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


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# Half-filled intermediate bands in doped inorganic perovskites for solar cells

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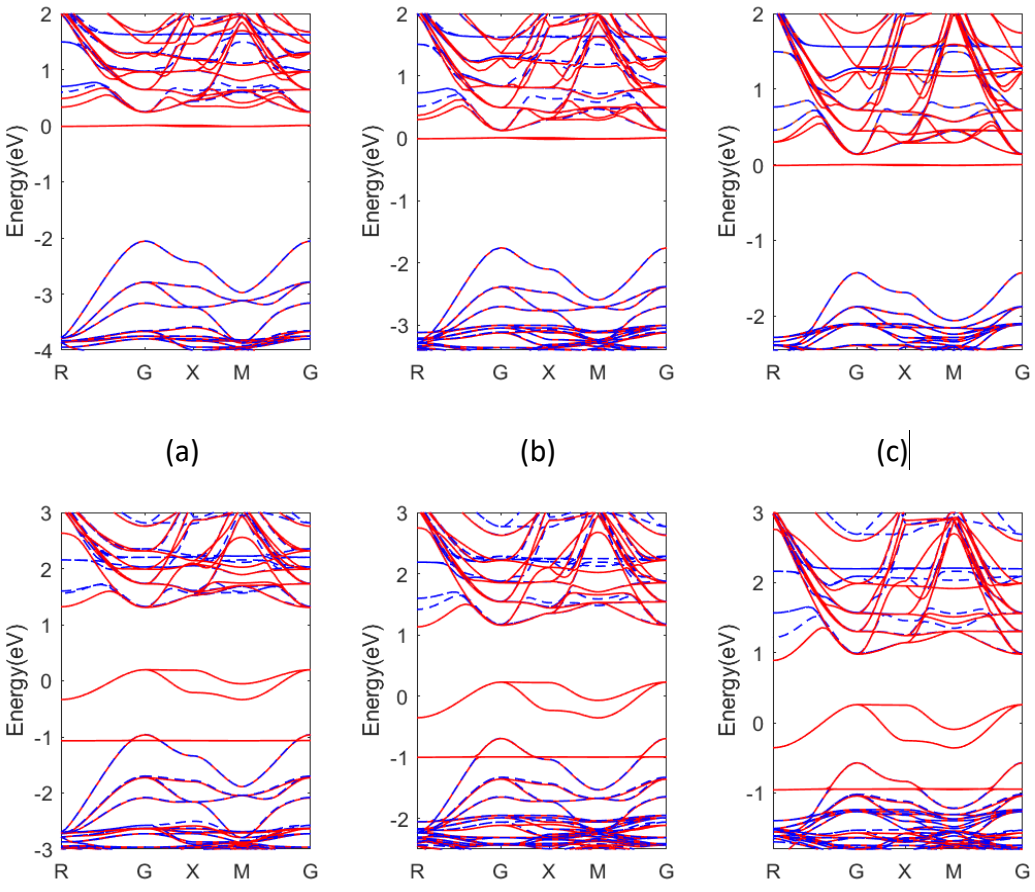
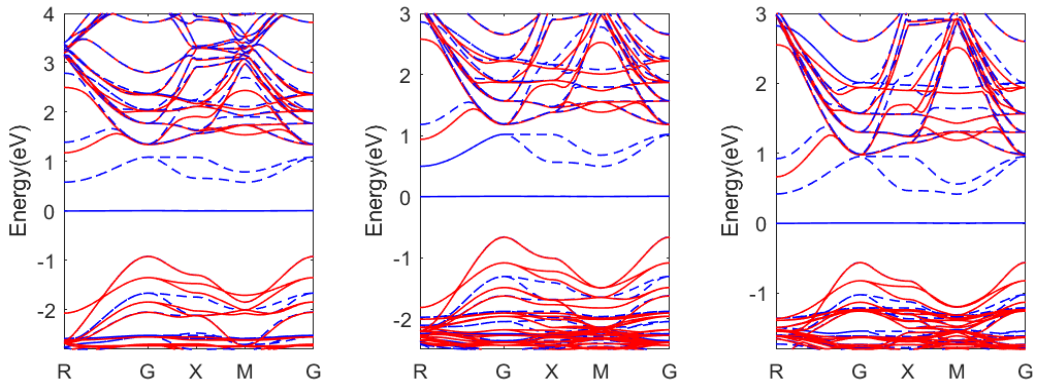


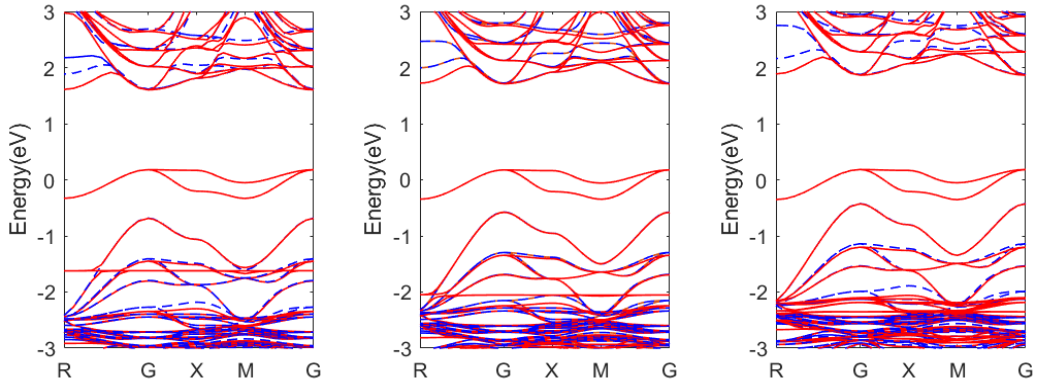

(a) (b) (c)

(d) (e) (f)

