

Supporting Information

Computational prediction of the low temperature ferromagnetic semiconducting two-dimensional SiN monolayer

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1. Structures of optimized two-dimensional C₂H, CN, SiN monolayers

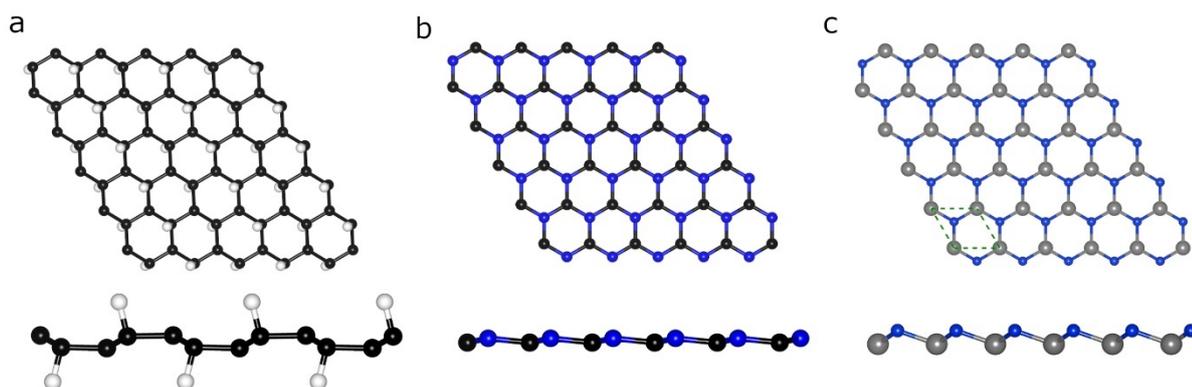


Figure S1. Top and side views of optimized two-dimensional (a) C₂H, (b) CN, and (c) SiN monolayers. Silicon atoms are gray, carbon atoms are black, nitrogen atoms are blue, and hydrogens are white.

2. Structure parameters of optimized two-dimensional C₂H, CN, SiN monolayers

C₂H-sheet ((<i>trans</i>)-semigraphan)	Direct coordinates of atoms: C: 0.0276160382167833 0.0276160382167762 0.5103013965200719 C: 0.5276160382167834 0.0276160382167762 0.4896986034799279 C: 0.1839107536550433 0.6839107536550290 0.4911098360029955 C: 0.6839107536550432 0.6839107536550290 0.5088901639970047 H: 0.1218065414615162 0.6218065414615020 0.4350275950777540 H: 0.6218065414615163 0.6218065414615020 0.5649724049222459 Translation vectors of Bravais lattice: 2.4547868738040846 -4.3547185038142207 0.0000000000000000 1.2719517068743600 2.2030849810704112 0.0000000000000000 0.0000000000000000 0.0000000000000000 20.0000000000000000 Free energy per unit cell= -40.372089 eV
CN-sheet	Direct coordinates of atoms: C: 0.0000000000000000 0.0000000000000000 0.4957574013043888 N: 0.33333333333333357 0.66666666666666643 0.5049888313986480 Translation vectors of Bravais lattice: 1.1965110185778463 -2.0724178759832856 0.0000000000000000

	1.1965110185778458 2.0724178759832856 0.0000000000000000 -0.0000000000000029 0.0000000000000011 15.0000000000000000 Free energy per unit cell= -16.003134 eV
SiN-sheet	Direct coordinates of atoms: Si: 0.0000000000000000 0.0000000000000000 0.4812810908815842 N: 0.3333333333333357 0.6666666666666643 0.5201357491998915 Translation vectors of Bravais lattice: 1.4471579128092174 -2.5065510315445265 0.0000000000000000 1.4471579128092174 2.5065510315445265 0.0000000000000000 0.0000000000000000 0.0000000000000000 15.0000000000000000 Free energy per unit cell= -13.787078 eV

