

Friday Morning, November 13, 2009

Magnetic Interfaces and Nanostructures

Room: C1 - Session MI-FrM

Molecular/Organic Based Magnetism

Moderator: A.N. Caruso, University of Missouri-Kansas City

8:20am **MI-FrM1 Molecular/Organic based Magnetism: New Chemistry, Physics, and Technologies**, *A.J. Epstein*, The Ohio State University **INVITED**

In recent years a broad range of magnetic and magnetotransport phenomena have been reported for organic semiconductors. Unpaired spins in the p orbitals of organic systems have been shown to yield new physics and be the basis of potential new technologies of broad interest. Organic-based magnets with magnetic ordering temperatures from a few K [1] to > 400 K [2] have been successfully synthesized. In addition, new magnetic phenomena have been discovered including fractal magnetism, photonically controlled magnetism, nanoscale magnetic bubbles, and fully spin polarized magnetic semiconductors[3]. Further, magnetotransport (MR) in magnetic and nonmagnetic organic semiconductors has revealed a host of heretofore unknown spin-dependent phenomena, including 20% change in resistance at room temperature for application of as little as 100 Oe to nonmagnetic organic semiconductors. The room temperature magnetic semiconductors $V[\text{TCNE}]_{x-2}$, (TCNE \equiv tetracyanoethylene) [2,3] has many new properties such as fully spin polarized energy bands and magnetism from 0 to 400 K and photonic response. The analogue $\text{Fe}[\text{TCNE}]_x$ forms monolayer thick spin layers that produce 'spin bubbles' upon application of a critical field.

These advances in science have prompted interest in the possibility of technologies based on these new materials. These new potential technologies will be discussed with emphasis on organic-based spintronics including tunneling magnetoresistance (TMR) and giant magnetoresistance (GMR) devices and also use of these materials as sensors in the emerging THz range.

This work was supported in part by NSF, DOE, AFOSR, and OSU Inst. for Mater. Res.

[1] S. Chittipeddi, K. Cromack, J.S. Miller, and A.J. Epstein, "Ferromagnetism in Molecular DecamethylferroceniumTetracyanoethenide ($\text{DMeFc}(\text{TCNE})$ ", *Phys. Rev. Lett.* 58, 2695 (1987).

[2] J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, and J.S. Miller, "A Room Temperature Molecular/Organic-Based Magnet", *Science* 252, 1415 (1991).

[3] A.J. Epstein, "Organic-based Magnets: Opportunities in Photoinduced Magnetism, Spintronics, Fractal Magnetism, and Beyond", *Mater. Res. Soc. Bull.* 28, 492-499 (2003).

[4] V.N. Prigodin, J.D. Bergeson, D.M. Lincoln, and A.J. Epstein, "Anomalous Room Temperature Magnetoresistance in Organic Semiconductors", *Synth. Met.* 156, 757 (2006).

[5] T. Francis, O. Mermer, G. Veeraraghavan, and M. Wohlgenannt, "Large Magnetoresistance at RoomTemp. in Semiconducting Polymer Sandwich Devices", *New J. Phys.* 6, 185 (2004).

9:00am **MI-FrM3 Tuning Molecule-Mediated Spin Coupling in Bottom-Up Fabricated Vanadium-TCNE Nanostructures**, *D. Wegner, R. Yamachika, X. Zhang, Y. Wang*, University of California, Berkeley and Lawrence Berkeley National Laboratory, *T. Baruah*, University of Texas, El Paso, *M.R. Pederson*, Naval Research Laboratory, *B.M. Bartlett, J.R. Long*, University of California, Berkeley, *M.F. Crommie*, University of California, Berkeley and Lawrence Berkeley National Laboratory

We have fabricated hybrid organic/inorganic magnetic molecules based on vanadium atoms and tetracyanoethylene (TCNE) ligands in an atom-by-atom fashion using a cryogenic scanning tunneling microscope. Using tunneling spectroscopy we observe spin-polarized molecular orbitals as well as a structure-dependent Kondo resonance. For complexes having two V atoms, the Kondo behavior can be switched on and off by a minute structural change that leaves the spin-containing orbital essentially unchanged. This can be explained by a tunable, structure-dependent change in the vanadium spin-spin coupling strength through the TCNE molecule, as confirmed by density functional calculations. The present findings offer a new route for designing molecular spin nanostructures with atomic-scale precision.

