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EMERSON CENTER Newsletter

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Emerson Center Welcomes New Subscribers: Prof. Lanny Liebeskind (Chemistry) & Prof. Tianquan (Tim) Lian (Chemistry)

The research of Dr. Lanny Liebeskind, Samuel Candler Dobbs Professor of Chemistry and Director of University Science Strategies, focuses on modern problems of medicinal, organometallic, materials, synthetic organic, and catalytic chemistry. Dr. Liebeskind's research requires an atomistic and molecular level understanding of fundamental principles of transition-metal catalyzed cross-coupling reactions (including carbon-heteroatom bond formation), which is vital for development of new and more effective synthetic protocols for the controlled formation of a covalent bond at a specific site on a complex molecule. One of examples is a novel and mechanistically unprecedented carbon-carbon coupling reaction discovered by Dr. Liebeskind: *the coupling of thiol esters with boronic acids at neutral pH under aerobic conditions in the presence of catalytic quantities of a Cu salt.* Dr. Liebeskind plans to use the Emerson Center facilities to elucidate the roles of Cu-centers in this important process. The acquired knowledge from these computational studies later will be applied to the selective carbon-carbon bond functionalization of small peptides using catalytic Cu under ambient and aerobic conditions. For more details see: http://www.chemistry.emory.edu/faculty/liebeskind.html

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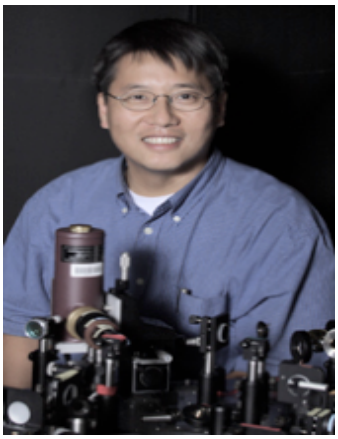
The research of Dr. Tim Lian, Professor of Physical Chemistry, is devoted to the understanding of structure-dynamics-function relationship in nanomaterials and biological systems. Dr. Lian's laboratory focuses on dynamical processes that both serve as good model systems for understanding fundamental aspects of chemical reactions and have potential practical applications. Dr. Lian's current interests include nanomaterials, nanoparticle-liquid interface, molecular solar cells, biomolecules and living cells. Recently, Dr. Lian along with his colleagues, Dr. Craig Hill (Chemistry) and Dr. Jamal Musaev (Emerson Center), was awarded by Department of Energy to develop solar-energy driven multi-electron transfer catalyst for water oxidation. The proposed three-component nanoassembly includes the well-established Grätzel cell (comprising nanoporous TiO_2 surfaces modified with Ru-tris(bipyridyl) derivatives) and a polyoxometalate (POM) catalyst. Designing of this complex nanoassembly requires an in detail understanding of electron transfer processes in this system, roles of linkage-groups, as well as molecular mechanisms of water splitting, H-H and O-O bond formation. Dr. Lian and his colleagues plan to use the Emerson Center facilities to shed light of these fundamental issues. For more details see: http://www.chemistry.emory.edu/faculty/lian.html



The Emerson Center Leadership Committee

The EC Leadership Committee Meeting was held on September 19, 2007. Various topics were discussed to include Computer Upgrades and Subscriber Membership. The committee agreed to increase the rent for the Emerson Center's Clairmont campus apartment. The rent for one bedroom is now $800.00 or $1600.00 for the entire apartment.

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EMERSON CENTER VISITING FELLOWSHIP

The Emerson Center offers visiting fellowships to interested scientists throughout the year. Scientists from academic institutions all over the world who want to perform intensive research in computational chemistry, biology, physics, and math & computer sciences for one to several months are encouraged to apply. Travel expenses and stipends are available. Although fully independent research is not excluded, collaboration with an EC subscriber is desirable, and EC subscribers are encouraged to make recommendations. The deadline for Emerson Center Visiting Fellowship applications for summer 2008-summer 2009 is February 1, 2008. To formally apply, please submit:

- 1-2 page research proposal
- CV including publication list
- Amount of financial support needed
- Length of stay with an approximate start/end date

Applications should be submitted to the Director of the Center, Dr. Jamal Musaev, by email at dmusaev@emory.edu.

