Supporting Information

Iodide vs. Chloride: Impact of Different Lead-Halides on the Solution Chemistry of Perovskite Precursors

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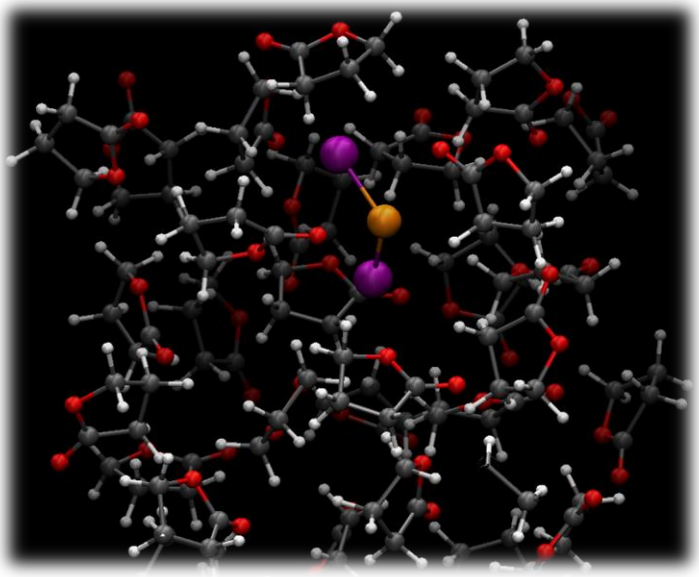

Figure S1. Simulation model of $PbCl_2$ in GBL solvent. The colors of the atoms are as follows: Pb (orange), Cl (purple), O (red), C (grey), H (white).

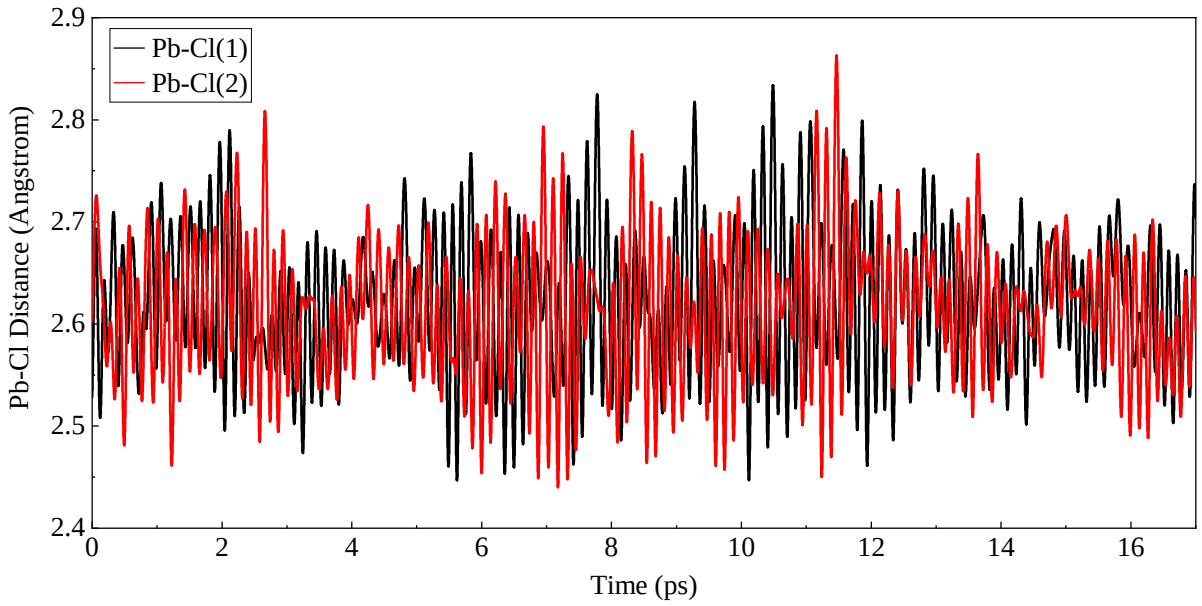

Figure S2. Time evolution of Pb–Cl bond lengths. Average bond lengths: 2.61±0.07 Å and 2.62±0.07 Å.

