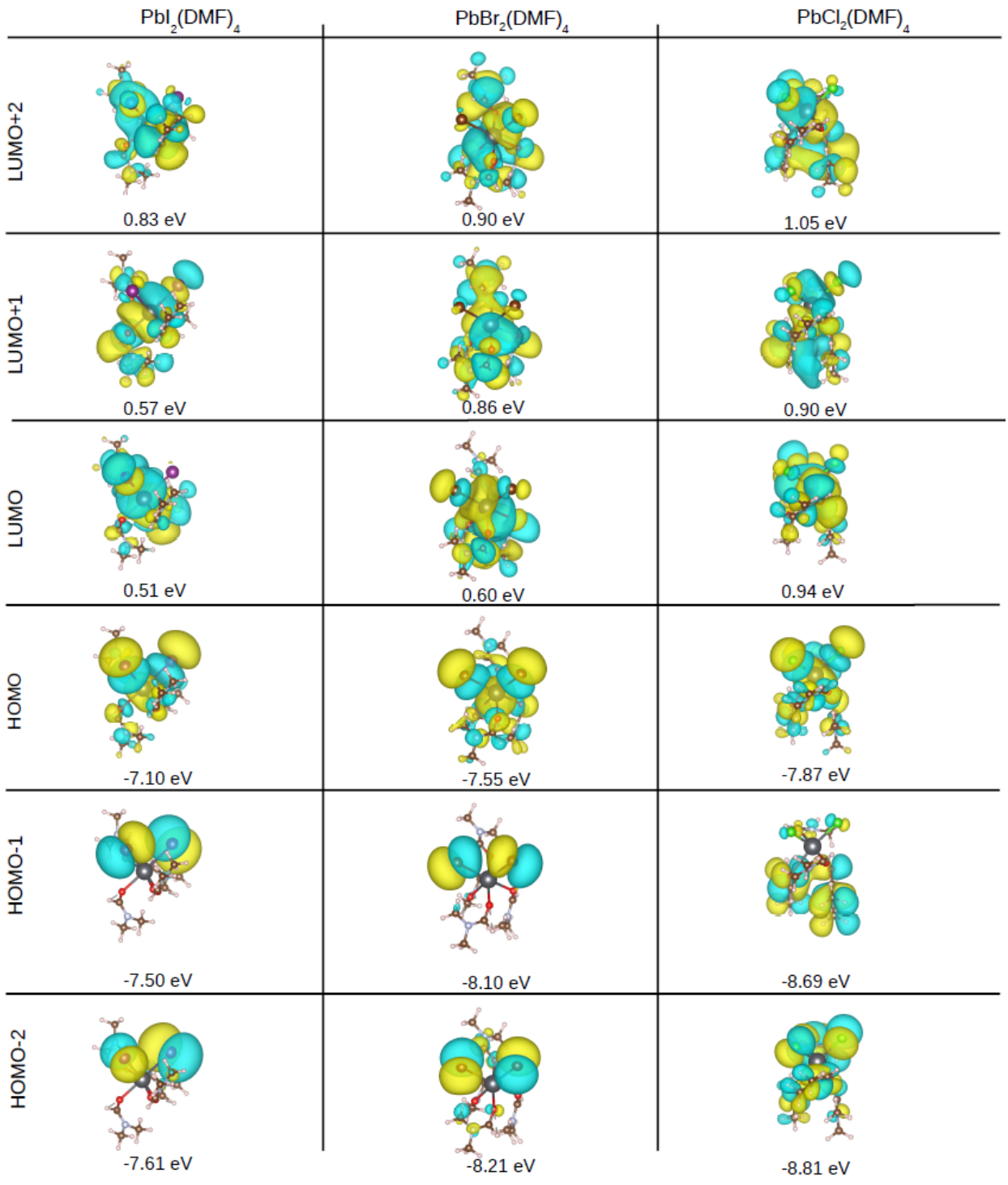

Figure S6: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(DMF)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