APPLICATION DEADLINE: February 1, 2008

My Stay at the Emerson Center as a Visiting Fellow

Dr. Nedialka Iordanova

To do a research at the Emerson center as a visiting fellow was a great experience. I have met many excellent scientists and I had the privilege to work under the guidance of Prof. Keiji Morokuma. My short time at the Emerson center was busy and very interesting. I was working on elucidating the mechanism of reactions involving phosphorous-containing compounds, that play an important role in the use, production, incineration, and accidental emission of chemical warfare nerve agents, pesticides, flame retardants, hydraulic fluids. My work at the Emerson center allowed me to use the great computer resources that the center and Prof. Morokuma's group have, as well as to enjoy many stimulating discussions with my colleagues.

Photo Left- Dr. Iordanova Right - Visiting Fellows with EC and Group Members

Hosting a Short-Term Visitor?

The Emerson Center may be able to help you house your short-term visitor. We have a continual lease on a 2-bedroom/2-bathroom apartment at the Clairmont Campus for the Center's visiting fellows. The apartment has vacancies from time to time and we would be happy to make the space available to other short-term visiting faculty on campus. The apartment has easy shuttle access to campus and is fully furnished with cable TV and internet access. The current rent, which includes all utilities and local telephone service, is $800 per room per month, or $40 per day if less than 30 days. Please call 727-0867 or email ttaitt@emory.edu for more information.

Letters from Fellows

Thanks to the Emerson Center Visiting Fellowship program for allowing me to visit Emory University and work with Prof. Michael Heaven and his group. During my stay here as an EC visiting fellow, I have spent a highly academic and wonderful time for it was extremely convenient to work in the center with powerful computers, abundant resources of the latest scientific information and serene ambience. Though I did not have prior experience working with Mac based computers and MOLPRO, special thanks to Dr. Jeremy Merritt whose valuable help and assistance during the initial stages helped me have a successful turn around consequently.

My goal in visiting Emerson Center at Emory was to enhance my knowledge of large-scale quantum mechanical computations for high qualify potential energy surfaces of a Rg-OH complex and I am sure this endeavor will take me a long way. I would like to extend my heartfelt gratitude to Prof. Heaven, who agreed to this collaborative research. I am also thankful to Dr. Jamal Musaev, director of the center, who was extremely helpful in resolving accommodation issues and other paper formalities which an international visitor like me have to overcome. Also, I would like to extend my thanks to secretaries Ms. Jianli Zhao and Mrs. Tara Taitt, Dr. Ioannis and many other post doctoral fellows of the center and Chemistry department, who helped me in many different ways during my stay.

Although I am eagerly looking forward to returning home to Varanasi, India, I'll miss the green grass and amicable Emory people very much.

Dr. Vipin Bahadur Singh
U.P. Autonomous College Varanasi, India

Emerson Center has got a new web-site:

Emerson Center's original website has had a major makeover and been moved to a web server in the North Decatur building. The old server is to be decommissioned in the near future. The structure and information content of the website have remained largely the same. The main difference is the presentation and design. With the generous help of Information Technology's multimedia developers Marianne Schneider and Steve Bean the website has taken on a more professional look, in line with the official websites of University's departments. We thank Jianli Zhao for pitching the original idea of redesign and organizing the workforce for reconstruction.

Report on Research Activities at the Emerson Center

The Emerson Center is supported, in part, by "subscribers" – faculty members, research groups or departments that purchase shares in order to gain access to its resources for their research projects. EC scientific staff members are also encouraged to conduct scientific in their own areas of specialty. The following is a research report from the Emerson Center:

Craig L. Hill, Chemistry Department

Computation aided study on designing a new and more efficient nano-scaled catalyst and unprecedented late-transition metal-oxo complexes.

