

## Surface-Adsorption of Metal-Phthalocyanine Molecules on Transition-Metal Dichalcogenides

How to improve the magnetic coupling in the films of transition metal phthalocyanines (TMPcs) and to introduce magnetism into transition metal dichalcogenides (TMDs) 2D materials are two subjects of intense research. The weak magnetic coupling between TMPc molecules in bulk phase hinders the use of TMPcs in spintronics.[1] Recent researches show that the interface hybridization offers an effective way to modulate the stacking structure of transition metal phthalocyanines (normally in the first two layers) and then hopefully enhances the magnetic coupling up to room temperature.[2][3] The predicted strongest magnetic coupling is 400K in CoPc films with a stacking structure of face to face.[4] On the other hand, compared with methods like hydrogenation, fluorination, strain, defect and doping, surface molecular doping is an effective way to induce magnetism in 2D materials with the advantages of easy preparing and precise control of doping concentration and location as well as providing extra electrons and magnetic source. Besides, TMDs have a variety of electronic properties from metallic to semiconducting with different band gaps, which providing more possibilities to control the hybridization, charge transfer and correlation between TMPcs and TMDs. Hence, here we would like to choose MPcs/TMDs systems to study the magnetic interactions between MPcs and semiconducting as well as metallic TMD materials. Since the participation of the 3d orbital of Co in HOMO and LUMO of CoPc molecule is greater than in other MPcs like NiPc and CuPc, and theoretical calculations predicted that the ferromagnetism of VSe<sub>2</sub> also mainly originates from the 3d orbital of V, We choose CoPc/VSe<sub>2</sub> as the first system we study.[5][6] Present experimental results show that compared with HOPG, VSe<sub>2</sub> has a very different influence on the electronic properties of CoPc, causing two distinct electronic states (see Figure 1). The switch between these two states can be controlled by applying different bias (Figure 2), which demonstrates that it is caused by charge transfer between CoPc and VSe<sub>2</sub>. Temperature dependence shows that both states are very stable against high temperatures up to 500K. The interaction between TMPcs and TMDs is of great interest and needs further study.

### References

- [1] S. Heutz, "Molecular spintronics: A warm exchange," *Nat. Mater.*, vol. 14, no. 10, pp. 967–968, 2015.
- [2] M. Gruber, F. Ibrahim, S. Boukari, H. Isshiki, L. Joly, M. Peter, M. Studniarek, V. Da Costa, H. Jabbar, V. Davesne, U. Halisdemir, J. Chen, J. Arabski, E. Otero, F. Choueikani, K. Chen, P. Ohresser, W. Wulfhekkel, F. Scheurer, W. Weber, M. Alouani, E. Beaupaire, and M. Bowen, "Exchange bias and room-temperature magnetic order in molecular layers," *Nat. Mater.*, vol. 14, no. 10, pp. 981–984, 2015.
- [3] X. Chen, Y. S. Fu, S. H. Ji, T. Zhang, P. Cheng, X. C. Ma, X. L. Zou, W. H. Duan, J. F. Jia, and Q. K. Xue, "Probing superexchange interaction in molecular magnets by spin-flip spectroscopy and microscopy," *Phys. Rev. Lett.*, vol. 101, no. 19, pp. 1–4, 2008.
- [4] M. Serri, W. Wu, L. R. Fleet, N. M. Harrison, C. F. Hirjibehedin, C. W. M. Kay, A. J. Fisher, G. Aeppli, and S. Heutz, "High-temperature antiferromagnetism in molecular semiconductor thin films and nanostructures.," *Nat. Commun.*, vol. 5, p. 3079, 2014.
- [5] A. Mugarza, R. Robles, C. Krull, R. Koryt??r, N. Lorente, and P. Gambardella, "Electronic and magnetic properties of molecule-metal interfaces: Transition-metal phthalocyanines adsorbed on Ag(100)," *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 85, no. 15, pp. 1–14, 2012.

