Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
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Supplementary Information for:

"First-principles investigation on tunable electronic properties and magnetism by polarization in PbTiO3/BiFeO3 2D ferroelectric heterostructures"

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Part I. Physical properties of the $PbTiO_3$ (PTO) and tetragonal $BiFeO_3$ (BFO) bulks

We relaxed the bulk structure and calculated the total and projected densities of states (DOS), which exhibit as an insulation both for the PTO and BFO bulk structure, as shown in Fig. S1. For tetragonal BFO, the adjacent Fe spins are antiparallel exactly shown in Fig. S1e, which manifest that the bulk BFO is G-type antiferromagnetic (G-AFM), being consistent with the experiment.[1] In addition, our calculated magnetic moment of Fe ions is ±4.15 μB, which is close to the experiment value of 4.34 μB.[2] These results reveal that the methods and calculation parameters used by us are reasonable.

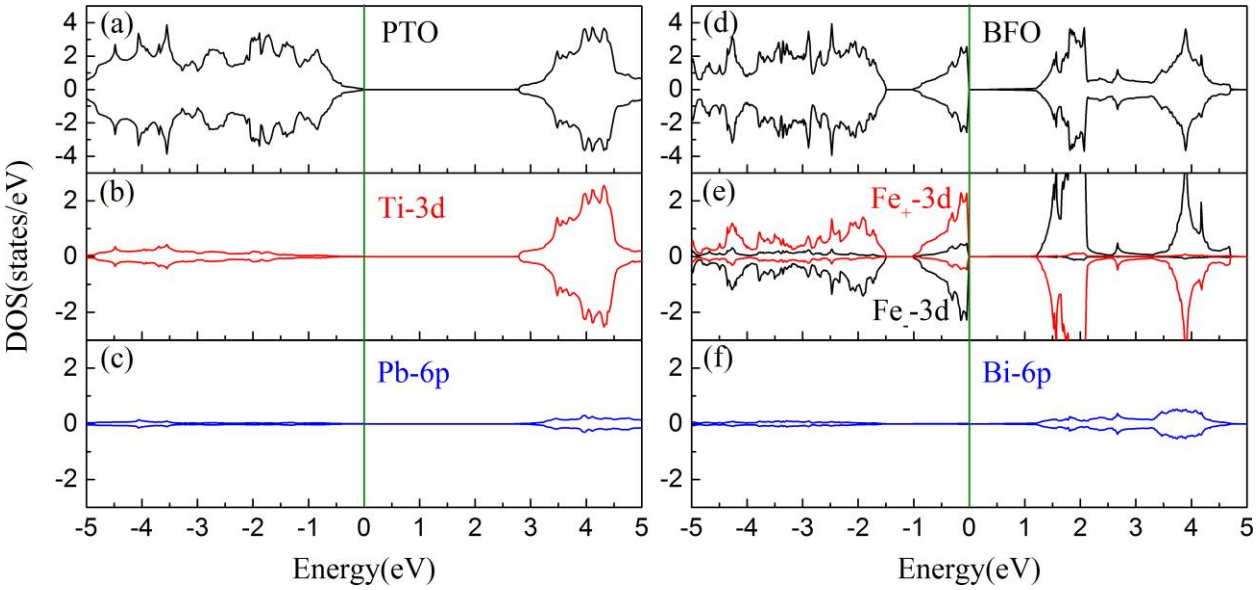

Fig. S1. (a-c) Total and partial DOS for the bulk PTO, (d-f) Total and partial DOS for the bulk BFO. The Fermi level is indicated by vertical lines and set to zero. Majority and minority spins are shown above and below the *x*-axes.

Part II. Magnetic and electrical conductivity of BB-type HSs

To understand the origins of these properties, we conducted a detailed analysis of the system from an orbital perspective for HS with 2.5 BFO monolayers (ML). From the projected DOS in Fig. S2a, we can see that the system is conductive in both polarization states, which mainly originates from the BFO part with a small contribution from the PTO part of the interface layer, and we noticed that the reasons for the conductive behavior under different polarization states are completely different. In the case of the $+P_{PTO}$ states, conducting carriers are massively accumulated within the BFO part due to the appearance of the head-to-head FE domain walls, as marked by the arrow in Fig. 3b, which further traps electrons in the domain walls. As a result, the conduction bands ultimately pass the Fermi level. We think that the magnetism still originates from the electron transfer from the e_g orbitals to the PTO part, which resembles the BF-type HSs. The unfilled e_g orbitals of for the majority spin have a double exchange effect with the O-2p orbitals, and thus causes the local FM ordering, which can be analyzed from the PDOS of the IV-FeO_2 layer given in Figs. S2b-e.

