THE UNIVERSITY OF MISSOURI—ST. LOUIS

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ST.LOUIS

The St. Louis metropolitan region, located around the confluence of the Missouri and Mississippi Rivers, has evolved through the centuries from the homes of ancient Native American civilizations to major fur trading center to the "Gateway to the West," marked by lasting French, Spanish and African influences. Today the area is a town with hospitable people rooted in a myriad of regional, ethnic, and cultural traditions reflective of our complex world, well supported by easy access to parks, educational centers, sports venues, museums, and historic sites.

Great ethnic and classic neighborhoods characterize the region. A cross-section of the area can provide examples of wonderful Victorian architecture, museum, gallery, and arts districts, farmers' markets, antique shops, boutiques and classic coffee houses, jazz clubs, great restaurants, and amazing ethnic foods, a world class botanical garden, and old warehouse buildings converted into lofts, shops and restaurants.

Forest Park, the urban St. Louis facility that is much larger than New York's Central Park, is home to bike trails, tennis courts, and golf courses. The Missouri Historical Society is a place to learn about interesting St. Louis history including the Lewis and Clark Expedition. The St. Louis Art Museum, designed by Cass Gilbert for the 1904 World's Fair, has a collection of art which is representative of the best of world art, its strengths being in Pre-Columbian and German art. The St. Louis Science Center has many educational interactive exhibits including an Omnimax theatre. And finally the St. Louis Zoo, home to more than 18,000 exotic animals, many of them rare and endangered, and set in the rolling hills, lakes and glades of Forest Park, is a great place to visit.

Activities and attractions are many, and St. Louis has a great variety of night life choices. Blues clubs and restaurants are tucked away in the red brick buildings of the historic Soulard neighborhood, while Dixieland and blues dinner cruises are available through the port of St. Louis. Clubs and restaurants are alive until early morning hours in the converted warehouses of the Landing, north of the Arch, and along the newly-developed "loft" neighborhood of Washington Avenue. Visitors to The Loop in University City can enjoy a game of darts between eating appetizers and dinner. The Fox Theatre, across the street from Powell Hall, the home of the Saint Louis Symphony Orchestra, hosts traveling Broadway musicals. There are special concerts at Riverport, the Peabody Opera House, the Pageant, Chaifetz Arena and, at Webster University, the summer season of Opera Theater, presented in English. Finally our own Touhill Performing Arts Center is the major newcomer to the cultural scene in St. Louis.

Sports of all sorts are an obsession in St. Louis. Cardinal baseball is a religion to many, the hockey Blues, and the NFL's Rams have large numbers of loyal and enthusiastic fans, and indeed all sports are available in town.

THE UNIVERSITY

The University of Missouri-St. Louis is one of four campuses that constitute the University of Missouri. Established in Columbia in 1839 on the ideals of Thomas Jefferson, the University of Missouri became a land-grant institution upon passage of the Morrill Act by Congress in 1862.

The university remained a single-campus institution until 1870, when the Rolla campus was opened as the Missouri School of Mines and Metallurgy. In the 1960s a movement began across the country toward creation of public universities located within metropolitan centers. That movement marked the most significant change in higher education in the twentieth century, and the University of Missouri-St. Louis is a product of that educational development. Two campuses were added in 1963. The private University of Kansas City became the university's Kansas City campus, and an entirely new campus was started in St. Louis.

The notion of a major public institution serving the St. Louis area evolved from a dream to a solid reality, which today exceeds the expectations of those who created it. Since the doors of the old Administration Building opened more than 50 years ago, UM-St. Louis has become the largest university serving St. Louisans and the third largest university in the state and the largest in the St. Louis metropolitan area. The university has grown from 30 faculty in 1963 to more than 1300 faculty members and more than 1,000 staff members, committed to the future of the St. Louis area through teaching, research, service and economic development.

One of the keys to this university's development as an outstanding institution has been the careful selection of faculty over the years. UM-St. Louis has attracted some of the top authorities in many fields. More than 90 percent of the full-time regular faculty members hold doctoral degrees, a figure that far exceeds the national average. These professionals develop new theories and new procedures, and in so doing attract millions of dollars each year in research funding.

Student enrollment, on and off-campus, has grown from 600 in 1963 to more than 17,000 in 2014. The numbers have changed, but not the spirit. Faculty and students are still most concerned with the education of new talent, which is the basis for the future social, intellectual, and economic health of Missouri's largest metropolitan area. From its beginning on what was once the site of a country club with a single building, UM-St. Louis has grown to a large modern campus of more than 320 acres with more than 60 buildings used to support academic and other University activities. In addition major construction projects, including a Wellness Center, a Science Learning Center among others, are underway on campus.

The curriculum has grown to include 54 undergraduate programs, 37 master's programs, seven pre-professional programs, 2 education specialists programs, 15 doctoral programs, and the only professional degree in optometry in Missouri. Programs address the particular needs of older students returning to school; of students pursuing pre-architecture, pre-law, pre-medicine, pre-pharmacy, pre-engineering, or pre-journalism courses, and of students interested in urban careers.

THE DEPARTMENT

THE CHEMISTRY & BIOCHEMISTRY DEPARTMENT was the first at the University to establish a Ph.D. program. That was in 1971-2, and in 1974 the M.S. program began. The first Ph.D. in chemistry was awarded in 1977 and in 2007 the department celebrated the 30th anniversary of the first MS and PhD graduates and the 40th anniversary of the first BS graduates. Through 2014 we have graduated 1,682 degree recipients including approximately 1,091 baccalaureates, 419 masters and 172 doctoral graduates. Included in the latter are graduates from the recently developed Biochemistry and Biotechnology Program run jointly with the Department of Biology. To date the program has generated almost 214 BS and 72 MS graduates. The Department of Chemistry & Biochemistry is housed in Benton Hall, the Research Building, and the William L Clay Center for Nanoscience, all within the Science Complex. In 2014 ground was broken for the Science Learning Center, a new 75,00 square foot building; part of the $32 million renovation of Benton and Stadler Hall, which will contain new teaching laboratories, some research and general-use space.

There are currently 18 faculty members, offering research opportunities in organic chemistry, inorganic chemistry, physical & analytical chemistry and biochemistry, and several active emeritus, research and adjunct professors. Recent faculty recruitment efforts have changed the demographics of the department and thus there are new opportunities in research for potential graduate students. There are more then 60 graduate students and postdoctoral fellows augmented by several undergraduate students involved in a broad range of research efforts.

The Chemistry & Biochemistry Department has developed a program that makes research and teaching excellence its top priorities. Papers and publications documenting departmental research are frequently presented at conferences and symposia and published in scientific journals throughout the world. The faculty serve on national and international committees and editorial boards. Several faculty members have written introductory textbooks and advanced specialized monographs and reviews. Advanced undergraduate and graduate classes are relatively small, allowing for considerable interaction between faculty and students. Undergraduate research is strongly advised for majors providing an opportunity for graduate students and postdoctoral fellows to assist in mentoring undergraduates thereby providing them all with valuable experience.

GRADUATE STUDY

THE DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY offers programs of study leading to the Ph.D. and M.S. degrees including a non-thesis M.S. for persons working full time. The Ph.D. degree is offered in the areas of Biological, Inorganic, Organic and Physical & Analytical Chemistry, and research on topics of current interest in these areas is being carried out by faculty, postdoctoral associates, graduate students and undergraduates. In addition, opportunities for research in interdisciplinary and materials related areas exist in a number of research groups. Incoming graduate students are free to undertake research toward an advanced degree with any faculty member of their choosing, depending on space and availability, and are encouraged to select their advisor and start research within their first year. Graduate courses covering more than two dozen subject areas are regularly offered by the Chemistry faculty. For persons working full time, there is convenient scheduling of courses in the late afternoon and early evening hours. A complete listing of Chemistry offerings is found in the *University of Missouri-St. Louis Bulletin* and online at *https://apps.umsl.edu/webapps/courseschedules/search_basic.cfm*.

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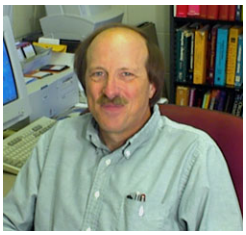
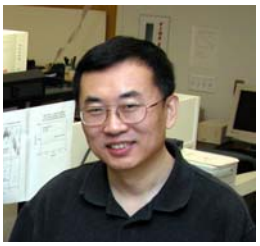
Fellowships, teaching or research assistantships are held by almost all full-time PhD students. Stipends for assistantships are competitive. Non-resident tuition fees are waived for all students on assistantships, although resident incidental fees must be paid. Research fellowships are also awarded on a competitive basis, and research assistantships are available, funded by research grants awarded to individual faculty members.

Faculty Research Interests

 **James K. Bashkin**	*Biological and Inorganic Chemistry*: Research involving the interface of chemistry and biology, including metabolism, "chemical genomics" and the design of antiviral and anticancer agents. Chemical synthesis and biochemical testing of sequence-specific DNA binding molecules designed to control gene expression. bashkinj@umsl.edu. 314-516-7352
 **Benjamin Bythell**	*Analytical, Computational and Biophysical Chemistry.* Structure, reactivity and chemistry of biologically- and industrially-important chemicals; mass spectrometry and mass spectrometry-related techniques; application of information gained in fundamental studies to practical problems. *bythellb@umsl.edu*. 314-516-5314
 **Eike Bauer**	*Organic, Organometallic.* Investigation of transition metal based catalysts systems; development of environmentally friendly iron based catalyst systems; new catalytic methods to activate propargylic alcohols; Green Chemistry. *bauere@umsl.edu* . 314-516-5340
 .**Alicia M. Beatty**	*Supramolecular and Materials Chemistry:* Synthesis of inorganic and organic molecular building blocks and their use in solid state synthesis; catalysis and molecular transport in porous solids; synthesis of clusters and nanoparticles using crystal engineering methods; chiral separations and magnetic solids. *beattya@umsl.edu* . 314-516-4383
 .**Janet Braddock-Wilking**	*Inorganic and Organometallic Chemistry; NMR Spectroscopy*. Synthesis and characterization of compounds containing transition metal to heavier group 14 element bonds. Cluster complexes containing Si, Ge, Sn and transition metals, NMR spectroscopy of organometallic and inorganic complexes. *wilkingj@umsl.edu*. 314-516-6436
 **James S. Chickos**	*Organic Chemistry*. Synthesis of chiral organo-deuterium compounds, thermal reactions of hydrocarbons, stereochemistry, heats of sublimation, isotope effects,; physical properties; measurement and estimation. *jsc@umsl.edu*. 314-516-5377

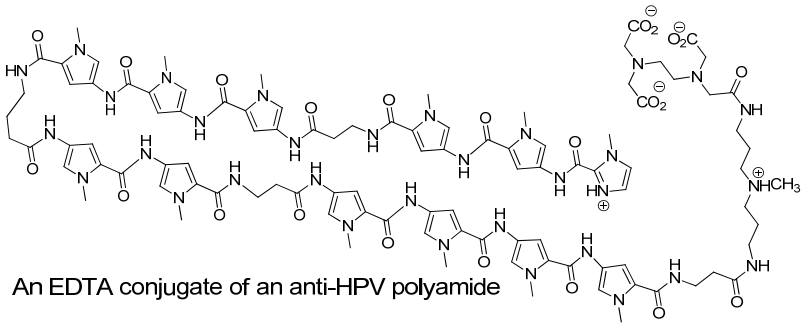
 **Valerian T. D'Souza**.	*Bioorganic Chemistry; Organic Chemistry*. Bioorganic chemistry, kinetics, mechanisms and structure-function relationships of organic reactions, particularly of biological processes; enzyme mechanisms, mimics and catalysis; cyclodextrin and modified cyclodextrin chemistry. *vally@umsl.edu*. 314-516-5324
 **Alexei V. Demchenko**	*Organic Chemistry; Carbohydrate Chemistry*. Novel synthetic methods, 1,2-cis-glycosylation, oligosaccharide synthesis, synthetic vaccines, synthetic glycopolymers and glycodendrimers, sialic acid containing glycoconjugates, chemo-enzymatic synthesis, solid phase chemistry, combinatorial chemistry. *demchenkoa@msx.umsl.edu*. 314-516-7995
 **Cynthia Dupureur**	*Biochemistry*. Enzyme structure-function relationships; inhibition of enzymatic drug targets; nucleic acid-ligand interactions . *cdup@umsl.edu*. 314-516-4392
 **George W. Gokel**	*Organic, Biological Chemistry, Supramolecular*. Chemical biology, synthesis of novel compounds that can serve as supramolecular receptors , cation channels in phospholipid bilayers or as mediators of anion transport through membranes. Examination of weak intermolecular ("supramolecular") forces that pervade chemical and biological phenomena. gokelg@umsl.edu. 314-516—5321
 **Wesley R. Harris.**	*Bioinorganic Chemistry; Inorganic Chemistry*. Complexation equilibrium with proteins and low molecular weight ligands. Metal ion exchange kinetics with serum transferrin. Linear free-energy relationships in coordination chemistry. *wharris@umsl.edu*. 314-516-5331
 **Stephen M. Holmes**	*Inorganic, Organometallic, and Materials Science:* Synthesis and characterization of polymerization catalysts, magnetic and photo-responsive materials, electron transfer, and molecule-based devices. holmesst@umsl.edu. 314-516-4382

 **Michael R. Nichols**	*Biochemistry*. Peptide/protein assembly mechanisms, macromolecular characterization, quantitative light scattering, atomic force and electron microscopy, cellular studies of inflammatory processes induced by protein assemblies. nicholsmic@umsl.edu . 314-516-7345
 **James J. O'Brien.**	*Materials Science; Physical Chemistry.* Gaseous species important in quantitative measurements obtained using plasma-assisted chemical vapor deposition processes studied by intracavity laser spectroscopy; techniques in intracavity laser spectroscopy; laboratory spectra of species important in planetary atmospheres. *obrienjja@umsl.edu*. 314-516-5717
 **Christopher D. Spilling**.	*Organic Chemistry*. Organic synthesis; new synthetic methods; chiral phosphonate and phosphonamides in asymmetric synthesis; asymmetric synthesis of heterocycles; total synthesis of marine natural products. *cspill@umsl.edu*. 314-516-5437
 **Keith J. Stine**.	*Physical Chemistry*. Surface modification of nanomaterials for life science applications; interactions in model membrane systems; supramolecular ordering in thin films and monolayers. *kstine@umsl.edu*. 314-516-5346
 **Chung F. Wong**.	*Computational Biochemistry.* Development and application of computational methods for studying biomolecular structure, dynamics, and function. Computer-aided drug design. Protein kinases and phospatases. *wongch@msx.umsl.edu* . 314-516-5218
 **Zhi Xu**.	*Materials Science. Physical Chemistry*. Nonlinear optics, solid-liquid interfacial chemistry; molecular electronics and optical switch storage devices. . *zhixu@umsl.edu* 314-516-5328

Emeritus, Founders' and Research Faculty

 **Lawrence Barton**.	*Inorganic Chemistry*. Synthesis. Structure and chemistry of borane and metallaborane cage compounds, transition metal borane complexes, organometallic chemistry. lbarton@umsl.edu. 314-516-5334
 **Joyce Y. Corey**.	*Inorganic Chemistry; Organometallics*. Synthesis and characterization of organometallic compounds containing elements form Group IV, with emphasis on catalyzed formation of polysilane oligomers and polymers from hydrosilanes. corey@umsl.edu. 314-516-5360
 **Harold H. Harris**	*Chemical Education; Physical Chemistry*. Chemical education; structure of self-organizing flames; electrically perturbed flames; computer simulations of molecular energy transfer; chaos and fractals in chemistry. hharris@umsl.edu. 314-516-5344
 **Rensheng Luo**	*NMR spectroscopy* The use of NMR for generating three-dimensional structural and dynamical information on biological macromolecules and organometallic complexes. Collaboration with scientists in chemistry, biochemistry, biology, medicine, physics and materials science. Development of techniques and implementation of new NMR experiments. luor@umsl.edu . 314-516-5330
 **Nigam. P. Rath**.	*X-ray Crystallography*. Structural chemistry; X-ray crystallography; crystallographic databases; organometallic chemistry. nigam_rath@umsl.edu. 314-516-5333
 **Rudolph E. K. Winter**	*Organic chemistry*: The chemistry of secondary plant metabolites, in particular terpenes and alkaloids. Isolation and identification of novel biologically significant compounds and biosynthesis and chemical ecology of plant materials. Mass spectrometry. rekwintr@umsl.edu. 314-516-5337

THE FACULTY



An EDTA conjugate of an anti-HPV polyamide

JAMES K. BASHKIN

Professor Bashkin, B.A. California-Irvine, D.Phil. Oxford, England, NIH postdoc at Harvard, was with Monsanto, Washington University in St. Louis, and again Monsanto (later Pharmacia and Pfizer) prior to joining the faculty at UMSL in 1999. He established a research program here in 2003 and started the biotech company NanoVir, LLC with Chris Fisher, and in 2012 was appointed Professor of Chemistry and Biochemistry.

