Supporting Information

Electronic Structure of $CsPbBr_3$ with Isovalent Doping and Divacancy: the Smallest Metal Pb Cluster

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Table S1 The space group, lattice parameters and total energies of the related solids adopted in the calculation of atomic chemical potential (μ_i) of $CsPbBr_3$.

Materials	Space group	Lattice parameters (Å)	Total energy (eV/atom)
Cs	*Fm*-3*m*	$a = b = c = 7.76$	-0.854
Pb	*Fm*-3*m*	$a = b = c = 5.02$	-3.577
CsBr	*Fm*-3*m*	$a = b = c = 7.39$	-6.107
$PbBr_2$	$P4_2/mnm$	$a = b = 7.17$, $c = 4.60$	-9.663

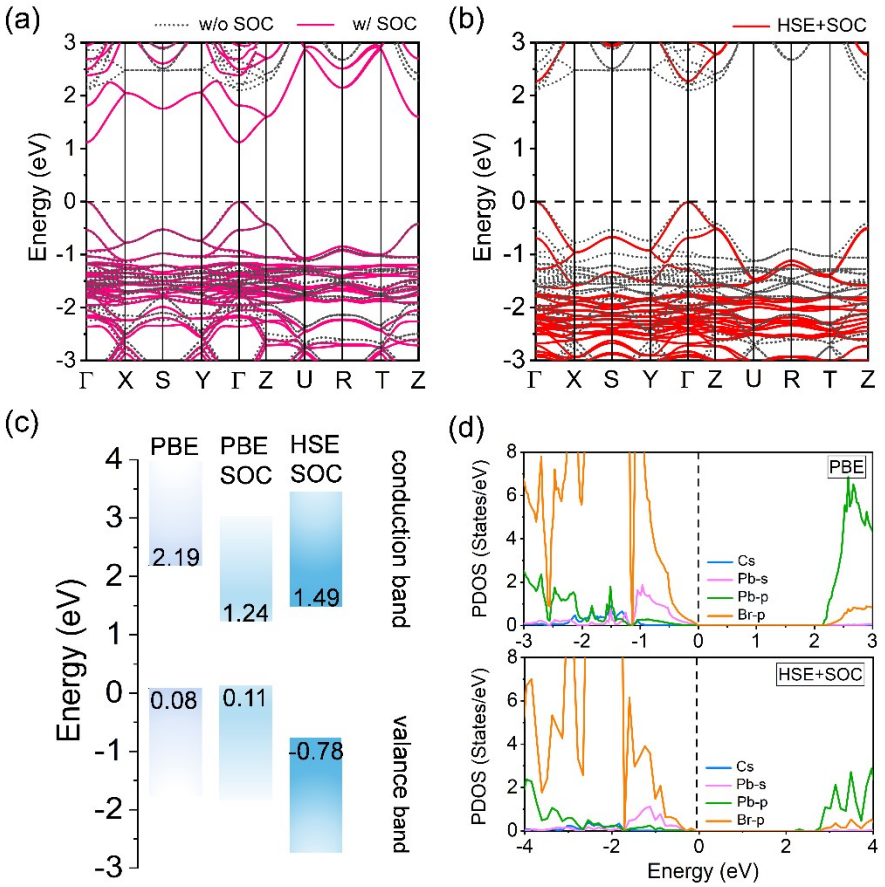

Fig. S1 The electronic properties of pristine $CsPbBr_3$. (a) Calculated band structure with- (pink lines) and without-SOC (gray dash lines) by PBE functional. (b) Band structure simulated by HSE hybrid functional combined with SOC (red solid lines). (c) Band alignment based on three schemes. (d) The results of PDOS under two types of functionals.

