A Single Molecule Kondo Switch: Multistability of Tetracyanoethylene on Cu(111)

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ABSTRACT Single tetracyanoethylene (TCNE) molecules on Cu(111) are reversibly switched among five states by applying voltage pulses with the tip of a scanning tunneling microscope. A pronounced Kondo resonance in tunneling spectroscopy indicates that one of the states is magnetic. Side bands of the Kondo resonance appear at energies which correspond to inter- and intramolecular vibrational modes. Density functional theory suggests that molecular deformation changes the occupancy in TCNE’s molecular orbitals, thus producing the magnetic state.

KEYWORDS Scanning tunneling microscopy, scanning tunneling spectroscopy, organic magnets, charge transfer, Kondo resonance, tetracyanoethylene

The ability of organic molecules to switch between states with distinct electrical or magnetic properties may enable a variety of organic-based information technologies.1 Such switching not only relies on molecular degrees of freedom but also depends on the interaction of the molecule with its local environment. Of interest to the emerging spintronics community is a family of organic semiconductors based on transition metal–tetracyanoethylene (TCNE: (CN)2C≡C(CN)2) complexes, which can serve as a spin injector in devices.2 Though underlying mechanisms are not completely understood, ferromagnetism in V[TCNE]2 for example, persists to 400 K 3 and can be reversibly switched by optical illumination.4

The STM can be used to study the emergence of magnetism in the building blocks of these materials, namely, single molecules.5 On Ag(100), magnetism in V4[TCNE]4 complexes produced a Kondo resonance in tunneling spectroscopy which depended on the number of species in the complex, as well as their bonding geometry.6 Kondo resonances arise from the many-body interaction between a local moment and surrounding conduction electrons.7 It has recently been demonstrated that the many-body interactions can be tuned by changing the local environment8,9 altering chemical composition,10 or deforming molecular structure.11,12 In this Letter, we report scanning tunneling microscopy (STM) studies of single TCNE molecules on Cu(111). Voltage pulses reversibly switch single molecules among any of five distinct states, one of which exhibits a pronounced Kondo resonance in tunneling spectroscopy. Thus, we demonstrate that a magnetic state of single TCNE molecules can be reversibly switched on and off. Our density functional theory (DFT) calculations suggest that this magnetic state is stabilized by a deformation which changes the distribution of charge among molecular orbitals.

All measurements were made with a Createc UHV LT-STM. A Zener-diode mounted at the base plate of the STM was used to vary the STM temperature from 5.3 to 55 K. A clean Cu(111) surface was prepared by repeated Ar+ sputtering and annealing cycles in an ultrahigh vacuum chamber (<10−10 mbar). A cut Ir tip was used to collect all images and spectroscopy. The tip was prepared with field emission and controlled contact with the sample. Auger electron spectroscopy was used to monitor sample cleanliness. TCNE molecules were introduced through a ultrahigh vacuum (UHV) leak valve in situ while the sample is cold (≈5.3 K). Tunneling spectra were collected by adding a ∼1.2 mVrms modulation to the sample voltage at the frequency of 855 Hz; a lock-in amplifier was then used to record the corresponding modulation in tunnel current.

Electronic and structural properties of the TCNE molecule adsorbed on Cu(111) surface were performed with first-principle density functional theory calculated using the SIESTA package.13 Simulated STM images were obtained within a scattering approach along with a semiempirical Hamiltonian using our SPAGS-STM software.14 For these calculations, a unit cell consisting of one TCNE molecule and a Cu(111) slab of three atomic layers (30 Cu atoms per layer) was considered, and both molecule and topmost Cu layer geometries were fully optimized at the DFT level prior to being used in the STM simulations. Electronic structure calculations and STM simulations followed the same procedure as in ref 15.