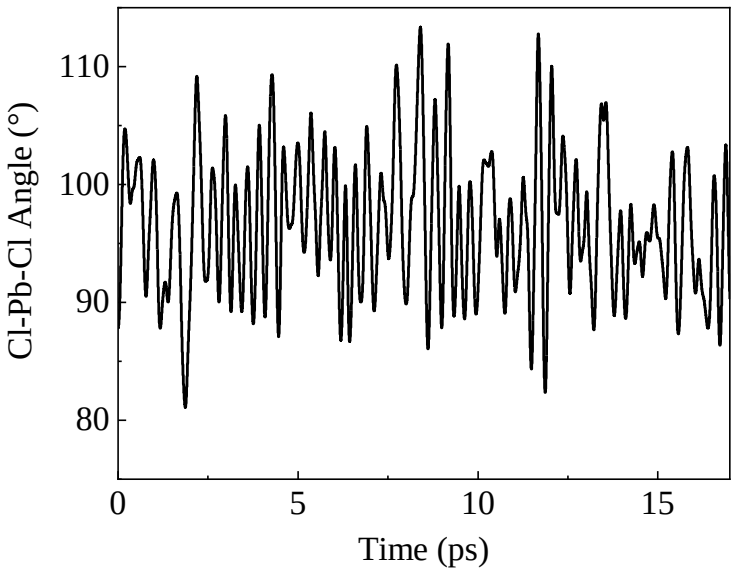

Figure S3. Time evolution of Cl–Pb–Cl bond angle. Average bond angle: 96.8° ± 6.0°.

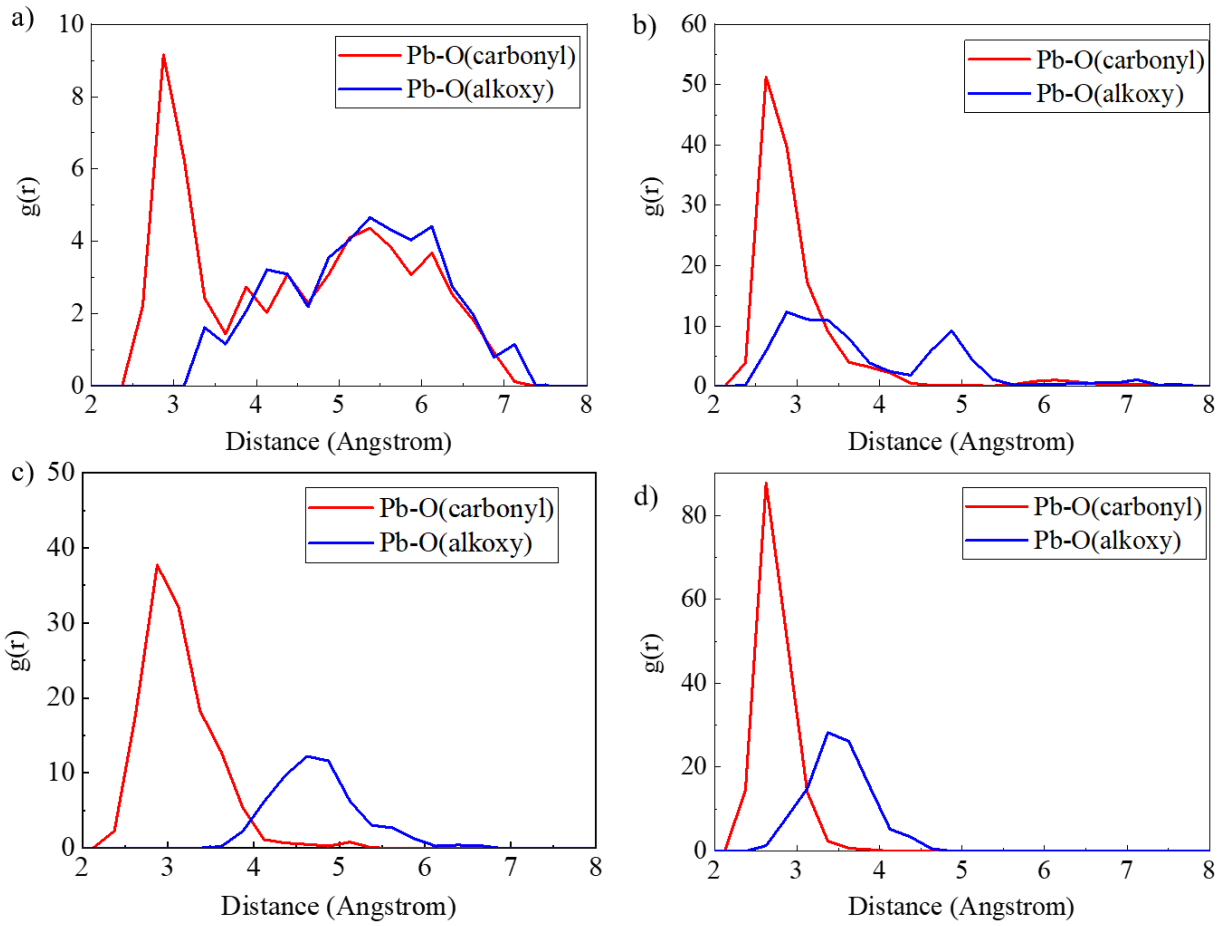

Figure S4. Radial distribution function, g(r), for (blue) Pb–O(alkoxy) and (red) Pb–O(carbonyl) of the GBL molecule participating in the solvation of Pb observed in the *ab initio* molecular dynamics simulations.

