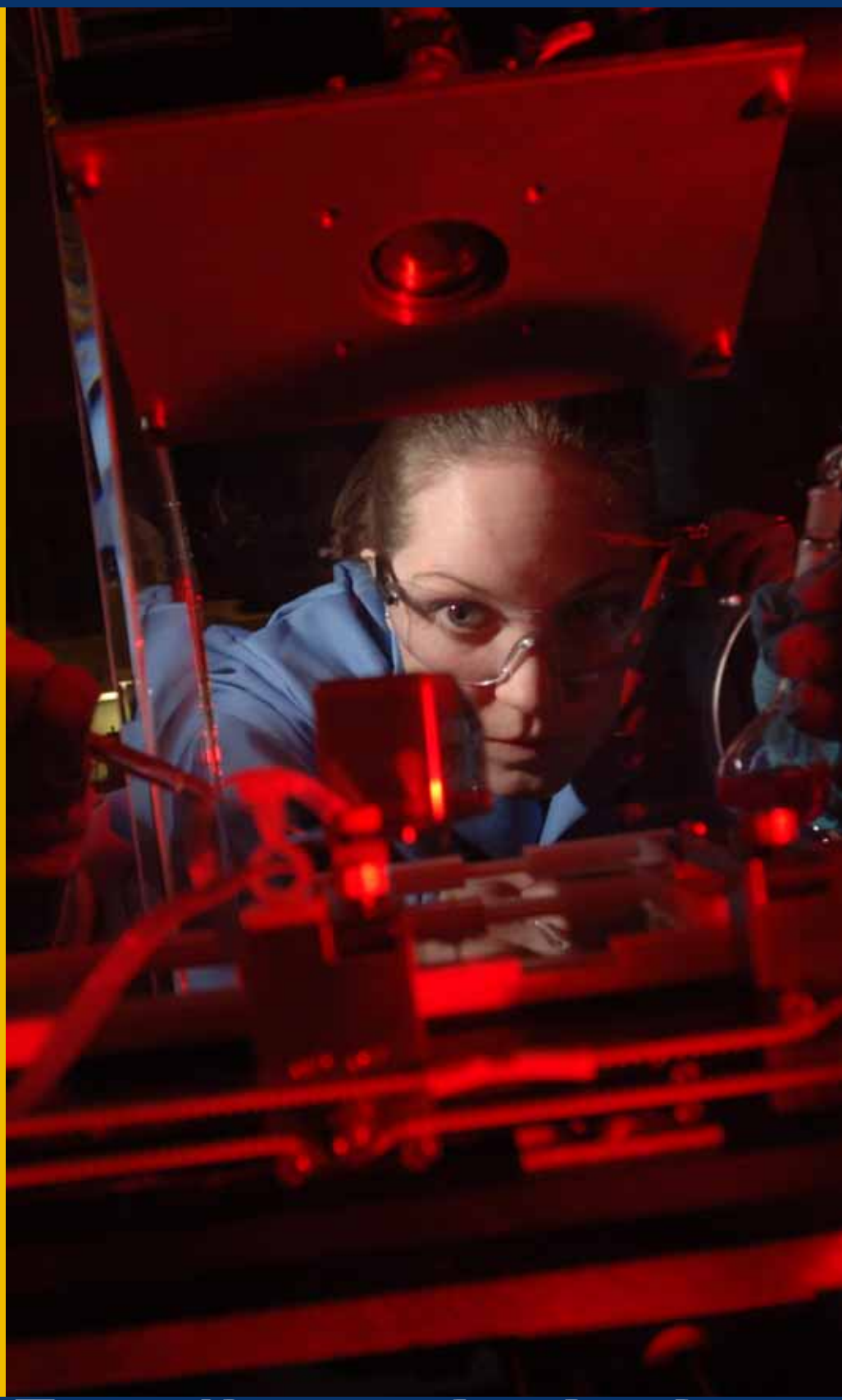
KENT STATE UNIVERSITY

Graduate Program in Chemistry and Biochemistry



Excellence in Action

Kent State Department of Chemistry and Biochemistry

Graduate Education:

The Gateway to a Successful Career

The Department of Chemistry and Biochemistry at Kent State University offers a modern graduate education leading to the Master of Science (M.S.) and Doctor of Philosophy (Ph.D.) degrees. Our outstanding faculty conducts world-class research in biochemistry as well as analytical, inorganic, organic, and physical chemistry. Many of the research topics that are being pursued by our exceptional graduate students are built around interdisciplinary themes in the areas of *biomedical research* (bioanalytical chemistry, bioinorganic chemistry, biophysical chemistry, biophotonics, nanomedicine, and molecular/cell biology) *materials science* (nanomaterials, liquid crystals, photonic materials, spectroscopy, separations, and surface science) and *environmental research* (atmospheric chemistry, environmental remediation). The research of our faculty is funded through grants from federal (e.g., NIH, NSF, NOAA, DOE) as well as state agencies.

Our campus is located in Kent, a small college town nestled at the Cuyahoga river in Northeastern Ohio. Kent offers a "hometown feel," yet still provides easy access to major cities like Akron and Cleveland. Our beautifully landscaped and safe campus is home to more than 25,000 students and offers state-of-the-art research facilities. The culturally rich campus life provides many opportunities to participate in social activities and Chemistry graduate students and faculty regularly socialize at events like picnics, bowling, ice-skating in the KSU ice arena and karaoke nights.

Graduate students in our program are currently offered highly competitive graduate stipends and a tuition waiver. The university provides low-cost access to quality health insurance (50% of the cost provided by the university).

Graduate students complete a program of core courses in their area of specialization and will also select elective courses in other areas of chemistry for their education. The extraordinary breadth of the program gives students considerable flexibility in curriculum design, ensuring a modern and dynamic graduate education. Students typically complete the doctoral program, including their thesis defense, within 5 years.

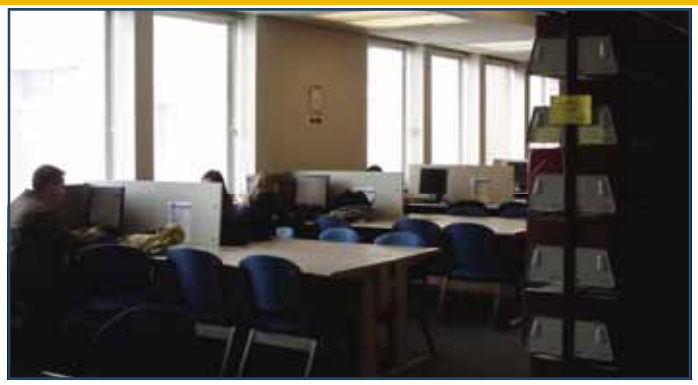
Many of our graduating students are offered post-doctoral research positions at prestigious institutions or assume positions in industry. Kent State Chemistry and Biochemistry Alumni work for Fortune 500 companies or pursue careers in smaller companies; they work for government and state agencies or are faculty members at colleges and universities.

Please take a moment and study the details of our graduate program and to familiarize yourself with the many research opportunities our department has to offer. Feel free to contact us for further information.

Research Facilities

Kent State University is home to world-class research facilities. The chemistry and biochemistry department has advanced NMR, x-ray, mass spectrometry, and proteomics core facilities. Research laboratories are located primarily in Williams Hall and the attached Science Research Laboratory. In addition, excellent materials' characterization facilities and one of the largest academic clean-room facilities in the nation are housed in the nearby Liquid Crystal Institute. A confocal microscopy core facility located in the Biology department is also available to chemistry students. Williams Hall houses two large lecture halls, classrooms, undergraduate and research laboratories, the Chemistry -Physics Library, chemical stockrooms, and glass and electronics shops. A machine shop, which is jointly operated with the physics department, is located in adjoining Smith Hall. Spectrometers include 500-MHz, 400-MHz (solids), and 300-MHz high-resolution NMR instruments; electrospray, MALDI-TOF, LC/ESI, protein chip SELDI mass spectrometers; various high-end FT-IR

spectrometers, including a focal plane array FT-IR microscope for spectroscopic imaging; photon-counting fluorometer; circular dichroism; ESR, FPLC, UV/visible spectrometers; AA/AE equipment; and an EDX-700 energy dispersive X-ray spectrometer. An X-ray facility includes a Siemens D5000 Powder diffractometer and a Bruker AXS CCD instrument for single-crystal structural elucidation. Equipment available in specialty areas includes a microwave spectrometer, an LCQ electrospray mass spectrometer with MS/MS capability, a phosphorimager, Microcal VP DSC and ITC calorimeters, surface plasmon resonance instrument, Bruker Vector 33 FTIR-NIR, Jobin Yvon Raman spectrometer with inverted microscope, laser tweezer instrumentation, particle sizer, Cary Eclipse



fluorescence spectrophotometer, MF^2 Jobin Yvon fluorescence lifetime spectrometer, fluorescence correlation spectrometer, ThermoFinnigan Polaris Q115W GC-MS, a BAS electrochemical analyzer, various preparative centrifuges, a molecular dynamic Typhoon 8600 imaging system, and PCR and DNA sequencing and cell culture facilities. Individual research groups in the Department of Chemistry and Biochemistry maintain a variety of computer systems, including PCs and workstations. High-performance computing is made possible with access to the Ohio Supercomputer Center, which maintains Cray T94, Cray T3E, IBM SP2, and SGI Origin 2000 supercomputers. The Department has advanced molecular modeling facilities, including Cerius, Felix, Hyperchem, InsightII/Discover, Macromodel, and Spartan packages for modeling surfaces and interfaces, polymers, proteins, and nucleic acids, as well as facilities for performing ab initio calculations of molecular properties and molecular dynamics. A 3-D immersive classroom equipped with a rear projection system that generates 6'x7' three-dimensional images when viewed with shutter glasses is available in Williams Hall and is frequently used for a variety of graduate classes. The chemistry/physics library in Williams Hall provides online access to virtually all chemical/biochemical journals as well as a broad variety of chemical databases, including the Chemical Abstracts SciFinder service.

Cost of Study, Living & Housing

Graduate students are generously supported through teaching and research assistantships and University fellowships. Students in good academic standing are guaranteed appointments for periods of at least 4 1/2 years (Ph.D. candidates) or 2 1/2 years (M.S. candidates). Stipends for 2009-10 range from $18,000 (M.S.) to $20,000 (Ph.D.) for a twelve-month appointment. A $1010 credit is made toward the University's health insurance plan. First-year bonuses and renewable merit fellowships providing an additional $2500 per year are available to outstanding doctoral applicants. In addition, first-year bonuses of $1250 are available for highly-talented students pursuing their Ph.D. in physical chemistry. Advanced Ph.D. students are typically funded through research assistantships ($20,000 or higher) provided by their respective advisors.

Graduate tuition and fees for the 2009-10 academic year are $6528, for which a tuition scholarship is provided.

Rooms in the graduate hall of residence are $2515 to $3360 per semester; married students' apartments may be rented for $669 to $699 per month (all utilities included). Information concerning off-campus housing may be obtained from the University housing office. Costs vary widely, but apartments typically rent for $500 to $600 per month.

Community & Student Group

The ethnically diverse and highly talented chemistry graduate student population currently numbers about 50. There are approximately 23,000 students enrolled at the main campus of Kent State University; 12,000 additional students attend the seven regional campuses.

Kent, a college town of about 28,000, is located 35 miles southeast of Cleveland and 12 miles east of Akron in a peaceful suburban setting. Kent offers the cultural advantages of a major metropolitan complex as well as the relaxed pace of semirural living. There are a number of music (e.g. Kent State's folk festival and free chamber music concerts in the summer), theater, and visual art groups at the University and in the community. Blossom Music Center, the summer home of the Cleveland Orchestra and the site of Kent State's cooperative programs in art, music, and theater, is only 15 miles from the main campus. This beautiful outdoor concert venue is also the site for many critically acclaimed rock concerts throughout the summer months. The newly expanded Akron and Cleveland art museums are within easy reach of the campus. Cleveland is also the home of the world-renowned Rock and Roll Hall of Fame and several professional sport teams. There are a wide variety of recreational facilities available on the campus and within the local area, including West Branch State Park and the Cuyahoga Valley National Park. Nearby Lake Erie and its beaches offer a broad range of water recreational activities. Winter activities include ice skating as well as downhill and cross-country skiing. Kent State's state-of-the-art recreation and wellness center is available for graduate

University History

Established in 1910, Kent State University is one of Ohio's largest and oldest state universities. Known as Kent State Normal School from its inception, it was originally intended to train public school teachers. It was constructed on land donated by William S. Kent, the son of Marvin Kent – the namesake for the city of Kent, Ohio. By 1915, the school was known as Kent State Normal College; upon receiving authorization to issue Bachelor of Arts and Bachelor of Science degrees, its name changed to Kent State College. In 1935, Kent State received university status when Governor Martin L. Davey signed a bill adding the school of business administration and graduate programs to Kent State.

The University is now an eight-campus system in northeastern Ohio; the main administrative center is located on the Kent Campus. The Kent campus contains 866 acres of wooded hillsides, with over 100 buildings, gardens and bike trails, as well as an airport and an eighteen hole golf course. Bachelor's, master's, and doctoral degrees are offered in more than thirty subject areas, and the full-time faculty numbers approximately 1,200.

Admissions

The general regulations of the university are followed along with the additional requirements listed below. A background of undergraduate courses consisting of one year each in analytical chemistry or biochemistry, organic chemistry, physical chemistry, calculus and physics is expected. A student not having all of the above courses may be accepted for graduate study if ability is shown in other courses. Deficiencies in undergraduate courses can be made up during the first year of graduate study, but no graduate credit will be earned from these courses.

Admission of a student to the doctoral program normally requires at least a 3.0 undergraduate grade point average and a 3.25 grade point average in any prior graduate coursework (if applicable). In addition, a minimum quantitative Graduate Record Examination (GRE) score of 600 is expected. Although the subject GRE is not required, candidates are encouraged to provide a subject GRE score to strengthen their file.

Applicants with grade point averages less than 3.0 may be considered for conditional admission if strong letters of recommendation and high Graduate Record Examination scores justify that admission.

The online application system for the graduate program is located at: **http://www.kent.edu/admissions/apply/**. To ensure full consideration, candidates for admission for the upcoming fall semester should ensure that all their application material is received by the

University no later than January 10th. However, applications will be accepted until all positions are filled. In the case that late applications cannot be considered for fall admission, they will be automatically considered for admission the following spring semester.

A limited number of positions are available for spring admission. Candidates should ensure that their application package is complete no later than September 1st.

Application material must include the following:

- All pertinent transcripts
- General GRE exam
- Personal statement
- Three letters of recommendation
- CV/resume

Foreign students also need to provide:

- TOEFL or IELTS exam scores. The minimum cutoff for the TOEFL is 525 on the paper-based exam, and 71 on the internet-based test. The minimum cutoff for the IELTS is a score of six.

Although the subject GRE is not required, candidates are encouraged to provide a subject GRE to strengthen their file.

Domestic applicants can send all application materials to:

Research & Graduate Studies
Office of Graduate Services
16 Cartwright Hall
Kent State University
P.O. Box 5190
Kent, OH 44242-0001

International applicants can send all application materials to:

Office of International Affairs
Kent State University
106 Van Campen Hall
21 Loop Road
Kent, OH 44242
USA

Program Information

Graduate students are required to complete a program of core courses in their area of specialization and at least one (for M.S. candidates) or two (for Ph.D. candidates) elective courses in other areas of chemistry. The extraordinary breadth of the program gives students considerable flexibility in curriculum design, ensuring a modern and dynamic graduate education. At the end of the second year, doctoral students must pass a written examination in their field of specialization and defend an original research proposal for their dissertation. Students typically complete their doctoral program with their thesis defense within 5 years.

Master of Science

Program Requirements

Each student must complete a total of 32 semester hours of courses including research and thesis. Of these, at least 18 hours must be for graduate credit other than research and thesis. Required courses include College Teaching of Chemistry (CHEM 60894; 1 hour) and, in the major area, two semester hours of Seminar (CHEM 62191, 62291, 62391, 62491 or 62591) and two semester hours of Problem Solving or Recent Development courses (CHEM 61191, 60291, 60391, 60491 or 60591). A total of 13 semester hours of graduate chemistry classroom courses are also required; one of these courses must be outside the major area.

A thesis presenting and interpreting the results of original research is required. The Department of Chemistry and Biochemistry considers research to be a fundamental part of the Master's of Science program.

Areas in which research may be carried out are analytical chemistry, biochemistry, inorganic chemistry, organic chemistry, and physical chemistry. The thesis must be successfully defended in an oral examination before the student's advisory committee.

Master of Arts

Program Requirements

A total of 32 semester hours of graduate credit is required, including at least 21 hours of classroom courses. The selection of these hours will be planned by the student and a faculty adviser to best fulfill the needs of the student. There is no research requirement for this degree. This program is only available with permission.

Doctor of Philosophy

Program Requirements

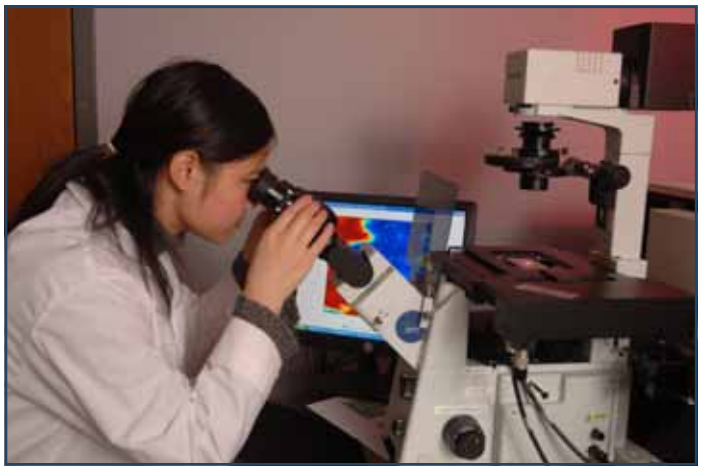
Each student must complete a total of 90 semester hours beyond the bachelor's degree or 60 hours beyond the master's degree including research and dissertation. Of these, at least 27 hours must be for graduate credit other than research and dissertation. Required courses include College Teaching of Chemistry (CHEM 70894; 1 hour) and, in the major area, four semester hours of Seminar (CHEM 72191, 72291, 72391, 72491 or 72591) and four semester hours of Problem Solving or Recent Developments courses (CHEM 71191, 70291, 70391, 70491 or 70591). A total of 18 semester hours of graduate chemistry classroom courses are required; one of these courses must be outside the major area.