We find that TCNE adsorbs onto terraces of a cold (5.3 K), Cu(111) surface in five different states, which we label
\(-, /\beta, \gamma, \delta, \text{ and } \varepsilon\)-TCNE (Figures 1 and 2). Analysis of STM images containing 1200 molecules gives a population probability of \((44:19:24:10:3)\), respectively. This probability distribution is not necessarily an indication of relative stability, as it may also be sensitive to details of the adsorption kinetics. We note that the desorption energy \((\sim 5 \text{ eV/TCNE from the DFT calculations discussed below})\) is likely to be much larger than the energy differences between these states, so that all states can be initially populated upon adsorption. On the square lattice of the Cu(100) surface, we only observe \(-\text{TCNE, suggesting that the triangular lattice of the (111) surface provides a more complex adsorption landscape. Adsorption onto the cold surface is necessary to observe these states, so, for example, Wegner et al. found that TCNE adsorbs in a single site on Cu(100) at room temperature.}^5

We are able to reversibly switch single TCNE molecules among these states by applying voltage pulses with the STM tip. Panels a–d of Figure 1 show a series of images where an individual TCNE molecule is switched among four of the configurations. For example, \(-\beta-\text{TCNE molecules can be switched to } \gamma-\text{TCNE by applying a voltage pulse of } \sim 0.5 \text{ V (Figure 1a,b). By applying a second } \sim 1 \text{ V pulse, } \gamma-\text{TCNE can be switched to } \delta-\text{TCNE (Figure 1c). The } \delta-\text{TCNE molecule can be switched back to } \alpha-\text{TCNE by applying a } +2 \text{ V pulse, or switched to } \varepsilon-\text{TCNE (Figure 1d) by perturbation at low voltage and higher current (e.g., } \sim 10 \text{ mV and } 1 \text{ nA) than typical imaging conditions. The solid black line represents occasional switching from } /\beta-\text{to } \alpha-\text{TCNE remote from the tip location (\sim 100 Å).}^5$

We coadsorbed CO molecules (e.g., dark spot in Figures 1a–d and 2a) to register the location of topmost Cu atoms,\(^1\text{e}\) and thus determine the adsorption sites of TCNE. We find that \(-\text{TCNE is adsorbed with the central } \text{C}==\text{C bond over a}
bridge site, and with the two C atoms nearly atop underlying Cu atoms in the surface (Figure 2c). Although \( \alpha, \beta \)-TCNE are nearly identical in qualitative appearance, they do differ in apparent height (0.4 and 0.5 \( \text{Å} \), respectively). The two configurations can be directly distinguished from Figure 2a, which shows that \( \beta \)-TCNE is oriented at 90° with respect to \( \alpha \)-TCNE, rather than the multiples of 120° expected from the triangular symmetry of the Cu(111) lattice. STM images indicate that \( \beta \)-TCNE is also adsorbed with a central C=C bond over a bridge site, but with the two central C atoms nearly centered on hollow sites instead of atop Cu atoms (Figure 2b).

Our DFT calculations indicate that the bridge site is the lowest energy binding site for TCNE on Cu(111), and that \( \alpha, \beta \)-TCNE molecules are bent compared to the planar gas phase molecule. For \( \alpha \)-TCNE, a deformation energy of 0.5 eV corresponds to a dihedral angle of \( \phi = 166° \) (Figure 1f). This bending brings the four CN groups closer to the Cu surface relative to the central C=C bond. We find that \( \beta \)-TCNE is more bent with a deformation energy of 0.91 eV and a dihedral angle of \( \phi = 145° \), which moves the C=C bond even further from the surface. The central C=C bond is also lengthened in both structures, with values of 1.49 \( \text{Å} \) for \( \alpha \)-TCNE and 1.50 \( \text{Å} \) for \( \beta \)-TCNE, compared to 1.39 \( \text{Å} \) for gas phase TCNE. On the basis of these structures, the simulated STM images in panels d and e of Figure 2 match well to our experimental images and also reproduce the relative apparent heights of \( \alpha, \beta \)-TCNE. While the \( \alpha, \beta \) configurations have very similar total energies, \( \alpha \)-TCNE is predicted to be more common due to the associated lower deformation energy.