9:20am **MI-FrM4 Resolving the Interface Magnetism of a Molecule-Based Spin Filter**, *J. Brede, S. Kuck, G. Hoffmann*, University of Hamburg, Germany, *P. Lazic, S. Blügel*, FZ Jülich, Germany, *R. Wiesendanger*, University of Hamburg, Germany, *N. Atodiresi*, FZ Jülich, Germany

The use of magnetic molecules opens a gateway to a flexible design of spintronic devices to store, manipulate, and read spin information at nanoscale level. Crucial is the precise knowledge of molecular properties at the interface towards an electrode. Progress into this field relies on resolving and understanding the physics at the relevant interface, the role of individual molecular constituents, and the impact of the atomic environment nearby on molecular properties. Here, we apply spin-polarized scanning tunneling microscopy to resolve the physics of such an interface formed of a magnetic metal-organic molecule adsorbed on a magnetic substrate to observe on an atomic scale the operation of single-molecule spin filter. The experimental data reveal a significant and strongly site dependent localization of spin split states at the interface. To understand the resulting spin-polarization, density functional theory calculations are performed with an extension to describe correlation effects present due to the close proximity of a molecule and a metallic substrate. The results of the joint work are presented and the physical processes at the molecule-electrode interface are discussed.

Acknowledgements: This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project "SPiDMe".

9:40am **MI-FrM5 The Densest Iron Coordination Network Based on Carboxylate Ligands**, *D. Eciija, C. Urban, M. Trelka*, Universidad Autonoma de Madrid, Spain, *C. Marti-Gastaldo, E. Coronado*, ICMOL & Universidad de Valencia, Spain, *J.M. Gallego*, ICMM-CSIC, Spain, *R. Otero, R. Miranda*, UAM & IMDEA-Nano, Spain

Over the last decade there has been a tremendous effort in order to create new kinds of supramolecular organic nanostructures on surfaces, with the prospect of possible catalytic, electronic, optical or magnetic applications. In particular, a lot of attention has been paid to metalorganic coordination networks (MOCNs), with the idea of creating functional metallo-supramolecular arrays on surfaces which combine the properties of their constituent metal ions and ligands.

Following this approach, the chemisorption of small molecules with ending carboxylic acids on metal surfaces has been extensively studied and deprotonation of the acid groups to produce carboxylate groups described [1]. These deprotonated groups can interact strongly with both metal surfaces and metal adatoms (either intentionally deposited or already existing as a 2D background gas that results from the emission of atoms from low coordination sites such as steps and kinks). This metal-to-carboxylate interaction, when properly addressed, leads to the formation of regular patterns of MOCNs. We have deposited oxalic acid, i.e. the smallest possible molecule with two carboxylic groups ($\text{C}_2\text{O}_4\text{H}_2$), on non magnetic Cu(100) surfaces, both clean and with a small pre-deposited amount of Fe. Scanning Tunneling Microscopy (STM) shows that moderate annealing of these systems lead to the formation of two different, new MOCNs: a rectangular copper-oxalate network, and a honeycomb iron-oxalate network, where the regularly spaced Fe spins have the smallest distance (5.2 Å) reported up to date, making the Fe-oxalate MOCN a promising system for an in-depth study of their magnetic properties.

[1] S. Stepanov, N. Lin, J. V. Barth, *J. Phys.: Condens. Matter* 20 (2008) 184002.

10:00am **MI-FrM6 Spatially Extended Kondo Resonance in Magnetic Molecules**, *U.G.E. Perera*, Ohio University, *H.J. Kulik*, Massachusetts Institute of Technology, *V. Iancu*, Ohio University, *L.G.G.V. Dias da Silva*, Oak Ridge National Laboratory and University of Tennessee, *S.E. Ulloa*, Ohio University, *N. Marzari*, Massachusetts Institute of Technology, *S.-W. Hla*, Ohio University

Molecules containing transition-metal complexes have great potentials in the emergent fields of spintronics and molecular electronics. Especially, controlling their spin states and spin polarization is a key challenge for future applications. Here, we report an extensive and unusual redistribution of spin density for self-assembled TBRPP-Co [5, 10, 15, 20 -Tetrakis -(4-bromophenyl)-porphyrin-cobalt] molecules adsorbed on a Cu(111) surface as a model system to investigate spin polarization, the effect of molecular orbital in Kondo resonances. The TBRPP-Co molecule has a spin-active cobalt atom caged at the center of porphyrin unit and four bromo-phenyl groups are attached to its four corners. STM imaging shows the molecules with four pronounced lobes. These molecules readily self-assemble and

form ordered, ribbon-like monolayer islands on Cu(111), with a preferential growth direction $\sim 7^\circ$ deviated from the [110] surface directions. We probe the spatially extended Kondo resonance of the molecules by monitoring the effective Kondo temperature with differential conductance (dI/dV) tunneling spectroscopy, finding it much larger on the macro-cycle itself than on the central cobalt atom. The origin of this effect is explained by means of first-principles and numerical renormalization group calculations, highlighting how it is possible to engineer spin polarization and electronic transport by means of adsorption chemistry. This work is supported by the US Department of Energy Basic Energy Sciences grant no. DE-FG02-02ER46012.