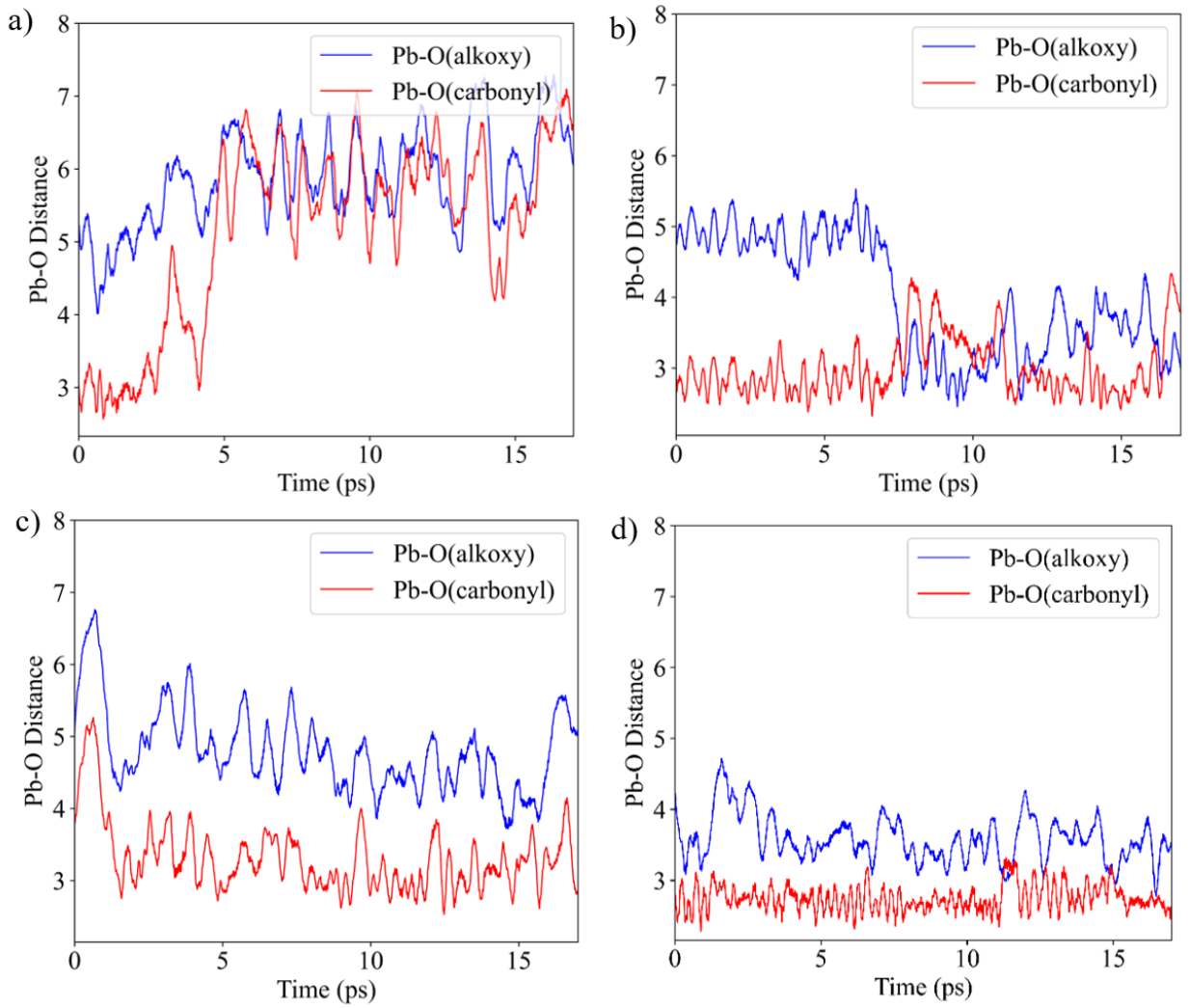

Figure S5. Time evolution of the (blue) Pb–O(alkoxy) and the (red) Pb–O(carbonyl) distance (unit in Å) of the GBL molecule participating in the solvation of Pb along the *ab initio* molecular dynamics simulations.