Research Interests

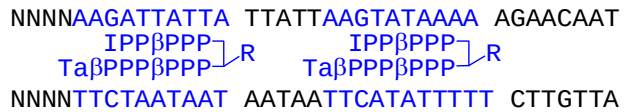
My group's research has recently been directed to the interface of chemistry and biology, in areas such as "chemical genomics," the design of antiviral and anticancer agents and Green Chemistry. Much of this work involves the chemical synthesis and biochemical testing of sequence-specific DNA binding molecules designed to control gene expression. Our main goals are the invention of new chemical methods to treat and diagnose diseases and the invention of new chemical reactions to eliminate toxic waste and other undesirable features of traditional chemistry.

Recently, we have worked toward prevention of cervical cancer. Most cervical cancer is caused by certain "high-risk" forms of Human Papillomavirus (HPV), primarily HPV16 and 18. We have designed potential antiviral agents that successfully eliminate HPV16 DNA from human cells in culture, with pseudo -IC50 values as low as 27 nM. Pyrrole-imidazole polyamides are used to target viral DNA sites such as the one shown below, bound to a DNA target. We have expanded our work to HPV18; all drug discovery and development have been collaborations with Dr. Chris Fisher of NanoVir LLC. Studies of the biophysics of polyamides interacting with HPV DNA have been collaborations with Dr. Cynthia Dupureur of this department.

All of our antiviral polyamides have been rather large molecules. To study the biophysics of smaller polyamides, both to help understand the larger polyamides and to design better leads for other human diseases, we have collaborated with biophysicist W. David Wilson of Georgia State University for several years.

Earlier work was concerned with the design of ribozymes mimics: molecules capable of sequence specific cleavage of RNA by the natural transesterification/ hydrolysis process. Applications include catalytic antisense agents that destroy target messenger RNA without requiring RNase H activation. We reported the first ribozymes mimic.

In addition to this biological chemistry, I have maintained a strong interest in environmentally-benign organic chemistry, known as Green Chemistry. This work involved developing organic reactions that eliminated toxic waste associated with traditional processes.



Code for building blocks: I = imdazole, P = pyrrole, Ta = triamine, β = beta alanine, and the hairpin turn is indicated by: R , where R= H or NH_2.

Selected Publications

″DNA binding polyamides and the importance of DNA recognition in their use as gene-specific and antiviral agents″, K. J. Koeller, G. D. Harris, K. Aston, G. He, C. H. Castaneda, M. A. Thornton, T. G. Edwards, S. Wang, R. Nanjunda, D. W. Wilson, C. Fisher and J. K. Bashkin, *Med. Chem.* **2014**, *4*, 338

"Binding studies of a large antiviral polyamide to a natural HPV sequence"' G. He, E. Vasilieva, G. D. Harris, K. J. Koeller, J. K. Bashkin and C. M. Dupureur, *Biochimie* **2014**, *102*, 83.

″Modulation of DNA-polyamide interaction by β-alanine substitutions: a study of positional effects on binding affinity, kinetics and thermodynamics″, S. Wang, K. Aston, K. J. Koeller, D. G. Harris, N. P. Rath J. K. Bashkin and W. D. Wilson, *Org. & Biomol. Chem.* **2014**, *12*, 7523.

"Differential thermodynamic signatures for DNA minor groove binding with changes in salt concentration and temperature," S. Wang, A. Kumar, K. Aston, B. Nguyen, J. K. Bashkin, D. W. Boykin and D. W. Wilson, *Chem. Commun.* **2013**, 8543.

"DNA Damage Repair Genes Controlling Human Papillomavirus (HPV) Episome Levels under Conditions of Stability and Extreme Instability," T. G. Edwards, T. J. Vidmar, K. Koeller, J. K. Bashkin and C. Fisher, *PLoS One*, **2013**, *8*, e75446.

"Mapping small DNA ligand hydroxyl radical footprinting and affinity cleavage products for capillary electrophoresis," G. He, E. Vasilieva, J. K. Bashkin and C. M. Dupureur, *Analytical Biochem.* **2013**, *439*, 99.

THE FACULTY

EIKE BAUER

Professor Bauer received his Vordiplom (B.S. degree) 1995, University of Erlangen-Nuremberg (Germany); Hauptdiplom (Thesis M.S. degree) 1999, University of Erlangen-Nuremberg; Ph.D., 2003, University of Erlangen-Nuremberg. He did a postdoc 2004-2005 at the University of California – Riverside and was Visiting Assistant Professor 2005-2006 at Illinois Wesleyan University prior to joining the Chemistry Department in the fall 2006. .

Research Interests

Dr. Bauer's research interests are in the area of Organic and Organometallic Chemistry. Organometallic chemistry is the study of compounds having metal-carbon bonds. Organometallic compounds often have unique geometries and exhibit reactivities as a result of the electronic properties of the metal. Organometallic compounds are important in catalysis, medicine, and the construction of molecular scale devices (nanoscience).

Phopshoramidite and phosphinooxazoline ligands have recently attracted considerable interest as ligands for a variety of transition metal catalyzed organic transformations. These ligands are easy to synthesize and can be sterically and electronically modified at several positions in their molecular framework.
Dr. Bauer designed and synthesized several novel, electronically and sterically fine-tuned phosphoramidite and phosphinooxazoline ligands. As a new class of ligands, thio derivatives of phosphoramidites were synthesized. These ligands were subsequently converted to a variety of ruthenium, rhodium, iridium and iron complexes. The impact of the ligand structure on the physical and chemical properties of its respective metal complexes was investigated.

The Bauer group has shown that phosphoramidite containing half sandwich complexes of ruthenium are catalytically active in the formation of β-oxo esters from propargylic alcohols and carboxylic acids (see graphics). The ligand structure has a profound impact on the catalytic activity of the corresponding metal complex. Structurally related chiral at metal ruthenium complexes have exhibited catalytic activity in the Mukaiyama aldol reaction.

Allenylidene complexes are cumulene-type compounds, which are readily accessible from propargylic alcohols and appropriate precursor metal complexes. The allenylidene complexes are of interest as possible intermediate in catalytic propargylic substitution reactions. Dr. Bauer has also demonstrated a route to chiral at metal allenylidene complexes, which were obtained from corresponding precursors with chirality transfer. Catalytic investigations are currently underway.

Iron is a cheap and non-toxic alternative to well-established, catalytically active transition metals. The Bauer group has demonstrated for the first time that phosphinooxazoline complexes of iron are catalytically active in the oxidation of benzylic methylene groups to ketones utilizing *t*-BuOOH as the oxidant.

Selected Publications

"New *bis*(imino)pyridine complexes of iron(II) and iron(III), and their catalytic-activity in the Mukaiyama aldol reaction", P. Shejwalkar, N. P. Rath and E. B. Bauer, *Synthesis*, **2014**, *46*, 57

"Ruthenium complexes of the general formula $[RuCl_2(PHOX)_2]$ and their catalytic activity in the Mukaiyama aldol reaction," N. Curvey, A. K. Widaman, N. P. Rath and E. B. Bauer, *Tetrahedron Lett*. **2014**, *55*, 3033.

"Etherification reactions of propargylic alcohols catalyzed by a cationic ruthenium allenylidene complex," D. F. Alkhaleeli, K. J. Baum, J. M Rabus and E. B. Bauer, *Catalysis Comm*. **2014**, *47*, 45.

"Polydentate pyridyl ligands and the catalytic activity of their iron(II) complexes in oxidation reactions utilizing peroxides as the oxidants," M. Lenze, S. Sedinkin and E. B. Bauer, *J. Mol. Catal. A: Chem.* **2013**, *373*, 161

"Iron(III) a-Aminopyridine Complexes and their Catalytic Activity in Oxidation Reactions: A comparative Study of Activity and Ligand Decomposition," M. Lenze, E. T. Martin, N. P. Rath and E. B. Bauer, *ChemPlusChem* **2013**, *78*, 101.

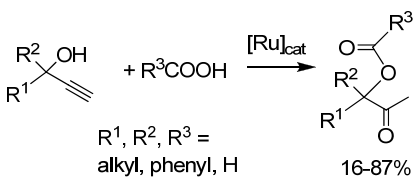
"Transition-metal-catalyzed functionalization of propargylic alcohols and their derivatives," E. B. Bauer, *Synthesis* **2012**, *44*, 1131 P. Shejwalkar, N. P. Rath and E. B. Bauer,

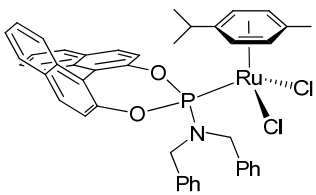
"Chiral-at-metal complexes and their catalytic applications in organic synthesis," E. B. Bauer, *Chem. Soc. Rev*. **2012**, *41*, 3153.

"New five-coordinate Ru(II) phosphoramidite complexes and their catalytic activity in propargylic amination reactions", A. K. Widaman, N. P. Rath and E. B. Bauer, *New J. Chem.* **2011**, *35*, 2427

"New iron(II) a-iminopyridine complexes and their catalytic activity in the oxidation of activated methylene groups and secondary alcohols to ketones", P. Shejwalkar, N. P. Rath and E. B. Bauer, *Dalton Trans*. **2011**, 7617.

"Synthesis and Structural Characterization of a Series of New Chiral-at-Metal Ruthenium Allenylidene Complexes", S. Costin, A. K. Widaman, N. P. Rath and E. B. Bauer, *Eur. J. Inorg. Chem*. **2011**,





THE FACULTY

ALICIA M. BEATTY

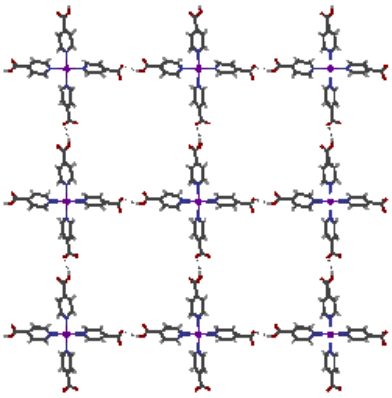
Professor Beatty received her B.S. degree from UM-St. Louis in 1989 and a Ph.D. from Washington University in St. Louis, in 1994. She held positions as a director of X-ray diffraction facility at Washington University, Research Associate and Senior Research Scientist at Kansas State University, and Research Associate Professor at the University of Notre Dame. She joined the faculty at Mississippi State University in 2003 and returned to UM-St. Louis in 2008.

Research Interests

The goal of our research is to create new, useful solid or polymeric materials through use of organic, inorganic and supramolecular synthesis especially using techniques developed through crystal engineering. These new materials will provide a foundation for systematic structure-property studies, initially focusing on: electroactive polymers, catalysis, chiral separations, magnetic solids. Projects will utilize common synthetic routes and methods of characterization in solution and the solid state.

We have demonstrated that, despite the competing intermolecular forces that exist in solutions of coordination complexes, hydrogen-bonding substituents on ligands may be used to predictably assemble coordination complexes. We can control the solid-state assembly of inorganic/organic hybrid materials either by changing the metal ion (thus the preferred coordination geometry) or by synthesizing ligands with hydrogen bonding substituents. For example, the figure above shows that square planar Pt(II)

(isonicotinic acid)2(isonicotinate)2 complexes are linked through carboxylic acid -carboxylate OH---O hydrogen bonds to form a square grid in the solid state.



Why crystalline solids? It is important to note that crystalline solids can, in some cases, be uniquely useful materials. By definition, single crystals are ordered, which means that structure-function (e.g. electronic or magnetic behavior) relationships can be determined by measuring the effect of systematic changes in the components of the crystal. In addition, channels or cavities organized in crystalline solids have equivalent environments, therefore the relative orientations of guest ions, molecules, or reactants are also constant, which is essential for: 1) uniform signaling in chemical sensors, 2) asymmetric catalysis, 3) stereochemically controlled solid state reactivity.

Selected Publications

″Solid phase microextraction (SPME) combined with TGA as a technique for guest analysis in crystal engineering,″ M. J. Fischer and A. M. Beatty, *CrystEngComm*, **2014**, 7313

Synthesis of some aminopicolinic acids," R. Bawa and A. M. Beatty, *J. Chem. & Chem. Eng.* **2012**, *6*, 372

"Stable Hydrogen-Bonded Coordination Network with Removable Guests", G. A. Hogan, N. P. Rath and A. M. Beatty, *Crys. Growth Des*. **2011**, *11*, 3740

"Exceptions to the rule: new hydrogen-bonded networks from an old reliable", O. Ugono, N. P. Rath and A. M. Beatty, *CrystEngComm* **2011**, *13*, 753

"2,2',5,5'-Tetrachlorobenzidine" O. Ugono, M. Douglas Jr, N. P. Rath and A. M. Beatty,*Acta Crystallogr. E,* **2010**, *66,* o2285.

"2,4,6-Triphenylaniline", O. Ugono, S. Cowin and A. M. Beatty, *Acta Crystallogr. E*,**2010**, *66*, o1777.

"Synthesis and Control of Single Layer and Polar 2-D Layered Architectures in a Series of Organic Layered Solids", O. Ugono, N. P. Rath and A. M. Beatty, *Cryst, Growth & Design* **2009**, *9*, 4595.

"Guest Inclusion and Structural Dynamics in 2-D Hydrogen-Bonded Metal-Organic Frameworks" C-L. Chen and A. M. Beatty, *J. Am. Chem. Soc*. **2008,** *130*, 17222

"*Reverse* engineering: toward 0-D cadmium halide clusters" C. E. Costin-Hogan, C-L. Chen, E. Hughes, A. Pickett, R. Valencia, N. P. Rath, and A. M. Beatty, *Cryst. Eng. Comm.,* **2008**, *10*, 1910

"From Crystal Engineering to Cluster Engineering: How to Transform Cadmium Chloride from 2-D to 0-D," C-L. Chen and A. M. Beatty, *Chem. Commun*., **2007**, 76.

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"Pillared clay mimics from dicarboxylic acids and flexible diamines," A. M. Beatty, C. L. Schneider, A. E. Simpson and J. L. Zaher, *Cryst. Eng. Comm*. **2002**, *4*, 282.

THE FACULTY

JANET BRADDOCK WILKING

Professor Braddock-Wilking received her B.A. degree from the University of Missouri-St. Louis and her Ph.D. from Washington University. She joined the UM-St. Louis faculty in 1993 following postdoctoral fellowships at Harvard University and Mallinckrodt Medical, Inc.

Research Interests

Dr. Braddock-Wilking's research focuses on the synthesis, characterization, and reactivity of compounds containing heavier Group 14 elements (E = Si, Ge). A major area of interest involves the chemistry of heterocyclopentadienes containing Group 14 elements, also known as metalloles (Figure 1), and related metallafluorenes and germafluoresceins (Figure 1). These heavy Group 14 molecules are known to exhibit unusual optoelectronic properties and high electron affinity and mobility and thus have potential application as components for electronic devices such as OLEDs and as chemical and biological sensors. Many of these molecules are weakly emissive in solution but show enhanced emission in the solid state due to the phenomenon of aggregation induced emission rendering them suitable for solid-state applications.

The research group is studying the structure-property relationship of these luminescent Group 14 molecules by exploring synthetic pathways that will allow for the incorporation of a variety of p-conjugated organic groups on the ring system enabling a range of emission colors (blue to red) and to promote aggregation-induced emission in the solid state. Figure 2 shows the molecular structure of an exceptionally stable germafluorene prepared in our laboratory that exhibits strong blue emission in solution and the solid state. The phenyl groups at the germanium center provide steric crowding that prevents close contact of adjacent molecules preventing aggregation-induced quenching which is commonly observed in the solid state with luminescent planar aromatic organic molecules.

They are also investigating the synthesis of related systems that incorporate linker groups that can bind to transition-metal centers for the preparation of novel fluorescent metal containing complexes as well as for applications in chemical sensing. Figure 3 shows two macrocyclic diplatinum complexes linked to a silole unit through an alkynyl group. Related structures are being examined with different chelating phosphines and nitrogen-based donors (Figure 4).

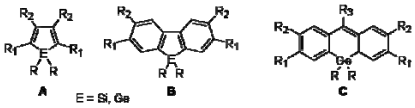


Fig. 1. General metallole and metalla-fluorene structures (M = Si, Ge)

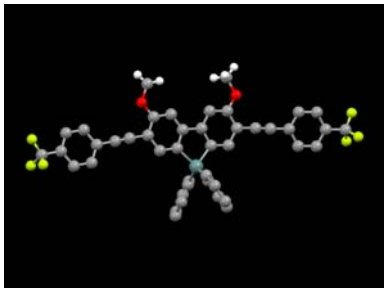


Fig. 2. Molecular structure of a germafluorene

Fig.3. Solid state fluorescence of a germafluorene on a TLC plate .

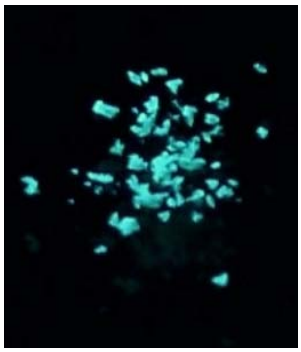


Fig.4. Solid state fluorescence of a germafluorene as crystals.

