

Electron Transport through Molecular Inorganic Clusters – A Convergent Approach toward Molecular Electronic and Magnetic Devices

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Overview and Objectives:

Over the past 40 years, we have witnessed a remarkable miniaturization trend in semiconductor-based electronic circuits, which, were it to be continued, would soon reach the size scale of molecules. For this reason, electron transport through molecules and clusters has received considerable attention recently as a possible paradigm for future electronic architecture. To date, most work on electronic transport through molecules has focused on organic or carbon-based molecules. From a materials standpoint, however, inorganic compounds provide even more exciting opportunities since they exhibit electronic and magnetic properties unparalleled by carbon-based materials. With the entire periodic table to choose from, molecules with much broader variations in their electronic and magnetic properties can be generated once inorganic atoms are incorporated into molecules. Furthermore, molecules containing multiple transition metal centers generally produce a much wider range of accessible redox states than encountered in carbon-based molecules of similar size. Indeed, the incorporation of inorganic clusters into molecular electronic elements should substantially extend their capabilities and provide the optimal route to diversify their functionalities.

Our research effort represents a convergent multi-investigator experimental and theoretical program for exploring potential device applications of molecular inorganic clusters, with particular emphasis on investigating their fundamental electronic and magnetic properties and exploring their device applications. The precisely determined properties of molecular clusters provide an inherent and unique advantage in designing and controlling functionality of molecular electronic and magnetic devices. The research effort is a synergistic collaboration between (i) the synthesis of novel inorganic clusters with diverse electronic and magnetic properties engineered via judicious control of synthetic parameters, (ii) the fabrication and characterization of molecular electronic devices built from individual clusters and low-dimensional cluster arrays, (iii) the electronic and magnetic characterization of these clusters using the state-of-the-art measurements, and finally (iv) the development of detailed understanding of cluster properties using high-level theoretical calculations, which will, in turn, guide the design of molecules and molecular electronic devices.

The synergy between our efforts will result in a fundamental understanding of the electronic and magnetic properties of molecular magnetic clusters, which, in turn, may lead to the applications toward novel molecular electronic and magnetic devices. The proposed collaboration between synthesis and characterization efforts will provide detailed experimental information on the electronic and magnetic properties of new molecular magnetic clusters, which can then be fed back into the cluster synthesis efforts to engineer desired characteristics. Moreover, the interplay between theory and experiment will allow for the development of a fundamental understanding of electron and spin motion in these clusters and will therefore aid the design of clusters with novel properties and devices with new functionalities.

The proposed research effort provides powerful educational opportunities for students at Harvard and Berkeley by exposing them to a broad collaboration that encompasses synthesis,

characterization, device fabrication, as well as theoretical calculations. The collaboration between Harvard, Berkeley, and IBM also provides a unique setting in which undergraduate, graduate, and postgraduate students can participate in a collaborative interdisciplinary research effort in nanoscience and technology, while also being exposed to research at world-class academic and industrial research institutions. This unique opportunity, which won't be available to students without this collaboration, will surely broaden their vista and be of aid in their career decisions.

Research Findings:

In the grant period of 2003, we have been working to build a range of molecular inorganic clusters with unique magnetic properties and to fabricate single-molecule transistors incorporating these clusters to investigate their properties. We are also working to build a theoretical model to explain the microscopic mechanism behind their behaviors. Recent effort at UC Berkeley has focused on the synthesis and characterization of molecules exhibiting unique electronic and magnetic properties. To that end, we have synthesized a variety of single-molecule magnets and mixed-valence compounds and characterized their structural and magnetic properties. The effort at Harvard has focused on incorporating these magnetic molecules into single-molecule-transistor devices and studying their transport characteristics. We are uncovering the unusual effects that a large magnetic moment has upon electron transport through single-molecule magnets. Collaboration between Harvard, Berkeley, and IBM has started, and we will further explore the material properties emerging from the combination of these molecules and metallic nanocrystals.

Synthesis of Molecular Inorganic Clusters:

Jeffrey Long and coworkers at UC Berkeley are working to build a range of molecular inorganic clusters with unique electronic and magnetic properties for study in single-molecule transistors and other possible molecular electronic or magnetic devices. The molecules are then sent to Harvard and IBM for incorporation and study in single-molecule transistors, molecular films, and devices. One area that we have been concentrating on is the synthesis of single-molecule magnets—high-spin molecules with axial magnetic anisotropy leading to an energy barrier for spin reversal. As a starting point, the most thoroughly characterized single-molecule magnet, $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$, was prepared, and its purity confirmed by X-ray powder diffraction and elemental analysis. Two analogous clusters with significantly shifted redox properties, $[\text{Mn}_{12}\text{O}_{12}(\text{CHCl}_2\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ and $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_2\text{BrCO}_2)_{16}(\text{H}_2\text{O})_4]$, were also synthesized. In each case, the one-electron oxidized species was generated chemically, and efforts to probe their magnetic ground states are ongoing. Several lines of investigation are being explored for producing new single-molecule magnets exhibiting redox activity and a larger spin reversal barrier. In one approach, we are attempting to generate sizable metal carbonyl clusters using magnetic metals such as Fe and Co. Here, the goal is to obtain clusters large enough to contain interior metal atoms with an environment similar to that in the bulk metal. In order to increase the nuclearity of the clusters beyond six, we have attempted to use heteroatoms as