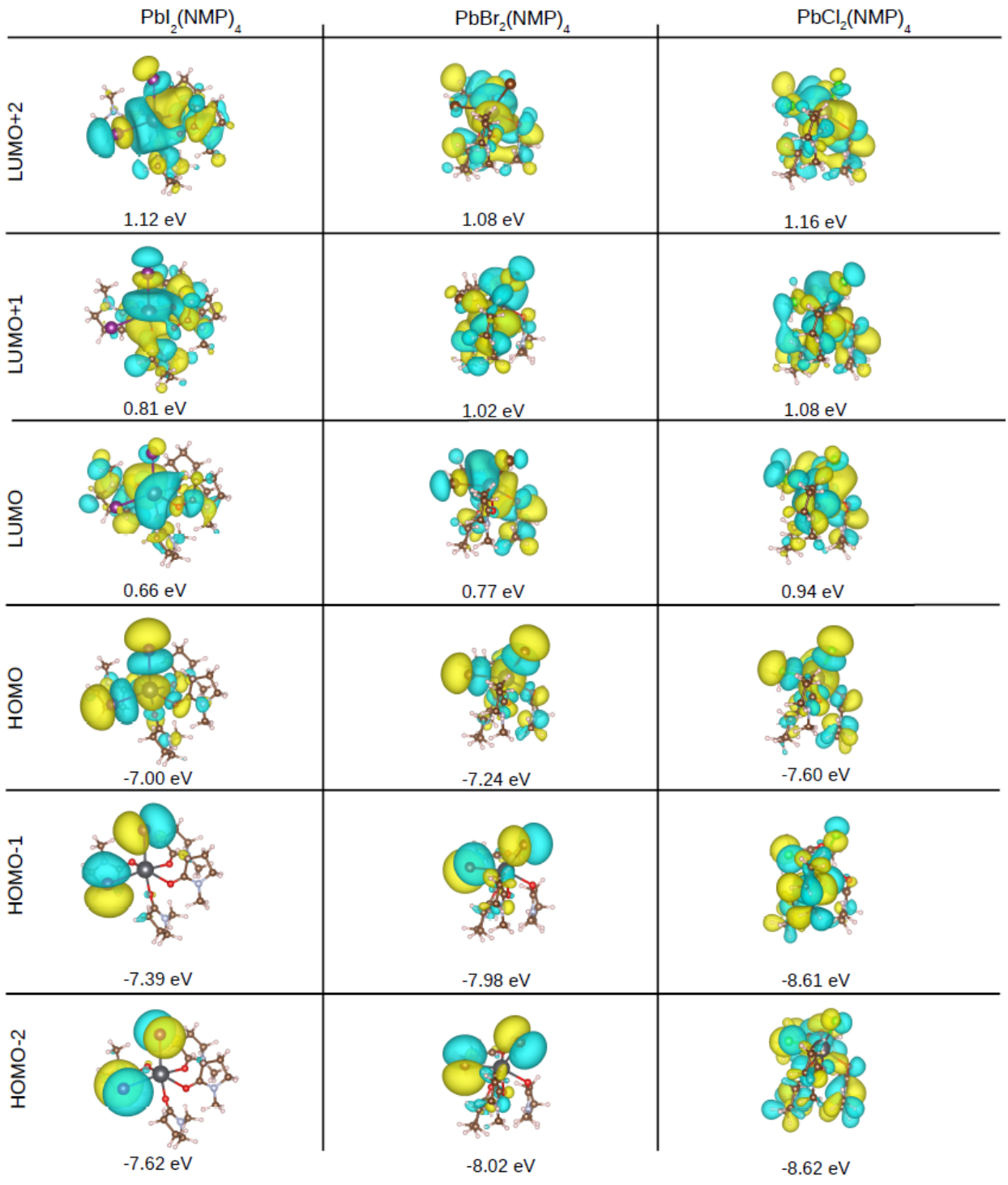

Figure S7: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(NMP)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