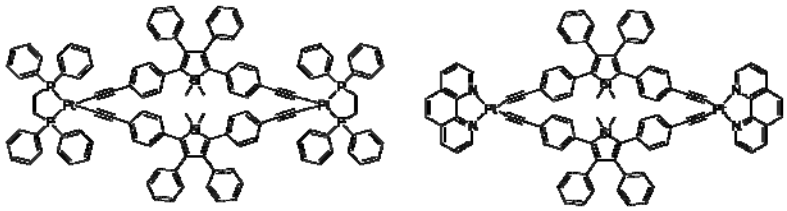


Fig. 5. Luminescent diplatinum macrocyles containing alkynyl-linked siloles.

Selected Publications

″Bis(alkynyl) PTA and DAPTA Complexes of Pt(II) and Pd(II)″, J. Braddock-Wilking, S. Acharya and N. P. Rath, *Polyhedron* **2014,** submitted.

″Synthesis and Characterization of Pt(II) and Pd(II) PTA and DAPTAcomplexes″, J. Braddock-Wilking, A. Sitaram and N. P. Rath, *Polyhedron* **2014**, *79*, 16.

"Synthesis of 2,5-substituted siloles and optical study of interactions with mercury(II), copper(II), and nickel(II) cations," J. B. Carroll and J. Braddock-Wilking, *Organometallics* **2013**, *32*, 1905.

T. L. Bandrowsky, J. B. Carroll, J. Braddock-Wilking, Synthesis, Characterization, and Crystal Structures of 1,1-Disubstituted-2,3,4,5-tetraphenylgermoles That Exhibit Aggregation-Induced Emission," *Organometallics* **2011**, *30*, 3559.

″Luminescent Platinum Complexes Containing Phosphorus-Linked Silole Ligands″, J. Braddock-Wilking, L. Gao, N. P. Rath, *Dalton Trans*. **2010**, *39*, 9321.

″Preparation and Photophysical Properties of Phosphino- and Phosphine Oxide-linked Siloles″, J. Braddock-Wilking, L. Gao, N. P. Rath, *Organometallics* **2010**, *29*, 1612.

THE FACULTY

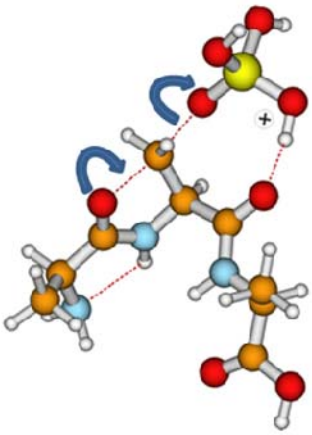
BENJAMIN J. BYTHELL

Professor Bythell received his MChem. degree from the University of Bath, UK, in 2002 and Ph.D. from Oregon State University in 2007. He held postdoctoral fellowships at the German Cancer Research Center in Heidelberg (2008-2010) and at the National High Magnetic Field Laboratory at Florida State University (2010-2013). He joined the faculty in the fall of 2013.

Research Interests

Dr. Bythell works at the interface between analytical, computational and biophysical chemistry where he strives to understand the structure, reactivity and gas-phase behavior of biologically- and industrially important chemicals. Fundamentally, chemical structure determines the properties and potential functions of any given molecule. Consequently, the gas-phase structures occupied by an analyte ion have direct influence on which fragmentation pathways are populated, and thus, on the resulting mass spectrum. The ability to decipher both the elemental composition ($C_cH_hN_nO_oS_sP_p$) and structural information on unknown compounds is highly desirable. To accomplish this successfully, an understanding of the gas-phase fragmentation chemistries in play is of substantial benefit.

He and his students work on how and why different analyte ions form particular conformations, and what effect this has on their gas-phase fragmentation chemistry. They utilize a wide assortment of analytical approaches based around mass spectrometry (accurate mass identification, HPLC, isotopic labeling, tandem mass spectrometry, hydrogen/deuterium exchange, "action" IR spectroscopy), and cutting edge computational methods (molecular dynamics, density functional theory, *ab initio*, and RRKM calculations). In so doing, students acquire a wide variety of valuable skills, and are exposed to multiple approaches to problem-solving.



Selected Publications:

"Targeted Petroleomics: Analytical Investigation of Macondo Well Oil Oxidation Products from Pensacola Beach, B. M. Ruddy, M. Huettel, J. E. Kostka, V. V. Lobodin, B. J. Bythell, A. M. McKenna, C. Aeppli, C. M. Reddy, R. K. Nelson, A. G. Marshall and R. P. Rodgers," *Energy and Fuels*, **2014**, *28*, 4043.

"Ion molecule reaction H/D exchange as a probe for isomeric fractionation in chromatographically separated natural organic matter", A. C. Stenson, B. M. Ruddy and B. J. Bythell, *Int. J. Mass Spec*. **2014**, *360*, 45.

"Insight into the Mechanism of grapheme Oxide Degradation via the Photo-Fenton Reaction", H. Bai, W. Jiang, G. P. Kotchey, W. A. Saidi, B. J. Bythell, J. M. Jarvis, A. G. Marshall, R. A. S. Robinson and A. Star, *J. Phys. Chem. C* **2014**, *118*, 10519.

"Unequivocal Determination of Site-Specific Protein Disulphide Bond Reduction Potentials by Top Down FTICR MS Characterization of the N and C Terminal Redox-Active Sites in Human Thioredoxin-1", J. Scotcher, B. J. Bythell and A. G. Marshall, *Anal. Chem.* **2013**, *85*, 9164.

"Heavy Petroleum Composition. 5. Compositional and Structural Continuum of Petroleum Revealed," D. C. Podgorski, Y. E. Corilo, L. Nyadong, V. V. Lobodin, B. J. Bythell, W. K. Robbins, A. M. McKenna, A. G. Marshall, and R. P. Rodgers, *Energy Fuels,* **2013**, *27*, 1268.

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"Vapors from Ionic Liquids: Reconciling Simulations with Mass Spectrometry Data," B. A. D. Neto, E. C. Meurer, R. Galav-erna, B. J. Bythell, J. DuPont, R. G. Cooks, and M. N. Eberlin, *J. Phys. Chem. Lett.,* **2012**, *3*, 3435.

"Tyrosine Side-chain Catalyzed Proton Transfer in the YG a_2 Ion Revealed by Theory and IR Spectroscopy in the 'Fingerprint' and X-H (X=C, N, O) Stretching Regions," B. J. Bythell, O. Hernandez, V. Steinmetz, B. Paizs, and P. Maître, *Int. J. Mass Spectrom.,* **2012,** *316-318,* 227.

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"Diagnosing the Protonation Site of b_2 Peptide Fragment Ions using IRMPD in the X-H (X = O, N, and C) Stretching Region," R. K. Sinha, U. Erlekam, B. J. Bythell, B. Paizs, P. Maître, *J. Am. Soc. Mass Spectrom.,* **2011**, *22*, 1645.

Bruker Maxis Plus (maXis HD) quadrupole time-of-flight mass spectrometer and UHPLC.

THE FACULTY

JAMES S. CHICKOS

Professor Chickos has been a member of the UM-St. Louis faculty since 1969. He received his undergraduate degree from the State University of New York-Buffalo, and his Ph.D. from Cornell University. He was an NIH Postdoctoral Fellow at Princeton University and the University of Wisconsin.

Research Interests

All scientific endeavors are dependent on the availability of reliable thermodynamic and physical property data. These data form the foundations on which our current understanding of the physical world is based. The measurement and collection of such data are a fundamental scientific task, common to all who practice the discipline.

We have had an interest in developing simple algorithms to model some of these physical properties. The purpose for doing so is to provide data in the absence of experiment and to provide a basis for the selection of a particular measurement in the presence of two or more discordant values. In addition, the process of distilling these physical data using these algorithms can sometimes produce parameters that can be used to evaluate molecular properties that cannot be measured directly.

Simple models have been developed to estimate condensed phase properties such as vaporization enthalpies, heat capacities, fusion entropies and enthalpies, vapor pressures and sublimation enthalpies of small molecules. The parameters generated by these algorithms have also been useful in estimating fusion enthalpies of polymers and conformational entropy changes in globular proteins. Models to estimate mp have also been developed.

The development of models to mimic physical properties requires extensive databases and a constant updating of these databases. As a result, we have developed a collaborative interaction with the National Institutes of Standards and Technology in Washington DC in which physical property data flow freely in both directions. We currently supply NIST with sublimation enthalpies of organic compounds.

Coupled with our interest to develop models for such properties is the need to obtain experimental data. A variety of physical properties are measured in our research laboratories that include measurements of vaporization, sublimation and fusion enthalpies. We are also examining new simpler methods of making these measurements. One such process recently developed, correlation gas chromatography, affords the vaporization enthalpy and vapor pressure of a solid or liquid at 298 K by simply using retention time measurements of knowns and unknowns.

Selected Publications

"Vapor Pressures and Vaporization Enthalpies of a series of χ- and δ-lactones by correlation gas chromatogrhaphy", M. Kozlovskiy, C. Gobble and J. S. Chickos, *J. Chem. Thermodynamics* **2014**, 73, 262.

″Feeling and investigating blue: On the enthalpy of formation of indigo″, M. S. Miranda, J. S. Chickos, J. C. G. Esteves Da Silva and J. F. Liebman, *J. Chem. Thermodynamics*, **2014**, *73*, 69

″Vapor pressures and vaporization enthalpies of a series of dialkyl phthalates by correlation gas chromatography″, C. Gobble, J. S. Chickos and S. P. Vererkin, *J. Chem. Eng. Data*. **2014**, *59*, 1353.

″Feeling and investigating blue: On the enthalpy of formation of indigo″, M. S. Miranda, J. S. Chickos, J. C. G. Esteves Da Silva and J. F. Liebman, *J. Chem. Thermodynamics*, **2014**, *73*, 69.

"Vapor Pressures and Vaporization Enthalpies of a series of c- and d-lactones by correlation gas chromatogrhaphy", M. Kozlovskiy, C. Gobble and J. S. Chickos, *J. Chem. Thermodynamics* **2014**, 73, 262

"Vapor Pressures and Vaporization Enthalpies of a series of Dialkyl Phthalates by Correlation Gas Chromatography", C. Gobble, J. S. Chickos and S. P. Verevkin, *J. Chem. Eng. Data.* **2014**, *59*, 1353

"Vapor Pressures, Vaporization, Sublimation and Fusion Enthalpies of Some Fatty Acids," J. A. Wilson and J. S. Chickos, *J. Chem. Eng. Data.* 2**013**, *58,* 322

"Some thermodynamic properties of benzocaine," C. Gobble, A. Gutterman and J. S. Chickos, *Struct. Chem*., **2013**, *24*, 1903.

"Vaporization Enthalpies and Vapor Pressures of Two Insecticide Components, Muscalure and Empenthrin, by Correlation Gas Chromatography″, J. Spencer and J. Chickos, *J. Chem. Eng. Data* **2013**, *59*, 3513.

"Thermochemistry of Uracils. Experimental and Computational Enthalpies of Formation of 5,6-Dimethyl-1,3,5-Trimethyl-, and 1,3,5,6-Tetramethyluracils", R. Notario, V. N. Emelyanenko, M. V. Roux, F. Ros, S. P. J. S. Chickos and J. F. Liebman, *J. Phys. Chem. A* **2013***, 117,* 244.

"Thermochemical and structural study of a dibenzocycloheptane cyanoenamine," S. Perisanu, I. Contineanu, A. Neacsu, N. P. Rath, J. S. Chickos, R. Notario and J. F. Liebman. *Struct. Chem*., **2013**, *24*, 1975.

THE FACULTY

ALEXEI V. DEMCHENKO

Professor Alexei Demchenko received his Diploma from the Mendeleev University of Chemical Technology of Russia, Moscow (1988) and his PhD in from the Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow (1993). He was a BBSRC post-doctoral research fellow at the School of Chemistry, University of Birmingham (UK) and a research associate at the Complex Carbohydrate Research Center, University of Georgia before joining the UM-St. Louis faculty in 2001. He was recipient of the Chancellor's Award for Research and creativity in 2013 and was appointed Curators' Professor of Chemistry in 2014.

Research Interests

Novel glycosylation reactions, methods and approaches. Stereocontrolled synthesis of 1,2-*cis*-glycosidic bond formation. Mechanistic aspects of glycosylation.

Thioimidates as glycosyl donors for stereoselective glycosylation and versatile building blocks for expeditious oligosaccharide synthesis.

Novel expeditious strategies for the synthesis of complex oligosaccharides and glycoconjugates: reactivity, selectivity, chemoselectivity, and orthogonality of modern glycosyl donors.

Transition metal complexes in synthetic carbohydrate chemistry: direction of the stereoselectivity of glycosylation, temporary deactivation, and activation for glycosylation.

Fully synthetic glycotherapeutics (anticancer, anti-inflammatory, antiseptic, antibacterial, *etc*.). Synthetic glycoproteins, glycopeptides, glycopolymers, glycolipids, glycoheterocycles, glycoaminoacids and combinations thereof. Synthetic glycoconjugate vaccines.

Solid phase and surface chemistry: application to stereoselective glycosylation and rapid assembly of complex oligosaccharides and glycoconjugates. New platforms and technologies for automated oligosaccharide synthesis: STICS and HPLC-based approaches.

Selected Publications (135 total)

"Hydrogen bond mediated aglycone delivery: Synthesis of linear and branched α-glucans," J. P. Yasomanee and A. V. Demchenko, *Angew Chem. Intl Ed.* **2014** (n press).

"Hydrogen-bond-mediated aglycone delivery: Focus on β-mannosylation," S. G. Pistorio, J. P. Yasomanee and A. V. Demchenko," *Org. Lett*. **2014**, *16*, 716

"Regenerative glycosylation under nucleophilic catalysis", S. S. Nigudkar, K. J. Stine and A. V. Demchenko, *J. Am. Chem. Soc.,* **2014**, *126*, 921.

"Super-arming of glycosyl donors by combined neighboring and conformational effects.," M. Heuckendorff, H. D. Premathilake, P. Pornsuriyasak, A. O. Madsen, C. M. Pedersen, M. Bols and A. V. Demchenko, *Org. Lett*. **2013**, *15* 4904

"Effect of remote picolinyl and picoloyl substituents on the stereoselectivity of chemical glycosylation," J. P. Yasomanee and A. V. Demchenko. *J. Am. Chem. Soc.,* **2012**, *134*, 20097.

"HPLC-assisted automated oligosaccharide synthesis," N. V. Ganesh, K. Fujikawa, Y. H. Tan, K. J. Stine, A. V. Demchenko. *Org. Lett.*, **2012**, *14*, 3036.

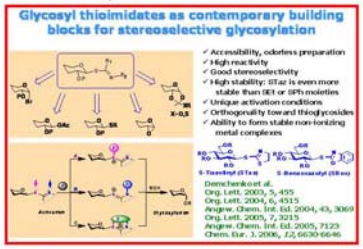
S. J. Hasty, M. Kleine, A. V. Demchenko. S-benzimidazolyl glycosides as a platform for oligosaccharide synthesis by an active-latent strategy. *Angew. Chem. Int. Ed.*, **2011**, *50*, 4197

Edited Books"

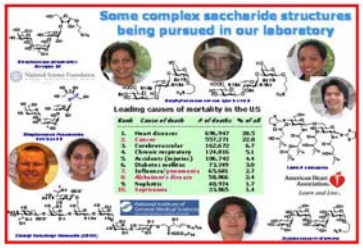
"Frontiers in Modern Carbohydrate Chemistry" Oxford Univ. Press, **2007**."

Handbook of Chemical Glycosylation." Wiley-VCH, **2008**.

Stereocontrolled glycosylation
NSF, CHE-0547566

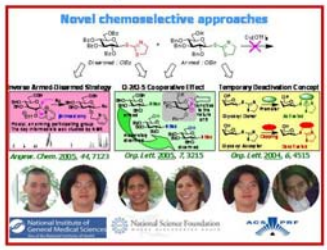


Biomedical applications
NIH-AI067494, AHA0855743G



RESEARCH AREAS

Oligosaccharide assembly
NIH, GM077170



Innovative technologies
NIH, GM090254

Research Group Members (09/2014)

Dr. Abhijeet Kayastha (post-doc)
Dr. J. Prithika Yasomanee (post-doc)
Xiao G. Jia (doctoral)
Saltvatore G. Pistorio (doctoral)
Satsawat Visansirikul (doctoral)
Tinghua Wang (doctoral)

Current Funding

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04/13-03/15 Mizutani Foundation
08/14-07/18 NIH R01GM111835

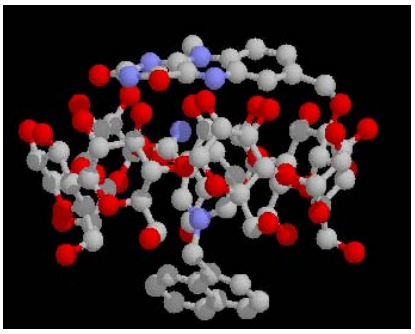
THE FACULTY

VALERIAN T. D'SOUZA

Professor. D'Souza received his M.Sc. from Bombay University, and his Ph.D from the University of Detroit. He held a postdoctoral position at Northwestern University prior to joining the UM-St. Louis faculty in 1987.

