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Electric field control of molecular magnetism in TMPc/Sc$_2$CO$_2$ van der Waals system

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Abstract: Controlling the magnetic states of molecular structures through electric fields is a major challenge in electron spin manipulation, which can be achieved by utilizing the sensitivity of the electron distribution at the heterostructure interface. Here, we found that the magnetic of transition metal phthalocyanine (TMPc) can be effectively controlled by switching the polarization state of the monolayer Sc$_2$CO$_2$ to achieve the transition between the nonmagnetic and magnetic states of some TMPc molecules. Moreover, the magnetic moment of some structures can be regulated by applying an external vertical electric field. These novel characteristics are caused by the effect of the intrinsic or external electric field on the $d$ orbital electron transfer and orbital splitting of the TMPc molecule. In addition, the $p$-$d$ orbital hybrid in AgPc will also be affected by the external vertical electric field and ultimately change the magnetic moment. Therefore, we are more interested in these different magnetic origins, the fascinating phenomena in this study guide the design of ferroelectric control in high-performance electric writing memories, high-density magnetic reading memories, sensors, and other spintronic devices.

Keywords: Electric field control magnetic states, Transition metal phthalocyanine molecule, Ferroelectric polarization heterostructure, First-principles calculations
INTRODUCTION

The magnetoelectric effect refers to the coupling of ferroelectricity (FE) and ferromagnetism (FM), which has great potential in multifunctional devices. Consequently, it is an effective control method to control the electron spin states of the nanostructure through the electric field. In general, there are two degenerate polarization states (P↑ and P↓) in the two-dimensional ferroelectric materials, the out-of-plane electric fields depends on polarization states, polarized electric field can effectively control the properties of magnetic materials. However, natural multiferroic materials are really rare and the magnetoelectric coupling is usually weak, on the other hand, the traditional ferroelectric and ferromagnetic materials have different electronic requirements for d orbit. Although there are materials that violate the d0 rule, in many cases, it is still pretty challenging to find the intense coupling between FE and FM.

In recent years, many two-dimensional (2D) FE materials have been widely studied, such as SnTe, In2Se3, Sc2CO3, AgBiP2Se4, CuInP2S6, monolayer WTe2, monolayer group IV chalcogenide, 2D honeycomb binary compound, Vertically polarized 2D ferroelectric BN, AlN, ZnO, MoS2, GaSe, transition metal dihalides, CrSnTe3. In addition, theory predicts the existence of a variety of two-dimensional multiferrous materials coexisting with FE and FM, such as C6H organic network23, CrN24, Hf2VC2F225, monolayer CrBr3.26

Van der Waals heterostructure provides multiple possibilities for artificial multiferroic materials, usually accompanied by novel physical phenomena and complex coupling principles. For example, the magnetic coupling of CrI3 bilayers can be switched by Sc2CO3 polarization state; by tuning the ferroelectric polarization state in In2Se/FeI2; the FeI2 monolayer transforms from ferromagnetic to antiferromagnetic, and the polarization state of the CuInP2S6 monolayer can be switched by the electric field. These reports indicate that vdW heterostructures provides a method to achieve artificial multiferroicity.

In this paper, a two-dimensional artificial multiferroic heterostructure is proposed, which is formed by the vdW interaction of a transition metal phthalocyanine molecule (TMPc) and a monolayer Sc2CO3. The monolayer Sc2CO3 has 1.60 μC/cm3 out-of-plane electric polarization, which has been studied in previous research, the position of carbon atoms mainly determines the polarization state,
and the energy barrier of up(P↑) and down(P↓) polarization is 0.52eV per unit\textsuperscript{31}. Besides, Phthalocyanine has been widely used in chemical catalysis\textsuperscript{32-33} and has been widely studied in spintronics\textsuperscript{34-35}.