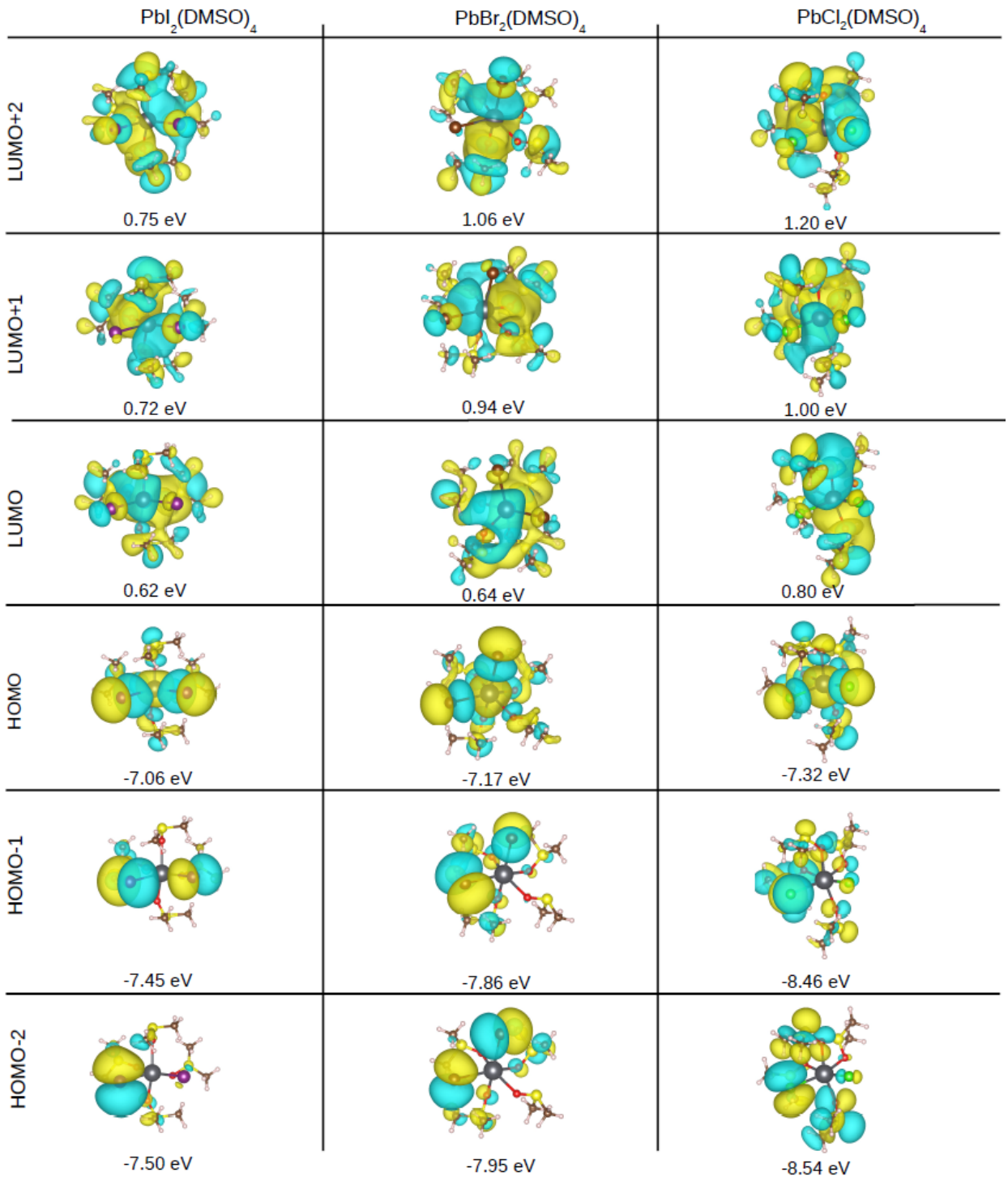

Figure S8: Energy and spatial distribution of the molecular orbitals of the considered $PbX_2(DMSO)_4$ compounds. All isovalues are fixed at 0.013 bohr^{-3}.

Optical Properties

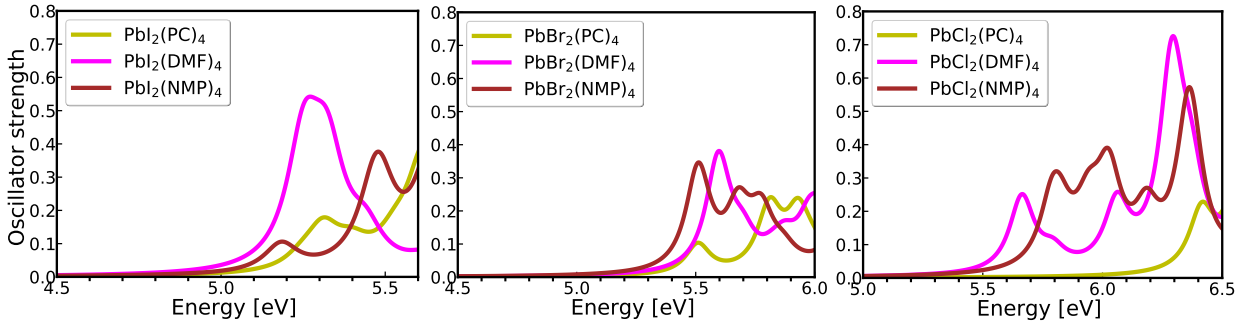

Figure S9: Optical absorption spectra of PbX_2PC_4, PbX_2DMF_4, and PbX_2NMP_4 with X = I (left), X = Br (middle), and X = Cl (right). A Lorentzian broadening of 125 meV is applied to all spectra.

Table S1: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(ACN)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition (weight)
E_1	5.08	0.02	H-1 → L+1(50%), H → L(36%)
E_2	5.14	0.02	H-1 → L(68%), H → L+1(14%)
E_3	5.21	0.02	H-3 → L (17%), H-2 → L (33%), H-2 → L+1 (20%), H → L+1 (12%)
E_4	5.24	0.08	H-2 → L+1 (16%), H-1 → L (11%), H → L+1 (57%)
E_5	5.27	0.02	H-3 → L+1 (25%), H-2 → L (27%), H-2 → L+1 (29%)
E_6	5.42	0.38	H-1 → L+1 (25%), H → L (48%),
E_7	5.52	0.01	H-3 → L+1 (58%), H-2 → L (24%)
E_8	5.53	0.01	H-3 → L (66%), H-2 → L+1 (22%)

Table S2: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(PC)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition (weight)
E_1	5.25	0.03	H-1 → L (48%), H → L (14%), H → L+1 (32%)
E_2	5.31	0.12	H-1 → L+1 (23%), H → L (56%)
E_3	5.40	0.06	H-1 → L+1 (56%), H → L (22%)
E_4	5.40	<0.01	H-2 → L (74%)
E_5	5.44	<0.01	H-3 → L (20%), H-3 → L+1 (32%), H-2 → L+1 (32%)
E_6	5.53	0.07	H → L+2 (81%),
E_7	5.62	0.36	H-1 → L (24%), H → L+1(40%)
E_8	5.76	<0.01	H-3 → L (32%), H-3 → L+1 (10%), H-2 → L+1 (53%)