Research Interests

The main goal of our research project is to build redox catalysts based on the chemistry of biological redox enzymes. The incredible power of the enzymes to bring about chemical transformations with large acceleration and high specificity has been mainly attributed to their ability to bind the substrate and catalyze specific reactions of the bound substrate. Thus, these redox catalysts are designed to have a binding site to bind particular molecules and a catalytic site to catalyze redox enzymes. We have synthesized the first generation of these artificial enzymes using cyclodextrins as a binding site and flavin derivatives as catalytic site shown in the figure.



This artificial enzyme can accelerate oxidation of benzyl alcohols up to 650-fold over that catalyzed by riboflavin. We are in the process of designing and synthesizing the second generation of artificial redox enzymes which should have enhanced catalytic ability. These enzymes are designed using computational chemistry techniques.

In the process of developing the methodology to build these artificial enzymes, we have also produced a method to synthesize custom-designed cyclodextrins. Cyclodextrins are cyclic oligosaccharides which have gained prominence in the last two decades as complexing agents for various organic molecules in artificial enzymes, foods, flavors, etc. However, the main shortcoming of this, otherwise remarkable, molecule is that the functionalities available for useful chemical processes are limited to simple hydroxyl groups. The new method developed by us enables us to synthesize cyclodextrins with various desired functionalities. We are presently investigating the binding and catalytic properties of these new cyclodextrins

Selected Publications

O. V. Shulga, K. Jefferson, A. R. Khan, V. T. D'Souza, J. Liu, A. V. Demchenko and K. J. Stine. "Preparation and Characterization of Porous Gold and Its Application as a Platform for Immobilization of Acetylcholinene Esterase." *Chem. Materials* **2007**, *19*, 3902.

J. N. Swamy, R. E. K. Winter, C. R. Jeffreys and V. T. D'Souza, "Synthetic methodology for cyclodextrin-dipyrromethane conjugates," *Tet. Lett.*, **2004,** *45*, 7595.

V. T. D'Souza, "Modification of Cyclodextrins for Use as Artificial Enzymes," *Supromolecular Chemistry,* **2003***, 15*, 221.

V. T. D'Souza, "Artificial redox enzymes," *Biologicheskii Zhurnal Armenii*, **2001**, *53*, 105.

A. R. Khan, P. Forgo, S. Tian and V. T. D'Souza, "Synthesis and properties of modified cyclodextrins," *Proceedings, 10th International Cyclodextrin Symposium*, Ann Arbor, MI, 2000, 673.

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A. R. Khan, P. Forgo, K. J. Stine and V. T. D'Souza, "Selective modifications of cyclodextrins,"*Proc. 9th Int. Symp.on Cyclodextrins,* Santiago de Comostela, Spain, **1999**, 33.

P. Forgo and V. T. D'Souza,"The Use of High Resolution NMR Spectroscopy in Supramolecular Systems," *Org. Lett.*, **1999**, *1*, 1543.

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K. J. Stine, D. M. Andrauskas, A. R. Khan, P. Forgo and V. T. D'Souza, "Electrochemical Study of Self-Assembled Monolayers of a ß-cyclodextrin Methyl Sulfide Covalently Linked to Anthraquinone," *J. Electroanal. Chem.* **1999**, *465*, 209.

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A. R. Khan, P. Forgo, V. T. D'Souza, R. M. Friedman and J. Liu "Structure and Electrochemical Behavior of a Flavin Sulfide Monolayer Adsorbed on Gold," *J. Electroanal. Chem.*, **1999**, *472*, 147.

P. Forgo and V. T. D'Souza, "The Use of High Resolution NMR Spectroscopy in Supramolecular Systems," *Org. Lett.*, **1999**, *1*, 1543.

P. Forgo and V. T. D'Souza, "An NMR Approach for Determination of the Substitution Pattern in Supramolecular Systems," T*et. Lett.*, **1999**, *40*, 8533.

THE FACULTY

CYNTHIA DUPUREUR

Professor Dupureur received her B.S. degree from Southwest Missouri State University, and her Ph.D. from Ohio State University. She joined the UM-St. Louis Chemistry faculty in 2001. She held a faculty position at Texas A&M following postdoctoral fellowship at the California Institute of Technology.

Research Interests

My group is interested in structure-function relationships, which is how the structure of a biomolecule dictates its behavior. For many years, we focused on metallonucleases, exploring aspects of DNA binding specificity and metal ion dependent behavior using various biophysical techniques. More recently, this had led to two newer collaborative drug discovery projects. Taking advantage of our long term experience in enzyme kinetics, we are evaluating synthetic inhibitors of esterases which are linked to Alzheimer's disease and diabetes. A project involving the conformational behavior of hormone sensitive lipase has evolved from this effort. The other project involves examining polyamide-DNA interactions in an effort to develop better HPV drugs. The group has experience in a wide array of techniques including fluorescence and NMR spectroscopies, mass spectrometry, calorimetry, enzyme kinetics, and capillary electrophoresis, among others. This provides excellent opportunities to master a number of biophysical and mechanistic approaches.

Recent Publications

″Structural Insights into the Interaction between a Potent Ant-inflammatory Protein, Viral CC Chemokine Inhibitor (vCC), and the Human CC Chemokine Eotaxin,″ N-W. Kuo, Y-G. Gao, M. Schill, N. Isern, C. M. Dupureur and P. J. Li Wang**,** *J. Biol. Chem.* **2014**, *289*, 6592.

"Binding studies of a large antiviral polyamide to a natural HPV sequence," G. He, E. Vasilieva, G. D. Harris, K. J. Koeller, J. K. Bashkin and C. M. Dupureur, *Biochimie* **2014**, *102*, 83.

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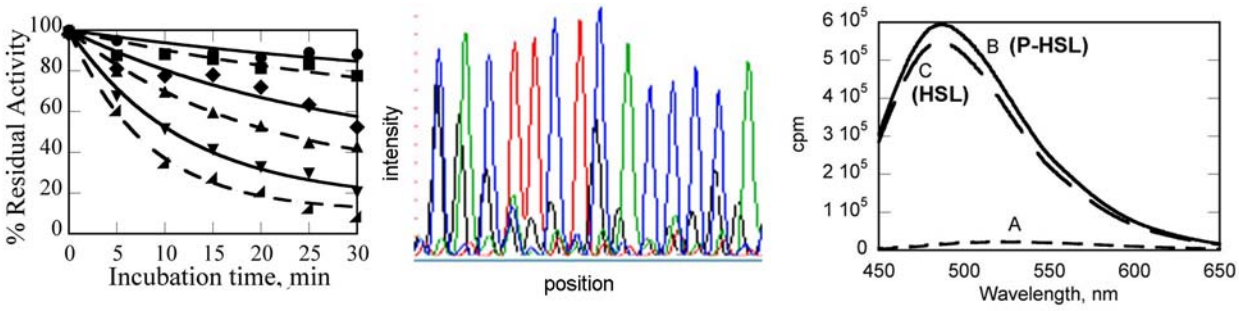
"Synthesis and kinetic analysis of some phosphonate analogs of cyclophostin as inhibitors of human acetylcholinesterase". S. Dutta, R. K. Malla, S. Bandyopadhyay, C. D. Spilling, and C. M. Dupureur, *Bioorg. & Med. Chem.* **2010**, *18,* 2265.



THE FACULTY

GEORGE W. GOKEL

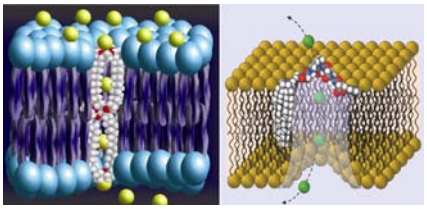
Professor Gokel attended Tulane University, New Orleans, LA, B.S. chemistry, 1968, University of Southern California, Los Angeles, CA, Ph.D. chemistry with I. K. Ugi, 1971 and UCLA, where he did a postdoctoral fellowship with D.J. Cram, 1972-1974. He served on the faculty at Penn State, Maryland and Miami prior to heading the Program in Chemical Biology, Washington University School of Medicine, St. Louis. He joined UM-St. Louis as Distinguished Professor in 2006 and was recently appointed Director of the Center for Nanoscience.

Research Interests

Synthetic Cation and Anion channels

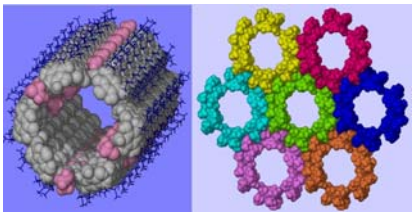
During the past decade, our lab has developed and elaborated a class of synthetic ion channels called hydraphiles. We use diaza-18-crown-6 macrocycles as head groups and entry portals for ion conduction. Hydrophobic spacer chains connect the headgroups and impart the appropriate length for the hydraphile to span the bilayer. A third, central macrocycle acts as an "ion relay." This subunit serves the same purpose as the recently discovered "water and ion-filled capsule" identified in the solid state structure of KcsA channel of *Streptomyces lividans*. A side arm of varying identity extends from the distal crown, providing anchoring and stabilization in the bilayer. These ion channels show antibacterial activity and we are currently developing this important aspect of their chemistry.

Anion, particularly chloride, permeability is essential for volume, pH, and membrane potential regulation in all cells. We have developed a chloride-selective channel in an attempt to model anion transport and explore these cellular requirements. Using known protein chloride channels as a guide, we have synthesized a chloride-selective transporter that is active in phospholipid bilayers. We use a broad range of biophysical methods to characterize the behavior of channels. These include dynamic light scattering, fluorescence techniques, ion selective electrodes, calorimetry, NMR, the Langmuir trough, and Brewster angle microscopy. The cation (left) and anion (right) channels are shown in the figure below.



Molecular Capsules and Nanotubes

It has been known for more than a century that phenols and aldehydes react to form macrocycles. We have been developing the chemistry of amphiphilic nanocapsules and nanotubes for drug delivery. The pyrogallol[4]arene compounds have a unique and nearly unexplored chemistry. We have found that they form ion channels and exhibit very unusual amphiphilic properties. The figure below shows a section of nanotube along with the adjacent tubes interlocked with it.



Selected Publications

″Improved Syntheses of Benzyl Hydraphile Synthetic Cation-Conducting Channels″ N. S. Curvey, S. E. Luderer, J. K. Walker and G. W. Gokel, *Synthesis*, **2014** (in press).

“Hydraphile synthetic ion channels alter root architecture in Arabidopsis thaliana,” M. B. Patel, A. Stavri, N. S. Curvey and G. W. Gokel, *Chem. Commun*. **2014** (in press).

"Ion transport through bilayer membranes mediated by pyrogallol[4] arenes ," S. Negin, R. Li, O. V. Kulikov, M. M. Daschbach and G. W. Gokel, *Inorg. Chim. Acta* **2014**, *417*, 177.

"Morphologies of branched-chain pyrogallol[4]arenes in the solid state," O. V. Kulikov, S. Negin, N. P. Rath and G. W. Gokel, *Supramolecular Chem*. **2014**, *26*, 506.

"Synthetic ion channels: From pores to biological applications," G. W. Gokel and S. Negin, *Acc. Chem. Res*., **2013**, *46*, 2024.

Properties of Long Alkyl-chained Resorcin[4]arenes in Bilayers and on the Langmuir Trough," P. Ogirala, S. Negin, C. Agena, C. Schäfer, T. Geisler, J. Mattay, and G. W. Gokel, *New J. Chem*. **2013**, *37*, 105.

"Anion Complexation and Transport by Isophthalamide and Dipicolinamide Derivatives: DNA Plasmid Transformation in E. coli," J. L. Atkins, M. B. Patel, M. M. Daschbach, J. W. Meisel, and G. W. Gokel, *J. Am. Chem. Soc.,* **2012**, *134*, 13546

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"Synthetic memberane active amphiphiles," G. W. Gokel and S. Negin, *Adv. Drug Delivery Rev.* **2012**, *64*, 784.

"Pyrogallo[4]arenes show highly Variable Amphiphilic Behavior at the Air-Water Interface Dependent Upon side Chain Length and Branching", M. M Daschbach, O. V. Kulikov, E. F. Long and G. W. Gokel, *Chem. A Eur*. J. **2011,** *17*, 8913

"In vivo cell death mediated by synthetic ion channels", B. A Smith, M. M.; Daschbach, S. T Gammon, S. Xiao, S. E Chapman, C. Hudson, M. Suckow, D. Piwnica-Worms, G. W Gokel and W. M. Leevy, *Chem. Commun.* **201**1, 79779.

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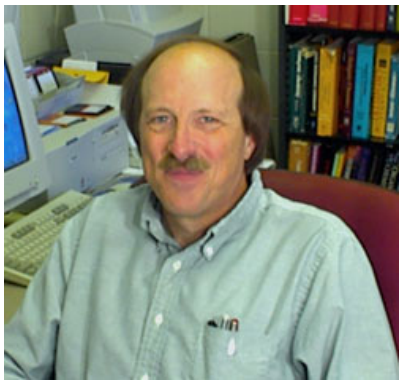


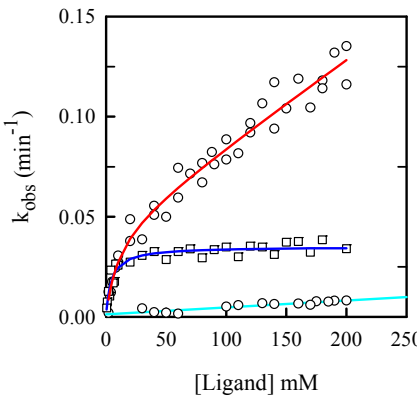
WESLEY R. HARRIS

Professor Harris joined the UM-St. Louis faculty in the Fall of 1988. He received both his B.S. and his Ph.D. from Texas A&M University, and was a Postdoctoral Associate at the University of California-Berkeley. Prior to joining UM-St. Louis, he held faculty positions at the University of California at Davis and the University of Idaho. He also serves as Associate dean of the Graduates School.

Research Interests

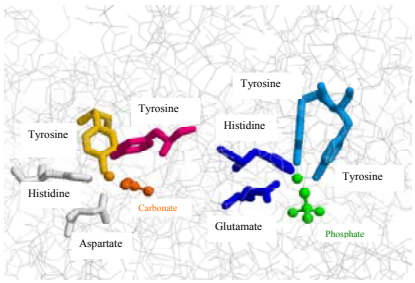
Although iron is an abundant element, the insolubility of Fe^{3+} at physiological pH requires specialized molecules to bind and transport this essential metal. The key iron transport agent in mammals is the serum protein transferrin. This protein binds iron as it enters the blood from the intestinal mucosal cells and controls the delivery of the metal to cells that need iron.

The Harris group studies the kinetics of iron release from transferrin to low-molecular-weight ligands. This process is relevant to the design of new ligands for treating iron overload. The rate of iron release appears to depend on the ability of the incoming ligand to displace the synergistic carbonate anion from the transferrin metal-binding site. As shown below, pyrophosphate (PP_i), which can substitute for the carbonate, removes iron more rapidly than tripolyphosphate (TPP), which cannot.



In collaboration with Dr. Spilling's lab, new ligands are being designed and evaluated for their ability to remove iron at pharmacologically relevant ligand concentrations.

In addition to its role in iron metabolism, transferrin also acts as the primary serum transport agents for a variety of toxic and therapeutic metal ions. Dr. Harris' group has reported the binding constants for transferrin with a number of other metal ions. This include physiological metal ions such as Zn^{2+} and Mn^{2+}, pharmaceutical metal ions such as Ga^{3+}, In^{3+}, and Gd^{3+} and toxic metal ions such as Al^{3+}. Recent work has focused on the binding of Al^{3+} to transferrin and to the low-molecular-weight ligands citrate and phosphate in order to construct an accurate computer model for the speciation of Al^{3+} in human serum.



Transferrin FBP

The studies on the mammalian protein transferrin have recently been expanded to include work on the binding and release of ferric ion from a bacterial iron transport protein known as FBP. This periplasmic transport protein is half the size of transferrin, but shares the key requirement for a synergistic anion in order to bind iron. While transferrin uses a carbonate anion, FBP uses phosphate as the synergistic anion. The metal binding sites for the two proteins are shown below.

New studies are underway on the binding of other trivalent metal ions to FBP. It may be possible to develop antbiotics based on the ability of other trivalent metal ions to block the uptake or iron by the pathogenic organisms that rely on FBP for iron uptake.

A collaborative effort to develop a new chelating resin is underway. Selective ligands are covalently attached to polymer beads for the removal of metal ions from solution. The relationship between the ligand binding affinity on and off the resin is being evaluated.

