Supplemental Materials for

Superexchange interactions and magnetic anisotropy in $MnPSe_3$ monolayer

Guangyu Wang,[1, 2, *] Ke Yang,[3, 1, *] Yaozhenghang Ma,[1, 2] Lu Liu,[1, 2] Di Lu,[1, 2], Yuxuan Zhou,[1, 2] and Hua Wu[1, 2, 4, †]

[1] Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, and Department of Physics, Fudan University, Shanghai 200433, China
[2] Shanghai Qi Zhi Institute, Shanghai 200232, China
[3] College of Science, University of Shanghai for Science and Technology, Shanghai 200093, China
[4] Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China

* These authors contributed equally to this work.
[†]E-mail: wuh@fudan.edu.cn

I. The magnetic exchange parameters

The value of J = 1.41 meV in the main text is obtained by considering only the first nearest neighboring magnetic coupling, i.e., the spin Hamiltonian is given by

$$H = \sum_{i,j} \frac{J}{2} \vec{S}_i \vec{S}_j + \sum_i \{D(S_i^c)^2 + E_n[(S_i^b)^2 - (S_i^a)^2]\}$$

where D and E_n are the magnetic anisotropy parameters. In this case, the calculated magnetic specific heat from our Monte Carlo simulations shows T_N = 47 K, which agrees well with the experimental 40 K.

We also compute the 1st, 2nd, and 3rd nearest neighboring magnetic couplings J_1, J_2 and J_3, using the supercells and four different magnetic states in Figs. S1 and S2. The spin Hamiltonian in this case is given by

$$H = \sum_{k=1,2,3} \sum_{i,j} \frac{J_k}{2} \vec{S}_i \vec{S}_j + \sum_i \left\{D(S_i^c)^2 + E_n \left[\left(S_i^b\right)^2 - (S_i^a)^2\right]\right\}.$$

Counting JS^2 for each spin pair, the magnetic exchange energies (per formula unit) of the four magnetic states are written as follows

$$E_{FM} = (\frac{3}{2}J_1 + 3J_2 + \frac{3}{2}J_3)S^2$$
$$E_{Neel} = (-\frac{3}{2}J_1 + 3J_2 - \frac{3}{2}J_3)S^2$$
$$E_{Stripy} = (-\frac{1}{2}J_1 - J_2 + \frac{3}{2}J_3)S^2$$
$$E_{Zigzag} = (\frac{1}{2}J_1 - J_2 - \frac{3}{2}J_3)S^2$$

The relative total energy results are shown in Table S1. Using those values and the above equations, we can calculate J_1 = 0.88 meV, J_2 = 0.08 meV, and J_3 = 0.54 meV.

Table S1. Relative total energies ΔE (meV/fu) for $MnPSe_3$ monolayer by GGA+*U*. The calculated three AF exchange parameters (meV) are listed.

States	FM	AF-Néel	AF-Stripy	AF-Zigzag
ΔE	26.4	0	13.6	9.0
J_1 = 0.88		J_2 = 0.08	J_3 = 0.54	

In the honeycomb structure of $MnPSe_3$ monolayer, the joint contribution of J_1 and J_3 ($J_1 + J_3$ = 1.42 meV) is equivalent to the exchange parameter J = 1.41 meV in the main text. With inclusion of the small J_2 but its higher six-coordination than three-coordination for J_1 and J_3, T_N is somewhat increased to 53 K, from 47 K according to the Monte Carlo simulation using J = 1.41 meV in the main text. Nevertheless, either 47 K or 53 K is in reasonable agreement with the experimental 40 K. Therefore, for the convenience of discussion, we assume the AF exchange parameter is 1.41 meV, as mentioned in the main text.

