Spin-Polarized Transport through Single Manganese Phthalocyanine Molecules on a Co Nanoisland

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ABSTRACT: We investigate spin-polarized (SP) electronic transport properties and hybrid states of a single manganese phthalocyanine (MnPc) molecule adsorbed on a Co nanoisland, with the SP scanning tunneling microscopy measurements and the first-principles calculations. Our analyses show that the MnPc molecule can pin the Co surface state to the Fermi level, forming hybrid stationary spin resonance states which, with an antiparallel-magnetization tip, give a resonant SP conductance peak. Our calculations further reveal that as the tip approaches the molecule, electronic and magnetic couplings in the junction are tuned as the Zener indirect exchange coupling becomes prominent, which switches the conduction carriers from s to d electrons and leads to the tailored magnetic moments and magnetoresistance.



INTRODUCTION

The organic-metal molecules possess unique magnetic characteristics which can be used to build multifunction spintronic devices and have attracted intensive interest. Recently, such molecular properties have been explored by X-ray magnetic circular dichroism $(XMCD)^{1-3}$ and spin-polarized (SP) scanning tunneling microscopy (STM),⁴⁻⁶ revealing various degree of hybrid states at the interface of molecules and substrates. These studies suggest the impacts of the hybrid states on spin injection⁷ and single-molecule conduction,⁸ facilitating the design of spin-based devices. For example, the surface state of a Co nanoisland located around -0.3 eV can be pinned to around the Fermi level by adsorbing a cobalt phthalocyanine (CoPc) molecule on the surface to form hybrid stationary spin resonance states, perpendicular to the surface,^{4,9} providing a promising way to engineer the spinterface.

Whereas the CoPc molecule can shift the Co spinterface states, first-principles calculations propose that the manganese phthalocyanine (MnPc) molecule owns higher magnetic moment and magnetocrystalline anisotropy energy than the CoPc molecule has,¹⁰ which would tune such states efficiently and achieve featured devices. While properties of MnPc molecules on metallic substrates have been investigated experimentally by the X-ray absorption spectroscopy^{2,11} or STM,^{12,13} a direct SP-STM transport measurement of the MnPc molecule adsorbed on a Co nanoisland, as applied to the CoPc molecule^{4,9} and the hydrogen phthalocyanine molecule,^{8,14} however is still absent.

Since a spintronic device would function in a shorter contact distance than the STM does, the effects of the tip and substrate on the molecule should take into account. For instance, both the unpolarized^{15–18} and polarized^{19–21} tips induce modifications to electronic structures of the sample. Recently, an *ab initio* study predicts the tailored tunnel magnetoresistance (TMR) in the antiferromagnetic junction consisted of a Co–Cr dimer and a SP-STM tip and suggests that by changing the distance between the tip and dimer, the hybrid states and magnetic couplings can be tuned and better understood.²² A direct correlation between the observed hybrid states and magnetic couplings in a molecular magnet junction thus is highly desired.

In this work, we show the features of SP transport through a magnetic junction consisted of the STM Co tip, the MnPc molecule, and the Co/Cu(111) nanoisland. Using low-temperature SP-STM and first-principles calculations, consistent SP tunneling spectra of the junction are obtained, where a resonant transmission peak appears at the Fermi level, due to electron tunneling between the hybrid stationary spin states of the Mn and Co atoms and the antiparallel-magnetization tip. Moreover, the coupling, the magnetic moments, and the magnetoresistance of the junction can be controlled by the tip—molecule separation, which helps us to clarify the nature of conduction channels and magnetic couplings in the junction and points to potential applications for spintronic devices.

METHODS

The SP-STM measurements were performed at a low temperature (4.2 K) and a pressure below 2×10^{-11} mbar.

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The Co/Cu(111) substrate and spin-sensitive tip were prepared as the same procedure described in our previous work.²³ After that, MnPc was sublimated onto the Co/Cu(111) surface by using a home-built thermal evaporation gun at deposition temperature around 450 °C. All above preparations were *in situ* performed at a pressure below 5×10^{-10} mbar. STM topographies were measured in a constant current mode, and differential tunneling conductances dI/dV were recorded simultaneously to topographic images by the lock-in technique with a voltage modulation of 20 mV_{rms} to bias voltage. When recording the spectroscopy data, the feed-back loop was closed for fixing tip–sample distances and the bias voltage swept from +1.0 to -1.0 V.