Selected Publications

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″Crystal structure of pyridoxal amino methyl phosphonic acid (PYRAMPA) and its stability constants with Al^{3+},″ Y. Z. Hamada, W. R. Harris and N. P. Rath, *Int. J. Green Nanotech,* **2013,** *5*, 1**.**

"Computer Simulation of the Interactions of Glyphosate with Metal Ions in Phloem," W. R. Harris, R. D. Sammons, R. C. Grabiak, A. Mehrsheikh, and M. S. Bleeke, *J. Ag. Food. Chem.* **2012**, *60*, 6077.

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"Chelating compounds and immobilized tethered chelators," R. A. Yokel, W. R. Harris, C. D. Spilling, R. J. Kuhn and S. Dawadi, *U.S. Pat. Appl. Publ.* **2012**, US 2012-0061325 A120120315

"Allosteric effects of sulphonate anions on the rates of iron release from Serum Transferrin", R. Sharma and W. R. Harris, *J. Inorg. Biochem*., **2011,** *105*, 1148

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THE FACULTY

STEPHEN M. HOLMES

Professor Holmes received his B.S. degree from Southwest Texas State University in 1992 and Ph.D. from the University of Illinois at Urbana-Champaign in 1999. He was a Postdoctoral Scholar at Cornell University from 1999-2001. He served on the faculty at the University of Kentucky before joining the Department of Chemistry & Biochemistry at UM-St. Louis in 2008. He is currently an NSF CAREER Awardee (2007-2012).

Research Interests

Magnetic Materials: Understanding the physical origins of single-molecule magnetic behavior in a series of structurally related cyanometalate clusters is an active area of study. Cyanometalates are excellent building blocks for constructing molecule-based clusters because cyanides generally form linear M (μ-CN)M´ linkages between two metal centers, stabilize a variety of transition metal centers and oxidation states, and efficiently communicate spin density information. Furthermore the sign and magnitude of the local exchange interactions can be controlled via substitution and predicted using simple orbital symmetry arguments. We have developed a synthetic methodology for preparing several well-defined clusters containing a variety of tricyanide complexes (building blocks). The building blocks exhibit significant orbital contributions to their magnetic moments, apparently a necessary feature for the observation of slow magnetic relaxation. Current efforts are focused on how late transition metal centers alter the magnetic (and optical) properties of structurally related clusters.

Photoresponsive Materials: Compounds that change their optical, magnetic, and electrical properties as a function of external stimuli is an exciting area of study in materials science. We recently reported that two polynuclear cyanometalate complexes exhibit reversible changes their optical and magnetic properties with temperature (up to 250 K) and light. If this is a general phenomenon, then substitution of the metal ions and ligands present may extend the operable switching temperatures of these materials above 300 K. Current efforts are directed at understanding the factors necessary for tuning the photoresponsive behavior in these clusters and one-dimensional networks.

Molecule-Based Devices: The increasing demand for higher information density and circuit miniaturization is rapidly approaching the limits of device scaling technologies, with potential cost and performance limits being realized within a decade. An overarching goal of molecule-based electronics is to insert easily modified molecules that function as switching elements into electronic devices, in principle allowing for information storage at the molecular level. Key challenges of this collaborative research effort are to (1) fabricate nm-scale electrode gaps that correspond to molecular length scales and (2) engineer tunable molecules for study. Recent measurements suggest that we have successfully integrated a series of magnetic clusters into electrical junctions. Future efforts will investigate how the clusters and metal ions present tune the electrical transport behavior of assembled devices.

Selected Publications

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Y. Zhang, D. Li, R. Clérac, M. Kalisz, C. Mathonière and S. M. Holmes, "Reversible Thermally and Photo-induced Electron Transfer in a Cyano-Bridged $\{Fe_2Co_2\}$ Square Complex," *Angew. Chem. Int. Ed.* **2010**, *49*, 3752.

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THE FACULTY

MICHAEL R. NICHOLS

Professor Nichols received his B.S. degree from Lindenwood College and Ph.D. from Purdue University. Prior to joining the UM-St. Louis faculty in Fall 2004, he completed a postdoctoral fellowship at the Mayo Clinic in Jacksonville, FL.

Research Interests

Protein assembly or aggregation is widely recognized as a significant contributing factor to a number of neurodegenerative diseases including Alzheimer's disease (AD), Parkinson's disease, Huntington's disease, and others. Remarkably, the proteins or peptides implicated in these diseases, while possessing different amino acid sequences, all self-assemble to form similar fibrillar structures termed amyloid. One such peptide is amyloid-β (Aβ), a 40-42-residue peptide and the primary component of the senile plaques found in AD brains. The leading hypothesis in AD research maintains that accumulation of aggregated Aβ is the primary cause of the disease.

One research area in my laboratory involves mechanistic studies of Aβ aggregation. Objectives include isolation and characterization of aggregation intermediates and investigation of conditions that influence aggregation. These studies utilize a variety of biophysical techniques to probe mechanistic and structural questions.

The other major research thrust in my laboratory addresses the question of how Aβ aggregates interact with, and are detrimental to, cells. One hypothesis is induction of a sustained inflammatory response causing the release of harmful cytokines such as tumor necrosis factor-α, interleukin-1β. We are studying these effects in monocyte/macrophage cells and primary microglia cells with the goal of understanding the cause of the inflammatory response, how it relates to cell toxicity, and identification of novel ways to regulate cytokine release.

Selected Publications

″CD47 does not mediate amyloid-β(1-42) protofibril-stimulated microglial cytokine release,″ S. Karki and M. R. Nichols, *Biochem Biophys Res Commun*, **2014**, in press

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"Stability of early-stage amyloid-β(1-42) aggregation species,″ K. A. Coalier, G. S. Paranjape, S. Karki, and M. R. Nichols, *Biochimica et Biophysica Acta*, **2013**, *1834*, 65

"Amyloid-β(1-42) protofibrils formed in modified artificial cerebrospinal fluid bind and activate microglia," G. S. Paranjape, S. E. Terrill, L. K. Gouwens, B. M. Ruck, and M. R. Nichols, *J Neuroimmune Pharmacol*, **2013**, *8,* 312

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"Isolated amyloid-β(1-42) protofibrils, but not isolated fibrils, are robust stimulators of microglia," G. S. Paranjape, L. K. Gouwens, D. C. Osborn, and M. R. Nichols, *ACS Chem Neurosci*, **2012**, *3*, 302.

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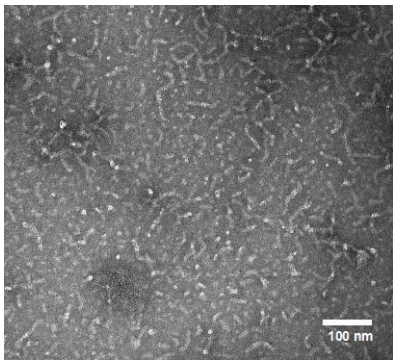
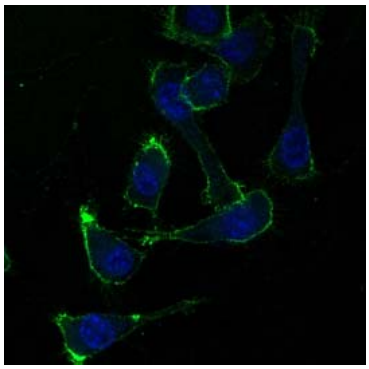
"Probing the amyloid-β(1-40) fibril environment with substituted tryptophan residues,"J. C. Touchette, L. L. Williams, D. Ajit, F. Gallazi, and M. R. Nichols *Arch. Biochem. Biophys,* **2010**, *494*, 192.

"Amyloid-β(1-42) fibrillar precursors are optimal for inducing tumor necrosis factor-α production in the THP-1 human monocytic cell line," D. Ajit, M. L. D. Udan, G. Paranjape, and M.R. Nichols, *Biochemistry,* **2009**, *48,* 9011.





(Left) Electron microscopy image (59k magnification) of isolated Aβ42 protofibrils. (Right) Binding of Aβ42 protofibrils (green) to BV-2 microglia. Cell nuclei are shown in blue.

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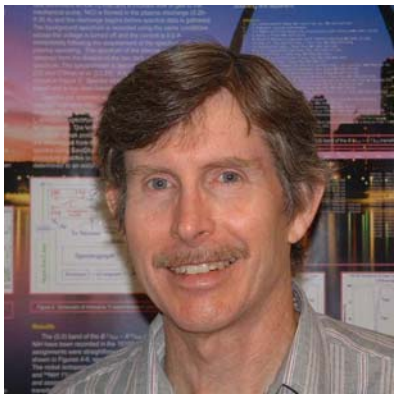

JAMES J. O'BRIEN

Professor Jim O'Brien received his B.Sc. (1st class Honors) from James Cook University and his Ph.D. from the Australian National University in Canberra. He had post-doctoral positions at the University of California-Berkeley (CSIRO Australia Fellowship), the National Research Council of Canada, Ottawa (NRC Research Associate), and the University of Arizona, Tucson.

Research Interests

Jim O'Brien is an experimental physical chemist who specializes in fundamental and applied, high-resolution laser spectroscopy and gas phase analytical chemistry. The primary tool employed is Intracavity Laser Spectroscopy. ILS techniques provide tremendously enhanced sensitivity for measuring absorption spectra quantitatively.

Research areas include: (1) determining absorption spectroscopy parameters (e.g., absorption coefficients) for methane and ammonia in the visible to near□IR spectral region to assist in interpreting reflected spectra from the outer planets (e.g., Neptune); (2) high-resolution electronic spectroscopy of small transition-metal diatomics (e.g., AuO, NiCl, NiH) with a view to locating excited electronic states in these species and comparing trends in bonding; (3) determining molecular constants from precisely measured line positions of species of atmospheric (e.g., O_2) and environmental relevance (4) the gas phase chemistries and species involved in a variety of plasma initiated chemical vapor deposition (CVD) processes; and (5) developing the intracavity laser spectroscopy technique for analytical purposes (e.g., in acquiring spectra at ultra□high spectral resolution) and extending its spectral range of application (e.g., use of other types of lasers that work in the IR).

Selected Publications

"High resolution electronic spectroscopy of the A2Σ- - X2Π1/2 transition of PtN," K. Womack, L. C. O'Brien, S. Whittemore, J. J. O'Brien, A. Li, and T. C. Steimle, J. *Chem. Phys.* **2014**, *141*, 084304/1

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"Reanalysis of the $[12.3]^2\Sigma$ - $X^2\Pi_{3/2}$, $[12.3]^2\Sigma$ - $X^2\Pi_{1/2}$, and $[12.3]^2\Sigma$ - $B^2\Sigma^+$ electronic transitions of nickel monochloride, NiCl," T. Dahms, K. Womack, L. C. O'Brien and J. J. O'Brien, *J. Mol. Spectrosc.***2013***, 292*, 5.

"Improved experimental line positions for the (1, 1) band of the b1S+-X3S transition of O_2," J. J. O'Brien, E. C. O'Brien and L. C. O'Brien, *J. Mol. Spectrosc.* **2012**, *273,* 34.

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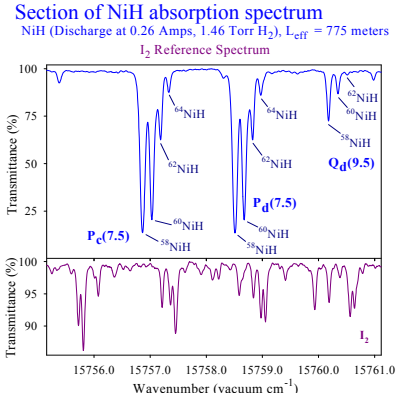
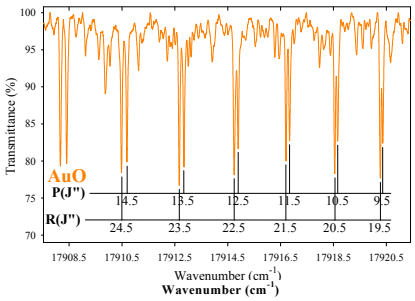
"Spectroscopy of NiF by intracavity laser spectroscopy: Identification and analysis of the (1,0) band of the [11.1] $^2P_{3/2}$-X $^2P_{3/2}$ electronic transition," R. A. Harris, L. C. O'Brien and J. J. O'Brien, *J. Mol. Spectrosc*. **2010,** *259*, 116.

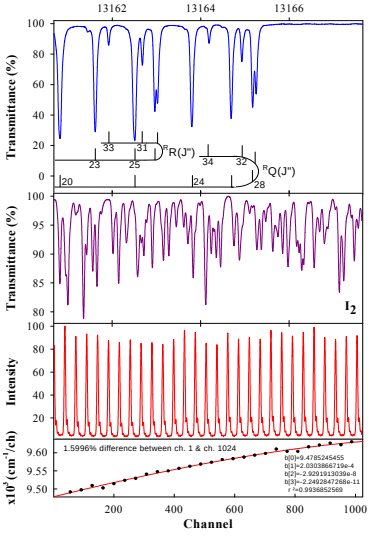
"Laboratory measurements of the (2,0) $B^2D_{5/2}$-$X^2D_{5/2}$ transition of nickel hydride using intracavity laser absorption spectroscopy," S. Shaji, A. Song, M. Li, J. J. O'Brien and L. C. O'Brien, *Can. J. Phys.* **2009**, *87*, 583

Section of NiH absorption spectrum

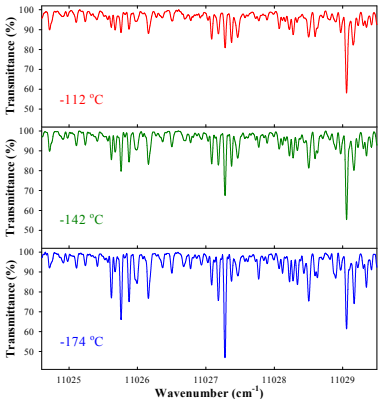


Gold oxide (2-0) $^4\Pi_{3/2} - X^2\Pi_{3/2}$ spectrum





ILS spectra of methane at 3 temperatures



THE FACULTY

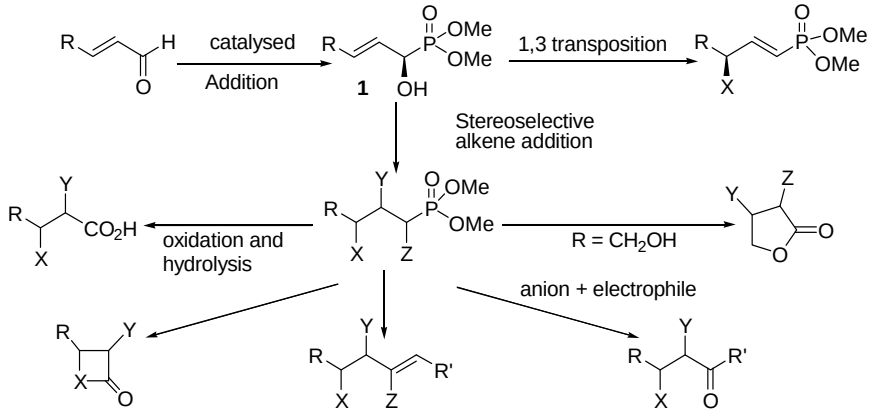
CHRISTOPHER D. SPILLING

Professor. Spilling received his B.Sc. (Hons.) degree and Ph.D. degree from the University of Technology, Loughborough, England. He was a Postdoctoral Associate at Northwestern University before joining the UM-St. Louis faculty in 1989. He became department chair in 2004.

Research Interest

The last decade has seen a rapid expansion in the interest in the asymmetric synthesis of 1-substituted phosphonates. The unique properties of phosphorus provide a fascinating and challenging approach to stereoselective reactions. Our goal is to examine the use of chiral phosphonamides and phosphonates in stereoselective reactions. We reported the first example of a lathanide chiral catalyst in the addition of simple phosphites to achiral aldehydes. More recently, we discovered some promising titanium alkoxide systems. We are attempting to expand the chemistry of allylic hydroxy phosphonamides and phosphonates formed in the chemistry discussed above. Allylic hydroxy phosphonates are similar to regular allylic alcohols and should undergo similar chemistry. However, the presence of the phosphonate significantly alters the electronics of the system, and enables control of both regiochemistry and stereochemistry. Our initial work focused on the palladium catalyzed addition of amines to the carbonate derivatives of allylic hydroxy phosphonates, and several examples of this reaction have performed. The rearrangement proceeds with complete retention of chirality. A number of 3,3 sigmatropic rearrangements and alkene addition reactions have been studied. The newly developed chemistry of the hydroxy phosphonates is being applied towards the synthesis of heterocyclic and carbocyclic natural products and enzyme inhibitors.

Psammapsylin, fistularin, and the bastadins are related metabolites isolated from sponges found worldwide. This family of highly brominated compounds possess wide ranging biological activity, including anti-HIV activity, and anti-tumor properties. They are related in their biosynthetic origin, as oxidation products of tyrosine. We are exploring biomimetic approaches to the synthesis of several of these metabolites. The development of new methodology is guided by the biosynthetic pathway proposed for the formation of the tyrosine metabolites. As an extension of this project, we recently initiated research into methods for the facile synthesis of unsymmetric biaryl ethers.



