Reversible Switching of Single FePc Molecule Structure on Giant Rashba Surface

Hung-Chin Lee[1*], Nitin Kumar[1], Yen-Hui Lin[1], Chen-Yu He[1], Jun-Quan Xiao[1], Pin-Jui Hsu[1]

[1] Physics Department, National Tsing Hua University

[*] Presenter: Hung Chin Lee, email: sean112022503@gapp.nthu.edu.tw

Abstract

The Rashba system, originated from strong spin-orbit coupling induces energy band splitting for electrons of opposite spins, exhibit distinctive interactions when coupled with a magnetic impurity. Previous STM/STS studies have demonstrated that the antiphase boundary of the Rashba system $BiAg_2$ stabilizes an alternative structure for manganese phthalocyanine (MnPc) molecules, resulting in a reversible magnetic switching system. In our research, we replaced MnPc with Iron phthalocyanine (FePc) and observed its ability to sustain two switchable phases. Notably, one of these phases manifests as a six-lobes pattern in STM topography in contrast with the previously observed four lobes, deviating from the typical molecular shape. This discovery highlights the potential unique electronic behavior of magnetic impurities within the Rashba system and may have far-reaching implications.

Introduction

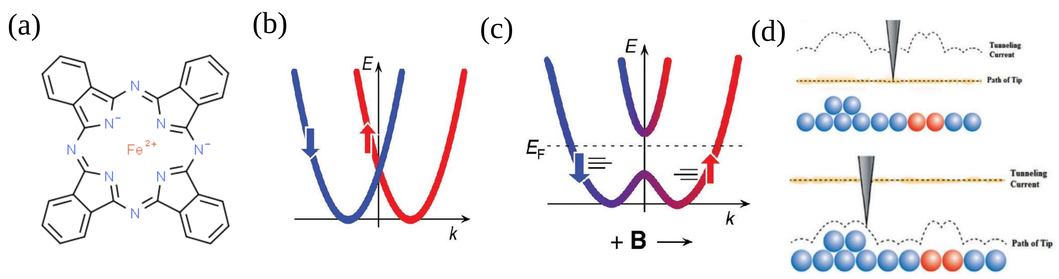
- **Rashba Effect** – Spin-orbital interaction leads to the splitting of energy bands for electron with opposite spins.
- **Tunneling current**

$$I = \frac{4\pi e}{\hbar}\int_{-\infty}^{\infty}[f(E_F - eV + \varepsilon) - f(E_F + \varepsilon)]\rho_S(E_F - eV + \varepsilon)\rho_T(E_F + \varepsilon)\left|M_{\mu\nu}\right|^2 d\varepsilon$$

At low temperature

$$I \propto \int_0^{eV}\rho_S(E_F - eV + \varepsilon)\rho_T(E_F + \varepsilon)\,d\varepsilon \quad \Rightarrow \quad \frac{dI}{dV} \propto \rho_S(E_F - eV)$$

- **Iron phthalocyanine (FePc)**



(a) The molecule structure of FePc, (b) Rashba effect will lead to spin-splitting band structure, (c) Band structure breaking the time-reversal symmetry by applying a magnetic field. [1] (d) The schematic diagram of STM.

Method

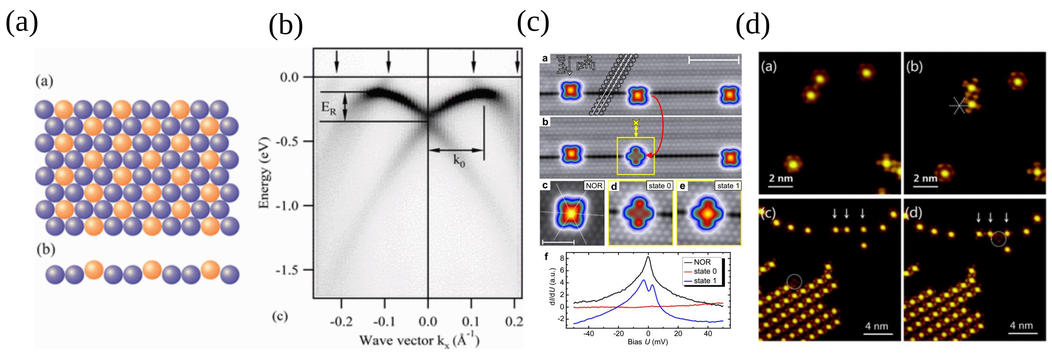
- **Sample Preparation**

Sputtering → Annealing → Depositing Bi → Cooling to 80K → Depositing FePc

- **Measurement** – Scan Tunneling Microscopy (STM), Scan Tunneling Spectrum (STS)