For quantum calculations, the optimized structure of MnPc on the Co/Cu(111) film was obtained, by using the Quantum Espresso package²⁴ with a kinetic energy cutoff of 25 Ry at Γ , as the atomic force was smaller than 0.001 Ry/bohr. MnPc was placed on two layers of cobalt (hcp) above two layers of copper(fcc) along (111) orientation, resulting in a supercell with 281 atoms.⁴ When the initial tip-molecule distance was 3.1 Å (3.0 Å), the relaxed one was 3.31 Å (2.74 Å). We thus estimated that the contact distance was 3.03 Å (about 5.34 Å of tip-substrate distance). Around the contact distance, the tip induced structure relaxations¹⁵ could affect our results, which were neglected to reduce the computational load. The spintransport calculations were performed by the Nanodcal code,²⁵ based on the nonequilibrium Green's function method and density functional theory, within the local-density approximation. Valence electrons were described by a double- ζ plus polarization basis set for the H, C, and N atoms and a double- ζ basis set for Co and Mn atoms. The converged criterion was 10^{-5} eV. Considering the highly localized measurement of STS, the optimized MnPc-Co/Cu(111) structure was modified to the tube-like structure as shown in Figure 2a. Five Cu (Co) buffer layers were included in the simulation box at the sample (the tip) site. The hexagonal closed-packed Co tip was manually constructed as a pyramid in the (001) direction with a single atom at the apex, giving 176 atoms in the simulation box.

RESULTS AND DISCUSSION

The STM topography of MnPc molecules on the Co/Cu(111)substrate is shown in Figure 1a, where the MnPc molecule with a cross shape can be clearly identified. Figure 1b plots the zoomed-in images of two MnPc molecules. Figure 1c shows a similar image with a Co-coated tip at $V_{\text{bias}} = -0.3$ V and I = 5 nA, where the MnPc molecules are well separated, and thus the intermolecular interactions can be ignored. Figure 1d shows the spin contrast of Co islands at a bias voltage (V_{bias}) of -0.295 V, which originates from localized spin minority $d_{3z^2-r^2}$ states.²⁶ While the magnetic orientation of a two-atomic layers high Co island is well understood to along the direction of the surface,⁴ parallel (P) or antiparallel (AP) with the SP tip is an issue to be determined. The AP one has been reported to be more conductivity than the P one at V_{bias} around -0.3 V.^9 As the dI/ dV spectrum of each island shown in Figure 1f (measured at the marked squares in Figure 1d) indicates, the bright (darker) island has AP (P) alignment of spin polarization with the SP tip, being consistent with the previous work.⁹ Moreover, these two Co islands are of the same crystal staking with similar sizes, and thus the electronic discrepancy due to the staking²⁷ and size²⁸ effects can be ruled out. The spin contrast of MnPc molecules on the Co islands at V_{bias} = 0.01 V is presented in



Figure 1. (a) STM topographic image of MnPc molecules on the Co/ Cu(111) substrate, taken by a W tip at $V_{\text{bias}} = -0.3$ V and I = 1 nA. (b) Zoomed-in images of two MnPc molecules. (c) A similar STM image with a Co-coated tip at $V_{\text{bias}} = -0.3$ V and I = 5 nA. (d) Spin-polarized conductance mapped at $V_{\text{bias}} = -0.295$ and (e) 0.01 V. (f) Spinpolarized tunneling spectra of the Co islands. (g) Spin-polarized tunneling spectra of the MnPc molecules.

Figure 1e. The dI/dV spectra of MnPc molecules, recorded from their central part, are shown in Figure 1g. A spin resonance from the AP configuration appears at the Fermi level, giving a larger conductance of the AP configuration than the P one. After the bias voltage is lower than -0.15 V, the conductivity between these two configurations reverses.

To shed insight into these experimental data, first-principles calculations were performed. After geometry optimization, the adsorbate favors the bridge site, 2.21 Å above the Co surface. In our transport modeling, the direction of the tip's magnetization is fixed, while the directions of the sample are set to be AP or P with respect to the tip's magnetization. The calculated transmission spectra are presented in Figure 2b. The feature of transmission spectra for the AP and P configurations at the tip–molecule distance (*D*) of 5.0 Å is consistent with the experimental outcome of Figure 1g, as the conductance, $G = (2e^2/h)T(E_f)$ in the linear response regime.²⁹ However, the calculated peak width (about 20 meV) is smaller than the measured one (about 150 meV). This discrepancy may come from the narrowed model we used in the calculations or from the potential drop which occurred on the contact resistance of



Figure 2. (a) Structure of MnPc molecule (left) and the model for transport calculations (right). (b) Transmission spectra for P and AP configurations under three tip–molecule distances. (c) Local density of states (LDOS) of the junction, for up-spin electrons in the AP configuration (the isovalue is $0.45 \times 10^{-3} e/Å^3$, and the energy range is within -15 to 15 meV).

the STM tip in the measurements. The transmission spectra and the up-spin transmission spectra are similar around the Fermi level (see Figures 2b and 3e), so that the conduction is dominated by the up (down) spin electrons in the AP (P) configuration (the case of P configuration is not shown here). To visualize the molecular states, local density of states (LDOS) for up-spin electrons in the AP configuration are plotted in Figure 2c, where the isovalue is $0.45 \times 10^{-3} e/Å^3$ and the integrated energy range is from -15 to 15 meV. For clarity, only states of the Mn atom, the Co atom at the tip's apex (Co tip), and the Co atoms underneath the Mn atom (Co_b) are presented. It is evident that up-spin electrons tunnel between the states of the Co tip atom and the hybridized states (D > 3.0 Å) of the Mn and the Co_b atoms.

Whereas the position of the STM tip makes influence on the transport properties in a Co–Cr dimer junction,²² the conduction behaviors and the magnetic couplings of the MnPc molecular junction can be further addressed, particularly in the contact regime. When the tip approaches the molecule to 3.8 Å, the transmission resonance peak for the AP configuration at the Fermi level enlarges and broadens (Figure 2b) due to the

much shorter D and the adjustment of couplings between the MnPc molecule, the substrate, and the tip. Although the LDOS of the tip's apex are reduced, the shorter D (Figure 2c) give better electronic couplings. When D becomes 3.0 Å, the resonance peak at the Fermi level reduces, and the wide peaks happen around 20 and -30 meV (Figure 2b). The LDOS of the Co tip are further decreased, and the LDOS of the Mn atom are narrowed and separated from those of the substrate (Figure 2c), so that the coupling between the molecule and the substrate is weaken in this energy range, though D is shorter.

To better understand the interactions, the projected density of states (PDOS) on the Mn, the Co_b, and the tip Co atoms, for up-spin electrons in the AP configuration, are shown in Figure 3a,b. For clarity, only featuring orbitals are plotted. When the tip positions at 5.0 Å above MnPc, the PDOS of the s orbital of the Mn atom have two major peaks at -5 and 38meV (Figure 3a). The PDOS of the tip Co atom do not depend on energy strongly (Figure 3b), indicating that the coupling between the molecule and the tip is weak. At this large D, electron tunneling behaviors are determined by the distance between the LDOS of the tip Co and the Mn atoms, on the s orbitals (Figure 3c,d). The PDOS product on the s orbitals of the Mn and Co tip atoms is similar to the up-spin transmission spectrum in the AP configuration (Figure 3e, where transmission coefficients are 7 times enlarged), suggesting that the PDOS of the s orbitals govern the tunneling events, being consistent with the Tersoff-Hamann approximation.³

When D decreases to 3.8 Å, the two PDOS peaks of the Mn's s states shift to -8 and 35 meV (Figure 3a). A PDOS dip of the Co-tip's s states appears around -5 meV (Figure 3b), indicating that the s states of the tip couple with the Mn atom. The LDOS on the s states of the Co tip are reduced largely, though those of the Mn atom are extended (Figure 3c). Moreover, the conduction channel near the Fermi level are switched from the s to the d orbitals (Figure 3d). The PDOS product on the s orbitals of the Mn and Co tip atoms deviates from the transmission spectrum (Figure 3e), suggesting that the hybridized d states of Mn and Co_b atoms dominate the conductance.

As D reaches 3.0 Å, the two PDOS peaks of the Mn's s states shift to -17 and 30 meV (Figure 3a), so that both peaks are away from the Fermi level, causing the decay of the transmission resonance peak as well as the reduction of the Mn's LDOS around the Fermi energy (Figure 2c). Two dips happen in the PDOS of the Co tip's s states at -10 and 35 meV, and the fluctuation occurs in the PDOS of the Co tip's d states (Figure 3b), due to the increased tip-molecule coupling. The LDOS on the s states of the Co tip vanish, and those of the Mn atom are reduced (Figure 3c), so that the d states support the conduction. However, as the tip extracts the states from the $Mn-Co_{h}$ hybridized ones (Figure 3d), the conductance decreases, though the width of the tunneling barrier (D)decreases. The PDOS product on the s orbitals of the Mn and Co tip atoms has the similar shape as the up-spin transmission spectrum in the AP configuration, except at the Fermi level, indicating that the d-orbital channel, consisting of the Mn, Co_b, and Co tip atoms, influences the conductance.

To investigate the couplings imparting to this system, magnetic moments of the Mn and Co tip atoms at various D are shown in Figure 4a. The magnetic moment (m) is acquired by calculating the spin-polarized charges $\sum_i (n_i^{\uparrow} - n_i^{\downarrow})$, and only the magnitude is presented. For example, the m of Mn in the AP configuration, shown in Figure 4a, is positive but not



Figure 3. (a) Projected density of states (PDOS) of the Mn and the substrate Co atoms, (b) PDOS of the tip Co atom, (c) LDOS on the s orbital, (d) LDOS on the d orbital, and (e) transmission spectra of the junction and PDOS products of the Mn and Co tip atoms on the s orbital, for up-spin electrons in the AP configuration under three tip–molecule distances. Only featuring orbitals are shown here. The PDOS is with an arbitrary unit. The isovalue of LDOS is $0.32 \times 10^{-3} e/Å^3$, and the energy range is within -15 to 15 meV.



Figure 4. (a) Magnetic moment (m) of the Mn and the tip Co atoms and (b) TMR ratio at the Fermi level as a function of tip-molecule distances.

negative value. When D decreases, the m of the Mn atom in both P and AP configurations and the m of the Co tip in the P configuration dwindle, especially for D below 3.8 Å where the coupling between the tip and the MnPc is enhanced. On the other hand, the m of Co tip in the AP configuration has an opposite tendency for D around 3.8 Å. As D is close to 3.8 Å, the Zener indirect exchange coupling becomes prominent, so that the d states of the Mn and Co tip atoms can be ferromagnetic coupled via the conduction electrons^{31,32} which are up (down) spin in the AP (P) configurations. However, in this system, the majority electrons of the Co tip atom are upspin in both configurations, and the majority of the electrons of the Mn atom are down (up) spin in the AP (P) configuration. Therefore, the conduction electrons increase the number of majority electrons for the Co tip atom in the AP configuration but increase the number of minority electrons for others. Since reducing the ratio of minority to majority electrons increases the *m*, only the *m* of the Co tip atom in the AP configuration increases. When *D* reaches to 3.0 Å, the direct exchange coupling (either FM or AFM type) and charge transfer can play roles to decrease the *m* again.

The TMR ratio³³ is estimated as

$$\Gamma MR = \frac{G_{AP} - G_{P}}{G_{AP}}$$

where *G* is conductance. The TMR values are calculated as a function of *D* (Figure 4b). Clearly, the TMR drops dramatically when D < 3.8 Å, as $T(E)_{\rm P}$ approaches $T(E)_{\rm AP}$ (Figure 2b), and the Mn states are coupled with the tip (Figure 2c). Thus, the TMR ratio of this single-molecule junction can be efficiently tuned, from ~0 to 100%.

CONCLUSIONS

In conclusion, spin-polarized tunneling spectra of MnPc molecules on the Co/Cu(111) surface are observed in SP-STM measurements, which are consistent with the calculated results from first principles, revealing the nature of the tunneling junction, consisted of the Co tip, MnPc molecule, and Co substrate. Particularly, the junction with a antiparallel magnetization between the tip and the molecule has higher conductance than the one with a parallel magnetization. As the tip approaches the molecule, the s states shift to lower energy and the d states dominate the conductance. The Zener indirect exchange coupling becomes prominent, and the d states of the Mn and Co tip atoms can be ferromagnetic coupled via the conduction electrons. Further reducing the tip–molecule distance to reach the contact regime, the conductance is

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decreased due to the dehybridization of the molecule and the substrate. As the molecular states are established on the subtle balance of the couplings between the tip, molecule, and substrate, they can be manipulated by the tip-molecule separation, leading to functional characteristics of the magnetic moments and the magnetoresistance in the molecular junction.

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Notes

The authors declare no competing financial interest.

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