Supplementary Information for:

"Valence mediated tunable magnetism and electronic properties by ferroelectric polarization switching in 2D FeI_2/In_2Se_3 van der Waals heterostructures"

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Part I. Relative energy of 6 different interface contact types

For the FeI_2/In_2Se_3 van der Waals heterostructure (HS), we constructed six different interfacial contact types and fully released the lattice constant in the *xy*-plane and spatial ion coordinates, as shown in Fig. S1. These types of relative energy (ΔE) and interfacial adsorption energy were calculated to confirm the most stable combination among them, as shown in Table S1. The interface adsorption energy of all structures that defined as $E_{\mathrm{ad}} = ({}^{E_{FeI_2/In_2Se_3}} - {}^{E_{FeI_2}} - {}^{E_{In_2Se_3}})/A$, where the ${}^{E_{FeI_2/In_2Se_3}}$ is the total energy of the HS, ${}^{E_{FeI_2}}$ and ${}^{E_{In_2Se_3}}$ represent the energy of the FeI_2 and In_2Se_3 parts with the same supercell constant, respectively. In addition, the area of interface in the HS is indicated by *A*. The physical meaning of the equation is that the energy released by combining the FeI_2 and In_2Se_3 part into a HS, which can describe the thermodynamic stability of the interface. Therefore, we calculated the interface adsorption energy, which ranges from –0.037 to –0.035 eV/Å^2. These negative values show that all structures are stable. By comparing the

relative energies, we finally determined that type-4 was the most stable structure applied in the calculations below.

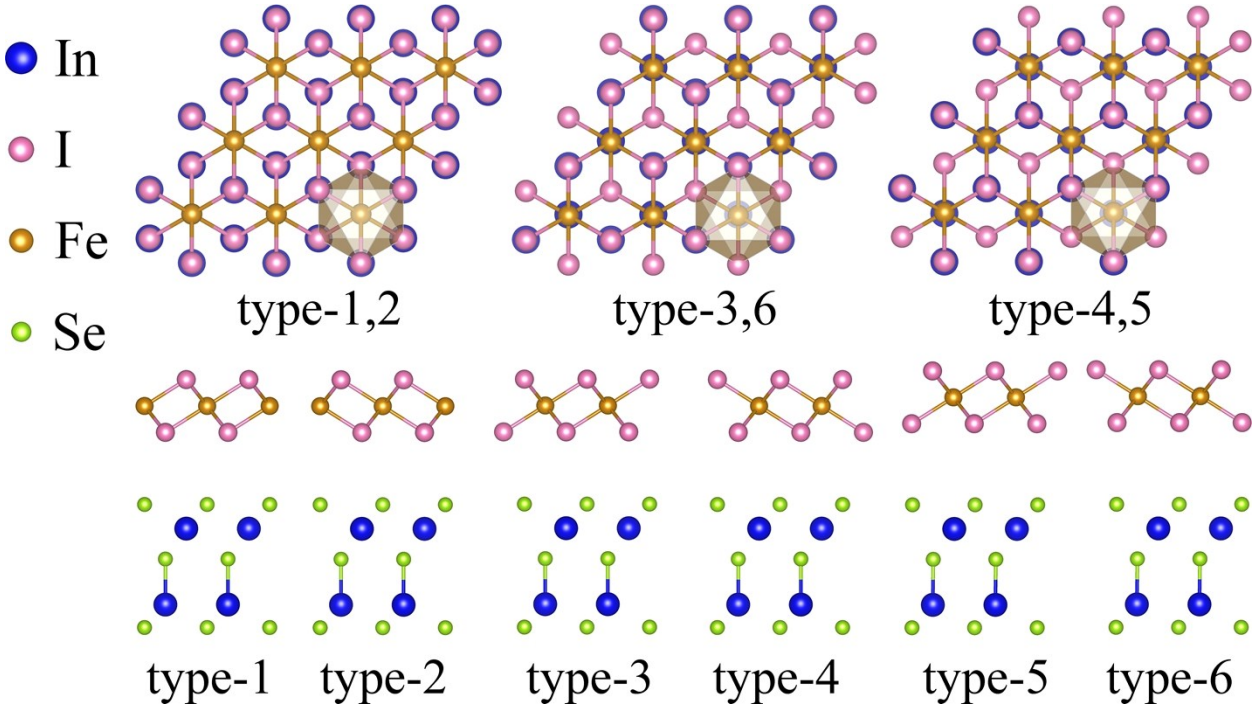

Fig. S1. Top view and side view of six different interfacial contact types for the FeI_2/In_2Se_3 HS. The type-*m*,*n* represents the top view of the type-*m* and the type-*n*.

