Resolving the unpaired-electron orbital distribution in a stable organic radical by Kondo resonance mapping

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Abstract: The adsorption geometry and the electronic structure of a Blatter radical derivative on a gold surface were investigated by a combination of high-resolution noncontact atomic force microscopy and scanning tunneling microscopy. While the hybridization with the substrate hinders direct access to the molecular states, we show that the unpaired-electron orbital can be probed with Angstrom resolution by mapping the spatial distribution of the Kondo resonance. The Blatter derivative features a peculiar delocalization of the unpaired electron orbital over some but not all moieties of the molecule, such that the Kondo signature can be related to the spatial fingerprint of the orbital. We observe a direct correspondence between these two quantities, including a pronounced nodal plane structure. Finally, we demonstrate that the spatial signature of the Kondo resonance also persists upon non-covalent dimerization of molecules.

The low spin-orbit coupling and hyperfine interaction in carbon-based materials allows the achievement of long spin coherence lifetimes[1–3] which are crucial for spin-based information processing. In this context, the development of synthetic methodologies capable of stabilizing organic radicals under ambient conditions provides new routes towards applications in molecular spintronics.[4–6] The stabilization of the radical species is typically achieved by means of steric protection of the reactive site, or through spatial delocalization of the lone electron orbital.[7–9] In this way, the spatial extent of the unpaired electron orbital can be engineered through chemical synthesis. This approach can then be used to tune the coupling to neighbors and electrodes.

Recently, Scanning Tunneling Microscopy (STM) has been applied to the study of several organic radicals deposited on metal surfaces.[10,11,20–24,12–19] In Scanning Tunneling Spectroscopy (STS) experiments, the presence of an unpaired electron can be detected through the measurement of the Kondo resonance, originating from the interaction between the unpaired electron spin localized on the molecule and the conduction electrons of a nonmagnetic substrate.[25,26] However, in most cases, the radical character of the molecule has been achieved through atomic manipulation and/or charge transfer from the surface, representing a non-scalable approach. Instead, less attention has been devoted to the study of stable organic radicals,[16,20,22,27–29] which make use of the possibilities enabled by chemical design. Among this class of open-shell systems, Blatter radicals exhibit a strongly delocalized unpaired electron orbital, resulting in a pronounced chemical stability even under ambient conditions.[9,30,31] Recent studies revealed that the open-shell configuration is retained upon adsorption on a Au(111) surface,[32] indicating that the molecule-metal and molecule-molecule interactions do not affect the radical character.

Here, we study the adsorption geometry and the electronic structure of a Blatter radical derivative adsorbed on Au(111) at the single molecule level using ultra-high vacuum (UHV) scanning probe microscopy and spectroscopy. Although the radical unpaired electron is strongly delocalized, its distribution does not extend over the entire molecule. STM and STS allow us to probe the spatial distribution of the Kondo resonance. These measurements therefore enable the spatial distribution of the Singly Occupied Molecular Orbital (SOMO) to be obtained, where a distinct nodal plane structure is also resolved. To unambiguously assign the spatial fingerprint of the Kondo resonance to the molecular structure, the three dimensional molecular structure is resolved by Atomic Force

Microscopy (AFM) with CO functionalized tips.[33] Finally, we reveal the presence of a specific bonding motif upon self assembly, consistent with molecular dipole-dipole interactions. The persistence of the Kondo resonance in the STS data indicates that the inter-molecular coupling does not affect the open-shell configuration of the molecule.

Figure 1a presents the chemical structure of a Blatter radical with two gold-binding thiomethyl groups (-SMe). The synthesis of this derivative was reported elsewhere.[32] An STM image of the Blatter radical deposited on Au(111) at 7 K is shown in Figure 1b. Detailed insights of the adsorption geometry are provided by AFM images acquired with a CO-functionalized tip.[33] In Figure 1c, the large bright feature seen due to a repulsive contribution can be ascribed to the phenyl ring bent out-of-plane because of steric hindrance.[34] Other pronounced features correspond to the two thiomethyl groups. Since the sulfur atoms are expected to bind through a donor-acceptor interaction directly to the gold surface,[35] the repulsive AFM features are assigned to the methyl groups, in particular to a C H bond pointing out of the surface towards vacuum.[36] The rest of the structure, lying closer to the surface, can be better observed in the corresponding high-pass (Laplace) filtered image (Figure 1d), where the benzotriazinyl core is clearly resolved.

