Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Halide-Driven Formation of Lead Halide Perovskites: Insight from *Ab Initio* Molecular Dynamics Simulations

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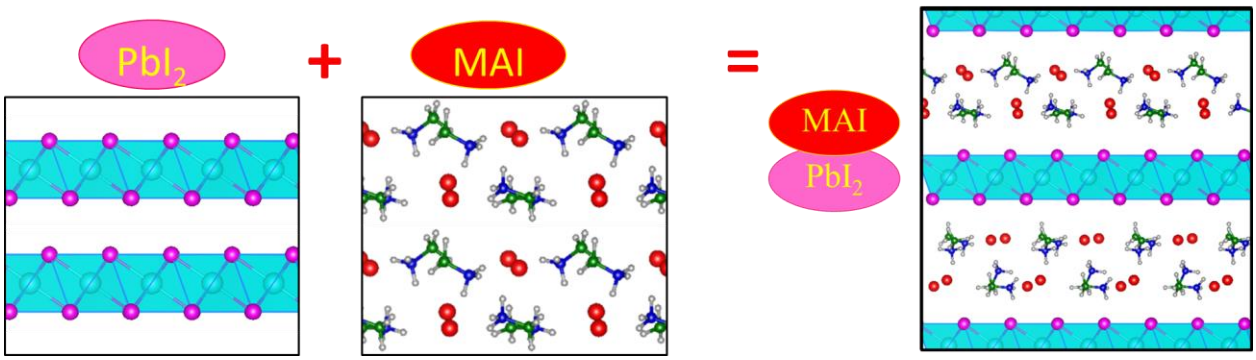

Figure S1. PbI_2•MAI supercell containing crystalline PbI_2 and MAI layers with a stochiometric 1:1 ratio.