Literature Review

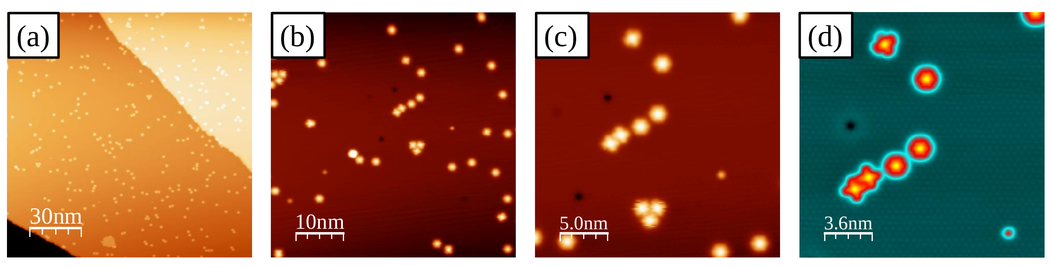
- **Giant Spin Splitting through Surface Alloying (2007)**
  - $BiAg_2$ $\sqrt{3}\times\sqrt{3}$ $R30°$ phase has strong rashba effect [2]
- **Reversible Magnetic Switching of High-Spin Molecules on a Giant Rashba Surface (2018)**
  - Result of MnPc on $BiAg_2$ $\sqrt{3}\times\sqrt{3}$ $R30°$ phase [3]
- **Monitoring and Manipulating single molecule rotors on the Bi(111) surface by the scanning tunneling microscopy (2017)**
  - Mangnese phthalocyanine (MnPc) can rotate on Bi(111) at 77K [4]



(a) The top view and side view of the $\sqrt{3}\times\sqrt{3}$ R30° Bi/Ag(111) surface, (b) Experimental band structure obtained by ARPES of $\sqrt{3}\times\sqrt{3}$ R30° Bi/Ag(111) surface, (c) Topography and STS of MnPc on $BiAg_2$, (d) Topography of MnPc on Bi(111).

Result and Discussion

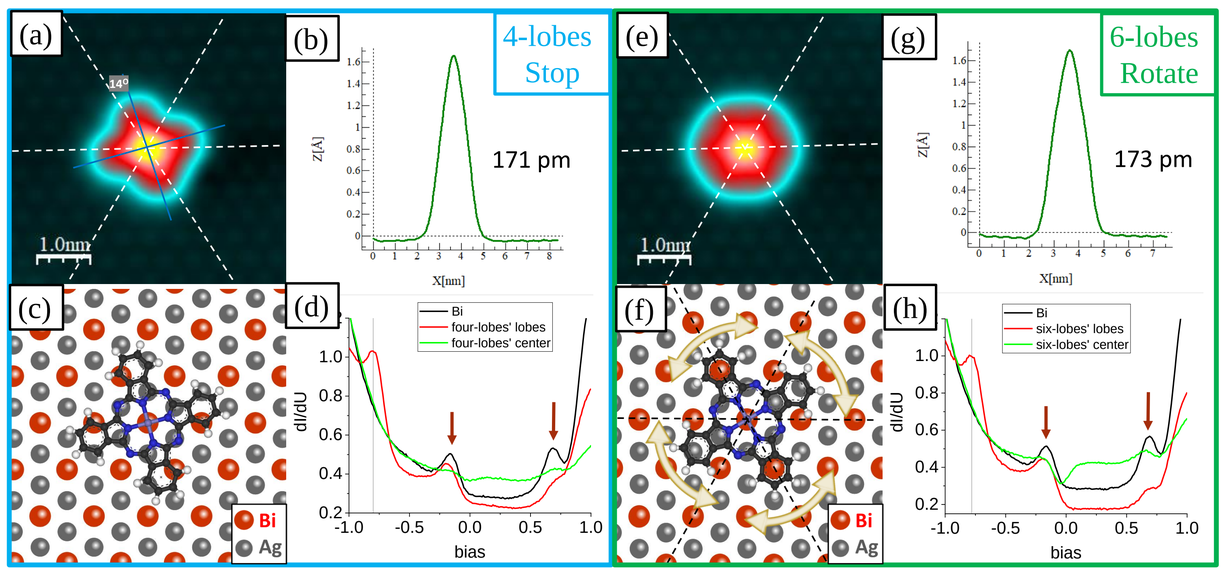
- **Topography of FePc single molecule on $\sqrt{3}\times\sqrt{3}$ $R30°$ Bi/Ag(111) surface**
  - Single FePc molecule deposited on $\sqrt{3}\times\sqrt{3}$ $R30°$ $BiAg_2$ surface.
  - FePc molecule appear four-lobes and six-lobes two phases.