Figure 2a shows a low-bias STM image (V = 5 mV) of an individual molecule, presenting pronounced intramolecular features. Notably, the presence of well-defined nodal planes is unusual in STM images of molecules adsorbed on metal surfaces. In fact, while orbital imaging has been demonstrated on weakly interacting metals such as Au(111),[37] hybridization with the substrate usually induces a pronounced blurring in the contrast of low-bias STM images. Conversely, the sharp features observed in Figure 2a indicate the presence of an additional channel of conductance, possibly related to the open-shell configuration of the Blatter radical. To elucidate this point, we investigated the electronic structure by performing spatially resolved STS. This allows for the distinguishing of specific electronic states and resonances from topographic effects that contribute to the overall contrast shown in Figure 2a. Tunneling conductance (dI/dV) spectra were acquired while placing the STM tip at different positions above the molecule (Figure 2b). The spectrum recorded at the center of the molecule (blue) exhibits a zero-bias peak (ZBP). Similar features were observed also in the spectra acquired above the tilted phenyl and one of the thiomethyl groups (indicated in yellow and orange, respectively). This feature is however absent over the other SMe group (violet). Given the open-shell configuration of the molecule,[9] the origin of the observed ZBPs can be ascribed to Kondo resonances.[32] The spectra in Figure 2b were fit with a Fano function:

where the fitting parameters are q (peak asymmetry), A and B (background and peak amplitudes, respectively), EK is the energy position of the resonance (relative to the Fermi level), and $2\Gamma(T)$ is the (temperature-dependent) full width at half maximum (FWHM) of the Kondo resonance. e denotes the elementary charge. The fits are shown on the experimental spectra in Figure 2b as solid lines. Following the approach for a Kondo impurity in the Fermi liquid regime, introduced by Nagaoka et al.[38], a value of the Kondo temperature (TK) can be extracted from the energy width:

where T is the sample temperature (6.1 K). Using this formula, we obtained a TK value of 26±3 K. In the spectra acquired above the center (blue marker), the thiomethyl group (orange) and tilted phenyl (yellow), shown in Figure 2b, differences in the asymmetry may be due to variation of the quantum interference between the unpaired electron orbital and continuum tunneling channels.[25]

We tentatively ascribe these differences to the non-planar adsorption configuration of the molecule (Figure 1c).

While the Kondo resonance-related ZBP is distributed on different molecular groups, it is absent in the region close to one of the SMe groups (violet marker in Figure 2a). This is in remarkable agreement with the calculated distribution of the SOMO of the Blatter radical in the gas-phase and the corresponding simulated STM image, shown in Figure 2c. The region exhibiting the Kondo resonance matches with the portion of the molecule where the SOMO is localized. This correspondence directly indicates that the SOMO distribution dictates the spatial extension of the spin-metal coupling.

No other spectroscopic feature related to the SOMO level[13,18,39] was observed in the dI/dV spectra acquired over a wider voltage range (Figure 2d). The absence of clear signature in dI/dV arising from tunneling resonantly through the SOMO level may result from an hybridization of the orbitals with the metal surface, leading to such a pronounced broadening of the molecular level[10] that no clear peak might be discernible against the background. While orbital hybridization with the metal substrate generally leads to a mixing of electronic states, the observed enhancement in the spatial resolution shown in Figure 2a arises from the state selectivity of the Kondo resonance, where only the singly occupied orbital contributes to the measured signal. Thus, despite containing topographic features (especially in the top part of the molecule shown in Figure 2a), the low-bias STM image is dominated by the contribution from the Kondo resonance. Interestingly, in addition to the spatial confinement, the nodal plane structure of the orbital involved (Figure 2c) is also imprinted into the Kondo signature (Figure 2a), showing that, despite the orbital level broadening due to hybridization with the metal substrate, the unpaired-electron orbital can be probed with Angstrom resolution through its Kondo resonance. Remarkably, at the moiety, at which the SOMO and consequently also the Kondo resonance has low weight, the STM image contrast does not show a clear nodal plane structure but appears rather washed out, providing further evidence that the nodal-plane structure is a fingerprint of the Kondo resonance imprinted from the singly-occupied orbital.

