**Optical and Mechanical Control of Single Molecule Transistors**

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**Overview**

With the trend toward miniaturization in electronics, there has been a great deal of research over the past few years focusing on the fundamental issues which arise when current flows through single molecules. Unlike circuit elements based on bulk metals or semiconductors, devices based on single molecules exhibit a wide range of quantum phenomena due to the discrete nature of the molecular energy levels. Our group has helped lead the development of single-molecule transistors [SMTs] – 3-terminal devices in which a gate voltage can be used to control the energy levels in a molecule, thereby changing its resistance. Having a three-terminal device allowed for detailed study of both Coulomb blockade and the Kondo effect in these systems [1-6], including the effects of molecular vibrations on transport [1,2,4] and the effects of ferromagnetic leads [5].

In most of the experiments described above, there are three "knobs" for the experimenter to vary: a bias (source-drain) voltage, a gate voltage and a magnetic field. Although we have learned a great deal about transport through single molecules by adjusting these parameters, additional techniques for manipulating the transport would be useful both for characterizing the structure of the devices and for enabling new device properties. We are currently studying two different ways to add additional "knobs" to the standard three-terminal SMT. In the first set of experiments, laser light is focused into the cryostat and onto the molecule in our transistor. This will allow us to excite the molecule and consequently study the effects of the excitation on the transport. In an additional development, we are fabricating our transistors using suspended electrodes on a thin Si wafer and using a motorized mechanism to bend the substrate in order to control the size of the gaps between the electrodes and the molecule. We have already employed these mechanical break junctions to study the effect that varying the coupling of the molecule to the electrodes has on Coulomb blockade [6] and are now investigating what effect varying the coupling has on the Kondo resonance.

The success of these new techniques depends crucially on the choice of molecule. For both the optically-modulated and the mechanically-adjustable transistors, we have synthesized monomers and oligomers of transition-metal/organic complexes which have been specifically designed to have both the redox properties desirable for general SMT operation, as well as specific optical/electronic properties necessary for the experiments described above.

**Optical Modulation of SMTs**

The goal of this class of experiments is to observe current through an SMT which is dependent on the presence of light of a given frequency. This may be accomplished in two ways: (i) optically exciting a molecule at low temperature so that the photoexcited electrons contribute directly to the current or (ii) optically switching a molecule between high and low resistance states.

For the first experiment, we have synthesized a ruthenium-TPPZ monomer and an osmium-TPPZ trimer (Fig. 1a) which were designed to have long excited state lifetimes, large absorption cross-sections and optical transitions in the frequency window of our experiment – all of which should help lead to increased photocurrents. According to our estimates, we will need intensities on the order of $10^6$ W/cm$^2$ at the excitation frequency of the ruthenium monomer to produce 1 nA of measurable current. This is within the range of our laser assuming a 1 $\mu$m$^2$ spot size. We also expect orders of magnitude of additional intensity enhancement due to surface plasmon excitations in the breakjunction gap.

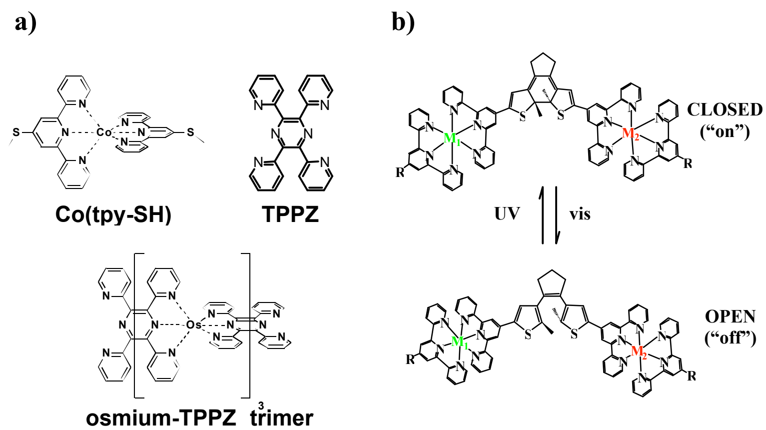

Figure 1. The molecules used in this work. They are coordination complexes of transition metals with terpyridine based ligands