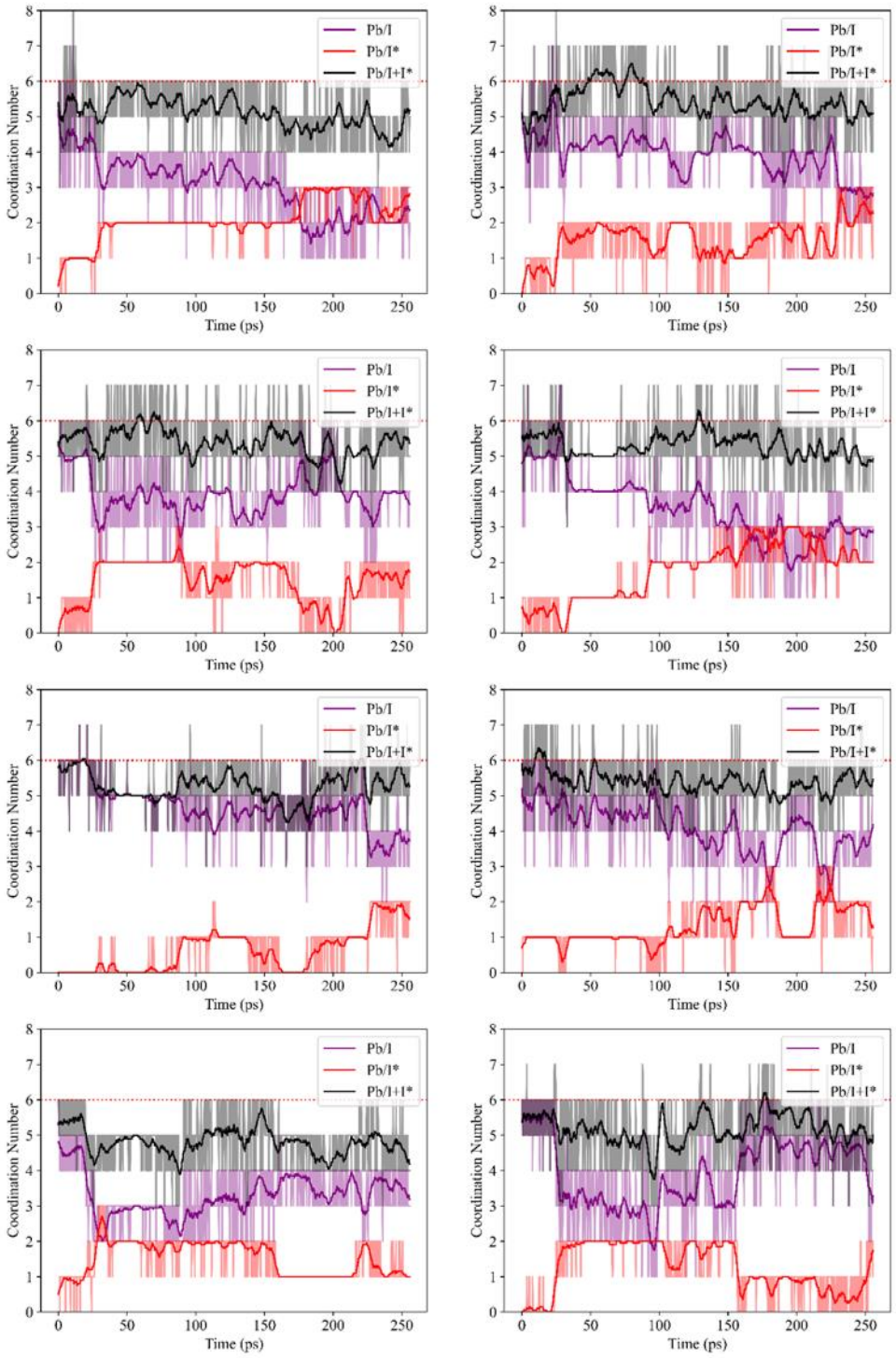

Figure S2. Time evolution of the coordination number of each lead ion with iodine coming from PbI_2 (Pb/I) and iodine coming from MAI (Pb/I*), and the sum of both contributions (Pb/I+I*).