Candidacy

To be admitted to candidacy for the doctoral degree, the student must pass a written examination in the field of specialization, the form and time of the examination being determined by each division (analytical chemistry, biochemistry, inorganic chemistry, organic chemistry or physical chemistry). Those failing this examination may repeat the examination once. After passing the written examination, the student must present a detailed written proposal for his/her dissertation research. The successful oral defense of this proposal and its acceptance by the advisory committee admits the student to candidacy for the Ph.D. degree.

Dissertation

The dissertation describes original research. The dissertation topic can be in/between the subdisciplines of analytical chemistry, biochemistry, inorganic chemistry, organic chemistry and physical chemistry. The written dissertation is reviewed and approved by the research advisor and the advisory committee prior to scheduling the final oral examination.



Student Life

Graduate students in the Department of Chemistry and Biochemistry have the opportunity to participate in external social events, such as bowling, ice skating, karaoke, evenings at the local wine bar, and so forth. These events provide a chance for undergraduate students, graduate students, faculty and staff to socialize outside of the department. Additionally, the university-wide Graduate Student Senate (GSS) holds monthly get-togethers at local pubs, known as "GradFest."

Alumni

Alumni of the chemistry graduate program have expressed gratitude for the direction their advisors have given them along the way. Hui Wang (Ph.D. 2007), found that the help his advisor offered allowed him to eventually solve his research problems independently: "I not only learned a lot of modern chemistry, but was also mentored by Dr. Twieg about how to think about different problems encountered in the research, how to solve them independently and so on. This really gave me a solid foundation for what I am doing now and what I will do in my future career; I am very grateful for that."

Another graduate from the chemistry program, Meng He (Ph.D. 2002), also felt that the program was a good foundation for his future career: "The research programs…aligned very well with the needs from many areas in chemical industry. The classes I took…provided me the right problem solving ability in any chemical business that requires the skills in Organic Chemistry. I still keep two things in my office desk: my Ph.D. dissertation and class notes… They not only remind me of my days at Kent State, and the working attitude of my Ph.D. supervisor, but also still help me generate new ideas whenever I open them."

Richard Lavrich, currently an Assistant Professor of Physical Chemistry at the College of Charleston, found the graduate program to provide an excellent environment for extensive interaction with faculty, for coursework and research. Science discussions took place among faculty and students, regardless of which division each belonged to.

After graduation, alumni have gone on to postdoctoral positions at institutions like the University of Colorado at Boulder, Georgia Tech, and the University of Connecticut; research positions at Promega, Lubrizol, and DuPont; and faculty positions at universities such as the Ohio State University and Tennessee State University.

Directions to Campus

From I-76:

Take the Kent/Route 43 exit (exit 33) and proceed north to Route 261. Turn right (east) onto Route 261. Proceed one-fourth mile to Campus Center Drive. At the traffic light, Williams Hall will be located on the right, at the corner of Summit St. and Risman Dr.

From I-80 (Ohio Turnpike):

Use exit 187/13 (Streetsboro). After the toll booth, proceed straight (follow Ravenna sign) onto Route 14 travelling southeast, go past Route 303 to Route 43. Turn right (south) on Route 43 and continue south for approximately six miles until you come to the traffic light at the dead end at Haymaker Parkway in the city of Kent. Turn left (east) onto Haymaker and follow until you reach the traffic light at the intersection of Lincoln and Haymaker. Turn right onto Lincoln and follow it until the next traffic light, located at the intersection of Lincoln and Summit St. Turn left onto Summit St. and follow for three traffic lights, until the intersection of Summit and Risman Dr. Williams Hall is located on the corner of Summit and Risman Dr.

From I-90:

Proceed toward Cleveland. Take I-271 south to I-480 east; stay on I-480 until it becomes Route 14 in Streetsboro. Turn right (south) on Route 43 and follow for approximately six miles until you come to the traffic light at the dead end at Haymaker Parkway in the city of Kent. Turn left (east) onto Haymaker Parkway and follow until you reach the traffic light at the dead end at Haymaker Parkway in the city of Kent. Turn left (east) onto Haymaker Parkway and follow until you reach the traffic light at the intersection of Lincoln and Haymaker. Turn right onto Lincoln and follow it until the next traffic light, located at the intersection of Lincoln and Summit St. Turn left onto Summit St. and follow for three traffic lights, until the intersection of Summit

Faculty Research

Dr. Soumitra Basu: Biochemistry

Dr. Nicola Brasch: Bioinorganic Chemistry

Dr. Scott Bunge: Inorganic Materials Chemistry

Dr. Farid Fouad: Organic Chemistry

Dr. Roger Gregory: Biophysical Chemistry

Dr. Songping Huang: Inorganic Materials Chemistry

Dr. Mietek Jaroniec: Mesoporous Materials

Dr. Anatoly Khitrin: NMR Spectroscopy

Dr. Hanbin Mao: Bioanalytical Chemistry

Dr. Grant McGimpsey: Physical Chemistry

Dr. Paul Sampson: Organic Synthesis

Dr. Alexander Seed: Organic Synthesis

Dr. Chun-che Tsai: Biochemistry

Dr. Michael Tubergen: Physical Chemistry

Dr. Robert Twieg: Organic/Materials Chemistry

Dr. John West: Physical Organic Chemistry

Bioinorganic and Medicinal Chemistry: Vitamin B_{12}—Small Molecule Interactions, Vitamin B_{12} Bioconjugates as Therapeutics and Vanadium (III) Coordination Chemistry

Research

Dr. Nicola E. Brasch
Associate Professor

Inorganic Chemistry
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Phone: (330) 672 9524

Education: BSc(Hons) and PhD University of Otago, New Zealand; Postdoctoral Research Associate University of Erlangen-Nuremberg and Colorado State University.

Honors, Awards and Fellowships: Graduate Student Mentorship Excellence Award, KSU (2007); American Chemical Society PROGRESS/Dreyfus Lectureship (2004); Inaugural Rita Cornforth Research Fellowship (Australian National University, 1997); Alexander von Humboldt Research Fellowship (1994).

Funding: ACS PRF, Juvenile Diabetes Research Foundation and Ohio Board of Regents.

Scientific Activities: Member of the Scientific Advisory Board for Cobalz Ltd; Licensing of IP to a US pharmaceutical company; reviewer for numerous journals and grant funding agencies.

Main research interests are the interaction of vitamin B_{12} derivatives with small molecules of biological interest, the development of vitamin B_{12} based therapeutics and the coordination chemistry of vanadium(III). Collaborative projects with cell biology labs are also underway. Students obtain training in a wide variety of techniques and instrumentation, including Schlenk (air-free) techniques, mechanistic studies, NMR, IR and UV-vis spectroscopy, mass spectrometry and HPLC.

Vitamin B_{12} Chemistry. The structure of vitamin B_{12} (cyanocobalamin, CNCbl) is shown in Figure 1 (X = CN^-). Cobalamins (= vitamin B_{12} derivatives) are cobalt-containing macrocyclic complexes which vary in the ligand occupying the upper axial site (= X, Fig. 1). Cobalamins are synthesized by microorganisms found in soil, water and the intestine of some animals; however humans cannot synthesize cobalamins and instead obtain their daily requirement (1-6 mg) from animal products. The MeCbl and AdoCbl forms of vitamin B_{12} (X = Me or Ado, Fig. 1) are cofactors for approximately 15 known enzyme reactions. A deficiency in vitamin B_{12} can lead to anaemia ("pernicious anaemia") and/or neurological disorders. Of the 15 or so vitamin B_{12} -dependent enzyme reactions known, two of these reactions, involving methionine synthase and methylmalonyl-CoA mutase, occur in humans. In the former reaction, the vitamin B_{12} derivative MeCbl is an intermediate in the methylation of homocysteine by methyl-tetrahydrofolate. A current "hot topic" in the medical literature is the recently demonstrated relationship between high serum levels of homocysteine and a greatly increased risk of strokes or heart attacks. In addition, it is now well established that individuals with high serum levels of homocysteine are more likely to develop neurological disorders. It has recently been estimated that 15-20% of the US population over the age of 65 years are B_{12} deficient.

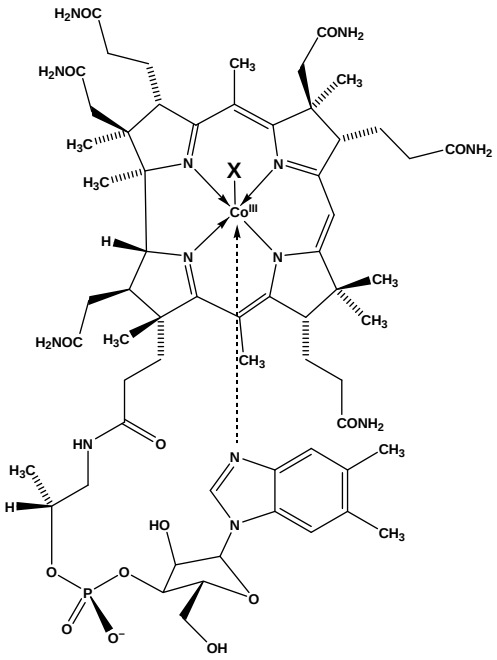

Figure 1: Structure of vitamin B_{12} and its derivatives. X = CN, Me, Ado, OH_2, GS, NO etc

Vitamin B_{12} - Small Molecule Interactions. We are interested in the interactions of vitamin B_{12} with small molecules of biological relevance. In collaboration with the lab of Dr. Donald Jacobsen, Department of Cell Biology, Lerner Research Institute, The Cleveland Clinic, we have recently shown that the glutathione derivative of B_{12}, glutathionylcobalamin (X = GS, Fig. 1) is naturally occurring in mammalian cells [1]. It was also recently proposed by Dr. Andrew McCaddon and co-workers that thiolatocobalamins may be more potent therapeutics than the currently available pharmaceutical forms of B_{12}. We have developed procedures for synthesizing thiolatocobalamins [2] and are interested in the chemical and biological properties of these complexes. *In 2007 the US pharmaceutical company Pamlab licensed out a patent concerning N-acetyl-L-cysteinylcobalamin from Kent State University and is exploring potential therapeutic applications of this compound.*

Our recent structure of the nitric oxide derivative of vitamin B_{12}, nitroxylcobalamin,[3] has attracted a lot of attention in the literature. Nitric oxide (NO) has important roles in biology including regulating

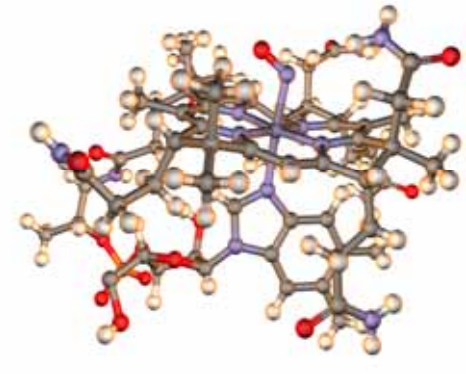

Figure 2: Ortep plot of NOCbl, nitroxylcobalamin.

vasodilation, cell proliferation and the immune response, and it has been proposed that B_{12} scavenges excess levels of NO to form NOCbl. In support of this, both mammalian B_{12}-dependent enzyme reactions are inhibited by NO and cobalamins have been found to inhibit a range of NO-induced physiologies and pathologies.

Vitamin B_{12} Bioconjugates and Therapeutics. Other areas of interest include the synthesis and properties of vitamin B_{12} bioconjugates. The ability of vitamins to act as drug carriers (or vectors) for transporting orally administered pharmaceuticals to cells has been recognized for some time. Only small, neutral, water-soluble molecules can pass across biological membranes to any degree by passive diffusion. Due to the large size of vitamins, these important biomolecules are therefore typically associated with active transport mechanisms for absorption and cellular uptake. This is especially important for vitamin B_{12}, given the very small amounts that are present in most foods. Utilizing vitamin B_{12} bioconjugates for the transportation of drugs has been shown to have applications in the uptake of peptides, proteins, imaging agents and chemo-therapeutics.

Vanadium compounds mimic and/or enhance nearly all of the known metabolic actions of insulin; however they are poorly absorbed. Recently we have prepared the first vanadium-vitamin B_{12} bioconjugate which could potentially be an active, orally administered pharmaceutical for the treatment of diabetes.[4] *This work was featured in Chemical & Engineering News* (Science & Technology Concentrate, 2008, June 30 issue).

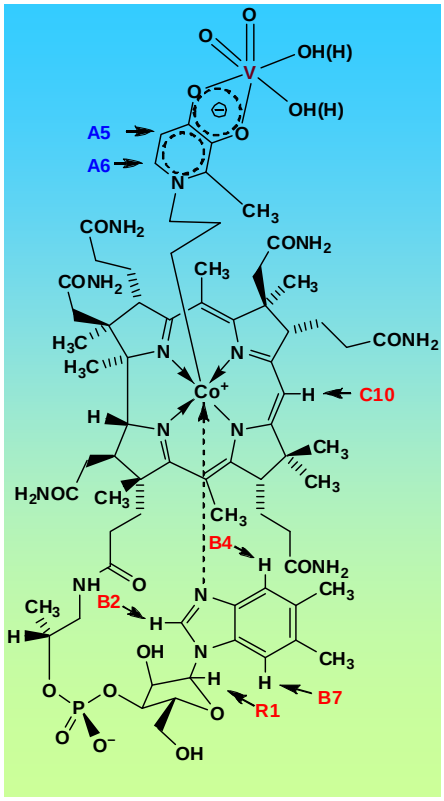

Figure 3: Structure of a vanadium-vitamin B_{12} bioconjugate incorporating a hydroxypyridinone.

The Coordination Chemistry of Vanadium(III). The +3 oxidation state of vanadium is of interest for several reasons. V(III) clusters spontaneously form in solution with interesting structures, spectroscopic properties, and magnetic properties. Furthermore, V(III) clusters can exhibit spin frustration and behave as single molecule magnets, and therefore have potential applications in data storage. V(III) complexes are also of interest with respect to their electron transfer properties and their potential to act as catalysts in industrially relevant processes and by mimicking the active sites of metalloproteins.

The importance of vanadium in biology first attracted attention through the work of Martin Henze and co-workers, who discovered high concentrations of vanadium(III) in the blood cells of sea squirts. Ascidians of the suborder *Phlebobranchia* are small marine animals that sequester vanadium(V) from seawater and reduce it to vanadium(III). How or why these creatures accumulate this metal ion is unknown.

The chemistry of vanadium(III) itself, especially in aqueous systems, is poorly defined compared with that of vanadium in the more stable oxidation states of +4 and +5. Our studies of vanadium(III) complexes have commenced with simple ligands such as amino acids, or ligands which model amino acids. Although it was proposed a number of years ago that V(III) complexes with nuclearity greater than two exist is aqueous solution, there is practically no structural data to substantiate this claim. Recently we structurally characterized and studied the aqueous solution chemistry of a series of trimeric and tetrameric V(III) complexes of acetate and related ligands [5]. ^{1}H NMR spectroscopy and ES-MS measurements demonstrated that the polynuclear complexes are not purely solid state phenomena, but retain their structural integrity in solution.

Figure 4: Structure of $[V_4(m\text{-}OH)_4(m\text{-}OOCCH_3)_4(OH_2)_8]Cl_4$, a novel tetranuclear V(III) complex spontaneously formed in water.

References

[1] Hannibal, L., et al. (2008) *Clin. Chem. Lab. Med.*, in press.

[2] Suarez-Moreira, E., et al. (2006) *Dalton Trans.*, 5269.

[3] Hannibal, L., et al. (2007) Angew. Chem., 46, 5140.

[4] Mukherjee, R., et al. (2008) *Chem. Commun.*, 3783.

[5] Mukherjee, R., et al. (2007) *Inorg. Chem.*, 46, 1575.

DNA G-Quadruplexes in Regulation of Transcription and RNA G Quadruplexes in Translation Control

Research

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Assistant Professor

Biochemistry

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Phone: (330) 672 3906

Education: **Ph.D., Kimmel Cancer Center, Thomas Jefferson University, Philadelphia; Postdoctoral Research Associate, Yale University, New Haven.**

The overall goal of my laboratory is to understand structure-function relationships in nucleic acids, with particular emphasis on non-canonical structures. We are interested in learning the role of such structures in the regulation of fundamental cellular processes, and utilize such molecules for therapeutic purposes.

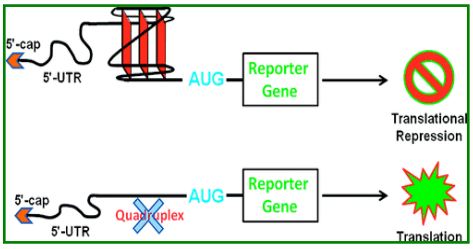
We are particularly interested in studying a structural form adopted by nucleic acids known as G-quadruplex. Both DNA and RNA sequences rich in guanosine residues can adopt this structural form. We intend to learn how DNA G-quadruplexes regulate transcription and how RNA G-quadruplexes can control translation. We will utilize biochemical and biophysical methods in tandem with molecular and cellular biology and techniques to achieve these objectives.