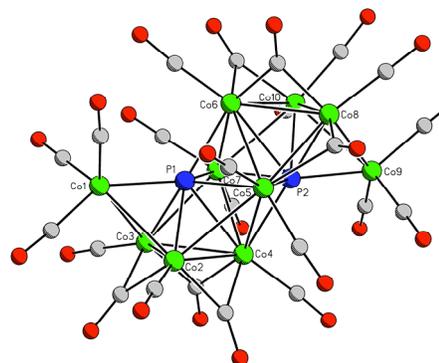


Fig. 1. Structure of the $[\text{Co}_{10}\text{P}_2(\text{CO})_{23}\text{H}]^{2-}$ cluster determined by X-ray crystallography. Green, blue, gray, and red spheres represent Co, P, C, and O atoms, respectively.

nucleation centers. For example, the reaction between $\text{Co}_6(\text{CO})_{16}$, $[\text{Co}(\text{CO})_4]^-$, and PBr_3 was found to generate a paramagnetic $[\text{Co}_{10}\text{P}_2(\text{CO})_{23}\text{H}]^{2-}$ cluster featuring two semi-interstitial phosphorus atoms (see Fig. 1).² The redox chemistry of this unprecedented species is now being explored, as are methods for adding additional cobalt centers to the structure.

Another area of focus is in using single-molecule transistors to probe electron delocalization and spin changes within mixed-valence multimetal clusters. In order to further our understanding of the behavior of devices incorporating the face-centered cubic cluster $[(\text{Me}_3\text{tacn})_8\text{Mo}_8\text{Ni}_6(\text{CN})_{24}]^{12+}$,³ we have attempted to replace the Ni^{II} centers in the molecule with Pt^{II} . Owing to the more diffuse d orbitals associated with Pt^{II} , this replacement is expected to enhance electronic communication within reduced forms of the cluster. The reaction of $[(\text{Me}_3\text{tacn})\text{Mo}(\text{CN})_3]$ with $[\text{PtCl}_4]^{2-}$ in aqueous solution indeed enabled assembly and isolation of an analogous $[(\text{Me}_3\text{tacn})_8\text{Mo}_8\text{Pt}_6(\text{CN})_{24}]^{12+}$ cluster. Efforts to improve the isolated yields of this molecule are ongoing. Other redox active molecules that we have prepared and characterized for related studies include $[(\text{Me}_3\text{tacn})_2\text{V}_2(\text{CN})_4(\mu\text{-C}_4\text{N}_4)]^{9+}$,⁴ $[\text{Mo}_2(\text{CN})_{11}]^{5-}$,⁵ $[(\text{cyclen})_4\text{Ru}_4(\text{pz})_4]^{9+}$,⁶ $[\text{Re}_6\text{S}_8\text{Br}_6]^{4+}$, and $[\text{W}_6\text{CCl}_{18}]^{2-}$.⁷

Transport Characterization of Single-Molecule Transistors: Hongkun Park and coworkers at Harvard are working to fabricate single-molecule transistors incorporating inorganic molecular clusters^{8,9} that are synthesized at Berkeley and to investigate how the electronic motion through individual molecules are coupled to various molecular degrees of freedom including molecular vibration and electronic spin. In this grant period, we have completed the fabrication and characterization of single-molecule transistors incorporating individual ferrocene and nickelocene molecules.¹⁰ These metallocene molecules can be considered as a simplest model system for more complex inorganic molecular clusters, and hence the transport investigations of metallocene molecules provide crucial information on the basic electron transport mode through transition-metal containing molecules. Current-voltage measurements at low temperatures show that electrons pass through these molecules one electron at a time via an individual quantum level, essentially dictated by Coulomb blockade. Analyses of the quantum level structures reveal that single-electron hopping on and off metallocene molecules excites the ring torsion and the center-of-mass oscillation, demonstrating the interplay between the molecular vibrations and single-electron tunneling.