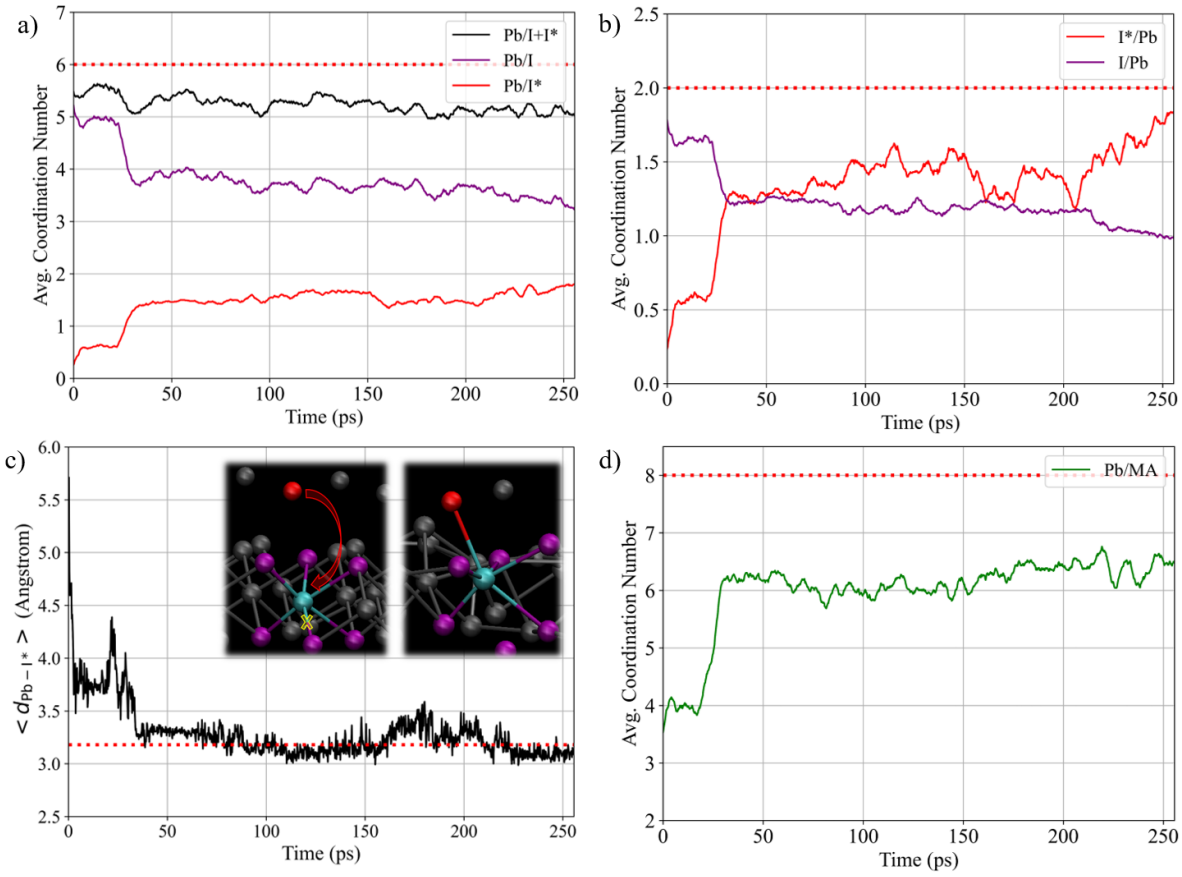

Figure S3. (a) Time evolution of the average Pb/I coordination number using a cutoff distance of 3.7 Å. We distinguish between bonds of Pb with iodine coming from PbI_2 (purple) and iodine coming from MAI (red). The black curve shows the sum of both contributions. (b) Time evolution of the average coordination number of iodine (I* and I) with lead. (c) Average minimum distance $\langle d_{Pb-I^*} \rangle$ of the Pb-I* bonds. The inset highlights the mechanism of the distance decrease by the nucleophilic attack of I* ions to Pb centers. The dashed line shows the Pb-I bond length of $MAPbI_3$ in the orthorhombic phase. (d) Time evolution of the average Pb/MA coordination number using a cutoff distance of 7 Å. All curves represent moving averages with time window of 5 ps. The raw data is shown in Figure S5, Supporting Information. The coordination number of (a) 6, (b) 2, and (d) 8, expected within $MAPbI_3$, are highlighted by dotted lines.