DNA G-Quadruplexes in regulation of transcription: Relationship to diabetes and cancer

Recent studies from several labs have shown the wide-spread occurrence of G-rich sequences within the human genome, suggesting involvement of such sequences in fundamental regulatory roles. One particular G-rich area of interest is the Insulin Linked Polymorphic Region (ILPR), which is located upstream of the Insulin gene. The ILPR region has been linked to juvenile or type I diabetes. The ILPR is unique among G-rich areas in the genome because of the unusual heterogeneity within a large cluster of G-rich sequences. The most well studied G-rich area in the human genome are the telomeric sequences, which are found at the end of chromosomes. However, the telomeric region consists of monotonic repetition of identical G-rich units. In contrast, the ILPR is known to harbor more than a dozen different G-rich repeats. As such, it presents a unique opportunity to study the structural polymorphism associated with G-quadruplex structures. The goal is to understand how such polymorphism influences the replication of this section in the genome and the transcription of Insulin.

Quadruplex DNA-Protein Interactions

Quadruplex DNA-protein interactions can be important in synergizing, accentuating or fine-tuning the regulatory role of quadruplexes. We are interested



not only in defining the chemical details of such interactions, but also understanding their role in modulating quadruplex function. Recently, we have defined, in molecular detail, the binding of the Insulin protein to some of the quadruplexes found within the ILPR, and in the process, were able to define some fundamental rules of Insulin's interaction to ILPR quadruplexes. We are also working to define how structural polymorphism in quadruplexes could affect the ability of helicase to unwind such structures.

RNA G-Quadruplexes in translation control and their role in cancer

Bioinformatics analyses have discovered prevalence of G-rich sequences in regulatory regions of mRNA. The 5'-untranslated region (5'-UTR) is known to control translation of mRNA. Recently, we and others have shown that G-rich sequences present in the 5'-UTR can adopt G-quadruplex conformation and repress translation. We are investigating in detail the role of such G-rich sequences in regulating translation of mRNA. We are particularly interested in understanding the roles played by such structures in regulating translation of mRNA genes that are related to cancer.

Selected Publications

[1] Morris, M. J., **Basu, S.** "An unusually stable G-quadruplex within 5'-UTR of the MT3 matrix metalloproteinase mRNA represses translation in eukaryotic cells." Biochemistry, 48:5315-5319 (2009).

[2] Schonhoft. J. D., Bajracharya, R., Dhakal, S., Yu, Z., **Mao, H., Basu, S.** "Direct experimental evidence for quarduplex-quadruplex interaction within the human ILPR." Nucleic Acids Res., 37:3310-3320 (2009).

[3]. Yu, Z., Schonhoft, J. D., Dhakal, S., Bajracharya, R., Hegde, R., **Basu, S., Mao, H.** "ILPR G-quadruplexes formed in seconds demonstrate high mechanical stabilities." J. Am. Chem. Soc., 131: 1876-1882 (2009).

[4] Tyagi, P., Banerjee, R., Basu, S. Yoshimura, N., Chancellor, M., Huang, L. "Intravesical antisense therapy for cystitis using TAT-peptide nucleic acid conjugates." Molecular Pharmaceutics, 3: 398-406 (2006).

[5] Basu, S., Strobel, S. A. "Identification of specific monovalent metal ion binding sites within RNA." Methods, 23: 264-275 (2001).

The Molecular Design of Metal-Organic Complexes

The primary objective of our research is to make a strong contribution to the fields of inorganic chemistry, nanoscale science and technology, and materials science. With this aim, our group utilizes a combination of a novel set of ligands in conjunction with a vast array of metals to produce well designed multi-functional inorganic/organic hybrid systems. Students working in this area frequently expand beyond the reaches of classical chemistry subjects and embrace additional areas, as required, for the successful execution of a specific project. Characterization methods include multinuclear NMR, X-ray crystallography, FT-IR and UV/VIS spectroscopy, TGA/DTA, SEM, TEM and X-ray powder diffraction.

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Research

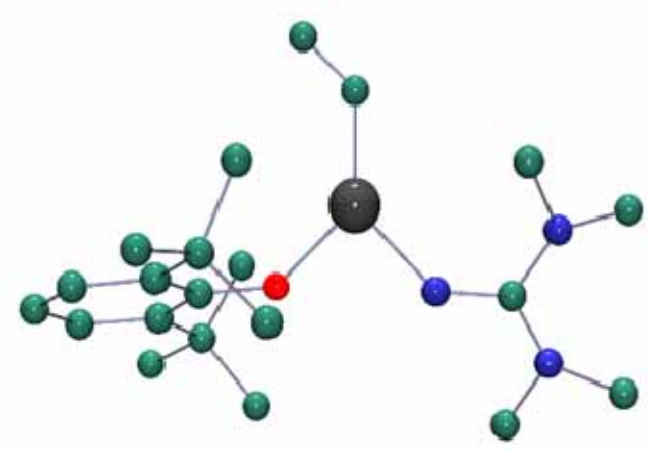
One component of our research is further elaborated on in the following paragraphs:

The Design of Metal-Organic Complexes Utilizing a Synergistic Approach

In a number of metalloproteins hydrogen bonding (5 to 15 kcal/mol) is used in conjunction with metal-ligand covalent bonds to control activity within bio-molecules. A current research challenge in synthetic inorganic chemistry is the incorporation of these types of interactions into well-defined metal compounds with the intension of developing enhanced catalytic and stoichiometric reactivity.

Conversely, difficulties arise in synthetic systems because their structures are often flexible, so H-bonds form with various other species present, such as solvent molecules or counterions. These intermolecular hydrogen bonds are often unwanted and interfere with the desired function. Therefore, as in metallo-proteins, synthetic complexes must have a combination of ligands placed within rigid frameworks located near the metal center(s) to ensure stable complex formation.

In our group, standard Schlenk and glovebox techniques are employed to synthesize low-coordinate air and moisture sensitive compounds. The stability and reaction chemistry of the resultant complexes is then investigated. Typically, complexes are isolated as crystalline solids and characterized via single crystal X-ray diffraction.



All of our investigations, while rooted in traditional aspects of chemistry, often involves students in collaboration with other research groups. Members generally have their own project; however, each group member's research has significant overlap with others in the group. As such, the students' depth of fundamental chemical principles becomes augmented by exposure to a breadth of additional concepts.

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[1] Scott D. Bunge; Jacob M. Lance; Jeffrey A. Bertke *Organometallics* 2007, *26*, 6320-6328.

[2] Jeffrey A. Bertke; Scott D. Bunge D*alton Transactions* 2007, 4647-4649.

[3] Travis L. Cleland; Scott D. Bunge *Polyhedron* 2007, *26*, 5506-5512.

Redox Reactions Involving Unusual Metal Centers

Research

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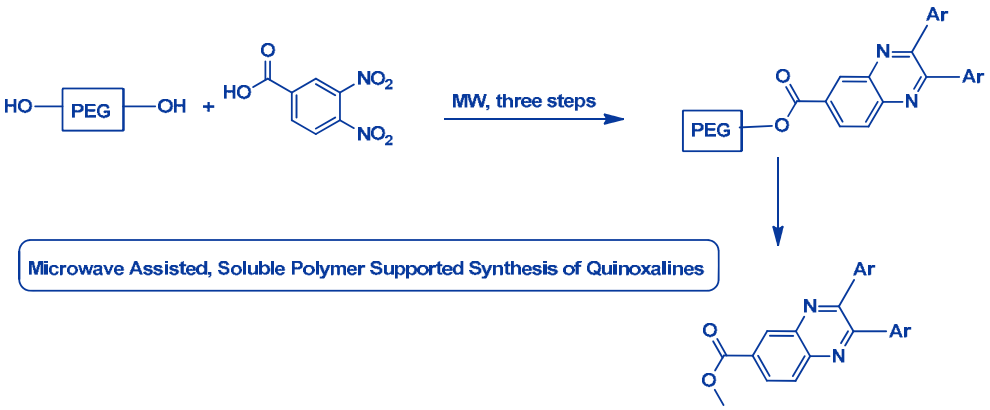
Our research interests are focused on the synthesis of heterocyclic compounds with potential applications in the fields of pharmaceuticals and material sciences.



Nitrogen, oxygen and sulfur heterocyclic compounds are key building blocks in medicinally and biologically active compounds. They are predominant among all types of pharmaceuticals and agrochemical products. Heterocyclic compounds also have many industrial uses as components in dyes, antioxidants, copolymers, bases and ligands. Both conventional and microwave-assisted synthetic techniques are adopted in our research. We have developed an efficient microwave-assisted synthesis of fused triazolo-benzopyridoxazepines for biological testing. Another area of interest is the synthesis of heterocyclic supramolecular compounds as liquid crystals, organic semiconductors and organic gelators. The structure of many heterocyclic compounds permits their self-assembly and aggregations via possible intermolecular hydrogen bonding, π-stacking, and metal coordination, making them attractive tunable, optical and electronic targets. Students in our laboratory will have the opportunity to learn and practice organic synthesis, structure elucidation and physical measurements.

Selected Publications

[1] **Fouad, Farid** S. Microwave-assisted soluble polymer supported synthesis of quinoxalines, benzodiazepines, and benzimidazoles. Abstracts of Papers, 240th ACS National Meeting, Boston, MA, United States, August 22-26, 2010

[2] Sane Komal M; Mynderse Michelle; Lalonde Daniel T; Dean Ivory S; Wojtkowiak Jonathan W; **Fouad Farid**; Borch Richard F; Reiners John J Jr; Gibbs Richard A; Mattingly Raymond R. A novel geranylgeranyl transferase inhibitor in combination with lovastatin inhibits proliferation and induces autophagy in STS-26T MPNST cells. The Journal of pharmacology and experimental therapeutics (2010), 333:23-33.

[3] Borch, Richard Frederic; Gibbs, Richard Anthony; Clark, Michelle Martin; **Fouad, Farid**. Prodrugs and conjugates of prenylation inhibitors. PCT Int. Appl. (2009), 47pp. CODEN: PIXXD2 WO 2009029849 A120090305 CAN 150:283238 AN 2009:258974

[4] Jonathan W. Wojtkowiak, **Farid Fouad**, Daniel T. LaLonde, Richard A. Gibbs, John J. Reiners, Jr., Richard F. Borch, Raymond R. Mattingly. Induction of apoptosis in Neurofibromatosis Type 1 malignant peripheral nerve sheath tumor cell lines by a combination of novel farnesyl transferase inhibitors and lovastatin. The Journal of pharmacology and experimental therapeutics (2008), 326:1–11.

[5] **Farid S Fouad**, Justin M Wright, Gary Plourde, Ajay S Purohit, Justin K Wyatt, , Ahmed El-Shafey, George Hynd, Curtis F Crasto, Yiqing Lin and Graham B Jones. Synthsis, and Protein Degradation Capacity of Photoactivated Enediynes. Journal of Organic Chemistry (2005), 70, 9789-9797

[6] **Farid S Fouad**, Curtis F Crasto, Yiqing Lin and Graham B Jones. Photoactivated Enediynes: Targeted Chimeras Which Undergo Photo-Bergman Cyclization. Tetrahedron Letters (2004), 45, 7753-7756

Inorganic, Materials & Nanopharmaceutical Chemistry: Towards New Generation Multiferroics, Multimodal Imaging Agents & Drug Delivery Vehicles

The current research work at my group is aimed at developing novel nanomaterials with useful magnetic, ferroelectric, photochemical properties, particularly nanostructured materials with two or three such properties combined in the same structure for microelectronics, photovoltaics and biomedical applications. Most of the compounds we synthesize fall into the realm of organic-inorganic hybrid materials.

Ferroelectric materials can exhibit a spontaneous electric polarization.[1] The direction of such polarization can be switched between equivalent states by the application of an external electric field. The movement and storage of electric charges and the manipulation of the electric fields they produce are the basis of the operation of computer processors and memories. The modern electronics industry demands an ever greater decrease in switching time and length scales, approaching the level of individual electrons and atoms.[2-3]

Although continued improvements in conventional semiconductor designs can, to some extent, address these needs, there is increasing motivation to consider alternative paradigms. In ferroelectric materials, electric polarization, bond charges, and large electric fields are produced by displacements of individual atoms, and devices based on ferroelectric materials therefore can be made in principle to operate on atomic scale. We have developed a new class of organic-inorganic hybrid materials that can show large ferroelectric effects.[4] Furthermore, several compounds in this class have magnetic properties that make them qualify as new generation ferroelectric-ferromagnetic materials or multiferroics. The latter have emerged as a topical research area in materials chemistry because these materials are expected to play a pivotal role in the future information processing and storage. On the other hand, some of the magnetic nanoparticles synthesized at my group show great potential as magnetic resonance imaging (MRI) contrast agents for both clinical diagnostic and biomedical research applications. Such nanoparticles can also be functionalized with either a radioactive isotope or an organic drug molecule, and to be used as a versatile platform for the simultaneous imaging and delivery of diagnostic and therapeutic agents to the human body *via* endocytosis. In addition, such magnetic nanoparticles may have applications in magnetic-field guided drug delivery and localization. In addition, we are also interested in developing this platform technology to form strong metal ion chelators that can deliver or remove metal ions from the human body for the purpose of maintaining metal ion homeostasis or treating diseases such as iron overload in thalassemia or heavy metal poisoning.

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Guest Professorship, University of Zurich, 2005
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Funding:

NSF and Ohio Board of Regents

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[1] W. Zhang, R. G. Xiong, S. D. Huang *J. Am. Chem. Soc.*, **2008**, *130*, 10468.

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[4] Q. Ye, Y. M., Song, S. D. Huang, et al *J. Am. Chem. Soc.*, **2006**, *128*, 6554.

Research

Protein Conformational Dynamics, Protein-Solvent Interactions, Proteomics and Protein Analytical Methods Development; Proteomics Studies of Multiple Sclerosis

Research

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Currently funded by NIH.

Our research interests are in protein conformational dynamics, protein-solvent interactions, and the characterization of dynamically distinct substructures in proteins and their role in protein function and stability. We employ a number of techniques to explore protein dynamics including ^{2}H NMR, and hydrogen isotope exchange measured by ^{1}H 2D COSY NMR and Electrospray Ionization Mass Spectrometry (ESI-MS).

Protein molecules are not rigid but undergo a variety of internal motions with amplitudes that range from a few hundredths of Angstroms to tens of Angstroms and over time scales that vary from picoseconds to seconds. The types of motion include high frequency, small amplitude vibrations of bonded atoms, rotations of amino acid side-chains, as well as a rich spectrum of slower, more collective rigid body motions, including helix and loop displacements and motions of protein domains. Protein conformational dynamics is important for a number of protein functions including ligand binding, enzyme catalysis and regulation, signal transduction, and the interaction of proteins with other macromolecules. The dynamic properties of proteins are also important for the protein folding process itself as well as for protein stability.

The dynamic properties of proteins are strikingly similar to the dynamic properties of many other complex systems, including glass forming liquids and synthetic polymers. For example, hydrated proteins display a dynamical transition at ~220 K and like synthetic polyamides are plasticized by water.

Globular proteins appear to be dynamically heterogeneous, consisting of rigid, solid-like regions embedded in a more mobile liquid-like matrix. These dynamically distinct regions were first identified in hydrogen isotope exchange experiments and we continue to characterize them and explore their role in protein function and stability.

We are currently studying the dynamic heterogeneity of the protein interior by a combination of hydrogen isotope exchange and deuterium NMR spectroscopy in collaboration with Dr. Mahinda Gangoda. Protein samples are kinetically labeled by hydrogen isotope exchange so as to select regions of the protein interior with different hydrogen isotope exchange rates. The location of deuterium labels within the protein structure and the hydrogen/ deuterium occupancy of each site are established by ^{1}H 2D COSY NMR (Figure 1). We then acquire ^{2}H NMR powder spectra using a quadrupole echo pulse sequence and employ the Lipari-Szabo model-free formalism to analyze the spin lattice relaxation times (Lipari, G.; Szabo, A. *J. Am. Chem. Soc.* 104, 4546, 1982). Spin-

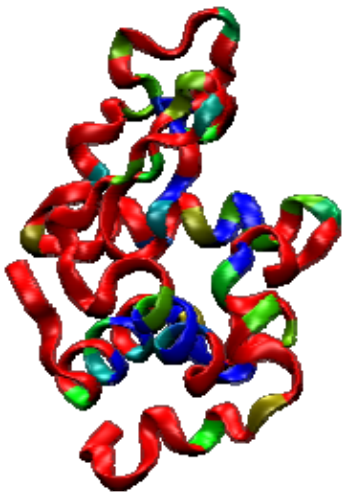


Figure 1: Location of the slowest exchanging protons (blue and green) in lysozyme determined from a ^{1}H 2D COSY NMR spectrum of the protein following kinetic labeling by deuterium-hydrogen exchange. The spectrum was obtained on a 500 MHz Varian NMR spectrometer by the method of Redfield et al [*Biochemistry,* **27**, 122, (1988)].

A second area of interest is the development of protein analytical methods including the development of novel chromatographic stationary phases for the separation of peptides, proteins, and metabolites, as well as the development of proteomics approaches to monitor protein chemical modification, oxidation and changes in protein stability. We also conduct proteomics studies of Multiple Sclerosis. Proteomics approaches include Surface Enhanced Laser Desorption and Ionization Mass Spectrometry (SELDI-MS), 2D HPLC, peptide mass fingerprint analysis, and various electrophoresis techniques including western blotting.