- [6] Y. Ma, Y. Dai, M. Guo, C. Niu, Y. Zhu, and B. Huang, "Evidence of the existence of magnetism in pristine VX<sub>2</sub> monolayers (X = S, Se) and their strain-induced tunable magnetic properties," *ACS Nano*, vol. 6, no. 2, pp. 1695–1701, 2012.

## Figures

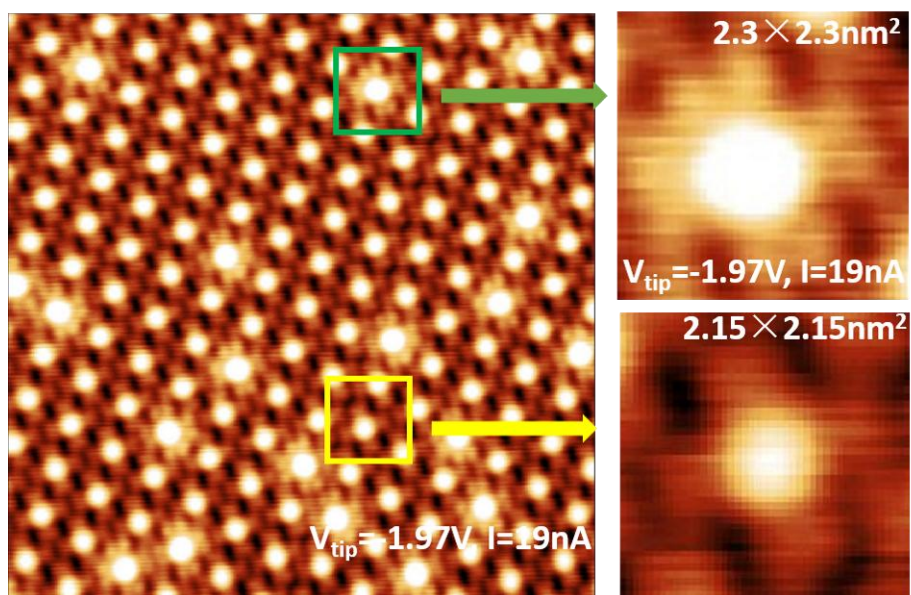


Figure 1: Two distinct electronic states of CoPc molecules on VSe<sub>2</sub>.

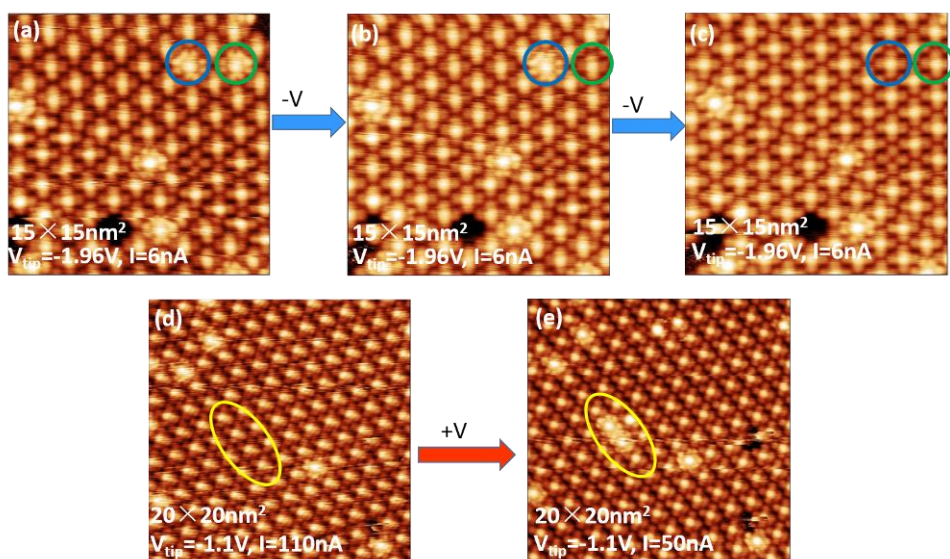


Figure 2: a-c: Negative bias (-2.5-0V) induced switch from bright to normal state. d-e: Positive bias (0-2.5V) induced switch from normal to bright state.