We consider the case where the central atom of TMPc is the transition metal of the fourth or fifth period. By first-principles calculation, we found that the magnetic state of TMPc can be switched through tuning the polarization state of Sc\textsubscript{2}CO\textsubscript{2} monolayer, the heterostructure can be switched from magnetic state to nonmagnetic state, and the external vertical electric field can control the magnetic moment of some heterostructures. Through further analysis, we know that the coupling variation between TMPc and Sc\textsubscript{2}CO\textsubscript{2} is caused by the significant change of structure arrangement and the charge transfer between layers, which mainly act on the d and p orbits. Moreover, the external electric field can further control the charge transfer between layers, so that the magnetic moment can be controlled. We also reveal the different magnetic variations origins of RuPc (P↑) and AgPc(P↑). Therefore, this research provides a novel method for designing artificial vdW multifunctional nanoelectronics and strong magnetoelectric coupling devices.

**CALCULATION METHODS**

All the results are based on VASP (Vienna ab initio Simulation Package)\textsuperscript{36}. We use the projector-augmented wave (PAW) method\textsuperscript{37} to indicate the ion potential. For dealing with the exchange-correlation effect between electrons, we chose the generalized gradient approximation (GGA) method established on Perdew–Burke–Ernzerhof (PBE) function\textsuperscript{38}, the Hubbard U correction describes the partial filling of the d orbit. U\textsubscript{eff}=U-J=3eV (U=3, J=0eV)\textsuperscript{39}, different U values do not affect the conclusion. The cutoff energy is 400eV, and we use 25Å vacuum space to minimize the influence between adjacent layers. In the relaxation structure, the convergence criterion is that the forces on all atoms are at least less than 0.02 eV/ Å as well as the energy variation is at least less than 10\textsuperscript{-5}eV. Grimme's zero dampings DFT-D3 method\textsuperscript{40} is used to describe the vdW effect of interlayer. We formed 5×5 Sc\textsubscript{2}CO\textsubscript{2} supercell to reduce the interaction of structures, the lattice parameters of Sc\textsubscript{2}CO\textsubscript{2} is 3.37 Å, this is similar to the previous studies\textsuperscript{27}, and dipole correction is considered. The differential charge distribution was drawn by using the software Vesta\textsuperscript{41}, and Bader\textsuperscript{42} is used for charge transfer analysis.
RESULTS AND DISCUSSION

Firstly, we relax the structure to find the lowest energy adsorption point of TMPc molecule on Sc$_2$CO$_2$, as shown in Fig. 1 (c). TMPc and Sc$_2$CO$_2$ relative monolayer position can be determined by referring to the Oxygen atom in the nearest neighbor layer. The relative position can be divided into top and bottom. Through rotation and translation, we find that system's energy at the top is lowest. The following research is based on this situation.

Fig 1: (a, b) Top views of metal phthalocyanine and 1×1 cell of Sc$_2$CO$_2$
(c) Side views of TMPc/Sc$_2$CO$_2$ system with the P↑ and P↓ configurations of the 5×5 Sc$_2$CO$_2$ supercell monolayer, the arrow points the out-of-plane polarization direction

As shown in Fig. 2 (a, b), the transition metals of the fourth period have no evident magnetic moment variation on Sc$_2$CO$_2$, this may be due to the electronegativity of the fourth-period transition metals is generally weaker than that of the fifth-period transition metals. The energy of electrons occupying 4$d$ and 5$s$ orbits is higher than that occupying 3$d$ and 4$s$ orbits, and they are easier to participate in the charge transfer process. In terms of the $D_{4h}$ symmetric ligand field structure of phthalocyanine, the magnetic variation can be explicated by the "4+1" splitting phenomenon\textsuperscript{43-44}. TMPc with central magnetic atom has four suborbits with similar energy in $d$ orbit, while the other one has much higher energy. For example, the bonding of central atom and ligands in VPc(3$d^6$4$s^2$) can cause the three electrons to be in close orbits with lower energy, so the total magnetic moment is 3μ$_B$. 
and with the further increase of $d$ orbital filling electrons, such as Mn (Fe, Co, Tc, Ru, Rh) Pc, the electrons occupy the opposite spin state, resulting in diminishing magnetic moments.