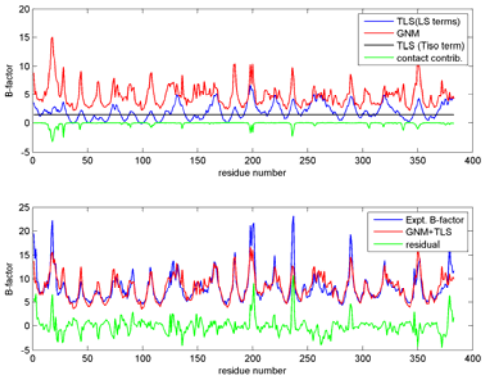


Figure 2: B-factor plot for sialidase (3sil.pdb). Upper plot: Contributions to the calculated B-factors from the TLS isotropic translation term (black) , the TLS libration-screw terms (blue), and the Gaussian Network model (red) as well as corrections for lattice contacts (green). Lower Plot: Experimental (blue) and calculated (red) B-factors and residuals (green) (corr. coeff. = 0.83)

lattice relaxation times of dry partially ^2H labeled lysozyme are found to correlate with the average solution exchange rate of the labeled sites, which presumably reflects the fact that both exchange rates and motional correlation times depend on the same intrinsic features of the protein structure, such as local packing density and the number of residue contacts about the N-^2H sites. These initial studies with lysozyme are being extended to other enzymes (ribonuclease A and adenylate kinase), where our interest is in exploring how protein conformational dynamic properties are perturbed by ligand binding and as the enzyme cycles through its catalytic reactions.

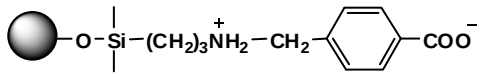
Another source of information about protein flexibility is the Debye-Waller factor or B-factor determined by X-ray crystallography. The isotropic atomic B-factor is given by:

$$\mathbf{B}_i = (8p^2/3)\langle D\mathbf{R}_i^2\rangle$$

where $\langle D\mathbf{R}_i^2\rangle$ is the atomic mean square displacement of the i^{th} atom. We are interested in modeling the atomic B-factors and in understanding the various contributions to B-factors from internal protein motions, rigid-body motions of protein molecules in the crystal, as well as the effects of crystal lattice contacts on B-factors. We are currently developing models (Figure 2) based on the Gaussian Network Model (GNM) [Haliloglu et al Phys. Rev. Lett., **79**, 3090, (1997)] and Local Density Model (LDM) [Halle, PNAS, **99**, 1274, (2002)] to account for internal motions in combination with the TLS model [Schomaker & Trueblood, Acta. Cryst., **B24**, 63, (1968)] to account for rigid-body motions of the protein within the crystal lattice.

A second area of interest is the development of protein analytical methods including the development of novel chromatographic stationary phases for the separation of peptides, proteins, and metabolites, such as 4-propylaminomethyl benzoic acid bonded silica (Figure 3), the development of multi-functional chromatographic stationary phases based on a reactive aldehyde silica platform, as well as the development of proteomics approaches to monitor protein chemical modification, particularly oxidation and changes in protein stability.

We employ SELDI-MS, 2D-LC and gel electrophoresis techniques in proteomics studies of Multiple Sclerosis (MS) and Experimental Autoimmune Encephalomyelitis (EAE) in collaboration with Dr. Jennifer McDonough (Dept. of Biological Sciences) and Dr. Ernie Freeman (Dept. of Biological Sciences). Oxidative damage plays an important role in a number of neurodegenerative diseases and appears to be important in MS where it may lead to mitochondrial dysfunction. We are attempting to identify proteins that are differentially expressed or chemically modified in MS and EAE brain tissue relative to controls. We are developing antibody pull-down methods coupled to SELDI-MS to identify protein peaks in the mass spectra and to identify oxidized proteins. These approaches are more rapid and convenient than current western blotting techniques.



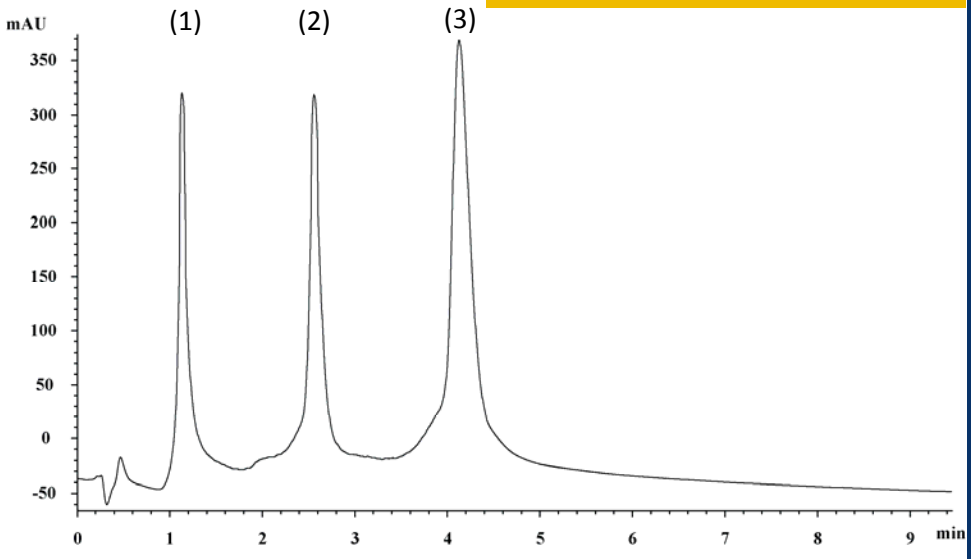


Figure 3: 4-propylaminomethyl benzoic acid (PAMBA) bonded silica – a versatile zwiterionic HPLC stationary phase which operates with high efficiency in cationic and anionic separation modes shown here separating (1) histidine, (2) lysine, and (3) arginine.

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Protein Hydration and Glass Transitions, Gregory, R.B., in "*The Role of Water in Foods*", Ed. D. Reid, Chapman-Hall, New York, 57-99 (1998).

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Surface Phenomena, Adsorption, Chromatography, and Chemistry of Conventional and Ordered Nanoporous Materials

Research

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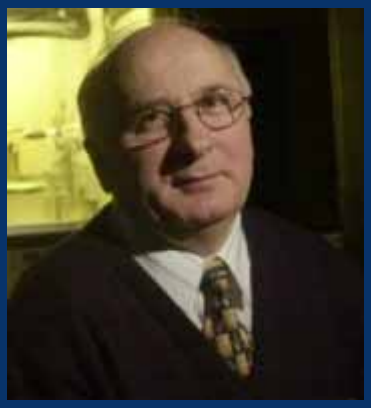

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Funding:
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Scientific Activities:
NSF Panel reviewer, vice-chair of 2nd, 3rd, 4th and 5th Int. Symposia on Nanoporous Materials held in Canada (2000, 2002, 2005, 2008); member of Editorial Boards of Adsorption, Adsorption Sci. & Technol. Chem. Mater., J. Porous Mater., J. Liquid Chromatography

Research interests and activities of Dr. Jaroniec and his group primarily revolve around interdisciplinary topics of interfacial chemistry, chemical separations and chemistry of nanomaterials with a special emphasis placed on physical adsorption at the gas/solid and liquid/solid interfaces, synthesis, modification and characterization of conventional and ordered nanoporous materials, as well as gas and liquid chromatography. A variety of techniques are used to study the aforementioned materials; namely, gas adsorption, thermogravimetry, elemental analysis, gas and liquid chromatography, power X-ray diffraction, scanning and transmission electron microscopy, solid-state NMR, infrared spectroscopy and related techniques.

Studies carried out in Jaroniec's lab include: (a) classical and statistical thermodynamics of adsorption processes at the gas/solid and liquid/solid interfaces, (b) theoretical and experimental studies of adsorption and chromatographic processes taking place on energetically heterogeneous sur-faces of nanoporous solids, (c) prediction of adsorption equilibria for multicomponent gas and liquid mixtures, (d) theory of gas and liquid chromatography, (e) development of advanced methods for analyzing surface heterogeneity, nanoporosity and fractal nature of adsorbents, catalysts and other materials, (f) characterization of carbon blacks, active carbons, active carbon fibers, polymeric sorbents, zeolities, silica, alumina, titania, and other nanoporous materials including chemically modified solids and recently discovered ordered mesoporous materials, and (g) synthesis, modification and applications of nanoparticles and monolithic nanomaterials, especially ordered mesoporous materials such as silicas, organosilicas, metal oxides, carbons and polymeric nano-materials.

The current research of Dr. Jaroniec and his group is focused on the synthesis, characterization and applications of novel ordered mesoporous materials (OMM) such as ordered mesoporous silicas (OMS)], periodic mesoporous orga-nosilicas (PMO), ordered meso-porous carbons (OMC), hierarchical porous materials and related hybrid nanomaterials for environmental and energy related applications. OMM can be prepared by

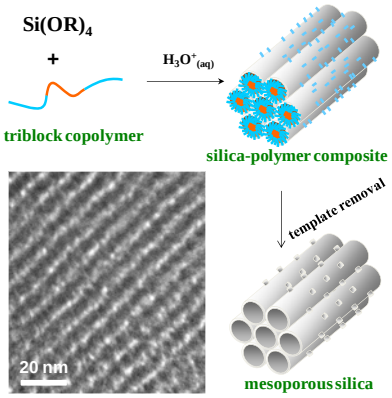

Figure 1: Schematic illustration of soft-templating synthesis of OMS by acid-controlled hydrolysis and condensation of TEOS in the presence of PEO-PPO-PEO triblock copolymer, Pluronic P123, as a soft template. The formation of hexagonally ordered OMS, known as SBA-15, is presented with TEM image of this ordered mesostructure. Microwave-assisted synthesis of this mesostructure is reported in [1].

using soft-templating (Fig. 1 & 2), hard-templating (Fig. 3) or combined synthesis routes.

The area of ordered nanomaterials has been growing remarkably since 1992, when the first hexagonally ordered mesoporous silica, MCM-41, synthesized via self-assembly of silica and cationic surfactant species, has been reported. The pore size of OMM can be tailored over the entire range of mesopores (pores with widths between 2 and 50 nm) by adjusting the size and chemical nature of the template (surfactants, block copolymers,

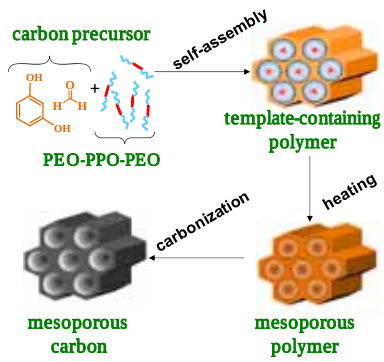

Figure 2: Schematic illustration of soft-templating synthesis of OMC by acid-catalyzed polymerization of resourcinol and formaldehyde in the presence of PEO-PPO-PEO triblock copolymer, Pluronic P123, as a soft template.

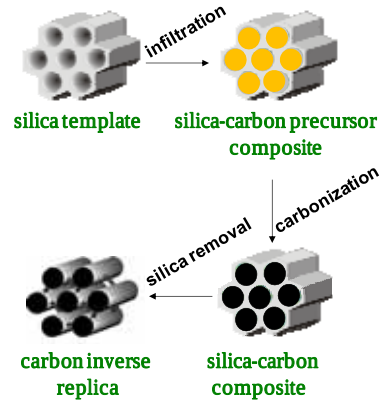

Figure 3: Schematic illustration of hard-templating synthesis of OMC by filling the mesopores of OMS such as SBA-15 with a carbon precursor followed by carbonization and silica dissolution [2]. The resulting OMC is an inverse carbon replica of the OMS template.

colloids), by adding molecular expanders and performing post-synthesis hydrothermal treatments.

There are tremendous opportunities in the design and synthesis of novel ordered nanostructures. For instance, the use of block copolymers with different chemical composition permits the synthesis of various nanostructures ranging from channel-like to cage-like materials. The latter are ordered structures consisting of interconnected sphe-rical mesopores. In addition, the use and/or incorporation of different inorganic and/or organic species via one-pot synthesis and/or post-synthesis modification can be employed to develop novel mesoporous materials for advanced applications in adsorption, catalysis, nano-technology, environmental and energy-related applications.

One of the major research activities in Jaroniec's lab is the synthesis of ordered nanomaterials and physico-chemical studies of their adsorption and structural properties. A special emphasis is placed on the development of nanomaterials with desired properties for environmental and energy-related applications. Examples of the OMM studied include the synthesis of monolithic

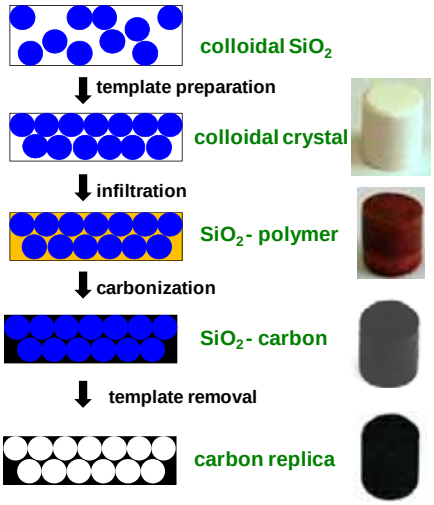

Figure 4: Schematic illustration of colloidal templating synthesis of mesoporous carbon monoliths by filling the mesopores of a colloidal silica crystal with a carbon precursor followed by carbonization and silica dissolution [3].

[3] and hierarchical carbons. Fig. 4 illustrates the colloidal templating synthesis of monolithic carbons with spherical mesopores.

Another example is the synthesis of ordered mesoporous organosilicas with different pendant and bridging organic groups [4]. Fig. 5 shows TEM image of benzene-silica with cubic structure [5], while Fig. 6 illustrates

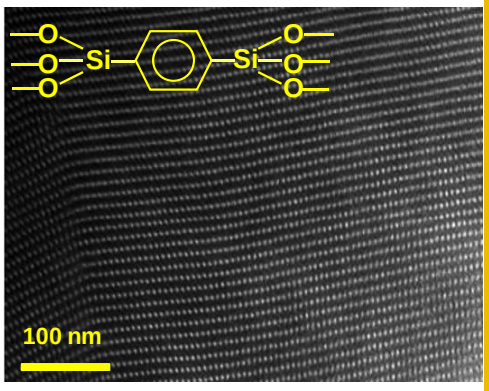

Figure 5: TEM image of cubic PMO with benzene bridging groups [5].

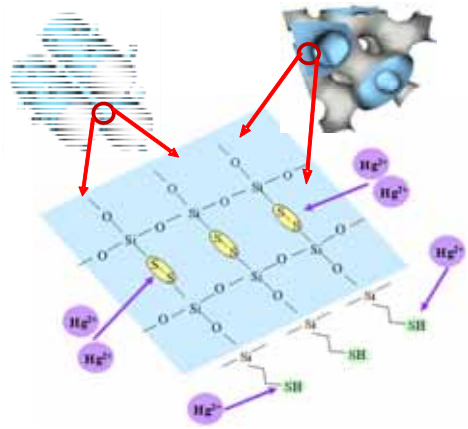

Figure 6: Illustration of sulfur-rich PMO with disulfide bridges and mercaptopropyl pedant groups for adsorption of mercury ions.

sulfur-rich PMO with disulfide bridging groups and mercapto-propyl pendant groups designed for adsorption (removal) of mercury ions from water. High-surface-area and large pore organosilicas and related materials are of great importance for environmental applications such as removal and detection of pollutants present in air and water.

Other examples of the nanomaterials studied are mesoporous oxides such as alumina [6], titania [7], metal organic framework (MOF)-boehmite [8] and OMC-alumina nanosheets composites [9] for catalysis, photocatalysis and energy-related applications.

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Development of New Spectroscopic and Imaging Techniques for NMR

Research

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Our group works on experimental and theoretical spin dynamics, quantum information processing, and developing new spectroscopic and imaging NMR techniques. We improved the methods of coherent spin control and were able to address and manipulate individual quantum states in clusters of up to twelve nuclear spins.

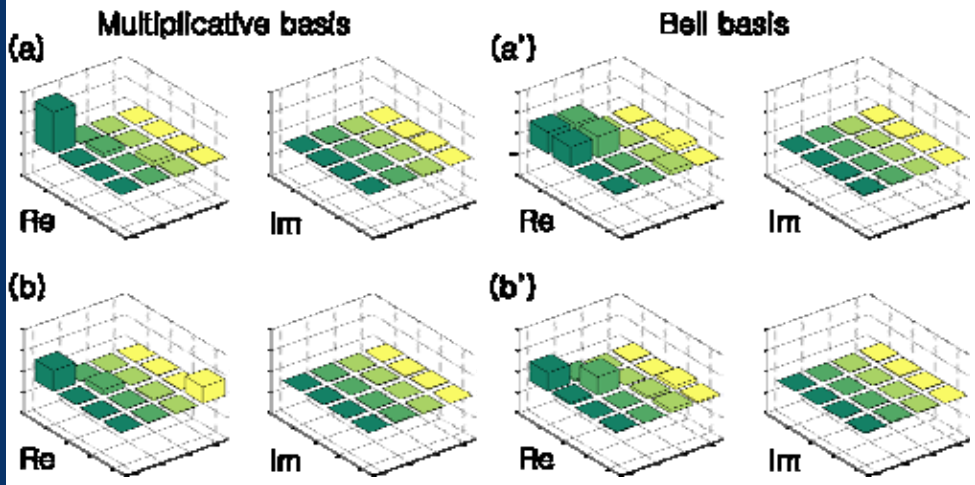

Figure 1: Reconstructed density matrices for the initial state $|\uparrow\uparrow>$ before (a) and after (b) projection on Bell states.

Today we use such systems to study relaxation and decoherence of individual states, and as experimental models for implementing quantum algorithms. We proposed a concept of quantum amplification and illustrated it by finding the exact dynamic solution and by experiments with clusters of coupled nuclear spins. The ideas from quantum information science help us designing the dynamics of complex quantum systems, while NMR "quantum toys" demonstrate feasibility of the proposed approaches. The work on NMR techniques includes creating more efficientschemes for decoupling, cross-polarization, measuring inter-nuclear distances in solids, imaging, and data processing.

