Molecular Nanomagnets: Magnetic and Electronic Properties of Novel Magnetic Nanostructures and Nanostructured Materials

NSF NIRT Grant 0103455

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The focus of this NIRT is synthesis of new nanoscale magnetic molecules, whose magnetic and electrical properties can be tailored by design, and development of techniques to assemble these molecular magnets and more conventional electronic and magnetic materials together to create new nanostructures and nanostructured magnetic materials. Research goals include: 1) designing and synthesizing new magnetic nanoscale molecules; 2) understanding the quantum properties of these large-magnetic-moment molecules; 3) assembling new magnetic nanostructures from these molecular and conventional micro/nanoscale building blocks that will exhibit magnetic and electronic effects useful for a wide range of novel applications; 4) understanding the interaction of these molecules and building blocks in complex nanostructures.

The research in the first year of the NIRT project was focused on: 1) synthesis of novel and modification of currently available Single Molecule Magnets (SMM) to generate new molecules with unique properties; 2) pilot studies for the SMM thin film and nanoparticle fabrication; 3) theoretical calculations of the SMM magnetic interaction with its environment to understand the previously documented, but poorly understood quantum behavior of the molecules; 4) development of structures for magnetic traps for observation and manipulation of large biomolecules; 5) enhancement of our experimental tools, particularly AFM, MFM and STM, for manipulation and characterization of these magnetic molecules and nanostructures. Highlights of progress to date is described below:

1) We are using magnetic anions of the type $[M(CN)_6]^{\{n-\}}$ to connect catonic cis-$[M(L\text{-}L)_2]^{\{n+\}}$ units into larger molecular architectures whose magnetic anisotropy leads to the observation of SMM behavior. Clusters such as open molecular pentamers and closed trigonal bipyramidal geometries have been prepared with Co or Ni ions together with Fe ions and with Mn ions. We have prepared the first incontrovertible example of a cyano-bridged SMM composed of Mn ions [1], and have been able to systematically prepare molecules of the same geometrical shape and nuclearity. (See Fig. 1 left.) Development of this SMM validates our proposed strategy for the synthesis of new magnetic clusters based on molecular architectures that have a unique axis of symmetry.

One goal in the manipulation of molecules that exhibit slow relaxation effects in their magnetization is their deposition on surfaces. We have sought to develop new Mn_{12} SMMs with different ligands. Data for a new Mn_{12} compound prepared in our laboratories indicates that the molecule retains its SMM nature upon substitution of trifluoroacetate ligands for acetate. (See Fig. 1 right.) Manipulation of the capping groups will be essential in efforts to control self assembly of the SMM's into useful composite structures. Succcessful substitution of triflouroacetate ligands on an SMM from the Mn_{12} oxide family is a major step since it should be possible to use this compound to prepare numerous other derivatives of Mn_{12} clusters.

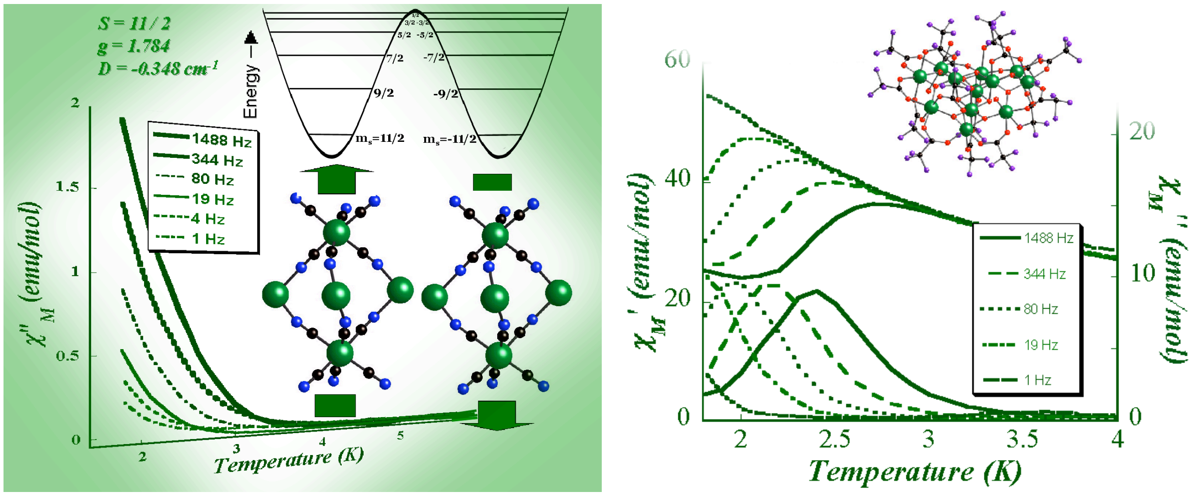

Figure 1. Left: $[Mn^{III}(CN)_6]_2[Mn^{II}(tmphen)_2]_3$, skeletal molecular structure and experimental data with potential energy diagrams, a New Cyano-Bridged SMM. Right: AC-susceptibility for the new SMM: $[Mn_{12}O_{12}(CF_3COO)_{16}(H_2O)_4]$