Table S3: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(GBL)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition (weight)
E_1	5.14	0.14	H → L (63%), H → L+2 (16%)
E_2	5.23	0.19	H → L (14%), H → L+1 (69%)
E_3	5.32	0.15	H-1 → L (13%), H → L+2 (60%)
E_4	5.37	0.04	H-1 → L (69%)
E_5	5.44	0.02	H-3 → L (35%), H-2 → L (53%)
E_6	5.52	< 0.01	H-3 → L (31%), H-2 → L (16%)
E_7	5.57	0.10	H-4 → L (37%), H-1 → L+1 (13%),
E_8	5.68	< 0.01	H-3 → L (21%), H-2 → L (15%)

Table S4: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(DMF)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition (weight)
E_1	5.25	0.37	H → L(90%)
E_2	5.32	0.31	H → L+1 (85%),
E_3	5.44	0.10	H → L+2 (82%)
E_4	5.62	0.03	H-1 → L (79%)
E_5	5.72	0.01	H-3 → L (36%), H-2 → L (40%)
E_6	5.75	<0.01	H-1 → L+1 (48%)
E_7	5.78	<0.01	H-3 → L (28%), H-2 → L (31%)
E_8	5.81	0.10	H-4 → L (12%), H → L+3 (42%)

Table S5: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(NMP)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy	OS	Composition (weight)
E_1	5.18	0.08	H L(91%)
E_2	5.48	0.32	H → L+1 (79%)
E_3	5.64	0.24	H-2 → L (22%),H → L+2 (57%)
E_4	5.67	0.08	H-3 → L (16%), H-2 → L (35%), H-1 → L (23%), H → L+2 (12%)
E_5	5.68	0.07	H-4 → L (10%), H-2 → L (12%), H-1 → L (54%)
E_6	5.82	0.04	H-4 → L (18%), H-4 → L+1 (11%), H-1 → L+1 (31%), H-1 → L+2 (17%)
E_7	5.84	0.04	H-3 → L (22%), H-3 → L+1 (19%), H-3 → L+2 (10%)
E_8	5.87	0.01	H-10 → L+3 (13%), H → L+3 (35%)

Table S6: **Energies, oscillator strength (OS), and composition in terms of transition of $PbI_2(DMSO)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy	OS	Composition (weight)
E_1	5.28	0.14	H → L (79%)
E_2	5.29	0.19	H → L+1 (77%)
E_3	5.38	0.43	H → L+2 (71%)
E_4	5.73	0.02	H-7 → L (15%), H-5 → L (13%), H-1 → L (15%), H-4 → L (11%),
E_5	5.78	< 0.01	H-1 → L+1 (28%), H-1 → L+2 (14%)
E_6	5.80	<0.01	H-1 → L (21%), H-1 → L+2 (22%)
E_7	5.82	0.01	H-2 → L (30%), H-2 → L+1 (11%), H-2 → L+2 (42%)
E_8	5.86	0.01	H-3 → L+1(24%), H-1 → L (16%)

Table S7: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(ACN)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.67	0.04	H-1 → L (40%), H → L+1 (33%)
E_2	5.73	0.12	H-1 → L+1 (13%),H → L (62%)
E_3	5.82	0.01	H-2 → L+1 (10%), H-1 → L (10%), H-1 → L+1 (51%), H → L (10%)
E_4	5.83	0.02	H-3 → L+1 (15%),H-2 → L(29%), H-2 → L+1 (29%)
E_5	5.87	0.01	H-3 → L (28%), H-2 → L (17%), H → L+2 (32%)
E_6	5.92	0.17	H-3 → L (15%), H-2 → L+1 (10%), H → L+2 (46%)
E_7	6.04	0.30	H-1 → L (22%), H → L+1 (37%), H → L+2 (12%)
E_8	6.14	0.02	H-3 → L (39%), H-2 → L (26%), H-2 → L+1 (19%)

Table S8: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(PC)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.51	0.09	H → L (91%)
E_2	5.81	0.19	H-1 → L+2 (10%), H → L+1 (66%)
E_3	5.93	0.17	H → L+2 (75%),
E_4	6.00	0.03	H-1 → L (69%)
E_5	6.04	< 0.01	H-1 → L (11%), H-1 → L+1 (77%)
E_6	6.07	0.01	H-3 → L+1 (11%), H-3 → L+2 (10%),
E_7	6.14	0.02	H-2 → L (12%),H-2 → L+1 (33%), H-1 → L+2 (31%)
E_8	6.18	0.01	H-3 → L+1(25%), H-2 → L(11%), H-2→L+1 (11%), H-2→L+1 (11%), H-2 → L+2 (30%)