10:20am **MI-FrM7 Pressure Dependent Magnetic and Optical Properties of M [TCNE] (MeCN)₂X (M= V, Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) Organic-Based Magnets.** *K.I. Pokhodnya, C. Olson, North Dakota State University, A. Midgley, M.B. Kruger, A.N. Caruso, University of Missouri - Kansas City*

M-TCNE molecule-based ferrimagnets demonstrate high magnetic ordering temperatures up to 400 K (M = V) due to strong AFM exchange between *d*-electrons of the metal and the anion-radical spin of the TCNE ligand. Magnetic and optical properties of the family of molecule-based 2D magnets [M(TCNE)(NCMe)₂] X (M=Fe, Mn, Ni; X=BPh₄, FeCl₄, SbF₆) will be discussed. Classical bonding-sensitive IR spectroscopy has difficulties distinguishing between the bonding and backbonding interactions (possibly mediating the strong superexchange), since their effects on CN bond stretching mode frequencies may cancel each other. In contrast, Raman active $\nu(\text{C}=\text{C})$ modes solely depend on charge transfer to/from the p^* antibonding orbital, and thus are only backbonding sensitive. The observed strengthening of the $\nu(\text{C}=\text{C})$ and $\nu(\text{N}^\circ\text{C})$ Raman modes for the compounds with higher T_c suggests the depopulation of the p^* orbital and enhanced ligand to metal charge transfer resulting in a hybrid $M3d$ -CN ground state with substantial admixture of ligand electron. The observed pressure-induced strengthening of the $\nu(\text{C}=\text{C})$ and $\nu(\text{N}^\circ\text{C})$ Raman modes is in accord with proposed backbonding model. The correlation between the frequency shift (degree of backbonding) and magnitude of T_c from M(T) is established.

10:40am **MI-FrM8 UV/Vis Magnetic Circular Dichroism of Fe[TCNE],** *S.Z. Janjua, A.N. Caruso, University of Missouri - Kansas City*
The unoccupied electronic structure of the $\text{Fe}^{II}[\text{TCNE}]_2\text{S}$ (TCNE = tetracyanoethylene; S = CH_2Cl_2) organic-based magnet has been studied using x-ray magnetic circular dichroism (XMCD) and standard x-ray absorption, but no clear picture of the binding energies nor their spin polarization has been determined. UV/Vis MCD studies have been completed, and will be presented within the ligand to metal charge transfer transition model, as a complimentary and possibly more sensitive means by which the unoccupied electronic structure may be determined. Further, the UV/Vis MCD were conducted to investigate the charge and intervalence transfer from ligand to metal orbital's.

11:00am **MI-FrM9 Perspectives in Multi-Functional Single-Molecule Magnets and Single-Chain Magnets.** *M. Yamashita, Tohoku University, Japan*
INVITED

Recently, the quantum molecular nano-magnets have been attracting much attention from the viewpoints of the basic sciences as well as the applied sciences such as memory storages, quantum computers, etc. So far more than 300 single-molecule quantum magnets have been reported, while about 20 types of single-chain quantum magnets have been reported. They have several interesting themes to be resolved as follows: (1) High blocking temperature, (2) Quantum GMR, (3) Memory storage into one quantum molecule magnet, (4) Quantum computer, (5) Quantum FET, (6) Glauber dynamics, (7) Multi-functionalities, (8) Kondo effect, etc.

As for (1), since the potential barrier of the double wells is defined as DS^2 and $(8J+D)S^2$ for the single-molecule magnets and single-chain magnets, respectively, we must increase the *D*, *S*, and *J* parameters to raise the blocking temperatures of these compounds. However, the control of the parameter *D* is very difficult. Then, we propose the conducting quantum molecular magnets. By the interaction between conducting electrons and localized quantum molecule magnets, the coherence among the quantum molecule magnets is strengthened and then the spin flips are made difficult, resulting in raising the blocking temperature. According to such a strategy, we have synthesized three types of conducting single-molecule magnets such as $[\text{Mn}_4(\text{hmp})_6(\text{MeCN})_2][\text{Pt}(\text{mnt})_2]_6$, $[\text{Mn}_2(5\text{-MeOsaltmen})_2(\text{MeCN})_2][\text{Ni}(\text{dmit})_7(\text{MeCN})]$, and $[\text{Mn}_2(5\text{-Rsaltmen})_2][\text{Ni}(\text{dmit})_2]$. As for (2), since in the quantum molecular magnets, we can create artificially the large spin numbers such as $S=10, 20, 30$, etc, we can anticipate new quantum GMR phenomena by interacting between large *S* and conducting electrons. According to such a strategy, we

try to synthesize a metallic single-molecule magnet. Otherwise, we have a plan to occur a photo-induced phase transition from semiconductor to metallic state in conducting single-molecule magnet. As for (3), we have accessed to one single-molecule magnet of Pc_2Tb by STM. We have a plane to input one memory into one single-molecule magnet and output it from one single-molecule magnet by using spin-polarized STM. We have observed Kondo Effect at 4.8 K in this compound by STS for the first time. As for (7), we have synthesized the single-molecule magnet with photo-induced switching and the single-chain magnet with absorption and desorption of crystal solvents reversibly like a spo

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