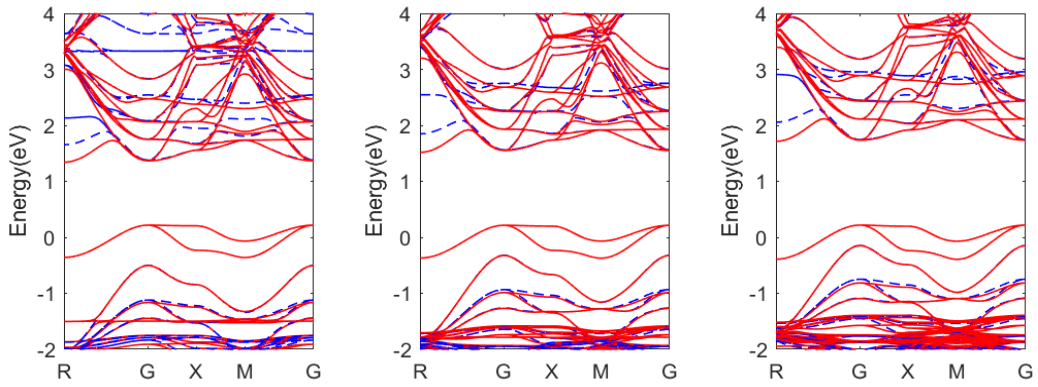



(g) (h) (i)

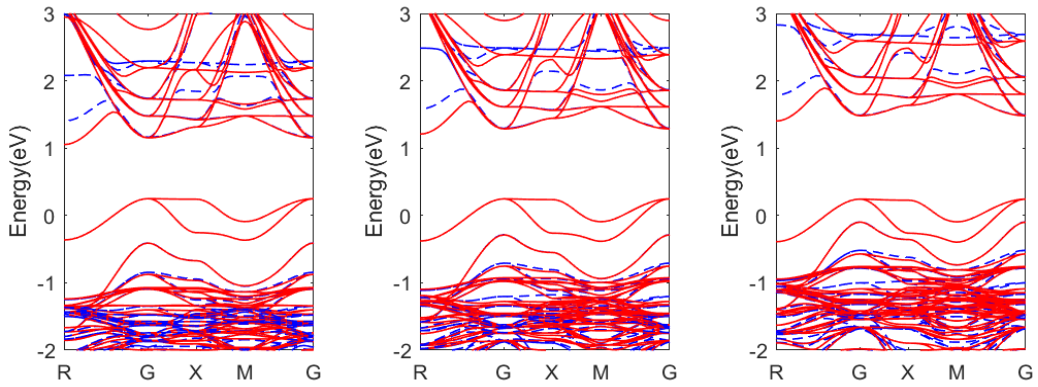
Fig. S1 Spin polarized band structures of Ti doped (a)(b)(c), Cr doped (d)(e)(f), and Fe doped (g)(h)(i) $CsPbX_3$ (X = Cl, Br, I) calculated with PBE and a 2×2×2 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.




(a) (b) (c)

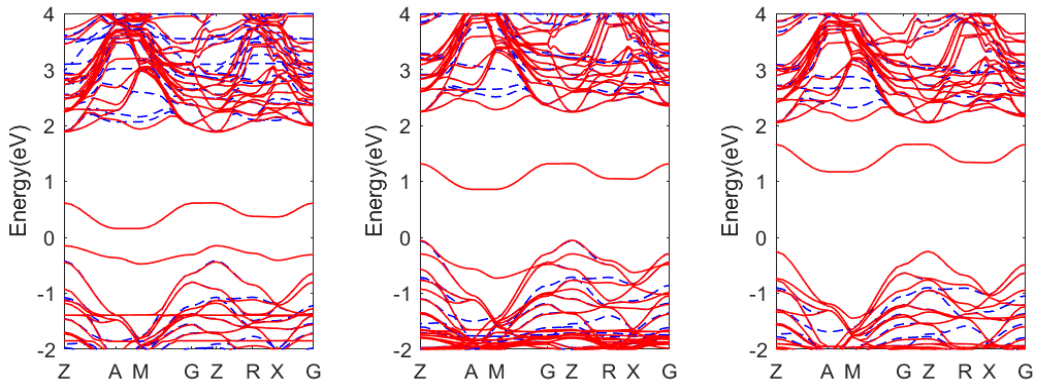



(d) (e) (f)



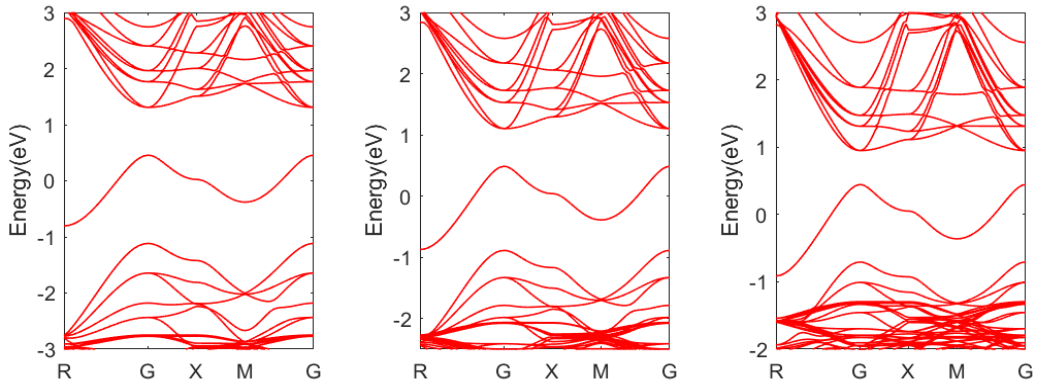

(g) (h) (i)

Fig. S2 Band structures of Cr doped (a)(b)(c) $CsPbCl_3$, (d)(e)(f) $CsPbBr_3$ and (g)(h)(i) $CsPbI_3$ calculated with PBE+U (U = 2, 3.8 and 6 eV, the value of 3.8 eV is adopted from the reference 1) using a 2×2×2 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.




(a) (b) (c)

Fig. S3 Band structures of Cr doped $CsPbCl_3$ calculated with (a) U = 2 eV, (b) U = 3.8 eV and (b) U = 6 eV modeled with a 2×2×3 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.