Table S9: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(GBL)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.53	0.13	H → L (81%)
E_2	5.74	0.06	H-1 → L (15%), H → L+1(37%)
E_3	5.79	0.01	H-6 → L (15%), H-6 → L+2 (26%)
E_4	5.82	0.01	H → L+3 (28%)
E_5	5.84	0.01	H-4 → L (10%), H-1 → L (39%)
E_6	5.91	0.04	H-3 → L (29%), H-2 → L (32%)
E_7	5.98	0.05	H-1 → L (12%), H → L+4 (22%)
E_8	6.03	0.07	H-2 → L (12%) ,H → L+4 (24%)

Table S10: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(DMF)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.60	0.34	H → L (66%)
E_2	5.60	0.08	H-12 → L (10%), H → L+1 (39%)
E_3	5.82	0.03	H-11 → L+3(26%), H → L+2(16%)
E_4	5.87	0.07	H → L+1 (14%), H → L+2 (31%)
E_5	5.98	0.13	H-12 → L (14%), H → L (14%)
E_6	6.05	0.11	H → L+4 (17%)
E_7	6.08	0.10	H → L+4 (15%)
E_8	6.21	0.04	H-2 → L (25%), H-1 → L(23%)

Table S11: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(NMP)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.51	0.31	H → L (84%)
E_2	5.68	0.18	H → L+1 (44%), H → L+2 (22%), H → L+3 (10%)
E_3	5.78	0.16	H → L+1 (27%), H → L+2 (19%), H → L+3 (21%)
E_4	5.87	0.05	H → L+2 (18%), H → L+3 (29%)
E_5	5.94	< 0.01	H-11 → L (42%), H-11 → L+2 (12%), H-10 → L (12%)
E_6	6.10	0.07	H → L+6 (21%)
E_7	6.13	0.11	H → L+8 (14%)
E_8	6.23	0.03	H-2 → L (15%), H-1 → L(52%)

Table S12: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2(DMSO)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.24	0.08	H → L (87%)
E_2	5.54	0.25	H → L+1 (71%),
E_3	5.63	0.29	H → L+2 (54%),
E_4	5.92	0.03	H-7 → L (10%)
E_5	5.97	0.08	H → L+2 (27%)
E_6	6.02	0.03	H-6 → L (22%), H → L+1 (10%)
E_7	6.08	0.01	H-4 → L (13%)
E_8	6.24	0.02	H-1 → L(74%)

Table S13: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(ACN)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	6.32	0.20	H → L (71%), H → L+2 (15%)
E_2	6.40	0.25	H → L (11%), H → L+1 (69%)
E_3	6.51	0.19	H → L+1(10%), H → L+2 (75%)
E_4	6.70	< 0.01	H-1 → L(46%), H-1 → L+1 (43%)
E_5	6.84	0.04	H-3 → L+1 (17%), H-2 → L+1 (30%), H-2 → L+2 (25%)
E_6	6.86	0.05	H-3 → L (21%), H-3 → L+2 (11%), H-2 → L (37%), H-2 → L+2 (11%)
E_7	6.86	0.06	H-1 → L (40%), H-1 → L+1 (40%)
E_8	6.89	0.10	H-2 → L+1 (10%), H-1 → L+2 (64%)

Table S14: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(PC)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	6.41	0.18	H → L (70%), H → L+1 (23%)
E_2	6.57	0.26	H → L (20%), H → L+1 (62%)
E_3	6.71	0.21	H-1 → L+1 (10%), H → L+2 (71%)
E_4	6.90	0.14	H-1 → L+1 (54%)
E_5	6.95	0.00	H-1→L (80%),
E_6	6.99	0.00	H-2 → L+1 (14%)
E_7	7.00	0.00	H-2 → L+1(26%), H-2 → L+2 (13%)
E_8	7.01	0.01	H-2 → L (10%)

Table S15: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(GBL)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.75	0.02	H-6 → L+1 (13%), H-6 → L+2 (10%), H-5 → L+1 (15%), H-5 → L+4 (13%), H→L+1 (11%)
E_2	5.77	0.03	H → L (26%)
E_3	5.81	0.01	H → L+3 (10%)
E_4	5.86	0.01	H-10 → L (12%), H-8 → L (10%) H-8 → L+2 (12%), H → L+2 (11%)
E_5	6.22	0.21	H → L (40%), H → L+3 (15%)
E_6	6.41	0.24	H → L+1 (57%)
E_7	6.61	0.14	H-1 → L (16%), H → L+3(14%) H → L+5 (27%)
E_8	6.72	0.12	H-2 → L (20%), H-1 → L (37%)

Table S16: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(DMF)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.66	0.23	H → L (62%)
E_2	5.79	0.05	H-11 → L+1 (20%), H → L+1 (20%)
E_3	5.81	0.01	H-10 → L+2 (20%), H-9 → L+2 (22%), H → L+2 (13%)
E_4	5.88	< 0.01	H-13 → L(12%), H-12 → L+3 (17%), H-11 → L (16%), H → L+3 (10%)
E_5	6.06	0.19	H-12 → L (17%), H → L (21%)
E_6	6.29	0.61	H → L+1 (45%)
E_7	6.37	0.21	H → L+2(38%), H → L+5(20%)
E_8	6.54	0.05	H-4 → L (16%), H-3 → L (26%), H → L+3 (18%)

