Kansas State University

AMERICAN CHEMICAL SOCIETY

Oct. 20-22
2004

Program
and
Abstracts

Hosted by :

The Kansas State University Local Section

at the Manhattan Holiday Inn Holidome

530 Richards Drive, Manhattan, KS

Acknowledgements

General Chair	Daniel A. Higgins
Program Chair	J. Vincent Ortiz
Symposia Chairs	
Crystal Engineering – Supramolecular Chemistry	Christer Aakeröy
Drug Discovery and Bioorganic Chemistry	Duy H. Hua
Environmental Chemistry	Larry E. Erickson
Methods of Electronic Structure Theory	J. Vincent Ortiz
Nanostructured Materials and Air Quality	Kenneth J. Klabunde
Sol-Gel Chemistry	Maryanne M. Collinson
Undergraduate Research	Stefan Kraft
Treasurer	Yasmin Patell
Exposition Chair	Earline Dikeman
Undergraduate Program	Janie Salmon
Audio/Video Resources	James R. Hodgson
Program Book	Ruth Hathaway
Printing/Publicity	Ellen Stauffer KSU Div. of Continuing Education
Website	KSU Div. of Continuing Education
Program Book Art	Jessa Talamentez KSU Div. of Continuing Education
Midwest Award	Leah O’Brien
ACS Regional Meeting Planner	John Michael Sophos

Welcome to the

39th Midwest Regional Meeting of the

American Chemical Society

October 20-22, 2004

Manhattan Holiday Inn Holidome

Manhattan, KS

Hosted by the Kansas State University Section

Local Sections of the Midwest Region

Of the American Chemical Society

Ames

Iowa

Kansas City

Kansas State University

Mark Twain

Mo-Kan-Ok

Nebraska

Omaha

Ozark

Sioux Valley

South Central Missouri

Southern Illinois

St. Louis

University of Kansas

University of Missouri

University of Arkansas

Wichita

Table of Contents

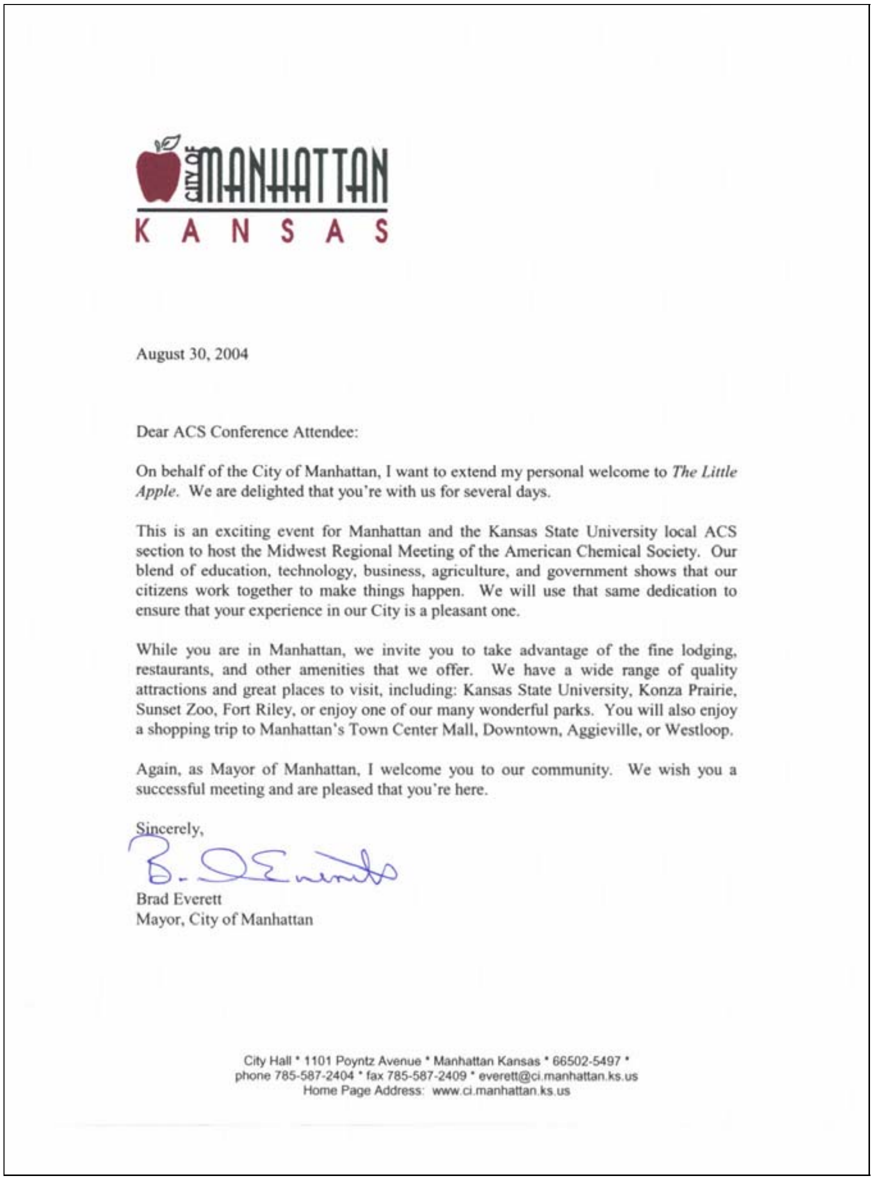
Special Greeting

Technical Program

  Special Symposia

General Sessions

Poster Sessions



CITY OF MANHATTAN
KANSAS

August 30, 2004

Dear ACS Conference Attendee:

On behalf of the City of Manhattan, I want to extend my personal welcome to *The Little Apple*. We are delighted that you're with us for several days.

This is an exciting event for Manhattan and the Kansas State University local ACS section to host the Midwest Regional Meeting of the American Chemical Society. Our blend of education, technology, business, agriculture, and government shows that our citizens work together to make things happen. We will use that same dedication to ensure that your experience in our City is a pleasant one.

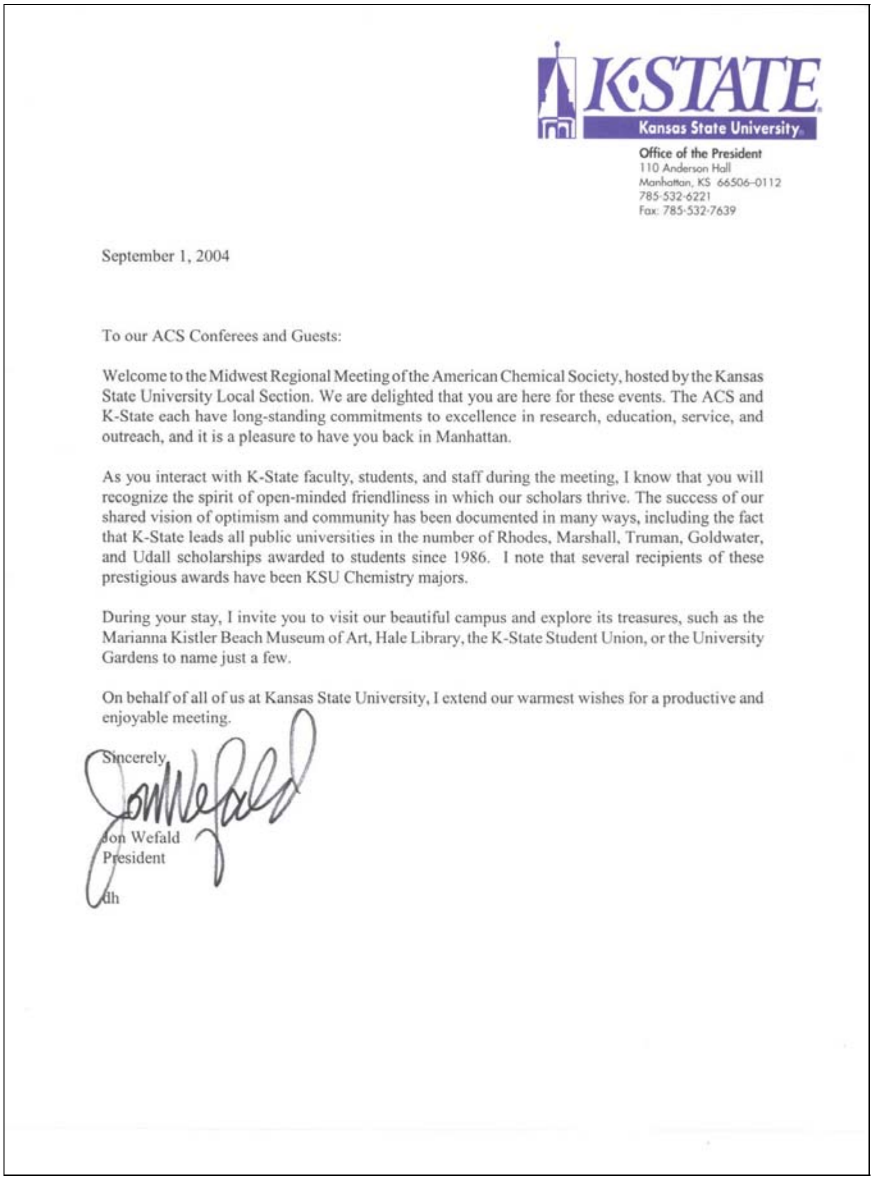
While you are in Manhattan, we invite you to take advantage of the fine lodging, restaurants, and other amenities that we offer. We have a wide range of quality attractions and great places to visit, including: Kansas State University, Konza Prairie, Sunset Zoo, Fort Riley, or enjoy one of our many wonderful parks. You will also enjoy a shopping trip to Manhattan's Town Center Mall, Downtown, Aggieville, or Westloop.

Again, as Mayor of Manhattan, I welcome you to our community. We wish you a successful meeting and are pleased that you're here.

Sincerely,

Brad Everett
Mayor, City of Manhattan

City Hall * 1101 Poyntz Avenue * Manhattan Kansas * 66502-5497 *
phone 785-587-2404 * fax 785-587-2409 * everett@ci.manhattan.ks.us
Home Page Address: www.ci.manhattan.ks.us



K·STATE
Kansas State University
Office of the President
110 Anderson Hall
Manhattan, KS 66506-0112
785-532-6221
Fax: 785-532-7639

September 1, 2004

To our ACS Conferees and Guests:

Welcome to the Midwest Regional Meeting of the American Chemical Society, hosted by the Kansas State University Local Section. We are delighted that you are here for these events. The ACS and K-State each have long-standing commitments to excellence in research, education, service, and outreach, and it is a pleasure to have you back in Manhattan.

As you interact with K-State faculty, students, and staff during the meeting, I know that you will recognize the spirit of open-minded friendliness in which our scholars thrive. The success of our shared vision of optimism and community has been documented in many ways, including the fact that K-State leads all public universities in the number of Rhodes, Marshall, Truman, Goldwater, and Udall scholarships awarded to students since 1986. I note that several recipients of these prestigious awards have been KSU Chemistry majors.

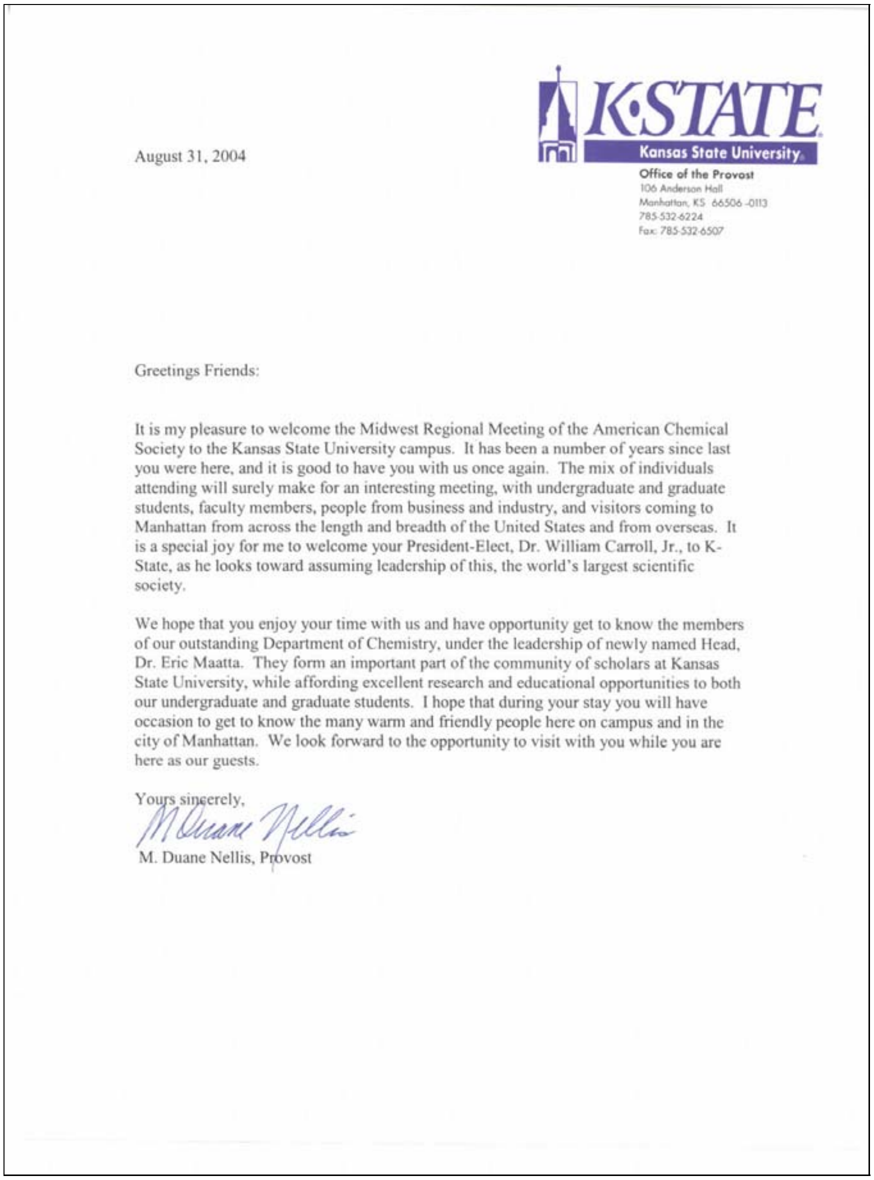
During your stay, I invite you to visit our beautiful campus and explore its treasures, such as the Marianna Kistler Beach Museum of Art, Hale Library, the K-State Student Union, or the University Gardens to name just a few.

On behalf of all of us at Kansas State University, I extend our warmest wishes for a productive and enjoyable meeting.

Sincerely,

Jon Wefald
President

dh



K·STATE
Kansas State University
Office of the Provost
106 Anderson Hall
Manhattan, KS 66506-0113
785-532-6224
Fax: 785-532-6507

August 31, 2004

Greetings Friends:

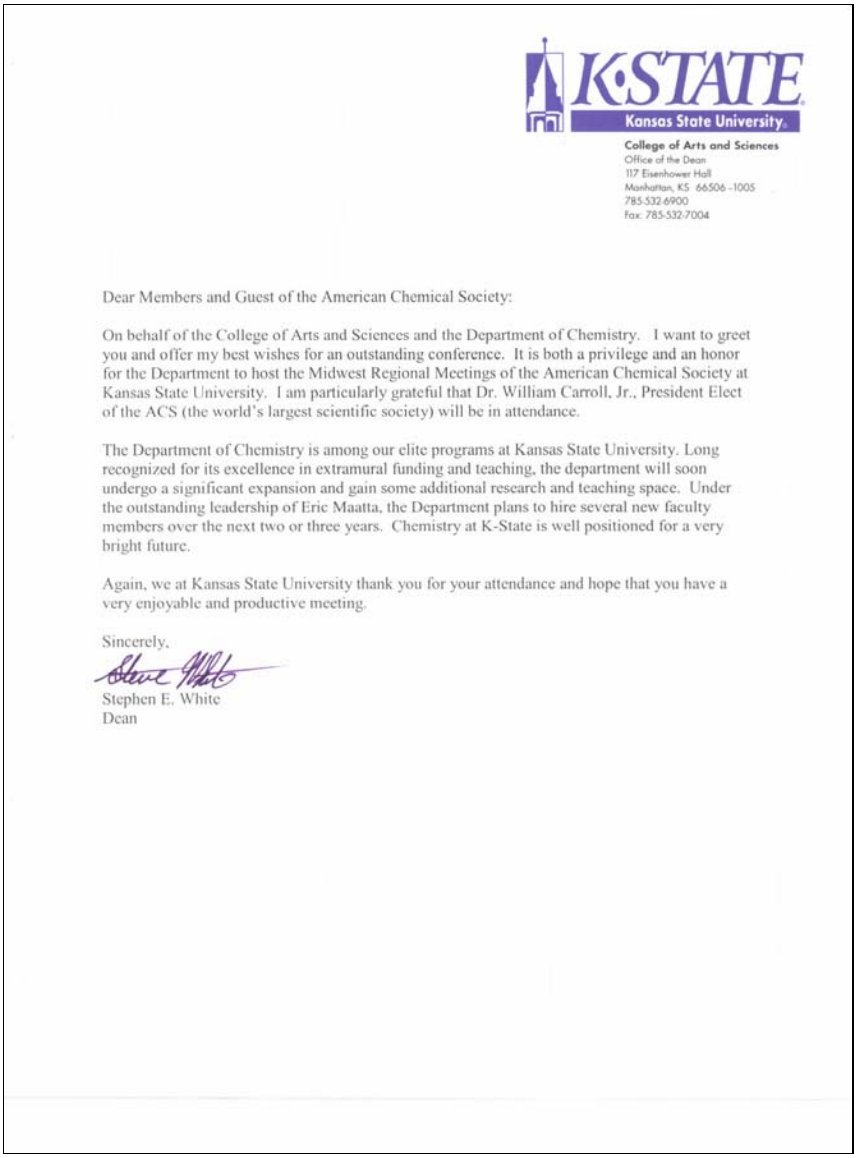
It is my pleasure to welcome the Midwest Regional Meeting of the American Chemical Society to the Kansas State University campus. It has been a number of years since last you were here, and it is good to have you with us once again. The mix of individuals attending will surely make for an interesting meeting, with undergraduate and graduate students, faculty members, people from business and industry, and visitors coming to Manhattan from across the length and breadth of the United States and from overseas. It is a special joy for me to welcome your President-Elect, Dr. William Carroll, Jr., to K-State, as he looks toward assuming leadership of this, the world's largest scientific society.

We hope that you enjoy your time with us and have opportunity get to know the members of our outstanding Department of Chemistry, under the leadership of newly named Head, Dr. Eric Maatta. They form an important part of the community of scholars at Kansas State University, while affording excellent research and educational opportunities to both our undergraduate and graduate students. I hope that during your stay you will have occasion to get to know the many warm and friendly people here on campus and in the city of Manhattan. We look forward to the opportunity to visit with you while you are here as our guests.

Yours sincerely,

M Duane Nellis

M. Duane Nellis, Provost



K·STATE
Kansas State University
College of Arts and Sciences
Office of the Dean
117 Eisenhower Hall
Manhattan, KS 66506-1005
785-532-6900
Fax: 785-532-7004

Dear Members and Guest of the American Chemical Society:

On behalf of the College of Arts and Sciences and the Department of Chemistry. I want to greet you and offer my best wishes for an outstanding conference. It is both a privilege and an honor for the Department to host the Midwest Regional Meetings of the American Chemical Society at Kansas State University. I am particularly grateful that Dr. William Carroll, Jr., President Elect of the ACS (the world's largest scientific society) will be in attendance.

The Department of Chemistry is among our elite programs at Kansas State University. Long recognized for its excellence in extramural funding and teaching, the department will soon undergo a significant expansion and gain some additional research and teaching space. Under the outstanding leadership of Eric Maatta, the Department plans to hire several new faculty members over the next two or three years. Chemistry at K-State is well positioned for a very bright future.

Again, we at Kansas State University thank you for your attendance and hope that you have a very enjoyable and productive meeting.

Sincerely,

Stephen E. White
Dean

MWRM 2004 MEETING AT A GLANCE

	10/20/04	10/21/04	10/21/04	10/22/04
Symposium	Wed PM	Thurs AM	Thurs PM	Friday AM
Analytical	1-5 PM	8 AM-noon		
Biochemistry		8 AM-noon		
Crystal Engineering	1-5 PM	8 AM-noon	1-4 PM	8 AM-noon
Drug Discovery			1-4 PM	8 AM-noon
Electronic Structure			1-4 PM	8 AM-noon
Environ. Chemistry	1-5 PM	8 AM-noon		
Inorganic				8 AM-noon
Nanoscale Materials			1-4 PM	
Organic	1-5 PM	8 AM-noon		
Physical	1-5 PM	8 AM-noon		
Sol-Gel Materials			1-4 PM	8 AM-noon
UG Res and Chem Ed				8 AM-noon
Posters	7-10 PM	9 AM-noon	1-4 PM	
Welcoming Mixer	7-10 PM			
UG Tour of KSU	1-4 PM			
UG Dinner, Lecture	4-7 PM			
Midwest Awards Symp.			4:30-6 PM	
Awards Banquet			6-9 PM	
Director's Breakfast				7:30-8:30 AM
Registration	11:30 AM-10 PM	7:30 AM - 5:00 PM		7:30-11 AM
Exposition	7-10 PM	8:00 AM - 4:00 PM		8-11 AM
Career Workshop/Assist		9 AM-noon	1-4:30 PM	

All times are approximate, see individual symposium listings for exact session times.

General Information

The Kansas State University Local Section of the American Chemical Society is proud to host the 39th Annual Midwest Regional Meeting (MWRM 2004). The meeting will be held at the Manhattan Holiday Inn Holidome from Wednesday, October 20, beginning at 1:00 PM, to Friday, October 22, at noon. The latest meeting information can be obtained from our website at http://www.dce.ksu.edu/chem/acs/index.html.

Registration

Registration and program booklet distribution will take place in the hallway just outside Conference Room I at the Holiday Inn. Registration hours will be from 11:30 AM – 10:00 PM on Wednesday, October 20, from 7:30 AM – 5:00 PM on Thursday, October 21 and from 7:30 AM–11:00 AM on Friday, October 22.

Technical Sessions

All technical sessions will be held in the Holiday Inn Conference Center. Specific locations for individual symposia are defined throughout the program booklet. A map of the conference center is included.

Exposition

An exposition featuring commercial vendors and academic institutions will be held throughout the meeting in Ballroom A of the Holiday Inn Conference Center. Technical poster sessions and coffee breaks will be held in this same location.

The exposition will be open from 7:00 – 10:00 PM on Wednesday, October 20, from 8:00 AM – 4:00 PM on Thursday, October 21 and from 8:00 AM – 11:00 AM on Friday, October 22.

Mixer and Opening Poster Session

The opening poster session and mixer will be held in Ballroom A of the Holiday Inn Conference Center from 7:00-10:00 PM on Wednesday, October 20, following the afternoon technical sessions that same day.

Awards

The Midwest Award for Outstanding Achievements in Chemistry, sponsored by the St. Louis Local Section of the American Chemical Society, will be given to Professor Mark S. Gordon of Iowa State University. A special award's symposium in his honor will be held from 4:30-6:00 PM on Thursday, October 21. This symposium will be followed by a reception and the Midwest Awards Banquet from 6:00 PM – 9:00 PM in Ballroom B at the Holiday Inn Conference Center.