Selected Publications

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″Support of academic synthetic chemistry using separation technologies from the pharmaceutical industry,″ E. L. Regalado, M. C. Kozlowski, J. M. Curto, T. Ritter, M. G. Campbell, A. R. Mazzotti, B. C. Hamper, C. D. Spilling, M. P. Mannino, L. Wan et al. *Org. & Biomolecular Chem*. **2014**, 12, 2161

″Relay Cross Metathesis Reactions of Allyl Vinyl Phosphonates,″ R. J. K. Malla, J. N. Ridenour and C. D. Spillng, *Beilstein J. Org. Chem*. **2014**, *10*, 1933.

"Enantioselective Inhibition of Microbial Lipolytic Enzymes by Nonracemic Monocyclic Enolphosphonate Analogues of cylcophostin," V. Point, R. K. Malla, F. Carriere, S. Canaan, C. D. Spilling and J-F. Cavalier, *J. Med. Chem*. **2013**, *56*, 4393.

"Synthesis and Kinetic Evaluation of Cyclophostin and Cyclophostins Phosphonate Analogs as Selective and Potent Inhibitors of Microbial Lipases," V. Point, Vanessa; R. K. Malla, S. Diomande, B. P. Martin, V. Delorme, F. Carriere, S. Canaan, N. P. Rath, C. D. Spilling and J-F**.** Cavalier, *J. Med. Chem*., **2012**, *55*, 1024.

"An Expeditious Total Synthesis of Both Diastereomeric Lipid Dihydroxytetrahydrofurans from Noptheia Anomala," S. Roy and C. D. Spilling, *Org. Lett*., **2012**, *14*, 2230.

"The First Total Synthesis of (±)-Cyclophostin and (±)-Cyclipostin P: Inhibitors of the Serine Hydrolases Acetyl Cholinesterase and Hormone Sensitive Lipase," R. K. Malla, S Bandyopadhyay, C. D. Spilling, S. Dutta and C. M. Dupureur, *Org. Lett.* **2011**, *13*, 3094.

"Concise synthesis of 1,3-di-O-substituted tetrahydropyran derivatives as conformationally stable pyranose mimetics," L. K. Mydock, C. D. Spilling and A. V. Demchenko, *Comptes Rendus Chim*. **2011**, *14*, 301.

"A Formal Synthesis of the C1-C9 Fragment of Amphidinolide C Employing the Tamaru Reaction," M. P. Paudyal, N. P. Rath and C. D. Spilling, *Organic Lett*. **2010**, *12*, 2954.

THE FACULTY

KEITH J. STINE

Professor Stine graduated with special honors with a B.S. in Chemistry from Fairleigh Dickinson University and received his Ph.D. from Massachusetts Institute of Technology. He was a postdoctoral fellow at UCLA and joined the UM-St. Louis Chemistry Department in the Fall of 1990.

Research Interests

Dr. Stine's research effort focuses on studies of monolayer-modified surfaces and nanostructures, and on model systems relevant to understanding the behavior of cell membranes. The surface modification of nanostructures is pursued with a focus on their prospective applications in bioanalytical chemistry such as in immunoassays for protein biomarkers of disease. Immobilization of proteins onto nanostructures of gold and other materials is pursued by adsorption or by covalent linkage to self-assembled monolayers. The characterization of these nanostructures by microscopy of various kinds (SEM, TEM, AFM) with UM-St. Louis Center for Nanoscience is a strong interest. The bioanalytical application of these materials is pursued using primarily surface plasmon resonance and electrochemical methods. The application of nanostructured materials in the supported organic synthesis of carbohydrates is an interest in collaboration with the Demchenko lab. Monolayers can serve as model systems providing insight into the physical properties of membranes and can be used to model molecular recognition processes occurring at membrane surfaces. Monolayers of surface-active molecules at the air-water interface (Langmuir monolayers) are studied using fluorescence microscopy, Brewster angle microscopy, and surface pressure versus molecular area isotherm measurements. The transfer of these monolayers onto solid supports for examination by microscopy, spectroscopy, or electrochemistry is another area of interest. Aggregates of biological relevance such as micelles, liposomes, and supported bilayers are of interest. The surface properties and membrane activity of selected natural products in the saponin family is a specific recent focus in this area.

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"Regenerative Glycosylation under Nucleophilic Catalysis", S. S. Nigudkar, K. J. Stine and A. V. Demchenko, *J. Am. Chem. Soc.,* **2014**, *126*, 921.

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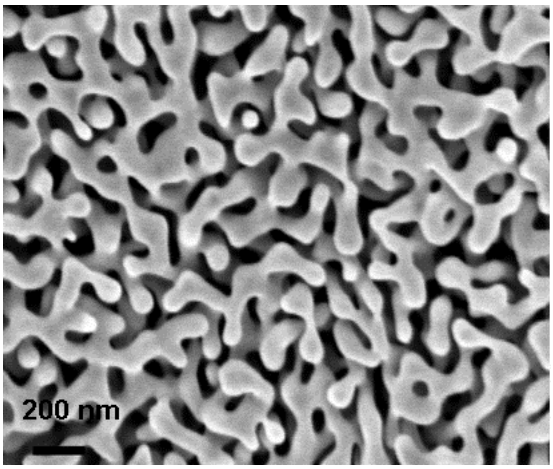
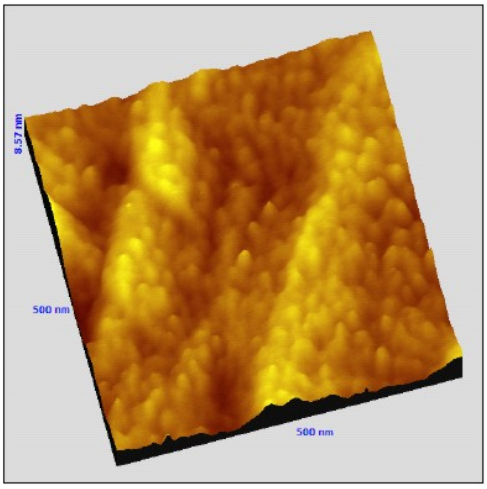
"Comparative Study of the Binding of Concanavalin A to Self-Assembled Monolayers Containing a Thiolated α-Mannoside on Flat Gold and on Nanoporous Gold," B. P. Pandey, Y-H. Tan, K. Fujikawa, A. V. Demchenko and K. J. Stine, *J. Carbohydrate Chem.* **2012**, *31*, 466.



SEM micrograph of nanoporous gold useful for assay development.



Tapping Mode Atomic Force Microscopy Image of Bovine Serum Albumin Immobilized on a Rough Gold Surface.

THE FACULTY

CHUNG F. WONG

Professor Chung F. Wong received his B.Sc. (Hons.) degree from the Chinese University of Hong Kong and his Ph.D. degree from the University of Chicago. He did his postdoctoral work at the University of Houston. Before joining the faculty of UM-St. Louis in the Fall of 2004, he held positions at the University of Houston, Mount Sinai School of Medicine, SUGEN, Inc., University of California-San Diego, and the Howard Hughes Medical Institute.

Research Interests

The Wong laboratory, situated in the Center for Nanoscience, utilizes a combination of quantum mechanics, statistical mechanics, computer simulation, molecular modeling, and informatics techniques to study biological macromolecules and their interactions with other molecules. Current projects include:

1. Computer-aided design of therapeutic drugs targeting protein kinases and phosphatases.
2. Elucidating the enzymatic mechanisms of protein kinases and phosphatases.
3. Understanding the molecular mechanisms of MALDI processes.
4. Development of computational tools that can help address the above problems.

Selected Publications

"Molecular simulation of drug-binding kinetics", C. F. Wong, *Molecular Simulation*, **2014,** *40*, 889 C.

"Drug design for Protein Kinases and Phosphatases: Flexible-Receptor Docking, Binding Affinity and Specificity, and Drug-Binding Kinetics," F. Wong and S. Bairy, *Curr. Pharm. Design* **2013**, *19,* 4739.

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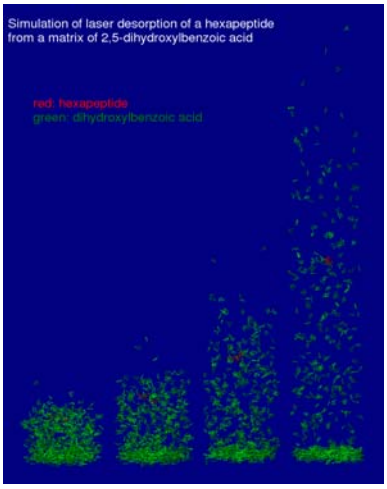
Z"Docking flexible peptide to flexible protein by molecular dynamics using two implicit-solvent models: An evaluation in protein kinase and phosphatase systems," . Huang and C. F. Wong, *J.Phys. Chem. B* **2009**, *113*, 14343.

"Beyond Thermodynamics: Drug Binding Kinetics Could Influence Epidermal Growth Factor Signaling," M. Goyal, M. Rizzo, F. Schumacher and C. F. Wong, *J. Med. Chem.* **2009**, *52,* 5582.

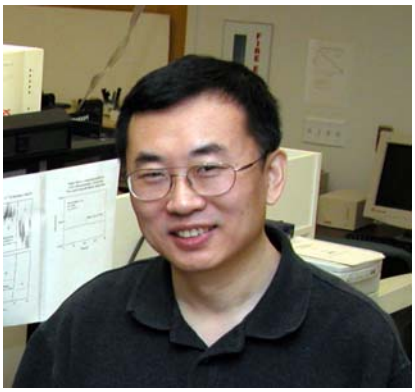
"A Computational Study of the Phosphorylation Mechanism of the Insulin Receptor Tyrosine Kinase" B. Zhou and C. F. Wong, *J. Phys. Chem. A,* **2009**, *113*, 5144.



$$\Delta G_{bind} = \int \rho_{ligand}^{complex}(\vec{r})\phi_{protein}^{complex} d^3\vec{r} + \int \rho_{ligand}^{complex}(\vec{r})\phi_{ligand}^{complex} d^3\vec{r} - \int \rho_{ligand}^{solvent}(\vec{r})\phi_{ligand}^{solvent} d^3\vec{r}$$
$$+ \left\langle \Psi_{ligand}^{complex} \middle| H^g \middle| \Psi_{ligand}^{complex} \right\rangle - \left\langle \Psi_{ligand}^{solvent} \middle| H^g \middle| \Psi_{ligand}^{solvent} \right\rangle + \Delta G_{protein}^{desolv} + \sigma \Delta A$$

A fixed - conformation QM/MM/PBSA model for rank - ordering protein - ligand binding affinity

THE FACULTY



ZHI XU

Professor Xu received his B.S. degree in Chemistry, an M.S. degree in Electrical Engineering from Tsinghua University, Beijing, China, and his Ph.D. in Chemistry from the University of Pittsburgh. He held a postdoctoral position at the University of Illinois, Urbana, prior to joining the UM-St. Louis faculty in 1994.

Research Interests

Development of new optical analytical instrumentation, investigation of new photonic materials, and study of solid-liquid interfacial chemistry are three major research areas in our group.

Development of New Optical analytical Instrumentation: Our basic research in optical spectroscopy has led to the invention of a new spectroscopic technology. The new technology has the potential to increase the sensitivity of most commonly used optical analytical instruments 100 to 1000 fold over that of state-of-the-art commercial instruments. Our current research is focused on the implementation of the new technology to a wide range of instrumentations including UV-Vis Spectrophotometry, Infrared (IR) Spectrophotometry, High Performance Liquid Chromatography (HPLC), Atomic Absorption (AA), Inductively Coupled Plasma Atomic Emission (ICP-AE), and Circular Dichroism (CD). This research could dramatically improve both qualitative and quantitative analytical capability in a broad range of chemical, biological, medical and other applications. Analyses from life science research to clinical diagnoses and from environmental analyses to forensic investigations will be favorably impacted. In healthcare, for example, the amount of blood or body fluid need for clinic analyses could be reduced to less than 1% of what is need today, and disease could be diagnosed much earlier and with better accuracy. In drug discovery, the time needed for identifying an efficient synthetic route could be significantly reduced. This could lead to the development of better and more economic medicine for decease treatment and prevention. In environmental protection, most chemical analyses can be carried out with unprecedented speed and accuracy, which could help to create a clearer living environment.

New Photonoc Materials: The research is aimed at developing new photonic materials that have applications in optical data storage, nonlinear optical conversion, and two-photon absorption. In particular, we are interested in the information storage by individual molecules and the structure-function relationship that governs the two-photon absorption (TPA) behavior of organic molecules. Our earlier study has demonstrated the feasibility of information storage by individual molecules in liquid phase based on intermolecular charge transfer. Our current investigation in this direction is to translate our successful model system from liquid phase into solid phase. In the research front of two-photon absorption, we have developed new transition theory based on quantum mechanics. A series of new molecular structures have been developed according to the prediction of the new theory. These new molecules have increased the TPA cross-section over 2000 times in comparison to traditional organic molecules with long electron conjugations. The extremely large TPA cross-sections of these new molecules make it possible to develop new optical media/devices for three-dimension optical storage, up-conversion of light to create blue and UV lasers, and the protection of human eyes and optical sensors from the permanent damage by lasers.

Chemistry at Solid-Liquid Interfaces: The goal is to achieve molecular level understanding of phenomena such as adsorption, molecular interaction, and chemical reactions occurring in solid-liquid interfacial systems of fundamental and industrial importance. Some of the industrial application areas for such studies are separation science, surfactants, electrochemistry, catalysis, and corrosion inhibition. By using a novel technique - nonlinear optical molecular probing (**NOMP**) method, we are able to extract the information of chemical interactions and chemical reactions in an interfacial region within 20 - 50 Å from the solid surface. This has created new research opportunities to understand the actual separation processes in HPLC and electrophoresis, and to develop new stationary phases that are highly selective for the separation of large organic and biomolecules.

Selected Publications

″New spectroscopic method for the determination of optical rotatory dispersion,″ Z. Han, Z. Xu and L. Chen, *Chinese Optics Lett*., **2014,** *12*, 081202.

″A three-spectrum method for accurate calibration of bi-plate zero-order retarder,″ Z. Han, Z. Xu and L. Chen, *Chinese Optics Lett*., **2014,** *12*, 031202.

″External/internal optical adapter with reverse biased photodiodes for FTIR spectrophotometry,″ Z. Xu, *U.S. 8,830,474*, U.S. Patent issued to the Curators of the University of Missouri, **2014**.

“External/Internal Optical Adapter for FTIR Spectrophotometer,” Z. Xu, *U.S. 8,766,191*, U.S. Patent issued to the Curators of the University of Missouri, **2014**.

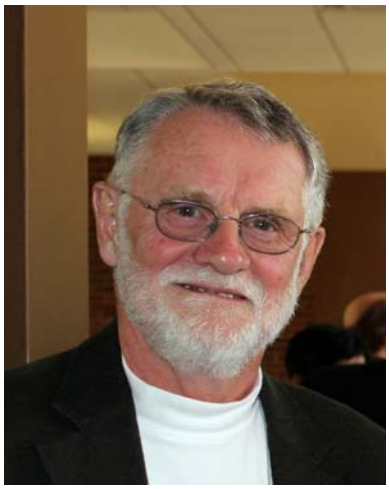
“Optical Spectroscopy Device for Non-Invasive Blood Glucose Detection and Associated Method of Use,” Z. Xu, *U.S. 8,552,359*, U.S. Patent issued to The Curators of the University of Missouri, **2013**

″Optical Device Components,” Zhi Xu, Hong Kong Patent No. *HK1151351*, Hong Kong Patent issued to The Curators of the University of Missouri, **2013**

“Optical Device Components,” Zh. Xu, Australian Letters Patent No. *2008307505*, Australia Patent issued to The Curators of the University of Missouri, **2013**.

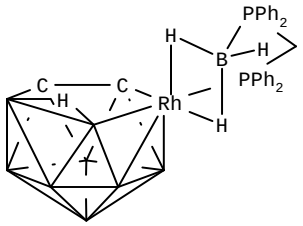
″Liquid Chromatography Detector and Controller Therefor," Z. Xu, R. Bose and J. M. Anderson, *U.S. 8,397,553,* U.S. Patent issued to The Curators of the University of Missouri, **2013**.