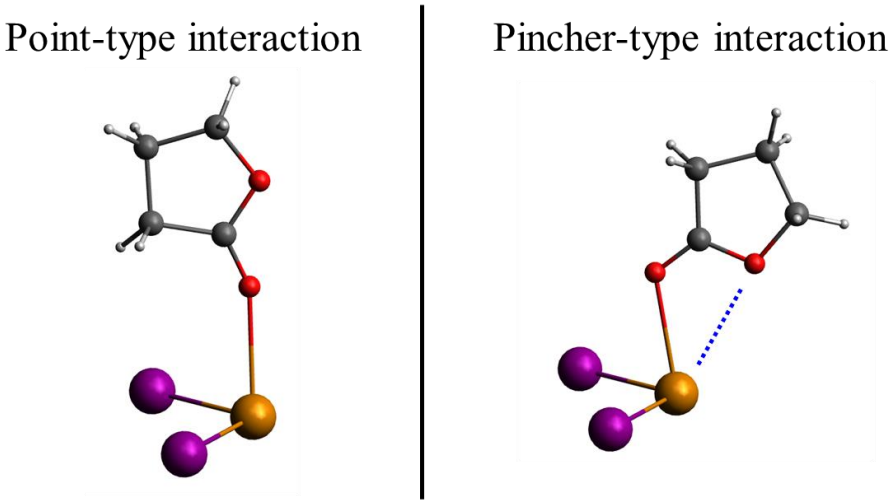

Figure S6. (left) Point-type interaction between the GBL molecule and the Pb ion, mediated by the carbonyl oxygen, and (right) pincher-type interaction characterized by a short bond between Pb and the carbonyl oxygen (~2.6 Å) and a short distance (~3.3-3.5 Å) between the Pb ion and the alkoxy oxygen, highlighted by dashed blue line.

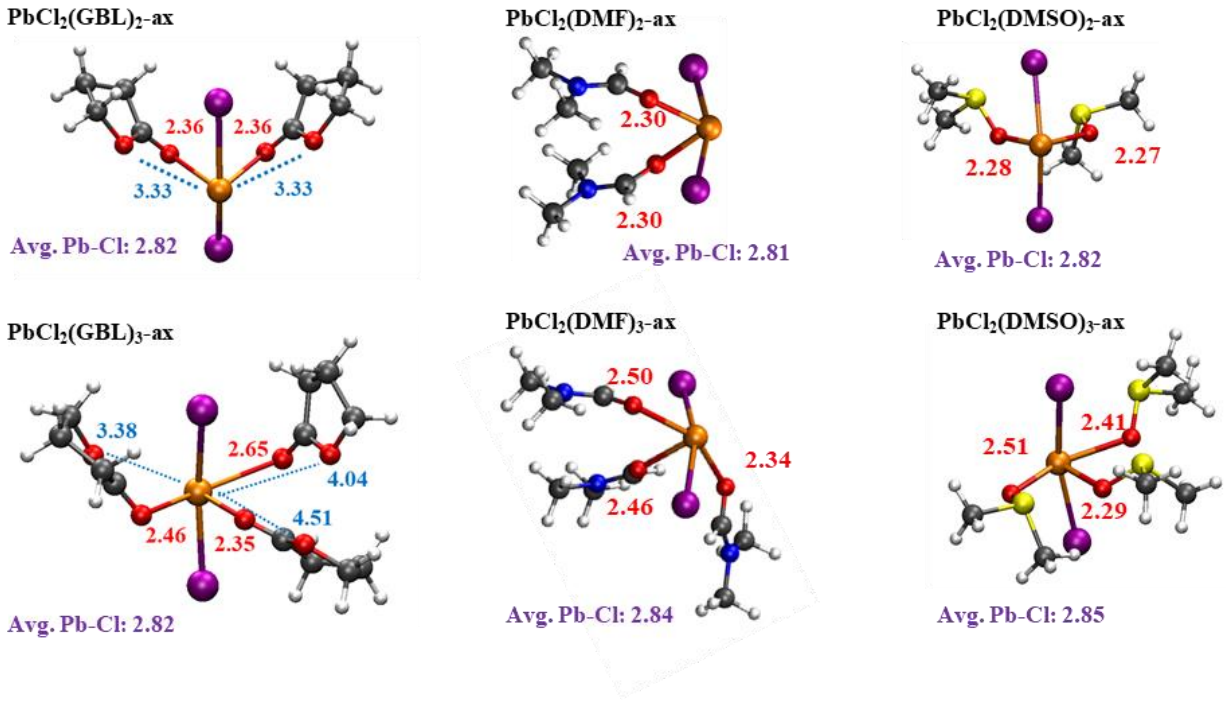

Figure S7. Optimized structure of $PbCl_2(solv)_n$ complexes with n=2–3 γ-butyrolactone (GBL), N,N-dimethylformamide (DMF), and dimethylsulfoxide (DMSO) solvent molecules with axial (ax) alignment of Cl–Pb–Cl bonds. Pb–O distances for each solvent molecule is given in red color (and blue for alkoxy oxygen in GBL); average Pb–Cl bond length reported in purple below each structure. All geometrical parameters are reported in Å. The colors of the atoms are as follows: Pb (orange), Cl (purple), O (red), S (yellow), N (blue), C (grey), H (white). Note that no stable configuration with n = 1 could be found.