Finally, we investigate whether intermolecular coupling occurring upon self assembly affects the radical character of this molecule. For this purpose, a sub-monolayer of molecules was imaged after annealing the substrate to 300 K (Figure 3a). Despite the observation of several isolated molecules and small clusters, a large fraction of the molecules form dimers in which the two molecules are always in the same relative orientation. In Figure 3b, a high-resolution image of a dimer is presented. The low-bias STM image (V = 5 mV) exhibits sub-molecular features, nearly identical to the monomers shown in Figure 2a. This indicates that the open shell configuration of the Blatter radical is preserved even in these dimers. Given the mild annealing temperature (300 K) and the large intermolecular distance (see models in Figure 3c), we can rule out that the dimers are covalently bonded together.[40] We therefore attribute dimer formation to a dipole-dipole interaction,[41] resulting from the asymmetric charge distribution. This gives rise to a large in plane electric dipole ($\mu \approx 2.7$ D), as evidenced by the molecular electrostatic potential (MEP) surfaces shown in Figure 3d, which steers the antiparallel alignment of molecular couples with the same chirality. A confirmation of the open shell character retained by the Blatter radical upon non-covalent dimerization is provided by the dI/dV spectrum, acquired above the center of one of the molecules (Figure 3c); again, an asymmetric ZBP is clearly visible. The spectrum closely resembles the one acquired on isolated molecules and gives a TK of 21 K. The decrease of TK upon dimerization (from 26 to 21 K, for the spectra acquired above the molecule's center) has been observed before in porphyrin assemblies on Cu(111).[42] In small clusters, the presence of neighboring molecules leads to a reduction of the surface state density, which is expected to lower the degree of coupling with the substrate being proposed as an explanation for the observed reduction of TK.[42]

In conclusion, we investigated the geometry and the electronic structure of the Blatter radical deposited on Au(111). The three dimensional structure has been resolved by means of AFM, allowing us to assign spin-related spectroscopic features to the molecular structure. We demonstrated that the extent of the Kondo resonance follows the spatial distribution of the unpaired electron and even exhibits the nodal plane structure of the corresponding orbital. These results provide direct proof of the state-selectivity of the Kondo resonance in accessing the molecular state responsible for the spin-metal coupling. This allows an enhanced imaging resolution to be obtained despite hybridization of the orbital with the metal substrate. Notably, such spatial signature persists also upon non-covalent dimerization of molecules, where the asymmetric charge distribution gives rise to a specific molecular arrangement. These results provide insights into the molecule-metal and molecule-molecule interactions of the Blatter radicals, shedding light on the coupling of the molecular radical with the environment.

Experimental Section

The Au(111) surface was prepared by repeated cycles of Ne+ sputtering (1.5 keV) and annealing to 830 K. Low temperature experiments were carried out with a home-built combined scanning tunneling / atomic force microscope, in ultrahigh vacuum ($p \approx 5\times10^{-11}$ mbar) at a temperature of 6.1 K. The atomic force microscope's qPlus tuning fork[43] was operated in the frequency modulation mode with sub-angstrom oscillation amplitudes (50 pm). Bias voltages are given as sample bias with respect to the tip. A small amount of CO was dosed onto the surface for tip functionalization. NaCl islands were grown to facilitate the pick-up of CO molecules. Bias voltages are given as sample bias with respect to the tip. Positive constant-height offsets Δz correspond to a distance decrease with respect to the STM set-point above the clean gold. The molecules were deposited onto the sample kept at ≈ 7 K inside the microscope. STS data (dI/dV) were acquired using lock-in detection of the tunnel current I by adding a sinusoidal voltage modulation Vmod at 185 Hz to the sample bias voltage V.

Calculations for the gas-phase molecule were performed using ORCA (4.0.1)[44] program package. The B3LYP density functional in combination with the Correlation-consistent Double-zeta (cc pVTZ) basis set was used.

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