Breakfast and Conversation with ACS Governance

All registered meeting attendees are invited to enjoy a complimentary continental breakfast, coffee and conversation with ACS governance on the morning of Thursday, October 21, from 7:30 AM – 8:30 AM. The breakfast will be held in the Saffron Restaurant of the Holiday Inn. Recent ACS Board of Directors' actions will be discussed and MWRM attendees will be given the opportunity to ask questions and present their own ideas.

ACS Career Services

The Career Resource Center at ACS will sponsor three professional development workshops on Thursday, October 21, 2004. These will include "Targeting the Job Market" at 9:00 AM, "Resume Preparation" at 10:00 AM and "Interviewing Skills" at 11:00 AM. These sessions will be held in the Sunflower Room (adjacent to the pool) at the Holiday Inn.

Individual 25-minute resume review appointments may be scheduled for Thursday, October 21 from 1:00-4:30 PM in the main registration area. Bring a copy of your resume. For more information about these workshops, call (800) 227-5558 x6210.

SPONSORS

ACS Environmental Chemistry Division (Environmental Chemistry and Nanostructured Materials Symposia)

Kansas State University Graduate School (Undergraduate Program)

Kansas State University Department of Chemistry

Kansas State University Information Technology Assistance Center

Kansas State University Center for Hazardous Substance Research (Environmental Chemistry Symposium)

Medicinal Chemistry Division of ACS (Drug Discovery and Biochemistry Symposium)

ACS Office of Regional Meetings (International Speaker Travel)

ACS Petroleum Research Foundation (Crystal Engineering – Supramolecular Chemistry Symposium)

ACS President's Office - ACS (Drug Discovery and Bioorganic Chemistry, Environmental Chemistry and Nanostructured Materials Symposia)

ACS Office of Undergraduate Programs (Undergraduate Program)

Kluwer Academic/Plenum Publishers (Crystal Engineering – Supramolecular Chemistry Symposium)

Linweld Inc. (Undergraduate Program)

EXHIBITORS

Commerical

Hayden McNeil Publishing Co.
Houghton Mifflin Co.
Prentice Hall Publishing Co.
Shimadzu Scientific Instruments, Inc
Varian, Inc.

Academic

Iowa State University, Dept. of Chemistry
Kansas State University, Dept. of Chemistry
Missouri Southern State university, Dept. of Chemistry
South Dakota State University, Dept. of Chemistry
University of Missouri at St. Louis, Dept. of Chemistry
Vanderbilt University, Dept. of Chemistry
Wichita State University, Dept. of Chemistry

2004 Midwest Regional ACS Award for Outstanding Achievements in Chemistry

Professor Mark S. Gordon

Iowa State University

Mark S. Gordon, the recipient of this year's Midwest Award of the American Chemical Society, grew up in and around New York City, received his B.S., Ph.D. and postdoctoral education at Rensselaer Polytechnic Institute, Carnegie-Mellon University (w. J.A. Pople) and Iowa State University (w. K. Ruedenberg). For 12 years he was on the chemistry faculty of North Dakota State University and rose to Distinguished Professor and Department Chair. During his subsequent 12 years at Iowa State University, he has become Distinguished Professor, has been the associate Department Chair and is Director of the Applied Mathematics Program in the Ames Laboratory USDOE. He has been a visiting scientist at the University of California-Irvine, the Minnesota Supercomputing Institute, the National Science Foundation, the Molecular Science Institute in Okazaki (Japan), the University of Tokyo and the Australian National University. He has been the Chair of the Theoretical Chemistry Subdivision of the American Chemical Society and the Secretary-Treasurer of its Physical Chemistry Division. He is a Fellow of the American Physics Society and a Fulbright Senior Scholar. He is on the editorial board of several journals.

Gordon's over 380 publications in quantum chemistry have had significant impact and won worldwide recognition, among "real" chemists as well as theorists, for his unique blend of systematic elucidations of important bonding and reaction mechanistic problems on the one hand and effective *ab initio* method developments on the other hand. The objects of his studies typically are potential energy surfaces, reaction paths, activation energies of transition states and reaction mechanisms.

Gordon has developed MCSCF centered methods, the Effective Fragment Method for solutions and liquids, a Molecular Orbital/Molecular Mechanics method for clusters on surfaces and several spin-orbit coupling methods. His localized analyses of electronic wavefunctions extract chemical meanings from complex computations, especially for the benefit of the non-theoretical chemists. To pursue this comprehensive program, he has developed, maintains and continues to expand the premier open quantum chemistry program system GAMESS, which is used by several thousand scientists worldwide.

Gordon's contributions cover many regions of the periodic table, notably carbon chemistry, silicon chemistry, organometallic chemistry and transition metal chemistry. He is particularly famous as a pioneer in elucidating how and why silicon chemistry differs from carbon chemistry. He discovered the near-isoergicity between silylenes and silenes; the small barriers for silylene insertion reactions; the *pi*-bonds of silicon with itself as well as carbon, nitrogen, oxygen, phosphorus and sulfur, including triple bonds; silicon's participation in aromatic systems; structure and strain of small rings and clusters containing silicon; geometric and electronic structures of molecules containing pentavalent silicon; reaction paths of pseudorotational isomerizations between axial and equatorial atoms. He has extended this work to germanium, tin and titanium.

Gordon has furthermore complemented his gas phase investigations by realistic studies of reactions in solution as well as on solid surfaces. His solvation theory has accurately produced metalloenzyme UV shifts, chemical reactions, protein pK_as and electrolyte dissociation dependence on solvation coordination. His surface model has yielded correct structures of Si surfaces and revealed mechanisms for reactions on this surface including oxidation, etching and addition of various substrates.

Notwithstanding the many complex mathematical and computational aspects of his investigations, it is the chemistry that drives all of Professor Gordon's work.

Midwest Regional ACS Award Address

Effective Fragment Potential: Theory and Applications

Professor Mark S. Gordon

Department of Chemistry
Iowa State University

The effective fragment potential (EFP) method, developed directly from quantum mechanics, is a sophisticated method that is capable of simulating cluster behavior, solvent effects and properties of bulk liquids. After an introduction to the theory, several applications of the method, drawn from both cluster and bulk studies, will be discussed.

Previous Midwest Award Recipients

Year	Recipient	Year	Recipient
1944	Lucuas P. Kyrides	1976	Stanley Wawsonek
1945	Carl F. & Gerty T. Cori	1977	Paul Kuroda
1946	Anderson W. Ralston	1978	Orville Chapman
1948	Paul L. Day	1979	Ralph Adams
1949	Robert D. Coghill	1980	Robert Hansen
1950	William S. Haldeman	1981	Donald W. Setser
1951	Henry Gilman	1982	Klaus Ruedenberg
1952	Edward Mallinckrodt, Jr.	1983	Jacob Kleinberg
1953	Roger Adams	1984	Norman Cromwell
1954	Richard M. Hixson	1985	John Corbett
1955	Carroll Hoochwalt	1986	Charles W. Gehrke
1956	Ray Q. Brewster	1987	Jacob Schaefer
1958	Charles D. Hurd	1988	C. David Gutsche
1959	Melvin DeGroote	1989	Robert W. Murray
1960	Charles D. Harrington	1990	Donald J. Burton
1961	Samuel I. Weissman	1991	Michael J. Welch
1962	Oliver H. Lowry	1992	Richard L. Schowen
1963	Herman Pines	1993	Daniel W. Armstrong
1964	Harold H. Strain	1994	Theodore Kuwana
1965	Richard W. Riley	1995	Thomas J. Barton
1966	Ralph G. Pearson	1996	Garland Ross Marshall
1967	Frank H. Spedding	1997	Reuben Rieke
1968	Byron Riegel	1998	Kenneth J. Klabunde
1969	Joseph J. Katz	1999	Dewey E. Holten
1970	Irving M. Klotz	2000	Joyce Y. Corey
1972	Myron L. Bender	2001	Vasu Nair
1973	Herbert S. Gutowsky	2002	Michael L. Gross
1974	Glen A. Russell	2003	Kristin Bowman-James
1975	Takeru Higuchi		

SPECIAL SYMPOSIA

Crystal Engineering

Organizer: Christer Aakeroy

Crystal Engineering I

Conference Room V
1:00PM – 5:00PM Wednesday
Mark Hollingsworth, Presiding

1. 1:00 STEREOCHEMISTRY AND CHIROPTICS IN COMPLEX ORGANIZED MEDIA. **Bart Kahr**, Werner Kaminsky and Claborn Kacey; University of Washington, Seattle, WA 86

2. 1:40 CHIRAL MOLECULAR GLASS: SYNTHESIS AND CHARACTERIZATION OF ENANTIOMERICALLY-PURE THIOPHENE-BASED [7]HELICENE. **Makoto Miyasaka**[1], Andrzej Rajca[1], Maren Pink[2] and Suchada Rajca[1]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]Indiana University, Bloomington, IN 86

3. 2:00 DIRECTING MOLECULAR CRYSTAL GROWTH WITH SELF-ASSEMBLED MONOLAYERS. **Rupa Hiremath**, Stephen W. Varney and Jennifer A. Swift; Georgetown University, Washington, DC 87

4. 2:20 POLAR ORDERING AND ELECTRIC FIELD-INDUCED DOMAIN REORIENTATION IN FERROELASTIC CHANNEL INCLUSION COMPOUNDS. **Jeremy R. Rush**, Mark D. Hollingsworth and Mark J. Abel; Kansas State University, Manhattan, KS 88

2:40 Break

5. 3:00 STRUCTURAL COMPARISONS OF ANION AND TRANSITION METAL ION COMPLEXES WITH MACROCYCLES. **Kristin Bowman-James**; University of Kansas, Lawrence, KS 88

Crystal Engineering I (continued)

6.	3:30	SYNTHETIC, ION-CONDUCTING TRANSMEMBRANE CHANNELS. **George W. Gokel**; Washington University School of Medicine, St. Louis, MO	89
7.	4:00	ROLE OF NON-COVALENT INTERACTIONS IN METAL ION-MEDIATED ACTIVATION OF SMALL MOLECULES. **Andrew S. Borovik**; University of Kansas, Lawrence, KS	90
8.	4:30	COORDINATION POLYMERS WITH 2,4,6-PYRIDINETRICARBOXYLATE: 1D CHAINS AND 2D TILES. **Robert P. Houser** and Deping Cheng; University of Oklahoma, Norman, OK	90

Crystal Engineering II

Conference Room V
8:10AM – 12:00PM Thursday
Jesus Valdes-Martinez, Presiding

179.	8:10	PERSPECTIVES IN MOLECULAR TECTONICS. **Mir Wais Hosseini**; Universite Louis Pasteur, Strasbourg, France	198
180.	9:00	TRIPLE PLAY: TERNARY SUPERMOLECULES BASED ON ASYMMETRIC BIPYRIDINES. **Brock D. Levin**, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS	199
181.	9:20	SYNTHESIS OF MOLECULAR TARGETS IN THE SOLID STATE *VIA* TEMPLATE-CONTROLLED REACTIVITY. **Tomislav Friscic**, Xiuchun Gao and Leonard R. MacGillivray; University of Iowa, Iowa City, IA	199
	9:40	Break	
182.	10:00	FROM MOLECULAR FUNCTION TO SUPRAMOLECULAR SYNTHESIS. **Christer Aakeröy**; Kansas State University, Manhattan, KS	200

Crystal Engineering II (continued)

183.	10:30	SUPRAMOLECULAR CHEMISTRY OF BORONIC ACIDS: A CARBOXYLIC ACID-AMIDE HYBRID? **Debra J. Salmon**, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS	201
184.	10:50	LINEAR TEMPLATES: TOOLS FOR ASSEMBLING AND CONSTRUCTING MOLECULES IN CRYSTALLINE SOLIDS. **Leonard R. MacGillivray**, Tomislav Friscic, Dushyant B. Varshney, Tamara D. Hamilton, Qianli Chu and Giannis S. Papaefstathiou; University of Iowa, Iowa City, IA	201
185.	11:20	RECIPE FOR MAKING TERNARY SUPERMOLECULES. **Joaquin F. Urbina**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS	202
186.	11:40	TARGETED SOLID-STATE SUPRAMOLECULAR ASSEMBLIES INVOLVING ANTHRACENE DERIVATIVES. **Tony N. Sokolov**, Tomislav Friscic and Leonard R. MacGillivray; University of Iowa, Iowa City, IA	203

Crystal Engineering III

Regency B I Ballroom
1:00PM – 4:10PM Thursday
Christer Aakeroy, Presiding

255.	1:00	SOLID-STATE REACTIONS WITHIN A SELF-ASSEMBLED DISCRETE CAGE. **Makoto Fujita**; The University of Tokyo, Tokyo, Japan	247
256.	1:50	DUAL RESPONSIBILITIES; MULTI-TASKING MOLECULES. **Nate C. Schultheiss**, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS	248

Crystal Engineering III (continued)

257.	2:10	"BLOCKING" LIGANDS FOR MOLECULAR TECTONICS. **Jesús Valdés-Martínez**; Universidad Nacional Autónoma de México, México, D.F., Mexico	249
	2:40	Break	
258.	3:00	HOW SOLID IS THE ORGANIC SOLID STATE? **Jerry L. Atwood** and Leonard J. Barbour; University of Missouri-Columbia, Columbia, MO	249
259.	3:30	CALIX[4]RESORCINARENES AS TEMPLATES FOR SOLID STATE REACTIONS. **Heba Abourahma** and Leonard R. MacGillivray; University of Iowa, Iowa City, IA	250
260.	3:50	TOWARDS GENERALITY IN TEMPLATE-CONTROLLED REACTIVITY: 'TEMPLATE SWITCHING' IN METAL-ORGANIC SOLIDS. **Qianli Chu** and Leonard R. MacGillivray; University of Iowa, Iowa City, IA	250

Crystal Engineering IV

Regency B I Ballroom
8:00AM – 12:00PM Friday
Leonard R. MacGillivary, Presiding

311.	8:00	RECENT ADVENTURES IN POLYMORPHISM. **Joel Bernstein**; Ben-Gurion University of the Negev, Beer Sheva, Israel	279
312.	8:50	CRYSTAL ENGINEERING OF SOME PHARMACEUTICALLY-ACTIVE CO-CRYSTALS. **Keith R. Lorimer**, Scott Childs and Lenard Chyall; SSCI Inc., West Lafayette, IN	280

Crystal Engineering IV (continued)

313. 9:20 PHARMACEUTICAL CO-CRYSTALS: SYNTHESIS, SCALE-UP AND PROPERTIES. **Matthew Peterson**, Magali B. Hickey, Julius F. Remenar, Sherry L. Morissette, Hector R. Guzman, J. Michael MacPhee and Örn Almarsson, TransForm Pharmaceuticals, Lexington, MA 281

9:40 Break

314. 10:00 DESIGN AND SYNTHESIS OF N-BASED LIGANDS FOR COORDINATION AND HYDROGEN-BONDED NETWORKS. **Eric Bosch**, Nate Schultheiss, Joseph Ellsworth and Ivan Georgiev; Southwest Missouri State University, Springfield, MO 281

315. 10:30 SOLID-STATE SYNTHESIS ENABLES CONSTRUCTION OF A POLYFUNCTIONAL LIGAND THAT GIVES RISE TO METAL-ORGANIC POLYGONS AND POLYHEDRA. **Tamara D. Hamilton**, Giannis S. Papaefstathiou, Qianli Chu and Leonard R. MacGillivray; University of Iowa, Iowa City, IA 282

316. 10:50 INVERTED METAL ORGANIC FRAMEWORKS CONSTRUCTED USING ORGANIC BUILDING UNITS DERIVED FROM THE ORGANIC SOLID STATE. **Claude L. Mertzenich**[1], Giannis S. Papaefstathiou[2], Tomislav Friscic[2], Dale C. Swenson[2] and Leonard R. MacGillivray[2]; [1]Luther College, Decorah, IA; [2]University of Iowa, Iowa City, IA 283

317. 11:10 HYDROGEN-BONDED INORGANIC-ORGANIC LAMELLAR SOLIDS AND THEIR POTENTIAL AS CLAY MIMICS. **Brian Helfrich**; Mississippi State University, Mississippi State, MS 284

Crystal Engineering IV (continued)

318.	11:30 AM	FROM FERROELASTICS TO FERROELECTRICS. **Mark D. Hollingsworth**, Matthew L. Peterson, Jeremy R. Rush, Mark J. Abel, Alexis A. Black, David A. Kesselring, Amanda G. Butenhoff, Kevin L. Pate and Julie A. Cooper; Kansas State University, Manhattan, KS	284

Drug Design and Bioorganic Chemistry

Organizer: Duy H. Hua

Drug Design and Bioorganic Chemistry I

Conference Room II
1:00PM – 4:05PM Thursday
Duy H. Hua, Presiding

261. 1:00 TRANSIENT PEPTIDE-INDUCED TRANSPORT OF DRUGS ACROSS BARRIER MEMBRANES. **John M. Tomich**; Kansas State University, Manhattan, KS 251

262. 1:45 INHIBITION OF S-ADENOSYLHOMOCYSTEINE HYDROLASE BY D-ERITADENINE ANALOGUES. **Fusao Takusagawa**[1] and Duy H. Hua[2]; [1]University of Kansas, Lawrence, KS; [2]Kansas State University, Manhattan, KS 252

263. 2:30 BLENDING PARALLEL SYNTHESES INTO MEDICINAL CHEMISTRY: DISCOVERY OF POTENT TIE-2 INHIBITORS. **Jinshan Chen**; Pfizer Global Research & Development, Groton, CT 253

264. 3:15 EFFECT OF MOLECULAR PROPERTIES ON THE SELECTIVE ACCUMULATION OF CHEMICALS IN TUMOR CELLS. **Stefan Trapp**[1] and Richard W. Horobin[2]; [1]Technical University of Denmark, Kongens Lyngby, Denmark; [2]University of Glasgow, Glasgow, United Kingdom 253

265. 3:40 STUDIES TOWARD A TOTAL SYNTHESIS OF (+)-MYRICERIC ACID A. **Angelo Aguilar**, Bernard Wiredu, Keil J. Regehr, Philine Wangemann and Duy H. Hua; Kansas State University, Manhattan, KS 254

Drug Design and Bioorganic Chemistry II

Conference Room II
8:00AM – 12:00PM Friday
Duy H. Hua, Presiding

	8:00	Introductory Remarks	
319.	8:10	NOVEL DESIGN AND SYNTHESIS OF NON-PEPTIDE AVP RECEPTOR ANTAGONISTS AND AGONISTS. **Kazumi Kondo**; Otsuka Pharmaceutical Co., Ltd., Tokushima, Japan	285
320.	8:55	DISCOVERY OF A SELECTIVE ITK INHIBITOR THAT BLOCKS T-CELL ACTIVATION AND REDUCES MURINE LUNG INFLAMMATION. **Jagabandhu Das**, John Wityak, Chunjian Liu, Robert V. Moquin, Joseph A. Furch, James Lin, Steven H. Spergel, Arthur Doweyko, Amrita Kamath, Hongjian Zhang, Kathleen D. O'Day, Becky Penhallow, Chen-Yi Hung, Steven Kanner, Tai-An Lin, John H. Dodd and Joel C. Barrish; Bristol-Myers Squibb Co., Princeton, NJ	286
	9:40	Break	
321.	10:00	DESIGN, SYNTHESIS AND EVALUATION OF INHIBITORS OF PYRIDOXAL PHOSPHATE DEPENDENT ENZYMES. **David B. Berkowitz**; University of Nebraska, Lincoln, NE	286
322.	10:45	3D MODEL OF A SUBSTRATE-BOUND LIGHT-CHAIN DOMAIN OF BOTOX PREDICTED BY MULTIPLE MOLECULAR DYNAMICS SIMULATION DOCKING: NEW APPROACH TO DOCKING FLEXIBLE MOLECULES WITH CONSIDERATION OF SOLVATION. **Yuan-Ping Pang**; Mayo Clinic, Rochester, MN	287
323.	11:10	TOTAL SYNTHESIS OF (±)-OVALICIN AND ITS ANALOGS. **Srinivas Battina,** Kaiyan Lou, Ana Jimenez and Duy H. Hua; Kansas State University, Manhattan, KS	287

Drug Design and Bioorganic Chemistry II (continued)

324. 11:35 TRICYCLIC PYRONES THAT BLOCK *BETA*-SHEET FORMATION AND AGGREGATION OF ALZHEIMER'S AMYLOID BETA-40 PEPTIDE. Hui-Chuan Wu[1], Erik Pettersson[1], Srinivas Battina[1], Ana Jimenez[1], Bernard Wiredu[1], Takeo Iwamoto[1], Gary A. Radke[1], Qianqian Li[2], Chao Xu[2], Jianjun Wang[2], Lee-Way Jin[3] and **Duy H. Hua**[1]; [1]Kansas State University, Manhattan, KS; [2]Southern Illinois University at Carbondale, Carbondale, IL; [3]University of Washington, Seattle, WA 288

Environmental Chemistry
Organizer: Larry Erickson

Environmental Chemistry I
Conference Room IV
1:00PM - 5:00PM Wednesday
Larry Erickson, Presiding

9.	1:00	BIODEGRADATION OF TOXIC COMPOUNDS BY PLANTS OR BY ASSOCIATED BACTERIA. **Stefan Trapp**; Technical University of Denmark, Kongens Lyngby, Denmark	91
10.	1:40	TREE CORE SAMPLING IN PLUME DELINEATION AND PHYTOREMEDIATION STUDIES. **Joel G. Burken**[1], Xingmao Ma[1], Garrett Struckhoff[1], Jeff Weishaar[1] and John Schumacher[2]; [1]University of Missouri Rolla, Rolla, MO; [2]United States Geological Survey, Rolla, MO	92
11.	2:10	EVALUATION OF CURRENT REMEDY AND RESEARCH INTO ADVANCED TECHNOLOGIES FOR REMEDIATION OF THE PPI SITE. **W. David Constant**; Louisiana State University, Baton Rouge, LA	92
	2:40	Break	
12.	3:00	BIOCHEMICAL BASIS FOR ENVIRONMENTAL MANAGEMENT OF AIRCRAFT DEICING WASTE USING VEGETATION. **Sigifredo Castro**, Larry E. Erickson, Lawrence C. Davis and Kenneth Dokken; Kansas State University, Manhattan, KS	93
13.	3:30	COMPARATIVE VALIDATION OF INNOVATIVE CAPPING TECHNOLOGIES ON THE ANACOSTIA RIVER. **W. David Constant** and Danny D. Reible; Louisiana State University, Baton Rouge, LA	93

Environmental Chemistry I (continued)

14. 4:00 TIME-DEPENDENT SORPTION-DESORPTION BEHAVIOR OF 2,4-DICHLOROPHENOL AND ITS POLYMERIZATION PRODUCTS IN SURFACE SOILS. **Mónica Palomo** and Alok Bhandari; Kansas State University, Manhattan, KS 94

15. 4:30 SORPTION OF THE MALODORANT TERTIARY BUTYL MERCAPTAN TO INDOOR MATERIALS FROM AIR AND WATER. **Alok Bhandari**, Aruna Suravajjala and Larry Erickson; Kansas State University, Manhattan, KS 95

Environmental Chemistry II

Conference Room IV
8:00AM - 11:55AM Thursday
Larry Erickson, Presiding

148. 8:00 USE OF LIGAND-MODIFIED COLLOID-ENHANCED ULTRAFILTRATION TO SELECTIVELY REMOVE HEAVY METALS FROM WATER. **Richard W. Taylor**, Kay K. Bjornen and John F. Scamehorn; University of Oklahoma, Norman, OK 178