Table S17: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(NMP)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.79	0.17	H → L (55%)
E_2	5.82	0.10	H → L+1 (22%)
E_3	5.92	0.02	H-9 → L (11%), H-9 → L+1 (16%), H-9 → L+2 (18%)
E_4	5.94	0.14	H → L+2 (28%)
E_5	6.03	0.27	H → L+1 (32%), H → L+2 (16%)
E_6	6.18	0.15	H-10 → L (18%), H → L (11%)
E_7	6.36	0.52	H → L+1(15%), H → L+3 (14%), H → L+6 (19%)
E_8	6.64	0.07	H-1 → L (16%), H-1 → L+1(15%)

Table S18: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2(DMSO)_4$. HOMO and LUMO are abbreviated by H and L, respectively. Only contributions above 10% are indicated.**

Exc	Energy [eV]	OS	Composition
E_1	5.39	0.21	H → L (81%)
E_2	5.59	0.13	H → L+1 (70%),
E_3	5.72	0.14	H → L+2 (54%), H-1 → L+1 (10%)
E_4	5.90	0.02	H-2 → L (20%), H → L+4 (10%)
E_5	6.14	0.02	H-3 → L (11%), H-3 → L (11%)
E_6	6.20	0.10	H-1 → L+1 (15%), H → L+1 (11%)
E_7	6.34	0.12	H → L+2 (10%),
E_8	6.39	0.05	H → L+3 (42%)

Optical properties of the PbX_2 compounds in implicit solvent

Table S19: Energies, oscillator strength (OS), and composition in terms of transition of PbI_2 backbone. HOMO and LUMO are abbreviated by H and L, respectively.

Exc	Energy	OS	Composition
E_1	3.55	0.01	H→L (99%),
E_2	3.85	< 0.01	H-1→L (100%)
E_3	4.21	0.04	H-2→L (95%), H-1→L+1 (2%), H→L+2 (2%)
E_4	4.55	< 0.01	H-3→L (86%), H→L+1(11%)
E_5	4.59	< 0.01	H-4→L (99%)
E_6	5.12	< 0.01	H-5→L (100%)
E_7	5.17	0.14	H→L+1 (82%) H-4→L+1 (7%), H-3→L (8%), H-1→L+2 (2%)
E_8	5.20	< 0.01	H-1→L+1 (77%), H→L+2 (21%)
E_9	5.30	< 0.01	H-2→L+1 (96%) H-3→L+2 (4%)
E_{10}	5.58	< 0.01	H-3→L+1 (75%), H-2→L+2 (24%)

Table S20: **Energies, oscillator strength (OS), and composition in terms of transition of $PbBr_2$ backbone. HOMO and LUMO are abbreviated by H and L, respectively.**

Exc	Energy	OS	Composition
E_1	4.07	0.03	H→L (100%),
E_2	4.50	< 0.01	H-1→L (100%)
E_3	4.90	0.03	H-2→L (94%)H→L+2 (3%),
E_4	5.22	0.01	H-4→L (100%)
E_5	5.25	< 0.01	H-3→L (87%)H→L+1 (11%),
E_6	5.82	< 0.01	H-5→L (100%)
E_7	5.98	0.14	H→L+1 (82%), H-4→L+1 (8%), H-3→L (8%)
E_8	6.04	< 0.01	H-1→L+1 (65%), HOMO→L+2 (33%)
E_9	6.20	< 0.01	H-2→L+1 (95%), H-3→L+2 (5%)
E_{10}	6.45	0.01	H-1→L+2 (89%), H-4→L+1 (6%), HOMO→L+1 (3%)

Table S21: **Energies, oscillator strength (OS), and composition in terms of transition of $PbCl_2$ backbone. HOMO and LUMO are abbreviated by H and L, respectively.**

Exc	Energy	OS	Composition
E_1	4.64	0.04	H→L (100%),
E_2	5.27	< 0.01	H-1→L (100%)
E_3	5.65	0.02	H-2→L (94%), H→L+2 (4%),
E_4	5.92	< 0.01	H-4→L (100%)
E_5	5.98	< 0.01	H-3→L (88%), H→L+1 (10%),
E_6	6.50	< 0.01	H-5→L (100%)
E_7	6.70	0.32	H→L+1 (86%) H-4→L+1 (4%), H-3→L (8%)
E_8	6.80	0.10	H-1→L+1 (39%), H→L+2 (59%)
E_9	7.14	< 0.01	H-2→L+1 (94%), H-3→L+2 (5%)
E_{10}	7.24	< 0.01	H-1→L+2 (90%), H-4→L+1 (9%)