(a) (b) (c)

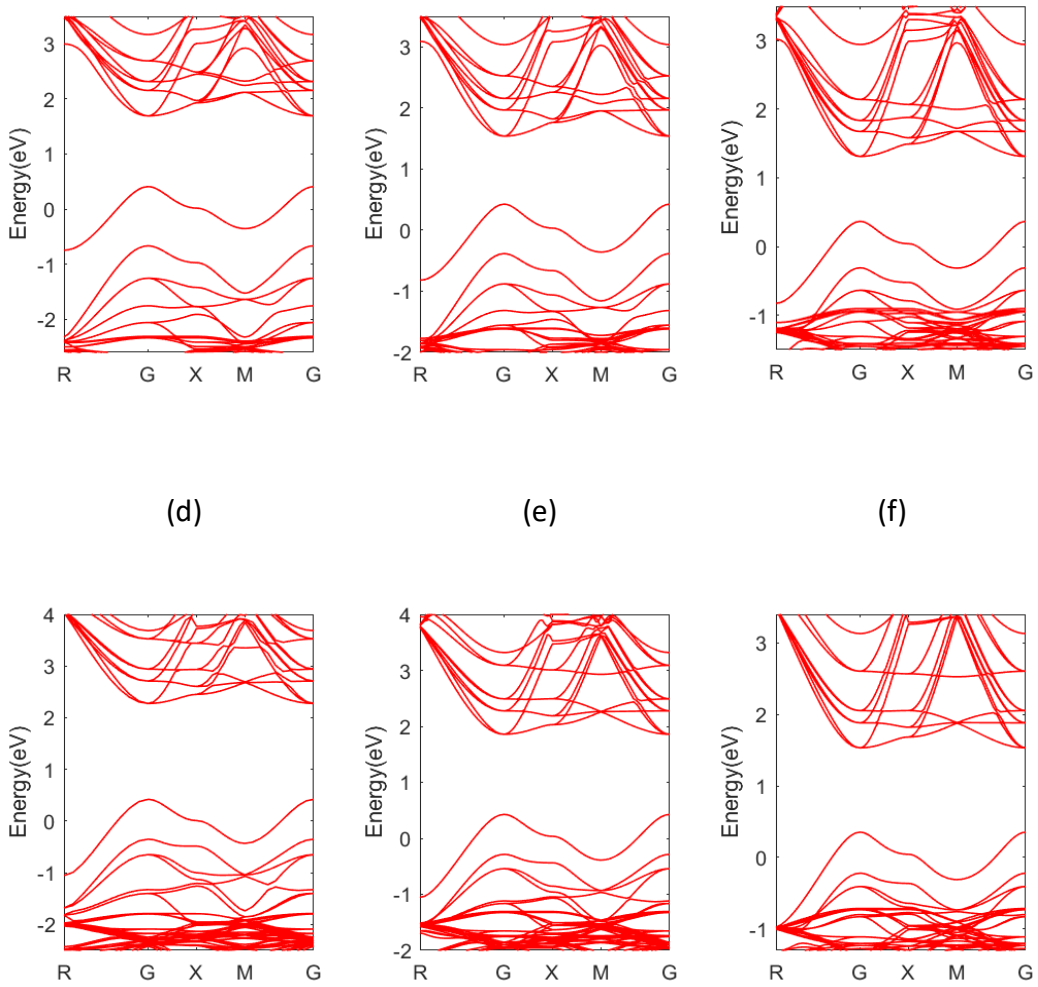
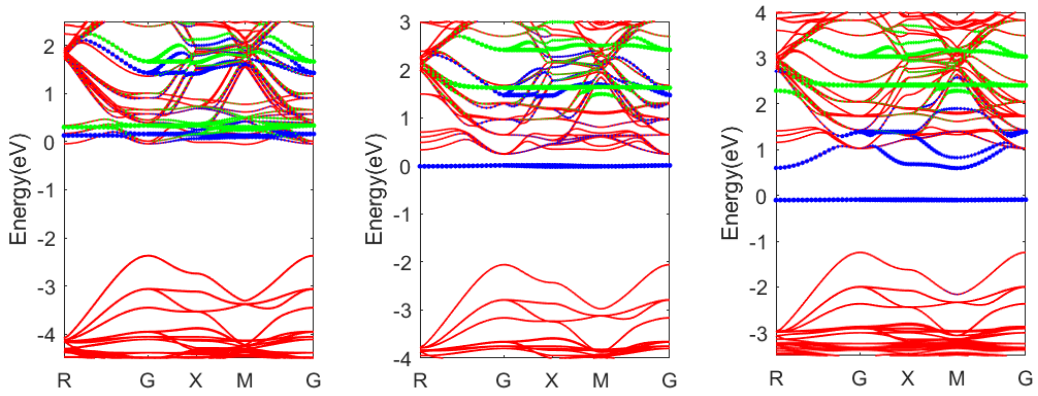



Fig. S4 Band structures of In doped (a)(b)(c), Ga doped (d)(e)(f), and Tl doped (g)(h)(i) $CsPbX_3$ (X = Cl, Br, I) calculated with PBE and a 2×2×2 supercell. The Fermi level is set to 0.



