Tuning Molecule-Mediated Spin Coupling in Bottom-Up-Fabricated Vanadium-Tetracyanoethylene Nanostructures

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We have fabricated hybrid magnetic complexes from V atoms and tetracyanoethylene ligands via atomic manipulation with a cryogenic scanning tunneling microscope. Using tunneling spectroscopy we observe spin-polarized molecular orbitals as well as Kondo behavior. For complexes having two V atoms, the Kondo behavior can be quenched for different molecular arrangements, even as the spin-polarized orbitals remain unchanged. This is explained by variable spin-spin (i.e., V-V) ferromagnetic coupling through a single tetracyanoethylene (TCNE) molecule, as supported by density functional calculations.

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Molecule-based spintronics raises new possibilities for chemically engineering electronic and magnetic device properties with unprecedented precision at the nanoscale [1,2]. For this concept to become reality, however, a more fundamental understanding of substrate-supported magnetic molecules is necessary since their charge, spin, and magnetic anisotropy can change as they come into contact with a surface [3,4]. Scanning tunneling microscopy (STM) and spectroscopy (STS) offer powerful tools for studying the local magnetoelectronic structure of such molecular nanostructures. Direct (atom-atom) and substrate-mediated (atom-substrate-atom) magnetic coupling between atomic spin centers has been measured previously using STM-based techniques [5–9]. Tunable spin coupling through a single molecular linker (atom-molecule-atom), however, has not yet been directly observed. One good candidate for such purposes is the strong π-electron acceptor tetracyanoethylene (TCNE). Bulk V(TCNE)$_x$ ($x \sim 2$), for example, is a molecule-based magnet with a Curie temperature $T_C \sim 400$ K [10–13].

Here we describe a bottom-up approach to create new magnetic nanostructures that display variable molecule-mediated spin-spin coupling using STM-based manipulation and characterization of individual V atoms and TCNE molecules at the surface of Ag(100). Central to this technique is our discovery that V and TCNE can be induced to form a rigid chemical bond through STM manipulation. The molecular orbital from which V-based spin is derived in the resulting complexes can be directly observed in our STS measurements. We find that, for complexes consisting of one V atom and either one or two TCNE molecules, this spin is screened by the Ag substrate via the formation of a Kondo resonance. For complexes consisting of two V atoms and one TCNE molecule, the Kondo effect can be switched on and off by a minute structural change that leaves the spin-containing orbital essentially unchanged. This is explained by a tunable, structure-dependent change in the V-V spin-coupling strength transmitted via a single TCNE molecule. This physical picture is supported by spin-polarized density functional theory (SP-DFT) calculations that suggest that V atoms are coupled through a TCNE molecule by a tunable ferromagnetic (FM) interaction. The present findings offer a new route for designing molecular spin nanostructures with atomic-scale precision.

The experiments were performed in ultrahigh vacuum using a home built STM operated at $T = 7$ K. A Ag(100) single crystal was cleaned by standard sputter-annealing procedures and then exposed at $T = 300$ K to TCNE molecules dosed through a leak valve [14]. After *in situ* transfer into the cryogenic STM, V atoms were deposited onto the cold sample using electron-beam evaporation. STS was performed by measuring the differential conductance dI/dV as a function of the sample bias V by standard lock-in techniques (modulation amplitude ~ 1 mV$_{\mathrm{rms}}$, frequency ~ 451 Hz) under open-feedback conditions.

Typical STM images of samples prepared in this way [Fig. 1(a)] show isolated V atoms as round protrusions adsorbed at hollow sites on Ag(100) terraces, while coexisting TCNE molecules are identified as faint oval protrusions (surrounded by a trench) centered over top sites [Fig. 2(a)] [14]. While isolated V adatoms cannot be moved on Ag(100), TCNE molecules can be slid with great precision along the surface using lateral STM manipulation [15] and can thus be attached to individual V adatoms [see arrows in Fig. 1(a)]. V-TCNE complexes formed in this way [Figs. 1(b) and 2(b)] display a merging of V and TCNE, as well as a strong change in apparent height. Once merged, the entire fused V-TCNE complex can be moved as a single unit along the surface by STM manipulation.