![Diagram](image)

**Fig 2:** (a,b) The effect of substrate polarization direction on the magnetic moment when the central atom of the structure is the transition metal of the fourth and fifth period (c) TMPc($\uparrow$) and TMPc($\downarrow$) layers distance ratio. (d) TMPc(fifth-period) is classified according to the change of magnetic moment.

For the fifth-period transition metal atoms, especially Nb, Ru, Rh, the Sc$_2$CO$_2$ ($P\uparrow$) has a significant effect on the magnetic moment of the structure. Especially, the magnetic moment of the RuPc($P\uparrow$) structure is 0 $\mu_B$, which means that the introduction of Sc$_2$CO$_2$ transforms the magnetic state of RhPc molecules. We mainly analyze the magnetic state transition of RhPc ($P\uparrow$) and the magnetic moment variation of RuPc ($P\uparrow$) in the following content. In order to explore the changes in the interlayer spacing of the heterostructure after the Sc$_2$CO$_2$ reversing, we plot a more concerned fifth-period interlayer spacing ratio, as shown in Fig. 2(c), the systems that are significantly affected by the polarization of the ferroelectric layer have obvious changes in the layer distance, which furtherly affects the electron density distribution and magnetic moment. We can divide the fifth period systems into three types, magnetic moment in type-a increases with the electrons occupying adjacent quadruple orbits, and the magnetic moment in type-b decreases as the electrons occupy the opposite spin state of the quadruple orbits. When the quadruple orbits are fully occupied, the magnetic moment is 0 $\mu_B$, the magnetic moment change in type-c is only related to the electron occupancy of the highest energy level suborbital.
Fig 3: (a, d) Density of states (DOS) and energy levels of $d$ orbital components of TMPc central atom (Rh) (b, c) DOS of the $d$ orbital component of TM atom (Rh) in two polarization structures (e) $d$ orbital electron arrangement of Rh(Ru) in Rh(Ru)Pc/Sc$_2$CO$_2$ (P↑ and P↓) and Rh(Ru)Pc molecule without Sc$_2$CO$_2$

To further study the system magnetic contribution of each sublayer of the $d$ orbit in RhPc, we have the following discussion. Fig 3 illustrates the arrangement of the $d$ orbital sublayer. According to the similarity of the "4+1" split phenomenon, the $d_{z^2}$ and $d_{x^2}$ of the pure RhPc molecule are degenerate. The two different spin states of the $d_{z^2}$ orbital split evidently, which mainly contribute to the magnetism. The energy level of the $d_{z^2}$ orbit is significantly higher than the $d_{xy}$, $d_{xz}$, $d_{yz}$, $d_{z^2}$ orbits. When the RhPc molecule is adsorbed on the Sc$_2$CO$_2$ monolayer, due to the electrons migrate to the $d_{z^2}$ orbit, the $d_{z^2}$ orbit moves to a lower energy level, and degenerates with $d_{xy}$ orbit.

As shown in Fig.3(e), firstly, the outer electron distribution of Rh is 4$d^85s^1$, after bonding, the $d$ orbital loses two electrons, then, the RhPc (P↑) obtains one electron from the interaction between the ligand and Sc$_2$CO$_2$, the total magnetic moment is 0μ$_B$, on the other side, Rh hardly obtains electrons in the P↓ structure, there is still an electron mismatch in the $4d$ orbit, the total magnetic moment of the structure is 1μ$_B$. Secondly, the outer electron arrangement of Ru is 4$d^75s^1$, and because the electronegativity of Ru is weaker than that of Rh, the electrons obtained in the P↑ structure are
slightly less than one, so the total magnetic moment is more than 1\(\mu_B\), the \(P_{\downarrow}\) structure has two electrons which do not match, the total magnetic moment of the structure is 2\(\mu_B\).