Summary

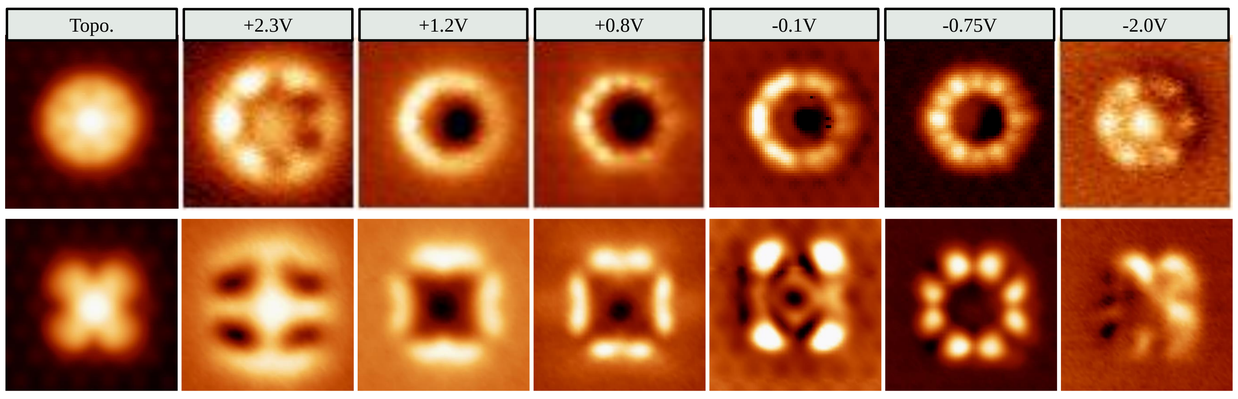
- We deposit the single FePc molecule on strong Rashba surface $BiAg_2$.
- By using high resolution STM, we successfully construct the atomic structure and HOMO/LUMO 2D mapping of the system.
- By using pulse, we success to manipulate the rotation of FePc molecule.
- FePc doesn't rotate below 4K.

- **Atomic resolution, structure model and STS of four-lobes and six-lobes molecule**
  - By (e), we suggest that six-lobes molecule is rotation of FePc molecule.
  - The molecule height of two types molecule almost same.
  - We can see the Rashba peak in $\pm 1V$ STS.

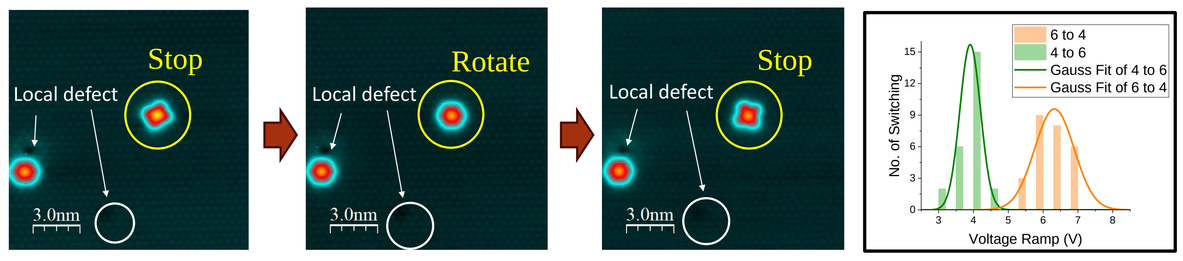


Four-lobes FePc molecule: (a) Atomic resolution, (b) Molecule height, (c) Atomic structure modle, (d) $\pm 1V$ STS curve, Rashba peak is mark by arrow; **Six-lobes FePc molecule:** (e) Atomic resolution, (f) Molecule height, (g) Atomic structure model, (h) $\pm 1V$ STS curve, Rashba peak is mark by arrow.

- **dI/dV mapping of four-lobes and six-lobes FePc molecule**
  - The molecule's dI/dV mapping higher than substrate at the energy we show below, which indicate the energy of HOMO/LUMO.

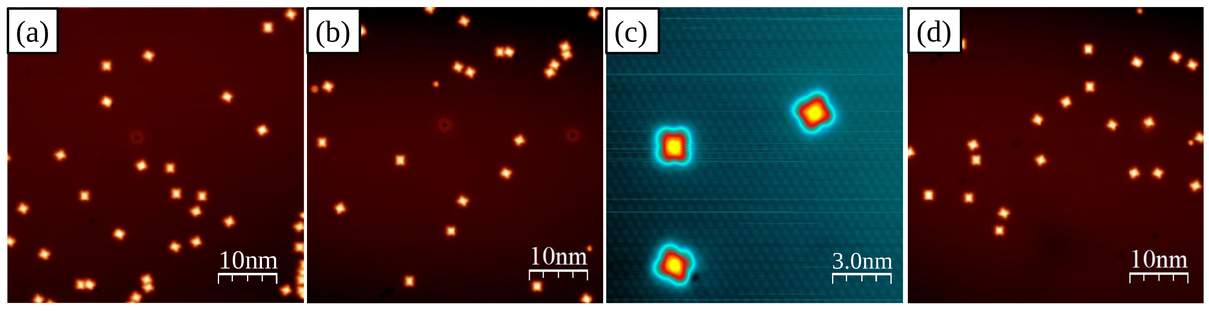


- **Switching phases of two type of molecule**
  - We can manipulate the molecule's rotation by pulsing the tip in STM.
  - By statistics, 3.9V pulsing make the molecule rotate, and 6.3V make molecule stop.



(a)-(c) When manipulating the molecule, we park the tip 3nm away from target molecule, and using specific large bias to do the pulsing. (d) we use Gauss fitting to find the center of to rotate is 3.9V and to stop is 6.2V.

- **Low Temperature Measurement**
  - There's no six-lobes FePc molecule being found in 4K and 0.32K measurement, which also support the idea that six-lobes molecule is rotation of four-lobes. (d) is 0.32K data.



Reference

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