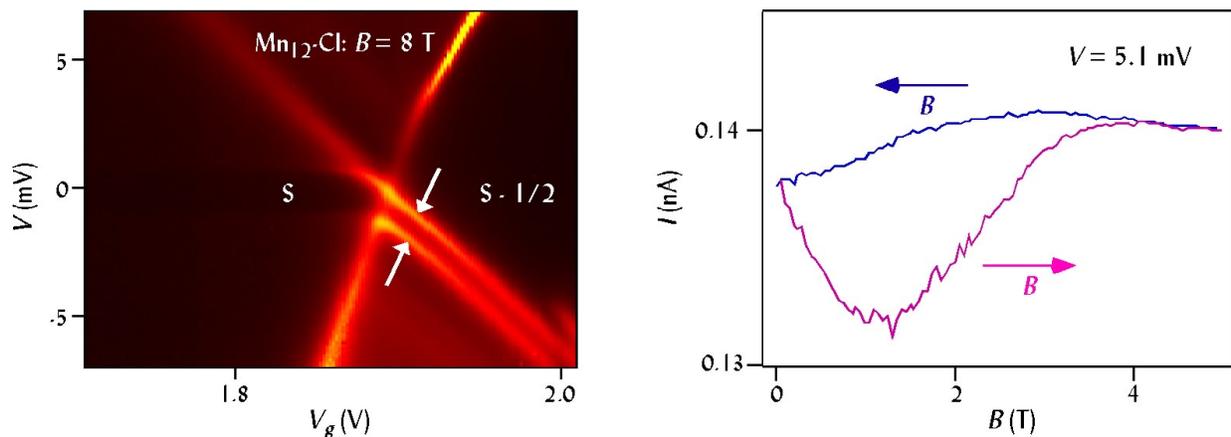


Fig. 2. Left: two-dimensional plot of differential conductance as a function of bias voltage (V) and gate voltage (V_g) obtained from a single-molecule transistor incorporating a single $[\text{Mn}_{12}\text{O}_{12}(\text{CHCl}_2\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ cluster. Right: a plot of current (I) as a function of the magnetic field (B) obtained from the same device, illustrating the magnetic hysteresis of the tunneling current.

In addition, we have also initiated in this grant period the transport characterization of individual $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ and $[\text{Mn}_{12}\text{O}_{12}(\text{CHCl}_2\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ clusters synthesized at Jeffrey Long's group at UC Berkeley.¹¹ Low-temperature transport measurements performed on single-molecule transistors incorporating these clusters show that the electrical conduction through individual clusters is governed by single-electron tunneling through individual quantum levels, as in the case of metallocene molecules. Most importantly, the current-voltage characteristics exhibit hysteresis of tunneling currents as a function of magnetic field (Fig. 2), illustrating that indeed the magnetic character of the molecule significantly influences the current transport even in the single-molecule level. We are currently investigating the microscopic mechanism for this magnetic hysteresis both experimentally and theoretically.

Characterization of Molecular-Magnet Thin Films: This past summer, a graduate student from UC Berkeley spent three months at IBM preparing and characterizing thin films and devices incorporating some of these molecules. Uniform, dense films of the $[\text{Mn}_{12}\text{O}_{12}(\text{CHCl}_2\text{CO}_2)_{16}(\text{H}_2\text{O})_4]$ clusters were obtained by spin-coating 0.5% (by weight) dichloromethane solutions onto silicon wafers. Characterization of the films by SEM revealed an unusual honeycomb pattern of 100-nm wide indentations within the films that presumably arises from the rapid evaporation of dichloromethane. Devices with gold electrodes spaced between 180 nm and 6 μm apart were prepared for measuring conductivity (and ultimately magnetoresistance) within these films; however, even at the smallest separations, the observed conductivities were low and did not scale linearly with distance. Further studies are required to establish conditions leading to better contact between the molecules and the gold electrodes.

Theoretical Studies of Single-Molecule Transistors: David Reichman and coworkers at Harvard are working to develop a theoretical model to explain the electronic and magnetic properties of inorganic molecular clusters as well as the basic electron transport mode through these molecules when they are incorporated into the single-molecule-transistor configuration. In this grant period, we have studied how electrons are transported in various inorganic clusters via the construction and numerical study of simple Hubbard models and applied it to the optical conductivity of the Creutz-Taube square clusters studied by Jeffrey Long and coworkers. Our model for the electronic structure of these clusters consists of sites both nuclei and bridge locations, and includes the effect of orbital contraction. The hopping and Coulomb parameters are chosen based on previous experiments, and the optical conductivity is computed exactly within the Lanczos scheme. We are currently including the vibrational degrees of freedom to make closer connection to the low energy experiments carried out by Hongkun Park and coworkers. We are also performing density functional calculations to make quantitative estimates of the parameters in the extended Hubbard model of charge hopping.

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