149. 8:25 OCCURRENCE AND FATE OF ANTIMICROBIALS IN MUNICIPAL WASTEWATER TREATMENT PLANTS: A NORTHEAST KANSAS PERSPECTIVE. **Alok Bhandari**, Larry Close, David Koch and Robert Hunter; Kansas State University, Manhattan, KS 179

Environmental Chemistry II (continued)

150.	8:50	DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN STREAMS, THE KANSAS CITY AREA. **Jing Tao**[1], Gary Welker[2], Donald Huggins[3], Jerry Dias[1] and James Murowchick[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]U.S. Environmental Protection Agency, Region 7, Kansas City, KS; [3]Kansas Biological Survey, Lawrence, KS	179
151.	9:15	ENVIRONMENTAL KNOWLEDGE AND ASSESSMENT TOOL (EKAT). **Ryan M. Green** and Terrie Boguski; Kansas State University, Manhattan, KS	180
	9:40	Break	
152.	10:00	COOKING PROCESS' RELATIONSHIP TO AIR QUALITY. **Julia A. Keen**; Kansas State University, Manhattan, KS	181
153.	10:25	LEAD, ZINC AND CADMIUM LEVELS IN PLASTER AND MORTAR FROM STRUCTURES IN JASPER AND NEWTON COUNTIES, MISSOURI. **Jeffrey W. Pavlik**, Richard N. Biagioni, Phyllis Perry and Ralph W. Sheets; Southwest Missouri State University, Springfield, MO	181
154.	10:50	OXIDATION KINETICS OF AQUEOUS ANTHRAQUINONE DYE IN AN *IN SITU* OZONE REACTOR AND CONVENTIONAL GAS-LIQUID CONTACTOR. **Kishora K. Panda** and Alexander P. Mathews; Kansas State University, Manhattan, KS	182

Environmental Chemistry II (continued)

155.	11:15	SAFETY OF GLYCOL, DIESEL FUEL OR COMBUSTION SMOKES IN THE PRESENCE OF MAGNESIUM OR TITANIUM DIOXIDE CLEARING AGENTS. **John Pickrell**[1], Gunjan Gakhar[1], Ravi S. Mulukutla[2], Ronaldo Maghirang[1], John S. Klabunde[2], Paul S. Malchesky[2], Ryan Green[1], Frederick Oehme[1] and Larry Erickson[1]; [1]Kansas State University, Manhattan, KS; [2]NanoScale Materials Inc., Manhattan, KS	183
156.	11:35	HALOGENATED METAL-OXIDE NANOPARTICLES FOR BACTERICIDAL AND SPORICIDAL USE. **Johanna A. Haggstrom**, Kenneth J. Klabunde and George L. Marchin; Kansas State University, Manhattan, KS	184

Methods in Electronic Structure Theory

Organizer: J. Vincent Ortiz

Methods in Electronic Structure Theory I

Conference Room III
1:00PM – 3:55PM Thursday
J. Vincent Ortiz, Presiding

	1:00	Introductory Remarks	
266.	1:05	COMPUTATIONAL MODELS FOR NANOTUBES AND NANOWIRES. **J. W. Mintmire**; Oklahoma State University, Stillwater, OK	254
267.	1:35	ENDOHEDRAL SILICON FULLERENES. **Xiao Cheng Zeng**[1], Soohaeng Yoo[1], Jijun Zhao[2] and Jinlan Wang[3]; [1]University of Nebraska-Lincoln, Lincoln, NE, [2]University of North Carolina, Chapel Hill, NC; [3]Argonne National Laboratory, Argonne, IL	255
268.	2:05	FIRST PRINCIPLES STUDY OF SCN/GAN AND SCN/INN SUPERLATTICES. **V. Ranjan**, Saad-Bin Omran and L. Bellaiche; University of Arkansas, Fayetteville, AR	255
	2:35	Break	
269.	2:55	TOWARD PRACTICAL ORGANIC POLYMER MAGNETS: LESSONS LEARNED FROM POLYARYLMETHYL POLYRADICALS. **Andrzej Rajca**; University of Nebraska-Lincoln, Lincoln, NE	256
270.	3:25	SYNTHESIS AND MAGNETIC STUDY OF MACROCYCLIC TETRARADICAL TETRACATION. **Kouichi Shiraishi**, Andrzej Rajca and Suchada Rajca; University Nebraska-Lincoln, Lincoln, NE	256

Methods in Electronic Structure Theory II: Symposium in Honor of Mark Gordon

Conference Room V
4:30PM – 6:30PM Thursday
J. Vincent Ortiz, Presiding

308.	4:30	PARALLELIZATION OF THE GAMESS ELECTRONIC STRUCTURE CODE. **Mike Schmidt**, Iowa State University, Ames, IA	278
309.	5:00	CONTROLLED CORRELATION ENERGY EXTRAPOLATION BY INTRINSIC SCALING. **Klaus Ruedenberg** and Laimutis Bytautas; Iowa State University, Ames, IA	279
310.	5:30	EFFECTIVE FRAGMENT POTENTIAL: THEORY AND APPLICATIONS. **Mark S. Gordon**; Iowa State University, Ames, IA	279

Methods in Electronic Structure Theory III

Conference Room III
8:00AM – 11:50AM Friday
J. Vincent Ortiz, Presiding

337.	8:00	SIXTEEN VALENCE-ELECTRON SPECIES CONTAINING BORON: STRUCTURAL DIVERSITY ABOUNDS. **Carol A. Deakyne**[1], Aaron K. Corum[1] and Joel F. Liebman[2]; [1]University of Missouri - Columbia, Columbia, MO; [2]University of Maryland, Baltimore County, Baltimore, MD	297
338.	8:30	ELECTRON PROPAGATOR THEORY CALCULATIONS OF PHOTOELECTRON CROSS-SECTIONS: BEYOND THE DIPOLE APPROXIMATION. **Gustavo Seabra**[1], I. Kaplan[2], V. G. Zakrzewski[1] and J. V. Ortiz[1]; [1]Kansas State University, Manhattan, KS; [2]Universidad Nacional Autonoma de Mexico, Mexico, D.F., Mexico	297

Methods in Electronic Structure Theory III (continued)

339.	9:00	POTENTIAL ENERGY SURFACE OF 1-METHYL-8-NITRONAPHTHALENE EXPLORED WITH HYBRID HARTREE-FOCK-DENSITY FUNCTIONAL THEORY METHODS. **Yuri V. Il'ichev**; Wichita State University, Wichita, KS	298
	9:30	Break	
340.	9:50	SEMIEMPIRICAL QUANTUM MECHANICAL STUDY OF THE CATIONIC HOMOPOLYMERIZATION OF 4-METHYL-[1,3]-DIOXAN-2-ONE (MDOO). Andrew J. Holder and **Yi Liu**; UMKC, Kansas City, MO	299
341.	10:20	WHERE ARE THE ELECTRONS IN A DOUBLE RYDBERG ANION? A THEORETICAL STUDY WITH THE ELECTRON LOCALIZATION FUNCTION. **Junia Melin** and J. V. Ortiz; Kansas State University, Manhattan, KS	300
342.	10:50	SCALING FACTORS FOR HARMONIC VIBRATIONAL FREQUENCIES CALCULATED BY USING CORRELATION-CONSISTENT BASIS SETS. **Ralph A. Wheeler**[1], Scott E. Boesch[1], Changming Gu[1], Pankaj Sinha[2] and Angela K. Wilson[2]; [1]University of Oklahoma, Norman, OK; [2]University of North Texas, Denton, TX	301
343.	11:20	ON THE MECHANISMS OF PROMOTION AND POISONING OF THE REACTIVITY OF METAL SURFACES. **Talat Rahman** and Sergei Stolbov; Kansas State University, Manhattan, KS	301

Nanostructured Materials and Air Quality

Organizers: Larry Erickson and Kenneth J. Klabunde

Nanostructured Materials and Air Quality

Conference Room IV
1:00PM – 4:00PM Thursday
Kenneth J. Klabunde, Presiding

271. 1:00 SOLVENT EFFECTS ON THE ADSORPTION AND REACTION OF 2-CHLOROETHYLETHYL SULFIDE AND OTHER CWA MIMICS. **Richard M. Narske**[1], Robert Zimmanck[1] and Kenneth J. Klabunde[2]; [1]Augustana College, Rock Island, IL; [2]Kansas State University, Manhattan, KS 257

272. 1:30 NANOPARTICLES IN NATURAL AND ENGINEERED SYSTEMS. **Vicki H. Grassian**; University of Iowa, Iowa City, IA 258

273. 2:00 NANOMACHINING OF METAL PARTICLES BY DIGESTIVE RIPENING USING THIOL LIGANDS. SYNTHESIS AND CHARACTERIZATION OF GOLD AND SILVER ALLOY NANOPARTICLES, AND THEIR FORMATION. **Alexander B. Smetana**, Kenneth J. Klabunde and Christopher M. Sorensen; Kansas State University, Manhattan, KS 258

274. 2:20 SYNTHESIS, CHARACTERIZATION, PHOTOCATALYTIC AND DIELECTRIC PROPERTIES OF NANOSIZED STRONTIUM AND BARIUM TITANATES. **Dmytro Demydov** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS 259

2:40 Break

275. 3:00 SYNTHESIS AND ELECTROCHEMICAL STUDIES OF METAL-OXIDE NANOPARTICLES. **Duane Bartak** and Adam Carlson; University of Northern Iowa, Cedar Falls, IA 259

Nanostructured Materials and Air Quality (continued)

276.	3:20	DIELECTROPHORETIC INTERCONNECTS COMPOSED OF SEMICONDUCTOR NANO-PARTICLES. **Bret Flanders** and Birol Ozturk; Oklahoma State University, Stillwater, OK	260
277.	3:40	TO BE ANNOUNCED. **Richard Colton**; Naval Research Laboratory, Washington, DC	260

Research at Undergraduate Institutions

Organizers: Vincent Ortiz

Research at Undergraduate Institutions

Conference Room V
8:30AM – 9:50AM Friday
Stefan Kraft, Presiding

352.	8:30	ARENEDIAZONIUM SALTS: CYCLIC VOLTAMMETRY AND NON-BONDED ELECTRON TRANSFER REACTION WITH CYTOCHROME C. **Surendra N. Mahapatro**, Hong T. Le, Nhan V. Pham and Rhiannon C. ReVello; Regis University, Denver, CO	307
353.	8:50	LEWIS STRUCTURES OF SO_2, SO_3 AND SO_4^{2-} USING *AB INITIO* CALCULATIONS. **Zeb C. Kramer** and Stephen A. Angel; Washburn University, Topeka, KS	308
354.	9:10	EFFECTS OF BASES, ALDEHYDE STRUCTURES AND WATER IN SOLID-STATE WITTIG REACTIONS. **Kevin Patrick Kent** and Stephen Angel; Washburn University, Topeka, KS	308
355.	9:30	INTRINSIC HYDRATION TENDENCIES OF LANTHANUM (III) COMPLEXES. **Jennifer Morrison** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS	308

Sol-gel Chemistry

Organizers: Maryanne Collinson

Sol-gel Chemistry I

Conference Room V
1:00PM – 4:00PM Thursday
Maryanne Collinson, Presiding

303.	1:00	STIMULI-RESPONSIVE ORGANOSILICA SOL-GELS: SYNTHESIS, CHARACTERIZATION, PROPERTIES, AND APPLICATIONS. **Bakul C. Dave**; Southern Illinois University, Carbondale, Carbondale, IL	275
304.	1:40	MECHANICALLY STRONG LIGHTWEIGHT POROUS MATERI-ALS (X-AEROGELS). **Nicholas Leventis**; NASA Glenn Research Center, Cleveland, OH	275
305.	2:20	ENZYMATIC CATALYSIS, PHOTOISOMERIZATION AND ELECTRON-TRANSFER RELAY REACTIONS IN NANOPOROUS SILICA. Jovica D. Badjic, Ekaterina V. Pletneva and **Nenad M. Kostic**; Iowa State University, Ames, IA	276
	3:00	Break	
306.	3:20	TEMPLATED DIRECTED FORMATION OF HEMISPHERICAL CAVITIES IN A SILICATE FILM AND THE CONTROLLED GROWTH OF CONDUCTING NANOPARTICLES. **Maryanne Collinson** and Mandakini Kanungo; Kansas State University, Manhattan, KS	277
307.	3:40	SINGLE-MOLECULE SPECTROSCOPY STUDIES OF DIFFUSION BY SILICATE-BOUND DYES IN SOL-GEL-DERIVED THIN FILMS. **Daniel Higgins**, Skylar Martin, Maryanne Collinson and Saroja Ginagunta; Kansas State University, Manhattan, KS	277

Sol-gel Chemistry II

Conference Room V
8:00AM – 12:00PM Friday
Maryanne Collinson, Presiding

344.	8:00	MOLECULAR-SCALE AND COARSE-GRAINED MODELING OF XEROGELS AND AEROGELS. **Lev D. Gelb**, Niny Z. Rao and Rafael Salazar; Washington University, St. Louis, MO	302
345.	8:40	EFFECT OF COULOMBIC INTERACTIONS ON THE MOBILITY OF GUEST MOLECULES. James W. Gilliland[1], Kazushige Yokoyama[2] and **Wai Tak Yip**[1]; [1]University of Oklahoma, Norman, OK; [2]SUNY Geneseo, Geneseo, NY	303
346.	9:20	HIERARCHICALLY-IMPRINTED NANOPOROUS SOL-GEL MATERIALS. **Sheng Dai**; Oak Ridge National Laboratory, Oak Ridge, TN	303
	10:00	Break	
347.	10:20	SENSOR FOR NERVE AGENTS USING SOL-GEL CHEMISTRY. **John C. DiCesare**, Starr N. Horne, Jennifer L. Parker, Sireesh Boya and Christopher J. Peeples; The University of Tulsa, Tulsa, OK	304
348.	10:40	ENCAPSULATED SOL-GEL SYSTEM FOR THE COLORIMETRIC DETERMINATION OF CHROMIUM(VI). **David L. McCurdy**, Niba Nchotu, Andrew Chambers, William Hodgson and Jon Johanning; Truman State University, Kirksville, MO	305
349.	11:00	LASER WRITING OF METAL NANOPARTICLES AND SEMICONDUCTOR QUANTUM DOTS. **Massimo F. Bertino**[1], R. Gadipalli[1], A. T. Tokuhiro[1], J. G. Story[1] and Nicholas Leventis[2]; [1]University of Missouri-Rolla, Rolla, MO; [2]NASA Glenn Research Center, Cleveland, OH	305

Sol-gel Chemistry II (continued)

350. 11:20 PREPARATION OF HIGH SURFACE AREA $VOHPO_4 \cdot 0.5H_2O$ WITH THE ALKOXIDE METHOD. **Juan M. Salazar** and Keith L. Hohn; Kansas State University, Manhattan, KS 306

351. 11:40 SOLVENT EFFECTS IN THE HYDROLYSIS OF MAGNESIUM METHOXIDE AND THE PRODUCTION OF NANOCRYSTALLINE MAGNESIUM HYDROXIDE: AN AID IN UNDERSTANDING THE FORMATION OF POROUS INORGANIC MATERIALS. **Ranjit T. Koodali** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS 307

GENERAL SESSIONS

Analytical Chemistry

Organizer: Daniel Higgins

Analytical Chemistry I

Conference Room II
2:00PM - 4:40PM Wednesday
Takashi Ito, Presiding

39.	2:00	NEW TERM OF pH/OH GLASS ELECTRODE. **K. L. Cheng**; University of Missouri-Kansas City, Kansas City, MO	109
40.	2:20	MICROCHIP-BASED RESISTANCE VESSEL MIMICS FOR THE DETECTION OF DEFORMATION-INDUCED ATP FROM ERYTHROCYTES. **Alexander K. Price**[1], R. Scott Martin[1] and Dana M. Spence[2]; [1]Saint Louis University, St. Louis, MO; [2]Wayne State University, Detroit, MI	109
41.	2:40	INTEGRATION OF AN IMMOBILIZED PC 12 CELL REACTOR WITH A MICROCHIP-BASED FLOW ANALYSIS SYSTEM. **Michelle W. Li** and R. Scott Martin; Saint Louis University, St. Louis, MO	110
	3:00	Break	
42.	3:20	STATUS AND DIRECTION OF THE ANALYTICAL SCIENCES DIGITAL LIBRARY. **Ted Kuwana** and Cyntha K, Larive; University of Kansas, Lawrence, KS	111
43.	3:40	SELF-ASSEMBLED PERYLENE-DIIMIDE/POLY-ELECTROLYTE COMPOSITES FOR ORGANIC THIN FILM PHOTOVOLTAICS. **Bei Liu**, Aifang Xie, Jeffrey E. Hall, Sarah L. Barron and Daniel A. Higgins; Kansas State University, Manhattan, KS	111

Analytical Chemistry I (continued)

44. 4:00 DETERMINING POLYMERIZATION VOLUME CHANGE OF EPOXIDES, METHACRYLATES AND CARBOXYLATES USING MERCURY DILATOMETRY. **Greg Giese**, James Code, Heather Vastlick, Jason Finley, Randall Michelson, Patrycja Wilczynska, Benjamin Iwai, Andrew Holder and Kathleen V. Kilway, University of Missouri-Kansas City, Kansas City, MO 112

45. 4:20 DETERMINATION OF SALVINORIN A IN BODY FLUIDS BY LC-MS/APCI. **Mark S. Schmidt**[1], Thomas E. Prisinzano[1], Kevin Tidgewell[1], Wayne Harding[1], Eduardo R. Butelman[2], Mary J. Kreek[2] and Daryl J. Murry[1]; [1]University of Iowa, Iowa City, IA; [2]Rockefeller University, New York, NY 113

Analytical Chemistry II

Conference Room II
8:00AM - 11:40AM Thursday
Takashi Ito, Presiding

130. 8:00 SINGLE-MOLECULE SPECTROSCOPY STUDIES OF LOCAL MATRIX ACIDITY IN SOL-GEL DERIVED FILMS. **Yi Fu**, Maryanne M. Collinson and Daniel A. Higgins; Kansas State University, Manhattan, KS 165

131. 8:20 CONTROLLING DIFFUSION IN HYDRATED SOL-GEL DERIVED GLASSES. **Mandakini Kanungo** and Maryanne M. Collinson; Kansas State University, Manhattan, KS 165

132. 8:40 MONOLITHIC PROTEIN STATIONARY PHASES PREPARED BY THE SOL-GEL METHOD FOR USE IN AFFINITY CAPILLARY LIQUID CHROMATOGRAPHY. **Jeffrey A. Crank** and Nenad M. Kostic; Iowa State 166

University, Ames, IA

Analytical Chemistry II (continued)

133. 9:00 PROGRESS TOWARDS A SEPARATION-BASED SENSOR FOR PEROXYNITRITE AND ITS METABOLITES. **Celeste Frankenfeld**[1], Matthew R. Rosebraugh[2] and Susan Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Drake University, Des Moines, IA 167

134. 9:20 CLINICAL APPLICATIONS OF HOMOCYSTEINE USING MICROCHIP CAPILLARY ELECTROPHORESIS WITH ELECTROCHEMICAL DETECTION. Leslie D. Wagner[1], **Walter R. Vandaveer IV**[2], Stephanie Pasas-Farmer[2] and Susan M. Lunte[2]; [1]Northern Arizona University, Flagstaff, AZ; [2]University of Kansas, Lawrence, KS 168

9:40 Break

135. 10:00 NEUROCHEMICAL APPLICATIONS OF PDMS MICROCHIPS FABRICATED USING CO_2 LASER ABLATION. **Barbara A. Fogarty**[1], Kathleen Heppert[1], Theodore Cory[2], Kalonie Hulbutta[3], R. Scott Martin[4] and Susan M. Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Drake University, Des Moines, IA; [3]Haskell Indian Nations University, Lawrence, KS; [4]Saint Louis University, St. Louis, MO 169

136. 10:20 NITRILE PRODUCT FROM THE CID OF $(b_3\text{-}1\text{+Cat})^+$ SEQUENCE IONS. Travis J. Cooper and **Michael J. Van Stipdonk**; Wichita State University, Wichita, KS 170

137. 10:40 INFLUENCE OF "ALTERNATIVE" AMINO ACIDS ON FORMATION OF $(B)_N$ AND $(Y)_N$ SEQUENCE IONS DURING PEPTIDE CID. **Travis J. Cooper** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS 170

Analytical Chemistry II (continued)

138. 11:00 MEASURING CLINICAL SALICYLATE LEVELS WITH LUTETIUM(III) PORPHYRIN-BASED ION-SELECTIVE ELECTRODES. **Erich D. Steinle**, Stacy W. Scranton, Monica N. Kinde and James M. Hastings; Southwest Missouri State University, Springfield, MO 171

139. 11:20 SEPARATION AND QUANTIFICATION OF N-ACETYL-L-CYSTEINE (NAC) AND N-ACETYL-CYSTEINE-AMIDE (AD4) BY HPLC WITH FLUORESCENCE DETECTION. **Wei Wu** and Nuran Ercal; University of Missouri-Rolla, Rolla, MO 171

Biochemistry

Organizer: Duy Hua

Biochemistry

Regency B II Ballroom
8:00AM – 11:00AM Thursday
John Tomich, Presiding

140.	8:00	ASSESSMENT OF SOME HEAVY METALS IN MUSHROOM SAMPLES FROM ONDO STATE, AKURE, NIGERIA. **Francis Olawale Abulude**; Federal College of Agriculture, Akure, Ondo State, Nigeria	172
141.	8:20	INFLUENCE OF NEEM LEAF EXTRACT ON THE *IN VITRO* NET PROTEIN VALUE OF HULLED AND DEHULLED COWPEA (*VIGNA UNGUICULATA L. WALP*) FLOUR. **Francis Olawale Abulude**; Federal College of Agriculture, Akure, Ondo State, Nigeria	173
142.	8:40	MOLECULAR CHARACTERIZATION OF DIGESTIVE PROTEINASES OF THE YELLOW MEALWORM, *TENEBRIO MOLITOR L.* **Sheila Prabhakar**[1], Mingshun Chen[1], Youping Deng[1], Yoonseong Park[1], C. Michael Smith[1], Elena N. Elpidina[2], Konstantin S. Vinokurov[2] and Brenda Oppert[3]; [1]Kansas State University, Manhattan, KS; [2]Moscow State University, Moscow, Russia; [3]Grain Marketing & Production Research Center, Manhattan, KS	173
143.	9:00	SEQUENCE FOR THE LOW MOLECULAR WEIGHT CR(III)-BINDING PEPTIDE? IMPLICATIONS FOR Cr BIOCHEMISTRY. **J. David Van Horn**, Deendayal Dinakarpandian and Vincent Morrissette; University of Missouri-Kansas City, Kansas City, MO	174
	9:20	Break	

Biochemistry (continued)

144.	9:40	DETERMINING THE FUNCTION OF HYPOTHETICAL PROTEIN SAV1430 FROM STAPHYLOCOCCUS AUREUS USING NMR SPECTROSCOPY. Kelly A. Mercier[1], **Michael Baran**[2], Rong Xiao[2], Robert Powers[1] and Gaetano T. Montelione[2]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]Rutgers University, Piscataway, NJ	175
145.	10:00	TETRACHLOROETHENE (PCE) DEGRADATION IN CONTAMINATED SOIL AND GROUNDWATER. **Jwan H. Ibbini**, Larry Davis and Larry Erickson, Kansas State University, Manhattan, KS	175
146.	10:20	PROLINE CATABOLIC ENZYMES: STRUCTURE, MECHANISM AND SCHIZOPHRENIA. **John J. Tanner**; University of Missouri-Columbia, Columbia, MO	176
147.	10:40	DESIGN OF CHANNEL-FORMING PEPTIDES WITH ALTERED TRANSPORT FUNCTION. **Maria A.B.L. Seabra**, Gabriel Cook, Robert Brandt, Bruce Schultz, Takeo Iwamoto and John Tommich; Kansas State University, Manhattan, KS	176

Chemical Education

Organizer: Vincent Ortiz

Chemical Education

Conference Room V
10:20AM - 12:00PM Friday
Jung Oh, Presiding

356.	10:20	SMILES-A REPLACEMENT FOR IUPAC NOMENCLATURE. **Robert Pavlis**; Pittsburg State University, Pittsburg, KS	309
357.	10:40	PERIODIC TABLE BY STUDENTS: CONNECTING LEARNING WITH STUDENTS' INTERESTS. **Jung R. Oh**; Kansas State University-Salina, Salina, KS	309
358.	11:00	ORGANIC CHEMISTRY MISCONCEPTIONS REVEALED BY TALK-ALOUD PROTOCOLS. **Robert A. Doyle**[1], Janet Bond-Robinson[2] and Randall Robinson[2]; [1]Creighton University, Omaha, NE; [2]University of Kansas, Lawrence, KS	310
359.	11:20	GENERAL CHEMISTRY "LATE SHOW": LECTURE VIDEOS IN LARGE-ENROLLMENT COURSES. **Brian D. Huesgen** and John E. Adams; University of Missouri-Columbia, Columbia, MO	310
360.	11:40	INTERACTIVE DEMONSTRATIONS FOR MOLE RATIOS AND LIMITING REAGENTS. **Bryan E. Breyfogle** and Crystal Wood; Southwest Missouri State University, Springfield, MO	311

Inorganic Chemistry
Organizer: Christer Aakeroy

Inorganic Chemistry
Regency B II Ballroom
8:00AM - 12:20PM Thursday
Chris Levy, Presiding

325.	8:00	CHROMIUM CLUSTER BREAKDOWN KINETICS. **Shveta Chaudhary** and J. David Van Horn; University of Missouri-Kansas City, Kansas City, MO	289
326.	8:20	ADSORPTION OF THIOPHENES OUT OF HYDROCARBONS USING SILVER-IMPREGNATED NANOCRYSTALLINE ALUMINUM OXIDE. **Jeevanandam Pethaiyan** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS	289
327.	8:40	PHOTOCATALYTIC OXIDATION OF 2-CEES (A CHEMICAL WARFARE AGENT SIMULANT) OVER NANOSTRUCTURED TiO_2-SiO_2 UNDER UV LIGHT. **Shalini Rodrigues**, S. Uma, I. N. Martyanov and K. J. Klabunde; Kansas State University, Manhattan, KS	290
328.	9:00	LAYERED PEROVSKITE PHOTOCATALYSTS. **S. Uma**, Shalini Rodrigues and Kenneth J. Klabunde; Kansas State University, Manhattan, KS	291
329.	9:20	FIRST BIOLOGICALLY-ACTIVE Pd(II) AND Pt(II) CYANOXIMATES. **Nikolay Gerasimchuk**, Paul Durham and Daniel Eddings; Southwest Missouri State University, Springfield, MO	291

Inorganic Chemistry (continued)

330. 9:40 PREPARATION AND STUDIES OF DISUBSTITUTED ARYLCYANOXIMES AND THEIR BIVALENT PLATINUM AND PALLADIUM COMPLEXES. **Leon Goeden**[1], Nikolay Gerasimchuk[1], Charles Barnes[2] and John F. Cannon[3]; [1]Southwest Missouri State University, Springfield, MO; [2]University of Missouri-Columbia, Columbia, MO; [3]Brigham Young University, Provo, UT 292

10:00 Break

331. 10:20 SYNTHESIS AND CHARACTERIZATIONS OF CHARGE TRANSFER HYBRIDS. **Jeonghee Kang**, James Nelson, Meng Lu, Degang Wang, Sheng Ye, Arindam Ganguly and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO 293

332. 10:40 MODEL COMPLEXES FOR NITRILE HYDRATASE. **David M. Eichhorn** and Bradley W. Smucker; Wichita State University, Wichita, KS 293

333. 11:00 SYNTHESIS OF NEW CHELATING DICARBENE LIGANDS AND THEIR APPLICATION IN SUZUKI-MIYAURA CROSS-COUPLING REACTIONS. **Adriana I. Moncada** and LeGrande M. Slaughter; Oklahoma State University, Stillwater, OK 294

334. 11:20 REVERSIBLE ALKENE COUPLING TO Pt(II) OXOCOMPLEXES. **Endre Szuromi** and Paul R. Sharp; University of Missouri-Columbia, Columbia, MO 294

335. 11:40 NEW MONOHELICAL TRANSITION METAL COMPLEXES. **Christopher J. Levy**, Alexander Wiznycia and Hellen Dyer, Kansas State University, Manhattan, KS 295

Inorganic Chemistry (continued)

336. 12:00 HELICAL IRON AND ZINC COMPLEXES DERIVED FROM TETRADENTATE SCHIFF BASE LIGANDS. **Alexander Wiznycia** and Christopher J. Levy; Kansas State University, Manhattan, KS 296

Organic Chemistry

Organizer: Duy Hua

Organic Chemistry I

Regency B I Ballroom
1:00PM - 5:20PM Wednesday
Stefan Bossmann, Presiding

16.	1:00	SYNTHESIS OF FUNCTIONALIZED BELTENES FOR SELF-ASSEMBLED NANOMATERIALS. **Kaiyan Lou**, Xiaodong Huang, Neil Brown, Huiping Zhao, Bernard Wiredu and Duy H. Hua; Kansas State University, Manhattan, KS	95
17.	1:20	3-DEOXYSCHWEINFURTHIN B: A SYNTHETIC SCHWEIN-FURTHIN WITH ANTICANCER ACTIVITY. **Jeffrey D. Neighbors**[1], Maya Salnikova[1], David F. Wiemer[1] and John A. Beutler[2]; [1]University of Iowa, Iowa City, IA; [2]National Cancer Institute at Frederick, Frederick, MD	96
18.	1:40	Ru-ASSISTED HORNER-WADSWORTH-EMMONS SPIROCYCLIZATION. **Rashmi Dalvi** and F. Christopher Pigge; University of Missouri-St. Louis, St. Louis, MO	96
19.	2:00	DIELS-ALDER REACTIONS OF A CYCLO-PENTADIENONE. Michael Harmata and **Maria G. Gomes**; University of Missouri-Columbia, Columbia, MO	97
20.	2:20	GENERATION OF 3-BROMOCYCLOPENTA-DIENONE AND SOME CHEMISTRY OF ITS DIMERIZATION PRODUCT. Michael Harmata and **Soo Yeun Kim**; University of Missouri-Columbia, Columbia, MO	98
21.	2:40	PALLADIUM-MEDIATED SYNTHESIS OF ISOXAZOLINES. **Katherine S. Frost**, Laura G. Emmerich and Michael D. Mosher; University of Nebraska at Kearney, Kearney, NE	98

Organic Chemistry I (continued)

22.	3:00	ANALOGUE OF ISO-1. **Michael D. Mosher** and Benjamin Anderson; University of Nebraska at Kearney, Kearney, NE	98
23.	3:20	SOLVENT IS A DETERMINANT IN THE ANION BINDING SELECTIVITY OF UREA-PICKET PORPHYRIN RECEPTORS. **Sumith A. Kularatne** and Dennis H. Burns; Wichita State University, Wichita, KS	99
24.	3:40	BIOACTIVE FLUORESCENT FARNESOL ANALOGS. **Roman Shchepin**, Patrick Dussault, Kenneth Nickerson and Raluca Dumitru; University of Nebraska-Lincoln, Lincoln, NE	100
25.	4:00	ASYMMETRIC ALLYLATION USING SELF-ASSEMBLED CHIRAL BIDENTATE P,P-LIGANDS. **Di Wu**, D. Sahadeva Reddy, Shin A. Moteki, Hector Palencia and James M. Takacs; University of Nebraska - Lincoln, Lincoln, NE	100
26.	4:20	STUDIES TOWARD THE TOTAL SYNTHESIS OF 1,2-DIOXANE POLYKETIDES. Patrick Dussault[1], **Chunping Xu**[1] and Joseph M. Raible[2]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]University of Kansas, Lawrence, KS	101
27.	4:40	SYNTHESIS OF ENDO-METACYCLOPHANES UTILIZING GRUBBS' CATALYST WHILE INCORPORATING A PORPHYRIN SCAFFOLD. **Charles L. Jayne**, Sumith A. Kularatne and Dennis H. Burns; Wichita State University, Wichita, KS	102
28.	5:00	SYNTHESIS AND PROPERTIES OF AZULENE-CONTAINING POLYMERS. **Xueyi Chen** and T. C. Sandreczki; University of Missouri-Kansas City, Kansas City, MO	103

Organic Chemistry II

Regency B I Ballroom
8:00AM - 12:00PM Thursday
Stefan Bossmann, Presiding

157.	8:00	WATER-SOLUBLE CONJUGATED POLYMERS: SYNTHESIS AND OPTICAL PROPERTIES. **Baohan Xie**, Meng Lu, Jeonghee Kang, Ruiyun Guo, Vikalp Thakor and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO	184
158.	8:20	SELENIUM CATALYZED HALOLACTONIZATION: NUCLEOPHILIC ACTIVATION OF ELECTROPHILIC HALOGENATING REAGENTS. **Shelli R. Mellegaard** and Jon A. Tunge; The University of Kansas, Lawrence, KS	185
159.	8:40	ALLYLATION OF NONSTABILIZED KETONE ENOLATES *VIA* THE TRANSITION METAL-CATALYZED CARROLL REARRANGEMENT. **Erin C. Burger** and Jon A. Tunge; University of Kansas, Lawrence, KS	185
160.	9:00	MODELING 'ANTENNA-REACTION CENTER' FUNCTIONALITY OF PHOTOSYNTHESIS: ENERGY TRANSFER FOLLOWED BY ELECTRON TRANSFER IN SUPRAMOLECULAR TRIADS COMPOSED OF BORON DIPYRRIN, ZINC PORPHYRIN AND FULLERENE. **Phillip M. Smith**[1], Melvin E. Zandler[1], Amy L. McCarty[1], Osamu Ito[2], Mitsunari Itou[2], Yasuyuki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan	186
161.	9:20	HALOGEN KINETIC ELEMENT EFFECT IN NUCLEOPHILIC AROMATIC PHOTOSUBSTITUTIONS. **Gene G. Wubbels**[1], Bryan Coughlin[2], Carol Peterson[2], Laura Flynn[3] and Heather A. Scholtz[3]; [1]University of Nebraska at Kearney, Kearney, NE; [2]Grinnell College, Grinnell, IA; [3]Washington College, Chestertown, MD	187

Organic Chemistry II (continued)

162.	9:40	PRELIMINARY STUDIES ON THE DEOXYGENATION OF FATTY ACIDS TO HYDROCARBON FEEDSTOCKS. **Amol A. More**, Keith Hohn and John R. Schlup; Kansas State University, Manhattan, KS	187
163.	10:00	SYNTHESIS OF 2-H BENZOPYRANS THROUGH C-C BOND FORMATION *VIA* IODOCYCLIZATION. **Shilpa A. Worlikar** and Richard C. Larock; Iowa State University, Ames, IA	188
164.	10:20	DEVELOPMENT OF CYCLIC ENOL PHOSPHONAMIDATES USING RING-CLOSING METATHESIS. **Stephen R. Sieck**, Matthew D. McReynolds and Paul R. Hanson; University of Kansas, Lawrence, KS	188
165.	10:40	FUNCTIONALLY-ACTIVE PHOSPHATE TETHERS IN SYNTHESIS. **Alan Whitehead** and Paul R. Hanson; University of Kansas, Lawrence, KS	189
166.	11:00	FUNCTIONALLY-ACTIVE PHOSPHATE TETHERS: HARNESSING LATENT LEAVING GROUP ABILITY IN BICYCLIC PHOSPHATE TRIESTERS. **Alan Whitehead** and Paul R. Hanson; University of Kansas, Lawrence, KS	189
167.	11:20	SOME UNUSUAL CHARACTERISTICS OF CRYSTALLINE ORGANIC COMPOUNDS UNCOVERED BY X-RAY STUDIES, *e.g.*, ROTATIONAL DISORDER AND H-BONDING VS. "MP (DEC.)". **Cal Y. Meyers**, Paul B. Sandrock, Aaron W. McLean and Paul D. Robinson; Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry, Southern Illinois University Carbondale, Carbondale, IL	190
168.	11:40	ENANTIOSPECIFIC SYNTHESIS OF (+)-Z-BISDEHYDRODOISYNOLIC ACID. **Yuqing Hou**; Southern Illinois University, Carbondale, IL	191

Physical Chemistry

Organizer: Vincent Ortiz

Physical Chemistry I

Conference Room III
1:00PM - 4:40PM Wednesday
Olga Dolgounitcheva, Presiding

29.	1:00	GAS PHASE REACTIONS OF UO_2^+ AND UO_2^{2+} WITH WATER. **Michael J. Van Stipdonk**, Winnie Chien and Kellis Bulleigh; Wichita State University, Wichita, KS	103
30.	1:20	ADSORPTION AND REACTION OF AMINES ON GERMANIUM AND SILICON SURFACES. **C. Michael Greenlief** and Pornpimol Prayongpan; University of Missouri-Columbia, Columbia, MO	104
31.	1:40	HYDRATION AND ALCOHOL-ADDITION REAC-TIONS OF GAS-PHASE LITHIUM-ALCOHOL COMPLEXES. **Sila Odour** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS	104
32.	2:00	SIMULATED VELOCITY DISTRIBUTIONS OF MOLECULES PASSING THROUGH ORIFICES INTO A VACUUM. **Phillip G. Wahlbeck**; Wichita State University, Wichita, KS	105
33.	2:20	SOLUBILITY AND TENSIOMETRIC STUDIES OF VARIOUS ALKALINE EARTH AND ANIONIC SURFACTANT COMPOUNDS. **Jim D. Roach** and Alan J. Oberley; Emporia State University, Emporia, KS	105
	2:40	Break	
34.	3:00	SAM1 STUDY OF THE HOMOPOLYMERIZATION OF SILICON DERIVATIVES OF TETRAOXASPIRO[5.5]UNDECANE. **T. P. Marshall** and Andrew J. Holder; UMKC, Kansas City, MO	106

Physical Chemistry I (continued)

35.	3:20	ELECTRIC-FIELD-INDUCED DYNAMICS IN RADIAL LIQUID CRYSTAL DROPLETS STUDIED BY MULTIPHOTON-EXCITED FLUORESCENCE MICROSCOPY: INTERFACIAL EFFECTS AND METASTABLE CONFIGURATIONS. **Aifang Xie** and Daniel Higgins; Kansas State University, Manhattan, KS	106
36.	3:40	ESR STUDIES OF A REORIENTING NICKEL COMPLEX. **Bruce A. Kowert**; St. Louis University, St. Louis, MO	107
37.	4:00	SURFACE-ENHANCED RAMAN SPECTROSCOPY USING SILVER NANOPARTICLES: THE EFFECTS OF PARTICLE SIZE AND HALIDE IONS ON AGGREGATION. **Paul W. Jagodzinski**[1] and Garry P. Glaspell[2]; [1]Colorado School of Mines, Golden, CO; [2]Virginia Commonwealth University, Richmond, VA	107
38.	4:20	FORMATION AND SURFACE-ENHANCED RAMAN SPECTRA OF METAL CYANIDE COMPLEXES IN GOLD COLLOID SOLUTION. **Paul W. Jagodzinski** and Michael B. Jacobs; Colorado School of Mines, Golden, CO	108

Physical Chemistry II

Conference Room III
8:00AM - 11:40PM Thursday
Paul Smith, Presiding

169.	8:00	ELUCIDATION OF CONDUCTIVITY IN A HIGHLY-CONJUGATED POLYMER USING ESR AND CONDUCTIVITY. **T.C. Sandreczki**[1], J. Park[1], J. Guthrie[2], F. Badrun[1], K. Rogers[1] and J. Bowen[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]University of Missouri-	192

Columbia, Columbia, MO

Physical Chemistry II (continued)

170.	8:20	INFLUENCE OF LIGAND VIBRATIONAL ENERGIES ON HYDRATION BEHAVIOR OF Ag(I) COMPLEXES IN THE GAS PHASE. **Dorothy A. Hanna**[1] and Michael Van Stipdonk[2]; [1]Kansas Wesleyan University, Salina, KS; [2]Wichita State University, Wichita, KS	192
171.	8:40	EQUILIBRIUM STRUCTURE OF *ORTHO*-BENZYNE. **Peter Groner**[1] and Stephen G. Kukolich[2]; [1]University of Missouri - Kansas City, Kansas City, MO; [2]University of Arizona, Tucson, AZ	192
172.	9:00	ENERGY TRANSFER AT A GAS-LIQUID INTERFACE. **Tamas Szabo**, Ali Siavosh-Haghighi and John E. Adams; University of Missouri-Columbia, Columbia, MO	193
173.	9:20	CHEMILUMINESCENCE FROM SURFACE REACTION ON METAL-OXIDE NANO-CRYSTALS. Hohn Keith and **Chien-Chang Huang**; Kansas State University, Manhattan, KS	193
	9:40	Break	
174.	10:00	*IN SITU* INFRARED STUDY OF THE CATALYTIC IGNITION OF METHANE ON Pt/Al_2O_3. **Chundi Cao**, Abdennour Bourane, John R. Schlup and Keith L. Hohn; Kansas State University, Manhattan, KS	194
175.	10:20	DFT MO CALCULATIONS ON PORPHYRIN-QUINHYDRONE DYADS: PREDICTION OF STABLE STACKED QUINONE-HYDROQUINONE ENTITIES WITH B3LYP/3-21G(*). Francis D'Souza[1], Paul A. Karr[2], **Melvin E. Zandler**[1] and Michael Beck[2]; [1]Wichita State University, Wichita, KS; [2]Wayne State College, Wayne, NE	195

Physical Chemistry II (continued)

176.	10:40	MOLECULAR DYNAMICS SIMULATIONS OF THE EFFECT OF PHOSPHORYLATION ON STRUCTURE AND DYNAMICS OF PHOSPHOLAMBAN IN MEMBRANE BILAYER. **Yao A. Houndonougbo**, Krzysztof Kuczera and Gouri S. Jas; University of Kansas, Lawrence, KS	196
177.	11:00	FT-IR STUDIES OF PHOTOCHEMICAL OXIDATION OF ORGANIC COMPOUNDS OVER TiO_2-SiO_2. **Dilip K. Paul**[1], D. A. Panayotov[2] and J. T. Yates[2]; [1]Pittsburg State University, Pittsburg, KS; [2]University of Pittsburgh, Pittsburgh	197
178.	11:20	ELECTRONIC STRUCTURE FOR POLYTYPES OF SEMI-CONDUCTING BORON CARBIDE. **Petru Lunca-Popa**, Snjezana Balaz, Carolina Ilie and Jennifer I. Brand; University of Nebraska, Lincoln, NE	197

POSTER SESSIONS

Poster Session I
Regency A Ballroom
7:00PM - 10:00PM Wednesday
Tanya Young and Dan Higgins, Presiding
 Analytical Chemistry
 Crystal Engineering
 Environmental Chemistry
 Organic Chemistry
 Physical Chemisty

Analytical Chemistry

46. MICROCHIP-BASED BLOOD BRAIN BARRIER MIMIC FOR MONITORING THE FATE OF ENDOTHELIUM-DERIVED NITRIC OXIDE. **Matthew K. Hulvey** and R. Scott Martin; Saint Louis University, St. Louis, MO 114

47. ALTERING ION TRANSPORT ACROSS NANOTUBE MEMBRANES. **Sai Sumana Penumetcha** and Erich D. Steinle; Southwest Missouri State University, Springfield, MO 114

48. BORON DIPYRRIN-BORONIC ACID CHEMOSENSORS FOR BIOCHEMICAL DETECTION OF *CIS* DIOLS. **Elena Lay**, Rodrigue Tchoufong, Raghu Chitta, Francis D'Souza and Ram Singhal; Wichita State University, Wichita, KS 115

49. CARBON-PYROLYZED ELECTRODES FOR MICROCHIP CAPILLARY ELECTROPHORESIS WITH DUAL-ELECTRODE ELECTROCHEMICAL DETECTION. **David J. Fischer**, Walter R. Vandaveer IV and Susan M. Lunte; University of Kansas, Lawrence, KS 116

50. DEVELOPMENT OF AN ON-LINE MICRODIALYSIS-MICROCHIP CE SYSTEM TO MONITOR NEUROTRANSMITTER RELEASE. **Pradyot Nandi**[1], Bryan Huynh[1], Barbara Fogarty[1], R. Scott Martin[2] and Susan Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Saint Louis University, St. Louis, MO 117

Poster Session I

Analytical Chemistry (continued)

51. EFFECT OF NON-POLAR SIDE CHAINS ON COLLISION-INDUCED DISSOCIATION OF CATION-IZED PEPTIDES. **Peter Hamlet**[1], Travis J. Cooper[2], Monohari Silva[2], Qun Wu[2] and Michael J. Van Stipdonk[2]; [1]Pittsburg State University, Pittsburg, KS; [2]Wichita State University, Wichita, KS 117

52. ELECTROCHEMICAL BEHAVIOR OF HORSE HEART CYTO-CHROME C IMMOBILIZED ON FULLERENE FILM-MODIFIED ELECTRODES. **Lisa M. Rogers**[1], Erin S. O'Dell[1], Agnieszka Kochman[2], Wlodzimierz Kutner[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Polish Academy of Sciences, Warsaw, Poland 118

53. INFLUENCE OF SPECIFIC AMINO ACIDS ON INTRA-MOLECULAR PROTON MIGRATION DURING CID. **Qun Wu**, Kellis Bulleigh and Michael J. Van Stipdonk; Wichita State University, Wichita, KS 119

54. INVESTIGATION OF ION-SELECTIVE ELECTRODES BASED ON ERBIUM(III) PORPHYRINS. **Joseph K. Mbugua** and Erich D. Steinle; Southwest Missouri State University, Springfield, MO 119

55. ION TRAP MS STUDY OF THE INFLUENCE OF SEQUENCE ON PEPTIDE FRAGMENTATION REACTION RATES. **Sammer Tekarli**, Travis Cooper and Michael J. Van Stipdonk; Wichita State University, Wichita, KS 120

56. MEASUREMENT OF METHANOL IN AQUEOUS ALCOHOL MIXTURES BY KROMOSCOPY. **David S. Cho** and Mark A. Arnold, University of Iowa, Iowa City, IA 120

57. MECHANISM OF ELIMINATION OF WATER FROM GAS-PHASE METAL-CATIONIZED TRIPEPTIDE ESTERS. **Erach Talaty**, Travis Cooper, Debra Piland, David Bateman, Adeel Syed and Michael J. Van 121

Stipdonk; Wichita State University, Wichita, KS

Poster Session I

Analytical Chemistry (continued)

58. MIXED REGIOSELECTIVITY IN THE ARG-177 MUTANTS OF CORYNEBACTERIUM DIPHTHERIAE HEME OXYGENASE AS A CONSEQUENCE OF IN-PLANE HEME DISORDER. **Yuhong Zeng**[1], Rahul Deshmukh[2], Gregori A. Caignan[1], Richard A. Bunce[3], Angela Wilks[2] and Mario Rivera[1]; [1]The University of Kansas, Lawrence, KS; [2]School of Pharmacy, University of Maryland, Baltimore, MD; [3]Oklahoma State University, Stillwater, OK 122

59. ON THE MECHANISM AND CONSEQUENCES OF HEMIN BINDING BY APOCYTOCHROMES B5: INSIGHT FROM STUDIES OF THE S71L MUTANT OF THE BOVINE MICROSOMAL PROTEIN. **An Wang**, Adriana Altuve, Aaron B. Cowley, David R. Benson and Mario Rivera; The University of Kansas, Lawrence, KS 123

60. POLYMERIZATION VOLUME CHANGE IN OXIRANES AND METHACRYLATES. **Jason Finley**, Randall Michelson, Patrycja Wilczynska, Benjamin Iwai, Heather Vastlick, Greg Giese, James Code, Andrew Holder and Kathleen V. Kilway; University of Missouri-Kansas City, Kansas City, MO 123

61. SOL-GEL MODIFIED POLY(DIMETHYLSILOXANE) MICRO-FLUIDIC DEVICES WITH HIGH ELECTRO-OSMOTIC MOBILITIES AND HYDROPHILIC CHANNEL WALL CHARACTERISTICS. **Gregory T. Roman**, Christopher T. Culbertson, Tyler Hlaus, Kevin Bass and Todd Seelhammer; Kansas State University, Manhattan, KS 124

62. SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATION OF PETUNIA PIGMENTS. James M. Chapman, Dale Harak and **Kyle Cummins**; Rockhurst University, Kansas City, MO 125

Poster Session I (continued)

Crystal Engineering

63. COMPLEXATION OF MONO- AND DICYANOVINYL-ARENES. **Cortnie Vogelsberg**[1], DeAnna Travis[1], John VanScoy[1], Douglas M. Ho[2] and Kathleen V. Kilway[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]Princeton University, Princeton, NJ 126

64. IF THERE WAS A FOURTH LITTLE PIG HE WOULD HAVE BUILT HIS HOUSE OUT OF THESE.....DESIGN, SYNTHESIS AND SUPRAMOLECULAR CHEMISTRY OF NEW AZAINDOLE-BASED MOLECULES. **Michelle Smith**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS 126

65. METAL-ORGANIC TEMPLATES THAT DIRECT REAC-TIVITY IN THE SOLID STATE. **Ivan G. Georgiev**, Giannis S. Papaefstathiou and Leonard R. MacGillivray; The Univerisity of Iowa, Iowa City, IA 127

66. N-SUBSTITUTED PYRAZOLE…"LEGO®" FOR CHEMISTS? **Benjamin M. T. Scott**, John Desper and Christer B. Aakeroy; Kansas State University, Manhattan, KS 127

67. TRIAROYLBENZENE: SUPER MOLECULES IN SUPRA-MOLECULAR CHEMISTRY. **Mayuri K. Dighe**, F. Christopher Pigge and Nigam P. Rath; University of Missouri-St. Louis, St. Louis, MO 128

Environmental Chemistry

68. AQUEOUS MERCURY ION ADSORPTION ONTO DIFFERENT TYPES OF PLASTIC CONTAINERS. **Daniel Dorn** and James L. Robinson, U. S. Environmental Protection Agency, Kansas City, KS 128

Poster Session I

Environmental Chemistry (continued)

69. RESEARCH-INTEGRATED CURRICULUM IN GEOENVIRONMENTAL ENGINEERING. Alok Bhandari, Lakshmi N. Reddi, David R. Steward, Stacy L. Hutchinson and **Larry Erickson**; Kansas State University, Manhattan, KS 129

70. SYNCHROTRON FOURIER TRANSFORM INFRARED MICROSPECTROSCOPY AS A TOOL TO MONITOR THE FATE OF ORGANIC CONTAMINANTS IN PLANTS. **Kenneth Dokken**[1], Larry Erickson[1], Lawrence Davis[1] and Nebojsa Marinkovic[2]; [1]Kansas State University, Manhattan, KS; [2]Albert Einstein Center for Synchrotron Biosciences, Upton, NY 129

71. ANAEROBIC BIODEGRADATION OF TETRACHLOROETHYL-ENE (PCE) IN SOIL AND GROUNDWATER. **Sathishkumar Santharam**, Larry Davis and Larry E. Erickson; Kansas State University, Manhattan, KS 130

72. ACCELERATED DEGRADATION OF HIGH EXPLOSIVES BY ZEROVALENT IRON IN THE PRESENCE OF SELECTED CARBON MATERIALS. **Jang-Eok Kim**[1], Bernard J. Kronschnabel[2], Jeong Park[3], Jong-Sung Kim[2] and Patrick J. Shea[2]; [1]Kyungpook National University, Daegu, South Korea; [2]University of Nebraska-Lincoln, Lincoln, NE; [3]University of Arkansas, Fayetteville, AR 131

73. NEW INSIGHTS INTO THE MECHANISMS OF THE THERMAL FENTON REACTIONS USING DIFFERENT IRON(II)-COMPLEXES. **Stefan H. Bossmann**[1], Esther Oliveros[2], Mark Kantor[2], Nabil Shahin[2], Sandra Niebler[2], Anna Bonfill[2], Michael Woerner[2] and Andre M. Braun[2]; [1]Kansas State University, Manhattan, KS; [2]University of Karlsruhe (TH), Karlsruhe, Germany 132

74. STUDY OF ILLITE PARTICLE AGGREGATION BY COMBINED STATIC AND DYNAMIC LIGHT SCATTERING. **Ildiko K. Lini** and James A. Rice; South 133

Dakota State University, Brookings, SD

Poster Session I
Environmental Chemistry (continued)

75.	*IN SITU* FTIR STUDIES OF REDUCTION OF NITRIC OXIDE EMISSIONS. **Jeremy VanAuker**, John Barriner and Dilip K. Paul; Pittsburg State University, Pittsburg, KS	133

Organic Chemistry

76.	PERIODIC TABLE FOR BENZENOID HYDROCARBON ISOMER CLASSES AND BEYOND. **Jerry R. Dias**; University of Missouri, Kansas City, MO	134
77.	SUPRAMOLECULAR COMPLEX COMPOSED OF A ZINC PORPHYRIN DIMER AND FULLERENE BEARING TWO AXIALLY COORDINATING PYRIDINE ENTITIES. **Suresh Gadde**[1], Melvin E. Zandler[1], Osamu Ito[2], Mitsunari Itou[2], Yasuyuki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan	134
78.	THREE-COMPONENT COUPLING/RING-CLOSING METATHESIS APPROACH TO THE SYNTHESIS OF FUNCTIONALIZED PHOSPHONOPYRROLES. **Shubhasish Mukherjee**, Jutta Wanner and Paul R. Hanson; University of Kansas, Lawrence, KS	136
79.	APPLICATION OF η^6-ARENE RUTHENIUM COMPLEXES IN SYNTHESIS. **Shobha R. Malgireddy** and F. Christopher Pigge; University of Missouri - St. Louis, St. Louis, MO	136
80.	APPLICATION OF PHOSPHATE TETHERS TO THE ASYMMETRIC SYNTHESIS OF SKIPPED POLYOL SUBUNITS. **Joshua D. Waetzig**, Alan Whitehead and Paul R. Hanson; University of Kansas, Lawrence, KS	137
81.	CATION STABILITY IN QUATERNARY AMMONIUM METHYLCARBONATES. **Justin G. Norberg**, Gary W.	137

Earl and Duane E. Weisshaar; Augustana College, Sioux Falls, SD

Poster Session I

Organic Chemistry (continued)

82. COMPLETE TWO-DIMENSIONAL NMR ASSIGNMENT AND CHARACTERIZATION OF SULFONATED AND UNSULFONATED POLY(ETHER ETHER KETONE) (PEEK) MONOMERS. **Scott E. McKay**[1], Robert W. Lashlee III[1], Brenda D. Moul[1], Bryce A. Holthouse[1] and Robert W. Kopitzke[2]; [1]Central Missouri State University, Warrensburg, MO; [2]Winona State University, Winona, MN 138

83. DESIGN AND SYNTHESIS OF AN OLIGODEOXY-UCLEOTIDE-DOTA CONJUGATE. **Samuel Sarsah** and Eric Trump; Emporia State University, Emporia, KS 138

84. DESYMMETRIZATION OF PSEUDO-C_2-SYMMETRIC MONO-CYCLIC PHOSPHATES. **James P. McParland**, Alan Whitehead and Paul R. Hanson; University of Kansas, Lawrence, KS 138

85. ENZYMATICALLY-CATALYZED ALCOHOLYSIS OF SOYBEAN OIL AS THE FIRST STEP OF ALKYD RESIN SYNTHESIS. **Tomas Vlcek**; Pittsburg State University, Pittsburg, KS 139

86. EXAMINATION OF THE SYNTHESIS OF NITRO-ALCOHOLS AND NITROALKENES TO YIELD PRECUR-SORS FOR ISOC REACTIONS. **William D. Buchanan**, Aaron K. Graumann, Steve J. Moore and Jetty Duffy-Matzner; Augustana College, Sioux Falls, SD 139

87. GENERATION OF N-HETEROCYCLIC CARBENE COMPLEXES THROUGH SILYLATED IMIDAZOLIUM SALTS. **Joseph Rashad Atkins** and Stefan Kraft; Kansas State University, Manhattan, KS 140

88. HPLC ANALYSIS IN BIOFRIENDLY QUATERNARY AMMONIUM SYNTHESIS. **Brian D. Rekken**, Gary W. Earl and Duane E. Weisshaar; Augustana College, Sioux 140

Falls, SD

Poster Session I

Organic Chemistry (continued)

89. IMPLEMENTATION OF ROMP-DERIVED DCC FOR LIBRARY GENERATION. **Punitha Vedantham**[1], Parul Jitendra Gor[1], Gunda I. Georg[1], Qi-Zhuang Ye[1], Daniel L. Flynn[2] and Paul R. Hanson[1]; [1]University of Kansas, Lawrence, KS; [2]Deciphera Pharmaceuticals Inc., Lawrence, KS 141

90. INVESTIGATING ANION STABILITY IN QUATERNARY AMMONIUM METHYL CARBONATES. **Michael W. Amolins**, Gary W. Earl and Duane E. Weisshaar; Augustana College, Sioux Falls, SD 141

91. INVESTIGATING THE POSSIBILITY OF CHELATION BETWEEN THE OXYGEN ON THE ENYNE AND THE METAL CENTER IN THE WULFF-KAESLER [2+2] CYCLOADDITION. **Kelsie Betsch**[1], Yiqian Lian[2] and William D. Wulff[2]; [1]Augustana College, Sioux Falls, SD; [2]Michigan State University, East Lansing, MI 142

92. MAGNESIUM PORPHYRIN-FULLERENE DYAD: ELECTRON TRANSFER REACTIONS. **Amy L. McCarty**[1], Suresh Gadde[1], Paul A. Kaar[1], Melvin E. Zandler[1], Osamu Ito[2], Mohamed E. El-Khouly[2], Yasuyaki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan 142

93. METHOXYPOLY(OXYETHYLENE)MALEIMIDES FOR SELECTIVE PROTEIN MODIFICATION. **Mary E. Hansen** and Reza S. Herati; Southwest Missouri State University, Springfield, MO 143

94. NEW ROUTES FOR ORGANOMETALLIC-MEDIATED SYNTHESIS OF HETEROCYCLIC RING SYSTEMS. **Erik R. Hoefgen** and F. C. Pigge; University of Missouri - St. Louis, St. Louis, MO 144

Poster Session I

Organic Chemistry (continued)

NITRONITROALKANE TAUTOMERIZATION. **Douglas Miller** and Melvyn W. Mosher; Missouri Southern State University, Joplin, MO

Poster Session I
Organic Chemistry (continued)

103. SEQUENTIAL ALKYLATION OF TRÖGER'S BASE. AN APPROACH TO NEW CHIRAL LIGANDS. Michael Harmata and **Kanok-On Rayanil**; University of Missouri-Columbia, Columbia, MO 148

104. SPECTROSCOPY OF 3,5-DISUBSTITUTED ISOXAZOLINES. **Laura G. Emmerich**, Katherine S. Frost and Michael D. Mosher; University of Nebraska at Kearney, Kearney, NE 149

105. STUDIES DIRECTED TOWARD DIMERIZATION OF LITHOCHOLIC ESTER DERIVATIVES USING GRUBB'S REAGENT. **Christopher G. Dallstream** and Jerry R. Dias; University of Missouri-Kansas City, Kansas City, MO 149

106. SYNTHESIS AND CHARACTERIZATION OF POLYMER NETWORKS *VIA* HYDROSILYLATION OF TRIGLYCERIDES. **Alisa Zlatanic** and Zoran Petrovic; Pittsburg State University, Pittsburg, KS 149

107. SYNTHESIS OF α,β-UNSATURATED-δ-LACTONES *VIA* PALLADIUM-CATALYZED COUPLING OF ALLENYL ESTERS, BORONIC ACIDS AND ALDEHYDES. **Chad D. Hopkins**[1], Lisa Guan[2] and Helena C. Malinakova[1]; [1]University of Kansas, Lawrence, KS; [2]Independence Community College, Independence, KS 150

108. SYNTHESIS OF 2,2,3,4-TETRASUBSTITUTED ^{2}H-1-BENZO-PYRANS *VIA* A PALLADIUM-MEDIATED ANNULATION OF UNSYMMETRICAL ALKYNES. **Genliang Lu**, John C. Hershberger and Helena C. Malinakova; University of Kansas, Lawrence, KS 151

109. SYNTHESIS OF A TETRAAZAMACROCYCLE FOR A 152

Poster Session I

Organic Chemistry (continued)

THE POSITION OF THEIR DOUBLE BOND AND WHOSE CRYSTALLINE FORMS APPEAR TO BE SUPERIMPOSED ONTO EACH OTHER. **Songwen Xie**, Cal Y. Meyers and Paul D. Robinson; [1]Southern Illinois University, Carbondale, IL

Poster Session I

Organic Chemistry (continued)

117. WHEN ARE EXPERIMENTALLY DETERMINED pK_a VALUES NOT "REAL pK_a" VALUES? **Aaron W. McLean**[1], Cal Y. Meyers[1], Yuqing Hou[1] and Paul D. Robinson[2]; [1]Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry; Southern Illinois University Carbondale, Carbondale, IL; [2]Southern Illinois University Carbondale, Carbondale, IL 157

Physical Chemistry

118. KIRKWOOD-BUFF DERIVED FORCE FIELD FOR AMIDES. **Myungshim Kang** and Paul E. Smith; Kansas State University, Manhattan, KS 158

119. *AB INITIO* STUDIES OF THE ALKYLATION OF BENZENE. **Dustin S. Hillman**, Shenmin Li and Ward H. Thompson; University of Kansas, Lawrence, KS 158

120. ANGULAR DEPENDENCE OF SINGLE IONIZATION OF HYDROGEN MOLECULES BY PROTON IMPACT. **Nora G. Johnson**[1], K. D. Carnes[2], Heather D. Baxter[1], I. Ben-Itzhak[2] and E. Wells[1]; [1]Augustana College, Sioux Falls, SD; [2]Kansas State University, Manhattan, KS 159

121. CHARACTERIZATION OF ISOCYANOAZULENE SELF-ASSEMBLED MONOLAYERS ON GOLD. **David R. Moody**[1], Cindy L. Berrie[2], Mikhail V. Barybin[2], Randall Robinson[2] and Edward Weintrob[2]; [1]Creighton University, Omaha, NE; [2]University of Kansas, Lawrence, KS 159

122. DERIVATIVES OF THE POLARIZATION PROPAGATOR IN-CLUDING ORBITAL RELAXATION EFFECTS. **Edmund L. Tisko**[1] and Katharine C. Hunt[2]; 160

[1]University of Nebraska at Omaha, Omaha, NE; [2]Michigan State University, East Lansing, MI

Poster Session I

Physical Chemistry (continued)

123. FLUORESCENCE MICROSCOPY INVESTIGATION OF PHOSPHOLIPID/SPHINGOMYELIN/CHOLESTEROL DERIVATIVES IN MIXED LANGMUIR MONOLAYERS. **Rose Rowden** and Alexa B. Serfis; Saint Louis University, St. Louis, MO 161

124. *IN SITU* NMR OF COMBUSTION USING OPTICALLY PUMPED ^{129}Xe. **Rachel L. Parris**[1] and Thomas Meersmann[2]; [1]Emporia State University, Emporia, KS; [2]Colorado State University, Fort Collins, CO 161

125. INVESTIGATIONS OF THE CONDUCTIVITY OF ORGANIC THIN FILMS USING CONDUCTIVE ATOMIC FORCE MICROSCOPY. **David Du Bose**, Cindy Berrie and Cornelius Kristalyn; University of Kansas, Lawrence, KS 162

126. MOLECULAR DYNAMICS OF LIQUID CLUSTERS: METHODS AND RESULTS. **John M. Schneiderman** and Brian G. Moore; Augustana College, Sioux Falls, SD 162

127. MONTE CARLO SIMULATION OF ABSORPTION AND FLUORESCENCE SPECTRA AND TWO-DIMENSIONAL FREE-ENERGY CALCULATIONS IN NANO-CONFINED SOLVENTS. **J. A. Gomez** and Ward H. Thompson; University of Kansas, Lawrence, KS 162

128. NANOARRAY-SURFACES BY RECONSTITUTION OF THE MSPA PORIN INTO STABILIZED LONG-CHAIN-LIPID-MONOLAYERS AT A GOLD-SURFACE. **Stefan H. Bossmann**[1], Katharine E. Janik[1], Sandra Niebler[2], Eliso Gogritchiani[2], Michael Woerner[2], Andre M. Braun[2] and Michael Niederweis[3]; [1]Kansas State University, Manhattan, KS; [2]University of Karlsruhe, Karlsruhe, 163

Germany; [3]University of Erlangen-Nürnberg, Erlangen, Germany

Poster Session I

Physical Chemistry (continued)

129. ULTRAFAST MODE-SELECTIVE STUDIES OF INTRAMOLECULAR ENERGY TRANSFER. Abhijit Chakraborty, Benjamin D. Prince, Beth M. Denk and **Hans U. Stauffer**; Iowa State University, Ames, IA 164

Poster Session II

Regency A Ballroom
9:00AM - 12:00PM Thursday
Tanya Young and John Desper, Presiding
- Drug Design and Bioorganic Chemistry
- Inorganic Chemistry
- Methods in Electronic Structure Theory
- Nanostructured Materials and Air Quality
- Sol-gel Chemistry
- Biochemistry
- Chemical Education

Drug Design and Bioorganic Chemistry

187. IMPROVED LOADING AND CLEAVAGE METHODS FOR SOLID-PHASE SYNTHESIS USING CHLOROTRITYL RESINS: SYNTHE-SIS AND TESTING OF A LIBRARY OF 144 DISCRETE CHEMICALS AS POTENTIAL FARNESYLTRANSFERASE INHIBI-TORS. **Kevin J. Langenwalter**[1], Jewn Giew Park[1], Yuan-Ping Pang[1], Patrick J. Casey[2] and Carolyn A. Weinbaum[2]; [1]Mayo Clinic College of Medicine, Rochester, MN; [2]Duke University Medical Center, Durham, NC 204

188. INHIBITION OF HUMAN TRYPTASE BY 1,2,5-THIADIAZOLIDIN-3-ONE-1,1-DIOXIDE-BASED HETEROCYCLIC SULFIDES. **Swathi Mohan**[1], Tzutshin Wong[1], 204

Christopher S. Groutas[1], Zhong Lai[1], Kevin R. Alliston[1], Nga Vu[1], Norman M. Schechter[2] and William C. Groutas[1]; [1]Wichita State University, Department of Chemistry, Wichita, KS; [2]University of Pennsylvania, Department of Dermatology, Philadelphia, PA

Poster Session II
Drug Design and Bioorganic Chemistry (continued)

189. ISOINDOLIN-1-ONE: A POWERFUL SCAFFOLD FOR THE DESIGN OF POTENT NON-COVALENT INHIBITORS OF SERINE PROTEASES. **Tzu Tshin Wong**[1], Christopher S. Groutas[1], Xiangdong Gan[1], Kevin R. Alliston[1], Laura S. Stevenson[1], William C. Groutas[1] and John R. Hoidal[2]; [1]Wichita State University, Wichita, KS; [2]University of Utah Health Sciences Center, Salt Lake City, UT 205

190. MECHANISM-BASED INACTIVATION OF HUMAN LEUKOCYTE ELASTASE *VIA* AN ENZYME-INDUCED SULFONAMIDE FRAGMENTATION PROCESS. **Xiangdong Gan**, Liuqing Wei, Zhong Lai, Kevin R. Alliston, Jiaying Zhong, Jeff B. Epp, Juan Tu, Asiri B. Perera, Michael Van Stipdonk and William C. Groutas; Wichita State University, Wichita, KS 206

191. MOLECULAR MODELING ON THE ACUTE TOXICITY OF THE ORGANOPHOSPHORUS COMPOUNDS ON THE ACETYLCHOLINESTERASE ENZYME. **Jianxin Guo**[1], Gerald Lushington[1], Margaret M. Hurley[2] and Jeffrey B. Wright[3]; [1]University of Kansas, Lawrence, KS; [2]U.S. Army Research Laboratory, Aberdeen Proving Ground, MD; [3]U.S. Army SBCCOM/Natick Soldier Center, Natick, MA 206

192. SERENDIPITOUS DISCOVERY OF AN UNEXPECTED REARRANGEMENT LEADS TO TWO NEW CLASSES OF POTENTIAL PROTEASE INHIBITORS. **Zhong Lai**[1], Jiaying Zhong[1], Christopher S. Groutas[1], Tzutshin Wong[1], Xiangdong Gan[1], Kevin R. Alliston[1], David Eichhorn[1], John R. Hoidal[2] and William C. Groutas[1]; [1]Wichita State University, Wichita, KS; [2]University of Utah 207

Health Sciences Center, Salt Lake City, UT

Poster Session II (continued

Inorganic Chemistry

193.	AMIDE-CONTAINING MODELS FOR NITRILE HYDRATASE. David M. Eichhorn and **Curtis E. Moore**; Wichita State University, Wichita, KS	208
194.	AZULENE AS A STRUCTURAL AND ELECTRONIC BRIDGE IN ELECTRON-RICH ORGANOMETALLICS. **Edward Weintob**[1], Randall E. Robinson[2], Thomas C. Holovics[2], Stephan F. Deplazes[2] and Mikhail V. Barybin[2]; [1]Columbia University, New York, NY; [2]University of Kansas, Lawrence, KS	208
195.	BIOACTINIDE CHEMISTRY-URANYL INTERACTIONS WITH -DAHK- AND DERIVATIVES. **Huan Huang**, Shveta Chaudhary and J. David Van Horn; University of Missouri-Kansas City, Kansas City, MO	209
196.	BONDING AND ELECTRONIC PROPERTIES IN THE ZINTL PHASES: THEORETICAL STUDIES OF $EuGe_2$, EuGaGe AND EuZnGe. **Tae-soo You** and Gordon J. Miller; Iowa State University, Ames, IA	209
197.	CHIRAL BIS(QUINALDINECARBOXAMIDE) LIGANDS FOR HELICAL COMPLEXES. **Dipesh Prema**; Kansas State University, Manhattan, KS	210
198.	CHROMIUM(III) BIOCOORDINATION CHEMISTRY: MODELS AND REACTIONS. **J. David Van Horn**[1], Shveta Chaudhary[1], Vincent Morrissette[1], Deendayal Dinakarpandian[1] and Brian Bennett[2]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]Medical College of Wisconsin, Milwaukee, WI	211
199.	CLUSTERS FORMED FROM THE REACTIONS OF GLYCOLIC ACID WITH COMBINATIONS OF SODIUM MOLYBDATE, SODIUM TUNGSTATE AND SODIUM HYDROGEN PHOSPHATE: CRYSTAL STRUCTURES AND ORGANIC PRODUCT ANALYSIS. **T. Adrian George**, David N. Kirk, Charles R. Ross II, Tom J. Brett, Patrick J. D. Kennedy and John J. Stezowski; University of Nebraska-Lincoln, Lincoln, NE	211

Poster Session II (continued

Inorganic Chemistry

200. COMPUTATIONAL AND SPECTROSCOPIC STUDIES OF Re(I) BIPYRIDYL COMPLEXES CONTAINING 2,6-DIMETHYLPHENYLISOCYANIDE LIGAND. Stanislav R. Stoyanov, John M. Villegas and **D. Paul Rillema**; Wichita State University, Wichita, KS 212

201. CYANOSCORPIONATE LIGANDS AND METAL COMPLEXES. David M. Eichhorn and **Peter Zhao**; Wichita State University, Wichita, KS 213

202. DESIGN OF NEW TYPES OF METAL-ORGANIC NETWORKS FOR ONE-DIMENSIONAL MIXED-VALENCE COORDINATION POLYMERS. **Daniel Robertson**[1], Nikolay Gerasimchuk[1], John F. Cannon[2] and Charles Barnes[3]; [1]Southwest Missouri State University, Springfield, MO; [2]Brigham Young University, Provo, UT; [3]University of Missouri-Columbia, Columbia, MO 213

203. DESIGN OF “TWISTED” MACROCYCLES. **Azadeh Lalehzari** and Christopher J. Levy; Kansas State University, Manhattan, KS 214

204. DEUTERIUM EXCHANGE FROM DMSO-d_6 TO POLYAMIDE CRYPTANDS. **Sung Ok Kang**, David VanderVelde, Douglas Powell and Kristin Bowman-James; University of Kansas, Lawrence, KS 215

205. ELECTROCHEMICAL STUDIES AND FUNCTIONALIZATION OF POLYOXOMETALATES. **Kristopher Mijares** and Eric A. Maatta, Kansas State University, Manhattan, KS 215

206. FIRST PLANAR-CHIRAL ISOCYANIDES. **Stephan F. Deplazes**, Thomas C. Holovics and Mikhail V. Barybin; University of Kansas, Lawrence, KS 216

207. HIGHLY PHOSPHORESCENT IRIDIUM COMPLEXES: SYNTHESIS AND USE IN ORGANIC LIGHT-EMITTING DIODES. **Betty Marie Jennifer Paulose** and Chien-Hong Cheng; National Tsing Hua University, Hsinchu 217

300, Taiwan

Poster Session II (continued

Inorganic Chemistry

208. HYBRID MOLECULAR DUMBBELLS OF TWO POLYOXOMETALATE CLUSTERS BRIDGED WITH AN ORGANIC CONJUGATED ROD. **Meng Lu**, Baohan Xie, Jeonghee Kang and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO 217

209. INVESTIGATION OF THE ELECTRONIC STRUCTURE OF PENTA- AND HEXACOORDINATED FERRIC HIGH SPIN (S=5/2) HEME PROTEINS BY ^{13}C NMR. **Aileen Y. Alontaga** and Mario Rivera; University of Kansas, Lawrence, KS 218

210. INVESTIGATIONS ON METALLOPORPHYRIN DIMERS FORMED BY CATION COMPLEXATION OF CROWN ETHER CAVITIES. **Raghu Chitta**, Lisa M. Rogers, Amber Wanklyn, Paul A. Karr, Pawan K. Kahol, Melvin E. Zandler and Francis D'Souza; Wichita State University, Wichita, KS 219

211. MODEL COMPLEXES FOR THE A-CLUSTER OF CODH/ACS. David M. Eichhorn and **Joshua Zimmerman**; Wichita State University, Wichita, KS 220

212. NEW VERSATILE ANIONIC AND CATIONIC MACROCYCLIC RECEPTORS. **Jerry A. Kut**, Rowshan A. Begum, Sung-Ok Kang, Douglas R. Powell and Kristin Bowman-James; University of Kansas, Lawrence, KS 220

213. NICKEL AND PLATINUM CORANNULENE DERIVATIVES. **Han Baek Lee** and Paul R. Sharp; University of Missouri, Columbia, MO 221

214. NITRIDO FUNCTIONALIZED POLYOXOMETALATES. **Louis M. Wojcinski II**[1], Sean Tomlinson[1], Christopher G. Hamaker[2] and Eric A. Maatta[1]; [1]Kansas State University, Manhattan, KS; [2]Illinois State University, Normal, IL 222

215. Pd AND Pt OXO CHEMISTRY SUPPORTED BY DI-*TERT*-BUTYLBIPYRIDINE. **Anupam Singh** and Paul R. 223

Sharp; University of Missouri-Columbia, Columbia, MO

Poster Session II (continued

Inorganic Chemistry

216. $RE_{2-x}Fe_4Si_{14-y}$ (RE = Y, Gd, Er, Tm, Yb) INTERGROWTH STRUCTURES: STRUCTURAL MODELS, PROPERTIES AND ELECTRONIC STRUCTURE. **Mi-kyung Han** and Gordon J. Miller; Iowa State University, Ames, IA 223

217. REDUCTION OF THE FERROUS α-VERDOHEME-CYTO-CHROME B_5 COMPLEX. **Christopher O. Damaso**[1], Nick D. Rubie[2], Pierre Moënne Loccoz[2] and Mario Rivera[1]; [1]The University of Kansas, Lawrence, KS; [2]OGI School of Science and Engineering at OHSU, Beaverton, OR 224

218. STRUCTURAL REINVESTIGATION ON BINARY Ga-Mn AND CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURAL INVESTI-GATIONS ON TERNARY Ga-Cr-Fe COMPOUNDS. **Hyunjin Ko**; Iowa State University of Science and Technology, Ames, IA 225

219. SYNTHESIS AND CHARACTERIZATION OF Au-Ge COMPLEXES. **Anandhi Upendran** and Paul R. Sharp; University of Missouri, Columbia, MO 225

220. SYNTHESIS OF NEW FUNCTIONALIZED POLYOXOMETALATES. **Jeffery D. Karcher** and Eric A. Maatta; Kansas State University, Manhattan, KS 226

221. TOWARD THE SYNTHESIS OF NOVEL 2,3,4,5-TETRAARYLSILOLES. **Barrett E. Eichler**, Amy E. Brown, Jill A. Webster, Christopher D. Thomas and M. Steven McClain; Northwest Missouri State University, Maryville, MO 227

Methods in Electronic Structure Theory

222. FIRST-PRINCIPLES OPTICAL CROSS-SECTIONS FOR SINGLE-WALLED CARBON NANOTUBES. **S. L. Elizondo**[1], Shagoto Nandi[2] and J. W. Mintmire[1]; 227

[1]Oklahoma State University, Stillwater, OK; [2]Boston University, Boston, MA

Poster Session II (continued

Methods in Electronic Structure Theory

223. ELECTRON PROPAGATOR CALCULATIONS ON SEVERAL PROPERTIES OF CH_3 AND CH_3^+. **Koevi A. Agbemehin** and J. V. Ortiz; Kansas State University, Manhattan, KS 228

224. INTERPRETATION OF THE PHOTOELECTRON SPECTRUM OF $ScC_6H_6^-$. **Srikanth Kambalapalli** and J. V. Ortiz; Kansas State University, Manhattan, KS 229

225. DENSITY FUNCTIONAL SIMULATION OF METALLIC CARBON NANOWIRES. **Ravi K. Vadapalli** and J. W. Mintmire; Oklahoma State University, Stillwater, OK 229

226. INDIVIDUAL CONTRIBUTIONS TO ELECTRON PROPAGATOR SELF-ENERGY AND THEIR COMPUTATIONAL COST. **V. G. Zakrzewski**, Olga Dolgounitcheva and J. V. Ortiz; Kansas State University, Manhattan, KS 230

227. STABILIZATION OF ZWITTERIONIC GLYCINE BY SOLVATING EFFECTS. **Mark R. Sterling**, Olga Dolgounitcheva, V. G. Zakrzewski and J. V. Ortiz; Kansas State University, Manhattan, KS 230

228. ELECTRON PROPAGATOR APPROACH TO IONIZATION ENERGIES OF PORPHYNE AND PORPHYRINS. **Olga Dolgounitcheva**, V. G. Zakrzewski and J. V. Ortiz; Kansas State University, Manhattan, KS 231

229. STRUCTURE AND ENERGETICS OF [B, N, O, H_2]: QUANTUM MECHANICS SHOWS MULTIPLE MINIMA. **Aaron K. Corum**[1], Carol A. Deakyne[1] and Joel F. Liebman[2]; [1]University of Missouri - Columbia, Columbia, MO; [2]University of Maryland, Baltimore County, Baltimore, MD 232

Poster Session II (continued)

Nanostructured Materials and Air Quality

230. EFFECTS OF NANOPARTICLE SIZE ON NEAR-IR REFLECTANCE. **Ravi S. Mulukutla**[1], Jeevanandam Pethaiyan[2], Mendy Phillips[2], Sambhudas Chaudhari[2], Paul S. Malchesky[1] and Kenneth J. Klabunde[2]; [1]NanoScale Materials Inc., Manhattan, KS; [2]Kansas State University, Manhattan, KS 232

231. METAL-OXIDE NANOPARTICLES FOR SMOKE CLEARING. John S. Klabunde[1], **Ravi S. Mulukutla**[1], Ronaldo G. Maghirang[2], Bernardo Predicala[2], Paul S. Malchesky[1] and Kenneth J. Klabunde[2]; [1]NanoScale Materials Inc., Manhattan, KS; [2]Kansas State University, Manhattan, KS 233

232. REACTION OF Pb NANOPARTICLES WITH 1-DODECANETHIOL. Zhiqiang Yang, **K. J. Klabunde** and Christopher M. Sorensen; Kansas State University, Manhattan, KS 234

Sol-gel Chemistry

233. BIOTEMPLATING OF SILICA THIN FILMS WITH *E. COLI*. **Andrew Chambers**; Truman State University, Kirksville, MO 234

234. ENCAPSULATION OF LACTATE DEHYDROGENASE IN SILICA BY ITS DIRECT REACTION WITH TETRA-METHOXYSILANE. **Igor I. Slowing** and Nenad M. Kostic; Iowa State University, Ames, IA 234

235. SINGLE MOLECULE STUDIES OF DYE-DOPED MESO-POROUS SILICATE FILMS. **William Sanders**, Daniel A. Higgins and Maryanne M. Collinson; Kansas State University, Manhattan, KS 235

Poster Session II (continued

Biochemistry

Poster Session II

Biochemistry (continued)

244. MELTING BEHAVIOR OF DNA COMPLEXES CONTAINING JOINED TRIPLEX AND HAIRPIN LOOP MOTIFS. **Sarah E. Betzold**[1] and Luis A. Marky[2]; [1]University of Nebraska Lincoln, Lincoln, NE; [2]University of Nebraska Medical Center, Omaha, NE 241

245. MODELING AND SIMULATION OF THE HUMAN DELTA OPIOID RECEPTOR. **Mahalaxmi Aburi** and Paul E. Smith; Kansas State University, Manhattan, KS 242

246. PROTEIN KINASE C AND ANNEXIN VI IN THE ROLE OF CELL ADHESION. **Heather E. Shinogle**, David S. Moore and Robert C. Dunn; University of Kansas, Lawrence, KS 242

247. PURIFICATION AND CHARACTERIZATION OF PHYTOCHROME FROM OAT SEEDLINGS. James M. Chapman[1], **Peter Simone**[1], Kyle Cummins[1], D. Philip Colombo, Jr.[1], Sheher Mohsin[2] and M. A. Lee[1]; [1]Rockhurst University, Kansas City, MO; [2]Agilent Technologies, Schaumburg, IL 243

248. ROSIGLITAZONE AMELIORATES ABNORMAL ACTIVITY OF PTP1B IN SKELETAL MUSCLE OF FAT-FED, STREPTOZOTOCIN-TREATED DIABETIC RATS. **Wu Yong**[1], Jingping Ou Yang[1], Ke Wu[1], Yunfeng Zhou[1] and Wen Chongyuan[2]; [1]Wuhan University, Wuhan, China; [2]Renmin Hospital, Wuhan University, Wuhan, China 243

249. SENSITIVE PROCEDURE FOR MEASURING NAD^+ AND NADH IN SERUM: THEIR CONCENTRATIONS IN HUMANS OF DIFFERENT AGE GROUPS. **Junqian Zhang**, D. Paul Rillema and Ram Singhal; Wichita State University, Wichita, KS 244

Poster Session II (continued)

Chemical Education

250. ACTIVITY COEFFICIENTS OF DIRTY DISTILLED WATER AND BEYOND. **Charles M. Greenlief**; Emporia State University, Emporia, KS 245

251. OLD TITRATION WITH A NEW TWIST: REINFORCING THE RELATIONSHIP BETWEEN TECHNICAL SKILL AND PRECISION IN QUANTITATIVE ANALYSIS. **Shauna L. Hiley**; Missouri Western State College, St. Joseph, MO 245

252. CHARACTERIZATION AND ANALYSIS OF A PRODUCT (CAP): A SEMESTER LONG GUIDED INQUIRY LABORATORY SEQUENCE FOR USE IN GENERAL CHEMISTRY. **Michael W. Ducey, Jr.**, Shauna L. Hiley, Benjamin D. Caldwell and Gerald L. Zweerink; Missouri Western State College, St. Joseph, MO 246

253. DETERMINATION OF THE FAT CONTENT OF PROCESSED MEATS BY NMR. **James M. Chapman** and **Matthew J. Francoeur**; Rockhurst University, Kansas City, MO 246

254. WHERE'S THE HEAT? A SURVEY OF HOT PEPPERS TO DETERMINE THE LOCATION OF THE CAPSAICIN WITHIN THE FRUIT. James M. Chapman and **Matthew J. Sullivan**; Rockhurst University, Kansas City, MO 247

Poster Session III
Regency A Ballroom
1:00PM - 4:00PM Thursday
John Desper and Dan Higgins, Presiding
Research at Undergraduate Institutions

Research at Undergraduate Institutions

278. RELIABLE RECIPE FOR MAKING BINARY COCRYSTALS. **Meg E. Fasulo**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS 260

279. CAPILLARY ELECTROPHORETIC ANALYSIS OF FORENSIC SAMPLES. **Robert A. Heegel**; Augustana College, Sioux Falls, SD 261

280. CHARACTERIZING REACTIVITY OF BENZYL ESTERS IN SODIUM DODECYL SULFATE MICELLES. Tram B. Hoang[1], Melissa Odorzynski[1], Alex Bulochnik[1], Gholam Mirafzal[2] and **Hassan Almoazen**[1]; [1]College of Pharmacy and Health Sciences, Drake University, Des Moines, IA; [2]Department of Chemistry, Drake University, Des Moines, IA 262

281. CHEMILUMINESCENCE FROM REACTION OF LUMINOL WITH SUPERBASIC SOLIDS. **Sean R. Tomlinson**, Chien-Chang Huang and Keith L. Hohn; Kansas State University, Manhattan, KS 263

282. DETECTION OF ENDOGENOUS THIOLS USING A CHEMICALLY-MODIFIED CARBON INK MICROELECTRODE. **Courtney D. Kuhnline** and R. Scott Martin; Saint Louis University, St. Louis, MO 263

283. DETECTION OF SUBSTANCE P IN BIOLOGICAL SAMPLES. **Brooke Shellaine Barrett**, Walter R. Vandaveer IV and Susan M. Lunte; University of Kansas, Lawrence, KS 264

284. EFFECT OF ACIDITY ON THE NONLINEAR BEHAVIOR OF THE CHLORITE-SULFITE pH OSCILLATOR IN A CSTR. **Rizia Bardhan**, Varun Talwar and Glen A. Frerichs; Westminster College, Fulton, MO 265

Poster Session III

Research at Undergraduate Institutions (continued)

Poster Session III

Research at Undergraduate Institutions (continued)

292. PHENOLIC ACID CONSTITUENT ANALYSIS OF *ECHINACEA SPP.* USING *μ*CE-EC. **Ryan J. Grigsby**[1], Walter R. Vandaveer IV[2] and Susan M. Lunte[2]; [1]Haskell Indian Nations University, Lawrence, KS; [2]University of Kansas, Lawrence, KS 269

293. PRODUCTION AND COLLISION-INDUCED DISSOCIATION OF GAS-PHASE, WATER AND ALCOHOL COORDINATED URANYL COMPLEXES CONTAINING HALIDE OR PERCHLORATE ANIONS. **Winnie Chien**, Victor Anbalagan and Michael Van Stipdonk; Wichita State University, Wichita, KS 270

294. PROGRESS TOWARD THE SYNTHESIS OF AN EXPANDED OXOPHLORIN. **Philip O. Suchi** and Sam H. Leung; Washburn University, Topeka, KS 270

295. REACTIVITY OF 1,1,-DICHLORO-2,3,4,5-TETRAPHENYLSILOLE. **Christopher D. Thomas**[1], Barrett E. Eichler[1], Jill A. Webster[1], M. Steven McClain[1], Amy E. Brown[1] and Douglas R. Powell[2]; [1]Northwest Missouri State University, Maryville, MO; [2]University of Kansas, Lawrence, KS 271

296. REMOTE CONTROL UV-VIS SPECTROSCOPY FOR SECONDARY SCHOOLS. **Daniel K. Unruh**, Gary Histand and Richard Zerger; Bethel College, North Newton, KS 271

297. SELECTIVE INHIBITION OF HEME OXYGENASE OF *PSEUDOMONAS AERUGINOSA*. **Matthew A. Siemer**[1] and Mario Rivera[2]; [1]University of Kansas, Bushton, KS; [2]University of Kansas, Lawrence, KS 271

298. SEPARATION OF NITRATE, NITRITE, AND PEROXYNITRITE USING CAPILLARY ELECTROPHORESIS. Matthew R. Rosebraugh[1], **Celeste Frankenfeld**[2], Barbara A. Fogarty[2] and Susan M. Lunte[2]; [1]Drake University, Des Moines, IA; [2]University of Kansas, Lawrence, KS 272

Poster Session III

Research at Undergraduate Institutions (continued)

299. STUDIES OF THE ROBINSON ANNULATION REACTION IN IONIC LIQUIDS. David C. Hawkinson and **Keith B. McCollister**; University of South Dakota, Vermillion, SD 273

300. SYNTHESIS OF A THIOL-SUBSTITUTED *ortho*-PHTHALALDEHYDE FOR THE DERIVATIZATION OF AMINO ACIDS. David C. Hawkinson, Miles D. Koppang and **Andy Mueting**, University of South Dakota, Vermillion, SD 273

301. TERTIARY TO TERTIARY CARBOCATION REARRANGEMENTS. **Robert Pavlis**, Katie Lemmon and Todd Francis; Pittsburg State University, Pittsburg, KS 274

302. MECHANISM OF AMINO ACID OXIDATION AT DIAMOND ELECTRODES: FLUORESCENCE IMAGING OF THE OXIDATION SITES. **Amanda Bakke** and Miles D. Koppang; University of South Dakota, Vermillion, SD 274

ABSTRACTS

1. STEREOCHEMISTRY AND CHIROPTICS IN COMPLEX ORGANIZED MEDIA.

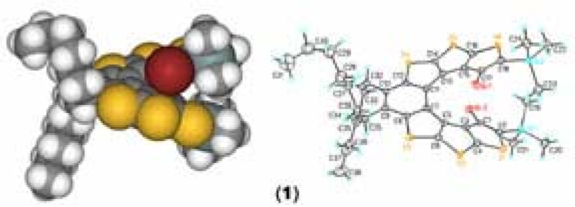
Bart Kahr, Werner Kaminsky and Claborn Kacey; University of Washington, Seattle, WA.

Chiroptical imaging techniques have not heretofore been implemented. This neglect has created a hole in the science of molecular chirality, particularly with respect to complex, heterogeneous, organized media. We built a circular extinction imaging microscope to examine chromophores in anisotropic hosts. With this instrument, images of mixed crystals were made *via* two mechanisms, intrinsic circular dichroism (CD) and a new effect that was discovered and called anomalous circular extinction (ACE). These phenomena address two outstanding questions in the investigation of dye-doped, ordered media: (1) The absolute configuration of the adsorbed dyes and (2) The absolute orientation of embedded dipoles with respect to the eigenmodes of the medium. With this instrument we are investigating the stereochemistry and chiroptical properties of organic compounds in crystals and crystalline tissues, furthering our long-standing inquiry into the process of dyeing crystals while at the same time undertaking a reinvestigation of chemical histology. Intrinsically chiral chromophores such as biaryls and triarylmethyls abound in organized media but have been silent with respect to their chirality and absolute orientation when so embedded.

2. CHIRAL MOLECULAR GLASS: SYNTHESIS AND CHARACTERIZATION OF ENANTIOMERICALLY-PURE THIOPHENE-BASED [7]HELICENE.

Makoto Miyasaka[1], Andrzej Rajca[1], Maren Pink[2] and Suchada Rajca[1]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]Indiana University, Bloomington, IN.

Synthesis of highly-functionalized thiophene-based [7]helicenes is developed for both design of organic chiral glasses with strong chiro-optical properties and further homologation to higher [n]helicenes. Based upon X-ray crystallographic determinations of the absolute configuretions for (+)-enantiomers of the diketone and the [7]helicene, stereochemical correlation between the (*R*) axial chirality of the diketone and (*M*) helical chirality of the [7]helicene is established. One of such enantiopure [7]helicene, which adopts "tetrahedral-like" shape in the racemic crystal (**1**), would not crystallize but forms a rare chiral molecular glass with strong chiro-optical properties. This relatively unexplored phenomenon is important because the significant part of applications for organic materials, especially involving optics and optoelectronics, requires strictly isotropic glasses. One such emerging application involves chiral waveguides with novel polarization modes, for which isotropic chiral glasses with enormous optical rotatory powers (optical rotations) are required.



(1)

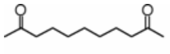
3. DIRECTING MOLECULAR CRYSTAL GROWTH WITH SELF-ASSEMBLED MONOLAYERS. **Rupa Hiremath**, Stephen W. Varney and Jennifer A. Swift; Georgetown University, Washington, DC.