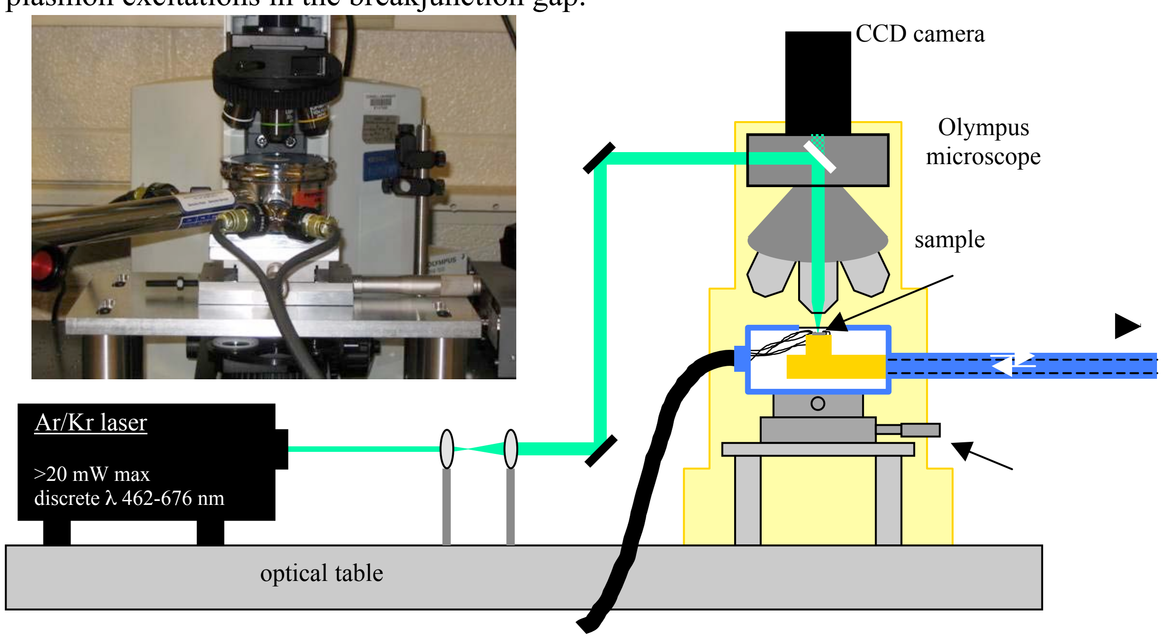

Figure 2. A schematic of the optical setup. The laser light is focused on a sample within the cryostat.

For the second experiment, we have synthesized an "optical switch" (Fig. 1b) which can be modulated from high (pi-conjugated) to low (unconjugated) conductance states upon application of light of two different frequencies (one for each transition). Fig. 2 is a picture of our setup for these experiments. An Ar/Kr laser will be coupled into an optical microscope that will focus the light into a microscopy cryostat (base temperature of 3 K).

## Mechanically-Adjustable SMTs

For this class of experiments, we will focus on the Kondo effect. The Kondo effect is based on the screening of an isolated spin by a surrounding continuum of electrons (such as in the electrodes of an SMT). The Kondo effect has already been observed using Co terpyridine monomers in standard SMTs [2]. With the mechanically-adjustable SMTs (Fig. 3), we can tune the coupling between the molecule and the leads by bending the flexible Si substrate while maintaining gating action.

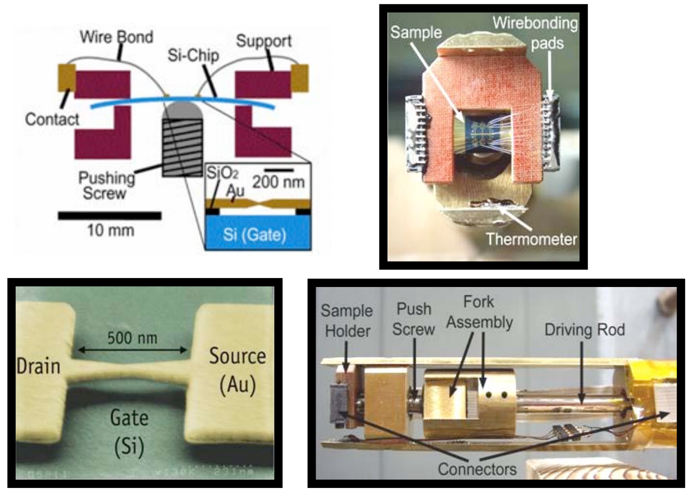


Figure 3. Schematics of mechanical break junctions

We are beginning to explore the transition from coherent (Kondo) to incoherent electron flow in devices containing $[Co(tpy\text{-}SH)_2]^{2+}$ synthesized within the group. We have measured devices which carry signatures of the Kondo effect, namely zero bias conductance peaks that exhibit a magnetic field splitting and logarithmic temperature dependence. Using mechanical motion, we have been able to tune parameters of the Kondo resonance (Fig. 4a). In addition, we have also observed split zero bias peaks that obey a non-monotonic temperature dependence, suggestive of a "Two-stage" Kondo effect (Fig. 4b). We are currently comparing the cobalt-ion transistors with ones made from ruthenium ions in order to elucidate the true nature of this data.

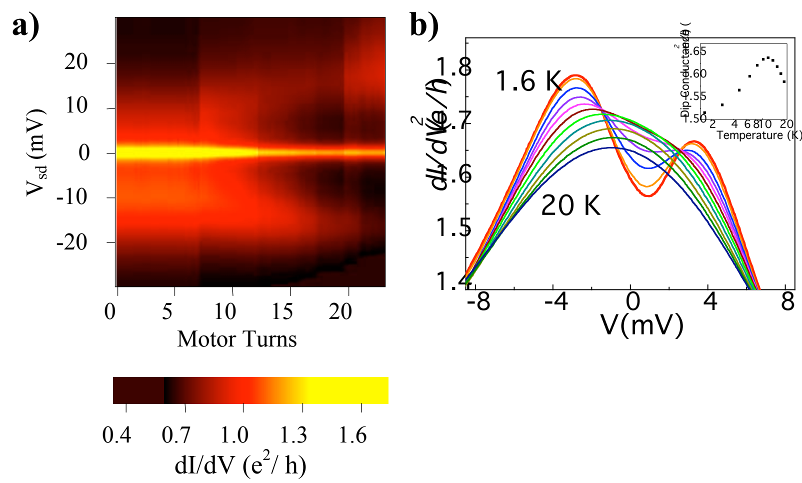


Figure 4.The mecahnical and the temperature dependence of Kondo effect seen in $[Co(tpy\text{-}SH)_2]^{2+}$


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