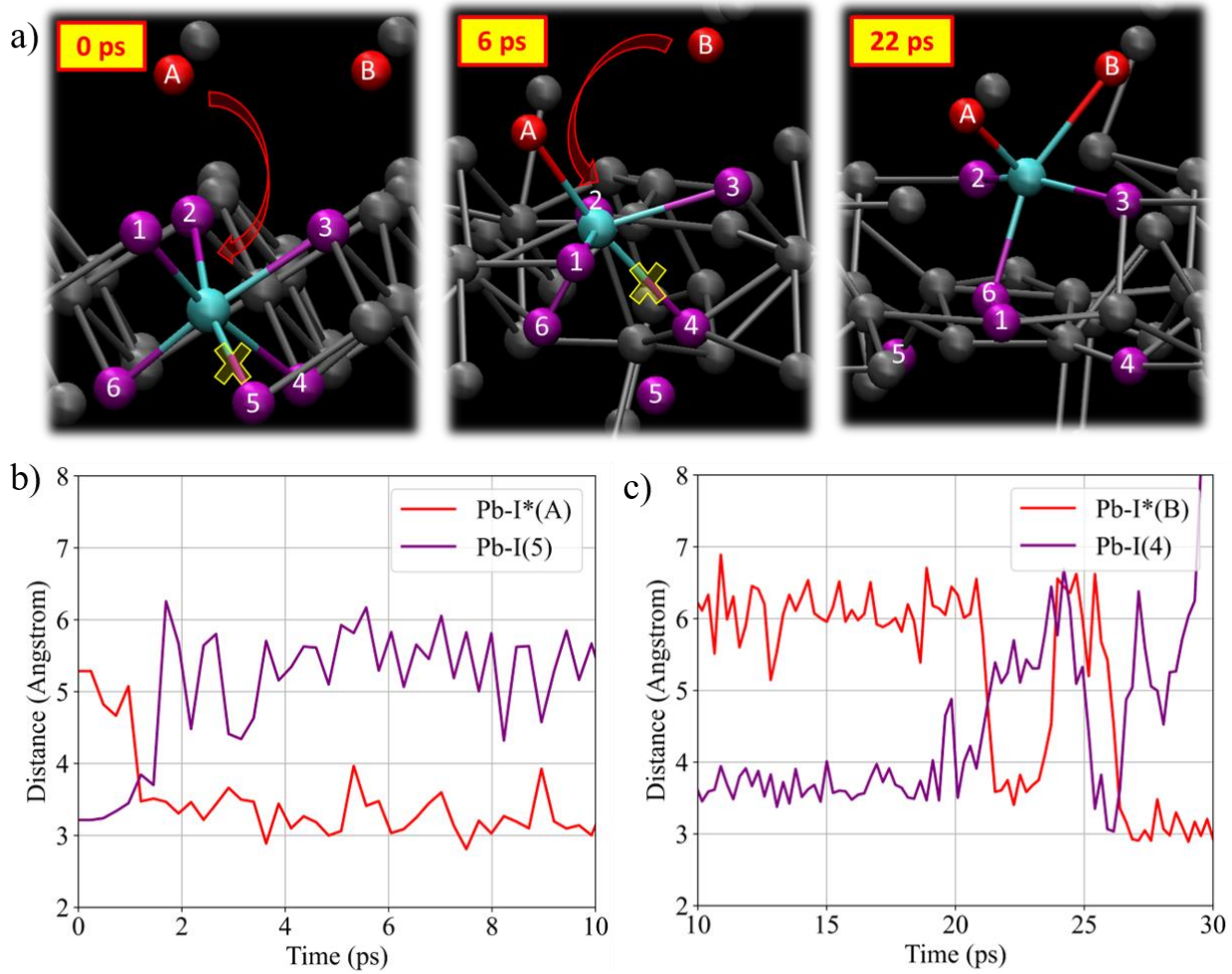

Figure S4. (a) Snapshots showing the breaking of the PbI_2 layer by the nucleophilic attack of iodine coming from MAI visualized for a particular Pb center. (b,c) Temporal evolution of the bond lengths between the Pb center and iodine ions that are involved in the nucleophilic substitution. Numbers and letters label each individual iodine coming from PbI_2 and from MAI, respectively, that are involved in the nucleophilic attacks.

