Supplementary Material: Perovskite Termination-Dependent Charge Transport Behaviors of the $CsPbI_3$/Black Phosphorus van der Waals Heterostructure

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GGA-1/2 method

The details of the GGA-1/2 method were given in refs [1, 2], which introduced a half-ionization state of individual atoms by removing 1/2 electron from the occupied levels that contribute the top of the valence bands. In this method, the atomic self-energy potential V_S is expressed as

$$V_S \approx V(0,r) - V(-1/2,r) \tag{1}$$

where $V(0,r)$ and $V(-1/2,r)$ denote the all-electron potentials of the atom and half-ion, respectively. To avoid the Coulomb tail (of 1/2 electron) penetrating into the neighboring atoms, the self-energy potentials should be trimmed as $V'_S = \Theta(r)V_S$ with a cutoff function $\Theta(r)$

$$\Theta(r) = \begin{cases} \left[1 - \left(\frac{r}{\mathrm{CUT}}\right)^n\right]^3 & (r \le \mathrm{CUT}) \\ 0 & (r \ge \mathrm{CUT}) \end{cases} \tag{2}$$

The occupation number n and cutoff radius CUT can be determined in a variation way to maximize the band gap of the crystal. In this work, the half ionizations are applied to the *p*-orbital of the P and I atoms. In details, the values of n and CUT (a.u.) are set as listed in the Table 1 according the refs [3, 4].

Table 1 Values of the occupation number n and cutoff radius CUT adopted in the GGA-1/2 calculations.

Atom	Half-ionized orbital	n	CUT (a.u.)
P	p	8	3.16
I	p	30	3.32

Model details

The optimized lattice parameters of the cubic $CsPbI_3$ bulk and monolayer BP are $a = b = c = 6.386$ Å, and $a' = 3.299$ Å, $b' = 4.621$ Å, respectively, which are in line with the previous reports.[5, 6] By following the same approach as that reported in our previous studies,[7,8] the $CsPbI_3$/BP vdW heterostructure can be constructed by stacking the 2×4 monolayer BP on the exposing (110) surfaces of 1×3 $CsPbI_3$ slab. The calculated $CsPbI_3$ cell parameters are employed to build the periodic super cell along x and y directions, leaving 20 Å vacuum along the z-direction to exclude

the interaction between the neighboring slabs. Moreover, the size and shape of the $CsPbI_3$ slab together with the positions of bottom two-layer atoms are fixed during the ionic relaxation of interface structures. In particular, there are PbI_2- and CsI-terminated surfaces for the $CsPbI_3$ slab, which are the most probably exposed surface under PbI_2-rich and PbI_2-poor conditions, respectively. Accordingly, we construct two types of $CsPbI_3$/BP heterostructures, namely PbI_2/BP (86 atoms) and CsI/BP (83 atoms) interfaces.

Table S1. Bader charge (in eV) of P atoms in BP calculated with GGA and GGA-1/2 methods.

	GGA		GGA-1/2	
	min	max	min	max
1L	4.993	5.007	4.994	5.006
2L	4.997	5.003	4.998	5.002
3L	4.994	5.006	4.992	5.008
4L	4.992	5.008	4.991	5.009
5L	4.994	5.006	4.992	5.008
Bulk	4.966	5.034	4.959	5.041

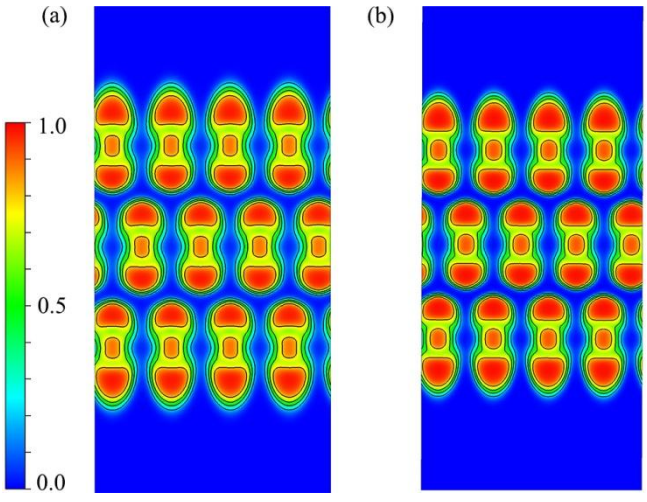

Fig. S1. 2D ELF slices crossing the interface atoms of the three-layer BP calculated with (a) GGA and (b) GGA-1/2 methods.