3. Calculated fluctuations of the total magnetic moment at 20K

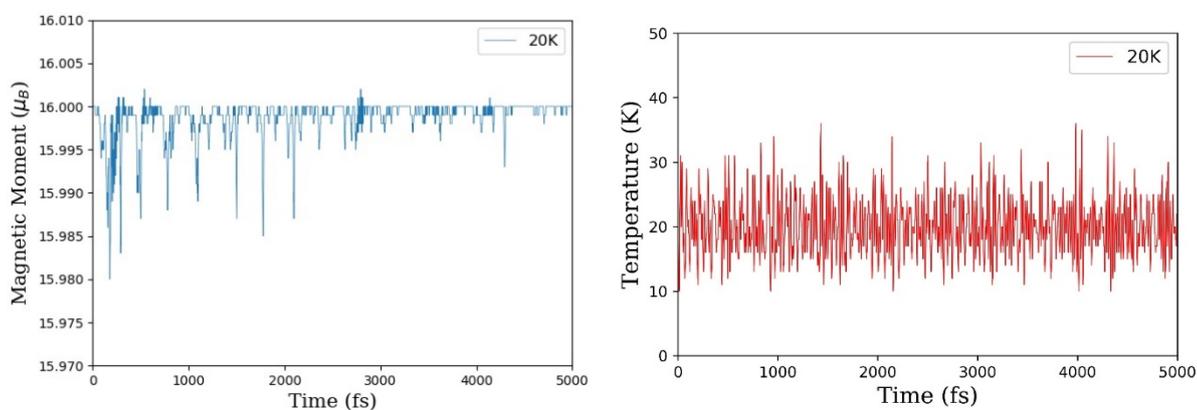


Figure S2. The fluctuations of temperature and ferromagnetic moment as a function of the molecular dynamic simulation step at 20K.

4. Spin ordering of different magnetic configurations

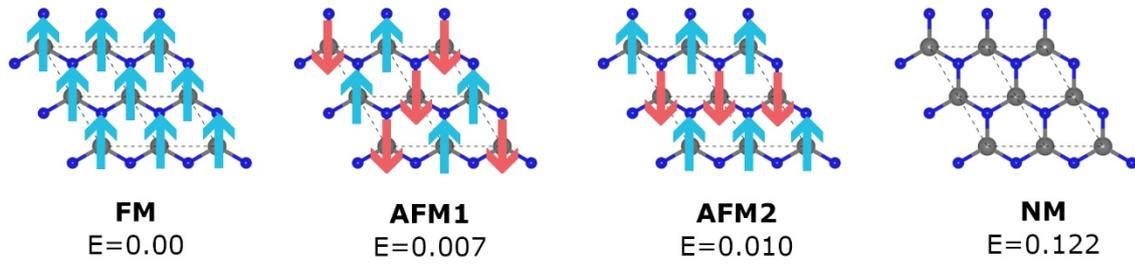


Figure S3. Magnetic ordering and relative total energies for $2 \times 2 \times 1$ supercell of 2D SiN-sheet. Energies are given in eV/atom.

5. Final frames of MD simulation test at 30K

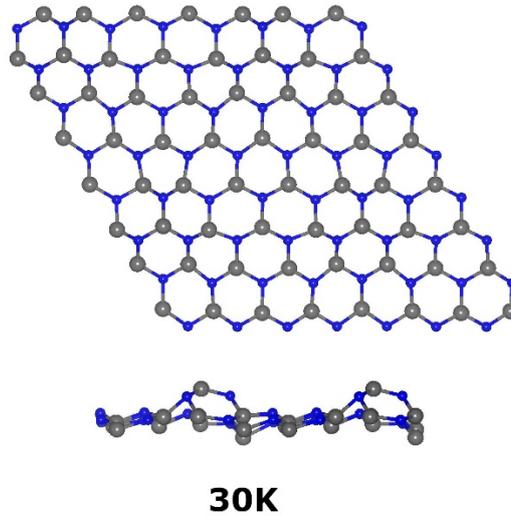


Figure S4. Top and side views of final frame of MD simulation test after 5 ps at 30 K..

6. Computational details

Optimized geometries were calculated using the density functional theory (DFT) via the plane-wave pseudopotential technique (PWPP) as implemented in Vienna *Ab initio* Simulation Package^[S1] (VASP) code. The projector-augmented wave^[S2,S3] (PAW) method was used to estimate the electron-ion interactions. The generalized gradient approximation (GGA) expressed by the PBE functional^[S4] was applied. Large 500 eV energy cut off with convergence threshold 10^{-6} eV for total energy were employed. The Brillouin zone has been sampled by the Monkhorst-Pack method^[S5] with an automatic generated $9 \times 9 \times 1$ Γ -centered k-point grid. To eliminate the interaction between the planes, a 15 Å gap for SiN and CN sheets and 20 Å gap for C₂H sheet were created along the z-axis. Band structure and DOS calculations for SiN-sheet were based on the screened hybrid functional of Heyd, Scuseria, and Ernzerhof (HSE06)^[54,55] with 400 eV cutoff energy.

