Electronic supplementary information

Ion migration mechanism in all-inorganic Ruddlesden-Popper lead halide perovskites by first-principles calculations

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Table S1. Optimized lattice constants a and c and bond length of Pb-X for all-inorganic 3D $CsPbI_3$, 2D RP Cs_2PbX_4 (X = Cl, Br, I) and mixed-halide RP $Cs_2PbI_2Cl_2$.

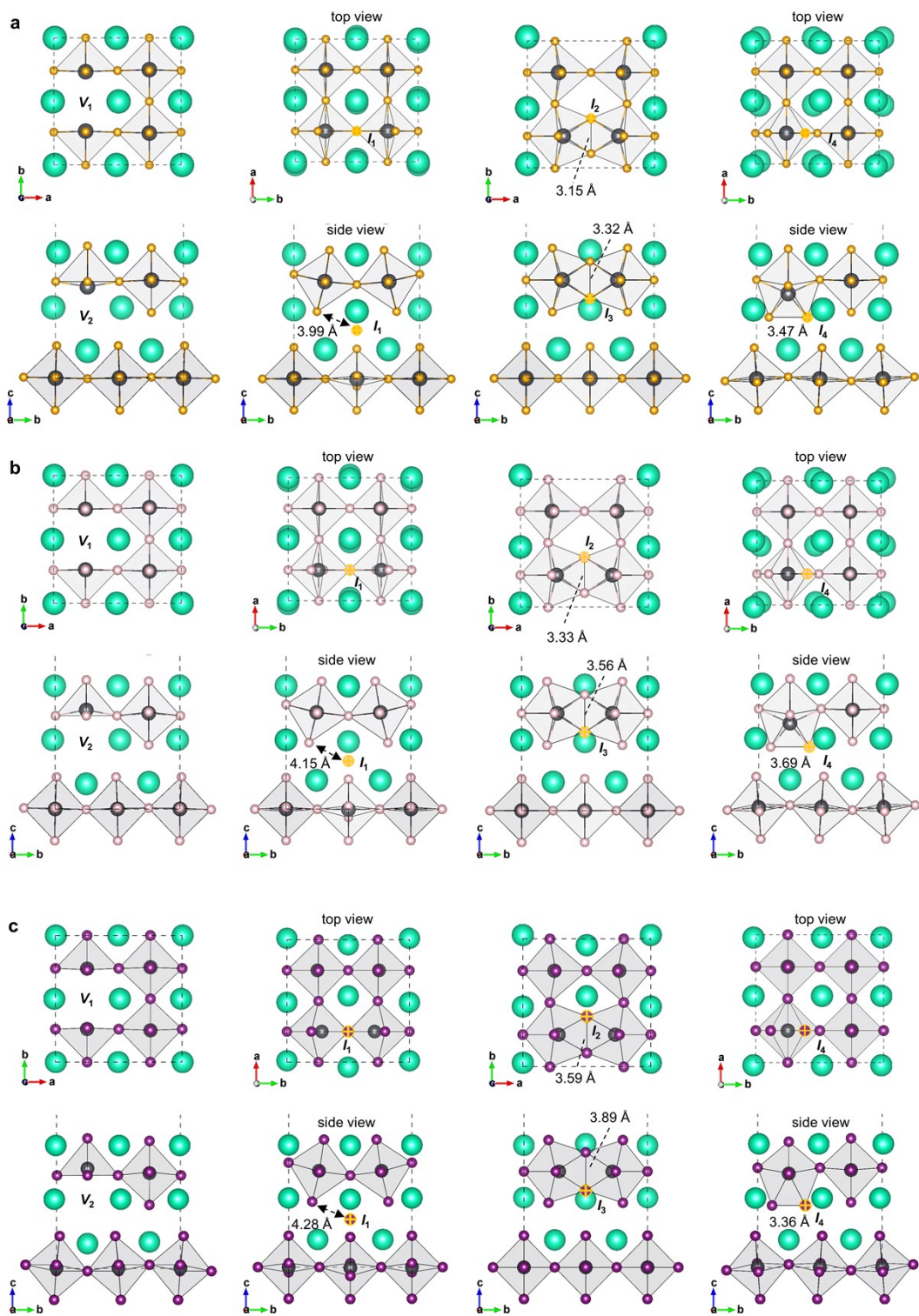|	a (Å)	c (Å)	r_{Pb-X} (Å)
$CsPbI_3$	6.38	-	3.19
Cs_2PbCl_4	5.71	17.58	2.85 ($\parallel$), 2.88 ($\perp$)
Cs_2PbBr_4	5.96	18.39	2.98 ($\parallel$), 3.03 ($\perp$)
Cs_2PbI_4	6.36	19.57	3.18 ($\parallel$), 3.23 ($\perp$)
$Cs_2PbI_2Cl_2$	5.75	19.50	2.87 ($\parallel$), 3.24 ($\perp$)

Figure S1. Optimized structures with different vacancies and interstitials for (a) Cs_2PbCl_4, (b) Cs_2PbBr_4 and (c) Cs_2PbI_4.
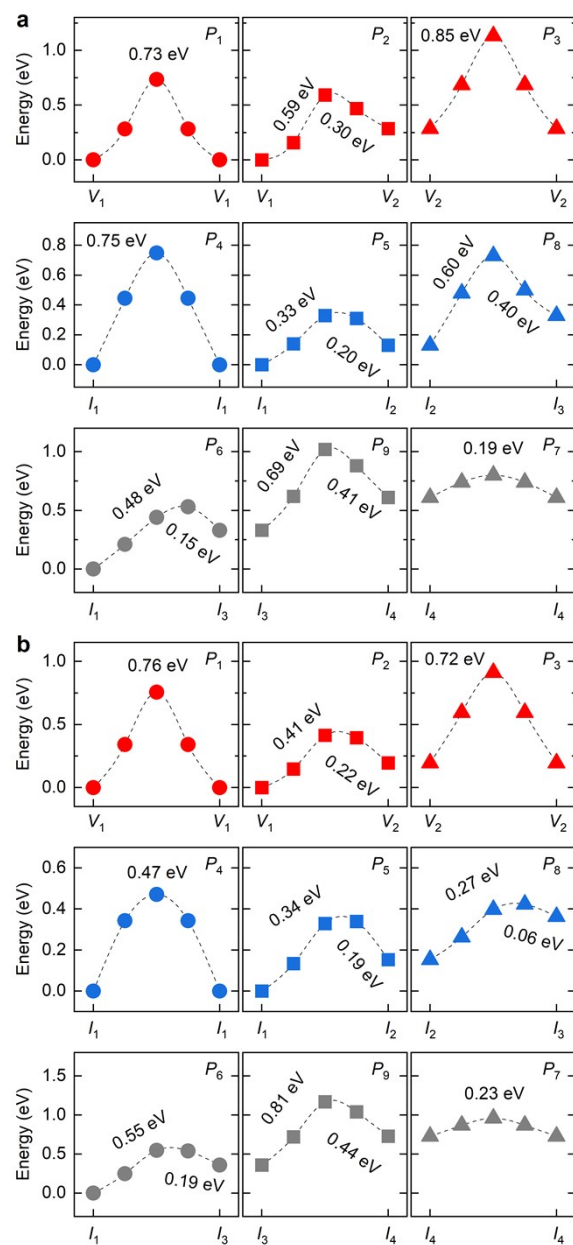
Figure S2. Calculated energy profiles for different migrations of halide vacancies and interstitials in (a) Cs_2PbCl_4 and (b) Cs_2PbBr_4 using the CINEB method.
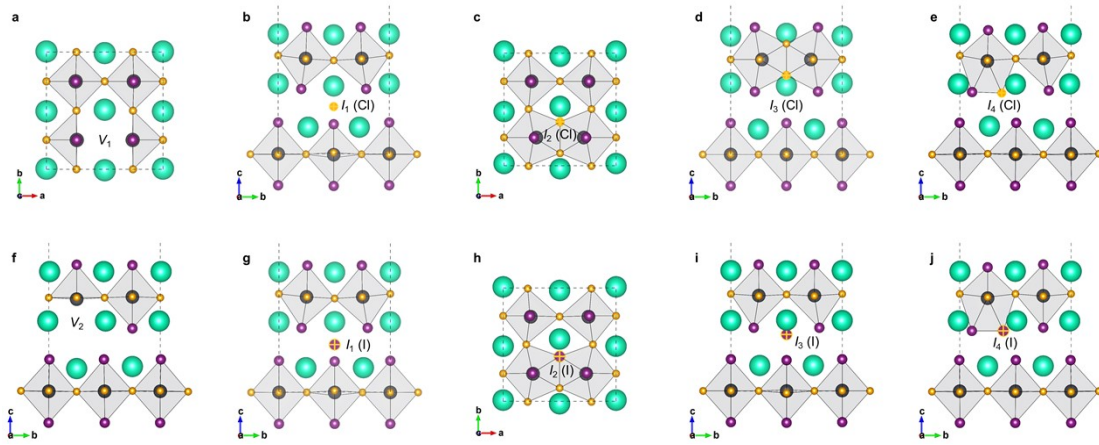
Figure S3. Optimized structures containing different defects in the mixed-halide RP $Cs_2PbI_2Cl_2$. (a) the vacancy at the $4c$ site; (b) the vacancy at the $4e$ site; the isolated I_1 interstitial of (c) Cl and (d) I; the I_2 interstitial of (e) Cl and (f) I; the I_2 interstitial of (g) Cl and (h) I; the I_2 interstitial of (i) Cl and (j) I.
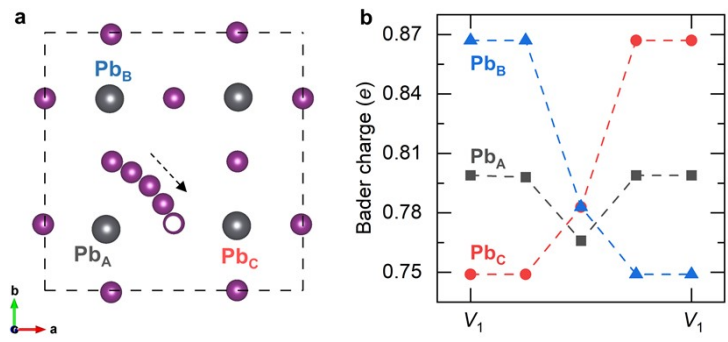
Figure S4. (a) The P_1 migration of RP Cs_2PbI_4, and (b) calculated Bader charges for Pb cations adjacent to the hopping I ions.