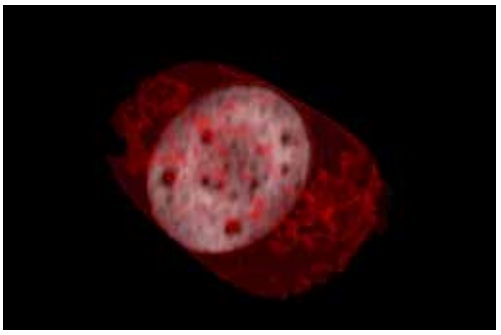

Figure 3: 3D NMR micro-image of pencil eraser.

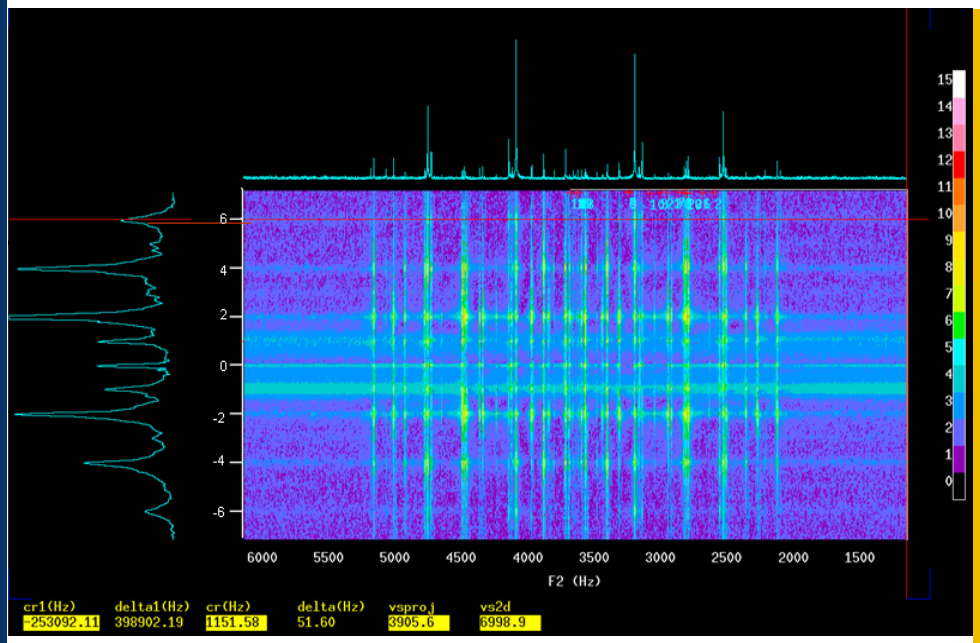

Figure 2: 2D spectrum of benzene in liquid crystal. The vertical axis is the multiple quantum dimension. The horizontal axis is the single quantum dimension. The trace is shown through the 6Q coherence.

Recent Publications

[1] Lee, J.-S., Khitrin, A. K. NMR quantum toys. *Concepts in Magn. Reson.* 30A: 194 –217 (2007).

[2] Lee, J.-S., Khitrin, A. K. High precision measurement of inter-nuclear distances using solid-state NMR. *Concepts in Magn. Reson.* 32A: 57–67(2008).

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Fundamental Studies for the Determination of Enzyme Activity in Cell Signaling Lipids and Chemical & Bio-analytical Separations

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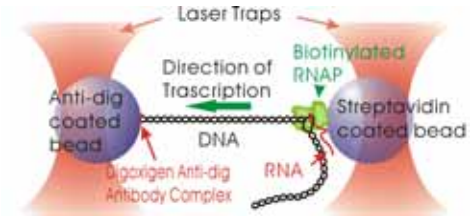
Research

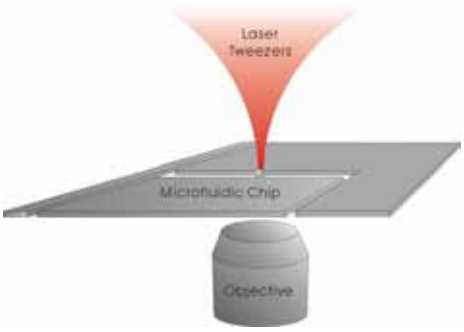
Towards the end of the twentieth century, two exciting techniques, laser tweezers and lab-on-a-chip, emerged. Our research group brings these two brand new techniques together to investigate scientific and technological problems in the fields of biophysics and bioanalytical chemistry, respectively. At the single molecular level, we are mechanically unfolding secondary structures of DNA G quadruplexes using laser tweezers, in an effort to understand the effect of these structures on DNA transcription. We are also placing laser tweezers in a tiny microfluidic channel to build highly sensitive biosensors for detection of biomolecules.

Laser tweezers, as a new technology emerged in the late nineteen eighties, can serve as a desirable tool to perform single molecular studies (see ref 1 and the figure above), as well as to rapidly and accurately identify biological agents. At the focal point of a laser beam, optical tweezers can trap and remotely manipulate *individual* dielectric particles, which include polymeric beads, cells and bacterial particles. The physical properties, such as size and dielectric constant, of a trapped particle can be determined by position sensitive photodetectors[2]; whereas the chemical property of the particle can be evaluated by confocal fluorescence or Raman spectroscopies[3]. These desirable features in a laser tweezers instrument not only enable the ultimate detection limit of single particles, but also facilitate the initial characterization of trapped particles.

Microfluidics is a critical component employed in the recently developed lab-on-a-chip field, in which chemical or biological assays are performed on a single chip as small as a few square centimeters in size. Sample solutions are often manipulated inside channels of micrometers in scale. The small size enables several inherent advantages. *First,* it conserves resources such as space, energy, materials, as well as labor. Compared to traditional techniques, this method occupies much less space and requires significantly less materials. In fact, with a highly



sensitive detection method using fluorescence or force for example, only a few molecules are needed. *Second*, due to the micrometer dimensions of a channel, its volume is on the order of picoliters to nanoliters. This small volume presents a homogeneous environment and miniscule dead volume, both of which increase the sensitivity through enhanced signal to noise ratio. The small volume also significantly decreases detection time. *Third*, the small cross section of a microchamber effectively increase the surveying area for point detection schemes such as those employed in the confocal or laser tweezers setup. This property implies higher concentration sensitivity for biosensors using microfluidics. The higher concentration sensitivity is of particular importance in our laser tweezers based biosensors. This is because the effective space a laser tweezers instrument can probe is on the order of femtoliters (laser spot has about one micrometer in radius). A simple calculation indicates that under standstill conditions, single biological molecules can be detected in real time only when they are in nanomolar concentrations. A continuous flow will dramatically increase this concentration sensitivity. By maintaining a flow inside a microfluidic channel where laser tweezers are placed, a convenient biosensor scheme can be accomplished (see the figure below).



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Biological Applications of Surface Chemistry

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Current support from US Army Medical Research and Material Command

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Journal and Proposal Reviewer

Main research topics include the chemical modification of surfaces in order to encourage cell growth, discourage microbial growth and promote* in vivo *cell behavior in cell culture. Work is currently funded and ongoing in several research areas such as: (a) creating surface chemistries that promote osseointegration of trans-dermal titanium implants in bone, initiate regeneration of soft tissues around implant sites, and limit incidence of infection that may result at the transdermal site; (b) chemical patterning of surfaces to promote controlled growth of neurons and non-invasive stimulation of neuronal action potentials; (c) studying the effect of surface roughness on cell morphology and expression; (d) bioreactor-based growth of tissue; (e) surface-based biosensors.

a.) Tissue Regeneration and Integration. We have worked with the US Army Medical Research and Material Command's Military Amputee Research program for the past 4 years to develop strategies to encourage the integration of implanted, trans-dermal titanium posts in the residual limbs of military amputees. Lower limb amputees who use traditional prosthetic solutions suffer from poor quality of life due to lack of mobility, pain caused by poor fit of stump and socket design, poor joint articulation in short residual limb amputees, and frequent falls. A new solution proposed for amputees is an implanted biocompatible titanium post that is fitted to the residual bone, biologically integrates with the bone, and has an external anchoring point that extrudes through the skin to which an external prosthetic device can be fitted. Such a solution is expected to bring more comfort, increase mobility to allow active exercise, and promote a return to a normal life. We are addressing several different scientific challenges in this work. These include creating an intimate seal between the bone and implant, encouraging revascularization at the implant site, and ensuring a skin seal around the trans-dermal component that will prevent migration of bacteria. We are investigating chemical and physical surface approaches in solving these challenges. Thus, we are chemically modifying the implant material surface to encourage mibration of bone into the post. Our approach involves the attachment of monolayer films to the implant that have chemical characteristics that cells 'like' or that have specific growth factors. We are also investigating the porosity of implant materials as a means to promote in-growth. Re-vascularization is also important at the implant site in order to maintain healthy tissue, particularly dermis/epidermis, since it is this tissue that will provide a barrier to infection. Therefore we are investigating the effect of depositing vascular growth factors the implant surface on the growth of new blood vessels. The chemical and physical properties of the implant surface are also being used in order to encourage a strong and rugged skin seal around the extruding implant. In addition we are investigating the use of surface chemistry to prevent the growth of microbial biofilms on substrate surfaces. **Students who work on this and other projects described below will acquire the following knowledge and skills:** tissue culture; surface modification techniques including chemical patterning and controlled roughness; surface characterization techniques such as contact angle gonimetry, optical spectroscopy (e.g., fluorescence, adsorption, grazing incidence IR), ellipsometry, electrochemistry, surface Plasmon resonance, microscopy, impedance spectroscopy, organic synthesis.

b.) Neural regeneration. We are investigating the use of surface

chemical modification for the regeneration of neural function. This work connects with the prosthetic work described above in that it is our eventual goal to allow the nervous system to control the externally-worn prosthetic limb. In order to achieve this it is necessary to make a functioning, 'living,' neural connection between the body and the prosthetic device. Our approach involves patterning surfaces with monolayers of chemicals that promote the deposition, adhesion and proliferation of neurons on the surface. To date we have achieved effective patterning of neurons on a conducting surface (see Figure 1).

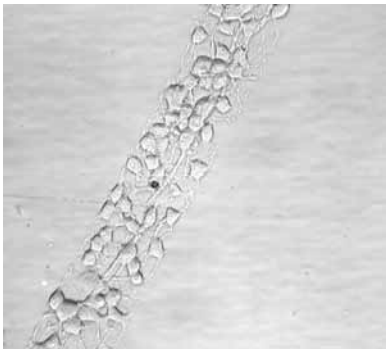

Figure 1: Light microscope image of cultured neurons growing on a conducting ITO surface patterned with 50 micron lines. Cells are growing on area consisting of amino-terminated monolayers. Other areas are 'back-filled' with methyl-terminated monolayers.

By applying a voltage to the surface, we have been able to induce an action potential in the neuron. This is a first step in regenerating neural function at a wound site. Our goal is to induce action potentials across newly formed synapses in neural assemblies. We have also recently induced action potential by light stimulation. **Students who are involved in this work will use the techniques described in project (a) above in addition to having an opportunity to train in electrophysiological techniques at a collaborator's site.**

c.) Cell-Surface Interactions. Traditional cell culture is carried out in tissue culture plastic or glass. It is clear that the chemical and physical surface properties of these materials have profound effects on cell morphology and protein expression in cells that are adherent. For example we have modified surface roughness in plastic and dramatically altered both the physical shape of cultured fibroblasts as well as gene expression—the cells became spindle-like, i.e., more *in vivo* in shape, and for some roughness domains substantially reduced the expression of extracellular matrix (ECM). It is particularly important that when cell culture is used to screen the effects of drug targets, cells behave in culture the same as they behave *in vivo*. We believe that our chemical and roughness approaches to surface modification will enable us to tune the behavior of the cells to their typical *in vivo* behavior. **Students who work on this project will use all of the techniques described above, including cell culture.**

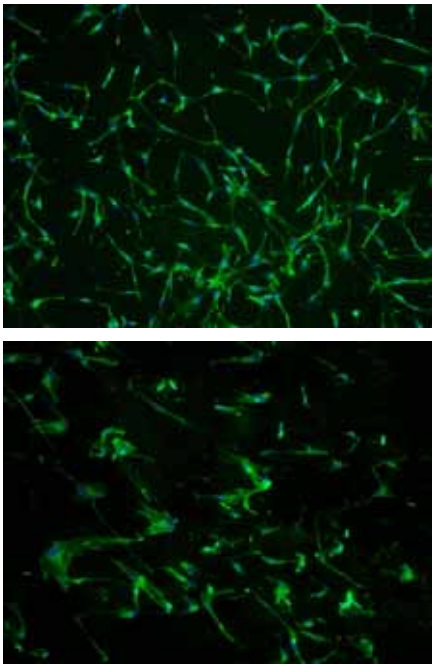

Figure 2: Fluorescence microscope images of neonatal fibroblasts on rough (top) and flat (bottom) PDMS surfaces.

d.) Tissue Regeneration in a Flow-Through Continuous Bioreactor. We have developed a continuous bioreactor for the *in vivo* growth of tissue. The patented technique involves the use of agarose beads doped with magnetic nanoparticles to which cells of different types (e.g., smooth muscle) are attached. The bead-cell assembly is suspended in flowing medium by means of an externally applied magnetic field. To date we have grown tube-like tissue suitable for use to template vascular growth.

e.) Biosensors. Our work in sensors has been ongoing for over ten years and has involved the creation of a microfluidic-based hand-held sensor device for measuring a panel of blood analytes including sodium, potassium and blood urea nitrogen (BUN). This work involves molecular modeling of large organic molecules to determine the likelihood of analyte binding, synthesis by solid or solution phase methods, testing and inclusion of the ligand into a sensor format. Sensor formats have included planar electrodes, optodes and more recently, surface-based monolayers. This work has resulted in several patents.

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New Heterocyclic Methodology Applied to the Synthesis of Liquid Crystal Materials for Transformative Display and Non-display Technologies

Research

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NE Ohio Regional Editor of *Molecules* (1999-2005); Associate Editor of *Liquid Crystals Today* (9/03-7/04); Editor of *Liquid Crystals Today* (7/04-6/08); EPSRC (Engineering and Physical Sciences Research Council) Panel Reviewer.

The main focus of our research is on the creation of new synthetic methodology (primarily heterocycle-based) and its application to the synthesis of novel self-organizing materials. Liquid crystal materials are at the forefront of flat-panel display technology and yet many liquid crystal phases are still relatively unexplored as are the potential technological applications. Our research is mainly targeted toward the synthesis of ferroelectric liquid crystals that show exceptional promise as materials for fast, high contrast displays with wide viewing angles. We employ a wide range of techniques in the physical evaluation of these materials including polarizing optical microscopy (POM) and differential scanning calorimetry (DSC).

Heterocycle-based materials have found a unique place in the field of liquid crystal display materials. Calamitic liquid crystals are typified by a rod like (or lath-like) shape with a high level of shape anisotropy. A large lateral dipole is a requirement for certain display technologies and the dipole is often created with the incorporation of polar groups that are attached to the rigid core such as fluorine and nitrile moieties. However, the incorporation of these relatively large lateral groups results in the weakening of lateral intermolecular association and therefore an accompanying reduction in mesophase stability.

Five-membered heterocycles such as 2,5-disubstituted thiophene, 2,5-disubstituted 1,3-thiazole, and 2,5-disubsituted 1,3,4-thiadiazole rings are relatively linear and yet have large lateral dipole moments built into the heterocyclic core. As a result liquid crystals containing these types of core often have high mesophase thermal stabilities as well as large in-built lateral dipoles.

Over the last few years our work has concentrated on the development of new methodology that has been utilized in the construction of materials incorporating heterocyclic core groups such as thiophene, 1,3-thiazole, 1,3,4-thiadiazole, and thieno[3,2-*b*]thiophene. We have established new flexible and high yielding synthetic methods that allow us to access new core structures that were previously inaccessible or proceeded in low yields. Incorporation of these cores has led to the synthesis of materials that have remarkable display properties. For example, we recently synthesized the first ferroelectric fluorothiophene-based liquid crystal (Figure 1) that appeared to show de Vries behavior (a lack of layer contraction upon cooling from the SmA

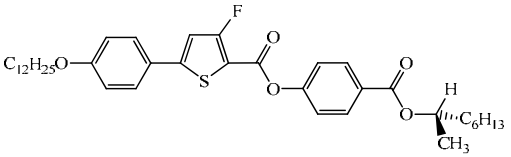

Figure 1. Ferroelectric fluorothiophene exhibiting de Vries-like behavior

to SmC phase). The vast majority of ferroelectric materials do not exhibit this behavior and as a consequence the layer contraction is manifested as lines on the display which render it useless.

This has been one of the major roadblocks to the commercialization of ferroelectric technology and as a result our work may lead to the transformation of the low-power flatpanel display industry.

New methodology has recently come to fruition in the synthesis of alkoxythiophenes (a system that was previously very difficult to prepare). γ-Keto esters were prepared and subjected to ring closure using Lawesson's reagent to give the alkoxythiophenes in excellent yields (Figure 2).

The prepared building blocks were then used in the construction of ferroelectric and high polarizabilty materials for non-linear optical applications.

1,3-Thiazoles are relatively rare in the liquid crystal field due to the few synthetic methodologies that are available for the preparation of systems other than 2,5-diaryl-1,3-thiazoles and 2,5-disubstituted systems with one aryl and one alkyl group. Recently our group has again exploited ring-closing methodology in the construction of 5-alkoxy-2 aryl-1,3-thiazoles (Figure 3). These systems are expected to be highly polarizable and

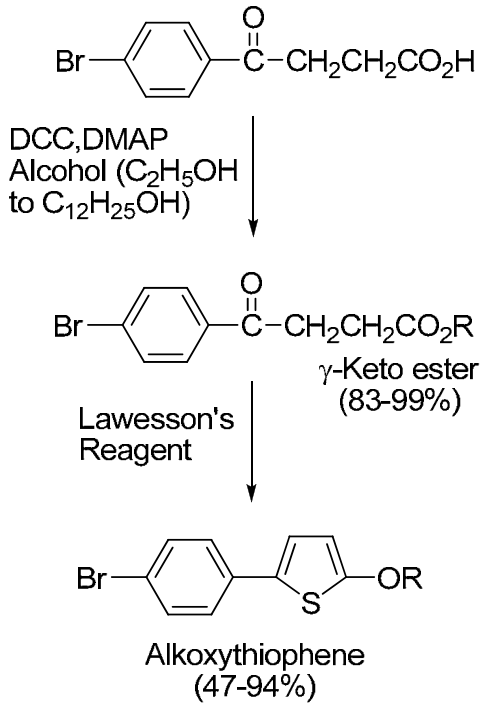

Figure 2. Efficient synthesis of flexible alkoxythiophene building blocks

this is reflected in their high transition temperatures. Again, ferroelectric materials (not shown) were prepared from alkoxythiazole building blocks. These materials display very unusual smectic C textures under the microscope and have yet to be fully identified (Plate 1).

