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

Supplementary Information

Two-Dimensional Vanadium Tetrafluoride with Antiferromagnetic Ferroelasticity and Bidirectional Negative Poisson's Ratio

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Table S1. The difference between calculated lattice constants and the experimental values for bulk VF_4 by different functionals and PBE+U methods with variant U values.

	PBE	LDA	optB88	optB86b	PBEsol	PBE+U		
						U=1	U=2	U=3
Δa	0.052	-0.079	0.041	0.063	0.022	0.067	0.101	0.095
Δb	0.005	-0.297	-0.189	-0.202	-0.187	0.010	-0.011	0.015
Δc	0.042	-0.256	-0.089	-0.075	-0.083	0.059	0.068	0.074

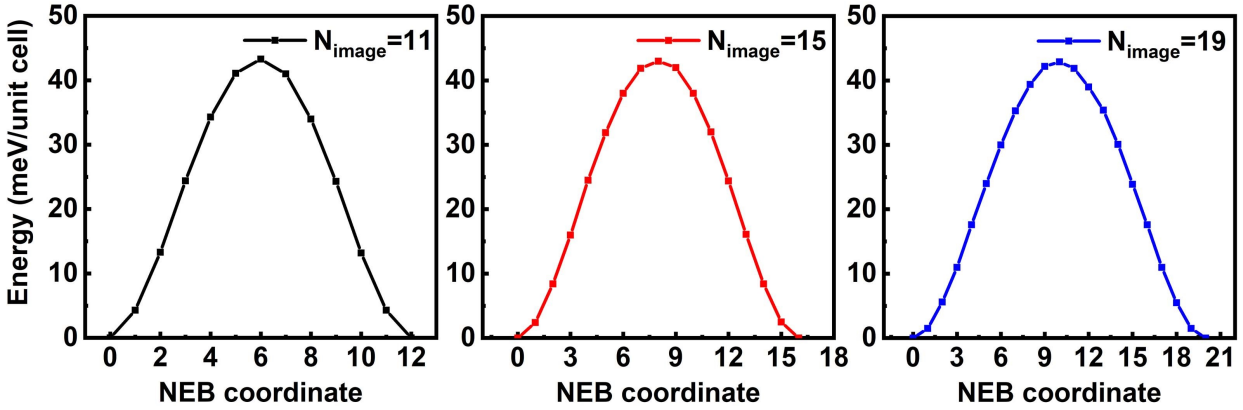

Figure S1. The NEB results calculated using 11, 15, and 19 images for the ferroelastic transition of VF_4 monolayer. The transition barriers calculated using 11, 15, and 19 images are 43.3 meV/unit cell, 43.0 meV/unit cell, and 42.9 meV/unit cell, respectively. Hence, the transition barrier can converge to 1 meV/unit cell even with a low number of image of 11.

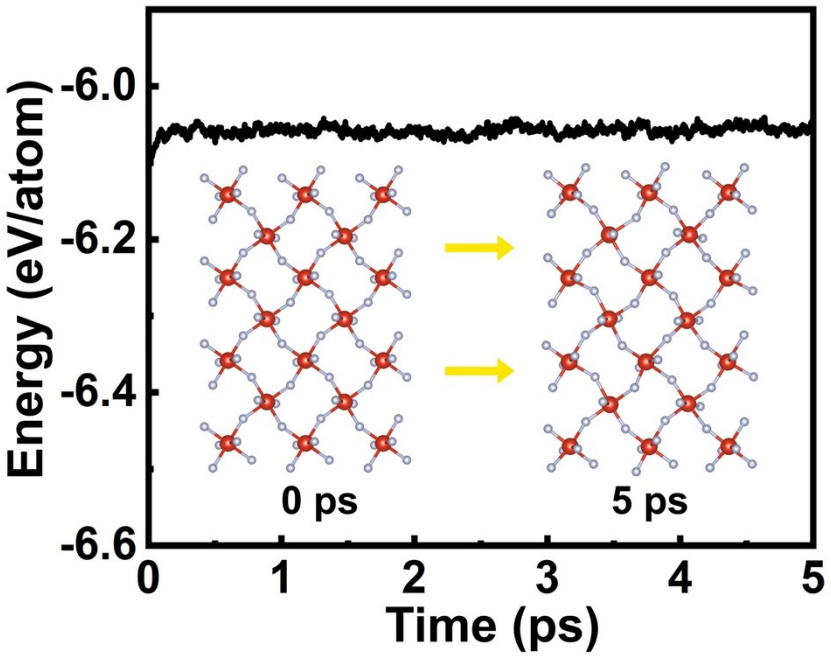

Figure S2. The energy evolution of VF_4 monolayer during AIMD of 5 ps at 300 K. The insets are the initial and final atomic structure.

Table S2. Total energy of VF_4 monolayer in different magnetic configurations. The energy of AFM-2 configuration is set to 0 for comparation. The energy of non-magnetic state is 1.54 eV/unit cell higher than the AFM-2 state, suggesting the robust magnetism in 2D VF_4.

Configuration	FM	AFM-1	AFM-2	AFM-3
ΔE (meV)	46.89	23.90	0	23.35

Table S3. The MAE (μeV per V atom) with respect to the easy-axis direction.

Direction	[100]	[010]	[110]	[101]	[011]	[111]	[001]
MAE	0	28.92	26.81	39.77	34.23	13.24	35.84

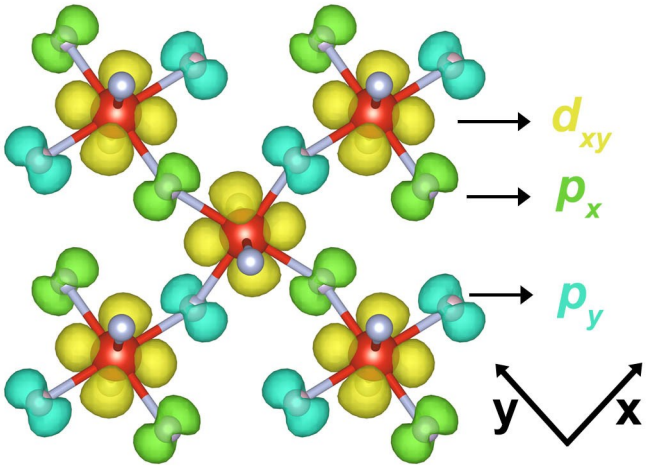

Figure S3. The real-space squared wave-function corresponding to the highest valence band at Gamma point. The global coordination axis is rotated to align the VF_6 octahedra. The d_{xy} orbitals of V atoms and $p_{x/y}$ orbitals of F atoms are vividly shown.