Further analysis of charge transfer in RhPc reveals the physical mechanism. It is illustrated by analyzing the density of states, charge transfer, and molecular structure of the two polarization situations. Fig 4(a, b) shows the density distribution of electron states in RhPc \((P_{\uparrow})\) and RhPc \((P_{\downarrow})\). It can be seen that the \(\text{Sc}_2\text{CO}_2\) \((P_{\uparrow})\) transfers 0.798 charges to RhPc, which is much more than the 0.016 charges transferred from RhPc to \(\text{Sc}_2\text{CO}_2\) \((P_{\downarrow})\), the Fermi level is lower for \(\text{Sc}_2\text{CO}_2(P_{\uparrow})\), which is different from the semiconductor state of \(\text{Sc}_2\text{CO}_2(P_{\downarrow})\), showing a metallic state. This transition differs from that of MPz/In\(_2\)Se\(_3\) charge transfer, but it is essentially the transfer and redistribution of charge under the effect of the polarized electric field. Fig 4(c) shows the internal transfer trend of electrons, where \(C_i\) refers to the carbon in \(\text{Sc}_2\text{CO}_2\) and \(C_T\) refers to the carbon in TMPC, \(C_{\text{Total}}=C_i+C_T\).

The number of electrons transferred has been subtracted from the intrinsic charges of the elements of TMPC and \(\text{Sc}_2\text{CO}_2\), Rh gains more electrons in the RhPc \((P_{\uparrow})\). According to Fig 4(d), the interlayer distance in the RhPc \((P_{\uparrow})\) is 2.95 Å, which is shorter than the 3.12 Å distance between the layers in the RhPc \((P_{\downarrow})\), this means that the interaction between TMPC and \(\text{Sc}_2\text{CO}_2\) is more intense in RhPc \((P_{\uparrow})\). The difference of interaction strength leads to the difference of charge transfer and orbital splitting.
finally makes the different magnetic state of TMPc in two polarization situations.

Fig 5: (a) Differential charge distribution after switching the direction of the electric field when the magnetic moments of RuPc(P↑) and AgPc(P↑) increase respectively (15.80 Å and 14.75 Å) (b) Magnetic moment variation of RuPc(P↑) and AgPc(P↑) in different electric fields (c) Charge transfer between RuPc(P↑) and AgPc(P↑) under electric field, (d) DOS of C and N in AgPc molecule in different directions of electric field (e) The magnetic moment of RuPc is significantly changed due to the inversion of Sc$_2$CO$_2$ in 0.05V/A electric field

Based on the response of TMPc to the Sc$_2$CO$_2$ polarized electric field, it can be predicted that the external electric field has a significant effect on the charge transfer and distribution and then affects the total magnetic moment of the systems. For the P↑ situation, the interaction between TMPc and Sc$_2$CO$_2$ is more intense. Therefore, the electric field controls the charge transfer more significantly.

Fig 5(a) further explains the origin of these two different magnetic moments. At the position of 15.80 Å (above the Pc structure), the covalent bond between the Ag atom and the neighboring N atom is
stronger. This is different from the almost no charge interaction between the Ru atom and the N atom.

The more complex bond relationship can be seen at 14.75 Å. The main reason for the increase of RuPc(P↑) magnetic moment is that the charges in Ru d orbit decrease, increasing of net magnetic moment, while the change of AgPc(P↑) magnetic moment is more sophisticated.

In Fig 5(b) the magnetic moment of AgPc(P↑) and RuPc(P↑) varies with the electric field, it can be judged that the origin of the magnetic moment variation of the two structures is quite different according to the differential charge density variation. Fig 5(c) illustrates the charge transfer under the electric field (the charge without the electric field has been subtracted). In the opposite electric field direction, Ru loses more electrons and dominates the variation of magnetic moment, while the Ag loses few electrons in different electric fields, the main contribution of the magnetic moment of the structure is N and C, which can be explained by the magnetic origin of carbonitride, in Fig 5(d), the px, py orbits are degenerate and contribute part of the magnetic moment due to the asymmetry of electrons occupying the spin-up and spin-down positions. AgPc(P↑) exhibits a semiconductor state in the reverse electric field and a half-metallic state in the forward electric field. The increase in magnetic moment mainly comes from splitting pz orbits of C and N near the Fermi level, which is different from the physical mechanism of RuPc/Sc2CO2(P↑).

