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Spatially Extended Kondo State in Magnetic Molecules Induced by Interfacial Charge Transfer

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An extensive redistribution of spin density in TBrPP-Co molecules adsorbed on a Cu(111) surface is investigated by monitoring Kondo resonances at different locations on single molecules. Remarkably, the width of the Kondo resonance is found to be much larger on the organic ligands than on the central cobalt atom—reflecting enhanced spin-electron interactions on molecular orbitals. This unusual effect is explained by means of first-principles and numerical renormalization-group calculations highlighting the possibility to engineer spin polarization by exploiting interfacial charge transfer.

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Molecular spintronics is an emergent field and a key challenge for future applications lies in probing and controlling the spin state of the molecules [1–16]. Recently, it was shown that charge-transfer processes can lead to the formation of novel states including magnetic [2], semiconducting [17] and even superconducting [18] states. The Kondo effect, originated from a many body screening of a magnetic moment by host electrons, has been studied in several molecular systems [1–16,19]. However, the effect of organic ligands and interfacial charge transfer on the Kondo state are nontrivial, and critical questions remain unanswered. The Kondo temperature ($T_K$), a measure of spin-electron interaction strength, can be significantly higher for molecules [5,6,12–16] than magnetic atoms [7–11] on metal surfaces although these molecules host only one spin-active atom. In the gas phase, the TBrPP-Co [5, 10, 15, 20-Tetrakis-(4-bromophenyl)-porphyrin-cobalt] molecules have their spin mainly localized at the Co atom. Contrary to this we will show that an interfacial charge-transfer process dramatically alters the spin distribution of the molecule when it is adsorbed on a Cu(111) surface and the entire molecule becomes spin active. This is a direct consequence of the ligands acquiring a spin polarization in competition with the spin density of the metal center.

The TBrPP-Co adsorbed on Cu(111) [6,15] is an excellent model system to investigate spin polarization, the effect of molecular orbitals in the Kondo state, and interfacial charge-transfer processes. TBrPP-Co has a porphyrin unit with a cobalt (Co) atom caged at its center [Fig. 1(a)]. The experiments were conducted using a custom-built low-temperature scanning tunneling microscope (STM) system operated in pressures below $4 \times 10^{-11}$ Torr and at 6 K. The Cu(111) sample was cleaned by repeated cycles of Ne ion sputtering and annealing to 800 K. A monolayer coverage of TBrPP-Co was vacuum deposited on a clean Cu(111) surface held at $\sim 120$ K that was further cooled to 6 K for measurements.

STM images [Fig. 1(b)] show the TBrPP-Co molecules on Cu(111) with four pronounced lobes. The TBrPP-Co is positioned on Cu(111) with its central Co atom directly located on top of a surface Cu atom and forms ordered ribbonlike islands [20]. The Kondo state of the molecules can be directly probed via $dI/dV$ tunneling spectroscopy, which reveals a prominent feature near zero bias. The $dI/dV$ tunneling spectroscopy and spectroscopic images are recorded with a lock-in amplifier by adding a 1 mV ac modulation at 720 Hz. The measured Kondo resonances are fitted by the Ujsaghy’s formula [19]. The $T_K$ at the center of a TBrPP-Co inside a self-assembled molecular layer is $\sim 105$ K [6]. Intuitively, one would expect the Kondo resonance to be stronger at the Co atom location because it is the only spin-active atom caged in the molecule. Surprisingly, we observe the Kondo resonance not only at the center but also throughout the entire porphyrin ring. This is confirmed unequivocally by a Kondo map ($dI/dV$ image, Fig. 2) acquired at a 5 mV energy window. The $dI/dV$ data reveal the Kondo state as a dip at $\sim \pm 25$ mV around the Fermi level. Accordingly, the spectroscopic image shows a depression in the two dimensional spectral region over which the Kondo signature is observed. The blue and black regions in Fig. 2(b) represent the Kondo map of a molecule inside a molecular layer, associated with the simultaneously acquired STM image [Fig. 2(a)]. The change in contrast, i.e., blue and black, is due to the variation of the $dI/dV$ curve slope and it does not necessarily represent the changes in $T_K$. To accurately measure the $T_K$ at each location, it is imperative to acquire a full spectrum (Fig. 3). The $dI/dV$ map in Fig. 2(b) clearly reveals that the entire porphyrin exhibits a Kondo signal. It is worth noting that a similar phenomenon is observed in isolated molecules on Cu(111) [20] and thus the observed Kondo phenomenon is driven by the molecule-substrate interactions, rather than by in-plane molecular interactions from self-organization.
The variation of $T_K$ across the molecule is clearly evident from the tunneling spectroscopy data measured along two outward paths: a diagonal (path 1, towards a bromophenyl unit) and across the molecule (path 2, along a Co-N bond), starting from the molecule center [Fig. 3(a)]. These $dI/dV$ spectra reveal the Kondo resonance to have higher $T_K$ values on the ring than at the center of the molecule [Fig. 3(b) and 3(c)]. The $T_K$ increases from 108 ± 5 K to 212 ± 6 K for path 1, and from 107 ± 4 K to 149 ± 3 K for path 2 as the tip is moved away from the molecule center [Fig. 3(d)]. Remarkably, the highest $T_K$ is found when the STM tip is located over a protruding lobe of the molecule, i.e., near a bromophenyl unit.

To understand the varied Kondo resonance across the molecule, we perform density functional theory (DFT) calculations [21] using the Perdew-Burke-Ernzerhof scheme [22]. In addition, a Hubbard-like potential energy term [23,24] is employed, which can greatly improve DFT descriptions of the transition-metal complexes [25–27]. A periodic boundary condition, plane wave basis, and an ultrasoft pseudopotential code are used for the computations. The pseudopotentials include both 3d and 4s orbitals in the valence for the Co and Cu. In both cases, the Hubbard $U$ is determined from a self-consistent linear-response procedure on the full system [25,26]; the calculated values for both gas-phase and adsorbed molecules are quite similar at 4.9 and 5.4 eV, respectively. We optimize the structures of both the isolated TBrPP-[Co,Cu] and the molecule-Cu(111) slab complexes. In the gas phase, the phenyl rings are constrained to lie in the plane of the porphyrin base to facilitate comparison to the molecule-slab complex, where a planar molecule geometry is preferred. For the molecule-Cu(111) slab, both the molecule and its relative distance to the surface (on average 2.5 Å) are optimized. The geometry optimization also allows the molecule to laterally adjust on Cu(111) and the most optimum geometry is achieved when the Co atom is located on top of a surface Cu atom (Fig. 4). Thus, the DFT result independently confirms the experimental adsorption geometry [20].

In the gas phase, the TBrPP-Co molecule has its spin density localized at the $3d^7$ Co(II) center (magnetic moment; $\mu_B = 1.08 \mu_B$) as expected [Fig. 4(a)]. However, when the molecule is adsorbed on the Cu(111) surface, the spin density delocalizes over the entire molecule with an actual decrease at the Co site, which becomes a $3d^8$ Co(I) state (magnetic moment; $0.06 \mu_B$). Now, the sites of greatest spin density in the molecule become the carbon atoms that connect to the bromophenyls [Fig. 4(b)], while portions of the pyrrole groups still exhibit spin densities about half as large. Interestingly, the calculations also reveal a sizeable charge transfer from the surface to the molecule [Fig. 4(c)]. The amount of charge transfer is estimated from Löwdin-charge differences, with a net charge increase in the molecule upon complexation of $\sim 2.25$ electrons from the surface ($\sim 0.5$ electrons to the Co and $\sim 1.75$ electrons distributing throughout the ring). The parts of the underlying surface that exhibit greatest charge depletion are the sites under the Co and those along the directions towards the pyrrole groups [Fig. 4(c)]. On the molecule, the greatest
charge increase is seen along the outer porphyrin edge, while the bromines are the only atoms that exhibit a slight depletion in charge upon complexation. In principle, charge transfer from the surface to the porphyrin should also occur in a similar molecule, TBrPP-Cu on Cu(111), where the central Co is replaced with a Cu atom. However, previous experiments [6,15] did not observe Kondo features in this system. For comparison, GGA + U calculations for the TBrPP-Cu on a Cu(111) are performed as well. We find that the majority of the 3d-derived molecular orbitals of the 3d^6 Cu(II) are located well below the surface Fermi level with the exception of a single 3d_x^2 - 3d_y^2 molecular orbital for the minority spin, which lies above the Fermi energy [Fig. 4(e)] [20]. For TBrPP-Co, the Cu(111) atoms in the axial position stabilize the double occupation of a 3dx^2 orbital that is located close to the surface Fermi level and has a maximal overlap with the surface. Charge transfer to the molecule causes the change in the ligand field that induces a transition from 3d^7 Co(II) to 3d^8 Co(I). It also causes the reorganization of the spin density, which is initially localized on the doublet Co (II) center, to delocalize and distribute throughout the porphyrin ring.