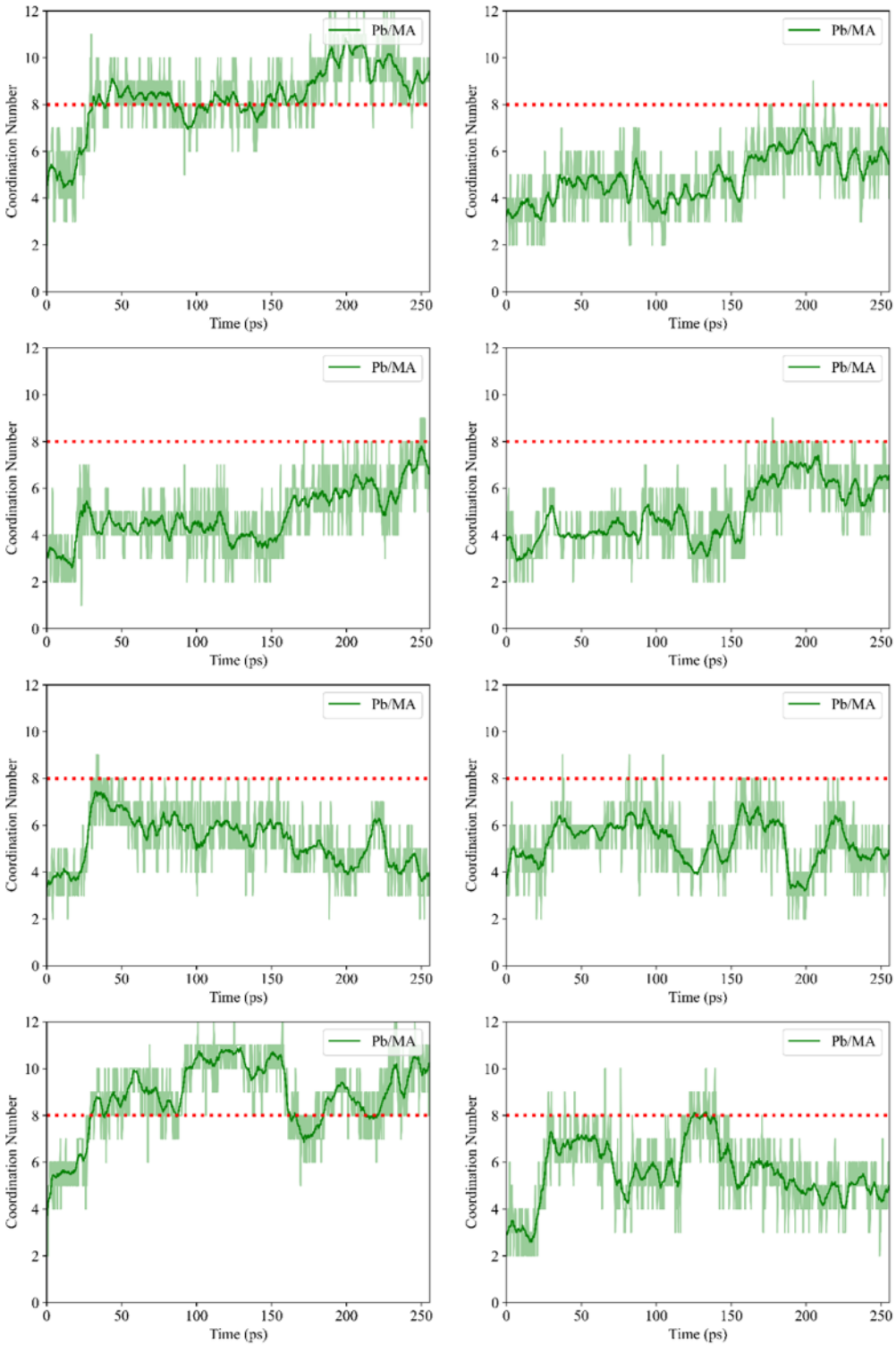

Figure S5. Time evolution of the Pb/MA coordination number for each lead ion. Nitrogen has been taken as reference for MA.

