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

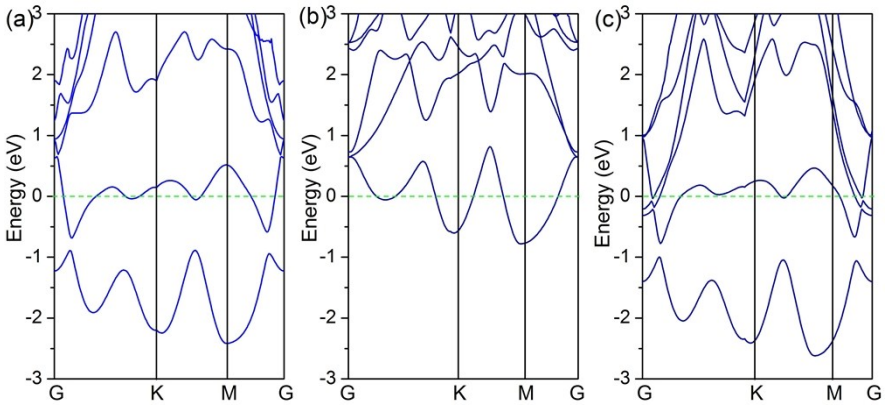

Figure S1 Calculated band structures of Hf_2NF_2 (a), Hf_2NO_2 (b) and $Hf_2N(OH)_2$ (c).

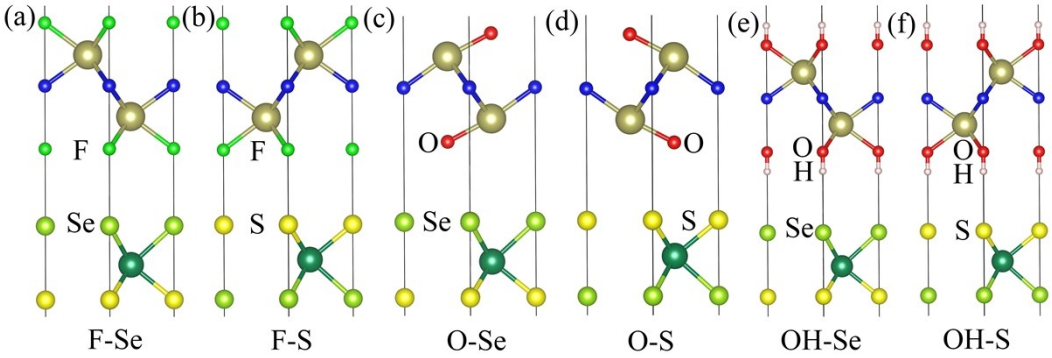

Figure S2 Six different interfaces for Hf_2NT_2/MoSSe heterostructures, including F-Se (a), F-S (b), O-Se (c), O-S (d), OH-Se (e) and OH-S (f).

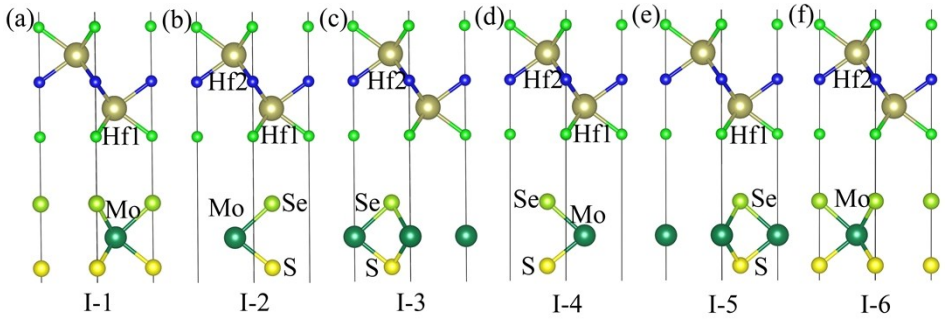

Figure S3 Aomic structures of the six typical stacking patterns of Hf_2NT_2/MoSSe. I-1 (a), I-2 (b), I-3 (c), I-4 (d), I-5 (e) and I-6 (f) refer to that Hf1 is placed above Mo, Hf2 is placed above Mo and Hf1 is placed above S (Se), Hf2 is placed above S (Se), Hf1 is placed above Mo and Hf2 is placed above S (Se), Hf1 is placed above S (Se), and Hf2 is placed above Mo, respectively.