Table S1. The relative energy (ΔE, in eV) and interfacial adsorption energy (E_{ad}, in eV/ Å^2) of six different interfacial contact types for the FeI_2/In_2Se_3 HS.

	type-1	type-2	type-3	type-4	type-5	type-6
ΔE	0.018	0.018	0.002	0.000	0.097	0.082
E_{ad}	–0.037	–0.037	–0.037	–0.037	–0.035	–0.036

Part II. The layer-resolved partial DOS of the FeI_2/bilayer In_2Se_3 HS

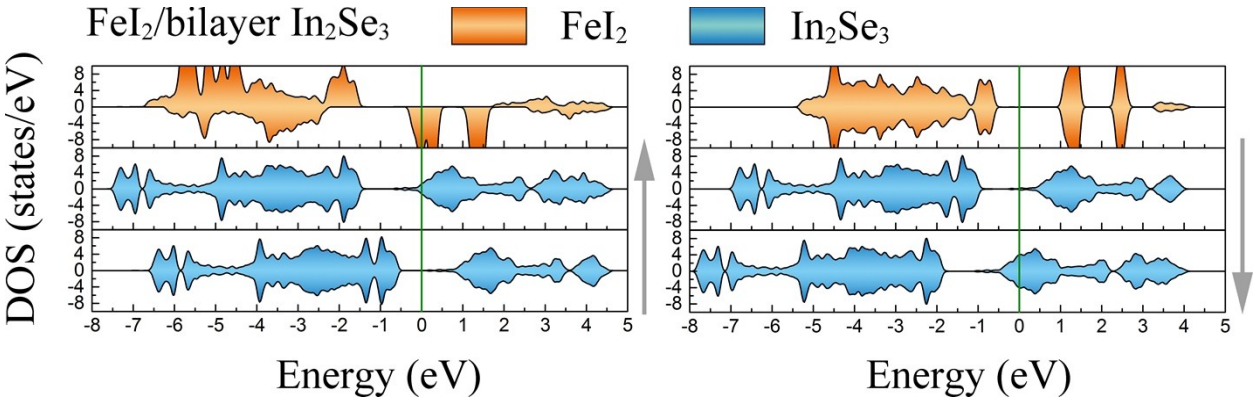

Fig. S2. The layer-resolved partial DOS of the FeI_2/bilayer In_2Se_3 HS. The gray arrow represents the direction of polarization.

Part III. The layer-resolved partial DOS of the MnI_2/In_2Se_3 and CoI_2/In_2Se_3 HS

We also calculated MnI_2/In_2Se_3 HS and CoI_2/In_2Se_3 HS, and their layer-resolved partial DOS is shown in Fig. S3. We found that they have the same conclusion as FeI_2/In_2Se_3 HS, that is, in the $+P$ case, the HS exhibits Ferromagnetic ordering, when it reverses to $-P$ case, the magnetic ordering changes from Ferromagnetic to antiferromagnetic ordering.

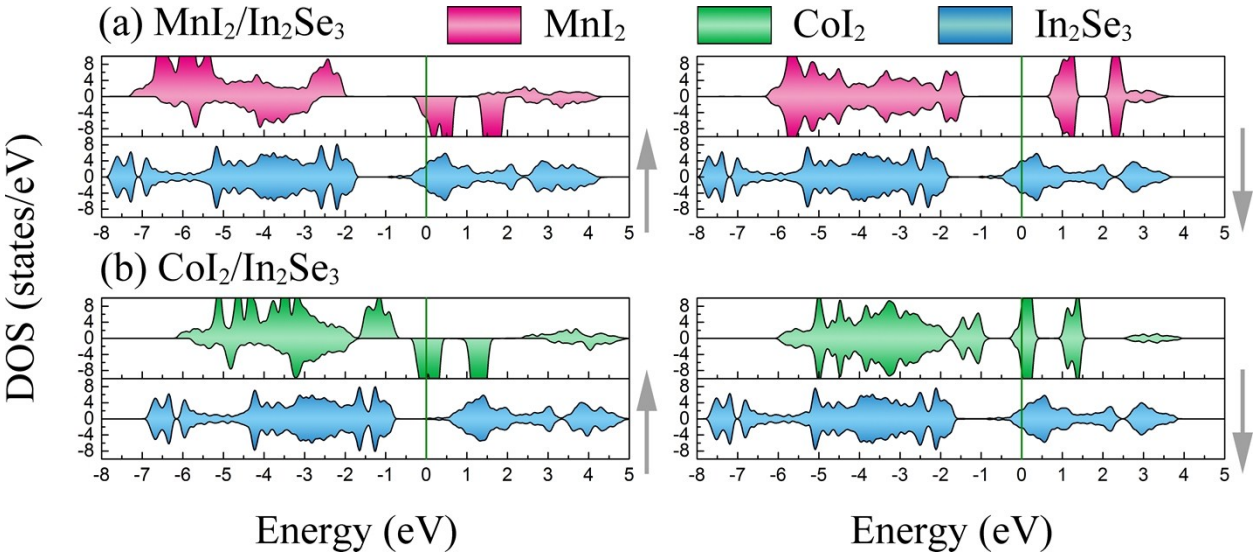

Fig. S3. The layer-resolved partial DOS of the MnI_2/In_2Se_3 and CoI_2/In_2Se_3 HS. The gray arrow represents the direction of polarization.