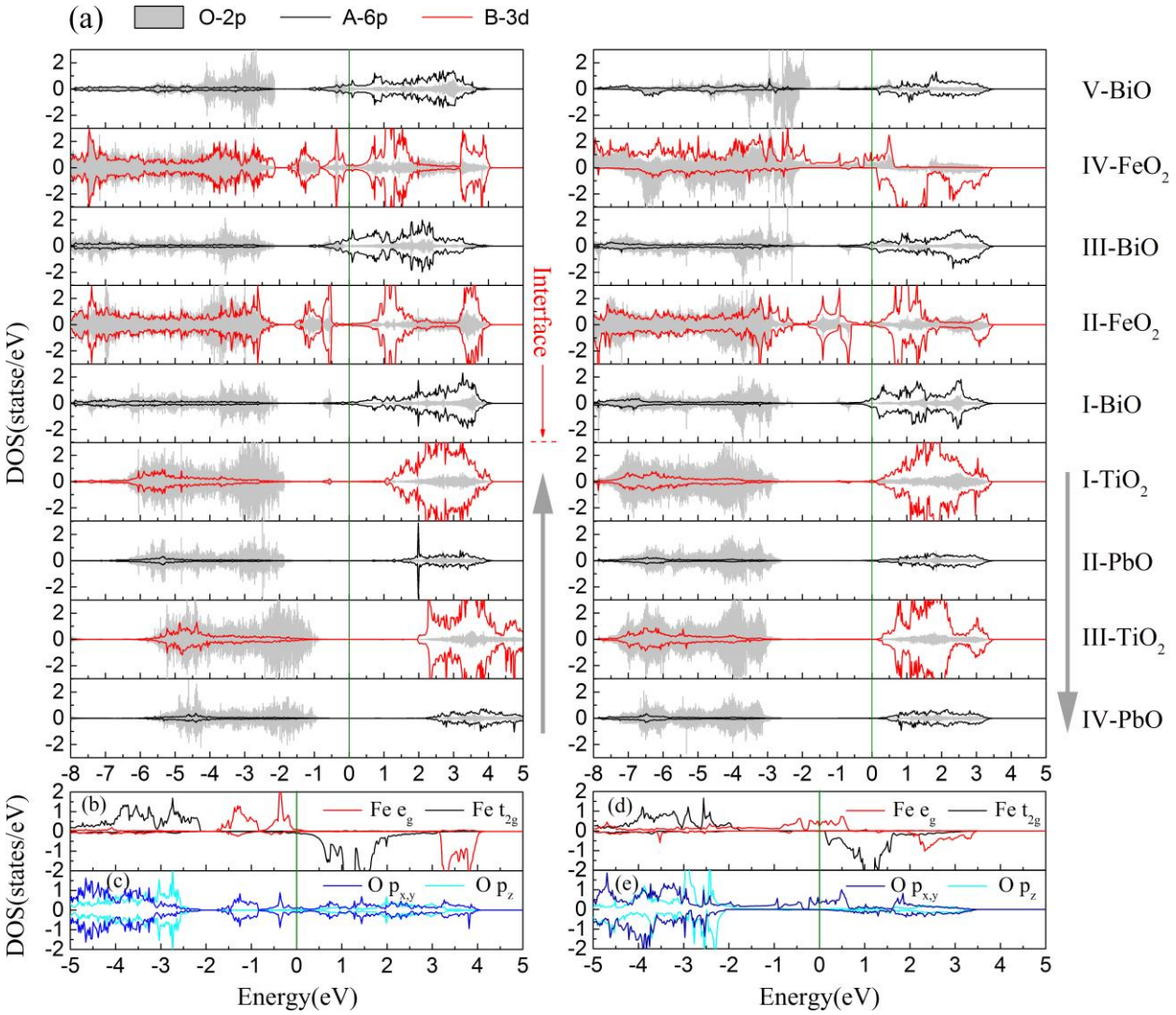

Fig. S2. The layer-resolved partial DOS (a) in different polarization directions for BB-type HSs with 2.5 BFO monolayers (ML). The gray arrows show the directions of the Ferroelectric (FE) polarizations. The projected DOS for I-FeO_2 of BB-type HSs with 2.5 BFO ML for the $+P_{PTO}$ states (b, c) and $-P_{PTO}$ states (d, e), respectively. (b) and (d) are Fe-3d states with the same spin direction (spin-up) in the two polarization states.