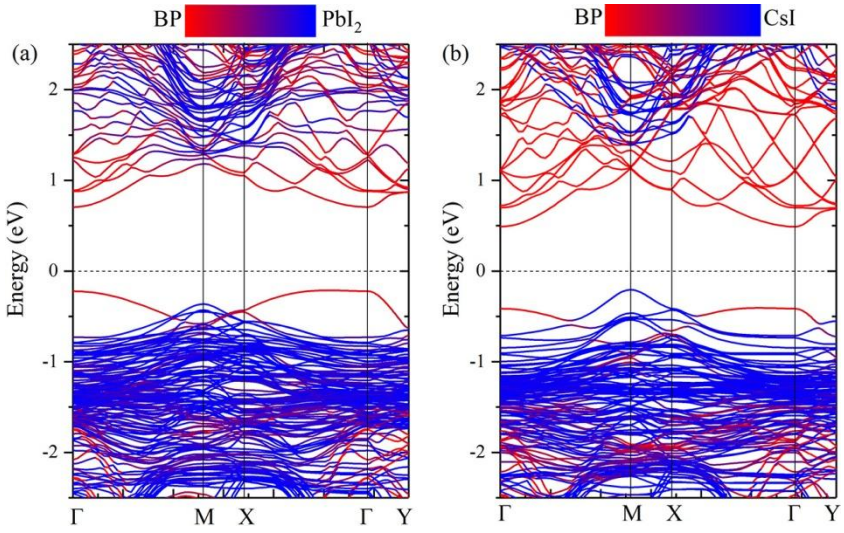

Fig. S2. Projected band structures of (a) PbI_2/BP and (b) CsI/BP interfaces calculated with GGA functional. The red and blue colors indicate the bands dominated by the monolayer BP and $CsPbI_3$ slab, respectively. The Fermi levels are denoted with dashed lines.

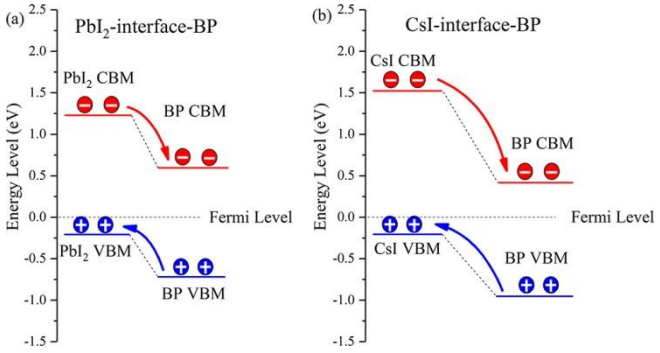

Fig. S3. Calculated energy levels with the GGA-1/2+SOC method for (a) PbI_2/BP and CsI/BP interfaces.

References

[1] Ferreira L G, Marques M and Teles L K 2008 *Phys. Rev. B* **78** 125116

[2] Ferreira L G, Marques M and Teles L K 2011 *AIP Adv.* **1** 032119.

[3] Guilhon I, Koda D S, Ferreira L G, Marques M and Teles L K 2018 *Phys. Rev B.* **97** pp.045426

[4] Jiang J, Onwudinanti C K, Hatton R A, Bobbert P A and Tao S 2018 *J. Phys. Chem. C* **122** pp. 17660-17667

[5] Huang Y, Yin W-J and He Y 2018 *J. Phys. Chem. C* **122** pp. 1345-1350

[6] Qiao J, Kong X, Hu Z-X, Yang F and Ji W 2014 *Nat. Commun.* **5** 4475

[7] Cao Y-H, Deng Z-Y, Wang M-Z, Bai J-T, Wei S-H and Feng H-J 2018 *J. Phys. Chem. C* **122** pp. 17228-17237

[8] Cao Y-H, Li Y-F, He J-W, Qian C-X, Zhang Q, Bai J-T and Feng H-J 2019 *Adv. Mater. Interfaces* **6** 1901330