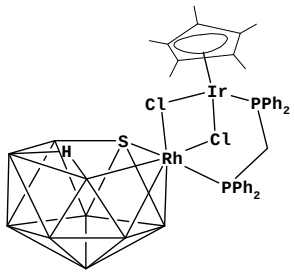
EMERITUS AND RESEARCH FACULTY

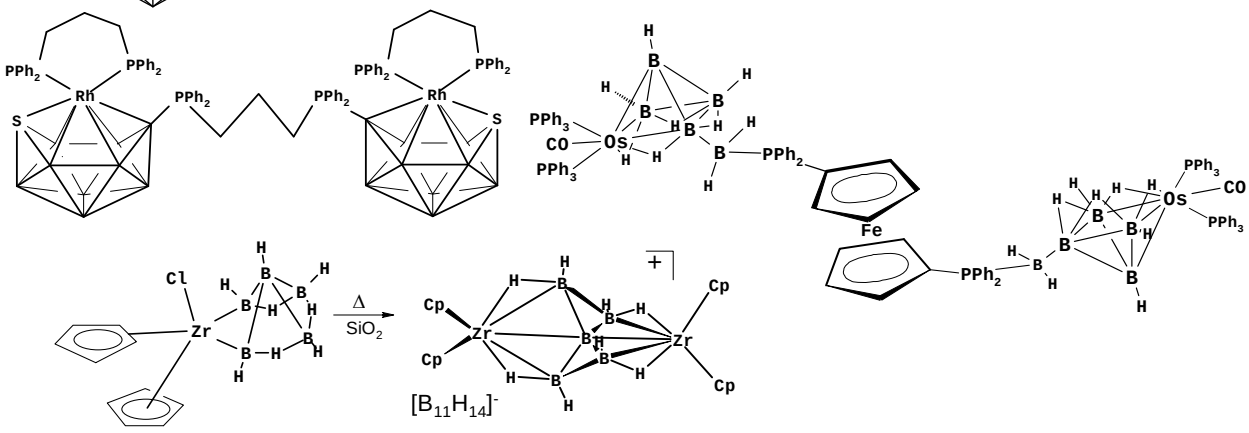


LAWRENCE BARTON

Professor Barton, B.Sc. (Hons) Liverpool University 1961, Ph.D. 1964, did a post-doc at Cornell University and joined the faculty at UM-St. Louis in 1966. He served as Department Chair from 1980 until 1998, Interim Director of the Center for Nanoscience from 1998-06, assumed Emeritus status in March 2007 and is no longer taking students.







Research Interests

Dr Barton and his students had several areas of research interest, as briefly described below. The work involves study of borane and metallaborane clusters.

A main group-element project led to the preparation of a series of metalloboranes based on B_6H_{10} and B_5H_9 using the main group metals Sn, Si, Zn, Cd and Hg. Another area involved the preparation bimetallaboranes based on small metallaborane templates. To this end they have thus far concentrated on the templates B_5H_9, B_6H_{10}, $(PPh_3)_2(CO)OsB_5H_9$ and $(PPh_3)_2(CO)IrB_5H_8$ and prepared a series of species containing the metal-boron combinations $IrFeB_2$, $IrOsB_3$, $IrOsB_4$, $OsRuB_4$, $IrOsB_5$, $IrPtB_5$, $IrFeB_5$, Ir_2B_5, Zr_2B_5, Hf_2B_5, Ti_2B_6 and Pt_2B_7.

Additional work on reactions of larger cage metallaboranes and boranes with small main group-containing molecules was a productive activity. For example formation of metallaheteroboranes from reactions of the unsaturated clusters [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] and [9,9-(PPh_3)-*nido*-9,7,8-$RhC_2B_8H_{11}$] and reactions of phosphines with these species. Related studies involving reactions of bases with small cage metallaboranes has revealed some novel reaction mechanisms and has led to the formation of linked cluster systems and hybrid bimetallaboranes. Some of this work is illustrated herein.

Selected Publications

O. Volkov, K. Radacki, R. Ll. Thomas, N. P. Rath and L. Barton "Another look at the *nido*-undecaborate system," *J. Organomet. Chem.* **2005**, *690/11*, 2736

P. McQuade, R. E. K. Winter, N. P. Rath and L. Barton. "Degradation and Modification of Metallaboranes Part 4: Synthesis and Characterization of a series of hybrid bimetallaborane clusters of the type [2,2,2-$(PPh_3)_2$(CO)-*nido*-2-OsB_4H_7-3-$(BH_2PPh_2)C_xH_yPPh_2RuCl_2$(*p*-cym)]," *Inorg. Chim. Acta.* **2005,** *358/5*, 1545.

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EMERITUS AND RESEARCH FACULTY

JOYCE Y. COREY

Professor Corey received her Ph.D. degree at the University of Wisconsin following a B.S. and M.S. at the University of North Dakota. She has held visiting faculty positions at the University of Wisconsin, and the Universite des Sciences et Techniques du Languedoc. She has been at UM-St. Louis since 1968. Dr. Corey assumed emeritus status in 2008 and is no longer taking students.

Research Interests

Unlike CH bonds in hydrocarbon chemistry, the SiH bond in hydrosilanes may be viewed as a functional group. However, transformations of SiH to other Si-element bonds usually require a catalyst. Typical coreactants are HEl species and if El represents another silicon unit, then homodehydrocoupling occurs to give silicon oligomers and polymers with H_2 as the only by-product. Titanium triad complexes are particularly effective for this transformation. Silicon analogs of substituted ethanes, propanes and butanes can be formed through the reaction of secondary silanes such as $PhMeSiH_2$ in the presence of the combination, Cp_2MCl_2 (M = Ti, Zr, Hf) and n-BuLi. With the availability of this simple dehydrogenative coupling reaction, the chemistry of short chains can be studied and developed. Examples include the removal of phenyl groups in $H(PhMeSi)_xH$ withl to x equivalents of triflic acid to give the corresponding silyl triflates, $H[(Ph)_{x-y}(OTf)_ySi_xMe_x]H$. Replacement of the triflate group by reaction with a number of nucleophiles may then take place to provide new oligomers. Oligomers with fluorosilane end groups have also been prepared through reaction with CuF_2 or $CuCl_2$/KF/KI. The disilanes, $F(PhMeSi)_2F$, which are formed as the statistical ratio of *meso* and *rac* forms (1:1) exhibit a novel spontaneous isomerization of the *rac*-isomer to the *meso*-isomer. The *meso*-form can be returned to the statistical mixture by adding catalytic quantities of fluoride ion. The spontaneous isomerization is a case of crystallization induced "asymmetric transformation" (AT) and is under current investigation.

Condensation of primary silanes with metallocene halides plus RLi provides polysilanes whose molecular weights vary with the structure of the metallocene. The mechanism for this condensation process is not entirely clear but probably involves sigma-bond metathesis steps and possibly radical processes. Strategies that will lead to an increase in molecular weight are under study and include modification of the basic metallocene structure as well as the development of new catalyst systems. Although earlier reports suggested that syndiotactic polysilanes were produced from metallocene catalysts, our recent studies have demonstrated that this is not the case and that the polymers are *atactic*. New challenges are to find catalysts that improve the molecular weights and control the microstructure of the polymer.

Metals from across the entire transition metal series will initiate a variety of reactions of SiH bonds although not by the same mechanism for electron poor metals vs. electron rich metals. In general the earlier transition metals promote metathesis reactions whereas oxidative addition of SiH to the metal probably initiates the reactions with electron rich metals. We are currently investigating the reaction pathways of secondary silanes that are also heterocyclic silicon compounds with electron rich metals with the objectives of building $[(Si\text{-}TM)]_x$ units (TM = transition metals; x >2) and determining the primary reaction events of these silanes. Studies also include the reactions of the corresponding germanes and stannanes as the ease of oxidative addition increases through the sequence Si < Ge < Sn.

Selected Publications

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THE FACULTY

HAROLD H. HARRIS

Professor Harris received his B.S. degree from Harvey Mudd College, and his Ph.D. from Michigan State University. He joined the UM-St. Louis Chemistry faculty in 1970 following a postdoctoral fellowship at the University of California -Irvine. He has spent leaves at University of Chicago, the Solar Energy Research Institute (Golden, Colorado), and Wright -Patterson Air Force Base (Dayton, Ohio). In fall 2012 he was appointed Founders' Professor of Chemistry and Biochemistry.

Research Interests

Professor Harris has published in diverse areas of physical chemistry and chemical education, including experimental studies of collision-induced dissociation of ions, chemical kinetics at suprahigh pressure, experimental and theoretical dynamics of molecular collisions, spectroscopy in supersonic jets, and the dynamics of cellular flames.

He originated and managed for nearly twenty years "The Chemical Education Resource Shelf", a unique bibliographic resource for textbooks and software, for the *Journal of Chemical Education*. This archive provided information about over 1600 chemistry textbooks and their publishers, as well as sources for molecular models, computer interfacing of experiments, and chemistry software. Associated with the Resource Shelf was "Hal's Picks of the Month", his recommendation of books and articles of interest to teachers of science. Over the years, well over two hundred items have appeared in this feature, which is archived and continues with his "Picks" in JCE ChemEd Xchange, http://www.chemedx.org. Professor Harris also edited over one hundred articles for his "Cost-Effective Teacher" feature of the *Journal of Chemical Education*. This feature emphasized the construction of economical alternatives to commercial products and other inventive ways to teach chemistry through laboratories and demonstrations. The feature was discontinued when *JCE* became co-published with the ACS and the Division of Chemical Education, but Professor Harris continues to review and edit articles with similar characteristics that appear intermittently in the *Journal*.

For nearly twenty years, Professor Harris taught and advised all of UMSL's students seeking certification to teach either chemistry or physics in Missouri high schools, and has worked closely with the science teachers in many of the region's school districts. His work has been honored with the St. Louis Area Physics Teachers' "Gene Fuchs Memorial Award" and the St. Louis Academy of Sciences' "Science Educator of the Year 2010".

With his appointment as a Founders Professor, Harris will be teaching a limited selection of courses in physical and introductory chemistry.

Selected Publications

(Book Review) "Essentials of Chemical Education" by Hans-Dieter Barke, Günther Harsch, and Siegbert Schmid, translated by Hannah Gerdau, *J. Chem. Educ.*, **2012**, *89* (11) (in press).

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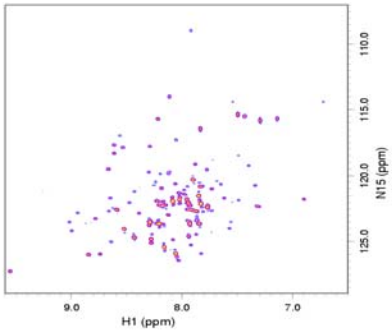
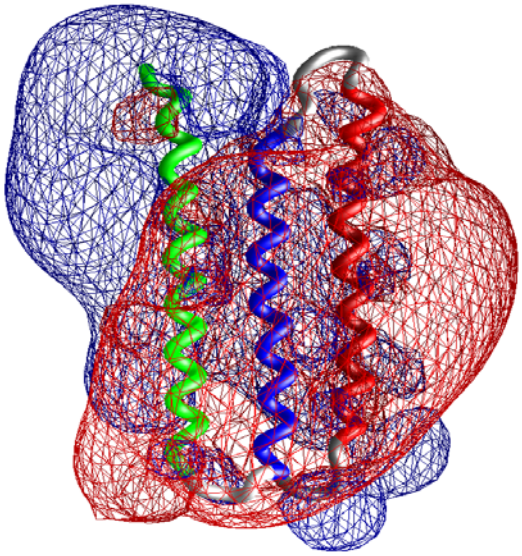
EMERITUS AND RESEARCH FACULTY

RENSHENG LUO

Professor. Luo received his Ph.D. degree from the Chinese Academy of Sciences. He was a Postdoctoral Fellow at the University of Illinois at Champaign-Urbana and St. Jude Children's Research Hospital prior to joining the UM-St. Louis faculty as Research Assistant Professor in the Spring of 2005 and promoted to Research Associate Professor in 2013..





Research Interests

Dr. Luo's research interests involve the use of NMR techniques for generating three-dimensional structural and dynamical information on biological macromolecules, organic compounds, and organometallic complexes. NMR is being increasingly applied in chemistry, biochemistry, biology, medicine, physics and materials science. Currently, Dr. Luo is the Director of the Nuclear Magnetic Resonance Facility. Current research interests also include collaboration with scientists in solving problems on all these and related subjects using NMR spectroscopy, as well as development of techniques and implementation of new NMR experiments for users at different areas.

Selected Publications

R. Luo, K. Tran, R. A. Levine, S. M. Nickols, D. M. Monroe, A. U. O. Sabaa-Srur and R. E. Smith, "Distinguishing Components in Brazilian Acai (Euterpe oleraceae Mart.) and in Products Obtained in the USA by Using NMR," *The Natural Products Journal,* **2012**, *2*, 86

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Y. Wang, I. Filippov, C. Richter, R. Luo, R. W. Kriwacki, "Solution NMR studies of an intrinsically unstructured Protein within a dilute. 75 kDa eukaryotic protein assembly; probing the practical limits for efficiently assigning polypeptide backbone resonances," *Chembiochem.,* **2005,** *6*, 2242.

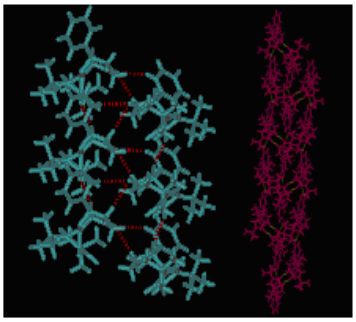
EMERITUS AND RESEARCH FACULTY

NIGAM P. RATH

Professor. Rath received B.Sc. (Hons.) and M.Sc. degrees from Berhampur University in India, and a Ph.D. from Oklahoma State University. He was a Postdoctoral Fellow and Assistant Faculty Fellow at the University of Notre Dame prior to joining the UM-St. Louis faculty as Research Assistant Professor in 1989. He was promoted to Research Associate Professor in 1996 and a Research Professor in 2004.

Research Interests

Dr. Rath is a X-ray crystallographer and he directs the X-ray diffraction facility. The use of single crystal X-ray diffraction studies can result in the most unambiguous structural information and threes dimensional structure of both small molecules and macromolecules. Dr. Rath's research interests involve the use of X-ray diffraction techniques for the determination of solid state-molecular structure of novel organic and organometallic compounds. His interests also include development of techniques and instrumentation for accurate data collection for small molecules.



Concomitant Polymorphism in a Spirobicyclic Dione: the 1-D rod-like structure of form A and supramolecular polycyclohexane network in form B

Selected Publications

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"A thiocynato-bridged copper(i) cubane complex and its application in palladium-catalyzed Sonogashira coupling of aryl halides,"M. Trivedi, G. Singh, A. Kumar Abhinav and N. P. Rath, *Dalton Trans.* **2013**, *42*, 12849.

Oxidative reactivity of $(N_2S_2)PdRX$ complexes (R = Me, Cl; X = Me, Cl, Br): involvement of palladium(II) and palladium(IV) intermediates," J. Luo, N. P. Rath, and L. M. Mirica, *Organometallics* **2013**, *32*, 3343

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"Role of Substitution at Terminal Nitrogen of 2-Oxo-1,2-dihydroquinoline-3-Carbaldehyde Thiosemicarbazones and the Coordination Behavior and Structure and Biological Properties of Their Palladium(II) Complexes," E. Ramachandran, D. R. Senthil, N. P. Rath and K. Natarajan, *Inorg. Chem*. **2013**, *52*, 1504.

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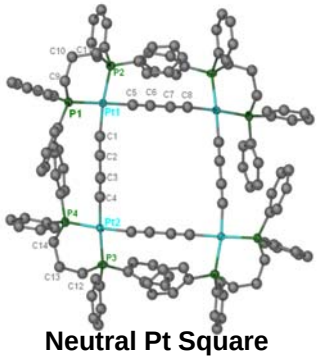
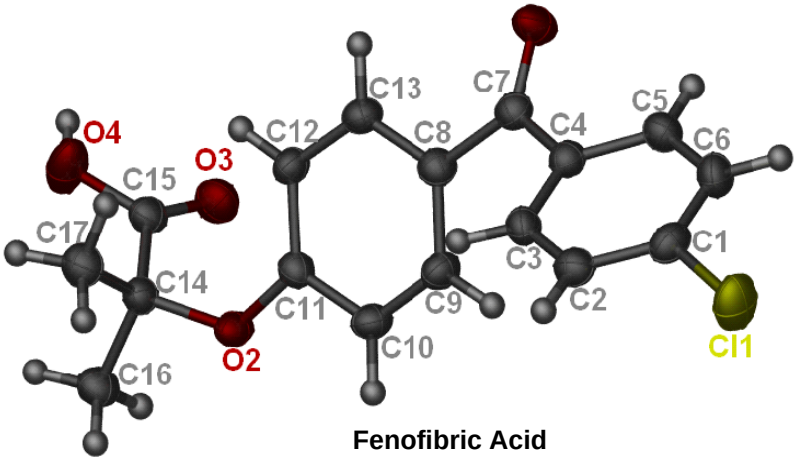


Neutral Pt Square



Fenofibric Acid

EMERITUS AND RESEARCH FACULTY

RUDOLPH ERNEST K. WINTER

Professor Winter received his A.B. degree from Columbia University and M.S. and Ph.D. degrees from The Johns Hopkins University. He held postdoctoral positions at Karlsruhe Technische Hochschule and Harvard University and was a member of the Polytechnic Institute of Brooklyn faculty before joining U. M. St. Louis in 1969. He has been a Visiting Research Professor at Cornell University, Visiting Scholar at the ETH Zürich and was also a Visiting Associate Professor (Biology) at Washington University (St. Louis) and now enjoys emeritus status at UM-St. Louis.