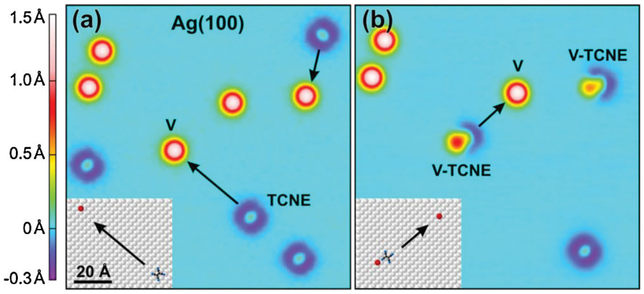

FIG. 1 (color). (a) STM image of TCNE molecules and V atoms adsorbed on Ag(100). (b) The same area after moving TCNE molecules toward V atoms using STM manipulation following arrows in (a), thus forming V-TCNE complexes. The arrow indicates how a V-TCNE complex will be moved toward a second V atom to form a V_2TCNE complex [see Figs. 2(d) and 2(e)]. Both STM images are plotted with the same scale bar for apparent height. Imaging parameters: 1 V and 5 pA.

Larger $V_x(TCNE)_y$ structures can be built reliably by connecting TCNE or V-TCNE with other building blocks. Figure 2(c) shows a complex after attachment of a second TCNE to a previously created V-TCNE complex. The newly formed $V(TCNE)_2$ complex again shows a rigid connection of both TCNE molecules to the interior V atom. Linear V_2TCNE complexes can be made by connecting a V-TCNE molecule to a V adatom [Figs. 1(b), 2(d), and 2(e)]. STM images of these different bottom-up synthesized molecules are shown in Fig. 2, along with structural models based on analysis of the images. In all cases the fused V atoms stay close to fourfold hollow sites on the Ag(100) surface, but the fused TCNE prefers bridge sites, thereby reducing the V-N distance. Linear V_2TCNE structures can be built reproducibly in two different forms that are distinguishable by the V-V angle relative to the [001] direction of the substrate: The first structure (V_2TCNE@27°) exhibits an angle of 27 ± 1° [Fig. 2(d)], while the second structure (V_2TCNE@11°) has an angle of 11 ± 1° [Fig. 2(e)]. These two isomers exhibit an overall difference in size, the distance between V atoms being slightly larger (by ~1 Å) in the V_2TCNE@27° molecule as compared to the shorter V_2TCNE@11°.

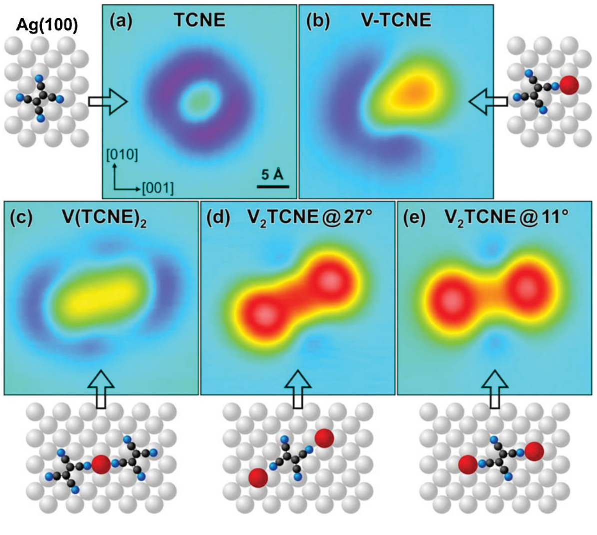

FIG. 2 (color). Highly resolved STM images and structural models of (a) TCNE, (b) V-TCNE, (c) $V(TCNE)_2$, (d) V_2TCNE@27°, and (e) V_2TCNE@11° on Ag(100). The models are derived from the STM images. Note that V_2TCNE@11° has a shorter V-V distance compared to V_2TCNE@27°. All STM images are plotted with the same height scale bar shown in Fig. 1. Imaging parameters: 1 V and 5–50 pA.