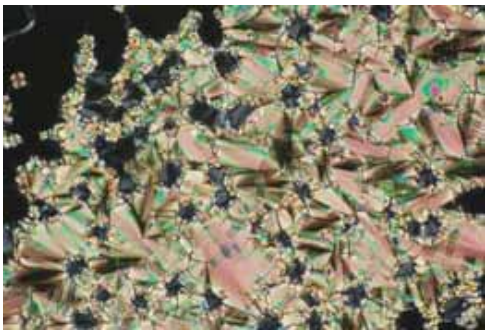

Plate 1. Unusual texture of ferroelectric 5-alkoxy-1,3-thiazoles

High polarizability materials have been utilized in nonlinear optical applications such as light valves and harmonic generators. Compact rigid core units packed with electron density such as thieno[3,2-*b*]thiophene would appear to be ideal cores but again are extremely rare in the LC field due to a dearth of methodology available for their synthesis. We have explored new approaches to these electron-rich cores that provide highly flexible substrates, in high yields and with straightforward purification (Figure 4). These building blocks often contain a bromine atom that provides a powerful handle for functional group transformation. Palladium-catalyzed cross-coupling and carbonylative couplings for example, are typically used for expansion of the rigid core and the introduction of carbonyl-based derivatives such as esters and ketones.

The exploration of new synthetic methodologies in the synthesis of thieno[3,2-*b*]thiophenes is central to our work and is currently being carried out by both graduate and undergraduate students. Expansion of this field will lead to the creation of new materials for semiconductor applications, all-optical switches, spatial light modulation etc. Preliminary evaluation of the targets shown in figure 4 reveals materials

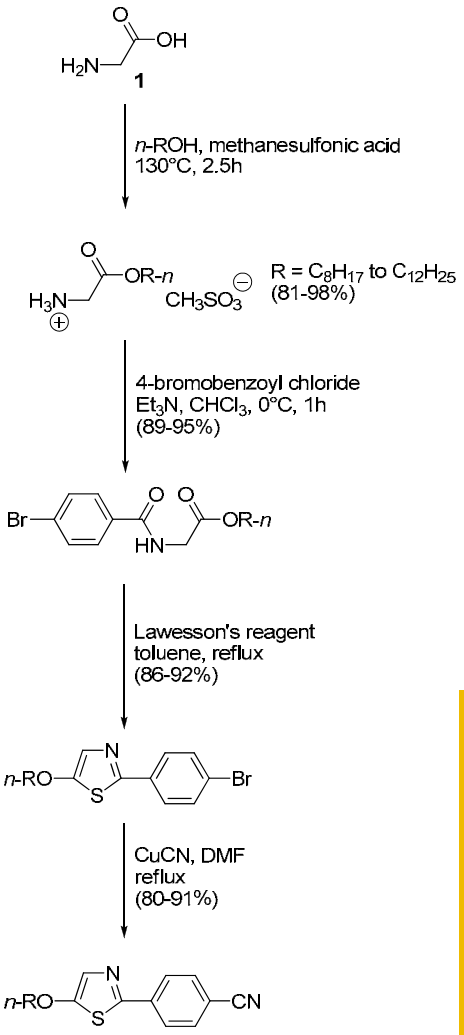

Figure 3. Efficient construction of 5-alkoxy-1,3-thiazoles

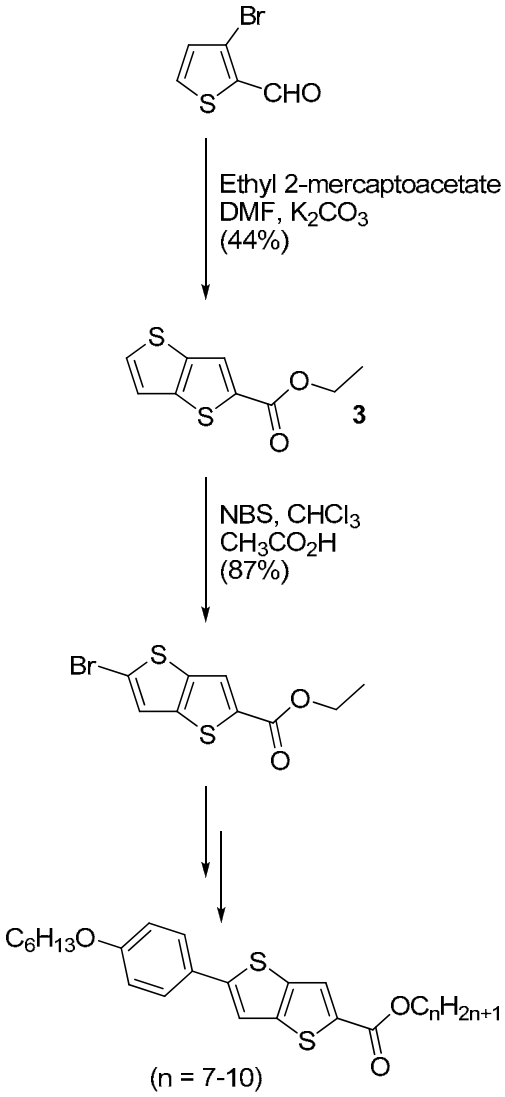

Figure 4 Synthesis of thieno[3,2-*b*]thiophene targets

that exhibit broad SmA phases. Careful modification of the molecular structure will be carried out in order to generate nematic phases for high birefringence applications, and tilted smectic phases for ferroelectric and antiferroelectric display and non-display devices. Ongoing work will additionally probe structure-property relationships of molecules incorporating this core in order to optimize mesophase thermal stability and other physical properties.

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Organic Synthesis: Synthetic Methods Development, Organofluorine Chemistry, Synthesis of Fluorinated and S-Heterocyclic Liquid Crystalline Materials, Synthesis of Fluorinated Bioactive Compounds

Research

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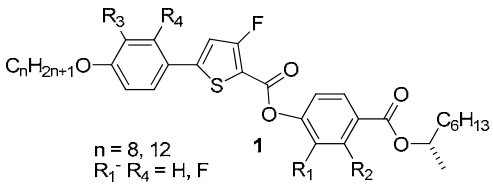
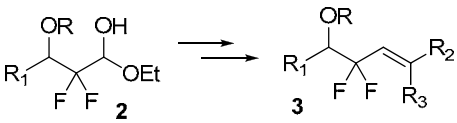
Research in the Sampson group is focused in the field of organic synthesis, with an emphasis on the development of new synthetic methods and their subsequent application in the synthesis of targets which either exhibit liquid crystalline properties or possess interesting biological activity. Several projects involve work in the field of organofluorine chemistry and S-heterocyclic chemistry, including the synthesis of fluorinated heterocycles.

Fluorine has a number of unique properties (e.g., small size, high electronegativity, strong C-F bond) that make it an attractive substituent for the manipulation of the electronic environment within a molecule, without unduly altering the steric requirements of the compound. We are exploiting these effects in several areas.

The strong lateral molecular dipole imparted by fluorine substituents within the core rings of liquid crystalline compounds is achieved with only a minimal impact on the molecular breadth. While fluorophenyl-based liquid crystalline cores are well-known, the incorporation of fluorine into heterocyclic cores is not well developed. We are working on new approaches for the construction of fluorinated thiophenes and other S-heterocycles, and are applying this chemistry in the synthesis of novel liquid crystalline materials containing these fluoroheterocyclic cores (e.g., **1**).[1]



In related studies, we are exploring new entries to alkoxy-substituted and other non-fluorinated S-heterocyclic cores for use in liquid crystal applications. Recent work in this area has focused on the synthesis of 1,3-thiazole-, 1,3,4-thiadiazole- and thieno[3,2-*b*]thiophene-2-carboxylate esters.[2]



We are also exploring the development of new approaches for the incorporation of difluoromethylene groups into organic targets based on the use of $BrCF_2CO_2Et$, an inexpensive precursor that does not suffer from the environmental disadvantages associated with many other simple halofluoroalkyl-containing building blocks. In one project, we have developed a convenient approach to hemiacetal **2** which serves as an excellent intermediate en route to a range of a,a-difluoroalkenyl targets **3** via Wittig- and metathesis-based approaches.

Fluorination is an established approach for manipulating the activity and/or metabolic stability of many biologically important compounds. Our group is interested in applying a number of the above fluorinated building blocks in the synthesis of fluoro-bioactive targets. (All of the above studies are being pursued in collaboration with Dr. Alex Seed's group.)

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Drug-Bioreceptor Interactions, Quantitative Structure Activity Relationships and Drug Design: Interactions of Drugs with Nuccleic Acids

Among the drugs currently under investigation as potentially useful anticancer drugs and/or antiviral agents, there are many which exert their pharmacological action by direct interaction with nucleic acids. We examine the interaction of drugs with nucleic acids; investigate the structure and activity of anticancer drugs, antiviral agents, antibiotics, and interferon inducers; and study the relationship between structure and biological function. We use a variety of techniques such as molecular co-crystallization/X-ray diffraction, solution spectroscopic techniques, bioassay and computer-assisted methods. The specific aims of our research are to elucidate the mechanisms of drug-nucleic acid interactions; to obtain a more comprehensive understanding of the chemical structure requirements and molecular mechanisms of anticancer or antiviral drug action and interferon induction; and to develop a rationale for the design of more effective and less toxic drugs for the treatment of neoplastic diseases, viral infections, and infectious diseases.

We are currently investigating a number of fascinating problems in biochemistry and computational chemistry such as drug-nucleic interactions, structure and activity of anticancer drugs, antiviral agents, antibiotics and interferon inducers, and structure-activity relationship studies. Some of the research projects which are under investigation include the following:

Interaction of drugs with biopolymers:

- Structural studies of drug-biopolymer complexes.
- *In vitro* antiviral studies of drug-biopolymer combinations.

In vitro antiviral, anticancer, antibacterial activity studies of polyphenols.

Computer-assisted molecular/drug design and quantitative structure-activity relationship (QSAR) studies:

- Structure and activity/property relationships of chemical compounds such as anti-viral agents, anticancer drugs, antibiotics, interferon inducers, and liquid crystal compounds.
- Modeling chemical transformation pathways using graph-theoretic transforms and structure-reactivity maps.
- Molecular modeling using similarly-based algorithms and techniques.
- Molecular design and mixture formulation of liquid crystals.
- Correlation and prediction of aqueous solubilities of organic pollutants and related compounds.
- The development and application of computer algorithms and software using molecular topology, chemical graph theory and chemical information theory for quantitative molecular similarity analysis (QMSA) and quantitative structure-activity relationship (QSAR) studies.

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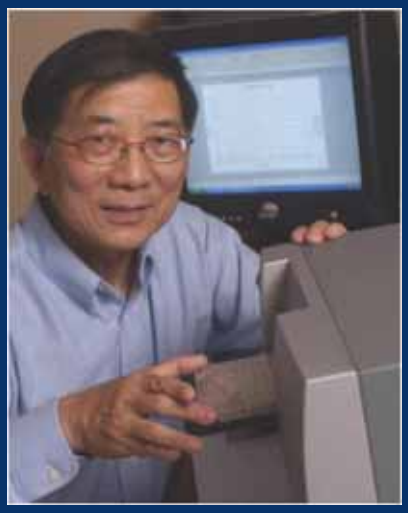

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High Resolution Rotational Spectroscopy as a Tool for Investigating Hydrogen Bonding, Biomolecule Conformations, and Solvent-Induced Conformational Changes

Research

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Funding:
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We investigate the conformational structures of small biomolecules using two Fourier-transform microwave (FTMW) spectrometers. The structural sensitivity of the technique allows us to systematically investigate the affects of hydrogen bonding on conformational structure. We have begun to investigate the conformational preferences of small peptides using a newly developed laser vaporization beam source for our spectrometers. We are also interested in the spectra of small chiral molecules and their hydrogen-bonded complexes, and we are seeking to record the spectra of diasteromeric complexes.

Rotationally-resolved spectroscopy provides the highest resolution structural information about molecules and molecular clusters. Transition frequencies, measured experimentally using Fourier-transform microwave (FTMW) spectrometers, are extremely sensitive to the molecular moments of inertia, and ultimately to the molecular structure. The technique is so sensitive to structure, that we are able to distinguish between the cis and trans forms of m-cyanophenol (Figure 1).

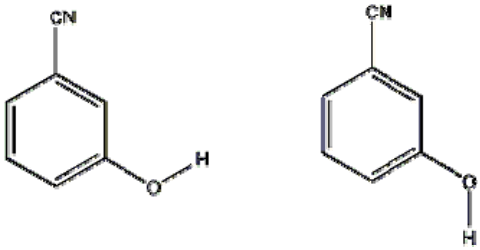

Figure 1: cis and trans m-cyanophenol.

The rotational transitions of these two conformational isomers are separated by about 20 MHz, and are easily resolved by our FTMW instruments which have a resolution of 2.4 kHz. The related species p-cyanophenol displays an interesting splitting of the rotational transitions caused by tunneling along the internal rotation coordinate of the hydroxyl group. We were able to use the measured splittings to determine the potential energy barrier to internal rotation to be 1413 cm^{-1}.

We have used FTMW spectroscopy to detect and identify the rotational spectra arising from four unique conformational isomers of 2-pentanol and 14 unique conformers of 2-hexanol [1]. A portion of the rotational spectrum of 2-hexanol is shown in Figure 2. The spectrum illustrates the resolution possible with rotational spectroscopy; features arising from five different rotational transitions of a single conformer are evident in the scan segment shown.

The high resolution of the technique is ideal for detecting changes in molecular structure brought about by interactions with neighboring molecules. Hydrogen bonding and van der Waals interactions, while weak, may sufficiently alter the potential energy landscape to change the structure of the most stable conformation of an isolated molecule. We have used our instruments to conclusively measure, for the first time, the structural changes brought about by intermolecular interactions. We have found

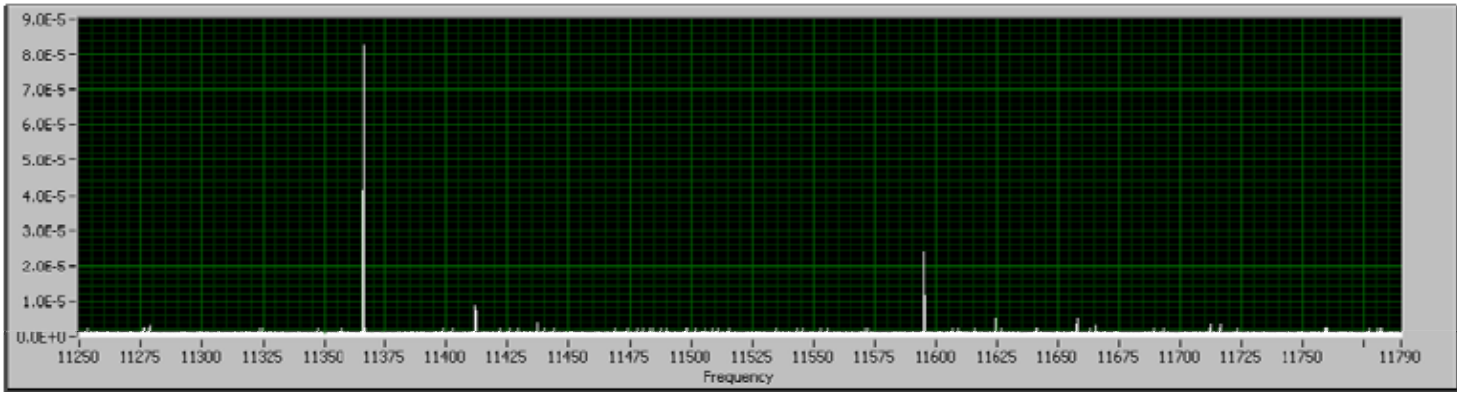

Figure 2: Portion of the microwave spectrum of 2-hexanol showing rotational transitions arising from the aaa carbon-backbone conformer.

that the O – C – C – N torsional angle in 2-aminoethanol increases from 58º to 71º upon formation of a hydrogen bonding network in the 2-aminoethanol-water complex [2]; see Figure 3. Formation of a network of intermolecular hydrogen bonds between glycidol and water drives a comparable increase of the O – C – C – O angle in the glycidol monomer from 41º to 50º [3].

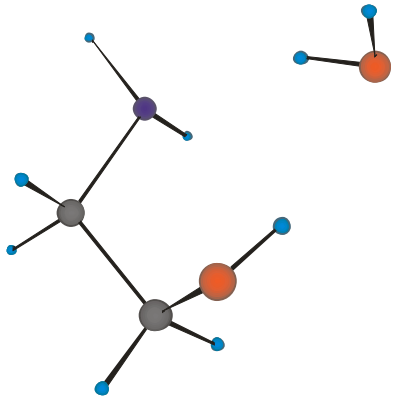

Figure 3: Structure of the 2-aminoethanol-water complex.

We are particularly interested in the three-dimensional structural preferences of biomolecules. The structures of these systems are often intimately related to their biological functions, yet the origins of their conformational preferences and the relative energies of related conformational structures are not fully understood, even for simple systems.

