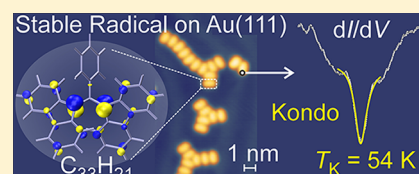


Surface-Supported Hydrocarbon π Radicals Show Kondo Behavior

Stefan Müllegger,* Mohammad Rashidi, Michael Fattinger, and Reinhold Koch

Institute of Semiconductor and Solid State Physics, Johannes Kepler University Linz, Altenberger Strasse 69, 4040 Linz, Austria

ABSTRACT: Stable hydrocarbon radicals are utilized as spin standards and prototype metal-free molecular magnets able to withstand ambient conditions. Our study presents experimental results obtained with submolecular resolution by scanning tunneling microscopy and spectroscopy from monomers and dimers of stable hydrocarbon π radicals adsorbed on the Au(111) surface at 7–50 K. We provide conclusive evidence of the preservation of the radical spin-1/2 state, aiming to establish α,γ -bisdiphenylene- β -phenylallyl (BDPA) on Au(111) as a novel Kondo system, where the impurity spin is localized in a metal-free π molecular orbital of a neutral radical state in gas phase preserved on a metal support.



■ INTRODUCTION

Since the first observations by Gomberg,^{1,2} stable free radicals are desirable spin standards, polarizing agents, and building blocks of carbon-based magnetic systems.^{3,4} Purely hydrocarbon stable radicals are gaining ground as versatile model systems for the development of novel π -magnetic systems^{3,5,6} along with other benzenoid compounds like graphene flakes,⁷ carbon nanotubes,⁸ fullerenes,⁹ and π -conjugated polymers.¹⁰ Recently, the real-space study of single unpaired electron spins on the atomic scale has become a reality with the help of electron-transport experiments in surface-supported metal impurities^{11,12} and metalorganic molecules^{13–15} inside the tunnel junction of a scanning tunneling microscope (STM). Such experiments utilize the Kondo effect,^{16,17} that is, the screening of a localized electron spin by delocalized conduction electrons at sufficiently low temperatures, as experimental proof of the spin system maintaining its unpaired electron.

Here we report on a low-temperature STM study of a new type of Kondo system based on metal-free stable hydrocarbon π radicals, BDPA (α,γ -bisdiphenylene- β -phenylallyl)¹⁸ (Figure 1a), that organize by self-assembly into different 1-D nanostructures on a Au(111) surface while maintaining their spin-1/2 state. Our results based on scanning tunneling spectroscopy (STS) reveal the characteristic properties of the surface Kondo effect for BDPA/Au(111) with submolecular resolution for isolated BDPA monomers and dimers. Compared with the monomer with a Kondo temperature, T_K , close to 50 K, an increase in T_K is observed for dimers, suggesting a stabilization of the Kondo state by the radical–radical interaction.

■ EXPERIMENTAL METHODS

BDPA recrystallized in benzene was thermally evaporated in ultrahigh vacuum (UHV) from a quartz crucible at 383 K after thorough degassing at 373 K. The single-crystal Au(111) surface was prepared by repeated cycles of 0.5 keV Ar^+ bombardment and annealing at 720 K. STM and STS experiments were carried out at 5–7 K employing electrochemically etched W tips deoxidized by annealing in UHV. The dI/dV

signal was obtained from the first-harmonic current signal detected by lock-in technique (0.5 to 2 kHz; 5–20 mV sinusoidal peak-to-peak voltage; average of 10 single spectra). Impurity and tip effects were minimized by careful sample preparation and multiple tip formings between the dI/dV experiments, resulting in Au-coated STM tips. Reliable tip performance was established by accurately reproducing the dI/dV signature of the Au(111) surface state from literature.²⁰ dI/dV spectra were recorded under constant-height conditions, the spectroscopic images (dI/dV maps) were simultaneously recorded with constant-current STM topographic imaging.