Research Interests

Dr. Winter's research interests are in the Organic and Bioorganic Chemistry of naturally occurring substances. Emphasis is on the isolation, structure determination and chemical interconversion of natural products of biological interest. He also has major interests in the application of mass spectrometry for characterization and structure determination and collaborates with faculty colleagues on those problems related to their research which are amenable to mass spectral measurements.

Selected Publications

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INSTRUMENTATION AND FACILITIES

High Field NMR Facility

The UM-St Louis High Resolution NMR Facility is located in the Department of Chemistry and Biochemistry on the second floor of Benton Hall (B210) and houses three NMR spectrometers: a Bruker ARX-500, a Bruker Avance 300 and a Varian Unity Plus 300. While these instruments are primarily for the use of the faculty, postdoctoral, and students in the Department of Chemistry and Biochemistry, other users (corporate other universities, and organizations) are welcome. The facility staff will provide NMR services as needed. For more information please contact to Dr. Rensheng Luo at (314) 516-5330.

Agilent DD2 600 MHz NMR

With support from NSF MRI-R2 grant (0959360), an Agilent DD2 600 MHz NMR spectrometer was purchased and installed in Benton Hall B207 in early 2012. This spectrometer is operated by a Linux PC with VnmrJ 3.2 software.

Two probes are available: a 5-mm three channel inverse gradient broadband and a 5-mm gradient broadband, each of which is capable of variable temperature experiments (-80 to +130°C). This spectrometer is a research-oriented instrument and primarily used to investigate the structures and dynamics of macromolecules and complex molecular systems as well as implement new NMR experiments for users at different areas. The instrument specifications include:

- The Agilent preminumCOMPACT magnet (54mm bore)
- Dell PC with Red Hat Linux
- ^{1}H-^{19}F/^{15}N-^{31}P, ^{15}N/^{13}C 5mm PFG triple OneNMR probe
- ^{1}H-^{19}F/^{15}N-^{31}P 5mm PFG autoX indirect detection probe
- ProTune accessory
- Variable temperature capability (-80°C to +130°C)

Bruker ARX 500 MHz NMR

The Bruker ARX-500 spectrometer is operated by a Silicon Graphics INDY R5000 workstation. It has two probes: a 5 mm broadband and a 5 mm inverse gradient broadband, each of which is capable of variable temperature experiments (-150 to + 200 ºC for liquids). The Bruker ARX-500 spectrometer is a research-oriented instrument. It is equipped with dual radiofrequency channels and used for molecules requiring better peak resolution, (complex) structure elucidation and variable temperature analyses on a wide range of organic, organometallic, inorganic, and biochemical systems, as well as natural products and host-guest systems. Experiments that are typically performed include 2D COSY, NOESY, ROESY, TOCSY, HSQC, HMQC, HMBC and selective excitation.

Bruker Avance 300MHz NMR

The Avance 300 spectrometer is currently equipped with a four-nucleus probe (^{1}H, ^{13}C, ^{19}F, and ^{31}P) with z-gradients. An additional 5 mm switchable broadband probe tunable for ^{1}H-^{19}F/^{15}N -^{31}P is also available. This instrument is used primarily for routine walk-on use for monitoring reactions and checking the purity of samples, but it is also used for longer run experiments such as 1D ^{13}C and routine 2D experiments: HMQC, HSQC, and HMBC in the evening and weekends.

Varian Unity Plus 300 MHz NMR

The Varian Unity Plus 300 is equipped with a wide bore Oxford superconducting magnet to accommodate probes for running solid state NMR experiments. It has two radiofrequency channels and is capable of broadband detection. This instrument is used primarily for detection of heteronuclei such as ^{11}B, ^{13}C, ^{31}P, ^{119}Sn, and ^{195}Pt, experiments that require long detection time. It has four probes: two 5 mm switchable broadband probes with boron-free glass insert, a 5 mm switchable inverse broadband probe, and a 7 mm magic angle probe for CP-MAS experiments.

INSTRUMENTATION AND FACILITIES

X-ray Diffraction Laboratory

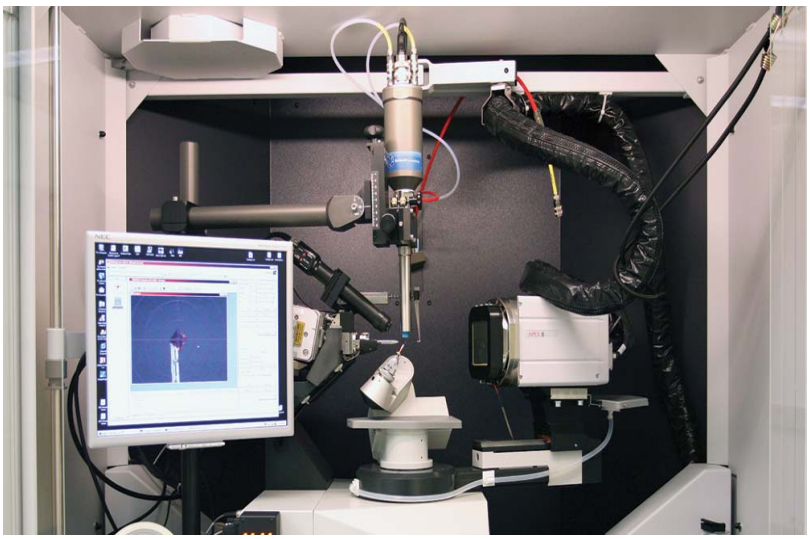
X-ray crystal structure determination is an important technique for most inorganic and organic chemists. The X-ray Diffraction Laboratory at UM-St. Louis supports the research programs of several research groups in the department. Also, we collaborate with a number of groups in the metropolitan St. Louis area and across the USA and in other countries in their solid-state structure determination research. The Laboratory is equipped with state-of-the-art instrumentation and computational facilities for solid state three dimensional crystal and molecular structure determinations. The facility is located in custom-designed laboratory space in the Center for Nanoscience, opened in November 1996, and currently houses single crystal and powder diffractometers. For more information please contact Dr. Nigam Rath at (314) 516-5333 or by email: ***rathn@umsl.edu***

Bruker SMART Apex II Single Crystal Diffractometer

Rigaku Ultima IV Powder Diffractometer

Single Crystal X-ray Diffraction Instrumentation

The Bruker APEX II Kappa diffractometer is equipped with an Oxford Cryostream low temperature device. Fast data collection can be carried out using this Kappa geometry diffractometer at 10-330K. Currently, most of the structure determinations are carried out using this system.



Bruker Kappa Apex II Single Crystal Diffractometer

The Bruker SMART APEX II Diffractometer: This CCD (Charge Coupled Device) area detector system was upgraded recently to the state of the art Apex II detector equipped with a 4K CCD chip and Oxford Cryostream low temperature device for use in small molecule crystallography. Currently, this instrument is primarily used for teaching and training of students and Post-doctoral researchers as well as for data collection by users.

Powder Diffraction Instrumentation

A Rigaku Ultima IV Powder Diffractometer is used primarily for bulk material characterization, including air- and moisture-sensitive samples. This provides a valuable analytical tool for the identification of single and multi-component solids by comparison with known published powder patterns. It is also used to determine the homogeneity of crystalline samples from which single crystals have been used for crystal structure determination. This instrument is also capable of data collection for small angle x-ray scattering (SAXS) experiments.

Computer Facilities and Other Instrumentation

The X-ray Laboratory Computing Facility has several workstations running crystallographic software. All computers in the lab are integrated with the university computer network. The Cambridge Structural Database is accessible to all university computer system users and is hosted through a Sun server and installed on all PCs.

The preparation laboratory is equipped with stereo microscopes for screening and mounting crystals; a fume hood, refrigerator and freezer for crystallization and sample storage, together with other necessary facilities for crystallization and crystal handling.

INSTRUMENTATION AND FACILITIES

Mass Spectrometry Facility

The mass spectrometry facility is housed in a 1000 sq ft laboratory located in the UMSL Research Building (R003). In addition to the mass spectrometers described below, there are areas for data processing, instrument maintenance, parts storage and sample preparation. The instrumentation is used primarily for support of research and teaching in the Department of Chemistry and Biochemistry, however in years past the MS facility has been a resource for the local business or members of the academic community which lack this instrumentation.. For more information contact Mr. Joseph Kramer: Tel: (314) 516-5120; e-mail: kramerj@umsl.edu

MALDI Micro MX by Micromass/ Waters. This has a mass range >60,000 and resolution 50 µmass

Hewlett Packard GC/MS System Model 5988A

For routine mass spectral analysis following capillary column gas chromatographic (GC) separation with:

- Electron impact (EI) and chemical ionization (CI) capabilities
- Positive and negative ion detection
- An extended-mass quadrupole
- A solids probe

JEOL MStation [JMS-700] Mass Spectrometer

A high-performance magnetic sector mass spectrometer for both high and low resolution mass spectral analysis equipped for:

- Fast Atom Bombardment (FAB) ionization, Electrospray Ionization (ESI),
- Atmospheric Ion Chemical Ionization (APCI) and EI and CI methods
- Positive and negative ion detection
- Linked scan measurements

Shimadzu 2010A LCMS

- LCMS System with 4 solvent pumps, column oven, diode array detector and single quad mass-spec.
- Positive and Negative Ion Detection

Bruker Maxis Plus (maXis HD) quadrupole time-of-flight mass spectrometer and UHPLC. It comes with Electrospray ionization, atmospheric pressure photoionization and a solids probe for ionizing solids directly. It can do m/delta m = 60,000 and collect up to 20 spectra per sec. (Available in Dr. Bythell's Lab)

INSTRUMENTATION AND FACILITIES

Molecular Modeling and Simulation

Computational scientists at UMSL perform molecular modeling and simulation to understand chemical and biological systems, and to design new materials such as molecular magnets, chemical and biological sensors, and therapeutic drugs. They also use bioinformatics tools in drug discovery, in associating genetic variations with diseases, and in disease diagnostics. The computer laboratories are located in the Center for Nanoscience, next to Benton Hall in which the office of the Department of Chemistry and Biochemistry is located. The laboratories are equipped with Dell workstations for fast computations and molecular visualization. Computational intensive calculations are done in the computer clusters in The University of Missouri Bioinformatics Consortium. For more information please contact Dr. Chung Wong at (314) 516-5318 or wongch@umsl.edu.

Computer Cluster Clark

An SGI Altix 3700 Bx2 containing 64 1.5GHz Itanium2 processors, 128 GB RAM, and 4 TB SGI InfiniteStorage. It is operated by the University of Missouri Bioinformatics Consortium, who provided this picture.

Software developed or enhanced by UMSL researchers

SRmapper: A program for assembling whole genome sequences from next-generation sequencing experiments. It aligns short reads from such experiments to reference genomes. It takes short reads data in fastq format and outputs results in SAM format for analysis by programs such as SAMtools.

UHBD: New features introduced by UMSL researchers and their collaborators include the interface with two quantum mechanical programs — PWSCF and SIESTA — to perform quantum mechanical calculations in solutions in which solvation effects are described by the Poisson-Boltzmann model, constrained Brownian dynamics simulation of peptides, and charge optimization at the interface between a protein and a ligand.

BDI: A program for performing Brownian dynamics simulation of ions surrounding proteins and DNAs.

MMTSB toolkit: UMSL researchers have modified this toolkit to perform flexible ligand-flexible receptor docking using a simulated annealing cycling strategy.

Other software packages

UMSL computational scientists also use other programs such as:

- Quantum mechanics: Gaussian 03, SIESTA, GAMESS, PWSCF, NWChem.
- Molecular dynamics simulation: CHARMM, NAMD.
- Electrostatics calculations: APBS.
- Genomics: BWA, Crossbow, Maq, SAMtools.
- Protein modeling: MODELLER

Computer Cluster Lewis

It contains more than 190 nodes with over 1200 Intel Xeon multi-core processors and a collective memory of 5100 GB. The largest computer nodes contain 24 processor cores and 512 GB of memory. Pictures provided by the University of Missouri Bioinformatics Consortium.

INSTRUMENTATION AND FACILITIES

Cell Culture Facility

Cell culture is an important tool for understanding basic biological processes and for analysis of compounds that may have therapeutic potential in a variety of human diseases. The department established a secure cell culture laboratory in 2007 in the Research building. The facility is utilized by multiple users who maintain and employ numerous mammalian and insect cell lines for research purposes. The facility currently houses three laminar flow hoods, a refrigerator/freezer, a manual defrost freezer, three water-jacketed carbon dioxide incubators, a liquid nitrogen cryosystem, a swinging bucket centrifuge, a multi-mode absorbance/fluorescence plate reader with computer, and two inverted microscopes (one with an attached digital camera). The facility is completely outfitted with all necessary items to support cell culture. Regular users of the facility attend semi-annual meetings regarding maintenance of the facility. The multi-user format fosters collaboration, the sharing of research ideas and troubleshooting.

Current cell culture users

Nichols Lab (Chemistry and Biochemistry)
Alzheimer's disease, inflammation, monocyte and microglial cells, neurons

Bashkin Lab (Chemistry and Biochemistry)
Human papilloma virus, therapeutics, epithelial cells

Dupureur/Spilling Lab (Chemistry and Biochemistry)
Diabetes, inhibitors/therapeutics, expression of proteins in SF9 insect cells

Olivas Lab (Biology)
Parkinson's disease, neurons

Steiniger Lab (Biology)
Expression of proteins in SF9 insect cells

The Center for NanoScience

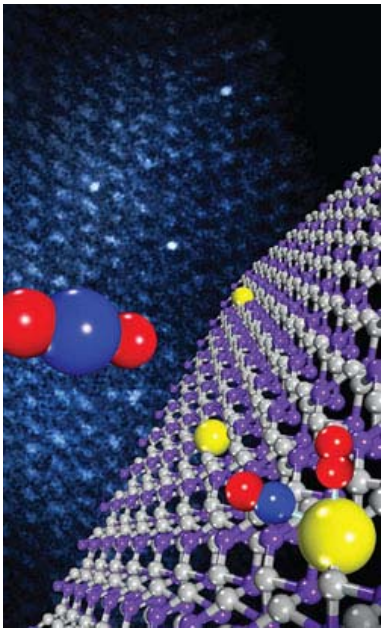
The Center for NanoScience (CNS) at the University of Missouri-St. Louis was established to both facilitate collaboration among university and industry scientists and engineers and provide interdisciplinary opportunities for faculty and students. Its mission is to enhance the research capacities of its faculty members and students and serve the region through research and technology transfer, cooperative and educational outreach programs and workforce development. For more information please contact Kendra Perry Ward at (314) 516-4626 or perryk@umsl.edu.

The CNS has approximately 16,000 square feet of assignable space, including 11,300 square feet for research laboratories and 2,700 square feet for research support space. In addition, there are 14 offices, and a conference room. The CNS also houses the Microscopy Image and Spectroscopy Technology (MIST) Lab and the X-ray Diffraction Facility.

Located in the William L. Clay building, the Center had its beginnings in a federal grant proposal initiated in 1988 by M. Thomas Jones, chemistry professor and deputy chancellor. The CNS facility took real shape with the help of Congressman William L. Clay and his support of a $10 million funding proposal that was awarded in July 1991 -- $7.5 million was used for building construction and $2.5 million was used for research instrumentation and building furnishings. The building, named in honor of Congressman Clay, was completed in early summer 1997.

Originally named the Center for Molecular Electronics, the facility was renamed as the Center for Nanoscience in early 2007 to better encompass the research being conducted by members. A new director, and associate director were hired in 2006 to help facilitate the goals of the Center. Dr. Gokel serves as Director and Dr. Eric Majzoub serves a Associate Director.

Members of the Center currently include the following Chemistry Department faculty members. L. Barton, J. K. Bashkin, A. M. Beatty, J. Braddock-Wilking, C. M. Dupureur, T. F. George, G. W. Gokel. S. M. Holmes, J. Liu, M. R. Nichols, J. J. O'Brien, N. P. Rath, C. D, Spilling, K. J. Stine, C. F Wong and Z. Xu.



Single platinum atoms (yellow balls and three bright spots in TEM image) on iron oxide (purple and gray) mediate conversion of CO to CO2.

This photograph shows the Jefferson National Expansion Memorial, also known as the Gateway Arch or simply the arch, which is located near the starting point of the Lewis and Clark Expedition on the Mississippi River

How to apply to our graduate program

For admission to our graduate program you must apply online on the Department website found at:
http://www.umsl.edu/chemistry/

Follow the link to Graduate Program and the instructions are provided.
For further information (or an information packet) please contact the department at:

Graduate Admissions Phone 1-314-516-5311
Department of Chemistry and Biochemistry
University of Missouri-St. Louis
St. Louis, MO 63121-4499, USA

Email: gradchem@umsl.edu

The website contains links to: The Ph.D. Program The M.S. Programs Graduate Brochure Biochemistry Division Handbook Graduate Study Handbook

Current graduate students should address any queries to: Director of Graduate Studies Dr. Stephen M. Holmes. Applicants should recognize that, normally, emeritus and research professors do not take doctoral students.