In order to understand the magnetoelectronic behavior of the newly synthesized $V_x(TCNE)_y$ complexes, we performed STS experiments on these structures with subnanometer resolution (Figs. 3 and 4). We observed three different features in this spectroscopy: (i) molecular orbital resonances, (ii) vibrational inelastic features, and (iii) Kondo resonances. Molecular orbital resonances are seen at "high" biases ($|V| > 100$ mV), while inelastic features are seen at "low" biases ($|V| < 50$ mV), and Kondo resonances are observed to straddle the Fermi energy at $V = 0$. The inelastic features reveal the nature of the V-TCNE bonding, while the molecular orbital resonances reveal the presence of spin in the V_xTCNE_y complexes. The Kondo resonance observations reveal how the molecular spins are coupled to their environment, including adjacent spins.

We first describe the inelastic features (marked with the label "E_{vib}" in Fig. 3). These are seen as steps in dI/dV or peaks (dips) at positive (negative) voltage in d^2I/dV^2, and they arise as new tunneling channels are opened due to molecular excitations [16]. For bare TCNE [Fig. 3(d)] a

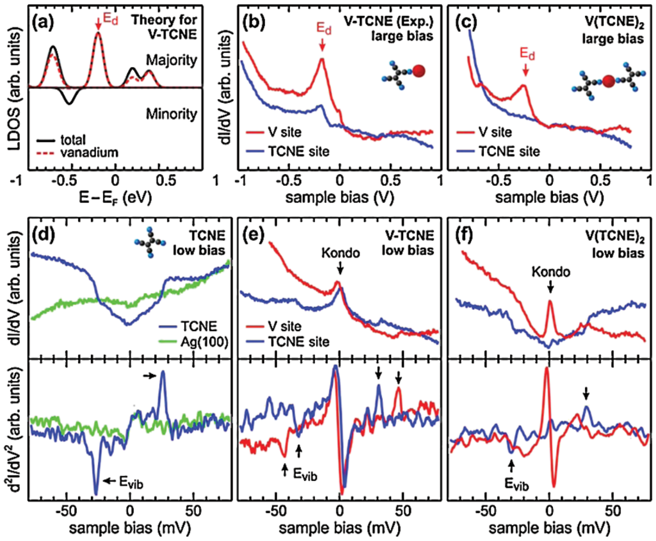

FIG. 3 (color). (a) SP-DFT-calculated spin-resolved LDOS of a free anionic V-TCNE complex. Large-bias STS spectrum is shown for (b) V-TCNE and (c) $V(TCNE)_2$. Highly resolved low-bias STS is shown for (d) TCNE, (e) V-TCNE, and (f) $V(TCNE)_2$. For clarity, the Ag-background signal [green curve in (d)] was subtracted from spectra in (b), (c), (e), and (f).

very clear inelastic mode exists at ~30 mV. We identify this as the TCNE rocking or wagging mode that is known to lie at this energy from optical spectroscopy measurements and DFT calculations [17,18]. When a single V atom is attached to a single TCNE molecule, however, a new mode appears at 45 mV that is localized to the V site [Fig. 3(e)]. We identify this as the V-N stretch vibration, and its energy corresponds well to the V-N stretch mode measured in other structures by optical spectroscopy [19]. The presence of the V-N stretch vibration provides strong evidence that V atoms connected to TCNE via STM manipulation are covalently bonded. When two TCNE molecules are connected to one V atom, the V-N stretch mode is no longer detectable, but the TCNE rocking/wagging mode is still seen over the TCNE molecules [Fig. 3(f)].