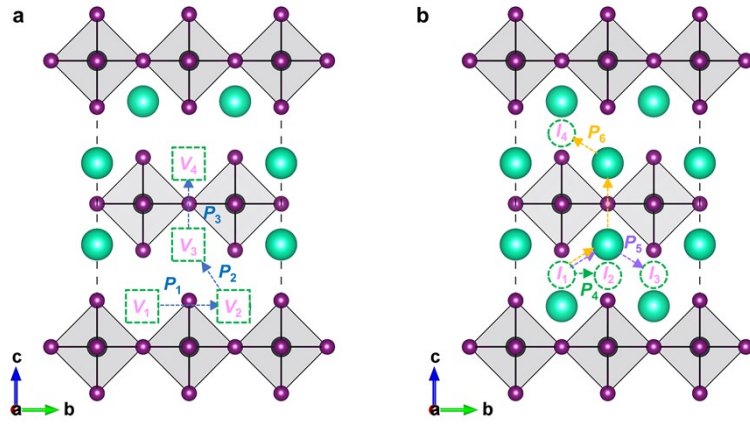
Figure S5. Simulated migration paths for Cs cations in these RP halide perovskites.
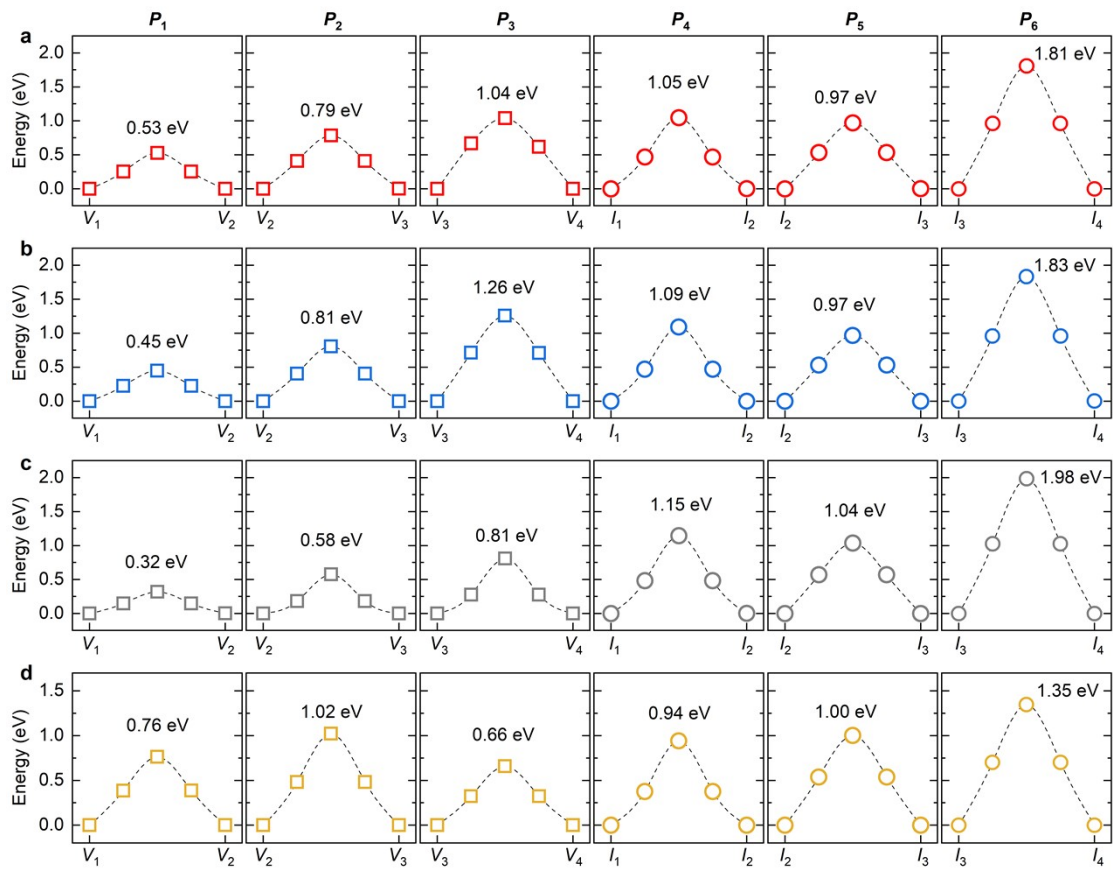
Figure S6. Calculated energy profiles of various migrations for Cs cations in (a) Cs_2PbCl_4, (b) Cs_2PbBr_4, (c) Cs_2PbI_4 and (d) $Cs_2PbI_2Cl_2$.