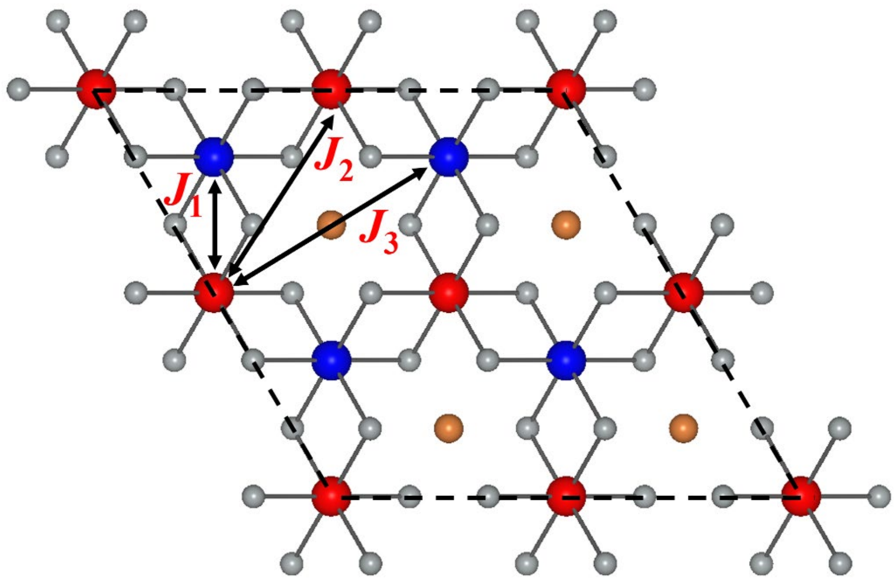

Fig. S1: The first (J_1), second (J_2) and third (J_3) nearest neighbor exchange interactions.

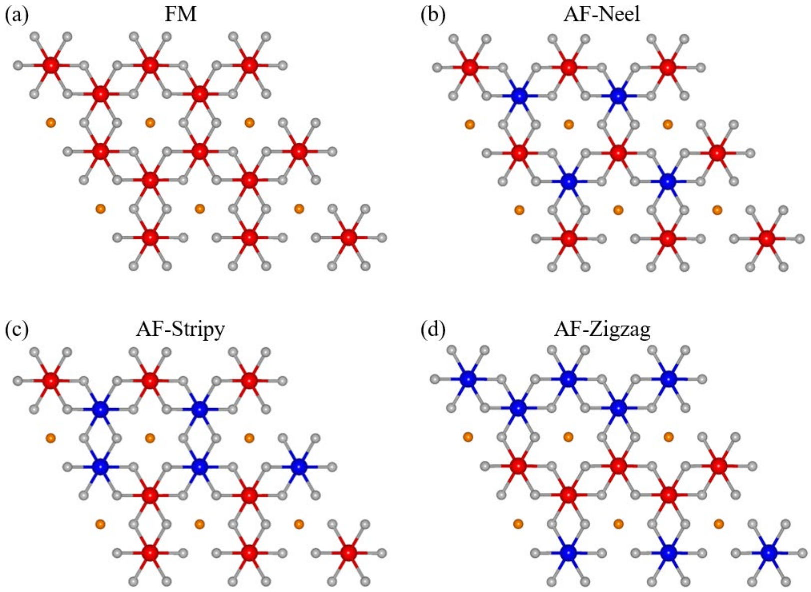

Fig. S2: Four different magnetic structures: (a) FM, (b) AF-Néel, (c) AF-Stripy, and (d) AF-Zigzag. Up (down) spins are represented by red (blue) balls.

II. Hopping integrals of spin-up channels

(a)

Mn2 \ Mn1	z^2	xz	yz	x^2	xy
z^2	0.04	0.02	0.02	0.00	0.02
xz	0.00	0.02	0.05	0.01	0.01
yz	0.00	0.05	0.01	0.01	0.01
x^2	0.00	0.03	0.02	0.11	0.02
xy	0.06	0.00	0.00	0.02	0.10

(b)

Se	Mn1 z^2	Mn1 xz	Mn1 yz	Mn1 x^2	Mn1 xy	Mn2 z^2	Mn2 xz	Mn2 yz	Mn2 x^2	Mn2 xy
p_z	0.06	0.27	0.03	0.14	0.04	0.10	0.07	0.53	0.12	0.01
p_x	0.37	0.12	0.00	0.61	0.10	0.03	0.07	0.03	0.01	0.73
p_y	0.03	0.02	0.01	0.08	0.30	0.54	0.04	0.13	0.94	0.06

(Color scale: eV, 0.0 – 1.0)

Fig. S3: (a): Hopping integrals of spin-up channels calculated by MLWFs basis set between 3d orbitals of Mn1 and Mn2. (b): Hopping integrals of spin-up channels between 3d orbitals of Mn and 4p orbitals of Se.

III. The distributions of MAE in the reciprocal space in the FM state

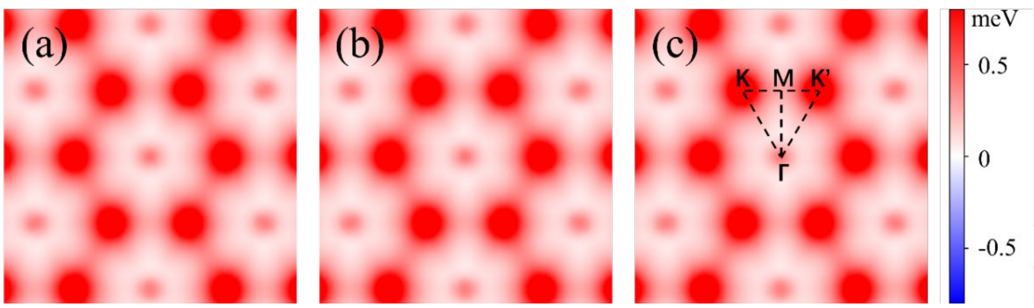

Fig. S4: The distributions of MAE in the reciprocal space in the FM $MnPSe_3$ monolayer. (a): $E^c - E^a$, (b): $E^{-c} - E^{-a}$, (c): $((E^c - E^a) + (E^{-c} - E^{-a}))/2$.