Functionalized self-assembled monolayer surfaces (SAMs) have the potential to combine the best of long-range geometric matching (epitaxy) and local chemical matching (dipole-dipole interactions) for the purposes of directing the nucleation of desired crystalline organic phases. Using SAMs templates constructed from benzene and/or biphenylthiols bearing polar substituents, we have been able to (1) control the alignment of polar nuclei at the monolayer-crystal interface and (2) selectively grow just one phase of known concomitant polymorphic systems. The nucleation and growth of polar 4-iodo-4'-nitrobiphenyl crystals can be achieved. The orientation of crystals grown on these SAMs templates suggests that dipole-dipole interactions at the SAMs-crystal interface dictate the polar orientation of the macroscopic crystal. Ongoing studies explore whether SAMs surfaces can also be used as a growth template to apply to other pharmaceutical systems and as a method to screen for new (perhaps metastable) as yet undiscovered polymorphic phases.

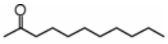
4. POLAR ORDERING AND ELECTRIC FIELD-INDUCED DOMAIN REORIENTATION IN FERROELASTIC CHANNEL INCLUSION COMPOUNDS. **Jeremy R. Rush**, Mark D. Hollingsworth and Mark J. Abel; Kansas State University, Manhattan, KS.

Urea inclusion compounds (UICs) consist of honeycomb-like networks of “host” ureas enclosing linear hydrocarbon “guests” or their analogues. When more than one kind of guest is present in the crystal growth medium, polar ordering of the guests can result, as demonstrated by second-harmonic generation and electric field-induced domain switching of the crystals. A striking example is presented by UICs containing mixtures of 2,10-undecanedione (**1**) and 2-undecanone (**2**). This work suggests that the incorporation of tailor-made impurities into known ferroelastics is a general strategy for the preparation of new ferroelectric materials.

To understand the crystal growth processes leading to polar ordering, it is important to dissect the occupancies of guests in different sites in mixed UICs. In conjunction with birefringence mapping, X-ray diffraction of mixed UICs containing heavy-atom analogues of 2-undecanone help reveal the molecular recognition events that give rise to the polar ordering of guests. The features of inclusion have potential consequences on macroscopic properties such as ferroelastic and ferroelectric behavior. For example, (**1**)/urea realizes plastic ferroelastic domain switching; however, the incorporation of (**2**) in amounts greater than ~13% into crystals of (**1**)/urea leads to elastic (spontaneously reversible) ferroelastic behavior. On the addition of even greater amounts of (**2**) electric field-induced domain reorientation is possible. Studies aimed at elucidating the mechanism of ferroelastic domain switching reveal surprising information that is helpful in tailoring the properties of these materials and in designing new materials with interesting and useful properties.



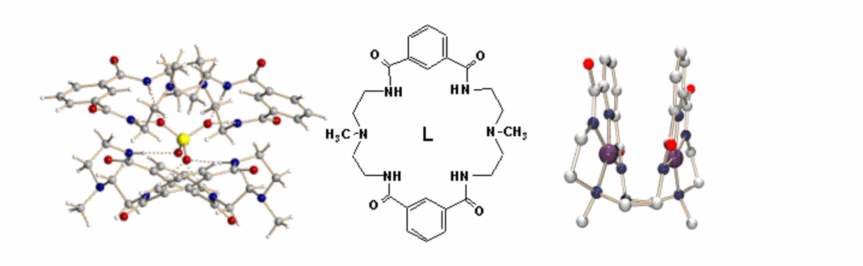
(1)



(2)

5. STRUCTURAL COMPARISONS OF ANION AND TRANSITION METAL ION COMPLEXES WITH MACROCYCLES. **Kristin Bowman-James**; University of Kansas, Lawrence, KS.

In our efforts to explore anion chemistry with macrocyclic receptors – or 'ligands', we have observed that these same 'ligands' also form transition metal complexes. Considerable work has been done by us and others, in exploring the area of amine (binding transition metals) and ammonium (binding anions) ligands. However, little effort has been directed to comparing amido- and thioamido-based macrocycles and their anion and transition metal complexes. Two examples are the sulfate sandwich complex (below left) and the dicopper complex (below right) with the tetraamido macrocycle L. The exquisite structural characteristics of both amine-based and amide/thioamide-based classes of ligands with and without anions or transition metal ions will be compared and discussed.



6. SYNTHETIC, ION-CONDUCTING TRANSMEMBRANE CHANNELS. **George W. Gokel**; Washington University School of Medicine, St. Louis, MO.

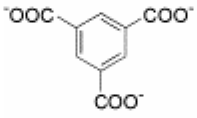
Macrocyclic polyether compounds are excellent cation binders and their complexation behavior has been extensively studied during three decades. We have incorporated macrocycles into structures that we have developed for use as model cation-conducting transmembrane channels. These compounds transport H^+, Na^+, K^+ through phospholipid membranes. Sodium transport has been assessed by dynamic ^{23}Na-NMR methods and proton flux has been measured by fluorescence techniques. Sodium and potassium fluxes have been determined in certain cases by bilayer clamp methods in phospholipid bilayers. Hydraphile channels are currently thought to form water- and sodium-filled pores through the bilayer. Issues such as position in the bilayer, conformation and biological activity will be discussed. In addition, this family of channels having systematically-varied lengths can be used to dynamically assess bilayer membrane thickness in liposomes.

7. ROLE OF NON-COVALENT INTERACTIONS IN METAL ION-MEDIATED ACTIVATION OF SMALL MOLECULES. **Andrew S. Borovik**; University of Kansas, Lawrence, KS.

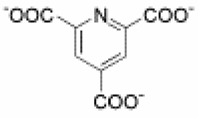
Non-heme enzymes are known to activate a variety of molecules during activity. In several of these metalloproteins, the unique protein-derived microenvironment surrounding the metal ion active site aids in regulating function. Structural and spectroscopic data on metalloproteins has revealed the important regulatory functions of hydrogen bond (H-bond) donors/acceptors within the secondary coordination sphere. We have used these principles of protein architecture to develop synthetic complexes that control the structure and function around metal ions by creating bio-inspired microenvironments. In particular, new systems have been designed and prepared that position H-bond donors proximal to metal centers. For instance, the tripodal ligands tris[(N'-*tert*-butylureaylato)-N-ethyl)]amine stabilize monomeric M—O and M—OH complexes by creating unique cavities around the coordinated metal ion. We have successfully isolated a series of monomeric metal complexes with terminal oxo, hydroxo, sulfido and selenido ligands, which are derived directly from dioxygen. This talk will describe the preparation, structural properties and reactivity of these complexes.

8. COORDINATION POLYMERS WITH 2,4,6-PYRIDINETRICARBOXYLATE: 1D CHAINS AND 2D TILES. **Robert P. Houser** and Deping Cheng; University of Oklahoma, Norman, OK.

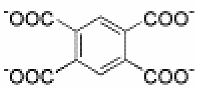
One particularly useful family of ligands that has been used to create a large number of coordination polymers contain carboxylato functional groups. Ligands with at least two, and up to four carboxylates can bridge between metal ions to create 1D chains, 2D sheets and 3D networks. In our laboratory we have explored the chemistry of transition metals with the aromatic carboxylic acids trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) and pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid, BTEC). Here we report three new coordination polymers synthesized with a new ligand, PTC (2,4,6-pyridinetricarboxylate), giving rise to linear chains containing cobalt(II) and 2D sheets containing copper(II) or zinc(II). The cobalt ions in the 1D chains are seven-coordinate, while the isostructural copper and zinc 2D sheets display novel tiling patterns.



TMA



PTC



BTEC

9. BIODEGRADATION OF TOXIC COMPOUNDS BY PLANTS OR BY ASSOCIATED BACTERIA. **Stefan Trapp**; Technical University of Denmark, Kongens Lyngby, Denmark.

Phytoremediation of toxic pollutants residing in soils or groundwater has been used frequently as a treatment method. The optimal solution is when toxic compounds are rapidly degraded.

Degradation by plant enzymes is described mathematically by the Michaelis-Menten kinetics, which has an upper limit (v_{max}). Bacterial growth is high at high doses, but low at low doses. It follows that degradation by plants would be superior at low pollution level, whereas bacterial degradation would dominate at high pollution levels.

An example for degradation by plant enzymes is the metabolism of hydrogen cyanide (HCN) by willows. The kinetics is described by Michaelis-Menten kinetics, with a maximum metabolic capacity v_{max} of 10 mg/kg/h. As long as the metabolism of cyanide was faster than the uptake, levels of cyanide inside the plants remained low. With increasing dose, cyanide can accumulate inside the plant and the plants died. Living willow trees did not accumulate free cyanide. A full-scale gas works phytoremediation was established in Denmark.

Closed-bottle tests with other chemicals than HCN showed no or only bacterial degradation. Although the toxicity to our willow trees was usually small, we could not find effective degradation of PAH, TBT, MTBE and BTEX by any investigated plant.

Bacteria living inside the vascular system of plants were determined, isolated and cultivated. These endophytic bacteria were equipped with genes that encode (bacterial) degrader DNA. The bacteria could reinvade the host plant and express degrader enzymes. The concept was proven using poplars and toluene, pea and 2,4-D, and other cases. The toxicity of these compounds decreased when endophytic degrader bacteria were present and the degradation of toluene was significantly higher.

10. TREE CORE SAMPLING IN PLUME DELINEATION AND PHYTOREMEDIATION STUDIES. **Joel G. Burken**[1], Xingmao Ma[1], Garrett Struckhoff[1], Jeff Weishaar[1] and John Schumacher[2]; [1]University of Missouri Rolla, Rolla, MO; [2]United States Geological Survey, Rolla, MO.

Tree coring methods have been used at numerous sites to delineate organic contaminant plumes and to track contaminant fate at phytoremediation sites. The contaminants range from single carbon molecules like carbon tetrachloride to polynuclear aromatic hydrocarbons. The sites range from urban settings to remote locations and from very shallow contaminant plumes to plumes more than 20 feet below ground level. Laboratory research supports the findings from the full-scale testing and elucidated some plant-contaminant interactions. Among the findings it was discovered that vadose zone contaminants can be removed by plant roots, potentially leading to a new remediation technique for unsaturated zone contaminants. Findings also allow for estimation of contaminant removal rates for full-scale remediation efforts.

11. EVALUATION OF CURRENT REMEDY AND RESEARCH INTO ADVANCED TECHNOLOGIES FOR REMEDIATION OF THE PPI SITE. **W. David Constant**; Louisiana State University, Baton Rouge, LA.

In 1989, LSU was appointed Expert to the U.S. District Court, Middle District of LA by the Honorable Frank J. Polozola. Since that time, the court assigned duties and tasks have been managed in the HWRC and HSRC/S&SW. The PPI Project is currently operating in Year 14, with a cumulative budget of over $3.5 million, supported by the Industry Defendants through the U.S. District Court, Middle District of LA. This presentation provides an overview of the research and court assigned duties over the last 13 years. The discussion includes site history, aspects of the role of the expert to the cleanup, examples of research projects and how they tie in with past and current remedies. Current and future activities are also described including research, monitoring and assessment of the remediation of the Petro Processors, Inc. sites.

12. BIOCHEMICAL BASIS FOR ENVIRONMENTAL MANAGEMENT OF AIRCRAFT DEICING WASTE USING VEGETATION.

Sigifredo Castro, Larry E. Erickson, Lawrence C. Davis and Kenneth Dokken; Kansas State University, Manhattan, KS.

Phytoremediation can be employed as a natural and feasible strategy for treating the waste generated by aircraft deicing operations. The environmental concern is due to the high oxygen demand of ethylene and propylene glycols and the toxicity associated with corrosion inhibitors, such as benzotriazole and methyl-benzotriazole. Benzotriazoles are non-volatile organic contaminants with an intermediate value of $\mathrm{LogK_{OW}}$. Land application of this waste can take advantage of vegetation by two mechanisms: enhancement of glycol biodegradation by the rhizosphere effect and transformation of benzotriazoles by plant enzymatic activities. This research focused on the uptake of benzotriazoles in hydroponic culture of sunflowers (*Helianthus annuus L.*). Several experiments were designed to establish the kinetics of the uptake process and the impact of environmental variables such as nutrients, temperature, pH, photoperiod, root-to-volume ratio, and mixing. A preliminary study with ^{14}C-radiolabeled methyl-benzotriazole was also performed. It was found that when enough nutrients are supplied, benzotriazoles can be transformed into two fractions: a methanol-soluble fraction containing by-products more polar than the original triazole and a fraction irreversibly bound to the plant structure, especially to the roots. The phytotransformation process followed Michaelis-Menten kinetics, was not directly linked to the photosynthetic activity of the plants and was not diffusion-limited.

13. COMPARATIVE VALIDATION OF INNOVATIVE CAPPING TECHNOLOGIES ON THE ANACOSTIA RIVER.

W. David Constant and Danny D. Reible; Louisiana State University, Baton Rouge, LA.

The Hazardous Substance Research Center/South and Southwest, Louisiana State University, is conducting comparative validation of innovative “active capping” technologies. The goal of ”active capping” is to ensure contaminants migrating through the cap are sorbed, chemically bound or degraded and not released into the overlying water. The project seeks to provide site-specific preliminary design information on the application of innovative technologies to the Anacostia River where historically industrial, municipal and military activities have resulted in potentially high hazardous levels of polynuclear aromatic hydrocarbons, polychlorinated biphenyls, metals and other contaminants. The project is currently demonstrating on a field scale the ability to design and construct caps that will provide treatment of sediment contaminants while simultaneously providing containment. Work was initiated in 2002 to select and characterize the site, followed by treatability testing of several technologies in 2003 and placement of the caps in early 2004. This presentation focuses on results of site characterization work, findings from laboratory testing of selected technologies for the Anacostia demonstration, efficiency of placement of the cap materials and initial post-capping monitoring and assessment.

14. TIME-DEPENDENT SORPTION-DESORPTION BEHAVIOR OF 2,4-DICHLOROPHENOL AND ITS POLYMERIZATION PRODUCTS IN SURFACE SOILS. **Mónica Palomo** and Alok Bhandari; Kansas State University, Manhattan, KS.

Contact-time dependent sorption-desorption of 2,4-dichlorophenol (DCP) and DCP polymerization products (DPP) was investigated with agricultural and woodland soils. DPP was generated in soil slurry reactors by the addition of H_2O_2 to solutions containing horseradish peroxidase (HRP) and DCP. Size exclusion chromatography results showed that DPP consisted primarily of dimers, trimers and tetramers. Removal of DCP in soil-free reactors occurred by DPP formation and sorption of DCP to the DPP precipitate. Removal of solute from the aqueous phase in HRP-amended reactors containing soil was attributed to (i) the sorption of DPP oligomers and residual DCP to soil and (ii) the cross-coupling of DPP and residual DCP to soil organic matter. Sorption of both DCP and DPP to soils was rapid and appeared to be complete within two days. DPP sorbed to a greater extent than DCP to both soils, especially at higher solute concentrations. Short-term desorption data indicated minor apparent hysteresis for DCP but significantly higher desorption resistance for DPP. Both DCP and DPP desorbed more readily from the woodland soil compared to the agricultural soil. Hysteresis increased with contact time indicating that sorbent-solute interactions proceeded long after apparent sorption equilibrium at the particle or aggregate scale. Results from this study show that “slow” sorption processes occurring at the molecular scale continue long after apparent sorption equilibrium at the particle scale. This “aging effect” was operational over longer periods for DPP than the parent DCP, thereby assuring long-term effectiveness of HRP-mediated humification processes in the reduction of contaminant mobility in soils and sediments.

15. SORPTION OF THE MALODORANT TERTIARY BUTYL MERCAPTAN TO INDOOR MATERIALS FROM AIR AND WATER.

Alok Bhandari, Aruna Suravajjala and Larry Erickson; Kansas State University, Manhattan, KS.

Tertiary butyl mercaptan (TBM) is widely used as an odorous tracer in natural gas due to its low toxicity and ability to be detected by the human nose at very low concentrations. TBM has also been proposed for use as a non-lethal agent in urban warfare or for crowd dispersal. In this paper, we present data on the sorption-desorption behavior of TBM in the context of common indoor surfaces such as carpet materials, wallpapers and soil. TBM sorption was evaluated in completely mixed batch reactors with air or water as the fluid phase. Sorption rates were determined by contacting TBM in air or water with indoor materials for periods of 1 to 35 days. Linear, Langmuir and Freundlich models were compared for their adequacy to describe TBM sorption behavior. Desorption was evaluated by sequential extraction with contaminant free air or water and the rates and extents of TBM desorption estimated. Sorption-desorption investigations were also performed with granular-activated carbon (GAC), a common adsorbent used for the removal of odorous contaminants. Results show that while sorption-desorption equilibria was rapidly attained for carpet materials and wallpapers, the approach to equilibrium was slower in the case of soil. GAC was effective in removing TBM from air and water.

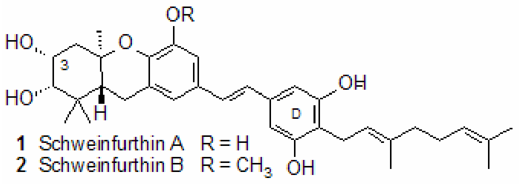
16. SYNTHESIS OF FUNCTIONALIZED BELTENES FOR SELF-ASSEMBLED NANOMATERIALS.

Kaiyan Lou, Xiaodong Huang, Neil Brown, Huiping Zhao, Bernard Wiredu and Duy H. Hua; Kansas State University, Manhattan, KS.

Studies of self-assembling nanotubes derived from functionalized beltenes containing a wide range of structural and functional capabilities will improve our fundamental understanding of non-covalent interactions and provide new applications in chemical, biological and materials sciences. We have initiated a multi-step synthesis of functionalized beltenes and studied their self-assembled nanotubes. The synthesis of novel beltenes started from a stereoselective double Diels-Alder reaction of triptycene bisquinone, 9,10-dihydro-9,10-[1,2]benzenoanthracene-1,4,5,8-tetraone, with two equivalents of 2,3-dimethylene succinic acid dimethyl ester to provide a quantitative yield of the corresponding di-adduct. After five functional-group transformation steps, the resulting tetraene was allowed to react with 1,4,5,8-tetrahydro-1,4,5,8-naphthalenetetraone and triptycene trisquinone separately to give the corresponding [8]- and [10]beltenes, respectively. Self-assembled nano-materials from these beltenes are being studied.

17. 3-DEOXYSCHWEINFURTHIN B: A SYNTHETIC SCHWEINFURTHIN WITH ANTICANCER ACTIVITY. **Jeffrey D. Neighbors**[1], Maya Salnikova[1], David F. Wiemer[1] and John A. Beutler[2]; [1]University of Iowa, Iowa City, IA; [2]National Cancer Institute at Frederick, Frederick, MD.

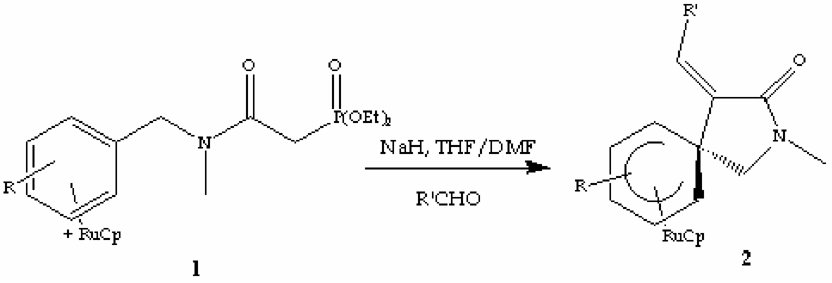
The schweinfurthins are a small set of prenylated stilbenes isolated from *Macaranga schweinfurthi*, and three of the four known compounds display significant anticancer activity. These three have a common "left-half" tricycle exemplified in the structures of schweinfurthins A (1) and B (2). The synthetic analogue 3-deoxyschweinfurthin B now has been prepared from vanillin. This analogue was examined in the NCI 60-cell line anticancer screen and was found to be more potent than any of the natural products while retaining the same interesting pattern of activity. The synthesis of 3-deoxyschweinfurthin B will be presented along with the syntheses and activity data for several analogs with D-ring modifications.



1 Schweinfurthin A R = H
2 Schweinfurthin B R = CH_3

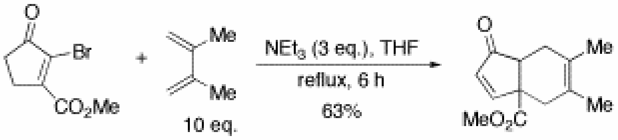
18. Ru-ASSISTED HORNER-WADSWORTH-EMMONS SPIROCYCLIZATION. **Rashmi Dalvi** and F. Christopher Pigge; University of Missouri-St. Louis, St. Louis, MO.

Reactions like nucleophilic aromatic substitution and nucleophilic aromatic addition, which are usually unfavorable, become amenable *via* metal-assisted synthetic routes. *η*6-Arene Ru complexes provide an example of this phenomenon. The metal moiety can be considered as an electron withdrawing group causing coordinated arene ligands to become susceptible to nucleophilic aromatic addition and substitution, as well as aromatic and benzylic deprotonation. Ru-mediated nucleophilic aromatic addition has been explored for the construction of spirocyclic compounds. β-Amido phosphonate complexes (**1**) participate in Ru-promoted cyclization to yield stable spirocyclic products. Upon addition of aldehyde olefination occurs to afford stable functionalized spirolactam complexes (**2**). Oxidative demetalation of these complexes then provides access to numerous unique spiroheterocyclic building blocks.



19. DIELS-ALDER REACTIONS OF A CYCLOPENTADIENONE. Michael Harmata and **Maria G. Gomes**; University of Missouri-Columbia, Columbia, MO.

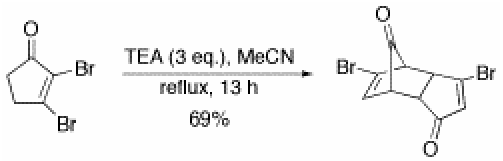
Treatment of methyl-2-bromo-3-oxocyclopent-1-enecarboxylate with an amine base in refluxing THF in the presence of electron-rich diens resulted in the formation of Diels-Alder adducts in moderate yields. Base was shown to be necessary for the reaction to occur. Current results and efforts directed toward optimization will be presented.



20. GENERATION OF 3-BROMOCYCLOPENTADIENONE AND SOME CHEMISTRY OF ITS DIMERIZATION PRODUCT.

Michael Harmata and **Soo Yeun Kim**; University of Missouri-Columbia, Columbia, MO.

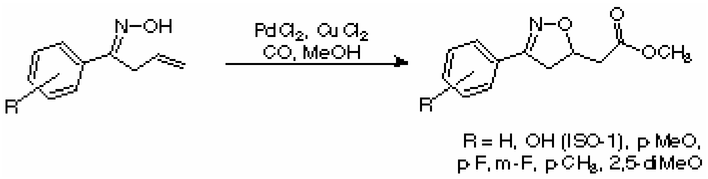
The reaction of 2,3-dibromocyclopent-2-enone with amine bases in acetonitrile affords the bicyclic product shown *via* generation of a cyclopentadienone and sub-sequent dimerization. Opti-mization of this reaction and studies of the chemistry of the dimer will be presented.



21. PALLADIUM-MEDIATED SYNTHESIS OF ISOXAZOLINES.

Katherine S. Frost, Laura G. Emmerich and Michael D. Mosher; University of Nebraska at Kearney, Kearney, NE.