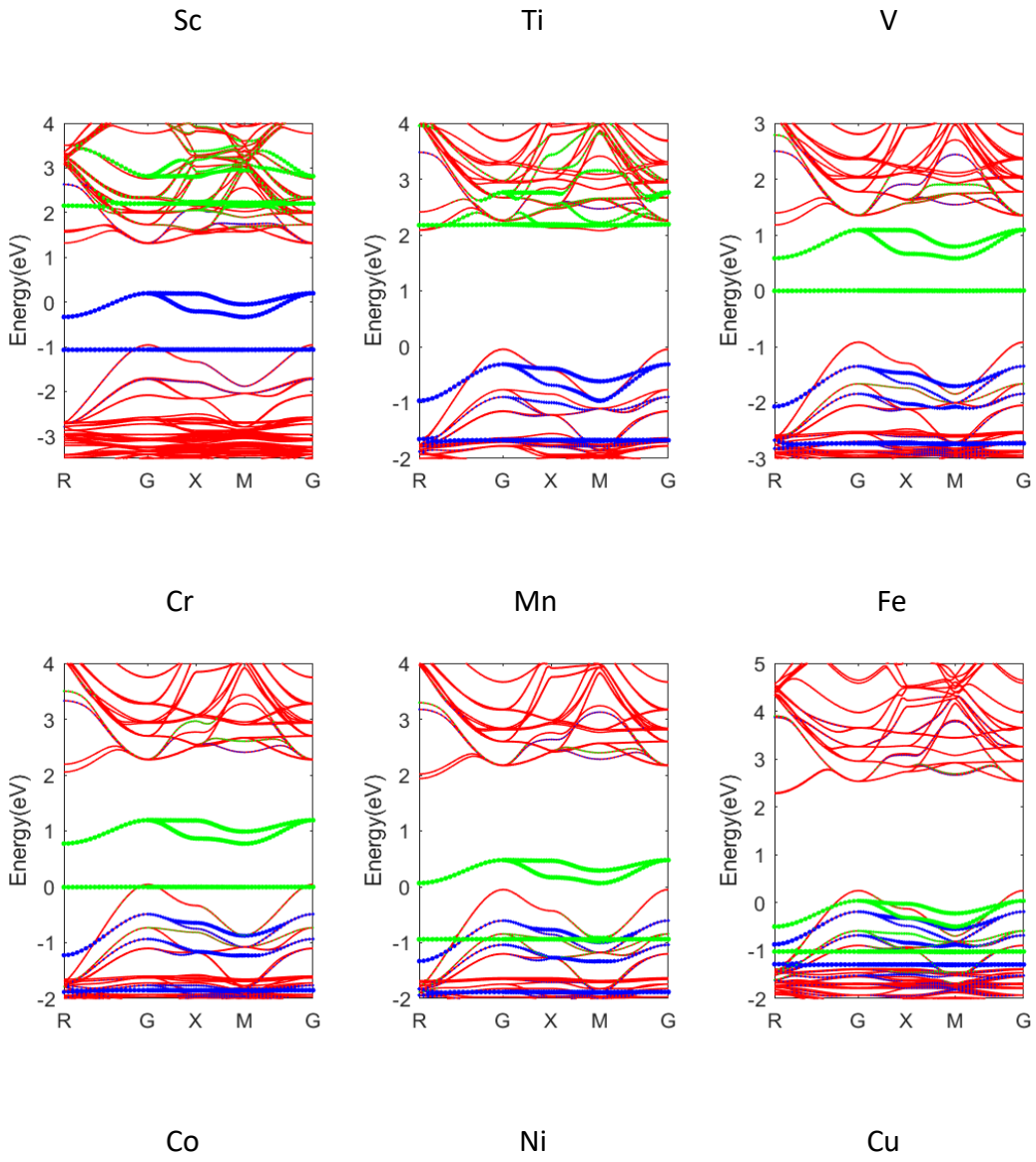



Fig. S5 Spin polarized projected band structures of M (M is transition metal in the fourth period) doped $CsPbCl_3$ calculated with PBE and a 2×2×2 supercell. The blue bands represent spin-up *d* orbitals of M and the green bands represent spin-down *d* orbitals of M. $e_g$ states are dispersive and $t_{2g}$ states are flat. The Fermi level is set to 0.