IV. Polar diagrams of MAE

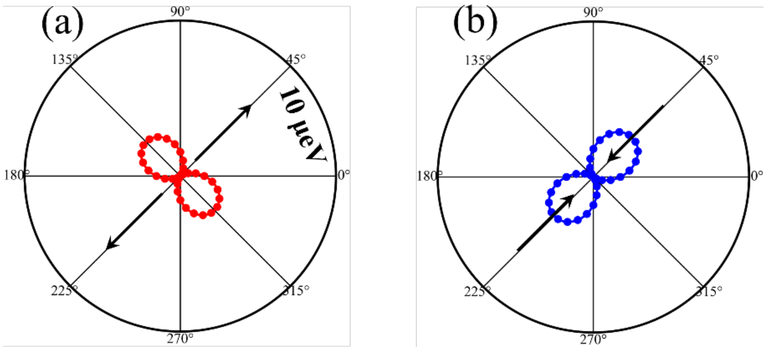

Fig. S5: (a): Polar diagrams of the MAE in the *ab* plane. The $MnPSe_3$ monolayer is under 2% uniaxial tensile strain with strain direction along 45° with respect to the *a* axis. (b): $MnPSe_3$ monolayer is under 2% uniaxial compressive strain with strain direction along 45° with respect to the *a* axis.

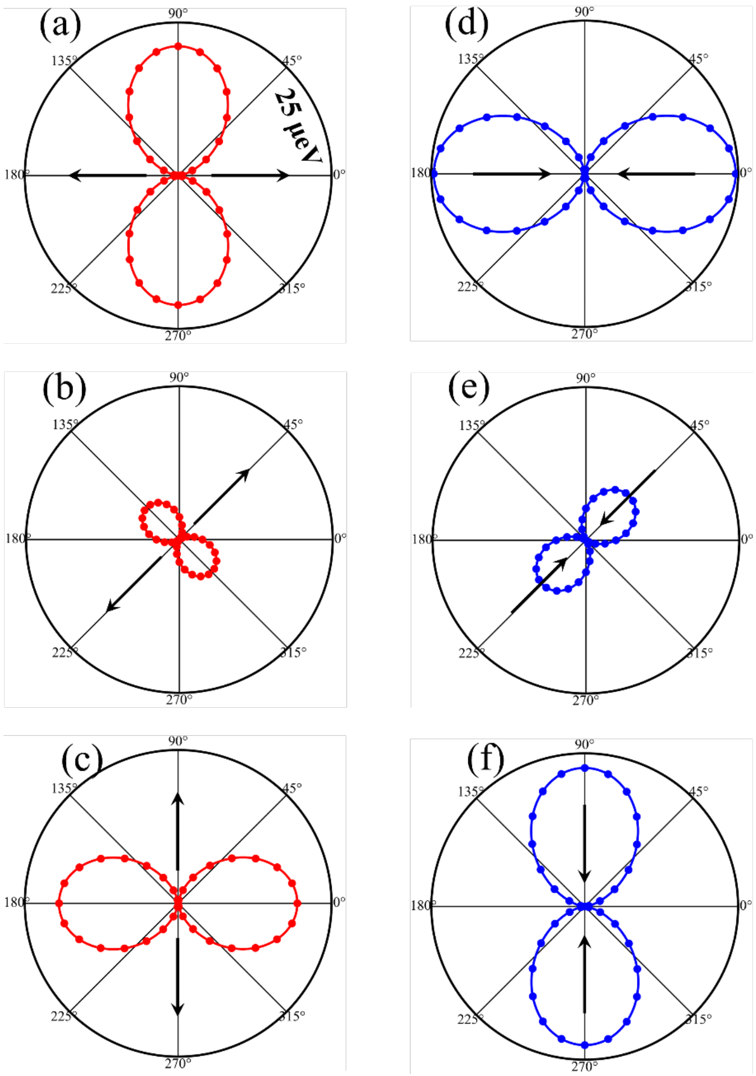

Fig. S6: Polar diagrams of the MAE in the *ab* plane. The $MnPSe_3$ monolayer is under 5% uniaxial tensile strain (a-c) and compressive strain (d-f).