Reversible Change of the Spin State in a Manganese Phthalocyanine by Coordination of CO Molecule

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We show that the magnetic state of individual manganese phthalocyanine (MnPc) molecules on a Bi(110) surface is modified when the Mn2+ center coordinates to CO molecules adsorbed on top. Using scanning tunneling spectroscopy we identified this change in magnetic properties from the broadening of a Kondo-related zero-bias anomaly when the CO-MnPc complex is formed. The original magnetic state can be recovered by selective desorption of individual CO molecules. First principles calculations show that the CO molecule reduces the spin of the adsorbed MnPc from $S = 1$ to $S = 1/2$ and strongly modifies the respective screening channels, driving a transition from an underscreened Kondo state to a state of mixed valence.

Control over the magnetic moment of a molecule and its interaction with a substrate is a key issue in the emerging field of molecular spintronics [1]. In metal-phthalocyanines and metal-porphyrins the metal center is usually coordinatively unsaturated and presents a local reactive site, which opens a unique possibility of controlling the magnetic moment *in situ* by external chemical stimuli [2–8]. The axial coordination of small molecules like CO, NO or O_2 to those complexes substantially alters their electronic properties, which has led to a successful implementation of phthalocyanines and porphyrins in gas sensors [9,10]. Studies specifically addressing the magnetic state are, however, scarce. Only recently it has been shown that the attachment of a NO molecule to a cobalt-tetraphenylporphyrin (CoTPP) quenches its spin due to the oxidation process [6]. The general picture is however more complicated, as the chemical bond to the reactant molecule causes the redistribution of charge in the *d* orbitals of the metal center and modifies the ligand field of the metal ion. This has critical consequences for the magnetic ground state of the complex [7,8]. On metal surfaces, the formation of a new ligand bond may additionally alter the hybridization of molecular and substrate states, thus affecting the electronic and magnetic coupling of the metal ion to the substrate [3–5]. Understanding the response of these effects to the change in chemical coordination is crucial to gain full control over the functionality of the magnetic system.

Here, we show that the magnetic moment of a manganese phthalocyanine (MnPc) molecule [see Fig. 1(a)] on a Bi(110) surface is reduced when coordinated to a CO molecule. Using a combination of a low temperature scanning tunneling microscopy (STM) and density functional theory (DFT) we find, first, that the spin of the MnPc molecule is reduced from $S = 3/2$ to $S = 1$ upon adsorption

and, second, that CO further reduces the spin of the MnPc from $S = 1$ to $S = 1/2$. The change in the magnetic ground state upon CO attachment is detected by the broadening of a characteristic zero-bias anomaly (ZBA). We interpret this broadening as a transition from a Kondo regime, for the bare MnPc on Bi(110), to a regime where charge fluctuations drive the CO-MnPc complex into a mixed valence state. We further show that the original magnetic state of MnPc is recovered after tip-induced desorption of the CO molecule.

Our experiments have been performed in a custom-made STM working in ultrahigh vacuum and at low temperature (5 K). As a semimetal, Bismuth has a low density of states
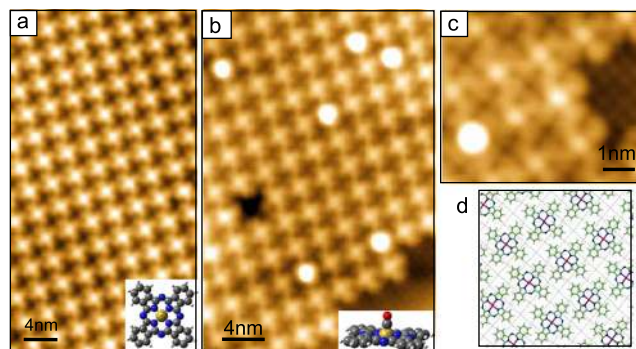

FIG. 1 (color online).   Adsorption of MnPc and CO-MnPc on Bi(110). (a) STM image of a highly ordered MnPc island ($I = 0.2$ nA, $V = 250$ mV, [44]). (b) MnPc island after exposure to CO ($I = 0.1$ nA, $V = 180$ mV). CO-coordinated molecules can be distinguished by different apparent heights. Inset images in (a) and (b) show schematic pictures of the chemical structure of MnPc and CO-MnPc. (c) High resolution STM image of bare and CO-ligated MnPc ($I = 0.1$ nA, $V = -250$ mV). (d) Adsorption model of MnPc on Bi(110).

close to the Fermi level [11], favoring that molecular adsorbates lie weakly affected by the surface [12]. We chose the (110) surface because it additionally presents dangling bonds that can eventually anchor the molecular species to a fixed site, creating a full commensurate layer. We exposed an atomically clean Bi(110) single crystal surface at room temperature to a flux of MnPc molecules (Sigma-Aldrich) thermally sublimed in vacuum from a crucible, and posteriorly cool it down for STM inspection.