The phonon dispersion analysis was carried out for the low-lying allotropes by using the Phonopy code^[6] with the finite displacement method, interfaced with the density functional perturbation theory as implemented in VASP. To obtain reliable results of phonon dispersion, more accurate DFT calculations were performed. On the basis of previously optimized SiN monolayer structure, we performed further optimization with more stringent criterion, i.e., $E_{\text{cut}} = 800$ eV, and k-points grid $31 \times 31 \times 1$, energy convergence criterion was set to 10^{-9} eV for the total energy and 10^{-6} eV/Å for the force convergence during the structure relaxation. On the basis of reoptimized structures, we performed the phonon calculation with the criterion, i.e., $E_{\text{cut}} = 660$ eV, energy convergence criterion was set to 10^{-9} eV for the total energy and k-points grid $11 \times 11 \times 1$.

To analyze the bonding pattern of the obtained structures, the solid-state adaptive natural density partitioning (SSAdNDP)^[51] algorithm was used. SSAdNDP is an extension of periodic NBO method^[57], which allows to obtain not only classical Lewis elements such as 1c-2e lone pairs and 2c-2e bonds but also delocalized bonding elements (nc-2e). A plane-wave calculation was performed using 400 eV energy cut off with convergence threshold 10^{-4} eV for total energy and k-points grid $21 \times 21 \times 21$. A projection algorithm was used to obtain the representation of plane-waves in the atomic orbital 6-311G** basis set for the subsequent application of the SSAdNDP algorithm. It was shown that the SSAdNDP is a powerful tool in analyzing chemical bonding in 2D materials.^[8-11, S8-S15]

To estimate the thermal stability of SiN monolayer, the *ab initio* Born-Oppenheimer molecular dynamics (BOMD) simulations, as implemented in VASP code, were carried out. $4 \times 4 \times 1$ supercell was used; a temperature control was performed using Nose-Hover method.^[S16] Simulation was performed during 5ps with a time step of 1fs.

7. References

- [S1] G. Kresse, J. Hafner, *Phys. Rev. B* **1993**, *47*, 558.
- [S2] P. E. Blöchl, *Phys. Rev. B* **1994**, *50*, 17953.
- [S3] G. Kresse, D. Joubert, *Phys. Rev. B* **1999**, *59*, 1758.

- [S4] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865.
- [S5] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B* **1976**, *13*, 5188.
- [S6] A. Togo, F. Oba, I. Tanaka, *Phys. Rev. B* **2008**, *78*, 134106.
- [S7] B. D. Dunnington, J. R. Schmidt, *J. Chem. Theory Comput.* **2012**, *8*, 1902.
- [S8] A. S. Ivanov, E. Miller, A. I. Boldyrev, Y. Kameoka, T. Sato, K. Tanaka, *J. Phys. Chem. C* **2015**, *119*, 12008.
- [S9] H. Zhang, Y. Li, J. Hou, A. Du, Z. Chen, *Nano Lett.* **2016**, *16*, 6124.
- [S10] Z. H. Cui, E. Jimenez-Izal, A. N. Alexandrova, *J. Phys. Chem. Lett.* **2017**, *8*, 1224.
- [S11] C. Pu, D. Zhou, Y. Li, H. Liu, Z. Chen, Y. Wang, Y. Ma, *J. Phys. Chem. C* **2017**, *121*, 2669.
- [S12] Y. Wang, M. Qiao, Y. Li, Z. Chen, *Nanoscale Horiz.* **2018**, *3*, 327.
- [S13] I. A. Popov, A. I. Boldyrev, *J. Phys. Chem. C* **2012**, *116*, 3147.
- [S14] X. F. Zhou, A. R. Oganov, Z. Wang, I. A. Popov, A. I. Boldyrev, H. T. Wang, *Phys. Rev. B* **2016**, *93*, 085406.
- [S15] I. A. Popov, K. V. Bozhenko, A. I. Boldyrev, *Nano Res.* **2012**, *5*, 117.
- [S16] G. J. Martyna, M. L. Klein, M. Tuckerman, *J. Chem. Phys.* **1992**, *97*, 2635.