The calculated spin densities along the two paths where the $T_K$ values are obtained [Fig. 4(d)] reveal similar trends as in experiment [Fig. 3(d)]: They increase toward the edge of the molecule and then drop passing the edge. Furthermore, the spin density along path 1 is higher than that of path 2, as in the experiment [Fig. 3(d)]. Since $T_K$ depends on the host density of states ‘‘ρ’’ and spin-electron coupling ‘‘J’’ as $k_B T_K \propto e^{-1/\rho J}$, the variation in spin density will vary the spin-electron coupling $J$, and so the $T_K$ will vary accordingly. A quantitative correlation of $T_K$ to the spin density can be extracted utilizing numerical renormalization-group (NRG) method [28,29]. Our NRG calculations take into account the delocalized molecular...
spin obtained from the DFT calculation and also incorporate the integrated densities. This provides an interesting scenario for Kondo physics, as the typical situation is that the magnetic moment of the Kondo impurity resides in a pointlike object. Here, the large molecule extends over several surface atoms, and the variation of the spin density at different locations on the molecule correlates with changes in $T_K$ across it. Although NRG calculations of $T_K$ in porphyrins have found variations with charge transfer [30], the detailed analysis of the spatial dependence seen by STM is beyond the scope of such treatment. Here we use a model where the spatial variation of the Kondo screening is associated with a position-dependent effective antiferromagnetic exchange coupling $J(x)$ between the surface and the molecule. Although $J(x)$ can be written as an exchange integral between metallic and unfilled $d$-like states (and therefore is implicitly associated with the spin density) a detailed derivation of $J(x)$ from first-principles is numerically demanding and lies beyond the scope of this work. Instead, guided by the DFT calculations, we assume the system can be described by an effective single-channel spin-1/2 Kondo model where the exchange coupling is modulated by the spin density as $J(x) = J_0 + A n_{DFT}(x)$. Here, $J_0$ and $A$ are the fitting parameters, and $n_{DFT}(x)$ is shown in Fig. 4(d). Using $J(x)$ as an input, $T_K$ is obtained from NRG magnetic susceptibility curves assuming a constant metallic density of states [28]:

$$\rho(x) = (2D)^{-1}.$$  

The band-discretization parameter ($\Lambda$) is fixed at $\Lambda = 2.5$, and up to 1000 states are kept on each NRG iteration. We obtain $\rho A = 0.2, \rho J_0 = 0.15$, and for a characteristic Cu half bandwidth, $D = 11$ eV. This two-parameter fit is able to describe the entire data set. The resulting position-dependent $T_K$ values are consistent with the experimental measurements [Fig. 4(g)] thereby confirming the DFT results. This excellent quantitative agreement supports the conclusion of $T_K$ increasing over the porphyrin as the direct result of the enhanced spin density in the molecular orbital.

In summary, we show that the spin polarization in a metallo-porphyrin (TBrPP-Co) can drastically change due to an interfacial charge transfer after molecular adsorption on a metal surface, where the macrocycle ring becomes spin active. This finding further illustrates that the interfacial charge transfer can dramatically affect the magnetic behavior of molecules, which could be used to tailor novel molecular complexes for future spintronic applications including spin injection and spin filtering processes. This work also paves the way for other experiments like x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) to study the magnetism of this molecular system.

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