We now describe the orbital resonances seen at larger biases for V_xTCNE_y complexes. In the data of Figs. 3 and 4, these resonances are marked by the label "E_d," since they are believed to arise from V d orbitals. STS of V-TCNE complexes [Fig. 3(b)] shows a pronounced broad molecular resonance at $E_d = -0.17$ V that has strong amplitude on the V site and slightly lower amplitude on the TCNE region of the complex. This resonance does not exist for bare TCNE on Ag(100) [14]. When two TCNE molecules are attached to a single V atom, the orbital resonance shifts to a slightly reduced energy $E_d = -0.25$ V [Fig. 3(c)] and becomes localized to the V atom and cannot be seen over adjacent TCNE molecules. When two V atoms are bonded to a single TCNE molecule [as shown in Figs. 2(d) and 2(e)], the molecular orbital shifts upward slightly to $E_d = -0.15$ V and has amplitude on both the V and the TCNE regions of the complex. This behavior is seen identically for both V_2TCNE@27° and V_2TCNE@11° [Figs. 4(a) and 4(b)].

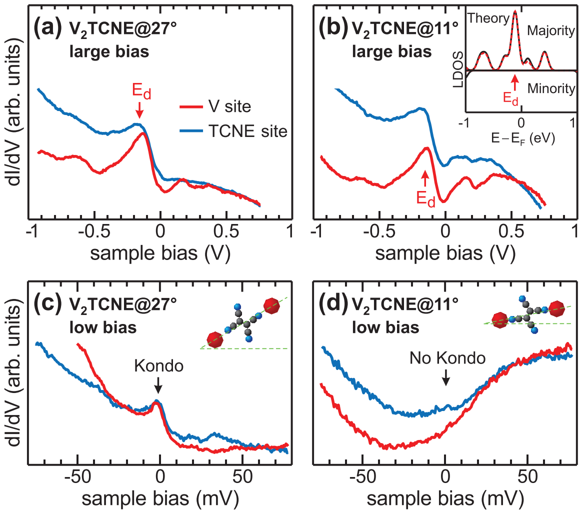

FIG. 4 (color). Large-bias (a),(b) and highly resolved low-bias (c),(d) STS spectra of V_2TCNE@27° and V_2TCNE@11°, respectively (Ag-background spectrum is subtracted). The inset in (b) shows the calculated spin-resolved LDOS of a free anionic V_2TCNE complex.

We now describe our observations of Kondo resonances in the low-bias spectra of V_xTCNE_y complexes. A Kondo resonance is the spectral signature of a many-body electron cloud that occurs as the itinerant spins of a nonmagnetic metal screen the spin of a local magnetic moment [20,21]. V-TCNE exhibits a Kondo resonance having amplitude on both the V atom and the adjacent TCNE molecule [Fig. 3(e)] with a width of $\Gamma = 11 \pm 2$ mV, indicating a Kondo temperature of $T_K \sim 65$ K. Figure 3(f) shows that the Kondo resonance remains for the $V(TCNE)_2$ complex ($\Gamma = 6 \pm 1$ mV, i.e., $T_K \sim 35$ K), except that it now has amplitude only on the V atom. The spatial dependence of the Kondo resonance for both V-TCNE and $V(TCNE)_2$ thus mirrors the spatial dependence of the molecular orbital at E_d. When two V atoms are connected to a single TCNE molecule in the V_2TCNE@27° configuration, the Kondo resonance also remains (in this case, $\Gamma = 10 \pm 2$ mV, i.e., $T_K \sim 60$ K), and again the spatial distribution of the Kondo resonance mirrors that of the E_d orbital resonance. Surprisingly, however, when two V atoms are connected to a TCNE molecule in the V_2TCNE@11° configuration, there is no Kondo resonance to be seen on either the V or the TCNE sites [Fig. 4(d)] despite the fact that the E_d orbital resonance amplitude remains unchanged across the entire V_2TCNE@11° complex.