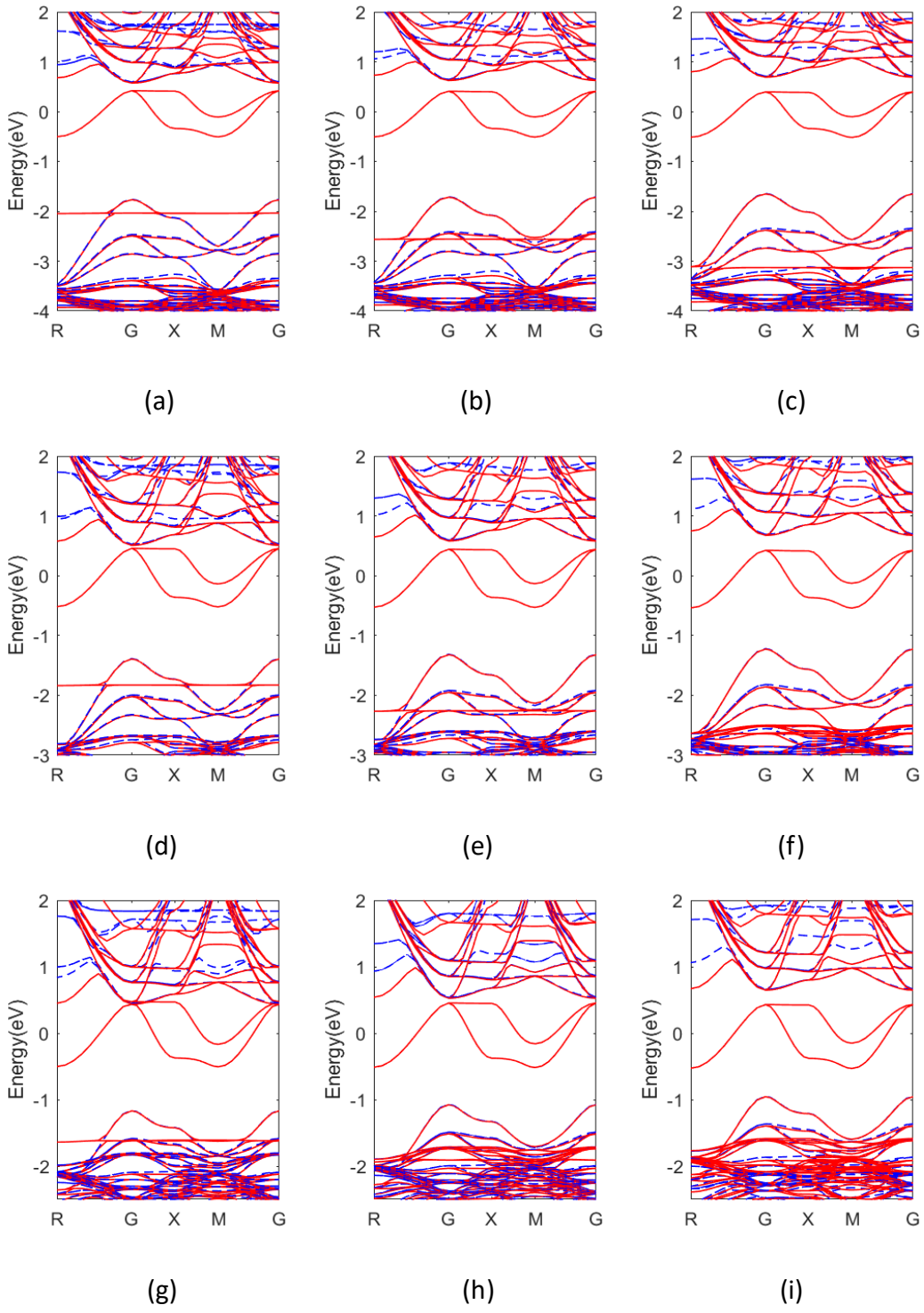



Fig. S6 Band structures of Mo doped (a)(b)(c) $CsPbCl_3$, (d)(e)(f) $CsPbBr_3$, (g)(h)(i) $CsPbI_3$ calculated with PBE+U (U = 2, 3.8, 6 eV) using a 2×2×2 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.

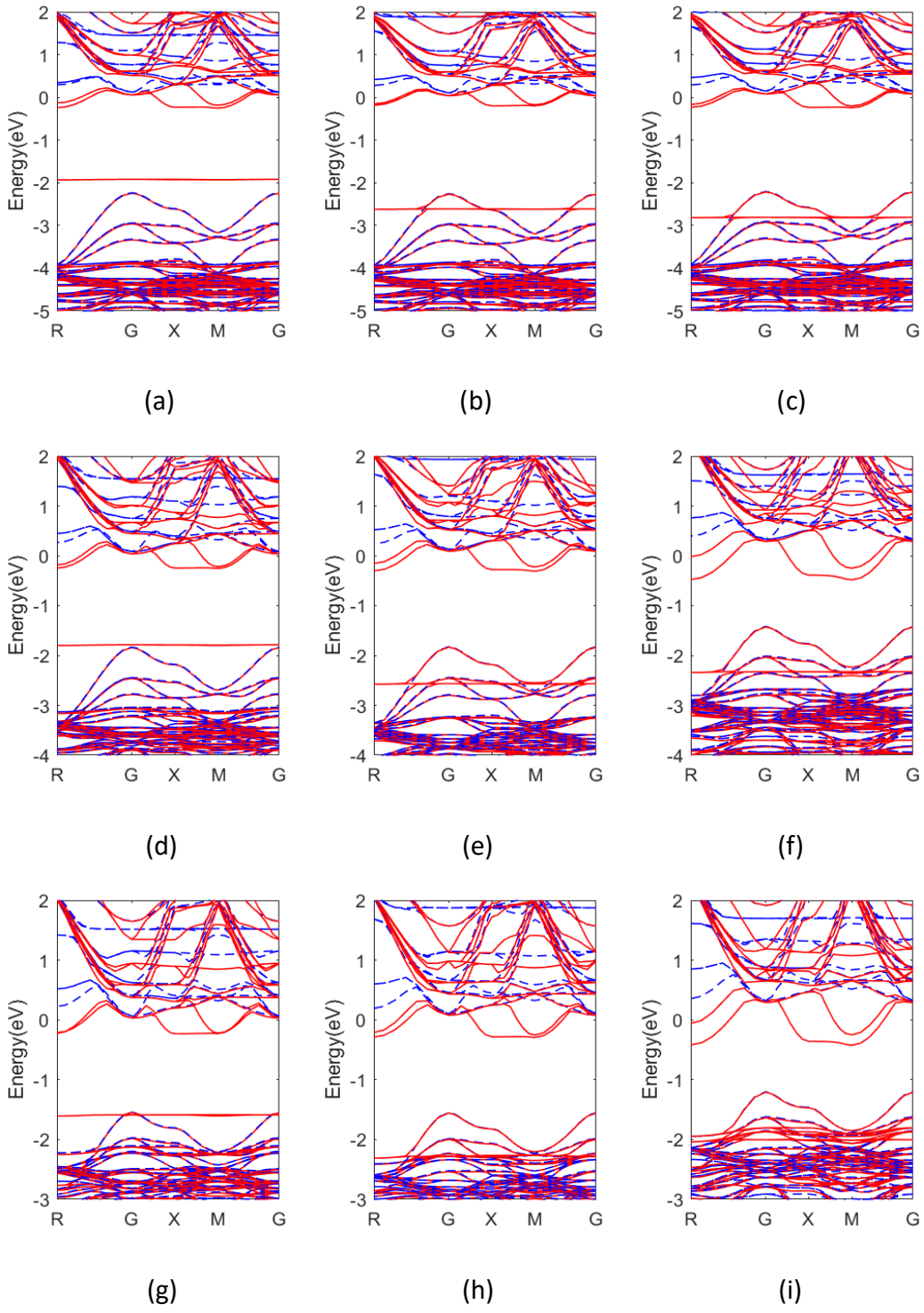
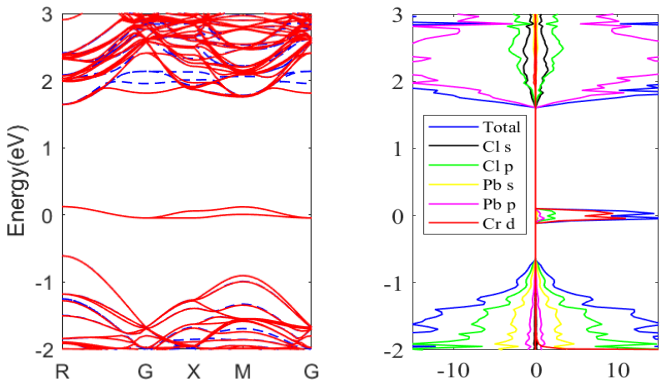
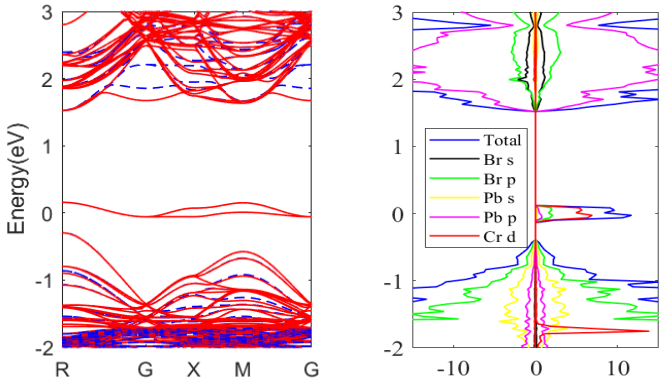


