Charge Transfer at the Single Molecule Level

STM Studies of Organic-Metal Interfaces

Since its discovery in the 1980s, scanning tunneling microscopy (STM) has been a powerful tool for exploring the nanoscale due to its capabilities for atomic-resolution imaging, tunneling spectroscopy, and atom/molecule manipulation. These unique capabilities of STM enable studies of problems related to the scaling of conventional information technologies to atomic dimensions, and provide opportunities for studying the fundamental bases of novel paradigms. For example, molecule-based devices are of interest for next-generation technologies due to the easy tunability of organic molecules with relatively simple chemical methodologies. This motivates our STM studies of organic-metal interfaces and metallo-organic complexes at the single molecule level.

Here, we provide an overview of our studies of the tetracyanoethylene (TCNE: (CN)₂C=C(CN)₂) molecule, a canonical charge acceptor whose high electron affinity facilitates chemical bonding and charge transfer with metals. Metal-TCNE complexes form a family of organic magnets with Curie temperatures exceeding room temperature [1], promising for spintronic devices [2]. We studied the molecules on conducting (Cu(100), Cu(111)) and insulating (Cu₂N/Cu(100)) surfaces to probe how aspects of the adsorption environment (binding site, surface orientation etc.) influence charge (and spin) transfer.

TCNE on Cu(111): A Single Molecule Kondo Switch

Figure 1 shows various configurations of TCNE molecules adsorbed on a cold (5K) Cu(111) surface. On Cu(111), we find five distinct states of the molecules labeled as α-, β-, γ-, δ-, and ε-TCNE [3]. On the square lattice of the Cu(100) surface, we only observe α-, γ-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, as for example, Wegner et al. found that TCNE adsorbs in a single site on Cu(100) at room temperature [4].

We are able to reversibly switch single TCNE molecules among these states by applying voltage pulses with the STM tip as seen in figure 1.
In order to probe the electronic and magnetic properties of these states, we measure dI/dV spectra by scanning tunneling spectroscopy (STS) as seen in figure 2. Tunneling spectroscopy not only probes the local density of states of surface, adsorbate and tip, but also excitations of the system, such as spin-flip, vibrational, or motional modes. One of the states (δ-TCNE) exhibits a pronounced Kondo resonance at V=0 in tunneling spectroscopy. The Kondo resonance arises from the many-body interaction between a local magnetic moment and surrounding conduction electrons; its presence thus indicates that δ-TCNE has a net spin. A magnetic switch is thus realized by cycling individual TCNE molecules among magnetic and nonmagnetic states. In δ-TCNE, we also find several sidebands in the spectra symmetric about V=0 in addition to the Kondo peak. These sidebands are interpreted as a convolution of the Kondo density of states with inelastic electron tunneling spectroscopy (IETS) of vibrational modes.

The relative prominence of Kondo resonance and vibrational sidebands is highly sensitive to tip placement, illustrating a complex interplay of spin, electronic and vibrational degrees of freedom. Our experimental results and density functional theory (DFT) calculations suggest that these configurations originate from multi-stable binding sites and molecular conformations with distinct charge and spin transfer between the TCNE molecule and the Cu surface [3].

**Decoupling TCNE Molecules from Cu via an Intervening Cu$_2$N Film**

Ultrathin insulating layers have recently been used for controlling electronic coupling at the nanoscale, while still permitting characterization via surface science techniques such as STM. Such layers suppress the substrate electron density, enabling direct imaging of molecular orbitals [5] and spin-flip spectroscopy of single magnetic atoms [6] with STM. We use one layer thick Cu$_2$N islands grown on Cu(100) to decouple TCNE molecules from the metal substrate [7]. Though one atomic layer thick, Cu$_2$N acts as an insulator with a ~ 6eV band gap [8, 9], thus
suppressing the substrate density of states. Figure 3 shows an STM image of a TCNE molecule adsorbed on the cold (5K) Cu$_2$N surface. TCNE on Cu$_2$N is readily moved on the surface by the STM tip during imaging at even pA-scale currents so molecules could only be studied when tethered to defects in the Cu$_2$N islands (e.g., N vacancies). In contrast to TCNE on Cu, the STM image of TCNE on Cu$_2$N closely resembles the lowest unoccupied molecular orbital (LUMO) of gas-phase TCNE, as calculated by DFT [3].

The dI/dV spectroscopy of TCNE on Cu$_2$N is also quite different compared to spectra taken on metal surfaces (Cu(100) and Cu(111)). For example, the spectra reveal steps at ±32 meV (=C-(CN)$_2$ in-plane rocking mode) and ±82 meV (CCN out of plane bending mode) when the tip is positioned over the central C=C bond. No such steps are observed for TCNE on bare Cu. These steps are relatively pronounced (changes in dI/dV~ 100%) compared to IETS steps from other molecules on metal surfaces (<10%). There is also no evidence for a Kondo resonance or spin-flip IETS.

This suggests the Cu$_2$N layer decouples the molecule from the metal substrate, thus increasing tunneling probability through vibrational modes and suppressing the interaction between any unpaired spin and the substrate electron density [10].

**Conclusion**

As a prototype model system for metal/organic charge transfer, we have studied TCNE molecules on various surfaces with STM. We find that individual TCNE molecules can be reversibly switched among 2-5 multi-stable states on Cu(111) and Cu(100). This multi-stability is associated with binding configurations with distinct charge and spin transfer. Tunneling spectroscopy of one state reveals a Kondo resonance due to a molecular spin, so that in essence we demonstrate that a magnetic state of single TCNE molecules can be reversibly switched on and off. On the other hand, TCNE on the Cu$_2$N insulating layer only shows IETS steps and no Kondo resonance, illustrating the decoupling effect of this thin film. Our results not only emphasize that the molecule/metal interface can be surprisingly complex, but that this complexity offers the potential for novel molecule-based devices.

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**References**

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