■ RESULTS AND DISCUSSION

BDPA Self-Assembly on Au(111). Deposition of sub-monolayer coverages of BDPA onto Au(111) at 300 K leads to the self-assembly of regular radical clusters. Details of the structural and electronic properties of BDPA clusters on Au(111) have been recently reported by our group.¹⁹ The STM topograph of Figure 1b shows a $15 \times 15 \text{ nm}^2$ frame of the sample surface. Individual BDPA radicals are imaged as protrusions with a characteristically curved “bean-like” shape. Single isolated BDPA monomers are rarely observed on the sample surface due to an increased surface mobility. Dimers are more stable due to pinning at surface defect sites¹⁹ and constitute the smallest BDPA clusters. Larger clusters are 1-D chains up to several nanometers long that start to grow at trimers with a characteristic three-fold symmetric arrangement acting as nucleation centers for the chain growth. (See Figure 1b.)

Evidence of Kondo Behavior. The resonance energies of BDPA’s frontier molecular orbitals (MOs) have been investigated in detail by our group in ref 19. Figure 1c shows as an example the dI/dV map at the energy of the highest occupied molecular orbital (HOMO). Here we focus on the

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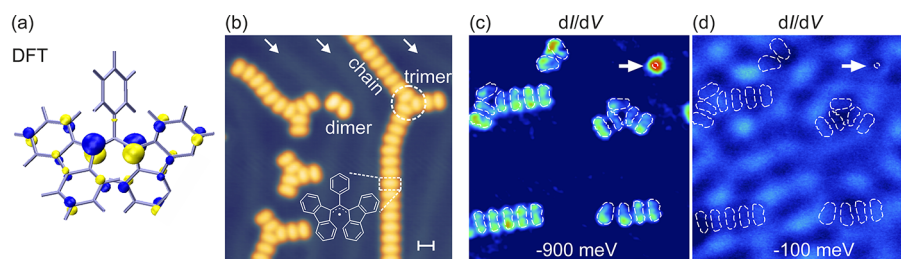


Figure 1. (a) DFT-calculated isodensity representation of the singly occupied molecular orbital (SOMO) of the stable π radical BDPA ($C_{33}H_{21}$) from ref 19. (b) STM topographic image of 0.2 monolayers of BDPA grown at 300 K on the Au(111) surface (+0.5 V, 50 pA, 7 K); scale bar = 1 nm. (c,d) Spectroscopic dI/dV maps at different electron energies ($6 \times 6 \text{ nm}^2$); overlaid contour lines (dashed) mark areas covered by BDPA molecules as extracted from STM topographs; arrows indicate a surface defect.