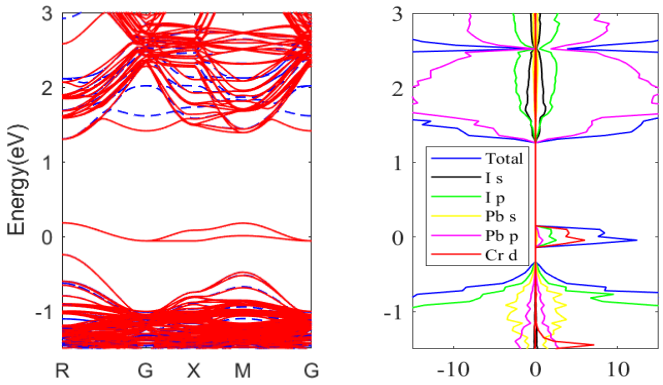

Fig. S7 Band structures of W doped (a)(b)(c) $CsPbCl_3$, (d)(e)(f) $CsPbBr_3$, (g)(h)(i) $CsPbI_3$ calculated with PBE+U (U = 2, 3.8, 6 eV) using a 2×2×2 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.




(a) (b)

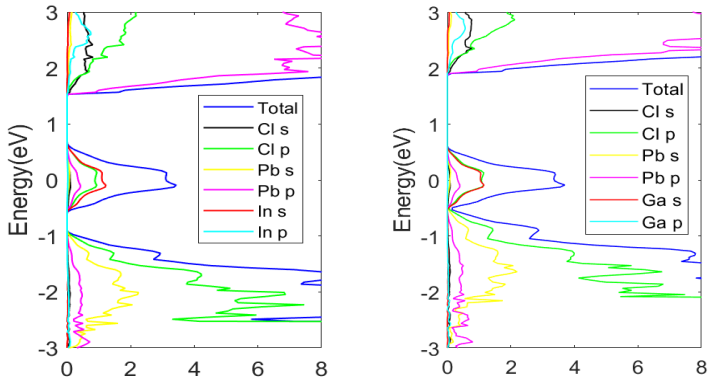



(c) (d)



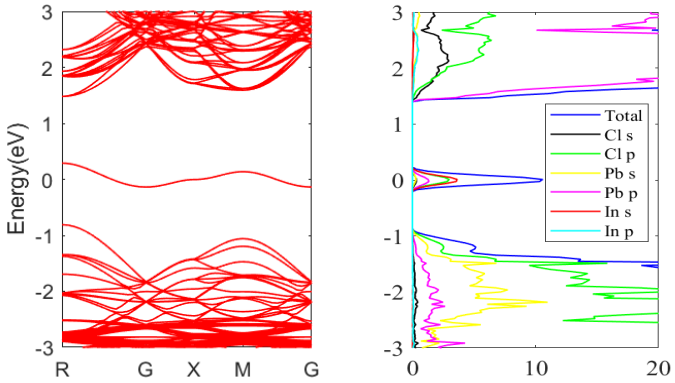

(e) (f)

Fig. S8 Band structures and PDOS of Cr doped (a)(b) $CsPbCl_3$, (c)(d) $CsPbBr_3$ and (e)(f) $CsPbI_3$ calculated with PBE+U (U = 3.8 eV) and a 3×3×3 supercell. Red solid lines and blue dotted lines in the band structures represent spin-up and spin-down bands. The Fermi level is set to 0.




(a) (b)

Fig. S9 PDOS of (a) In and (b) Ga doped $CsPbCl_3$ calculated with PBE using a 2×2×2 supercell. The Fermi level is set to 0.




(a) (b)