This behavior can be explained by identifying the filled orbital resonance at E_d as the signature of a local magnetic moment. The presence (or absence) of the Kondo resonance then indicates how this local moment couples to its environment. In the case of V_2TCNE, our data indicate that, although nearly identical local spin moments exist for V_2TCNE@27° and V_2TCNE@11°, the V-V spin coupling is very different for these two complexes. The V spins in V_2TCNE@11° appear to be FM coupled through the TCNE molecule with a larger exchange energy than for the more weakly coupled V_2TCNE@27° complex. The signature of this tunable V-V exchange coupling is the disappearance of the Kondo effect in the more strongly coupled V_2TCNE@11° case [22]. This interpretation of the data is supported by SP-DFT calculations as well as by differences in V geometry between V_2TCNE@27° and V_2TCNE@11°, as described below.

First-principles SP-DFT calculations of the magnetoelectronic structure of isolated V_xTCNE_y complexes were performed using the NRLMOL code [23–26]. All atoms in the calculation were treated within an LCAO formulation at the all-electron level. The basis sets used here are roughly equivalent to triple-ζ or better. The generalized gradient approximation was used to approximate the exchange-correlation functional [27]. Structures were relaxed until all forces were below 0.001 Hartree/Bohr. Figure 3(a) shows the local density of states (LDOS) calculated for a V-TCNE complex. The majority-spin LDOS shows a pronounced filled state at $E_d = -0.20$ eV, implying that the experimental orbital resonance seen at this same energy is a majority-spin state arising from a V d orbital. Calculations of a V_2TCNE complex [Fig. 4(b), inset] also show a dominating V d resonance at $E_d = -0.12$ eV, similar to what is seen for the experimental case [Figs. 4(a) and 4(b)]. This agreement between theory and experiment occurs only when the simulated V-TCNE and V_2TCNE complexes are charged with one electron, which we assume is drawn from the Ag substrate in the experiment [28]. In this case the FM state is lower in energy than the antiferromagnetic state by 170 meV. The SP-DFT calculations thus support the conclusion that orbital resonances seen experimentally at E_d indicate the presence of a local moment and that these moments are FM coupled for anionic V_2TCNE.

The reason that the Kondo effect is quenched for V_2TCNE@11° and not for V_2TCNE@27° is because the 11° complex is more strongly FM coupled through the TCNE molecule than the 27° complex. Although our SP-DFT calculations are not accurate enough to distinguish between these two cases, we can see from the structure of the 11° complex [Fig. 2(e)] that the V atoms are closer together than for the 27° complex [Fig. 2(d)]. This couples them more strongly to the TCNE ligand, thus providing stronger FM coupling. As this coupling strength rises above the single-moment Kondo temperature, the two V atoms form a FM complex rather than two individually screened magnetic moments. FM coupled spin complexes are well known to have a lower Kondo temperature than single impurities, thus explaining why the Kondo effect is quenched for the 11° complex [22]. The fact that the binding energies of the spin-containing orbital states at E_d, as well as their widths (i.e., their hybridization with the substrate), are identical for both V_2TCNE@11° and V_2TCNE@27° provides further evidence that quenching of the Kondo effect comes from tunable ligand-induced FM exchange coupling rather than a simple shifting of the single-impurity Kondo temperature.

We emphasize that the separation between the two V atoms in V_2TCNE@11° (~10 Å) is relatively large. Strong FM coupling over such distances is possible only due to molecular ligand-induced exchange coupling [5,8]. This direct use of a molecule as a mediating unit between spin centers enables a new type of spin-coupling engineering. For example, the influence of molecular size on magnetic coupling might be studied systematically by replacing TCNE with closely related molecules [e.g., tetracyanoquinodimethane (TCNQ)], or the effects of chemical interactions might be studied by varying functional end groups. Such a bottom-up strategy opens new paths for designing quantum spin structures with atomic-scale precision.

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[28] Isolated V adatoms on Ag(100) are neutral, while TCNE molecules are negatively charged on that surface [13]. Comparison of experimental data with simulations of isolated V_xTCNE$_y$ complexes in the neutral, −1, and −2 charge states supports the assumption that no additional charge transfer with the substrate occurs as these building blocks are bonded.