On this surface MnPc molecules self-assemble in densely packed islands [Fig. 1(a)]. MnPc molecules appear as a cloverlike protrusion with a bright center corresponding to the metal ion. The adsorption configuration could be established with precision by resolving simultaneously the intramolecular structure of MnPc and atomic structure of the underlying substrate [see e.g., Fig. 1(c)]. As shown schematically in Fig. 1(d), MnPc adsorbs on Bi(110) with its Mn ion located directly on top of a dangling bond of the surface. This configuration suggests the formation of a local bond between MnPc and the dangling bond of the bismuth atom.

The MnPc covered sample was subsequently annealed up to 130 K and exposed to CO gas at partial pressure of 10^{-7} mbar for 90 s. After CO exposure the structure of the molecular islands remains unchanged, but several molecules ($\sim 10\%$) now exhibit larger apparent height [Fig. 1(b)]. We identify these new molecules as CO-ligated MnPc. Figure 1(c) shows a high resolution STM image of the new species embedded in the MnPc island. Similarly to MnPc, the CO-coordinated molecules exhibit fourfold symmetry, with a central protrusion appearing 0.8 Å higher than in the case of MnPc, indicating that a single CO molecule bonds directly to the transition metal ion. We find only singly coordinated CO-MnPc, contrary to previous studies reporting doubly coordinated porphyrin molecules [13,14].

The differential conductance (dI/dV) spectra measured close to E_F reveals a pronounced anomaly at zero bias with a diplike line shape on MnPc [Fig. 2(a)]. We interpret it as a fingerprint of the Kondo effect, as it has been observed before for MnPc and other metal-phthalocyanines on surfaces [15–18]. The zero-bias anomaly exhibits a clear Fano line shape [Figs. 2(a) and 2(b)], commonly observed for Kondo ground states of magnetic adsorbates [19]. Other possible effect which could also cause a zero-bias anomaly, as e.g., inelastic spin flip excitation, have been carefully excluded by studying the temperature dependence of the line shape. A Kondo temperature of $T_K^{MnPc} = 22(\pm 6)$ K can be approximated from a fit to the anomaly's line shape using the Fano equation [20,21].

When similar spectra are measured on CO-MnPc molecules, the ZBA appears much broader, with a slightly different line shape [Fig. 2(a)]. The broadening of the zero-bias resonance indicates that the coordination to CO modifies the magnetic state of the molecule. This modification is
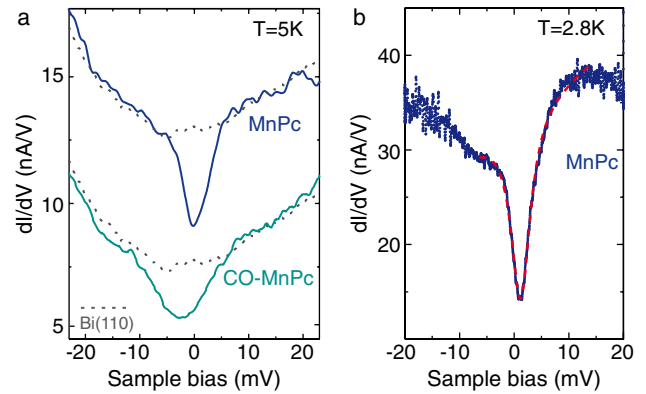

FIG. 2 (color online). (a) dI/dV spectra of MnPc and CO-coordinated MnPc in the bias range close to E_F, showing the zero bias anomaly. The dotted plots are the spectra measured on a bare Bi surface as a reference. (b) Zero-bias feature of MnPc measured at reduced temperature $T = 2.8$ K. The feature exhibits a clear Fano line shape. The dashed line (red) corresponds to the fit by Fano equation.