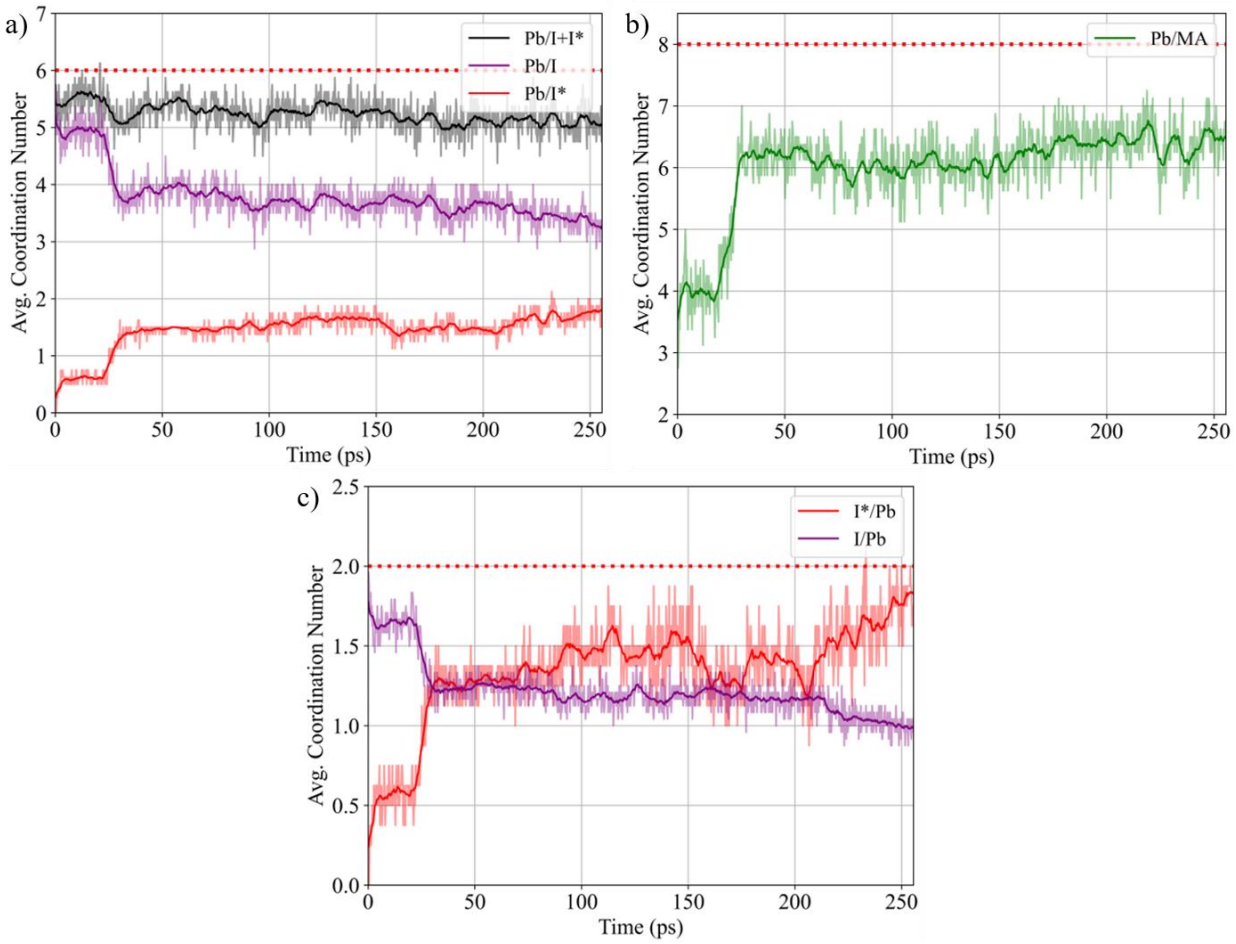

Figure S6.Time evolution of the average coordination number of (a) lead with iodide coming from PbI_2 (Pb/I) and iodide coming from MAI (Pb/I*), and the sum of both contributions (Pb/I+I*); (b) Pb/MA coordination number; (c) I*/Pb and I/Pb coordination number. The solid lines show a moving average with time window of 5 ps. The dotted red line highlights the expected coordination number of bulk $MAPbI_3$.