![Figure 6](image)

**Fig6:** The effect of the distance d between layers of heterostructures on the magnetic moment and energy of the system

In order to further explore the influence of interlayer exchange effect intensity on magnetic
variation, we calculated the magnetic moment of the RuPc structure with the change of the interlayer spacing of the heterostructure, as shown in Fig.6, since there is no obvious difference in magnetic moment between RuPc/Sc$_2$CO$_2$(P↓) structure and RuPc molecular, we mainly study RuPc/Sc$_2$CO$_2$(P↑) structure, $E_\Delta = E_d - 2.2\Delta - E_d$. The $d=2.7\text{Å}$ marked in the figure, it is the optimized result of RuPc/Sc$_2$CO$_2$(P↑) in this paper. When the interlayer spacing is too large, the result gradually approaches two independent molecules in a vacuum. When the interlayer spacing is too small, the repulsion between electrons is strong, resulting in a drastic change in the structure distribution and the destruction of magnetism.

**Conclusions**

In summary, we propose and study a two-dimensional van der Waals heterostructure composed of transition metal phthalocyanine (TMPc) molecule and ferroelectric monolayer Sc$_2$CO$_2$ by first-principles calculation. The magnetic state of RhPc and the magnetic moment of NbPc and RuPc can be controlled through switching the polarization of Sc$_2$CO$_2$ through the electric field. The physical origin of this phenomenon is that the ferroelectric interface polarization leads the charge transfer and redistribution, which is similar to the “4+1” splitting phenomenon. The variation of the magnetic moment of AgPc (P↑) and RuPc (P↑) under the external electric field is predicted, and the different physical mechanisms are revealed. For the AgPc (P↑) structure, carbon and nitrogen contribute to the magnetism and can be further regulated by the electric field. Therefore, our research provides a theoretical method for higher density nonvolatile magnetic memory and may further accelerate research in related fields.

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Reference

1. Bader, S. D.; Parkin, S. S. P., Spintronics. Annu Rev Conden Ma P 2010, 1, 71-88.
2. Heron, J. T., et al., Deterministic Switching of Ferromagnetism at Room Temperature Using an Electric Field. Nature 2014, 516, 370-+
3. Scott, J. F., Data Storage - Multiferroic Memories. Nat Mater 2007, 6, 256-257.
4. Barnes, S. E.; Ieda, J.; Maekawa, S., Rashba Spin-Orbit Anisotropy and the Electric Field Control of Magnetism. Sci Rep-Uk 2014, 4.
5. Wolf, S. A.; Awschalom, D. D.; Buhrman, R. A.; Daughton, J. M.; von Molnar, S.; Roukes, M. L.; Chtchelkanova, A. Y.; Treger, D. M., Spintronics: A Spin-Based Electronics Vision for the Future. Science 2001, 294, 1488-1495.
6. Hill, N. A.; Filippetti, A., Why Are There Any Magnetic Ferroelectrics? J Magn Magn Mater 2002, 242, 976-979.
7. Wang, K. F.; Liu, J. M.; Ren, Z. F., Multiferroicity: The Coupling between Magnetic and Polarization Orders. Adv Phys 2009, 58, 321-448.
8. Tan, H. X.; Li, M. L.; Liu, H. T.; Liu, Z. R.; Li, Y. C.; Duan, W. H., Two-Dimensional Ferromagnetic-Ferroelectric Multiferroics in Violation of the D(0)Rule. Phys Rev B 2019, 99.
9. Chang, K., et al., Discovery of Robust in-Plane Ferroelectricity in Atomic-Thick SnTe. Science 2016, 353, 274-278.
10. Cui, C. J., et al., Intercorrelated in-Plane and out-of-Plane Ferroelectricity in Ultrathin Two-Dimensional Layered Semiconductor In2se3. Nano Lett 2018, 18, 1253-1258.
11. Ding, W. J.; Zhu, J. B.; Wang, Z.; Gao, Y. F.; Xiao, D.; Gu, Y.; Zhang, Z. Y.; Zhu, W. G., Prediction of Intrinsic Two-Dimensional Ferroelectrics in In2se3 and Other Iii2-Vi3 Van Der Waals Materials. Nat Commun 2017, 8.
12. Chandrasekaran, A.; Mishra, A.; Singh, A. K., Ferroelectricity, Antiferroelectricity, and Ultrathin 2d Electron/Hole Gas in Multifunctional Monolayer Mxene. Nano Lett 2017, 17, 3290-3296.
13. Xu, B.; Xiang, H.; Xia, Y. D.; Jiang, K.; Wan, X. G.; He, J.; Yin, J.; Liu, Z. G., Monolayer Agbip2se6: An Atomically Thin Ferroelectric Semiconductor with out-Plane Polarization. Nanoscale 2017, 9, 8427-8434.
14. Belianinov, A.; He, Q.; Dziaugys, A.; Maksymovych, P.; Eliseev, E.; Borisevich, A.; Morozovska, A.; Banys, J.; Vysochanskii, Y.; Kalinin, S. V., Cuinp2s6 Room Temperature Layered Ferroelectric. Nano Lett 2015, 15, 3808-3814.
15. Si, M. W., et al., Room-Temperature Electrocaloric Effect in Layered Ferroelectric
16. Fei, Z. Y.; Zhao, W. J.; Palomaki, T. A.; Sun, B. S.; Miller, M. K.; Zhao, Z. Y.; Yan, J. Q.; Xu, X. D.; Cobden, D. H., Ferroelectric Switching of a Two-Dimensional Metal. *Nature* 2018, *560*, 336−338.