Part III. The layer-resolved partial DOS for FB-type HSs

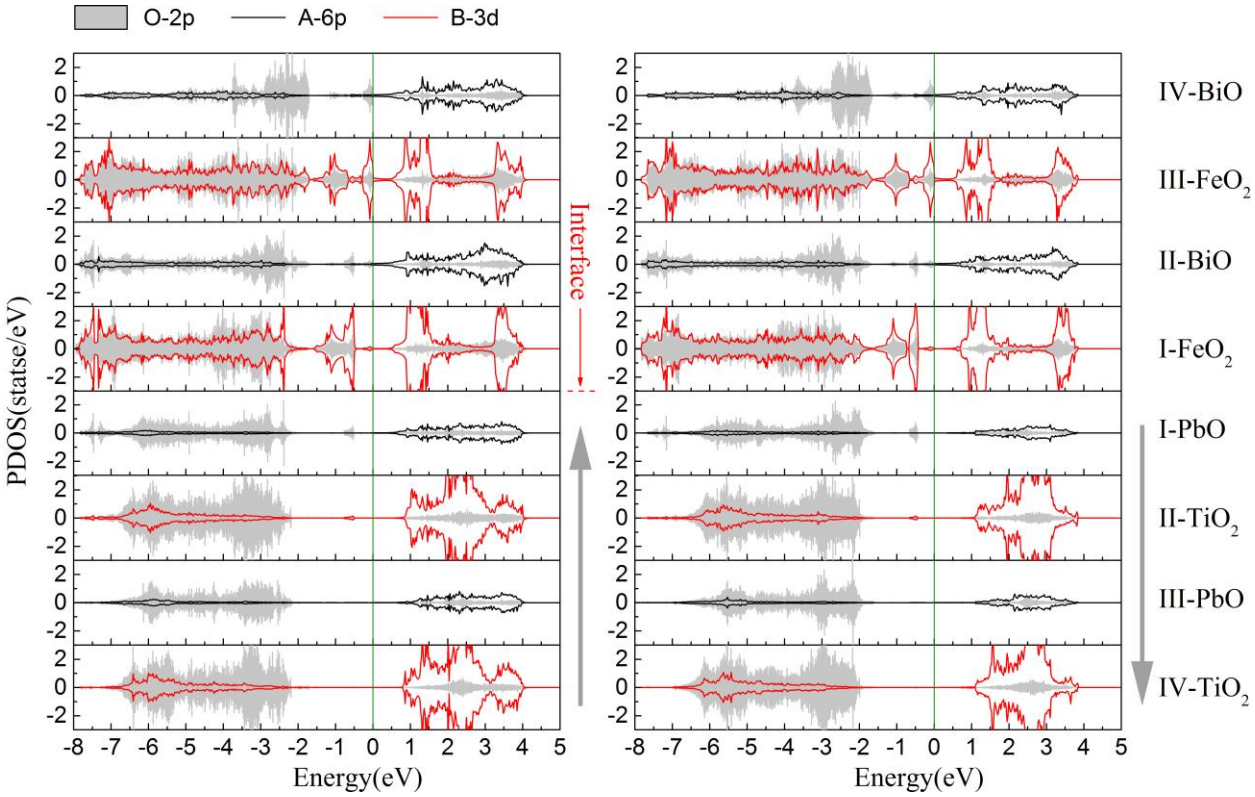

Fig. S3. The layer-resolved partial DOS in different polarization directions for FB-type HSs with 2 BFO ML. The gray arrows show the directions of the FE polarizations.

References

(1) H. Yamada, V. Garcia, S. Fusil, S. Boyn, M. Marinova, A. Gloter, S. Xavier, J. Grollier, E. Jacquet and C. Carrétéro, *Acs Nano*, 2013, **7**, 5385.

(2) T. P. Comyn, T. Stevenson, M. Al-Jawad, S. L. Turner, R. I. Smith, A. J. Bell and R. Cywinski, *Journal of Applied Physics*, 2009, **105**, 094108.