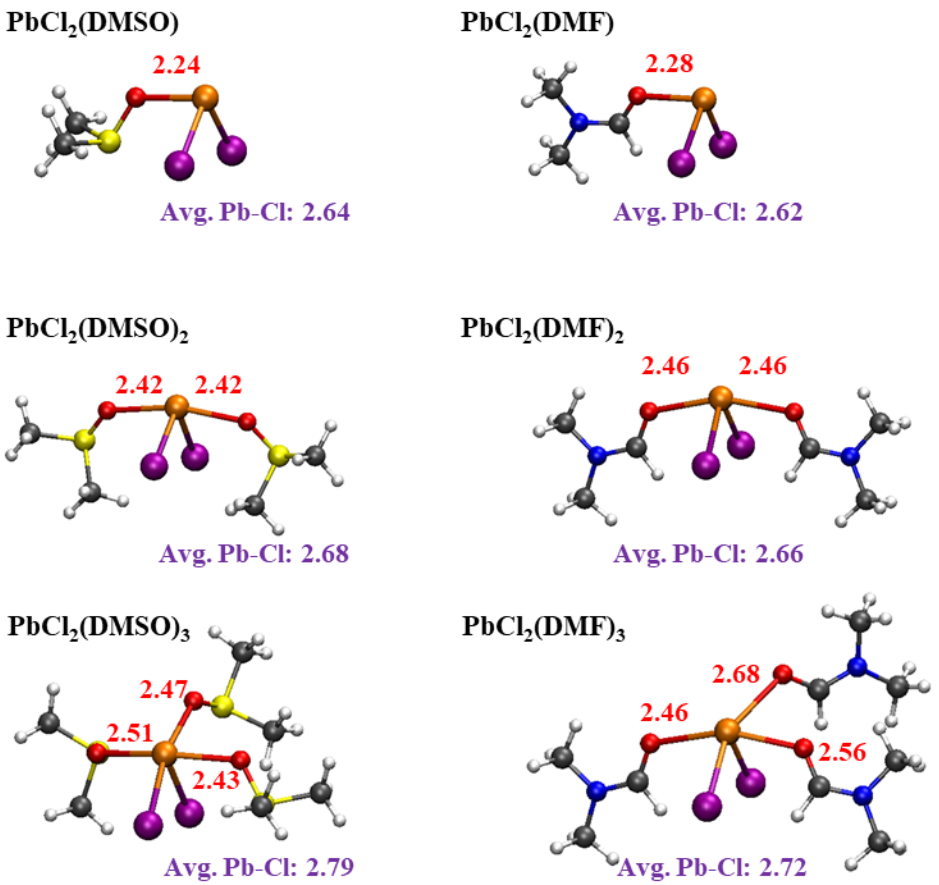

Figure S8. Optimized structure of $PbCl_2(solv)_n$ complexes (n=1 to 3) with dimethylsulfoxide (DMSO) and N,N-dimethylformamide (DMF) solvent molecules with equatorial (eq) alignment of Cl–Pb–Cl bonds. Pb–O distance for each solvent molecule is given in red color; average Pb–Cl bond length reported in purple below each structure. All geometrical parameters are reported in Å. The colors of the atoms are as follows: Pb (orange), Cl (purple), O (red), S (yellow), N (blue), C (grey), H (white).