17. Fei, R. X.; Kang, W.; Yang, L., Ferroelectricity and Phase Transitions in Monolayer Group-Iv Monochalcogenides. *Phys Rev Lett* 2016, *117*.

18. Fei, R.; Kang, W.; Yang, L. Robust Ferroelectricity in Monolayer Group-Iv Monochalcogenides 2016.

19. Di Sante, D.; Stroppa, A.; Barone, P.; Whangbo, M. H.; Picozzi, S., Emergence of Ferroelectricity and Spin-Valley Properties in Two-Dimensional Honeycomb Binary Compounds. *Phys Rev B* 2015, *91*.

20. Li, L.; Wu, M. H., Binary Compound Bilayer and Multilayer with Vertical Polarizations: Two-Dimensional Ferroelectrics, Multiferroics, and Nanogenerators. *Acs Nano* 2017, *11*, 6382-6388.

21. Bruyer, E.; Di Sante, D.; Barone, P.; Stroppa, A.; Whangbo, M. H.; Picozzi, S., Possibility of Combining Ferroelectricity and Rashba-Like Spin Splitting in Monolayers of the 1t-Type Transition-Metal Dichalcogenides Mx2 (M = Mo, W; X = S, Se, Te). *Phys Rev B* 2016, *94*.

22. Zhuang, H. L. L.; Xie, Y.; Kent, P. R. C.; Ganesh, P., Computational Discovery of Ferromagnetic Semiconducting Single-Layer Crsnte3. *Phys Rev B* 2015, *92*.

23. Tu, Z. Y.; Wu, M. H.; Zeng, X. C., Two-Dimensional Metal-Free Organic Multiferroic Material for Design of Multifunctional Integrated Circuits. *J Phys Chem Lett* 2017, *8*, 1973-1978.

24. Luo, W.; Xu, K.; Xiang, H. J., Two-Dimensional Hyperferroelectric Metals: A Different Route to Ferromagnetic-Ferroelectric Multiferroics. *Phys Rev B* 2017, *96*.

25. Zhang, J. J.; Lin, L. F.; Zhang, Y.; Wu, M. H.; Yakobson, B. I.; Dong, S., Type-Ii Multiferroic Hf2vc2f2 Mxene Monolayer with High Transition Temperature. *J Am Chem Soc* 2018, *140*, 9768-9773.

26. Huang, C. X.; Du, Y. P.; Wu, H. P.; Xiang, H. J.; Deng, K. M.; Kan, E. J., Prediction of Intrinsic Ferromagnetic Ferroelectricity in a Transition-Metal Halide Monolayer. *Phys Rev Lett* 2018, *120*.