My research greatly benefits from the use of the Emerson Center resources. The central thrusts of my integrated experimental and computational (in collaboration with Dr. Jamal Musaev, Emerson Center) research program are (1) to obtain an atomistic and molecular-level understanding of the structural and dynamic factors underlying the design of catalysts for selective reductant-free O_2 oxidations, and (2) to elucidate fundamental principles of designing new and more efficient materials.

The focus of my first project is on oxygenation catalysts that contain two proximal and synergistically interacting redox-active metal centers in the active site because molecules with such sites, including the di-iron centered polyoxometalate (POM), $[\gamma(1,2)\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$ (Figure 1), relate to both methane monooxygenase (MMO) and related enzymes and some of the most effective or promising synthetic oxygenase-like catalysts known.

Previously, the complex $[\gamma\text{–}(1,2)\text{-}SiW_{10}\{Fe(OH_2)\}_2O_{38}]^{6-}$ (**1**) has been reported to catalyze the much sought reductant-free selective O_2-based epoxidation of alkenes in chlorocarbon-acetonitrile solution. The challenge of reproducing catalysis by **1** led us to examine this chemistry in detail. In H_2O, a desirable solvent for catalysis, **1**, does not exist in the proposed organic-medium form in which the two iron atoms are in the binding pocket defined by the equatorial oxygens and, importantly, by two oxygens bound to the central Si heteroatom. Instead, **1** in H_2O initially forms an unusual trimer $[\{Fe_2(OH)_3(H_2O)_2\}_3(\gamma\text{-}SiW_{10}O_{36})_3]^{15-}$ (**2**). The X-ray structure of **2** shows that the Fe-O_{Si} bonds are cleaved and new bonds (μ-hydroxo bridges) form between these Fe centers and those of the neighboring $[\gamma\text{–}(1,2)\text{-}SiW_{10}Fe_2]$ units. Computational studies were instrumental for understanding chemistry of this specie. Structural, physical and computational evidences indicate that if the bonds between the d-electron center, M (Fe in the case of **1** and **2**) and the terminal ligands on M are stronger than the M-O_x bonds, then the out-of-pocket form is more stable and is the one observed. Significantly, **2** in H_2O forms an intermediate that catalyzes the effective aerobic oxidation of sulfur compounds (mercaptoethanol is oxidized to the corresponding disulfide by O_2 at ambient pressure and temperature). All experimental findings are consistent with dissociation of a γ-SiW_{10} Keggin unit from the trimer, **2**, to form the catalytically active species.

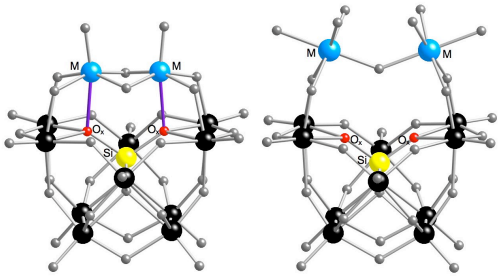


Figure 1. Two distinct structural forms of the polyanion with adjacent interacting d-electron centers ("M" in blue; M = Fe^{III} , for **1**).

Computational studies also allowed us to elucidate the roles of chemical composition (X, M and M_{FW}) of di-transition-metal-substituted γ-Keggin polytungstates and polymolybdates, $[(X^{n+}O_4)M_2(OH)_2(M_{FW})_{10}O_{32}]^{(8-n)-}$, on the geometry, electronic structure, magnetic properties, and reactivity of these species. We have shown that:

Changing the heteroatom X from the electropositive Al^{III} to the more electronegative S^{VI} stabilizes high-spin states of the M_2-γ–Keggin POMs and increases the magnitude of antiferromagnetic coupling constant, *J*. We predicted that the oxidizing power of $[(X^{n+}O_4)M_2(OH)_2(M_{FW})_{10}O_{32}]^{(8-n)-}$ increases via X = Al < Si < P < S.