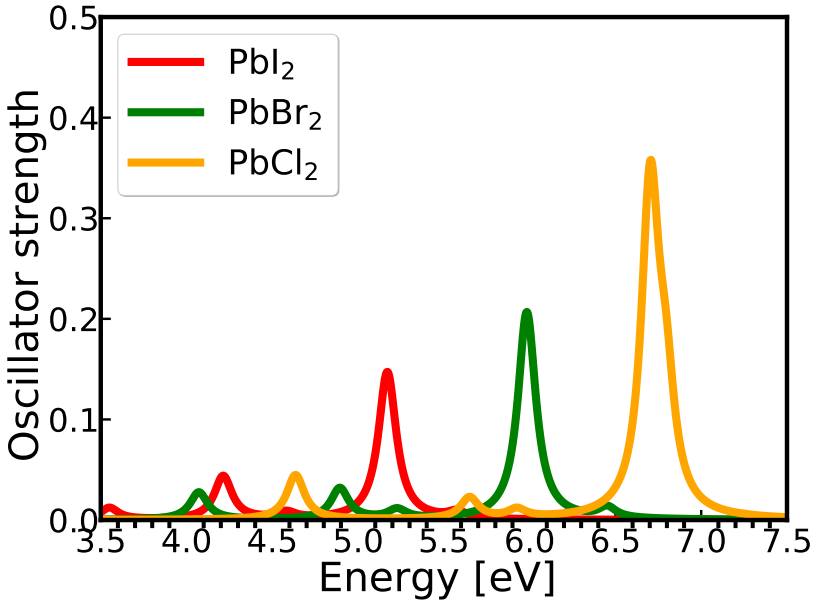

Figure S10: Optical spectra of the PbX_2 compounds computed in implicit solvent from TDDFT+PCM.

Electronic and optical properties of PbI_2Sol_4 *in vacuo* from many-body perturbation theory

In this section, we present the analysis of $PbI_2(Sol)_4$ compounds investigated *in vacuo* from density-functional theory and many-body perturbation theory. These calculations were performed with the code MOLGW[1] adopting the range-separated hybrid functional CAM-B3LYP,[2] Gaussian-type cc-pVDZ basis sets for the light atoms and effective core potential (ECP) cc-pVDZ-PP basis sets for Pb and I atoms.[3] Spin-orbit coupling is included in the ECP at the scalar relativistic level. In these calculations, the resolution-of-identity approximation is employed.[4]

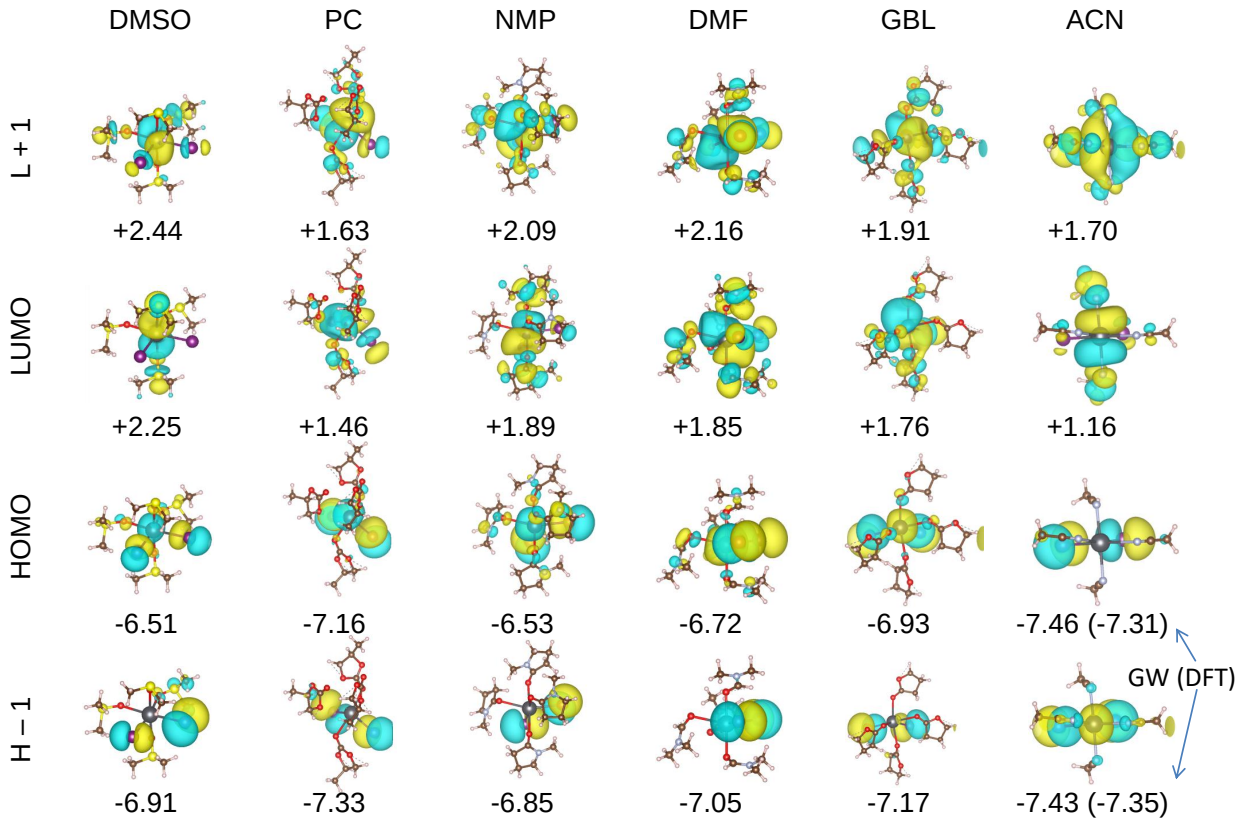

Figure S11: Molecular orbitals from DFT with G_0W_0 energies in eV.