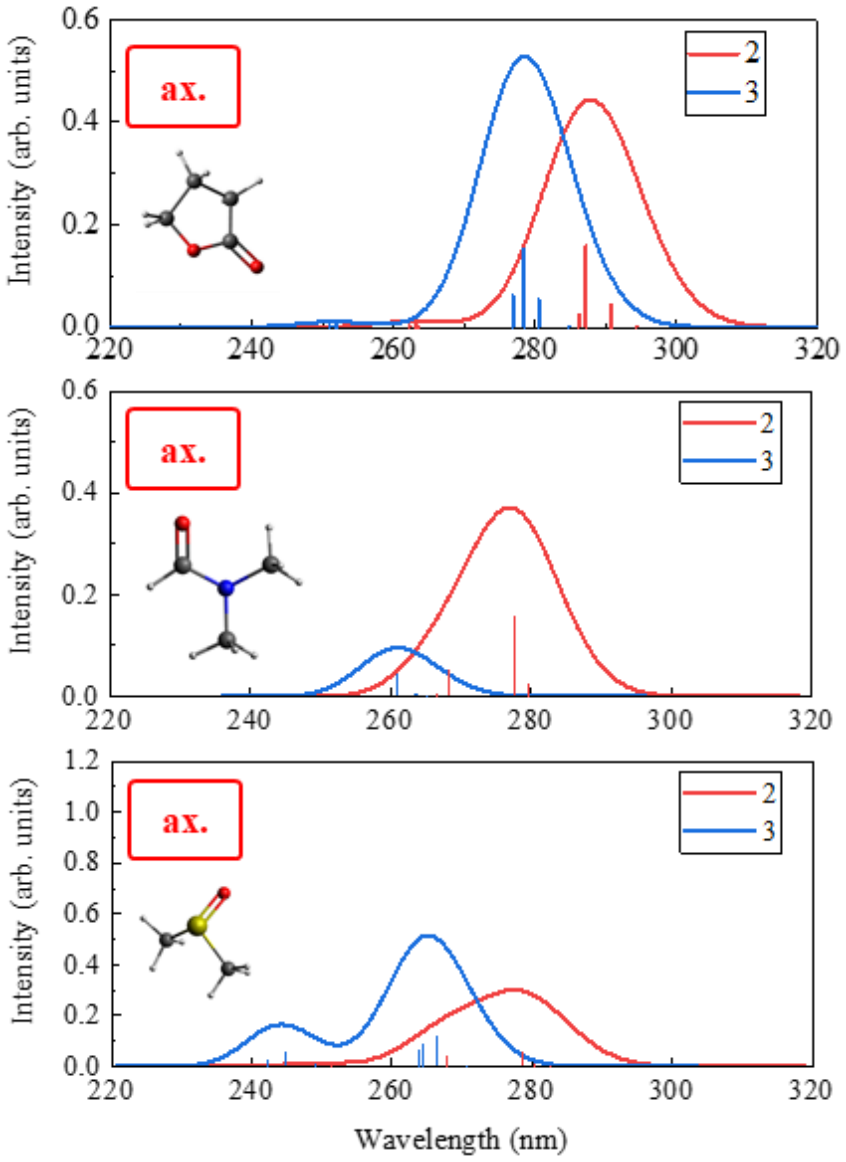

Figure S9. Calculated absorption spectra for (top) $PbCl_2(GBL)_n$, (center) $PbCl_2(DMF)_n$ and (bottom) $PbCl_2(DMSO)_n$ for n=2–3 in axial configuration.

Table S1. Absorption maxima (nm units) of simulated absorption spectra and energy difference (eV units) between axial (ax) and equatorial (eq) configurations for $PbCl_2(solv)_n$ (solv = DMSO, DMF, GBL and n=1–3) for all the stable complexes. The eq configuration is set as zero energy reference.

n	**DMSO**			**DMF**			**GBL**		
	λ_{eq}	**λ_{ax}**	**ΔE**	**λ_{eq}**	**λ_{ax}**	**ΔE**	**λ_{eq}**	**λ_{ax}**	**ΔE**
1	257	-	-	255	-	-	263	-	-
2	256	277	-0.039	258	277	-0.061	255	288	-0.257
3	264	265	0.154	261	261	0.057	265	279	-0.005