The change of the redox-active center M in M_2-γ-Keggin POMs from Mn to Fe slightly increases the M-(XO_4) interaction and the magnitude of antiferromagnetic coupling between the M-centers. Simultaneously, it stabilizes the LUMO of $[(X^{n+}O_4)M_2(OH)_2W_{10}O_{32}]^{(8-n)-}$. As a result, $[(X^{n+}O_4)Fe_2(OH)_2W_{10}O_{32}]^{(8-n)-}$ shows stronger oxidant character than $[(X^{n+}O_4)Mn_2(OH)_2W_{10}O_{32}]^{(8-n)-}$. The HOMO of M = Fe involves principally M-based orbitals, while in the M = Mn it involves, mainly, framework atom-based orbitals. In the other words, the di-Fe-substituted γ-Keggin POMs are predicted to exhibit more Fe-type chemistry, while their Mn-analogs are predicted to show mainly M_{FW}-based activities.

Upon changing the framework atoms M_{FW} from W to Mo, (a) the geometry of Keggin "cage" becomes slightly smaller, (b) the interaction of redox-active centers (Fe) with the central XO_4-unit becomes stronger, (c) the magnitude of antiferromagnetic *J*-coupling constant becomes larger, and (d) the nature of the LUMO changes from M–O_X anti-bonding for M_{FW} = W to Mo-O anti-bonding for M_{FW} = Mo.

Computation analyses were instrumental in designing a new class of compounds that also exhibits proximal and synergistically interacting redox active metal centers. (Figure 2). These molecules contain late transition metal centers (M) with terminally bound oxygens. There has been considerable discussion in the literature and at conferences over the last 35 years on the existence and importance of late transition metal oxo (LTMO) units and commensurate experimental efforts over this period to prepare and investigate these species. However, the intrinsic instability of this inorganic functional group (that derives in good measure from high occupation of σ* and π* antibonding M=O orbitals) has conspired to render all these attempts futile until our work in this program. Based on our computational analyses, we have concluded that the interaction of empty delocalized W-based orbitals on the POM ligands with the π* orbitals of the metal oxo unit can lower the energy of the latter orbitals and reduce the electron population in them (see Scheme 1). Armed by this computational support we have now prepared and thoroughly characterized LTMO species of the work-horse elements for catalysis, and catalytic oxidation in particular (Pt, Pd, Au, and Ir).

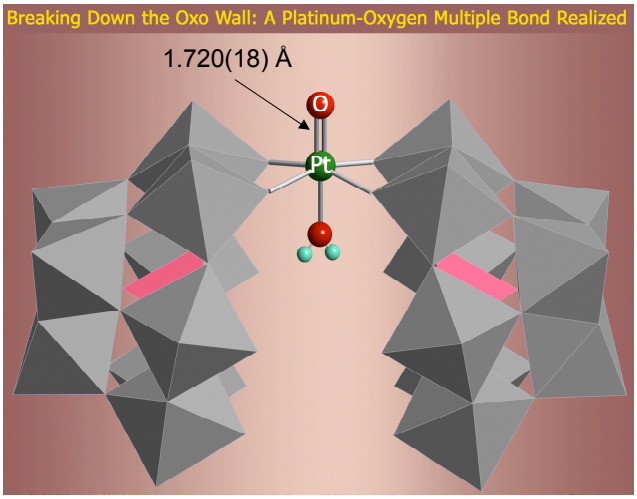
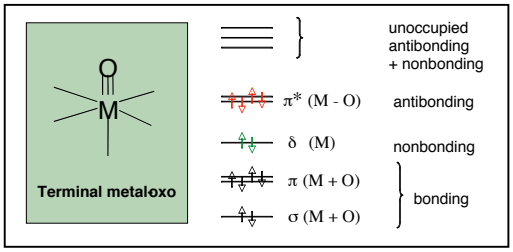


Figure 2. X-ray structure of a terminal M=Pt-oxo complex (Hill et. al., Science 2004, 306, 2074)



Scheme 1.