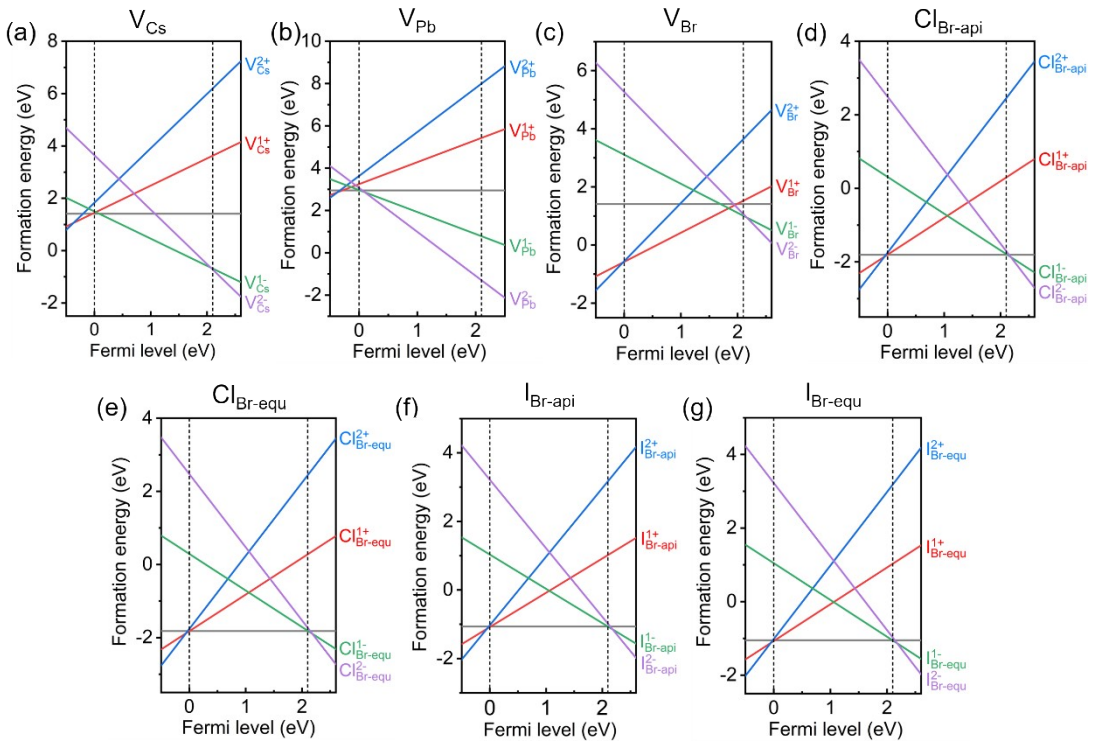

Fig. S2 Formation energies of charged point defects under Pb-rich growth condition, where the charge states are shown adjacent to lines. The solid lines with grey represent the formation energies of defective $CsPbBr_3$ at neutral state.

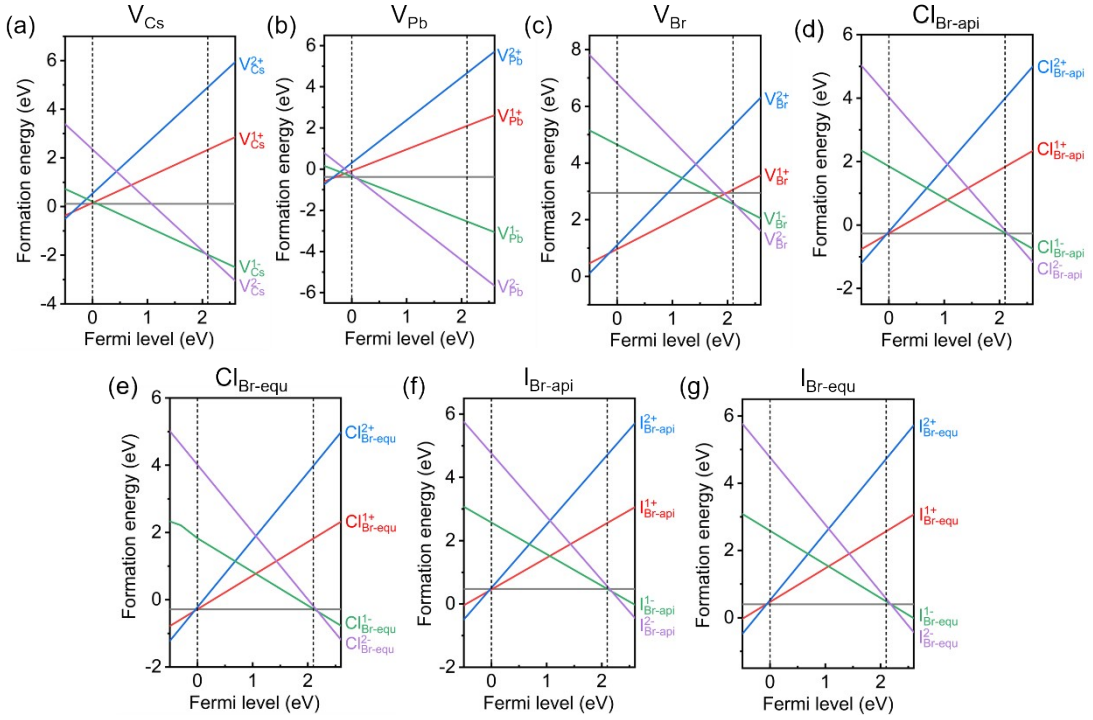

Fig. S3 Formation energies of charged point defects under Br-rich growth condition,

where the charge states are shown adjacent to lines. The solid grey line represents the formation energy under neutral state.