The asymmetric shapes of \( \gamma \) - and \( \varepsilon \)-TCNE make it difficult to unambiguously determine adsorption sites from our STM images. Simulated STM images of TCNE adsorbed at other, less stable adsorption sites did not well reproduce the asymmetric shapes observed experimentally. This suggests that there are deformed molecular structures involving excited states of adsorbed TCNE which are not easily predictable within the DFT approach used here. The appearance of \( \varepsilon \)-TCNE suggests the bending of one C=C bond away from the surface or perhaps a buckling of one Cu atom out of the surface plane. The more asymmetric appearance of \( \gamma \)-TCNE may represent a bending of multiple C=C-CN bonds or the C=C bond itself. A similar interpretation was reported for TCNE on Au(111).\(^5\)

We find that \( \delta \)-TCNE appears much taller (2 \( \text{Å} \)) than the other configurations and exhibits a butterfly-like shape (Figure 1c). Surprisingly, Figure 2f shows that the adsorption site and orientation of \( \delta \)-TCNE are identical to \( \beta \)-TCNE, so that this distinct appearance is not due to a different adsorption site. We believe that \( \delta \)-TCNE represents an additional deformation related to the central C=C bond of the molecule. Discussed further below, redistribution of charge due to this deformation changes the local density of states and leads to the much larger apparent height of \( \delta \)-TCNE.

To establish the relative energies of these various states, we increased the sample temperature from 5.5 to 55 K. We observed that all \( \gamma \) - and \( \delta \)-TCNE switch to \( \beta \)-TCNE by 54 and 24 K, respectively, which indicates that \( \beta \)-TCNE is a lower energy state, consistent with our DFT calculations. We did not observe any interconversion among \( \alpha, \beta, \varepsilon \)-TCNE at these temperatures. The \( \alpha, \beta \)-TCNE molecules are stable until \( \sim 55 \text{ K} \), at which point they start diffusing on the surface.

We studied the switching from \( \delta \)-TCNE to \( \beta \)-TCNE in more detail by measuring the lifetime of \( \delta \)-TCNE as a function of temperature. For these measurements, we initialized a group of TCNE molecules to \( \delta \)-TCNE by voltage pulsing. We then repeatedly imaged the area (~10 s/image) to measure the duration each molecule remained in the \( \delta \)-TCNE state (Figure S1, Supporting Information). We found that the switching from \( \delta \) - to \( \beta \)-TCNE is thermally activated, with Arrhenius behavior that gives an activation energy of \( \sim 43 \text{ meV} \) and an attempt frequency of 1 GHz. These numbers should be considered estimates however, because we find that lifetime of \( \delta \)-TCNE is affected by proximity of the STM tip. A dependence of the switching rate on voltage polarity may reflect an interaction between the local electrostatic field and a surface dipole associated with \( \delta \)-TCNE.

We probe the local density of states (LDOS) of TCNE with tunneling spectroscopy. Unlike TCNE on Au(111) or Ag(100) surfaces,\(^5\) we do not observe any peaks that can be attributed to molecular orbitals for any of the states of TCNE on Cu(111). It is possible that these peaks lie outside the voltage range we can access, which is limited to \( \pm 0.5 \text{ V} \) due to the molecules’ stability on Cu(111). Within this range, we find that \( dI/dV \) spectra on \( \alpha, \beta, \gamma \), and \( \varepsilon \)-TCNE do not exhibit any significant features above the background signal on Cu(111) (Figure 3a). In contrast, a pronounced peak at the Fermi energy, \( E_F \) (i.e., 0 mV) is observed in \( dI/dV \) from \( \delta \)-TCNE, taken with the tip positioned over a corner of the molecule (Figure 3b). We interpret this peak as a Kondo resonance, which occurs due to the interaction between a local magnetic moment and surrounding conduction electrons. The nearly Lorentzian line shape represents a limit case of the well-known Fano line shape in tunneling spectroscopy of Kondo systems.\(^17\) To confirm this interpretation, experimental \( dI/dV \) spectra were corrected for thermal broadening, and then fit using the Fano equation

\[
\frac{dI}{dV}(V) \propto \frac{(\varepsilon' + q)^2}{1 + \varepsilon'^2}
\]