27. Lu, Y.; Fei, R. X.; Lu, X. B.; Zhu, L. H.; Wang, L.; Yang, L., Artificial Multiferroics and Enhanced Magnetolectric Effect in Van Der Waals Heterostructures. *Acs Appl Mater Inter* 2020, *12*, 6243-6249.
28. Sun, W.; Wang, W.; Chen, D.; Cheng, Z.; Wang, Y., Valence Mediated Tunable Magnetism and Electronic Properties by Ferroelectric Polarization Switching in 2d Fei2/In2se3 Van Der Waals Heterostructures. *Nanoscale* 2019, 11, 9931-9936.

29. Li, L. Z.; Zhou, B. Z., Theoretical Investigation of Nonvolatile Electrical Control Behavior by Ferroelectric Polarization Switching in Two-Dimensional Mncl3/Cuinp2s6 Van Der Waals Heterostructures. *J Mater Chem C* 2020, 8, 4534-4541.

30. Tang, X.; Shang, J.; Ma, Y. D.; Gu, Y. T.; Chen, C. F.; Kou, L. Z., Tuning Magnetism of Metal Porphyrazine Molecules by a Ferroelectric In2se3 Monolayer. *Acs Appl Mater Inter* 2020, 12, 39561-39566.

31. Chandrasekaran, A.; Mishra, A.; Singh, A. K., Ferroelectricity, Antiferroelectricity, and Ultrathin 2d Electron/Hole Gas in Multifunctional Monolayer Mxene. *Nano Lett* 2017, 17, 3290-3296.

32. McKelvey, N. B., *Phthalocyanine Materials: Synthesis, Structure, and Function*; Cambridge University Press: Cambridge, U.K.; New York, 1998, p xvi, 193 p.

33. Sorokin, A. B., Phthalocyanine Metal Complexes in Catalysis. *Chem Rev* 2013, 113, 8152-91.

34. Bogani, L.; Wernsdorfer, W., Molecular Spintronics Using Single-Molecule Magnets. *Nat Mater* 2008, 7, 179-186.

35. Shirota, Y.; Kageyama, H., Charge Carrier Transporting Molecular Materials and Their Applications in Devices. *Chemical Reviews* 2007, 107, 953-1010.

36. Kresse, G.; Furthmuller, J., Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys Rev B* 1996, 54, 11169-11186.

37. Blochl, P. E., Projector Augmented-Wave Method. *Phys Rev B Condens Matter* 1994, 50, 17953-17979.

38. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Phys Rev Lett* 1996, 77, 3865-3868.

39. Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P., Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An Lsda+U Study. *Phys Rev B* 1998, 57, 1505-1509.

40. Grimme, S., Semiempirical Gga-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J Comput Chem* 2006, 27, 1787-99.

41. Momma, K.; Izumi, F., Vesta 3 for Three-Dimensional Visualization of Crystal, Volumetric and Morphology Data. *Journal of Applied Crystallography* 2011, 44, 1272-1276.

42. Bader, R. F., Atoms in Molecules. *Accounts of Chemical Research* 1985, 18, 9-15.
43. Cho, W. J.; Cho, Y.; Min, S. K.; Kim, W. Y.; Kim, K. S., Chromium Porphyrin Arrays as Spintronic Devices. *J Am Chem Soc* **2011**, *133*, 9364-9369.

44. Liao, M. S.; Scheiner, S., Electronic Structure and Bonding in Metal Porphyrins, Metal=Fe, Co, Ni, Cu, Zn. *J Chem Phys* **2002**, *117*, 205-219.

45. Li, X.; Zhou, J.; Wang, Q.; Kawazoe, Y.; Jena, P., Patterning Graphitic C-N Sheets into a Kagome Lattice for Magnetic Materials. *J Phys Chem Lett* **2013**, *4*, 259-63.

46. Du, A.; Sanvito, S.; Smith, S. C., First-Principles Prediction of Metal-Free Magnetism and Intrinsic Half-Metallicity in Graphitic Carbon Nitride. *Phys Rev Lett* **2012**, *108*, 197207.