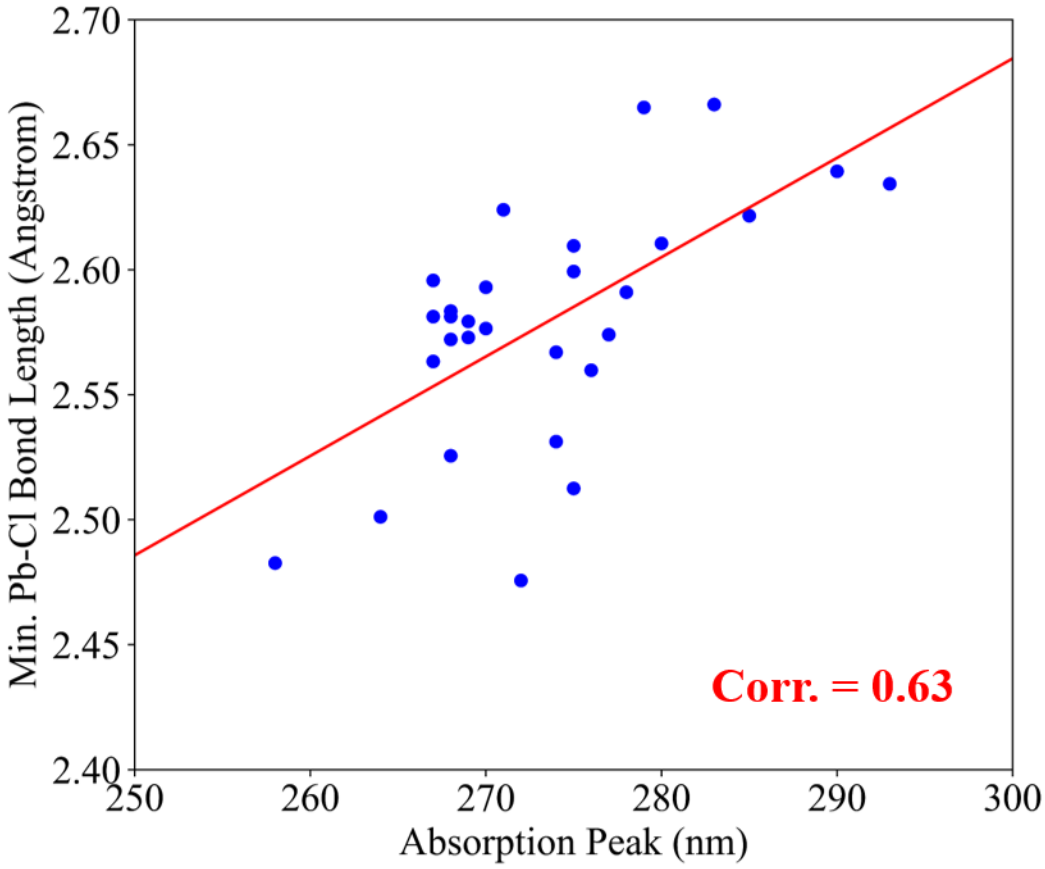

Figure S10. Scatter plot of the minimum Pb–Cl bond length versus absorption peak. Each dot represents one snapshot of the ab initio molecular dynamics simulations. The minimum Pb–Cl bond shows largest correlation across all considered measures (min., max., avg.) of the Pb–Cl and Pb–O(alkoxy) and Pb–O(carbonyl) bonds with the absorption peak, having a Pearson correlation coefficient of 0.63. The correlations with the other properties are as follows: Corr. = 0.35 for max. Pb–Cl bond length, Corr. = 0.57 for average Pb–Cl bond length; Corr. = 0.27 for average Pb–O(carbonyl) bond length, Corr. = 0.32 for min. and Corr. = 0.22 for max. Pb–O(carbonyl) bond length; Corr. = 0.27 for average Pb–O(carbonyl) bond length, Corr. = -0.36 for min. and Corr. = -0.02 for max. Pb–O(alkoxy) bond length.

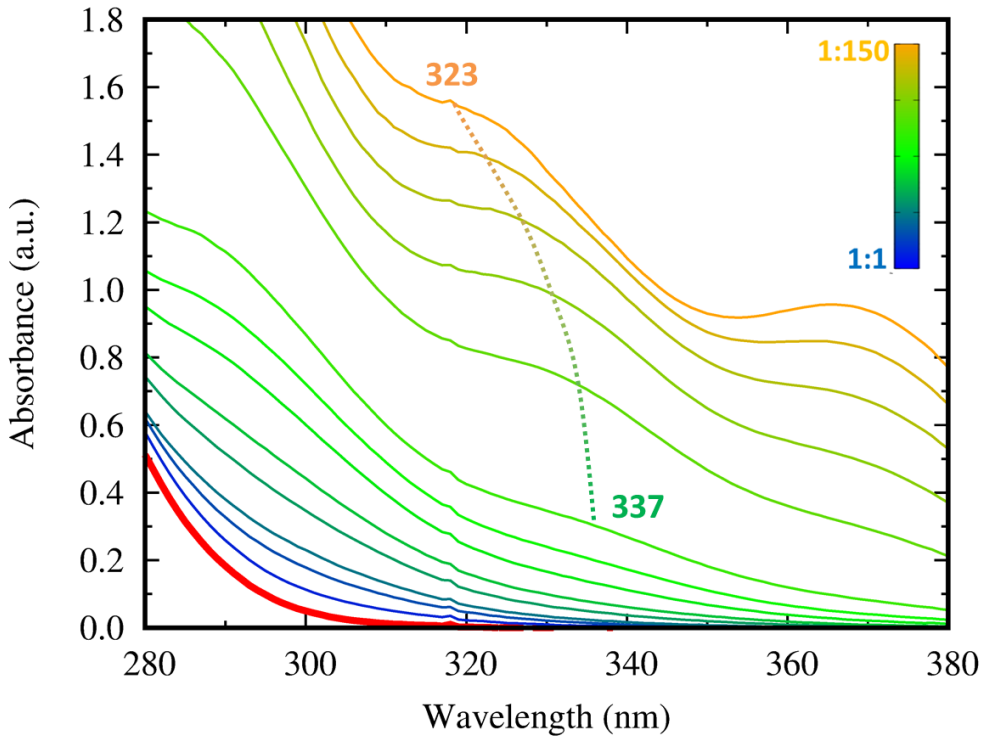

Figure S11. Blue-shift of the [PbI_2] absorption peak, highlighted by the dotted line, from 337 nm to 323 nm by the change of $PbCl_2$:MAI molar ratio from 1:1 to 1:150.