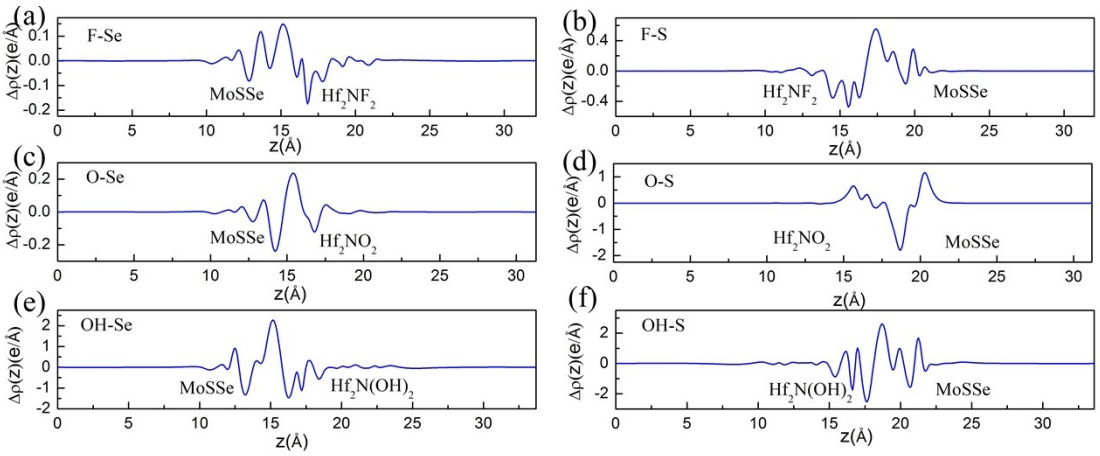

Figure S4 Plane-integrated electron density difference for F-Se (a), F-S (b), O-Se (c), O-S (d), OH-Se (e) and OH-S (f) interfaces in Hf_2NT_2/MoSSe heterostructures.

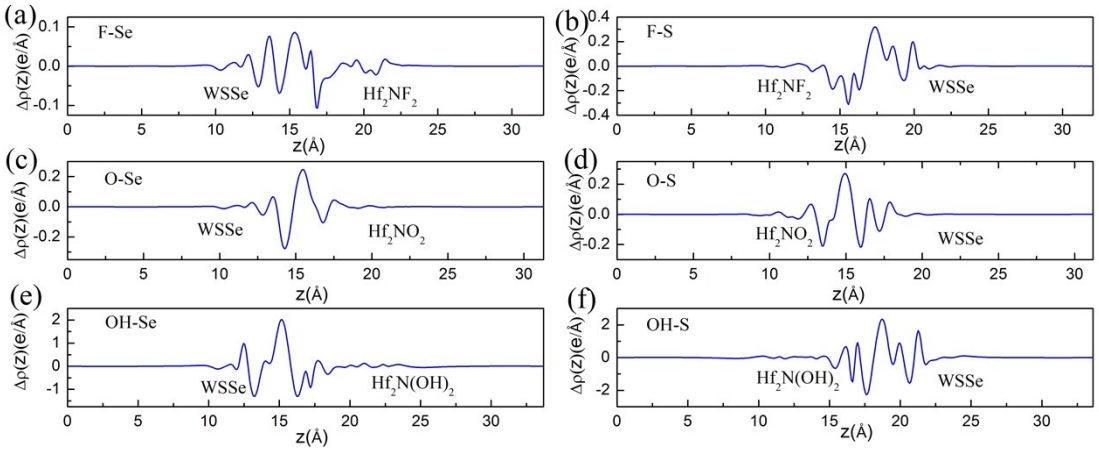

Figure S5 Plane-integrated electron density difference for F-Se (a), F-S (b), O-Se (c), O-S (d), OH-Se (e) and OH-S (f) interfaces in Hf_2NT_2/WSSe heterostructures.