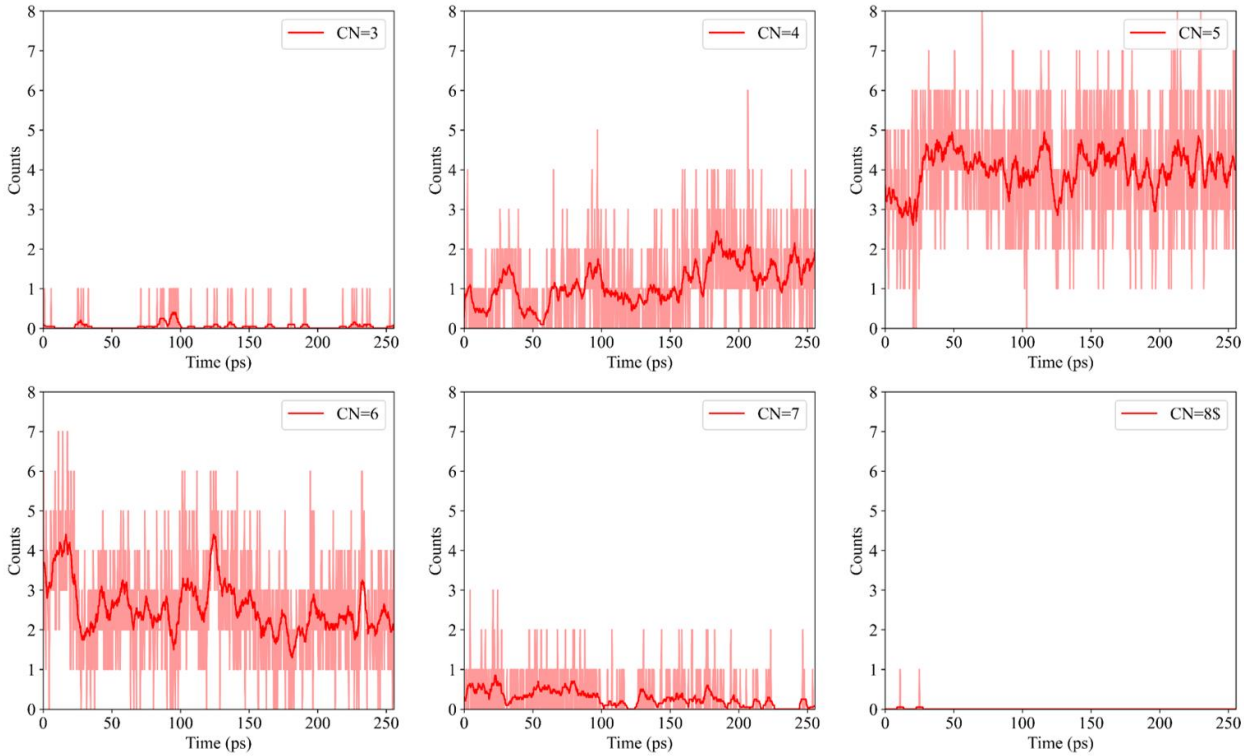

Figure S7. Time evolution of the number of Pb centers with Pb/I coordination number of 3 to 8.

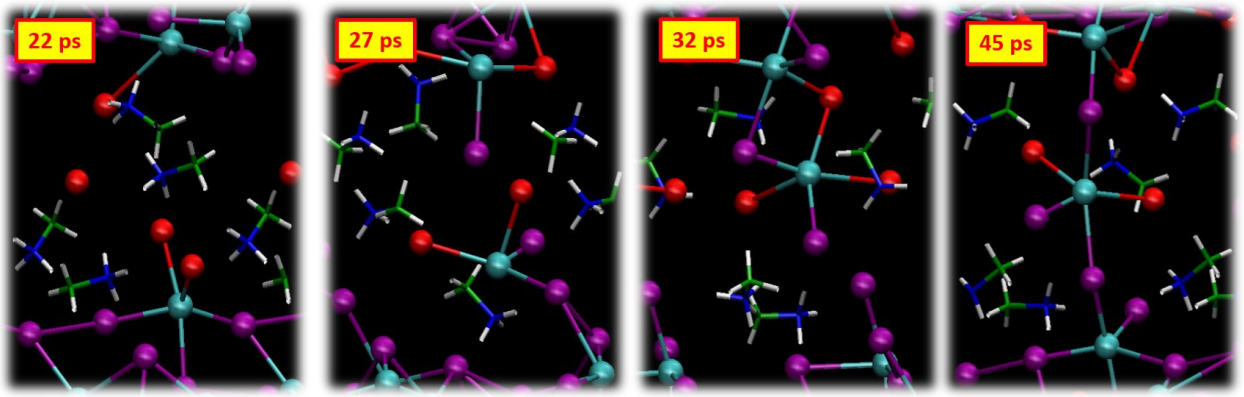

Figure S8. Snapshots visualizing the time evolution of the formation of the 3D perovskite framework.