reversible and can be controlled by selective removal of CO molecules using a STM tip. In order to detach an individual CO from its site, the STM tip was placed over CO-MnPc molecule, the feedback loop was opened and the sample bias was ramped. The resulting current-voltage characteristics are shown in Fig. 3(a). A sudden drop of the tunneling current at a certain threshold voltage indicates detachment of the CO molecule from its coordination
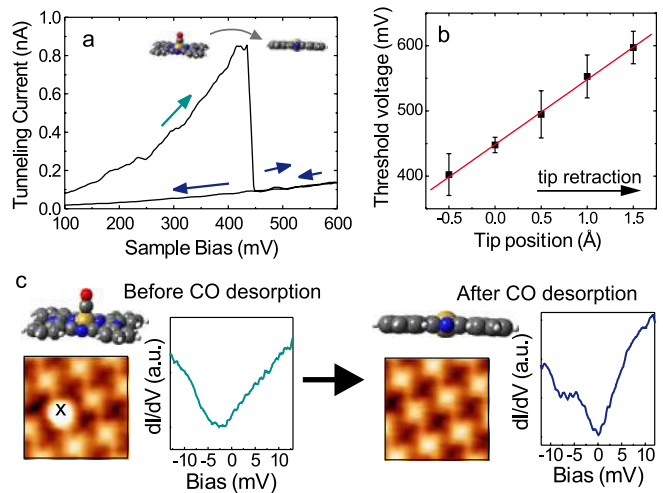

FIG. 3 (color online). Desorption of CO molecules from MnPc islands. (a) I-V characteristics recorded during desorption of CO. A sudden drop in current marks the threshold voltage for CO detachment. (b) Threshold voltage plot versus tip-sample distance. Zero position of the tip corresponds to the feedback parameters $V_f = 100$ mV and $I_f = 100$ pA. Each point is an average of over 30 measurements. Linear fit of the data indicates that the process is driven by electric field of 1 V/nm. (c) STM image and dI/dV spectrum of the molecule before and after controlled CO desorption.

site (in most cases to a new site in a neighbor MnPc molecule). The resulting species recovers the usual clove-like shape and a narrower zero-bias anomaly characteristic of a bare MnPc molecule [Fig. 3(c)]. To establish the underlying mechanism of CO detachment we note that the threshold voltage increases linearly with the distance between the tip and the molecule, as shown in Fig. 3(b). This behavior indicates that the desorption of CO is induced by the electric field at the tunnel junction. A critical value of electric field $\varepsilon \cong 1$ V/nm can be extracted from the slope of the line.

The origin of the zero-bias anomaly on the CO-MnPc molecules cannot be deduced directly from our experiments. One could associate it to a fingerprint of a Kondo ground state with a larger Kondo temperature [$T_K^{\text{CO-MnPc}}$ about 50($\pm$10) K can be fitted]. This is, however, unprovable considering the π-acceptor character of the CO ligand. As a strong field ligand, CO affects the magnetic state of MnPc in two ways: (i) it increases the splitting of the d orbitals, and thus favors the low spin configuration in the complex [8]; (ii) it withdraws the electron density from the bond to the ligand in the opposite coordination site (here the Bi dangling bond) and hence reduces the coupling of the d orbitals to the substrate [2–4]. The latter effect, known in coordination chemistry as trans effect, should reduce the Kondo temperature, contrary to our experimental observation.

To rationalize the experimental results we performed DFT calculations of free and adsorbed MnPc and CO-MnPc molecules. All calculations were performed using the Green's function formalism implemented in our code ANT.G, which interfaces with GAUSSIAN03/09 [22,23]. We used a general gradient approximation (GGA) with the Becke and Perdew-Becke-Ernzerhof exchange-correlation functional [24] in combination with a common double local basis set LANL2DZ [25,26]. Different views of the computed system are shown in Fig. 4(a). The Bi(110) surface was described using two bilayers embedded on a tight-binding Bethe lattice. Following the experimental results (Fig. 1), MnPc and CO-MnPc molecules were placed with the manganese atom directly on top of a Bi atom with an optimized distance to the surface and rotated seven degrees with respect to the high symmetry axis of the Bi(110) surface. In this configuration, four carbon atoms of the phthalocyanine cycle and the central Mn ion are in direct contact with Bi(110) dangling bonds.