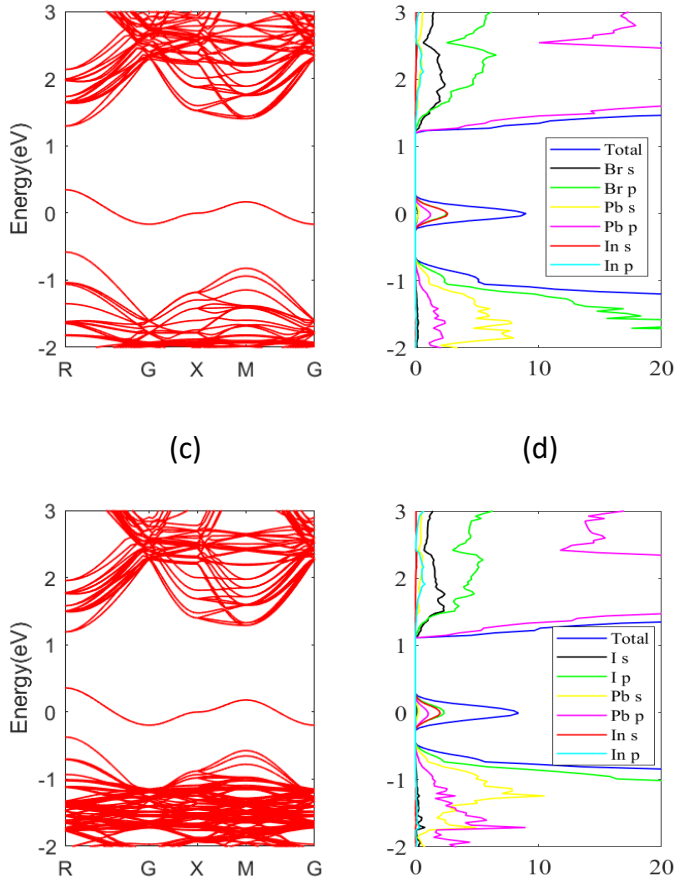
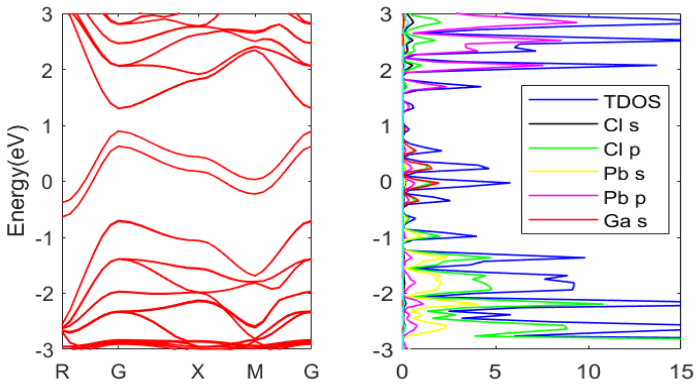
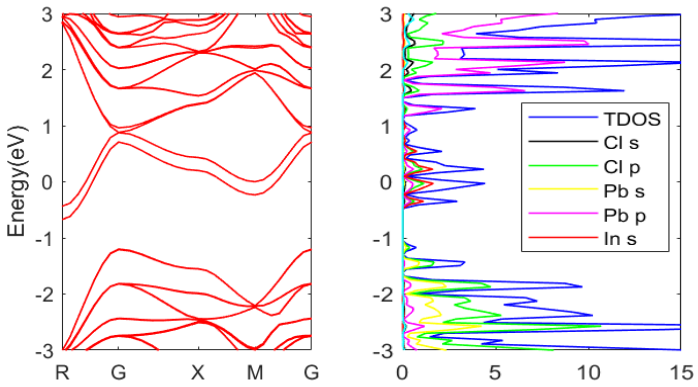



Fig. S10 Band structures and PDOS of In doped (a)(b) $CsPbCl_3$, (c)(d) $CsPbBr_3$ and (e)(f) $CsPbI_3$ calculated with PBE using a 3×3×3 supercell. The Fermi level is set to 0.

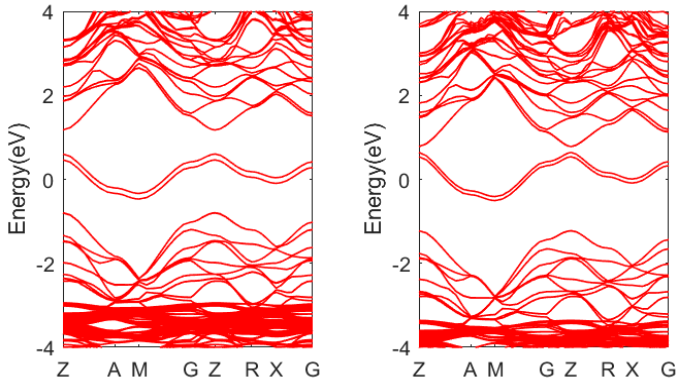



(a) (b)



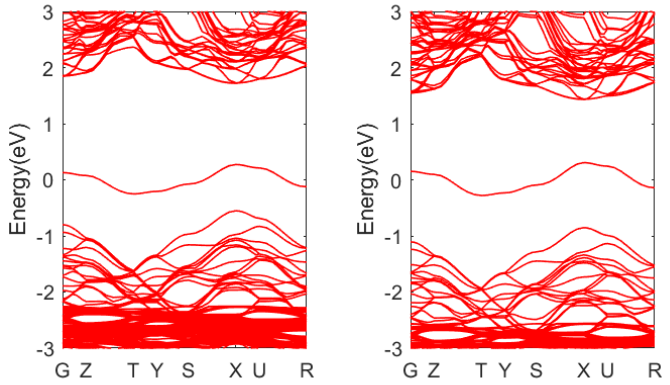

(c) (d)

Fig. S11 Band structures and PDOS of (a)(b) Ga and (c)(d) In doped $CsPbCl_3$ calculated with HSE+SOC using a 2×2×2 supercell. The Fermi level is set to 0.




(a) (b)

Fig. S12 Band structures of (a) Ga and (b) In doped $CsPbCl_3$ calculated with HSE+SOC using a 2×2×3 supercell. The Fermi level is set to 0.




(a) (b)

Fig. S13 Band structures of (a) Ga and (b) In doped $CsPbCl_3$ calculated with PBE using a 2×3×4 supercell. The Fermi level is set to 0.