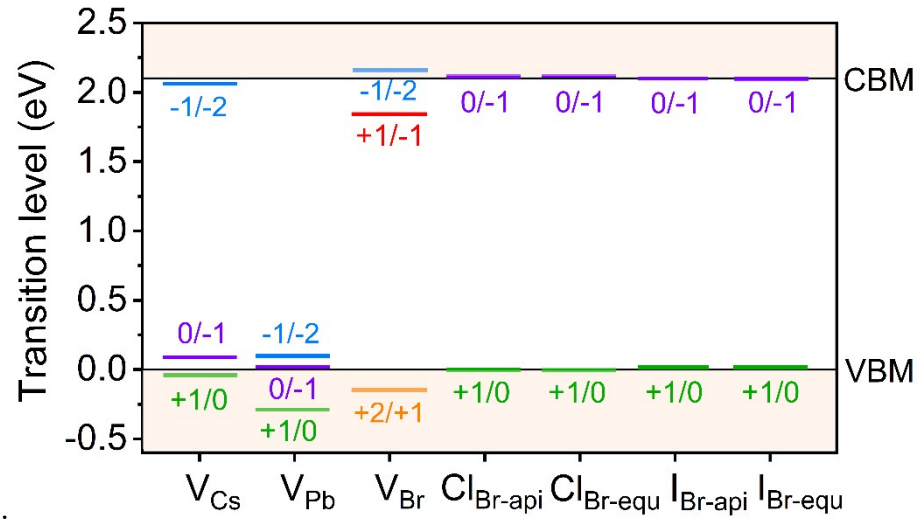

Fig. S4 Charge transition energy levels of point defects in $CsPbBr_3$ under Br-rich growth condition.

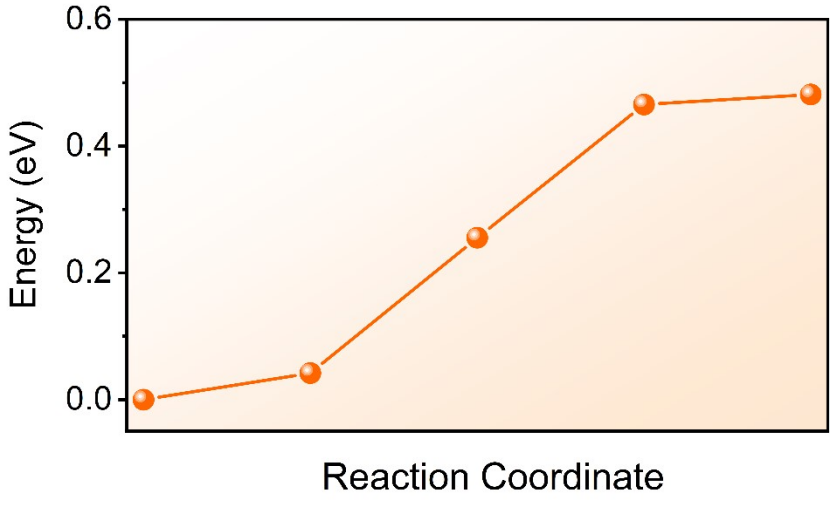

Fig. S5 The reaction energy for migration process of the V1- Br, where the initial and final state is V1- Br (dimmer-like) and V1- Br (unbound) structure, respectively.

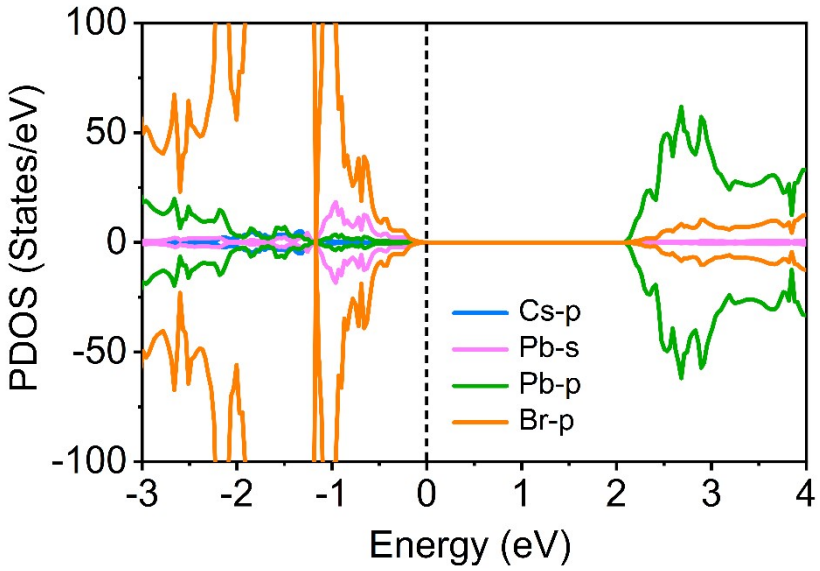

Fig. S6 PDOS of single Br vacancy with positive charge V1+ Br, where black dash line shows the location of E_F.