We simulate first the electronic and spin configuration of the free MnPc molecule, obtaining results in close agreement with previous studies [27–29]. The molecule has a spin state $S = 3/2$ due to three unpaired electrons localized on the manganese orbitals d_{xz}/d_{yz}, d_{z^2}, and d_{xy}. The d_{xz}/d_{yz} orbitals, hosting three electrons, are strongly hybridized with the phthalocyanine ring of the molecule, masking the atomic character of its localized spin. The d_{xy} orbital hosts the most localized unpaired electron.
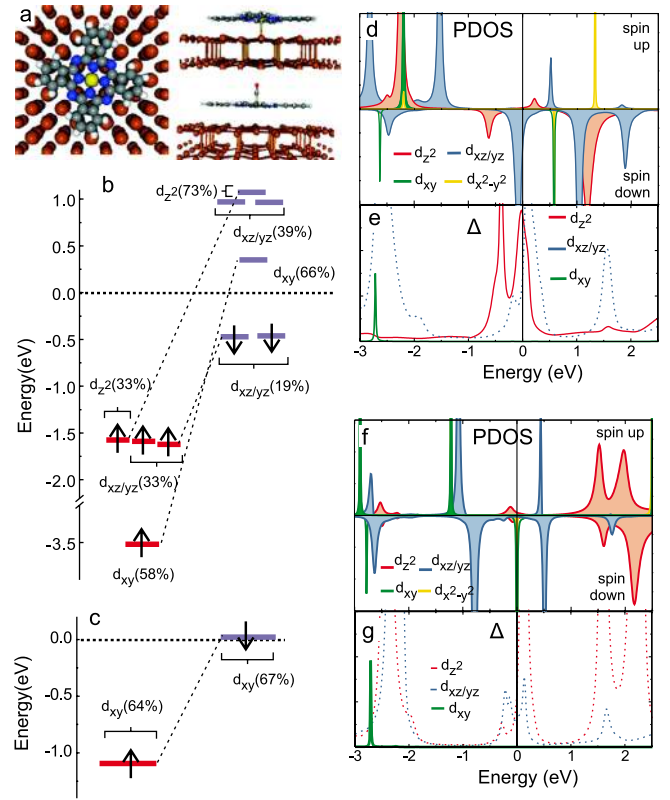

FIG. 4 (color online).   (a) Model of computed system: top view (left) and side view (right) of CO-MnPc (top) and MnPc (bottom). (b),(c) Energy spectrum of adsorbed MnPc (b) and CO-MnPc (c), showing the relevant spin states. Bars in left (right) show the up (down) eigenvalues. The rate in parentheses gives the atomic character of the molecular orbital. (d),(f) Local density of states (PDOS) and (e),(g) hybridization function (Δ) projected on d orbitals of adsorbed MnPc (d),(e) and CO-MnPc (f),(g). The dotted lines in (e) and (g) refer to the orbitals which are not relevant for the magnetism of the molecule.

On the Bi(110) surface, MnPc keeps two unpaired electrons in the d orbitals. The net spin density in the d_{xz} and d_{yz} orbitals is reduced and now results from four occupied molecular orbitals with different atomic contribution depending on the spin orientation [Fig. 4(b)]. In addition, a spin polarization arises in the ligands, opposite to that in the Mn core. Thus, the total spin is reduced to $S = 1$, with two identifiable and localized unpaired electrons in the the d_{z^2} and d_{xy} orbitals [Fig. 4(b)]. We also find that a spin polarized density arises on Bi atoms directly underneath the adsorbed molecule, antiferromagnetically coupled to the spin on the Mn core and thus supporting the emergence of Kondo screening.

The strength of a Kondo screening channel depends, to a first approximation, on the hybridization with the substrate. For MnPc on Bi(110), the spin-polarized local density of states (LDOS) projected on the Mn-d orbitals shows that each orbital hosting an unpaired electron interacts differently with the surface [Fig. 4(d)]. The Mn-d_{z^2} orbital

hybridizes with a dangling bond of Bi and broadens substantially. The d_{xy} orbital appears as narrow peaks in the PDOS spectrum. This indicates that this state remains highly decoupled from the surface, probably to the absence of the z component. The result is that the two unpaired spins are screened via Kondo screening channels with a very different energy scale and, thus, Kondo temperature [17]. Such a scheme suggests an underscreened spin if the experimental temperature lies between the Kondo temperatures of each screening channels [30,31].

In the DFT framework, the orbital-substrate coupling is represented by a hybridization function which allows for a qualitative analysis of the feasible Kondo channels [32,33]. The hybridization function is given by $\mathbf{\Sigma_d}(\omega) = (\omega + \mu)\mathbf{I} - \mathbf{H_d^{KS}} - (\mathbf{G_d}(\omega))^{-1}$, where ω and μ are the energy and the chemical potential, respectively, $\mathbf{I}$ is the identity matrix, $\mathbf{H_d^{KS}}$ is the Kohn-Sham Hamiltonian and $\mathbf{G_d}$ is the one electron Green's function projected onto the d-subshell. Only the imaginary part of the hybridization function is relevant in this work ($\Delta = -\text{Im}\mathbf{\Sigma_d}(\omega)/\pi$). Specifically, the prerequisite for the Kondo effect of the host orbital having a finite coupling to the electron bath is equivalent to having nonzero value of the hybridization function Δ at the Fermi level [34]. The value of Δ calculated for different Mn d orbitals of adsorbed MnPc is shown in Fig. 4(g). The d_{z^2} orbital shows a peak in the hybridization function at the Fermi level indicating that this orbital is strongly screened by the substrate. On the contrary, the hybridization function of the d_{xy} orbital has a zero value in a broad energy window in the vicinity of the Fermi level. These results suggest that the Fano resonance in the spectra of the MnPc molecule is a fingerprint of a Kondo channel opened to screen the d_{z^2} orbital. The unpaired spin of the d_{xy} orbital remains decoupled from the electron bath and this Kondo channel is closed. On the basis of these simulations, we conclude that the MnPc molecule retains part of its magnetic moment on the surface, lying in an underscreened many-body ground state. This is a consequence of the huge disparity in hybridization functions between spin channels, making this system unique in this regard.

Next, we perform a similar analysis for the CO-MnPc molecular complex. The CO molecule stays perpendicular to the MnPc molecular plane [Fig. 4(a)]. It is anchored to the manganese ion via its carbon atom through a synergic π^* backbonding, which strongly modifies the electron population and the spin of the Mn d orbitals in the following manner. The d_{z^2} and the d_{xz}/d_{yz} orbitals lose their magnetic moment: the former is emptied due to the overlap with a nonbonding orbital of CO and the latter is fully occupied due to the bond with the p_x and the p_y orbitals of CO. The spin-resolved LDOS of the adsorbed CO-MnPc projected on the Mn d orbitals [Fig. 4(f)] confirms that the spin-polarization of the d_{z^2} and d_{xz}/d_{yz} orbitals is reduced. Only the d_{xy} orbital appears to be relevant for

the magnetism of the complex. The total spin of the MnPc-CO complex is reduced to $S = 1/2$, stemming from an unpaired electron localized in a molecular orbital with strong atomic d_{xy}-orbital character but a finite contribution from the phthalocyanine cycle [see Fig. 4(c)].

It thus appears clear that the modification of the experimentally observed Kondo resonance upon CO coordination is a direct consequence of the redistribution of the d electrons of the Mn atom. However, the ZBA broadening cannot be understood as an increase in the Kondo screening because the responsible level is very localized. As seen in Fig. 4(g), the d_{xy} hybridization function is zero in the vicinity of the Fermi level, which confirms that also now no Kondo effect can be mediated by this orbital.

This apparent inconsistency with the experimental observations can be bypassed by noting that the PDOS on the d_{xy} orbital shows a highly localized branch pinned at the Fermi level. This state thus belongs to the lowest unoccupied orbital of the molecule (LUMO), and is the only one responsible for the chemical potential lineup between the molecule and the substrate [35]. In these circumstances, charge fluctuations are expected to occur at the d_{xy} orbital. When electronic correlations are considered, a mixed-valence regime is likely to emerge, as it is known for the f-electron compounds [34]. In this situation, one expects a resonance to appear in the differential conductance spectra at zero bias, similar to that in the Kondo regime but characterized by a larger width [36,37]. It is interesting to note that the small hybridization with the surface prevents the finite spin in the d_{xy} orbital from quenching, in contrast with the scenario reported in related systems [38,39]. This allows for a many-body correlated state to emerge.

Finally, we comment on the possible role of the surface states in the screening process on Bi(110). As a semimetal, bismuth is characterized by a low density of bulk states at the Fermi level; its surfaces are, however, strongly metallic due to the presence of the surface states. Therefore, the Kondo effect on bismuth can be expected to involve surface states rather than bulk states. However, strong spin-orbit coupling induces the spin polarization of the surface states through the Rahsba effect [11]; the concept of screening in such system is not straightforward [40]. The Kondo effect involving the chiral spin states has been recently intensively discussed in the context of topological insulators [41–43] and can be understood assuming a complex structure of the Kondo cloud with a nontrivial spatial and spin dependence [43].

In summary, we have demonstrated that the magnetic ground state of individual metal-organic molecules can be reversibly modified by chemical coordination to external molecular species acting as ligands. Using a combination of low-energy scanning tunneling spectra and *ab initio* calculations, we find that the bonding of a CO molecule to the Mn^{2+} center of MnPc molecules on Bi(110) leads to

a substantial modification of its spin state. Our results indicate that the chemically induced magnetic transition corresponds to a change from a high-spin underscreened Kondo state to a mixed-valence state, where charge fluctuations destroy the spin 1/2 state of the CO-MnPc complex. Our results thus emphasize the ultimate limits of manipulating magnetic states of individual molecules by using a combination of tunneling electrons and chemical control over the molecular spin, which could facilitate molecular scale patterning of magnetic motifs in molecular thin films.

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