2) Efforts to grow thin films and adsorbed layers of these SMM's are in progress. Two of the more promising approaches under investigation include the use of matrix assisted pulsed laser deposition for thin films and self assembly induced by nanostructured magnetic templates for patterned adsorption.

3) Theoretical efforts were focused on the interaction of SMM/nanomagnets with the environment, which includes studies of the Landau-Zener problem for better understanding of the process of the magnetic moment tunneling [2,3] and on the SMM/nanomagnet interaction with a superconducting film [4,5] which is the crucial design element of a micro or nanoSQUID magnetometer. In a real SMM with organic ligands the large electronic spin associated with the ferromagnetically coupled 3-d elements interacts strongly with the many chaotically oriented nuclear spins. This hyperfine interaction should completely distort the Landau-Zener tunneling probabilities; however, recent experiments on Fe_8 SMM's by Wernsdorfer and Sessoli are well described by Landau-Zener tunneling. Our detailed analysis shows that, for fast sweeps of the magnetic field used in that experiment, the decoherence effects produced by the hyperfine interaction are precisely compensated by the multiplicity of the interacting nuclear spins. The corollary prediction is that the Landau-Zener formula fails for slow sweeps of the field.

4) We have proposed [6] use of micro/nanometer size magnets (magnetic dots, nanowires) to capture and manipulate with magnetic fields diamagnetic objects such as macromolecules (DNA, proteins), nanoparticles and cells. The key to this approach is the very high magnetic field gradients available at the micro/nanometer scale. Trapping and manipulation of micron size objects with magnetic fields, like the rod-like array of red blood cells captured in a magnetic "bottle" shown on Fig. 2, has been successfully demonstrated by Igor Lyuksyutov in our NIRT.

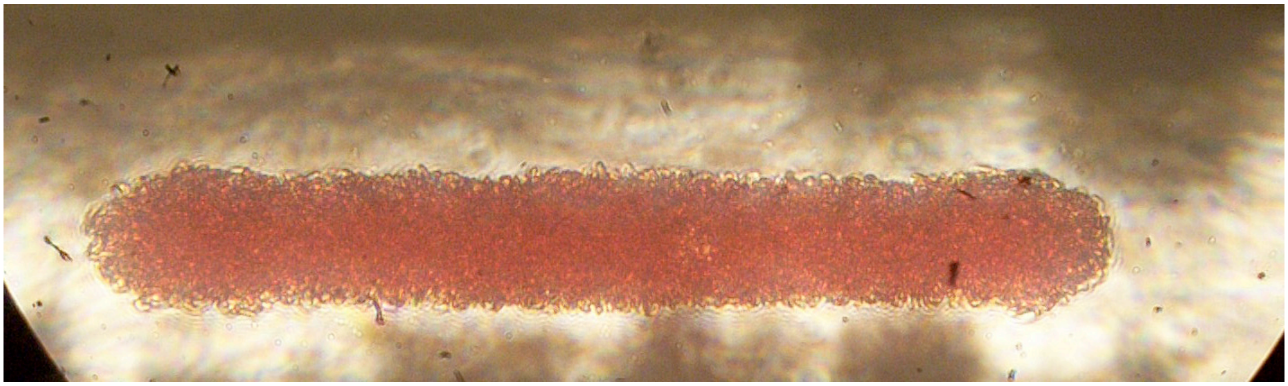

Figure 2. Red blood cells captured in "magnetic bottle" created by assembly of micron scale magnets. The diameter of the "bottle" is about 50 microns.

5) A new low temperature AFM/MFM system is being installed to probe the thin film and adsorbed layer structures. We plan to use this system to manipulate SMM's in situ at low temperatures, and to study the magnetic interactions of SMM's and magnetic nanostructures. A novel combination AFM/STM for inelastic electron tunneling spectroscopy (IETS) has been designed and is under construction with its low temperature UHV system. It would be capable of simultaneous atomic imaging and chemical characterization by the vibrational spectra of a single molecule as well as study of the molecule's electronic coupling to the substrate.

References:
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