We have investigated a number of amino acid derivatives as part of a larger effort to characterize the structural preferences of biomolecules. Rotational spectra have been used to identify the C^b-exo/C^g-endo structure of prolinamide [4], determine the structures of alaninamide [5], valinamide [6], and leucinamide, and investigate the structure of the alaninamide-water complex [7]. We have collaborated with colleagues at the National Institute of Standards and Technology to identify the C_7^{eq} structure of the alanine dipeptide mimetic, N-acetyl-alanine-N'-methylamide by measuring the internal splittings in the rotational spectrum [8]. The C_7^{eq} structure is characterized by a 7-membered ring, stabilized on one side by an intramolecular hydrogen bond from the methylamide to carbonyl. Interestingly the C_7^{eq} structure is calculated to be the most stable conformation of alanine dipeptide isolated in the gas phase, even though alanine dipeptide adopts a polyproline-II conformation with as few as four surrounding water molecules [9].

Larger biological molecules have intrinsically low vapor pressures and are therefore difficult to study by rotational spectroscopy. Glycine, for example, decomposes before it reaches its melting point of 290ºC [10]. We have developed a unique laser-vaporization source for our FTMW spectrometers, so that we can quickly vaporize these thermally unstable molecules without decomposition.

Laser light from a Continuum MinLite Nd:YAG laser (second harmonic; 532 nm, 20 mJ/ pulse) is focused onto a sample film coating a drum; see Figure 4.

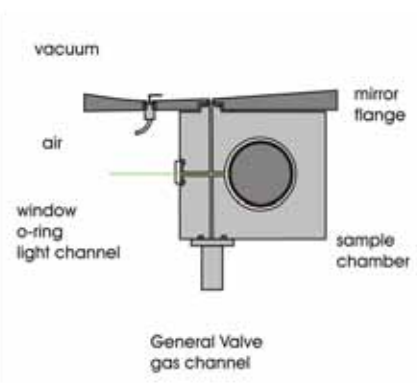

Figure 4: Design of the laser vaporization source.

The pulse of laser radiation vaporizes the sample into a stream of argon gas flowing over the surface; the argon gas carries the sample through the mirror flange and into the resonant cavity of the FTMW spectrometer. Each laser pulse completely vaporizes a spot of film, so the sample drum is continuously rotated and translated to expose fresh sample film to each pulse of focused laser radiation. A picture of the laser vaporization source is shown in Figure 5.

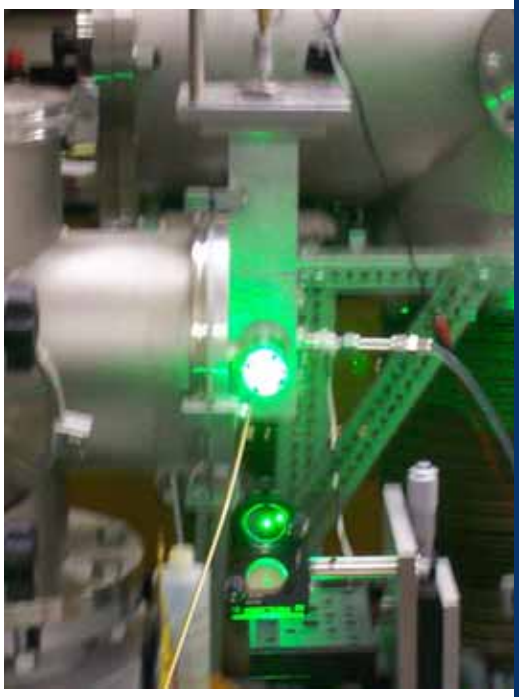

Figure 5: Laser vaporization source for FTMW spectrometer.

Our laser vaporization source is one of only five worldwide on FTMW instruments. We are using our new source to investigate the rotational spectra of peptides and to look for the spectral signatures of peptide secondary structural motifs such as alpha helical turns.

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Research

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Our research activities concentrate on the design and synthesis of organic materials with selected electronic and optical properties such as semiconductor behavior and fluorescence. The range of materials we study encompasses small molecule single crystals, molecular glasses, liquid crystals and polymers. As materials scientists we seek to discover and optimize new, interesting and useful physical properties of materials and therefore we collaborate closely with specialists to fully understand and exploit the materials. Whenever possible, and certainly whenever necessary, we will enhance or develop the appropriate synthetic methodologies required for the ultimate practical preparation of our materials.

Our current research interests and repertoire of projects involves quite a broad subject area. Here a brief description of just a few active projects is provided.

In the area of liquid crystals (LCs) we are pursuing projects driven by both basic and applied issues. On the more basic science side we are investigating some aspects of the fundamental boundary conditions of mesogenic behavior. Conventional calamitic LCs are characterized by a dimensional aspect ratio wherein the long axis is usually comprised of a combination of hard and soft segments. Perturbations of this aspect ratio that result from hard segment bending (so called *bent-core* materials) are currently a popular area of study in which we participate, especially with the goal of looking at cybotactic structures or the generation of biaxiality in nematics.[1] We are also examining perturbations in the aspect ratio and their behavioral ramifications based on bending at the junctions of hard and soft segments. This latter simple and fundamental *bent-junction* structure modification has thus far been examined significantly less than *bent-core* systems and it remains to be seen if this structure modification will be of any utility.

A relatively new LC project deals with control of light absorption in selected spectral regions, especially in the infrared. Absorptions in the IR region of interest are due to relatively high strength bonds and/or bonds to hydrogen. Of course conventional LCs contain numerous bonds like these. Strategies to reduce (or ideally eliminate) this absorption involve the substitution of deuterium for hydrogen (which just shifts the absorption instead of eliminating it) and replacement of hydrogen by fluorine. The latter approach is especially interesting but is fraught with side effects resulting from a significant level of fluorination producing dramatic changes in phase identity, temperature range and enthalpy. Nonetheless, we have prepared a large number of interesting highly fluorinated LCs and simultaneously we have developed some alternative approaches to address the overall absorption problem.

We are pursuing a project in organic semiconductors (OSCs) with applications in transistors and solar cells in collaboration with Prof. Ellman in the KSU Department of Physics. LCs also serve as an appealing media as OSCs. The ability of LCs to self assemble into organized structures is particularly relevant for device fabrication as sophisticated deposition tools are not required. Charge transport in condensed organic matter is highly influenced by structural features including those that promote intermolecular orbital overlap and/or attenuate polaron binding. We have prepared and evaluated a variety of heterocycle (especially pyridine) containing calamitics due to a propensity of this heterocycle to deliver crystal-like high order smectic phases. Time of flight (TOF) measurements of some of these LCs indicate large and useful ambipolar charge mobilities approaching 1 cm^{-2}/Vs. [2]

In the area of single crystal organic semiconductors we are examining structure features that promote high charge mobility. One approach, seen in **Fig. 1**, involves selective localized fluorination in order to promote highly cofacial organization. The electrostatic interaction between perfluorinated and nonfluorinated aromatics is well known and we have been able to adapt it to some large polynuclear aromatics.[3] An undesirable side effect of such fluorination has been the creation of dipolar molecular structures, which themselves tend to impede charge

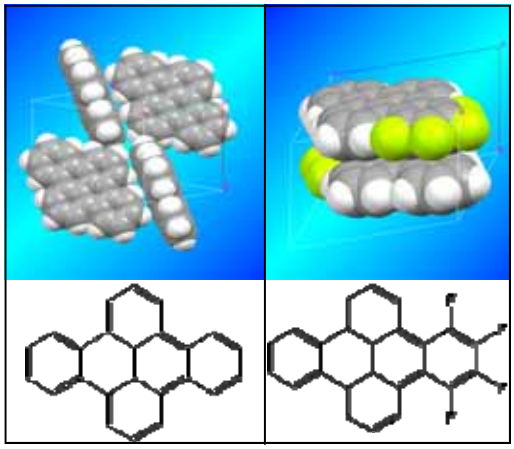

Figure 1: Left. Dibenzo[*fg,op*]naphthacene crystallizes in a herringbone fashion. Right. Selective 1,2,3,4-tetrafluorination of the dibenzo[*fg,op*]naphthacene results in highly cofacial crystallization. Note the molecular dipoles oppose each other. Ref [3].

transport. We are now working on a scheme to deliver the requisite cofacial interaction but with zero dipole moment. An alternative approach to high mobility materials entails the intentional introduction of high Z elements, thus providing two simultaneous potential benefits. First, as in the case of 1,4-diiodobenzene, which has hole mobility in excess of 10 cm^2/Vs, close I-I contacts provide a path for charge transport in addition to more typical p-p interactions.[4] Second, the iodine atoms reduce the deleterious effects of molecular vibrations on charge mobility.

A major area of emphasis in our research is the development of fluorescent tags for biological imaging.[5-7] In particular, we are developing special photoswitchable (fluorogen-fluorophore) systems [8] that are protein targeted and operate at the single molecule level for superresolution (SR) imaging. In SR imaging the diffraction limit (DL) is defeated by examination of an evolving sparse set of fluorophores. Since typical organic fluorophores can emit significantly more photons than average fluorescent proteins, organic fluorophores have an advantage in SR imaging schemes, but targeting to specific cellular proteins must be provided.

A current project with colleagues at Stanford University (located in the Departments of Chemistry, Radiology and Developmental Biology) is typical about how we like to undertake collaborative research. We perform the synthesis work here on the single molecule fluorogens designed in conjunction with our collaborators. Next, the fluorophore photophysics is evaluated and then the bioconjugation and single molecule imaging is performed at Stanford. A recent accomplishment involving targeted single molecule SR imaging in a living organism is noteworthy. The results of labeling *C. crescentus* bacteria are seen at top in **Fig. 2.** Imaging using standard amino-DCDHF (top left) is diffraction limited while imaging using the azido DCDHF fluorogen (top right) is obtained with superresolution. In both cases the DCDHF is functionalized with a HaloTag™ that reacts with the complementary fusion site on both polar and mid plane proteins. With SR the detailed course of cell division can be observed with about a 30 nm scale of precision (~10X that available under DL conditions). This method has also been applied to living and fixed mammalian cells, as seen bottom **Fig 2.** Preliminary experiments with Azido DCDHF and fixed BS-C-1 cells demonstrate that the SR technique delivers ~5X resolution enhancement vs. the standard DL imaging of microtubule structures.

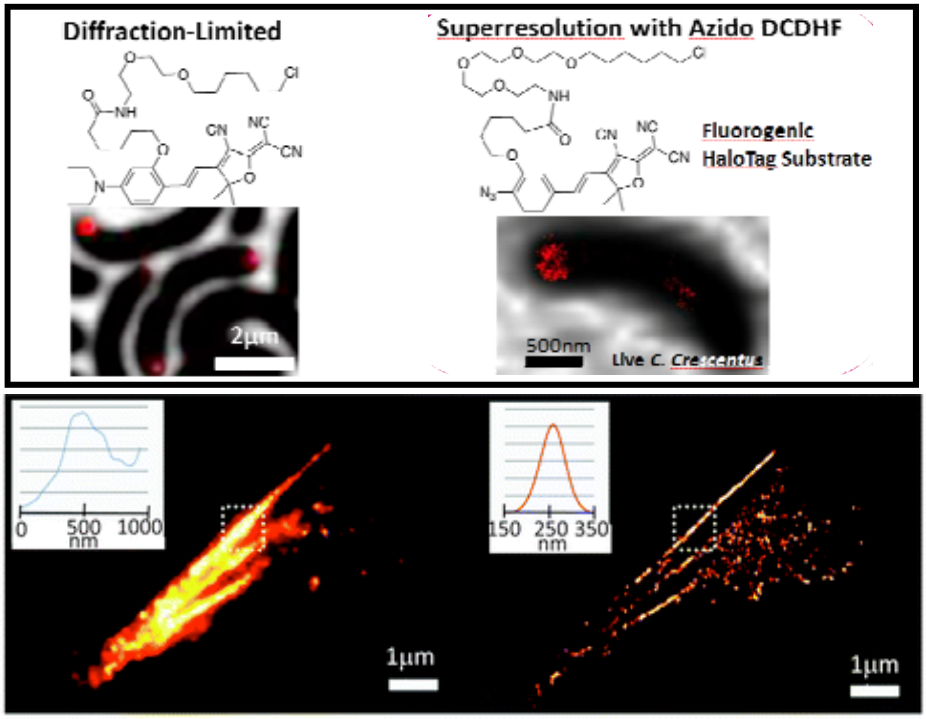

Figure 2: Superresolution imaging techniques based on sequential imaging of sparse subsets of single molecules require fluorophores whose emission can be photoactivated. **Top:** Living bacteria are ideal candidates for SR imaging. HaloTag-DCDHFs were used to highlight protein localization patterns in live *Caulobacter crescentus* bacteria, which possess the biologically interesting ability to divide asymmetrically. SR images produced by photoactivation of a DCDHF azide fluorogen not only display the expected localization patterns but also reveal additional detail unseen in DL images. For PopZ at the cell pole, the protein forms an asymmetric cap-like structure with a curvature that hugs the shape of the bacterial membrane. **Bottom:** (left) Fixed BS-C-1 cells expressing HaloEnz-a-tubulin labeled with DCDHF fluorogen and using conventional DL imaging. Here the indicated microtubule measures 450±40nm FWHM. (right) The same cell as at left but now examined with SR imaging. Here the same microtubule measures 85±15nm FWHM. Images from Ref [8].

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Liquid Crystal Dispersion for Displays and Related Electro-Optic Devices

Research

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Doolittle Prize of the American Chemical Society (1989)
Goodyear Corporate Inventor Award (1997)
National Science Foundation Pioneer Award (2003)

Funding:
Ohio Third Frontier Industry

My research focuses on the development of polymers or particles dispersed in liquid crystals. My lab is developing nano-structured polymer dispersions that have high transmission, fast switching speeds and large phase shifts, useful for high speed displays and beam steering devices. We are also developing ferroelectric nanoparticle/liquid crystals dispersions as a means of enhancing the physical properties of the host. With funding from Ohio Third Frontier, we are designing and synthesizing high twisting power chiral designed to improve the performance of bistable cholesteric displays. Most recently my lab has used electro-spinning to form liquid crystal fibers that offer great scientific challenges and opportunities for entirely new applications. Finally we are working with collaborators locally and around the world to develop flexible liquid crystal displays.

We are all familiar with the liquid crystal display, found in our cell phones, laptop computers and flat screen TVs. However, their applications and importance reach well beyond displays. For example, liquid crystals are used extensively in fiber optic communications while essentially all biological membranes are liquid crystalline. My research focuses on developing liquid crystal dispersions that have enhanced or entirely new properties and applying these materials for entirely new applications and products.

Liquid Crystal / Polymer Dispersions:

My lab helped pioneer the development of polymer/liquid crystal dispersions.[1] In our most recent research we are using electrospinning to form liquid crystal fibers.[2] The liquid crystal and suitable polymer are dissolved in a common solvent. With proper selection of materials, concentration and spinning voltage the liquid crystal phase separates into a well aligned core encased in a polymer shell. As shown in Figure 1 the resulting fibers have a uniform shape and thickness and are highly birefringent. Because the liquid crystal phase separates into aligned domains, the fibers respond to an applied external field in a similar manner to the liquid crystal materials found in modern displays. Our research is now focused on understanding the complex details of the fiber formation and how the large electric fields inherent in electro-spinning serve to uniformly align the liquid crystal domains. We are also exploring application of these fibers in a range of electro-optic devices. In the future these fibers may be woven into textiles and used to incorporate displays and sensors directly into clothing.

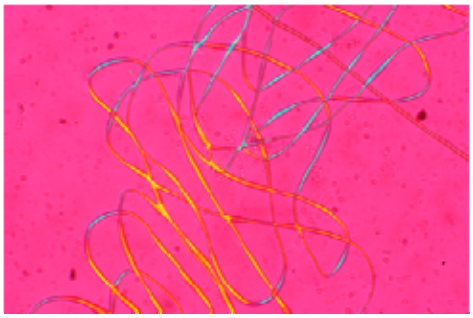

Figure 1: Polarizing optical microscope image of electrospun liquid crystal containing fiber viewed through cross polarizers and a retardation plate.

Ferroelectric nanoparticle / liquid crystal dispersions:

Working with collaborators in the Ukraine and Colorado we disperse ferroelectric nanoparticles in a nematic host.[3] We use both chemical synthesis and mechanical grinding to produce particles of $BaTiO_3$ or $Sn_2P_2S_6$ large enough (>50nm) to retain their ferroelectric properties but small enough (<200nm) to not create a defect in the liquid crystal. In this size range the particles act as a chemical dopant, changing the order parameter of the liquid crystals along with all of the related properties such as birefringence and dielectric anisotropy. Because the particle size is just below the minimum required to form a defect it may be possible to form well ordered structures of these particles in the liquid crystal phase.

Chiral materials:

Addition of chiral materials to a nematic liquid crystal twists the director. This results in a periodic variation in the refractive index of the liquid crystal and a Bragg reflection of light incident on the materials. The materials are therefore colored. These materials have been used for temperature sensors and for low power reflective displays. Improvement in these devices requires enhanced chiral

materials with high helical twisting power. With support from the Third Frontier and collaborating with local companies, we are designing and synthesizing materials where the chirality is the result of the conformation of a twisted core. These cores typically consist of rigid ring structures that are often aromatic. Alkyl chains attached to these cores introduce the required flexibility to the molecule while also enhancing the twisting power.

We are striving to understand the mechanism of chiral induction and how the twisting power varies with temperature. Specifically, for these high helical twisting power materials we are investigating how the specific conformation of the material changes with temperature and how this change affects the twisting power.

