Electronic Supplementary Information (ESI) for

Electronic structures and band alignments of monolayer metal trihalide semiconductors MX₃

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1. Phonon dispersions of monolayer MX₃

In order to study dynamical stability of the monolayer MX_3 , we calculated the phonon dispersion by using Phonopy code based on a supercell approach. A $4 \times 4 \times 1$ supercell was used in phonon dispersion and the forces were obtained from VASP ^[1,2]. From the phonon dispersions for all these monolayer MX_3 , we can see that there is no imaginary frequency along all the symmetric directions. Hence, the predicted structures of monolayer MX_3 are dynamically stable.



Fig. S1 (Color online) Phonon dispersions for a series of monolayer MX₃ along the high symmetry line from Gama to M to K to Gama.



2. The electronic structures and optical properties of metal trihalides MX₃



Fig. S2 (Color online) The electronic band structures of bulk MX₃ with PBE functional, monolayer MX₃ with PBE and HSE functional. The red and blue lines indicate the valence band and conduction band. The Fermi level indicated by horizontal black dashed lines is set as zero. The dark green arrows connect VBM and CBM. The imaginary part of dielectric function $\varepsilon_2(\omega)$ of monolayer MX₃ with PBE and HSE functional are also plotted. Red lines indicate the $\varepsilon_2(\omega)$ spectra along *x* and *y* directions, dark green lines indicate the $\varepsilon_2(\omega)$ spectra along *z* direction.



Fig. S3 (Color online) The density of states (DOS) and the partial density of states (PDOS) with PBE functional for monolayer MX_3 . Black lines represent the total DOS, while the red and blue lines represent DOS for X-*p* orbital and M-*d* or M-*p* orbital, respectively. The Fermi level indicated by black dashed lines is set to zero.



Fig. S4 The electronic band structures of (a) monolayer, (b) bilayer, (c) trilayer and (d) bulk YBr₃ with PBE functional without SOC. The electronic band structures of (e) monolayer, (f) bilayer, (g) trilayer and (h) bulk YBr₃ with SOC. The red and blue lines indicate the valence band and conduction band. The Fermi level indicated by horizontal black dashed lines is set as zero. The dark green arrows connect VBM and CBM.





Fig. S5 (Color online) The electronic band structures of (a) monolayer and (b) bulk MX_3 with PBE functional including the spin-orbit coupling (SOC) effect. The Fermi level indicated by horizontal black dashed lines is set as zero. The red and blue lines indicate the valence band and conduction band. The dark green arrows connect VBM and CBM.



Fig. S6 The charge density isosurfaces of VBM and CBM in various monolayer MX_3 . The isovalue is set to be 0.02 e Å⁻³.

References

- [1] A. Togo, F. Oba and I. Tanaka, Phys. Rev. B, 2008, 78, 134106.
- [2] A. Togo and I. Tanaka, *Scripta Materialia*, 2015, **108**, 1–5.