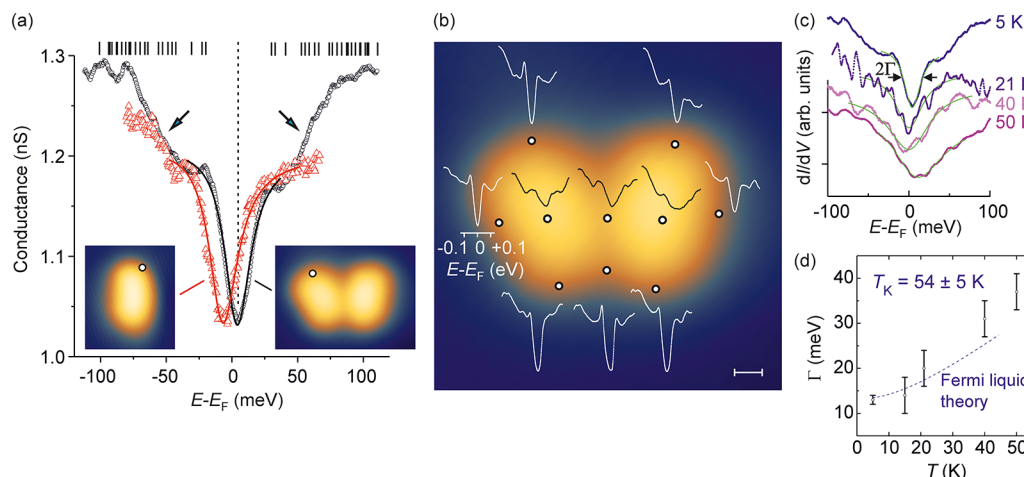


Figure 2. STS results of BDPA on Au(111). (a) dI/dV spectrum of BDPA monomer (red) and a dimer (black) recorded at 5 K over positions marked by circles in the STM topographic insets; the feedback loop has been opened at +1 V, 50 pA, and a z -offset of 70 pm; the zero-bias conductance of pristine Au(111) was calibrated to 1.3 nS; solid lines are numerical Fano fits of the Kondo antiresonance (fit parameters see Table 1); arrows mark broad shoulders attributed to inelastic excitations (details see text); and vertical bars indicate energies of possible collective vibrational modes obtained from DFT calculations relative to the Kondo dip of the dimer marked by the dashed line. (b) dI/dV Kondo spectra over different positions (O) of a BDPA dimer; scale bar = 0.2 nm. (c) dI/dV Kondo spectra of the BDPA dimer at different temperatures; the feedback loop has been opened at +1 V, 50 pA, and a z -offset of 70 pm. (d) Temperature-dependent broadening of the Kondo signal for the BDPA dimer recorded over similar STM tip position close to the rim of BDPA; the dashed line represents best-fit based on the formalism proposed by Nagaoka et al.²²

energy range of $\pm 100 \text{ meV}$ close to E_F , where Kondo features are typically expected. At -100 meV , BDPA is almost invisible in the dI/dV map against the conductance background of the Au(111) surface,¹⁹ where only the standing-wave pattern of the 2-D surface state of Au(111) is observed (Figure 1d). In addition to MO resonances, typical dI/dV spectra of BDPA/Au(111) exhibit a narrow conductance minimum (dip) close to E_F , whose amplitude is significantly larger than the modulation ("ripples") of the surface-state band by the herringbone reconstruction of Au(111).²¹ Figure 2a shows this conductance minimum recorded with the STM tip over a single isolated BDPA monomer (red curve) and a BDPA dimer (black curve). The tip position is marked by a circle (O) in the insets showing the respective STM topographic images. The maximum amplitude of the conductance dip is observed whenever the STM tip is near the rim of BDPA. Amplitudes of up to 20% of the zero-bias conductance of the pristine substrate are observed with our best STM tips (Figure 2a). Over intramolecular positions the conductance dip decreases (Figure 2b). A detailed analysis of our STS results on the conductance minimum confirms a number of characteristic properties of the transmission Kondo effect^{11–14,22} for BDPA/Au(111):

(i) Energetic position: The conductance minimum is centered at an energy offset, $|\Delta E| = E - E_F$, of a few millielectronvolts around E_F (Figure 2a). The width of the signal is larger than the offset, $2\Gamma > \Delta E$, so that it spans over both the filled and empty state regimes, that is, below and above E_F . According to Fermi-liquid theory, the value of ΔE is related to the electron–hole asymmetry.¹⁷ The asymmetry is determined by the alignment of the MO level that is singly occupied (SOMO) relative to E_F and the Coulomb charging energy U that separates SOMO from the singly unoccupied level (SUMO). For BDPA/Au(111), the SOMO was found to lie several hundred millielectronvolts below E_F ,¹⁹ and BDPA exhibits a large U on the order of 1.4 eV.²³ The large U value is responsible for the high stability of the radical state and strongly reduces electron tunneling for the SOMO/SUMO levels in STM experiments (consistent with the small q value obtained from the Fano fits below). This hampers an accurate determination the electron–hole asymmetry by tunneling spectroscopy. We observe $\Delta E < 0$ for monomers and $\Delta E > 0$ for dimers (Table 1), suggesting that ΔE is affected by the presence of neighboring BDPA radicals.