where \( q \) is related to the relative tunneling probability from STM tip to TCNE molecule or Cu substrate, \( E_0 \) is the resonance energy (0 mV in our measurements), and \( \Gamma \) is the half width.
FIGURE 3. Tunneling spectroscopy of TCNE. (a) Spectra taken with the tip centered over α,γ,ε-TCNE. No distinct vibrational or orbital features are visible above the Cu(111) background. Spectra are offset from α-TCNE by 0.5 pA/mV for clarity. The tip height was set at +0.1 V, 0.2 nA. (b) Spectra with the tip over a corner of δ-TCNE showing a Kondo resonance at 0 mV. Spectra at different temperatures are offset from the 18 K data by 0.5 pA/mV for clarity. The inset shows the intrinsic line width of resonance peak, after correction for temperature-dependent experimental broadening. The solid line shows a fit to Kondo theory. (c) Comparison of spectra with the tip over the corner and center of δ-TCNE at 5.3 K. Kondo side bands corresponding to inter- and intramolecular vibrational modes are more prominent with the tip over the center of the molecule. The inset is a spatial map of the dI/dV signal at 35 mV. Scale bar = 5 Å.

width at half-maximum. Theory predicts a temperature-dependent line width:

\[ \Gamma(T) = \frac{1}{2} \sqrt{(a k_B T)^2 + (2 k_B T)^2} \]

which defines the Kondo temperature, \( T_K = \Gamma(0)/k_B \). The inset of Figure 3b shows that good agreement between the measured \( \Gamma(T) \), and the fit is obtained for \( T_K = 29 \pm 1 \text{ K} \).

The tunneling spectra in Figure 3b also show weak side bands which are symmetric about \( E_F \). When the tip is positioned over the center of δ-TCNE (Figure 3c), the Kondo resonance is not observed, but the side bands are much more pronounced. In total, we observe seven side bands at 5.1 ± 0.2, 13.5 ± 0.3, 21.9 ± 0.7, 35.7 ± 0.1, 57.8 ± 0.4, 66.9 ± 0.5, and 74.1 ± 0.4 mV. The errors quoted here represent the standard deviations of measurements on 15 different δ-TCNE molecules. A number of these side bands correspond to vibrational modes that have been measured using other techniques. For example, the side bands at ±35.7 mV (285 cm\(^{-1}\)) may be assigned to the \( \text{C} \equiv \text{C} \) rocking mode observed with Raman spectroscopy. The distinct shape of the side bands can be explained by a two-stage tunneling process. First, tunneling electrons can transfer energy to vibrational modes of the molecule once the magnitude of the voltage exceeds \( h v_{\text{mode}} \). This inelastic tunneling process typically produces steplike features in \( \frac{dI}{dV} \) that are symmetric about \( V = 0 \). In the case of δ-TCNE, the inelastically scattered electrons probe the Kondo density of states at \( E_F \) before reaching the Cu substrate. As a result, the side bands represent the convolution of a steplike feature with the Kondo resonance. Simulations of this convolution are in good agreement with the measured spectra (Figure S2, Supporting Information). By recording the \( \frac{dI}{dV} \) signal at fixed voltage during STM imaging, we can spatially map these sidebands over the molecule. The inset to Figure 3c shows, for example, that the 35 mV sideband is preferentially excited when the tip scans over the \( \text{C} \equiv \text{C} \) bond, which is qualitatively consistent with our assignment as a rocking mode.

We utilize DFT calculations to understand the distribution of charge in the five states of TCNE that we observe. Figure 4 shows the calculated LDOS for adsorbed β-TCNE compared to isolated molecules in the deformed and planar geometries. While not shown here, the calculated LDOS for α-TCNE was qualitatively similar. For clarity, orbitals are labeled by their occupation in planar TCNE. For reference, the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of isolated, planar (i.e., gas phase) TCNE. We find that the deformation and adsorption of β-TCNE significantly influence the energy and ordering of these orbitals. For example, the deformation of β-TCNE relative to the planar geometry exchanges the LUMO+1 and LUMO+2. The LUMO lies \( \sim 0.5 \text{ eV} \) below \( E_F \) for adsorbed β-TCNE, so that two electrons from the Cu substrate will readily occupy this orbital upon adsorption. This occupation should produce a singlet state with zero spin, consistent with the absence of a Kondo resonance in Figure 3a. Mulliken population analysis gives a net charge transfer from Cu to TCNE of \( \sim 0.4 \text{ e} \), which indicates that \( \sim 1.6 \text{ e} \) are transferred from lower-lying orbitals of TCNE near \( E_F \) to Cu in a back-donation process.
electron spin in these lower-lying orbitals is not expected to contribute a Kondo resonance, which only reflects states near $E_F$. The similarity of $\gamma, e$-TCNE to $\alpha, \beta$-TCNE in spectroscopy and imaging suggests that the deformations responsible for the asymmetric shapes of $\gamma, e$-TCNE do not significantly change this charge distribution.