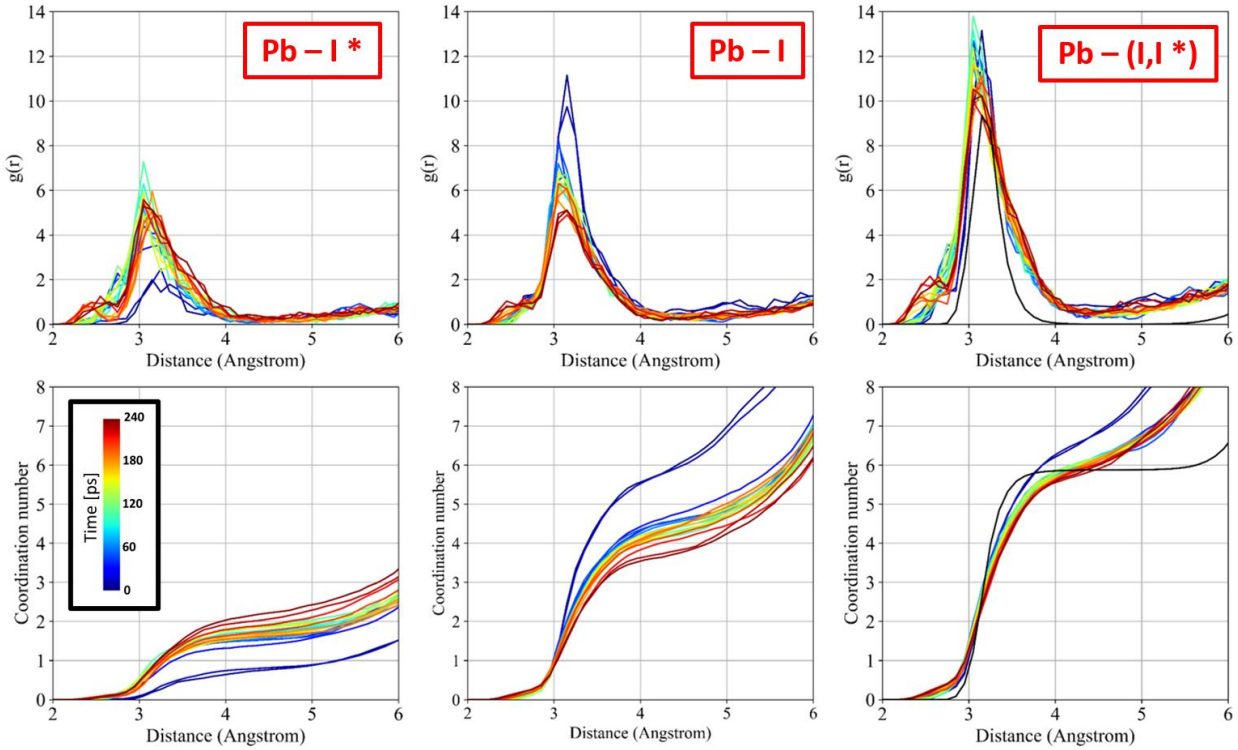

Figure S9. Time evolution of the (top) radial distribution function g(r) and (bottom) coordination number of (left) Pb-I*, (mid) Pb-I, and (right) the sum of both. The colors capture the time information: blue = initial distribution, red = final distribution. In the right subplots, the black line shows the expected g(r) and coordination number for the orthorhombic phase of $MAPbI_3$.

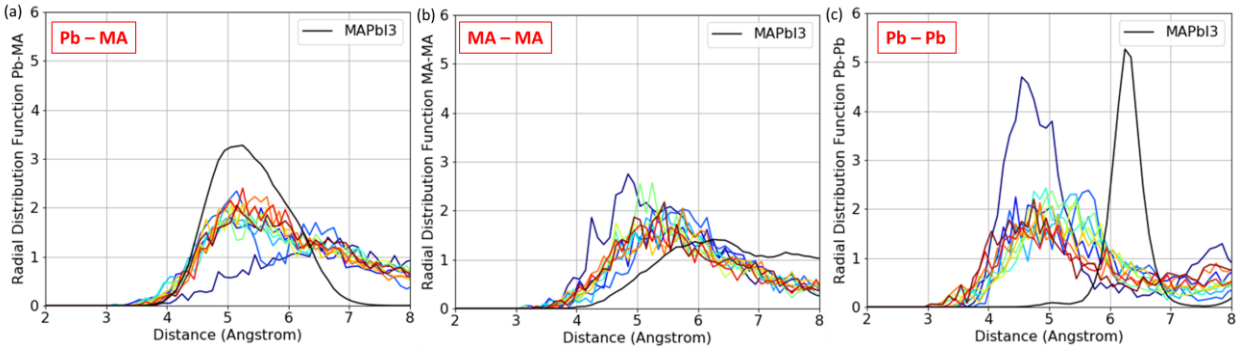

Figure S10. Radial distribution functions (RDF) for (a) Pb-MA, (b) MA-MA, (c) Pb-Pb. Nitrogen has been used as a reference for the methylammonium cation. The black line shows the expected cumulative RDF for the perovskite phase of $MAPbI_3$. The colors capture the time information of the RDF: time increases from blue to red. All curves show averages across 100 trajectory snapshots (~25 ps).