(ii) Spectral shape: The spectral shape of the conductance minimum of Figure 2a is well-fitted by the Fano function²⁴

Table 1. Fano Parameters of BDPA/Au(111)^a

	q (± 0.1)	ΔE (± 0.7 meV)	Γ (± 1 meV)
monomer	-0.15	-5.9	11
dimer	-0.23	+2.3	13

^aFano fit parameters of the BDPA monomer (average of four) and dimer (average of three) adsorbed on Au(111) at 5 K; asymmetry parameter q , energy offset ΔE , and half-width Γ .

(compare experimental spectra with numerical fits shown as black and red solid lines in Figure 2a). The values of the fit parameters are listed in Table 1. In the Fano picture, the shape of the resonance is described by the asymmetry parameter, q . The numerical value of q depends on the quantum mechanical phase difference between different coherent spin-conserving tunneling paths of electrons between STM tip and Kondo system^{25,26} and determines whether a dip (reduced conductance) or peak (increased conductance) is observed. For BDPA/Au(111), we obtain an almost constant value of $q \approx -0.2$ for monomers and dimers. (See Table 1.) The small absolute value of q indicates that electrons tunnel predominantly between the tip and the continuum of substrate states rather than the molecular impurity state.

(iii) Temperature dependence: Their lower surface mobility compared with monomers facilitates the recording of dI/dV spectra of BDPA dimers up to 50 K (Figure 2c). With increasing temperature, the signal width, 2Γ , increases and the amplitude decreases simultaneously, as expected for surface Kondo systems.^{11,12} Numerical values of Γ determined by Fano fits of each spectrum are plotted against the substrate temperature in Figure 2d for the BDPA dimer. We have further analyzed the temperature broadening based on a Fermi liquid description put forward by Nagaoka et al.²² The least-squares fit based on this formalism, $\Gamma = 2((\pi k_B T)^2 + 2(k_B T_K)^2)^{1/2}$, is shown as a dashed curve in Figure 2d and yields a nominal value of $T_K = 54 \pm 5$ K for the BDPA dimer. This value is consistent with the requirement of Fermi liquid theory for the existence of Kondo physics¹⁷ that the width of the resonance, 2Γ , has to be much smaller than the spectral energy of the bare impurity level (see above).

(iv) Vibrational satellites: The conductance minimum is accompanied by two broad shoulders symmetrically offset above and below the Kondo dip (marked by arrows in Figure 2a). The shoulders indicate inelastic excitation of molecular vibrations by the tunneling electrons. This is common for molecule-based Kondo systems, where the impurity orbital is spatially extended and thus sensitive to geometric changes of the molecular backbone.^{13,27} The shoulders in Figure 2a range from ~ 25 to 90 meV above and below the Kondo dip. This is significantly larger than the expected thermal broadening of a single vibrational mode and points to the excitation of a number of different vibrational modes with wave numbers between ~ 200 and 750 cm^{-1} . Most likely, collective backbone vibrations of BDPA are involved because plain C–H vibrations typically exhibit wave numbers higher than 1000 cm^{-1} . This interpretation is supported by density functional theory calculations of BDPA in the gas phase performed previously by our group.¹⁹ The vertical bars in the top part of Figure 2a mark the calculated energies of collective backbone vibrations; they are symmetrically aligned above and below the Kondo minimum of the dimer (marked by dashed line). Indeed, a number of calculated energies lie within the broad symmetric shoulders of the spectrum.

In Figure 2b, the inelastic excitations are not as clearly distinguishable from the Kondo signal as in Figure 2a, which hampers the accurate determination of the Kondo parameters with respect to the precise location over the BDPA molecule. We attribute the spectral deviations to different tip structures, varying adsorption sites, excitation of lateral motion (diffusion) and noise in the dI/dV signal. Nevertheless, Figure 2b evidences considerable variations of the Kondo amplitude over different positions of the radical. The Kondo amplitude of BDPA reaches maximum values close to the rim compared with decreased values over the radical, similar to metal–organic adsorbates with significant spin contributions from the hydrocarbon backbone.^{28,29} The spatial distribution of the Kondo amplitude over the molecule is commonly assigned to the distribution of the unpaired spin in the impurity orbital.²⁹ In that respect, Figure 2b is consistent with the SOMO of BDPA obtained by calculation.¹⁹