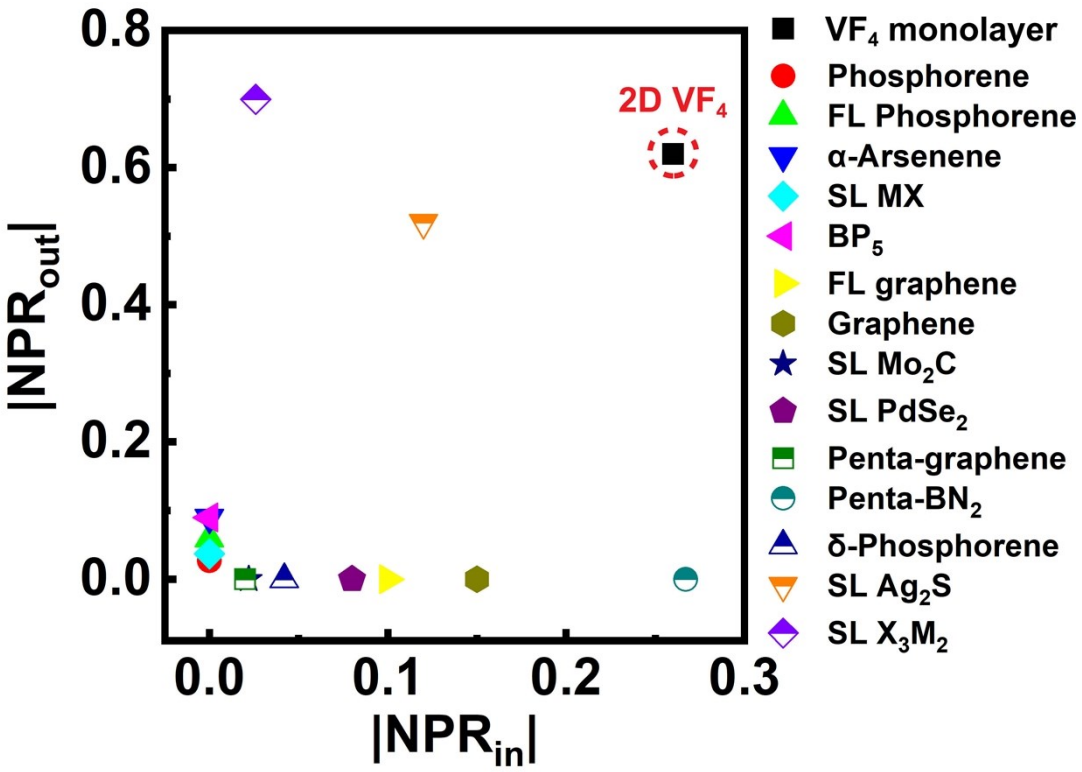

Figure S4. The in-plane and out-of-plane NPRs for 2D VF_4, phosphorene,[1] few-layer (FL) phosphorene,[2] α-arsenene,[3] single-layer (SL) MX (M = Ge, Sn; X = S, Se),[4] BP_5,[5] FL graphene,[6] graphene,[7] SL Mo_2C,[8] SL $PdSe_2$,[9] penta-graphene,[10] penta-BN_2,[11] δ-phosphorene,[12] SL Ag_2S,[13] and SL X_3M_2.[14] For clarity, we plot the absolute values here and if it does not exist, we set it to 0. It can be seen that 2D VF_4 possess balanced bidirectional auxeticity and the values of NPR along both directions are among the highest values reported so far.

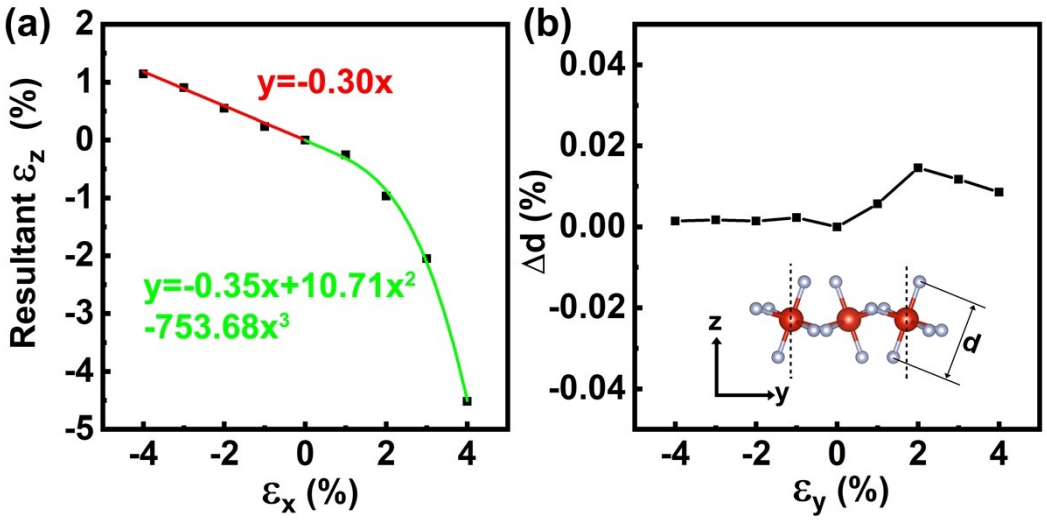

Figure S5. (a) Resultant out-of-plane strain as a function of applied strain along the x-direction. The v_{out} is obtained by fitting $\varepsilon_{rs} = -a\varepsilon_s + b\varepsilon_s^2 + c\varepsilon_s^3$,[13] where ε_s and ε_{rs} represent the applied and resultant strain respectively, and then a can be regarded as v_{out}. The calculated v_{out} is 0.30 and 0.35 for compressional and tensile strain applied along the x-direction, respectively. (b) The variation of the distance between the upper and lower F atoms in a VF_6 octahedron upon strain along the y-direction. Clearly, the variation is quite small (less than 0.02%).

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