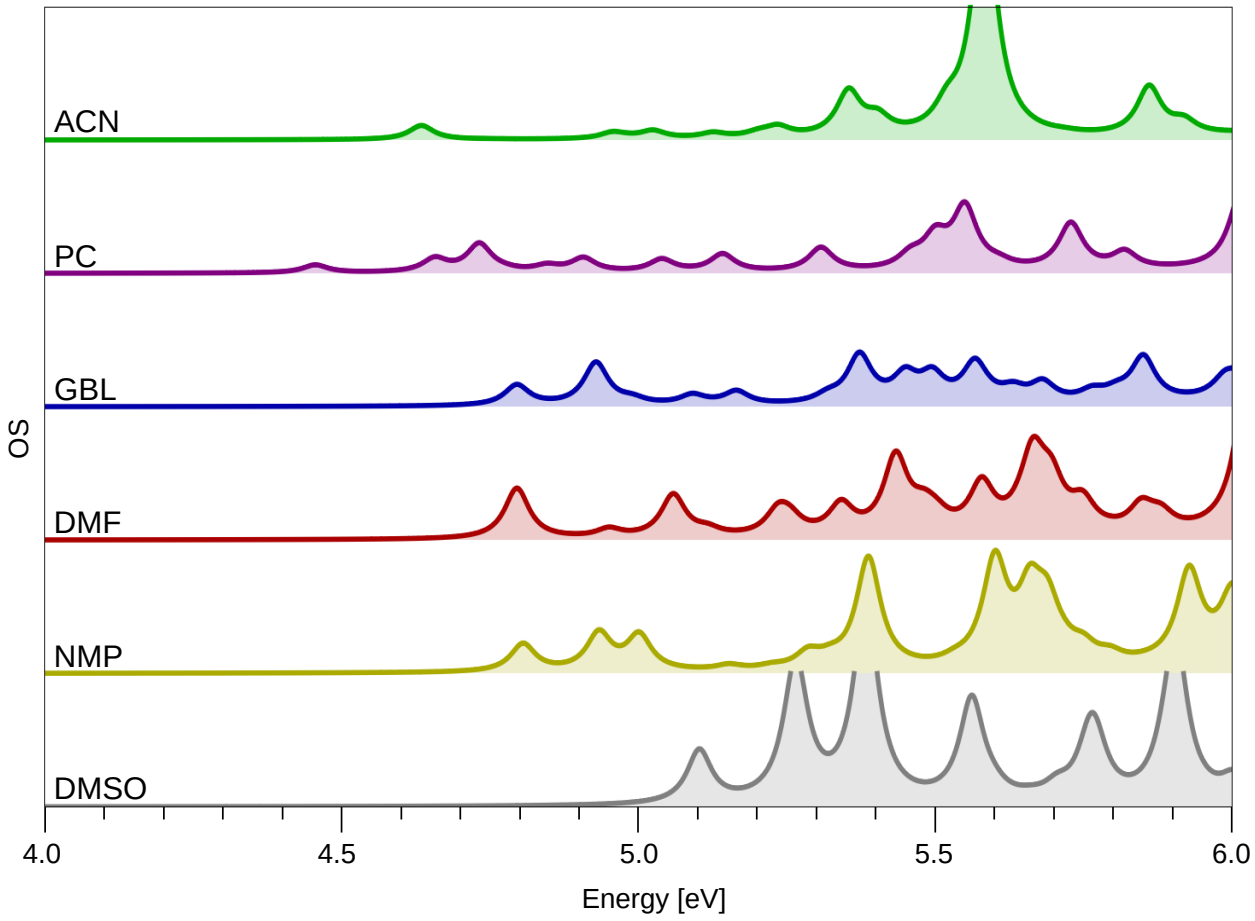

Figure S12: Optical spectra from the solution of the BSE on top of the G_0W_0 electronic structure *in vacuo*. A Lorentzian broadening of 50 meV is applied to all spectra.

Table S22: Analysis of the first excitation in terms of energy (E_1), electronic gap from G_0W_0 (E_{gap}) and difference thereof, oscillator strength (OS), and relative contribution (in %) of the HOMO→LUMO transition.

	E_1 [eV]	E_{gap} [eV]	E_{gap} - E_1 [eV]	OS	HOMO→LUMO
ACN	4.66	8.59	3.93	0.018	96%
PC	4.49	8.62	4.13	0.008	56%
GBL	4.82	8.69	3.87	0.021	51%
DMF	4.83	8.57	3.74	0.057	91%
NMP	4.84	8.42	3.58	0.034	86%
DMSO	5.13	8.76	3.63	0.068	91%

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