Spin and Charge States of BDPA/Au(111). The existence of a Kondo signal indicates that the BDPA radicals remain magnetic after adsorption on Au(111). Our recent electron spin resonance (ESR) experiments on samples with BDPA monolayer coverage on Au(111)/mica substrates have yielded $g = 1.96$ at 7 K.¹⁹ This value is in good agreement with the isotropic g factor of $g = 2.008$ of the BDPA crystalline bulk phase at 4 K and $g = 2.0026$ at room temperature.³⁰ The observed ESR activity of monolayer BDPA/Au(111) together with the small g shift compared with bulk phase suggest that a possible charge transfer from the Au substrate to the adsorbed BDPA is small. This is corroborated by the standing wave pattern of the Au(111) surface state shown in Figure 1d, where we find no evidence of an enhanced electrostatic scattering potential at the BDPA radicals that would indicate a significant charge transfer.³¹ The above results corroborate that the BDPA radicals preserve the initial radical spin-1/2 state upon adsorption on the Au(111) surface.

Surface-State Contribution to Kondo Screening.

Figure 3 illustrates the results of distance-dependent STS measurements along a specific high-symmetry direction of a BDPA dimer. STS spectra were recorded with the STM tip over positions at increasing lateral distance, r , from the center of BDPA, as marked by the circles in Figure 3a. The respective spectra shown in Figure 3b exhibit the characteristic Kondo dip

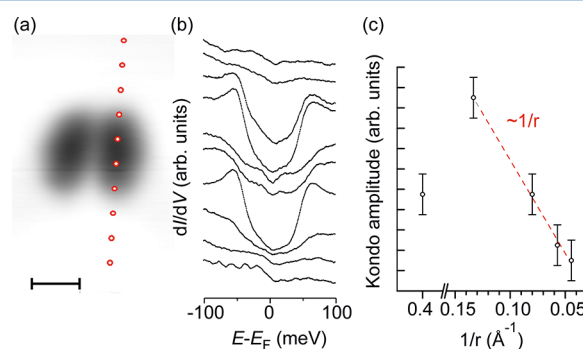


Figure 3. Decay of the Kondo signal with lateral distance. (a) STM topography of BDPA dimer recorded at +1 V and 50 pA; scale bar = 1 nm. (b) dI/dV Kondo spectra recorded at different tip positions marked by the circles in panel a; the feedback loop has been opened at +1 V, 50 pA, and a z -offset of 70 pm. (c) Decay of the Kondo amplitude with increasing lateral distance, r , from the center of BDPA; dashed line is a fit of $1/r$.

even over the pristine Au(111) surface at large lateral distance of up to 1.5 nm from the center of the radical. Outside of BDPA the signal amplitude decreases monotonically according to $1/r$. (See detailed analysis in Figure 3c.) The $1/r$ dependence suggests that 2-D electronic states contribute to Kondo screening.^{26,32} In the present case, this points to the surface-state band of Au(111), which acts as a 2-D electron gas.

Our experimental results indicate that the two BDPAs of a dimer are individual spin-1/2 Kondo systems. Nevertheless, their spins appear to be correlated through the surface-state: The two Kondo screening clouds are so large that they may readily overlap; that is, the two BDPAs of the dimer share part of a common Kondo cloud. This seems to stabilize the individual screened states, as evidenced by the higher T_K of dimers compared with monomers. (See Table 1.)

CONCLUSIONS

In conclusion, our experimental STM and STS results obtained at submolecular resolution from monomers and dimers of stable hydrocarbon π radicals on Au(111) provide conclusive evidence of establishing BDPA/Au(111) as a novel Kondo system, where a radical state in gas-phase is preserved after adsorption on a metal surface.

AUTHOR INFORMATION

Corresponding Author

*E-mail: stefan.muellegger@jku.at. Phone: +43 (0)732 2468 9624.

Notes

The authors declare no competing financial interest.

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