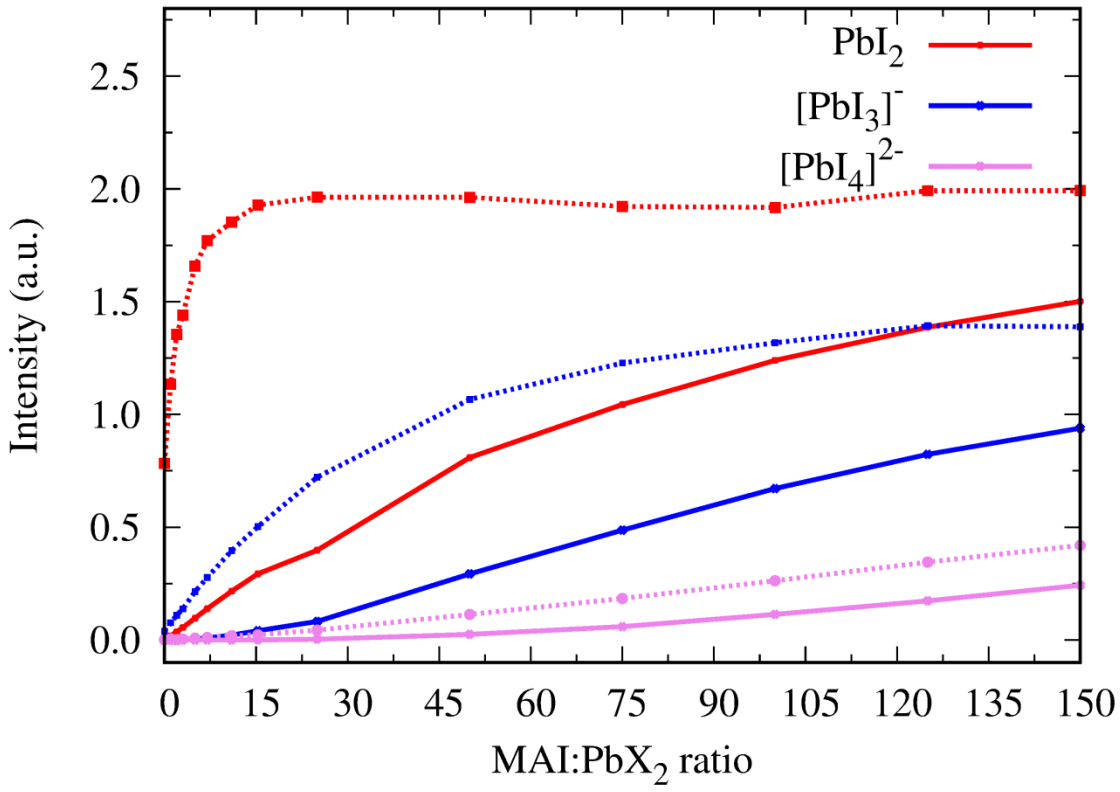

Figure S12. Intensity of the absorption shoulders for different iodoplumbates ($[PbI_2]$, $[PbI_3]^-$ and $[PbI_4]^{2-}$) for the case of $PbCl_2$ (continuous lines) and PbI_2 (dotted lines) with increasing MAI:PbX_2 ratio (X = I, Cl). The absorbance values at 323, 370 and 423 nm were taken as an approximation for the concentration of $[PbI_2]$, $[PbI_3]^-$ and $[PbI_4]^{2-}$, respectively.

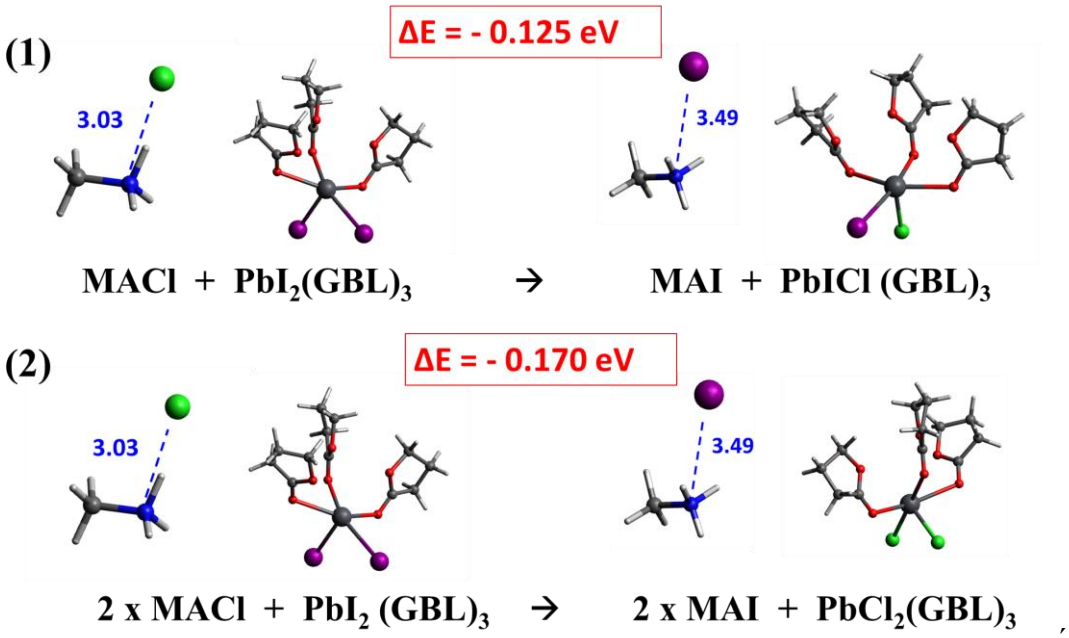

Figure S13. DFT calculation of the energy of replacing (1) one and (2) two iodine ion(s) from the Pb center, coordinated by 3 GBL molecules, in presence of MACl: (1) MACl + $PbI_2(GBL)_3$ → MAI + $PbCl(GBL)_3$ and (2) 2×MACl + $PbI_2(GBL)_3$ → 2×MAI + $PbCl_2(GBL)_3$. 2xMACl (MAI) refers to twice the energy of a single MACl (MAI) complex in solution.