***FLEXMatters*:**

Working with regional companies, development agencies and universities I established FLEXMatters. FLEXMatters is a Northeast Ohio initiative to support a growing industrial cluster manufacturing flexible electronic devices. Over the next decade flexible electronics will gradually come to dominate the industry, displacing the current silicon based electronics industry. Because

Figure 2: Boogie Board electronic writing tablet. Picture courtesy of Kent Displays.

they are organic, liquid crystals are ideally suited for use with plastic substrates. Local companies, many using technology developed at KSU, are manufacturing the first generation of flexible LCD devices. For example, Kent Displays is manufacturing and selling the Boogie Board, a low power, electronic writing tablet, Figure 2. The high chirality material mentioned in the last section will be used to improve the contrast and overall performance of the Boogie Board. With support from and collaboration with the Korean Institute of Machinery and Materials we are developing printed displays, using conducting polymers and appropriate liquid crystal materials. We are also developing techniques to produce polymer walls around the pixels in a flexible liquid crystal display. The segregation of polymer walls into the interpixel region provide the mechanical support required without lowering the optical response of the liquid crystal materials, Figure 3.[4] Our goal is to develop materials and processes that can be used now to fabricate commercially viable displays and related electro-optic devices on flexible plastic substrates.

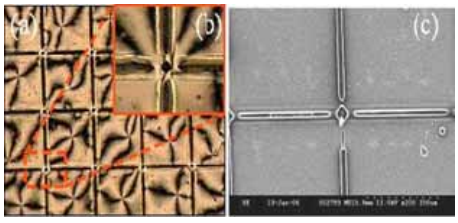

Figure 3: Polymer walls formed by a patterned electric field in a liquid crystal display.

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Graduate students in chemistry may not use the following courses to fulfill degree requirements:

5/70000, 5/70093, 5/70361, 5/70362, 5/70481, 5/70555, 5/70556, 5/70557, 5/70558, 5/70570 and 50795.

Non-chemistry majors may take any of these courses for credit with the permission of their major department and the Department of Chemistry.

Unless otherwise indicated, the prerequisite for 50000-69999 level courses is graduate standing. Unless otherwise indicated, the prerequisite for courses 70000 and higher is doctoral standing.

CHEM 50093/70093
VARIABLE TITLE WORKSHOP IN CHEMISTRY (1-6)
S/U grading. Prerequisite: Special approval and graduate standing.

CHEM 50795
CURRENT TOPICS IN CHEMICAL EDUCATION (1-3)
Designed to present recent advances in chemical research, instrumentation and theory to chemistry educators. S/U grading. Prerequisite: Special approval and graduate standing.

CHEM 60894/70894
COLLEGE TEACHING OF CHEMISTRY (1)
Experience in teaching of chemistry at college level. S/U grading.

Analytical Chemistry

CHEM 50112/70112
ADVANCED ANALYTICAL CHEMISTRY (2)
An advanced study of the theory and applications of analytical chemical equilibria: acid base, precipitation, compexation and redox. Prerequisite: CHEM 40555.

CHEM 50113/70113
CHEMICAL SEPARATIONS (3)
Theory, instrumentation and applications of chemical separations for chemical analysis with emphasis on gas and liquid chromatography. Prerequisite: CHEM 30106.

CHEM 50114/70114
ELECTROANALYTICAL CHEMISTRY (3)
The physical basis of electrochemistry; instrumentation and applications in chemical analysis. Polarography, coulometry, voltammetry and ion-selective electrodes. Lecture 3 hours weekly. Prerequisite: CHEM 40555.

CHEM 60111/70111
THEORY OF CHEMICAL INSTRUMENTATION (2)
General survey course on theory of instruments. Special emphasis on data interpretation and problem solving. Prerequisite: Permission.

CHEM 60115/70115
ANALYTICAL SPECTROSCOPY (3)
An advanced study of the fundamental principles, instrumentation and experimental techniques associated with different analytical spectroscopic methods.

CHEM 61191/71191
SEMINAR: PROBLEM SOLVING IN ANALYTICAL CHEMISTRY (1)
Discussion of recent chemical analysis methods, sample preparation and data handling, as well as practical student experience involving characterization of real samples. IP permissible.

CHEM 62191/72191
SEMINAR: ANALYTICAL CHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 70195
ADVANCED TOPICS, ANALYTICAL (1-3)
Advanced topics in analytical chemistry. Repeat registration permitted. Prerequisite: permission.

Biochemistry

CHEM 50245
BIOCHEMICAL FOUNDATIONS OF MEDICINE (4)
Introduction to chemistry and metabolism of important compounds in biological systems; enzymes and characteristics of enzyme catalysis; regulation of metabolism at molecular, cellular and organism levels; inborn and induced errors of metabolism. Designed and scheduled for, and priority given to, students in integrated life science program. Prerequisite: CHEM 30481 or equivalent.

CHEM 50247/70247
PRINCIPLES OF BIOCHEMISTRY (4)
Introduction to biochemical principles, including chemistry and metabolism of biochemically important compounds, biological catalysts and metabolic regulation. May be taken for graduate credit by chemistry majors. Prerequisite: CHEM 20481 or 30481 and 40555 or 40567 or permission.

CHEM 50248/70248
ADVANCED BIOLOGICAL CHEMISTRY (3)
Chemistry of biologically important molecules. Advanced topics in: metabolic and enzyme regulation; enzyme kinetics and mechanism; DNA replication, recombination, and repair; gene transcription and translation; recombinant DNA technology; selected areas in molecular physiology. Three hours weekly. Prerequisite: CHEM 30284 or CHEM 40245 or CHEM 40247; graduate standing.

CHEM 50263/70263
PHYSICAL BIOCHEMISTRY I (3)
Principles and techniques of physical chemistry used in studying biomacromolecules and biological systems. Topics covered are thermodynamics, spectroscopy, structure and properties of biological molecules. Prerequisite: CHEM 40555 or permission.

CHEM 60249/70249
BIOCHEMICAL TECHNIQUES (2 EACH)
Laboratory work emphasizing modern methods of biochemical investigation. Experiments illustrating use of spectrophotometric, chromatographic and isotopic methods. May be taken for graduate credit by chemistry majors. S/U grading; IP permissible. Co– or prerequisite: CHEM 60247 or CHEM 70247.

CHEM 60250/70250
BIOCHEMICAL TECHNIQUES (2 EACH)
Laboratory work emphasizing modern methods of biochemical investigation. Experiments illustrating use of spectrophotometric, chromatographic, and isotopic methods. May be taken for graduate credit by chemistry majors. S/U grading; IP permissible. Co– or prerequisite: CHEM 60249 or CHEM 70249.

CHEM 60265/70265
ENZYMOLOGY (2)
Basic principles of steadystate and rapid enzyme kinetics; theory and experiment; catalytic mechanisms for selected enzymes. Prerequisite: Permission.

CHEM 60269/70269
NMR: THEORY AND APPLICATION IN BIOCHEMISTRY (1 OR 2)
Basic principles of high-resolution nuclear magnetic resonance will be applied at a general level in the study of biochemical structure and function. Prerequisite: CHEM 30284, 40551 or equivalent.

CHEM 60291/70291
SEMINAR: RECENT DEVELOPMENTS IN BIOCHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 62291/72291
SEMINAR: BIOCHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 70251
COMPREHENSIVE BIOCHEMISTRY I (5)
Molecular and metabolic aspects of biochemistry including: chemistry of metabolism of low molecular weight biochemical structures; biopolymers; enzymes; bioenergetics; molecular basis of organismic systems.

CHEM 60252/70252
COMPREHENSIVE BIOCHEMISTRY II (2)
Supramolecular and cellular aspects of biochemistry including: DNA structure and function; regulation of transcription and translation; principles of supramolecular structure and assembly; membranes; motile systems.

CHEM 60253/70253
COMPREHENSIVE BIOCHEMISTRY III (1)
Supermolecular structure and self-organization of proteins and nucleic acids in chromatin, viruses, ribosomes, motile processes muscle, flagella and axonal transport. Prerequisite: permission.

CHEM 60254/70254
COMPREHENSIVE BIOCHEMISTRY IV (2)
Biological membranes; composition, structure, dynamics and biogenesis; membrane transport and energy transduction. Prerequisite: permission.

CHEM 70295
ADVANCED TOPICS IN BIOCHEMISTRY (1-3)
Advanced topics in biochemistry. Repeat registration permitted. Prerequisite: permission.

Inorganic Chemistry

CHEM 50302
INORGANIC CHEMISTRY II
Physical techniques in inorganic chemistry, molecular structure and bonding, metallic and ionic solids, organometallic chemistry, homogeneous and heterogeneous catalysis; solid-state and materials chemistry, Nanomaterials, nanoscience and nanotechnology. Prerequisite: CHEM 30301 and graduate standing.

CHEM 50303
INORGANIC CHEMISTRY III (2)
Molecular symmetry, molecular orbital theory of polyatomic molecules and octahedral complexes, electronic spectra and reaction mechanisms of d-block complexes, periodic trends Groups 1 and 2 and d-block, bioinorganic chemistry. Prerequisite: CHEM 50302 and graduate standing.

CHEM 50352/70352
INORGANIC MATERIALS CHEMISTRY (3)
Broad survey of the synthesis, properties, characterization and applications of inorganic materials.

CHEM 50365/70365
BIOLOGICAL INORGANIC CHEMISTRY (3)
Physical methods, s-block metals, metal-induced stabilization, electron transfer proteins, oxidoreductases, hydrolases and lyases, metal transport and storage, nitrogenases, group-atom transfer and metals in medicine. Prerequisite: CHEM 30360 and graduate standing.

CHEM 60327/70327
MODERN INORGANIC CHEMISTRY (3)
Synthesis, structure and reactivity of inorganic compounds, including transition metal and organometallic complexes. Prerequisite: CHEM 40362 or equivalent.

CHEM 60337/70337
INORGANIC MAGNETIC SPECTROSCOPY (3)
Applications of magnetic resonance spectroscopic techniques (NMR, EPR and Mossbauer) in inorganic and organometallic compounds.

CHEM 60347/70347
CHEMICAL CRYSTALLOGRAPHY (3)
Structure solution and refinement methods of X-ray diffraction data. Emphasis will be placed on single-crystal techniques.

CHEM 60391/70391
SEMINAR: RECENT DEVELOPMENTS IN INORGANIC CHEMISTRY (1)
Presentation and discussion of current research papers in inorganic chemistry. Participation by students and faculty. IP permissible.

CHEM 62391/72391
SEMINAR: INORGANIC CHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 70395
ADVANCED TOPICS, INORGANIC (1-3)
Advanced topics in inorganic chemistry. Repeat registration permitted. Prerequisite: Permission.

Organic Chemistry

CHEM 50451/70451
ORGANIC MATERIALS CHEMISTRY (3)
Broad survey of the synthesis, properties, characterization and applications of organic and polymeric materials.

CHEM 50476/70476
SPECTROSCOPIC IDENTIFICATION OF ORGANIC COMPOUNDS (2)
Strategies for structural elucidation of organic compounds from analysis of infrared, proton and carbon NMR and mass spectrometric data through lectures and problem solving. Prerequisite: CHEM 30482 and graduate standing.

CHEM 50478/70478
SYNTHESIS OF ORGANIC LIQUID CRYSTALS (3)
Synthesis of organic thermotropic liquid crystals including nematic, smectic and discotic variants. Evaluation of the phase types using polarizing microscopy and DSC. Brief introduction into their use in display devices. Prerequisite: CHEM 30482 and graduate standing.

CHEM 60471/70471
ADVANCED ORGANIC CHEMISTRY—MECHANISTIC ASPECTS (3)
Discussion of organic reaction mechanisms. Chemistry of reactive intermediates, aromaticity, addition/elimination, nucleophilic/electrophilic substitution, bonding theories and other fundamental topics governing organic reactions. Prerequisite: CHEM 30482 and graduate standing.

CHEM 60472/70472
ADVANCED ORGANIC CHEMISTRY—SYNTHETIC ASPECTS (3)
Disconnection approach to organic synthesis. Modern methods for carbon bond formation and functional group interconversion, and their application to natural product synthesis. Prerequisite: CHEM 30482 and graduate standing.

CHEM 60473/70473
STEREOSELECTIVE ORGANIC SYNTHESIS (3)
Modern methods of asymmetric synthesis; introduction to selected methods for Stereoselective N-heterocycle synthesis; application of these methods in natural product synthesis. Prerequisite: CHEM 30482 and graduate standing.

CHEM 61491/71491
SEMINAR: PROBLEM SOLVING IN ORGANIC CHEMISTRY (1)
Practical experience in solution of current problems of structure, synthesis and mechanism in organic chemistry. Participation extends throughout nine-month academic year. Repeat registration permitted. IP permissible.

CHEM 62491/72491
SEMINAR: ORGANIC CHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 70495
ADVANCED TOPICS, ORGANIC (1-3)
Advanced topics in organic chemistry. Repeat registration permitted. Prerequisite: Permission.

Physical Chemistry

CHEM 50555/70555
ELEMENTARY PHYSICAL CHEMISTRY (3)
Fundamental concepts of physical chemistry, with example problems chosen emphasizing application in chemistry and the biological science. Prerequisite: CHEM 10061 and MATH 22005 and PHY 23102 and graduate/doctoral standing. Pre– or corequisite: CHEM 30107.

CHEM 50556/70556
ELEMENTARY PHYSICAL CHEMISTRY (3)
A continuation of CHEM 50555. Areas covered are chemical kinetics, quantum chemistry and the solid state. Prerequisite: CHEM 50555 or PHY 45301; graduate standing.

CHEM 50557/70557
PHYSICAL CHEMISTRY LABORATORY (2)

Experiments in numerous areas of physical chemistry, including the interpretation and reporting of obtained experimental data, correlation of results with theory and an introduction to the computer treatment of data. Pre– or corequisite: CHEM 5/70555. Special course fee: $40 per credit hour (subject to change).

CHEM 50558/70558
PHYSICAL CHEMISTRY LABORATORY (2)
Experiments and interpretation, reporting, and correlation of data with theory. Emphasis on gases, liquids, solutions, surface properties, thermodynamic variables, rates of reaction, transport phenomena and spectral properties. Pre– or corequisite: CHEM 5/70556.

CHEM 50570/70570
INTERMEDIATE PHYSICAL CHEMISTRY (2)
Special topics of physical chemistry, with applications to problems of chemical interest that are not covered in the basic course. Prerequisite: CHEM 5/70556.

CHEM 50571/70571
SURFACE CHEMISTRY (2)
Treatment of basic principles and concepts in surface and colloid chemistry. Relationship to practical systems emphasized. Prerequisite: CHEM 40555 or 40567.

CHEM 50575/70575
MOLECULAR SPECTROSCOPY (3)
Survey of the fundamental principles of the interaction of radiation with matter, with an emphasis on the interpretation of microwave, infrared and ultraviolet-visible spectra. Introduction to group theory and its application to spectroscopic interpretation. Description of modern experimental techniques. Prerequisite: CHEM 40556 and graduate standing.

CHEM 50583/70583
PHYSICAL CHEMISTRY OF MACROMOLECULES (2)
A course designed to cover the basic principles of polymer science. Structure, properties and characterization of polymeric systems will be discussed. Prerequisite: CHEM 40555 or 40567.

CHEM 60541/70541
ADVANCED PHYSICAL CHEMISTRY (3)
Covers basic materials of modern physical chemistry in two broad areas: thermodynamics and introductory quantum mechanics. Prerequisite: CHEM 50556 or equivalent.

CHEM 60542/70542
ADVANCED PHYSICAL CHEMISTRY (3)
Covers basic materials of modern physical chemistry in the area of application of wave mechanics to atomic structures, chemical bonding and reactivity.
Prerequisite: CHEM 50556 or equivalent.

CHEM 60543/70543
STATISTICAL THERMODYNAMICS (3)
Theory and applications of statistical thermodynamics and mechanics on non-interacting and interacting particles of real and model systems; gases, solutions, crystals, polymers; dielectric and magnetic phenomena. Prerequisite: CHEM 6/70542.

CHEM 60563/70563
QUANTUM CHEMISTRY (3)
Basic principles of quantum mechanics. Those aspects of theory of special interest to chemistry emphasized.
Lecture 3 hours weekly. Prerequisite: CHEM 6/70541.

CHEM 60591/70591
SEMINAR: RECENT DEVELOPMENTS IN PHYSICAL CHEMISTRY (1)
Presentation and discussion of original papers from current literature. IP permissible.

CHEM 62251/72251
SEMINAR: PHYSICAL CHEMISTRY (1)
Students register once each year. Participation extends throughout the academic year. IP permissible.

CHEM 70595
ADVANCED TOPICS, PHYSICAL (1-3)
Advanced topics in physical chemistry. Repeat registration permitted. Prerequisite: Permission.

Research, Thesis and Dissertation

CHEM 60050/70050
CHEMISTRY RESEARCH PROPOSAL (3)
The student will prepare an independent and original research proposal that is completely distinct from the thesis project.

CHEM 60199
THESIS I (2-6)
Thesis students must register for a total of 6 hours, 2 to 6 hours in a single semester, distributed over several semesters if desired. IP permissible.

CHEM 60299
THESIS II (2)
Thesis students must continue registration until all degree requirements are met. S/U grading; IP permissible. Prerequisite: CHEM 60199.

CHEM 60898
MASTER'S RESEARCH (1-15)
Research for master's students. Credits earned may be applied toward degree if department approves. Repeat registration permitted. S/U grading; IP permissible.

CHEM 80199
DISSERTATION I (15)
Doctoral dissertation, for which registration in two semesters is required, first of which will be semester in which dissertation work is begun and continuing until the completion of 30 hours. S/U grading; IP permissible. Prerequisite: Admission to candidacy.

CHEM 80299
DISSERTATION II (1 OR 15)
Continuing registration required of doctoral students who have completed the initial 30 hours of dissertation and continuing until all degree requirements are met. S/U grading; IP permissible. Prerequisite: CHEM 80199.

CHEM 80898
RESEARCH (1-15)
Research for doctoral students. Credits earned may be applied toward degree if department approves. Repeat registration permitted. S/U grading; IP permissible.

Correspondence and Information

General Correspondence

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