The occupation of molecular orbitals in $\delta$-TCNE must be distinct from the other states however, since unpaired spin near $E_F$ is required for the Kondo resonance in Figure 3b,c. Because $\delta$-TCNE and $\beta$-TCNE share an identical adsorption site, we believe an additional deformation of the molecule or surface is required to produce the metastable $\delta$-TCNE state. Recent STM studies have suggested that deformation of thin insulating surfaces can stabilize different charge states of adatoms or molecules. Furthermore, prior DFT calculations of TCNE on Cu(100) do suggest a surface buckling which leads to self-assembly of TCNE into chains. However, we have repeated these calculations and do not find any significant buckling for TCNE on Cu(111), which suggests that a molecular deformation occurs to stabilize $\delta$-TCNE.

While it is difficult to identify excited states of adsorbed species using any standard DFT methods, we can vary molecular parameters to study their influence on the electronic structure. We found that variation of the dihedral angle (Figure 1f) from 180 to 120° shifts the LUMO 0.6 V away from $E_F$ but does not significantly shift the LUMO+2. We also varied the central C=C bond length from its gas phase value of 1.39 Å up to 1.74 Å and found significant shifts of both the LUMO (0.6 V away from $E_F$) and the LUMO+2 (1.2 V toward $E_F$) as the bond length is increased. On the basis of this calculation, we suggest that a lengthening of the C=C bond leads to a partial occupation of the LUMO+2 in $\delta$-TCNE. The calculated LUMO+2 corresponds well to spatial maps of the Kondo resonance, recorded at a fixed voltage of +1 mV (Figure 4). Both, for example, show nodal structures perpendicular to the central C=C bond and a similar butterfly-like shape. This interpretation is qualitatively consistent with our additional time-dependent DFT (TD-DFT) calculations, which indicate that single—singly and singlet—triplet transitions occur at lower energy in deformed TCNE compared to planar TCNE. The C=C bond’s stretching mode (~161 meV or 1500 cm$^{-1}$ in gas phase TCNE) should shift due to this elongation. Similar shifts have been used to infer charge states of TCNE in bulk transition metal complexes and on surfaces. Although some of the Kondo side bands from $\delta$-TCNE correspond well to other vibrational modes in the literature, we do not observe the central C=C stretching vibration in any state of TCNE. The absence of vibrational modes in STM-based inelastic electron tunneling spectroscopy is common, and the selection rules which may govern this process are not well understood.

In conclusion, we discovered that single TCNE molecules on Cu(111) can be reversibly switched among any of five distinct states. Our STM and DFT results suggest that these states reflect different deformations of the TCNE molecule. In the case of $\delta$-TCNE, these deformations redistribute charge in such a way as to produce a magnetic state, which is probed via tunneling spectroscopy of a Kondo resonance. We thus have demonstrated that a magnetic state of single TCNE molecules can be reversibly switched on and off. Such multistability may enable new paradigms for parallel computing with organic materials on the nanometer scale.

Acknowledgment. We thank J.-W. Yoo for helpful discussions and are grateful for support from NSF CAREER Award No. DMR-0645451, and the Center for Emergent Materials, an NSF-funded MRSEC (DMR-0820414). A.R. and S.B. are grateful to the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support, and to the Résseau québécois de calcul haute performance (RQCHP) for providing computational facilities. S.B. thanks the Fonds québécois de la recherche sur la nature et les technologies (FQRNT) for a scholarship.

Supporting Information Available. Figures showing thermal switching from $\delta$-TCNE to $\beta$-TCNE and simulations of Kondo side bands. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES