Probing Superexchange Interaction in Molecular Magnets by Spin-Flip Spectroscopy and Microscopy

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The superexchange mechanism in cobalt phthalocyanine (CoPc) thin films was studied by a low temperature scanning tunneling microscope. The CoPc molecules were found to form one-dimensional antiferromagnetic chains in the film. Collective spin excitations in individual molecular chains were measured with spin-flip associated inelastic electron tunneling spectroscopy. By spatially mapping the spin-flipping channels with submolecular precision, we are able to explicitly identify the specific molecular orbitals that mediate the superexchange interaction between molecules.

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Orbital overlapping, the origin of chemical bonding, magnetism, and so on, generally results in short-ranged interaction between atoms due to the localization of atomic wave functions. To achieve interaction over a large distance, usually the superexchange mechanism [1,2], where a bridging molecule or ion mediates higher-order virtual hopping processes, has to be invoked. The superexchange interaction is responsible for the magnetism in a wide range of materials including transition metal oxides [3] and strongly correlated electronic systems [4]. It also exists in the ultracold atoms in optical lattices [5], as well as in the charge and energy transfer of molecular systems [6]. As a typical superexchange pathway in molecular magnetism [7–9], the nonmagnetic ligands mediate the magnetic coupling between well-separated transition metal ions. Owing to the lack of real-space imaging techniques with high spin sensitivity, the superexchange pathway was usually identified by model calculation.

In the present Letter, we studied the mechanism of superexchange interaction by the spin-flip inelastic electron tunneling spectroscopy (IETS) and microscopy with a scanning tunneling microscope (STM). IETS is one of the most sensitive tools to probe excitations in molecules [10–12]. The latest success of STM-IETS was the measurement of spin excitations, where the tunneling electrons transfer energy to the spin degree of freedom of individual Mn atoms or atomic chains via the spin-flip process [13–15]. Together with external magnetic field, spin-flip spectroscopy provides information of spin coupling, and therefore opens new avenues to probe magnetism at the nanometer scale.

The experiments were conducted with a Unisoku ultra-high vacuum STM at the base temperature of 0.4 K by means of a single-shot 3He cryostat. A magnetic field up to $B = 11$ T can be applied perpendicularly to the sample surface. Pb(111) islands with flat-top surfaces were prepared on the Si(111) – (1 × 1) – Pb substrate [16,17].
and increase the lifetime of spin excitations. The residual coupling between the substrate and the molecules in the second layer leads to the Kondo effect [17,20] with a Kondo temperature below 10 K. The $dI/dV$ spectra in Fig. 2(b) document the Kondo resonance and its splitting under the magnetic field.

The spin of a molecule on the second layer can be released from the Kondo screening of the substrate by dragging the molecule away from the top sites of the first CoPc layer with the STM tip. A magnetic field is needed to observe the IETS [Fig. 2(c)] of a single CoPc molecule with spin-1/2. Above a threshold bias voltage at $E/e$ (where $E$ is the spin-flip excitation energy and $e$ is the charge on an electron), tunneling electrons may lose their energy through the spin-flip processes and tunnel inelastically [13–15]. The threshold is represented by a steplike increase in $dI/dV$ at $E/e$. The Zeeman splitting $\Delta = g\mu_B B$, where $\mu_B$ is the Bohr magneton and $g$ is the Landé factor in the direction perpendicular to the molecular plane, allows the spin-flip excitation at an energy proportional to the applied magnetic field $B$. Fitting the data to a line gives $g = 1.88$ [Fig. 2(d)], which is in good agreement with the ESR measurement [21].

We subsequently detect the spin excitations of the chain-like stacks formed by the CoPc molecules from the second to the fifth layers [Fig. 1(e)] by STS measurements. A magnetic field of 1.5 T was applied to completely quench the superconductive state of Pb. Figure 3(a) shows the $dI/dV$ spectrum at the center (Co$^{2+}$ ion) of a CoPc molecule in the third monolayers. The inelastic tunneling feature [indicated by arrows in Fig. 3(a)] is clearly noted. The single step in Fig. 3(a) splits into three distinct steps [Fig. 3(b)] under magnetic field, suggesting that the observed IETS originates from the antiferromagnetic coupling [22] between two adjacent CoPc molecules in a chain. The split steps correspond to the transitions from the singlet ground state.
where excitations can be well described by the Heisenberg junction under voltage reversal \[23\]. The observed spin-flip voltage, possibly due to the asymmetry of the tunneling IETS signals are visible at only one polarity of the bias barrier height less than 1 meV. The observed antiferromagnetic ordering of the molecular chain is a result of the superexchange interaction, which has been proposed previously to explain the magnetism in MnPc \[24,25\]. The superexchange interaction arises when an electron of the well-developed \(\pi\) system of phthalocyanine ring hops to the \(d_\perp\) orbital of a Co\(^{2+}\) ion and the remaining unpaired electron on the \(\pi\) orbital enters into a direct exchange with the \(d_\perp\) orbital of another Co\(^{2+}\) [Figs. 4(a) and 4(b)]. As a result, the two adjacent Co\(^{2+}\) ions are magnetically linked.

We can resolve the specific molecular orbitals that are involved in the superexchange interaction using the spin-flip imaging together with the first-principles simulation. The bridging orbital in superexchange is magnetically coupled to the central Co\(^{2+}\) ion. Therefore, the local electronic density of states of the bridging orbital, which is detected by STS, can be visualized by the \(dI/dV\) mapping when the dc bias voltage was fixed at the conductance step [see the spectra in Fig. 4(c)]. The obtained spatial mapping of the inelastic tunneling channels [Fig. 4(d)] is considerably distorted from the \(D_{4h}\) symmetry of a CoPc molecule: the charge density is reduced at the benzene ring adjacent to the intervening N atom [indicated by a dashed circle in Fig. 4(d)].

To identify the bridging orbital, we carried out the structural optimizations and total-energy calculations using the DMol\(^3\) package \[26,27\] within the spin-polarized density functional formalism. The electronic structure of two interacting CoPc molecules indicates that only one orbital with \(E_g\)-like symmetry [Fig. 4(e)] can reproduce the spatial distribution of electron density in Fig. 4(d). The overall shape of the \(dI/dV\) mapping agrees well with that of the \(E_g\)-like orbital, although no details (such as the nodal

\[
H = J \sum_{i=1}^{N-1} S_i \cdot S_{i+1} \tag{1}
\]

where \(S_i\) is the spin for the \(i\)th site, \(J\) is the exchange parameter and \(N\) is the number of molecules in the chain. A positive \(J\) value corresponds to an antiferromagnetic coupling. Figures 3(c) and 3(e) show the excitation spectra calculated by diagonalizing Eq. (1) with \(S = 1/2\). The exchange parameter \(J \sim 18\) meV is obtained by comparing the threshold voltages in Figs. 3(a) and 3(d) with the excitation energies of the Heisenberg chain (Table I). \(J\) may vary by 10\% for different molecules due to the inhomogeneity in the molecular film. All the detectable IETS steps follow the selection rule that \(|\Delta S_e| = 0\) or 1, where \(S_e\) is the total spin of the chain. The interchain interaction, dominated by noncovalent binding forces, has negligible effect on the magnetic coupling: similar spectra were obtained on a molecule that was dragged out of the ordered molecular layer and placed at any equivalent stacking positions by the STM tip.

### Table I. Comparison of the spin excitation energies observed by IETS with the calculation based on the Heisenberg model.

<table>
<thead>
<tr>
<th>(N)</th>
<th>2</th>
<th>3</th>
<th>4</th>
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<tbody>
<tr>
<td>1st excitation</td>
<td>IETS</td>
<td>18 ± 2</td>
<td>19 ± 2</td>
</tr>
<tr>
<td></td>
<td>model</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>2nd excitation</td>
<td>IETS</td>
<td>28 ± 2</td>
<td>25 ± 2</td>
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planes) can be resolved due to the spatial resolution limit of STM. The theoretical analysis and experimental measurement suggest that the superexchange pathway involves an \(E_g\) orbital of the \(\pi\) system of the phthalocyanine ring, the \(3d_{z^2}\) of the same molecule, and the \(3d_{z^2}\) of the neighboring molecule.

Molecular magnetic materials show great potential in spin-based electronics and quantum information technology\(^{[28–30]}\) as a result of the rich structure of organic chemistry. However, the structure-property relations turn out to be remarkably intricate. The spin-flip spectroscopy and microscopy reported here provide direct information of spin distribution and coupling, and enable our study and understanding of molecular magnetism down to the single molecular level. The information is of great importance for rational design of molecular magnetic materials with desired properties.

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\[\text{FIG. 4 (color online). Superexchange mechanism.}\]

(a) Illustration of the superexchange interaction in a molecular chain. (b) Spin configuration in superexchange. The bridging N atom is marked by a dot. The nodal plane (dashed line) of the \(E_g\) orbital passes through two pyrrole N atoms and the central Co\(^{2+}\) ion. (c) The spectra at different locations of the molecule. (d) Spin-flip image of a CoPc molecule on the third layer at \(T = 0.4\) K. The bias voltage was fixed at \(-17.2\) mV [indicated by arrows in (c)] during mapping. The mapping with positive bias has similar shape, but less contrast. The modulation was 2 mV at 799 Hz. The molecular structure is superimposed on the image. The dashed circle indicates the bridging N atom. (e) Charge density of \(E_g\) orbital yielded by the first-principles calculation.

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\[^{[1]}\] H. A. Kramers, Physica (Amsterdam) 1, 182 (1934).


\[^{[20]}\] A. Zhao \textit{et al.}, Science 309, 1542 (2005).


\[^{[22]}\] A ferromagnetic ground state can not lead to the explicit splitting in Fig. 3(b) at the temperature of 0.4 K.