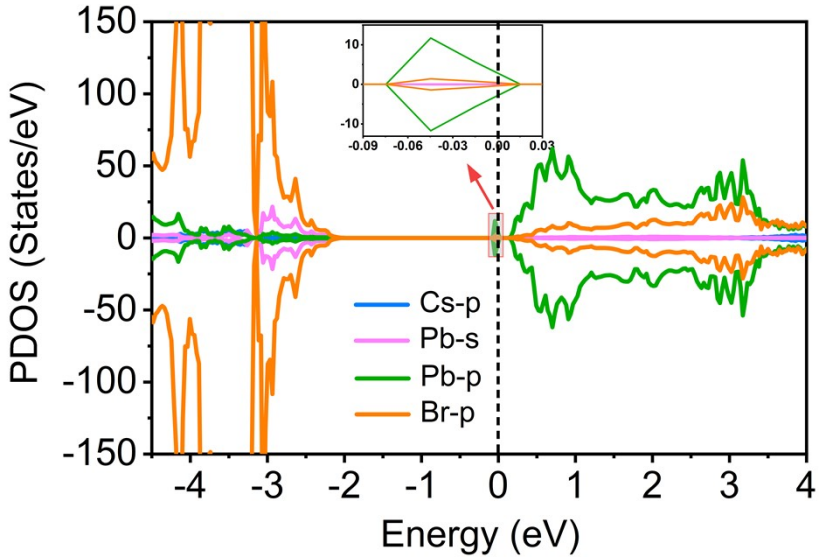

Fig. S7 The PDOS of evenly separated DV_{Br}, with the inset provides an enlarged view of the defect state near the E_F.

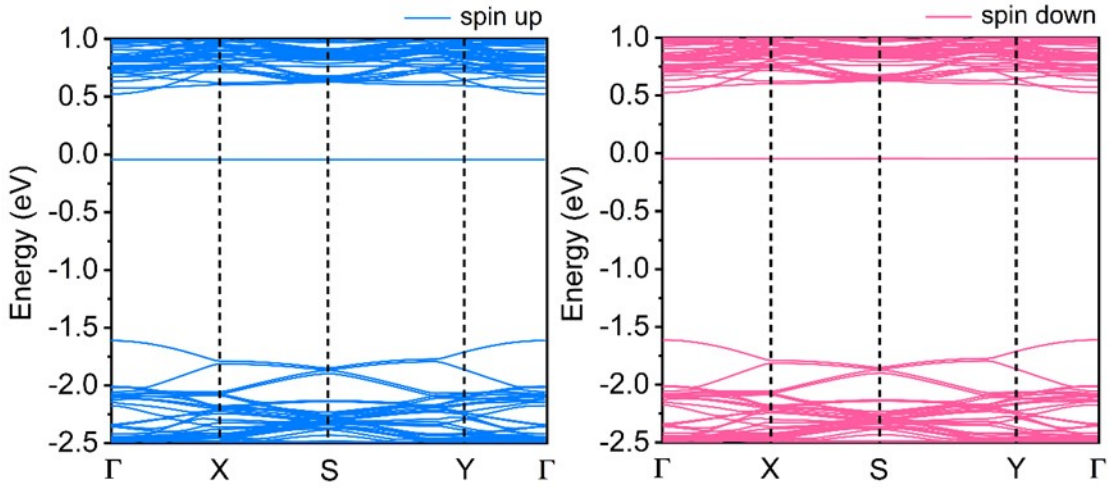

Fig. S8 Band structure of Br divacancy. Blue lines represent the spin-up states (left), and the pink lines represent the spin-down states (right).

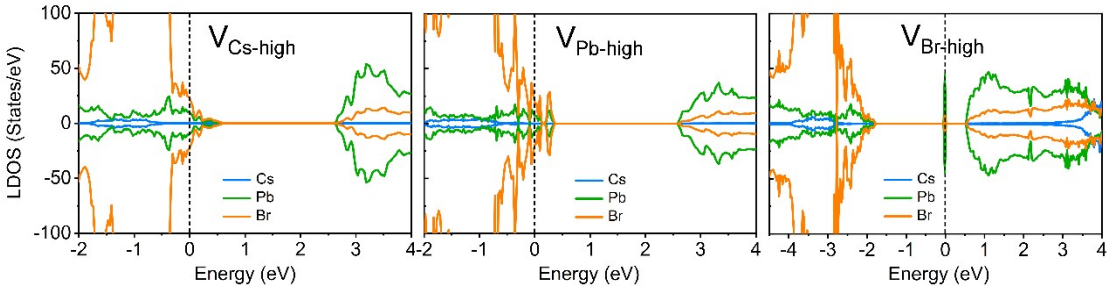

Fig. S9 LDOS of defected $CsPbBr_3$ at high defect concentrations, where black dash line shows the location of E_F.