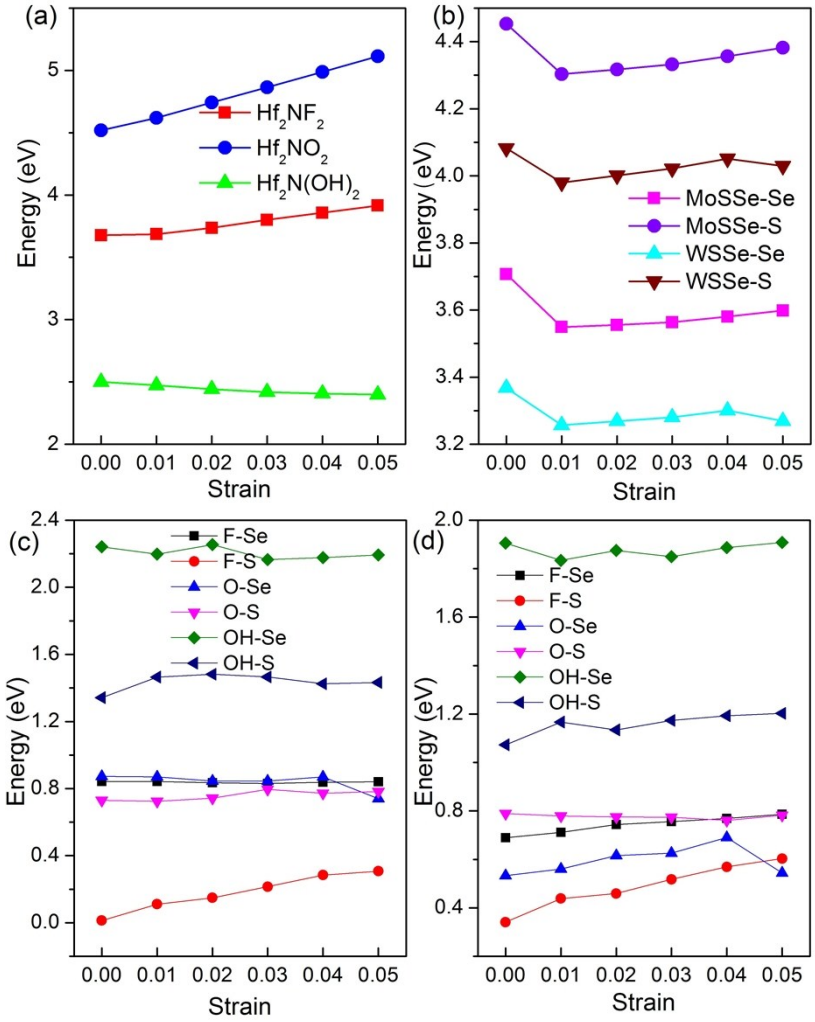

Figure S6 Work functions of Hf_2NT_2 (T=F, O, OH) (a), electron affinities of MoSSe and WSSe (b), potential steps of various interfaces in Hf_2NT_2/MoSSe (c) and Hf_2NT_2/WSSe (d) heterostructures under the increased compressive strain.

Table S1 Calculated binding energies of different stacking patterns for various interfaces. The unit is eV.

Hf_2NT_2/MoSSe						
	I-1	I-2	I-3	I-4	I-5	I-6
F-Se	-0.209	-0.228	-0.227	-0.205	**-0.229**	-0.171
F-S	-0.205	**-0.244**	-0.230	-0.234	-0.238	-0.206
O-Se	-0.257	**-0.269**	-0.269	-0.204	-0.205	-0.261
O-S	-0.257	-0.267	-0.195	-0.195	**-0.274**	-0.253
OH-Se	-0.472	**-0.49**	-0.47	-0.479	-0.477	-0.474
Oh-S	-0.597	-0.557	-0.572	-0.557	-0.573	**-0.601**
Hf_2NT_2/WSSe						

F-Se	-0.215	-0.234	-0.233	-0.230	**-0.234**	-0.216
F-S	-0.165	**-0.241**	-0.233	-0.241	-0.235	-0.208
O-Se	-0.264	**-0.275**	-0.214	-0.212	-0.274	-0.268
O-S	-0.262	-0.269	-0.201	-0.201	**-0.276**	-0.259
OH-Se	-0.42	**-0.446**	-0.424	-0.436	-0.431	-0.422
F-Se	-0.532	-0.514	-0.516	-0.504	-0.51	**-0.537**

Table S2 Calculated average interfacial distances for various heterostructures. The unit is Å.

Hf_2NT_2/MoSSe						Hf_2NT_2/WSSe					
Se-F	S-F	Se-O	S-O	Se-OH	S-OH	Se-F	S-F	Se-O	S-O	Se-OH	S-OH
2.75	2.61	2.89	2.62	1.98	2.06	2.78	2.62	2.85	2.68	2.00	2.01

Table S3 Calculated potential steps of different stacking patterns for various interfaces. The unit is eV.

	Hf_2NT_2/MoSSe						Hf_2NT_2/WSSe					
	I-1	I-2	I-3	I-4	I-5	I-6	I-1	I-2	I-3	I-4	I-5	I-6
Se-F	-0.85	-0.83	-0.90	0.88	-0.85	-0.85	-0.79	-0.70	-0.74	-0.77	-0.69	0.80
S-F	0.09	-0.01	-0.01	-0.01	-0.01	0.08	0.34	0.34	0.33	0.32	0.33	0.40
Se-O	-0.84	-0.62	-0.92	-0.87	-0.72	-0.80	-0.68	-0.53	-0.45	-0.82	-0.56	-0.75
S-O	0.61	0.80	0.60	0.59	0.73	0.65	-0.62	-0.86	-0.58	-0.65	-0.79	-0.74
Se-OH	-2.15	-2.24	-2.33	-2.25	-2.24	-2.18	-1.84	-1.91	-1.91	-1.94	-1.90	-1.86
S-OH	-1.36	-1.35	-1.32	-1.35	-1.34	-1.34	-1.09	-1.12	-1.07	-1.08	-1.07	-1.07

Table S4 Calculated potential steps and charge transfer for various interfaces.

	Hf_2NT_2/MoSSe					
Interfaces	F-Se	F-S	O-Se	O-S	OH-Se	OH-S
ΔV_1(eV)	-0.10	-0.76	0.13	-0.02	-1.50	-2.09
Charge (*e*)	0.004e	-0.019	0.007	-0.005	-0.140	-0.144
	Hf_2NT_2/WSSe					
Interfaces	F-Se	F-S	O-Se	O-S	OH-Se	OH-S
ΔV_1(eV)	0.025	-0.37	0.18	0.07	-1.16	-1.79
Charge (*e*)	0.008	-0.007	0.008	-0.002	-0.128	-0.134