EC Hardware/Software Report *Dr. Alex Kaledin, Emerson Center*

New scientific software were added:

Scientific software additions to the EC libraries include (i) NWChem 5.0 (parallel), which features the celebrated Car-Parrinello Density Functional Molecular Dynamics, an efficient approach to simulating real time dynamics of large scale systems in gas phase and solvent; (ii) MOLPRO 2006.1 parallel -- the long-awaited parallel capability has been added to this popular software. Since the scaling is known to be poor, only 2 processors per parallel job will be allocated; (iii) NAMD_2.6 integrates structural information with bioinformatics databases and molecular dynamics simulations; high performance molecular visualization and simulation (www.ks.uiuc.edu); (iv) TINKER 5.0 suite of molecular design codes, performs MD simulations, geometry optimization, annealing, etc. for biological macromolecules and nanoassemblies. This version features a large scale vibrational analysis module developed and implemented by EC staff in collaboration with Professor Jay Ponder at Washington University (dasher.wustl.edu/tinker).

System software has been upgraded with the following packages, Intel Fotran 10.0, advanced optimization, multi-threading, and processor support that includes automatic processor dispatch, vectorization, auto-parallelization, OpenMP, data prefetching, loop unrolling, substantial Fortran 2003 support, and an optimized math processing library; Global Arrays, an efficient and portable shared-memory programming interface for distributed-memory computers.

A new high performance computer array, Emory High Performance Computing Clusters (EHPCC), is now open to the Emory community:

Emory has acquired a large high performance computer cluster for use by the Emory community. EHPCC Executive Committee has established "The Cluster Use policy". *Importantly, cluster will incur a charge for CPU usage*. This new facility is accessible to Emerson Center (EC) Subscribers. In order to synchronize the use of this new computing facility by EC's Subscribers and make use of this large cluster most effective for EC's users, the Emerson Center Leadership Committee (ECLC) has proposed to establish the following policy on an experimental basis, which will be reviewed sometime in December 2007.

If you are an EC subscriber who wishes to use the EHPCC facility you need to contact Alex Kaledin (akaledi@emory.edu) or Jamal Musaev (dmusaev@emory.edu) to establish your own EHPCC account for billing purpose and give the names of the users who will be associated with you, and whose computer usage can be billed to your account. Please copy your request to EC's Director at dmusaev@emory.edu, too.

Please note that EHPCC time must be paid for directly by the PIs, and that these charges are not part of your EC subscription fee.Emerson Center staff will install the widely used (by EC's users) Software (Gaussian, Molpro, NWChem, etc, for which EC holds site license) to EHPCC computers and make them accessible to EC's users. EC staff will provide scientific consultations on how to use this software at EHPCC computers. However, EC staff will NOT have access to hardware, queuing system and system software. EHPCC staff will be in charge of those issues and should provide all necessary assistance. Installation of your specific software by EC staff to EHPCC computers will be done only on individual basis and may require additional charges.

The use of EC's facilities (hardware, software (on EC's computers), scientific expertise, Visiting Fellow Program, and other) will be continued as before, based on your subscription to EC.

PS: In brief, the new cluster features 250 SUN's X2200 2.6GHz (Opteron) nodes with 4 cores per node. The server and the nodes run the well-known Red Hat Linux operating system equipped with IBRIX Fusion file system. The queuing system is run via the Sun's Grid Engine batch queue.

Currently, there are three queues set up for general use. They are, "long.q" ($.025/CPU hour) with no hard or soft job/time limits, "all.q" ($.03/CPU hour) with a 12 hour job limit, and "express.q" ($.05/CPU hour) with a 2 hour job limit. (For more details, please contact to EHPCC staff).