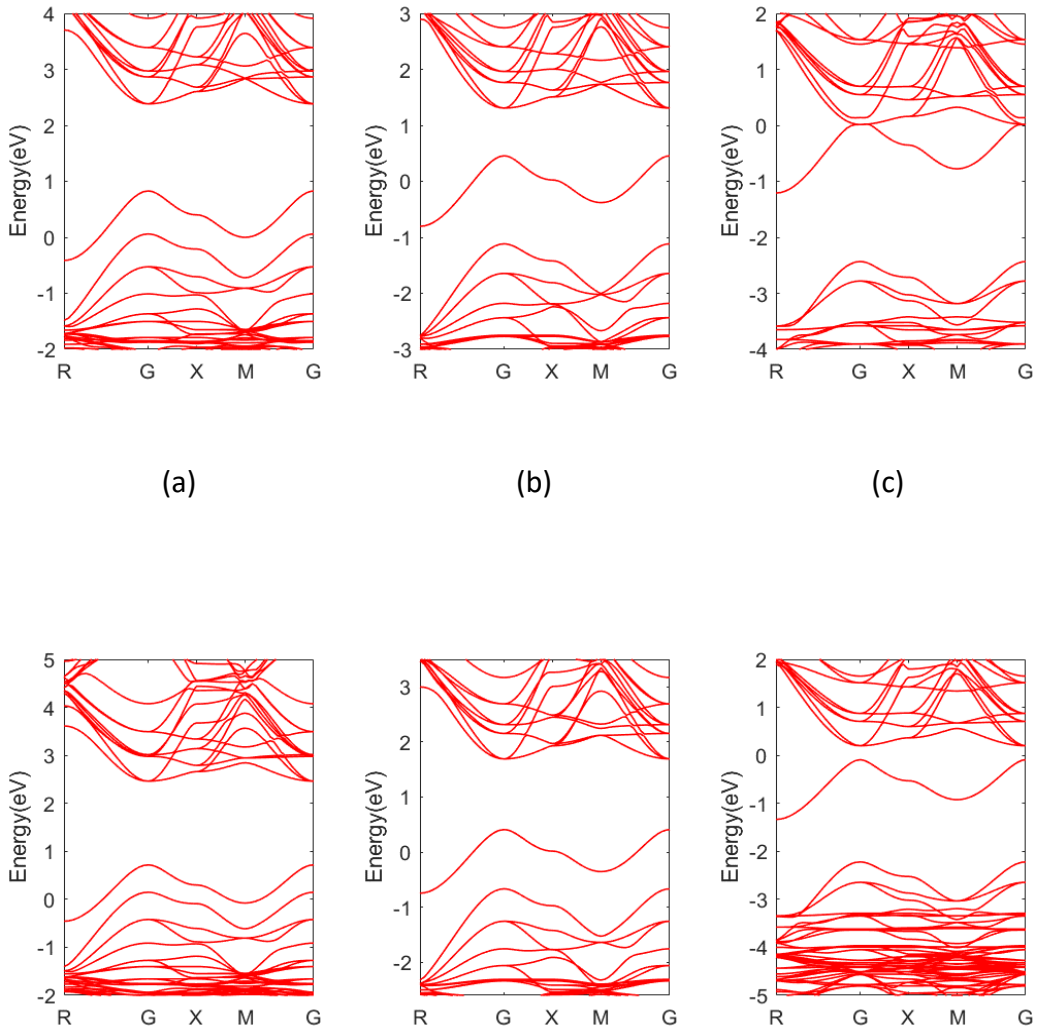



Fig. S14 Band structures of (a)(b)(c) In and (d)(e)(f) Ga doped $CsPbCl_3$ calculated with PBE using a 2×2×2 supercell at the charge state of $q$ = +1, 0, -1. The Fermi level is set to 0.

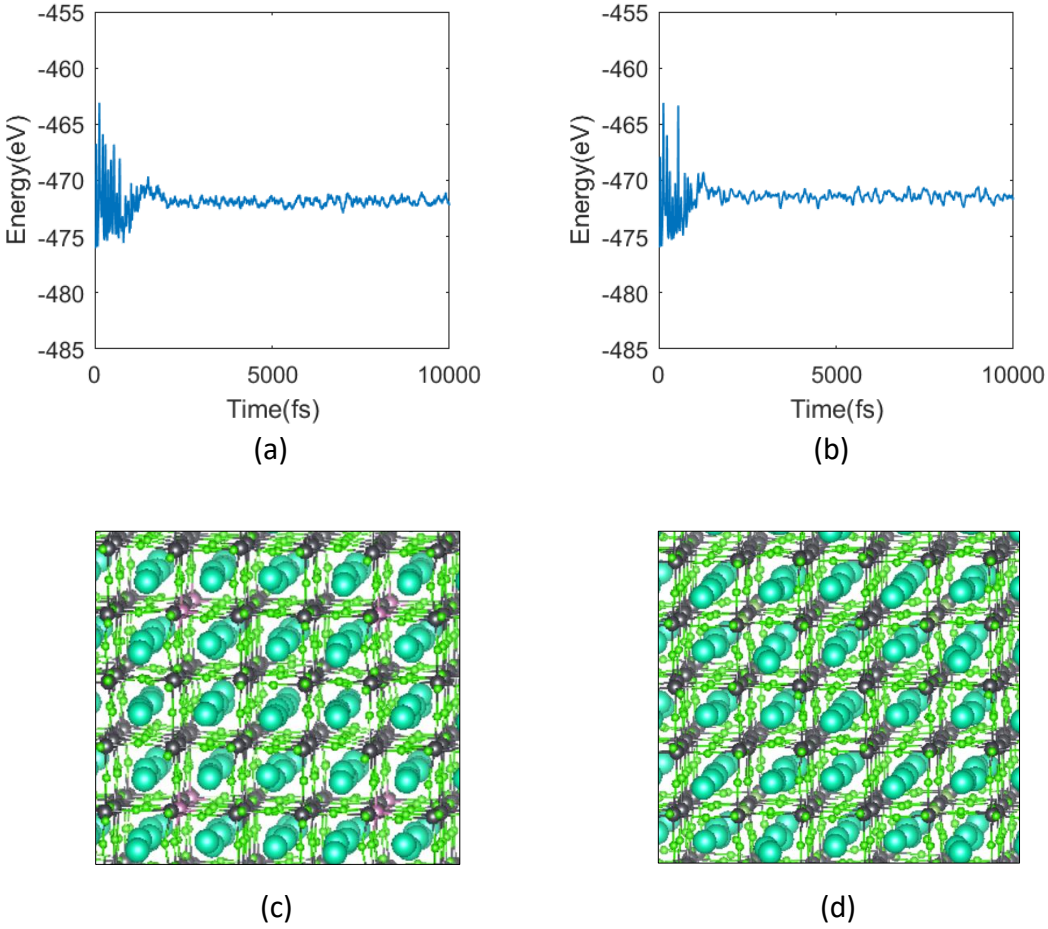



Fig. S15 Fluctuation of total potential energy and the snapshot at 10 ps for (a)(c) In and (b)(d) Ga doped $CsPbCl_3$ during the AIMD simulations at 300 K.

## References

1 A.Hermann, B.Vest, P.Schwerdtfeger, *Phys. Rev. B* 2006, **74**, 224402.