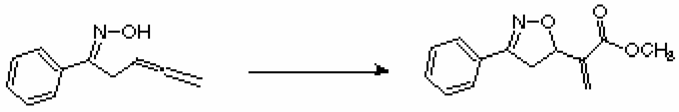
Recently, it was announced that ISO-1 (methyl 3-(*p*-hydroxyphenyl)-5-isoxazolinylacetate) inhibits the production of macrophage Migration Inhibitory Factor. This antagonism results in suppression of the development of hyperglycemia and can be a possible therapeutic pathway for the treatment for diabetes. We have investigated a synthetic route to ISO-1 and its derivatives *via* the palladium-mediated nucleometalation/methoxycarbonylation of *beta*,*gamma*-unsaturated oximes. Herein, we report the results of this synthetic route for a series of isoxazolines.



22. ANALOGUE OF ISO-1.

Michael D. Mosher and Benjamin Anderson; University of Nebraska at Kearney, Kearney, NE.

Isoxazolines, as a class, have been implicated as therapeutic agents for the treatment of diabetes, cancer, the common cold and other human maladies. Our interest in this class of molecules has focused on their preparation *via* the palladium-mediated cyclization of *beta*-allenyl oximes. This methodology provides a convenient route to the preparation of 3,5-disubstituted isoxazolines. Specifically, 1-phenyl-3,4-pentadien-1-one oximes give rise to acrylate substituted isoxazolines. The synthesis and proposed mechanistic details will be presented.

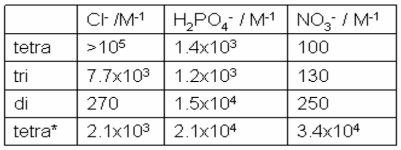


23. SOLVENT IS A DETERMINANT IN THE ANION BINDING SELECTIVITY OF UREA-PICKET PORPHYRIN RECEPTORS.

Sumith A. Kularatne and Dennis H. Burns; Wichita State University, Wichita, KS.

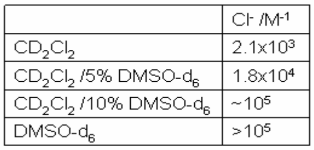
Water plays many essential roles in biological systems, including structural roles. However, studies that systematically probe and quantify these types of solvent-recognition effects with model receptor are lacking. Previously we reported the preparation and anion binding behavior of a series of tetra picket porphyrins. These receptors bind strongly to Cl^- in the highly competitive solvent DMSO-d_6 (K_a M^{-1}>10^5), forming 1:1 anion receptor complex. X-ray crystal structure showed Cl^- binds to two urea pickets and a DMSO molecule that hydrogen bonded to a third urea picket. Recently we prepared a series of tetra-, tri- and di-urea picket porphyrin receptors to evaluate the solvent effect because tri-urea provides a more open pocket and di-urea contains no extra urea picket. A remarkable reversal in the selectivity of anion complexation is observed between the receptors, wherein the binding constants ratios change over three orders of magnitude as the receptor's number of urea pickets change from four to two in DMSO-d_6.The association constant's decrease for Cl^- with the change from a competitive receptor bound solvent to non-competitive solvent, and association constant for other anions increases. However, K_a increases even in the presence of a small percentage of DMSO. ESMS competition studies proved that tetra- and tri-urea bind strongly to Cl^- in DMSO whereas they bind strongly to $H_2PO_4^-$ in CH_2Cl_2.

Table 1: Ka for tetra-, tri-and di- with tetra-butylammonium salt in DMSO-d6 and tetra* in CD2Cl2

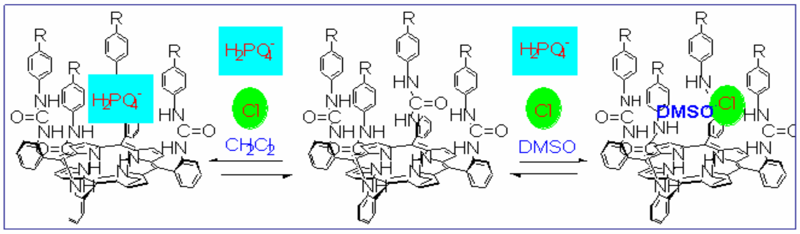


	Cl^- /M^{-1}	$H_2PO_4^-$ / M^{-1}	NO_3^- / M^{-1}
tetra	>10^5	1.4x10^3	100
tri	7.7x10^3	1.2x10^3	130
di	270	1.5x10^4	250
tetra*	2.1x10^3	2.1x10^4	3.4x10^4

Table 2: Ka for tetra- in different solvent ratios



	Cl^- /M^{-1}
CD_2Cl_2	2.1x10^3
CD_2Cl_2 /5% DMSO-d_6	1.8x10^4
CD_2Cl_2 /10% DMSO-d_6	~10^5
DMSO-d_6	>10^5



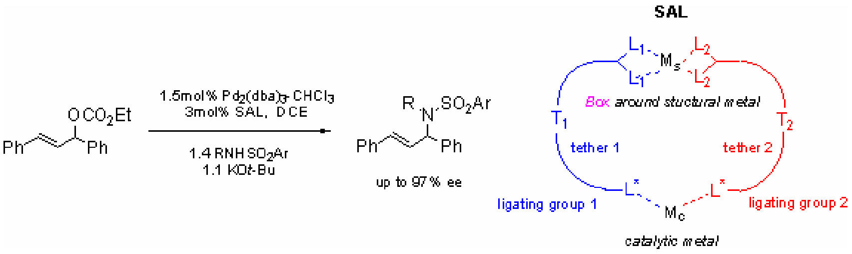
24. BIOACTIVE FLUORESCENT FARNESOL ANALOGS. **Roman Shchepin**, Patrick Dussault, Kenneth Nickerson and Raluca Dumitru; University of Nebraska-Lincoln, Lincoln, NE.

A number of fluorescent farnesol analogs have been prepared and characterized with respect to both bioactivity and fluorescent properties. Several of the compounds demonstrated significant activity as quorum-sensing molecules in *Candida albicans*, an organism normally responsive to farnesol. The results of spectroscopic studies suggest the compounds will be useful for cell imaging and in investigations of farnesol binding proteins or receptors.

25. ASYMMETRIC ALLYLATION USING SELF-ASSEMBLED CHIRAL BIDENTATE P,P-LIGANDS. **Di Wu**, D. Sahadeva Reddy, Shin A. Moteki, Hector Palencia and James M. Takacs; University of Nebraska - Lincoln, Lincoln, NE.

A library of chiral bidentate P,P-ligands has been synthesized. Its design is based on self-assembly of bifunctional subunits around a structural metal (Zn(**II**)) positioning a second set of ligating groups to complex a catalytic metal (Pd, Rh etc.) to effect the catalytic asymmetric reaction.

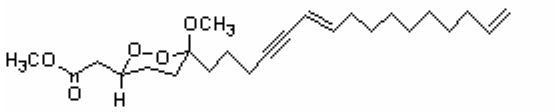
Each ligand contains three basic parts: a *bisoxazoline* (Box subunit, *L_1 or L_2*) to complex the structural metal, a **ligating group** for the *catalytic site* (*L**) and a **tether** *bridging the Box and ligating groups* (*T_1 or T_2*). The key feature of this project is to build up the ligand backbone at the last step in a combinatorial manner, allowing a large number of different ligands to be made in a short time. The ligand library has been successfully applied to a simple asymmetric allylic amination and giving enantiomeric excess up to 97%.



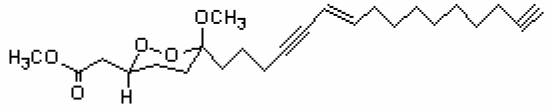
26. STUDIES TOWARD THE TOTAL SYNTHESIS OF 1,2-DIOXANE POLYKETIDES.

Patrick Dussault[1], **Chunping Xu**[1] and Joseph M. Raible[2]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]University of Kansas, Lawrence, KS.

Cyclic peroxides isolated from marine organisms often exhibit antimicrobial, ichthyotoxic, and cytotoxic activities. Dioxane polyketides **1** and **2** have been isolated from the Red Sea sponge *Acarnus cf. berquistae* and the $CHCl_3$ extract of the marine sponge exhibited cytotoxicity against P-388, A-549 and HT-29 tumor cells with an IC_{50} of 0.2 *μ*g/ml. Synthetic approches for these two compounds have not been reported. We have recently intiated efforts to develop a convergent and stereocontrolled synthesis of these dioxane polyketides. The key methodology synthetic steps are the construction of the 1,2-dioxane ring and the introduction of enyne functional group. Progress toward the completing the total synthesis of cyclic peroxide **1** and **2** will be presented.



1



2

27. SYNTHESIS OF ENDO-METACYCLOPHANES UTILIZING GRUBBS' CATALYST WHILE INCORPORATING A PORPHYRIN SCAFFOLD.

Charles L. Jayne, Sumith A. Kularatne and Dennis H. Burns; Wichita State University, Wichita, KS.

Our group has synthesized several endo- and exo-cyclophanes of various annulus sizes in the past without the benefit of a template and yields were considered moderate to good. The yields of the exo-cyclophanes were better than the endo- due to “self-templating”. Wishing to improve yields of the endo-cyclophanes, we have incorporated into its synthetic scheme a porphyrin as a template to direct the macrocycle's formation.

Using a tetra-*alpha*-5,10,15,20-tetrakis(2-aminophenyl)porphyrin as the basic scaffold, its amino groups were transformed into isocyanates. *In situ*, the isocyanates were reacted with our bis-*ortho*-elaborated bisphenol to rigidly secure two sides of the cyclophane to the porphyrin by way of the newly formed carbamate groups. The *ortho*-allyl groups were metastasized using Grubbs' second generation to furnish the cyclophane ring. The carbamates can then be hydrolyzed separating the cyclophane from the porphyrin.

The porphyrin isocyanates were also reacted with our 2,6-bis-allyl-4-*tert*-butyl phenol model system in attempts to metastasize four sites using Grubbs' catalyst to furnish the cyclophane ring.

Future elaborations include various functional groups at the *para* position of the cyclophane ring and conformational analysis.

28. SYNTHESIS AND PROPERTIES OF AZULENE-CONTAINING POLYMERS.

Xueyi Chen and T. C. Sandreczki; University of Missouri-Kansas City, Kansas City, MO.

Preparations of polyazulene derivatives with pure hydrocarbon backbones lead to new electro-conductive polymers which exhibit unique electronic properties. Presented here is a summary of synthetic methods developed in our lab, a survey of promising building blocks and oligomers leading to conductive polymers and a description of some of the properties of those compounds. Early results indicate that a radical cation generated from a polyazulene derivative by doping with iodine vapor may account for its conductivity.

29. GAS PHASE REACTIONS OF UO_2^+ AND UO_2^{2+} WITH WATER.

Michael J. Van Stipdonk, Winnie Chien and Kellis Bulleigh; Wichita State University, Wichita, KS.

The reactivity of uranium is a topic of sustained interest because species-dependent chemistry controls processes ranging from nuclear fuel processing to mobility in the geologic subsurface. The solution chemistry of uranium is dominated by the uranyl ion, UO_2^{2+}, for which recent theoretical studies suggest specific interaction with solvent is likely to influence the physico-chemical behavior of the metal and its complexes in the environment. Explicit control over the interactions of solvent with the uranyl ion is difficult, which complicates the study of species-dependent uranium behavior. To gain a better understanding of the intrinsic interactions between different uranium species and solvent, we have turned to investigations of uranyl-anion complexes in the gas phase. We recently demonstrated that electrospray ionization (ESI) and multiple stage collision-induced dissociation can be used to generate singly-charged uranyl-hydroxide, nitrate or alkoxide cations for subsequent investigation of intrinsic ligand-addition reactions. To date, bare, doubly-charged cations such as UO^{2+} and UO_2^{2+} have proven difficult to produce in the gas phase for similar studies. We report here that gas-phase UO^{2+}, UO_2^{2+}, UO_2^+, UO_2OH^+ and $UO_2NO_3^+$ can be generated by ESI of solutions containing uranyl nitrate dissolved in mixtures of water and acetonitrile. In this talk a comparison of the reactivity of these cations when isolated in an environment of N_2, O_2 and predominantly H_2O in a He bath gas will be discussed. We found that UO_2^+ reacts slowly to add up to four ligands (H_2O and/or acetonitrile).

The U(V) species is unique in that it reversibly binds an O_2 ligand at long reaction times. Isolation of the UO_2^{2+} ion under the same conditions and in the same environment instead leads to formation of UO_2^+, presumably by oxidation of gas-phase water. The other U(VI) species, UO_2OH^+ and $UO_2NO_3^+$ react by adding up to three H_2O or acetonitrile ligands.

30. ADSORPTION AND REACTION OF AMINES ON GERMANIUM AND SILICON SURFACES. **C. Michael Greenlief** and Pornpimol Prayongpan; University of Missouri-Columbia, Columbia, MO.

The bonding and structure of organic molecules with semiconductor surfaces is important for a variety of potential applications. This work examines the interactions between small organic amines, ethylamine and allylamine, with Si(100)-2x1 and Ge(100)-2x1 surfaces. *Ab initio* calculations are used to investigate the transition states and predicted adsorption products for the reactions between these molecules and a dimer cluster model of the semiconductor surfaces. The cluster models include Si_9H_{12}, Ge_9H_{12} and a mixed cluster, $Ge_2Si_7H_{12}$. Ultraviolet and x-ray photoelectron spectroscopy are used to examine the chemical bonding of the adsorbed products. This work will examine the effect of electron-donating organic molecules with semiconductor surfaces. The selectivity and reactivity of functional groups in the surfaces will be described. According to our recent experimental and theoretical studies, the adsorption products for the interaction between amine molecules with Si(100)-2x1 and Ge(100)-2x1 surfaces are temperature dependent. Low temperature adsorption favors dative bonding of the amine with either surface, whereas different adsorption geometries are observed for adsorption at higher surface temperatures.

31. HYDRATION AND ALCOHOL-ADDITION REACTIONS OF GAS-PHASE LITHIUM-ALCOHOL COMPLEXES. **Sila Odour** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

In this study, the intrinsic hydration and alcohol addition reactions of Li^+ cationized alcohols (ethanol, *n*-propanol, 2-propanol, *n*-butanol and 2-butanol) were investigated using ion-trap mass spectrometry. In general, the gas-phase reactions observed included the formation, from $[Li(ROH)]^+$, of $[Li(ROH)(H_2O)]^+$, $[Li(ROH)(H_2O)_2]^+$, $[Li(ROH)_2]^+$ and $[Li(ROH)_2(H_2O)]^+$. Experimental measurements of ligand-addition reaction rates were made by monitoring changes of precursor and product ion abundance as a function of isolation and storage time. Reaction rate constants were determined using the Chemical Kinetics Simulator program. The overall trend in hydration tendency for $[Li(ROH)]^+$ with respect to ROH was *n*-butanol > 2-butanol > *n*-propanol > 2-propanol > ethanol. For the larger alcohols, rates for the addition of second H_2O and ROH ligands decreased, suggesting a steric effect. Trends in reactivity are also supported by *ab initio* investigation of most-probable complex conformations.

32. SIMULATED VELOCITY DISTRIBUTIONS OF MOLECULES PASSING THROUGH ORIFICES INTO A VACUUM. **Phillip G. Wahlbeck**; Wichita State University, Wichita, KS.

Calculations have been performed to simulate the flow of gases through orifices into vacuum. The simulation considers molecular collisions occurring between molecules with randomly selected velocities (speeds and directions) in a gas container with an orifice. The speed distributions are required to agree with the Maxwellian distribution. Isotropy failure theory was applied to the results. In isotropy failure theory, molecular directions from the orifice opening (the vacuum outside the gas container) are not allowed. Classical mechanics are applied to the collision process. Numbers and velocities of molecules exiting the orifice are calculated. The simulations were performed at various Knudsen (Kn) numbers between 0.01 and 1000 using 10 million collision. The number of molecules effusing increase in accordance with isotropy failure theory as the Kn decreased. The velocity distributions show an increase in the average velocity as Kn decreased. These results are compared with experimental results.

33. SOLUBILITY AND TENSIOMETRIC STUDIES OF VARIOUS ALKALINE EARTH AND ANIONIC SURFACTANT COMPOUNDS. **Jim D. Roach** and Alan J. Oberley; Emporia State University, Emporia, KS.

Anionic surfactants have a myriad of industrial and domestic uses which include wastewater remediation and water softening. These anionic surfactants form insoluble complexes with many ions and, in particular, with divalent cations. Solubility and surface tension measurements of dodecylsulfate and dodecylbenzenesulfonate salts were obtained as part of this study. Surfactant concentrations were determined spectrophotometrically using a methylene blue extraction technique. Solubilities for calcium dodecylsulfate, calcium dodecylbenzenesulfonate, magnesium dodecylsulfate and magnesium dodecylbenzenesulfonate were determined and the values verified through flame atomic absorption. Room temperature surface tension isotherms were also obtained for each aforementioned compound.

34. SAM1 STUDY OF THE HOMOPOLYMERIZATION OF SILICON DERIVATIVES OF TETRAOXASPIRO[5.5]UNDECANE. **T. P. Marshall** and Andrew J. Holder; UMKC, Kansas City, MO.

SAM1 calculations were carried out to investigate the acid catalyzed homopolymerization of several silicon derivatives of tetraoxaspiro[5.5]undecane. Mechanisms leading to single- and double-ring opening for expansion upon polymerization were investigated for 1,5,7,11-tetraoxa-6-sila-spiro[5.5]undecane, 1,5,7,11-tetraoxa-2,8-disila-spiro[5.5]undecane, 1,5,7,11-tetraoxa-3,9-disila-spiro[5.5]undecane and 1,5,7,11-tetraoxa-2,4,8,10-tetrasila-spiro[5.5]undecane. Activation energies and enthalpies of reactions for these monomers were then compared to elucidate relative reactivities and probable products. The accuracy of the models employed was evaluated using experimental evidence.

35. ELECTRIC-FIELD-INDUCED DYNAMICS IN RADIAL LIQUID CRYSTAL DROPLETS STUDIED BY MULTIPHOTON-EXCITED FLUORESCENCE MICROSCOPY: INTERFACIAL EFFECTS AND METASTABLE CONFIGURATIONS. **Aifang Xie** and Daniel Higgins; Kansas State University, Manhattan, KS.

Time-resolved multiphoton-excited fluorescence microscopy is used to study electric-field-induced reorientation dynamics in single liquid crystal (LC) droplets within polymer-dispersed liquid crystal films. Films comprised of nematic LC dispersed in a poly(isobutyl methacrylate) matrix are characterized. An electric field is applied laterally across each droplet, using two parallel copper wires embedded in the film. Three-photon excited fluorescence images are recorded with 200 ms time resolution as the field is modulated on and off. Orientational relaxation of the LC in different droplet regions was observed to occur on dramatically different time scales following removal of an applied electric field. Droplet relaxation was driven by interfacial LC, with the LC configuration passing through a transient, metastable axial organization that quickly relaxed to the original radial configuration after a short delay. These effects are attributed to polymer/LC interfacial interactions and relaxation of the LC through a transient, metastable organizational state. The imaging methods employed in these studies, as well as the results presented for E7/PiBMA droplets promise to provide an enhanced understanding of field-induced dynamics in PDLC materials.

36. ESR STUDIES OF A REORIENTING NICKEL COMPLEX. **Bruce A. Kowert**; St. Louis University, St. Louis, MO.

Electron spin resonance spectra of the planar bis(maleonitrile-dithiolato)nickel anion radical have been simulated in several polar solvents using axially symmetric reorientation. The rotational diffusion about the long in-plane axis is three to four times faster than that about the two axes perpendicular to it. The reorientational model needed to produce agreement with experiment is either in or close to the Brownian rotational diffusion limit. The solvents are 4-allyl-2-methoxyphenol (eugenol), dimethyl phthalate, tri-*n*-butyl phosphate, tris(2-ethylhexyl)-phosphate and 2-methoxyethyl ether (diglyme), ethyl alcohol and a dimethylformamide-chloroform mixed solvent. The reorientational rates from the simulations are in general agreement with those from line width analyses. These reorientational results are compared with those obtained from the translational diffusion constant of the complex.

37. SURFACE-ENHANCED RAMAN SPECTROSCOPY USING SILVER NANOPARTICLES: THE EFFECTS OF PARTICLE SIZE AND HALIDE IONS ON AGGREGATION. **Paul W. Jagodzinski**[1] and Garry P. Glaspell[2]; [1]Colorado School of Mines, Golden, CO; [2]Virginia Commonwealth University, Richmond, VA.

A surfaced-enhanced Raman spectroscopic investigation of the aggregation of silver nanoparticles formed *via* laser vaporization controlled condensation was undertaken. Using Rhodamine 6G as the adsorbate, nanoparticles with diameters in the range 5 to 50 nm were studied with the results from 8nm, 11nm and 15nm diameter particles reported to highlight the effects of particle size and halide ion concentration on particle aggregation. It was found that with 647.1 nm excitation maximum enhancement is observed using particles with 11 nm diameters. Aggregates formed from particles of this size also exhibit significantly greater enhancements compared to aggregates formed from the other size particles. Upon addition of sodium halides, enhancement is proportional to the size of the anion for F^-, Cl^- and Br^-. Maximum enhancement was observed when the concentration of the anion was approximately equal to the concentration of the adsorbate. These observations are explained in terms of electromagnetic contributions to the enhancement.

38. FORMATION AND SURFACE-ENHANCED RAMAN SPECTRA OF METAL CYANIDE COMPLEXES IN GOLD COLLOID SOLUTION.

Paul W. Jagodzinski and Michael B. Jacobs; Colorado School of Mines, Golden, CO.

Cyanide ions adsorbed onto gold colloids produced *via* chemical reduction methods have been previously studied using surfaced-enhanced Raman spectroscopy (SERS).[1,2] In addition, it is well known that cyanide ions form complexes with gold (I) and gold (III) ions, *e.g.*, $[Au(CN)_2]^-$ and $[Au(CN)_4]^-$.[3] We have performed a SER investigation of the formation of gold-cyano complexes in colloidal solution and their subsequent attachment to the gold colloid surfaces. We believe that the cyanide ions form complexes with gold ions that have not been reduced during the formation of the colloid despite a large excess of reducing agent. We will discuss our work to identify and quantify the gold ions in solution, the complexes that they form and interpret the associated SER spectra.

1. B. Pettinger, G. Picardi, R. Schuster and G. Ertl, *J. Electroanal. Chem*. **554**, 293 (2003).
2. M. R. Mahoney, R. P. Cooney and *J. Chem. Soc. Faraday Trans.* 1, **81**, 2115 (1981).
3. K. Cho, Y. S. Jang, M.-S. Gong, K. Kim and S.-W. Joo, *Appl. Spectrosc.* **56**, 1147 (2002) (and references therein).

39. NEW TERM OF pH/OH GLASS ELECTRODE. **K. L. Cheng**; University of Missouri-Kansas City, Kansas City, MO.

The questionable pH term has been one of most popular and common misleading terms in chemistry. Unfortunately such errors still exist, though modern progress in this area has been known in the last two decades. Among the acid-base theories of Arrhenius, Bronsted and Lewis, the Bronsted theory is generally accepted. This author prefers Arrhenius because Bronsted neglects hydroxide ions and Lewis covers practically all chemical reactions. This demonstrates that protons, as a ghost, are generally used for explanation of all alkaline situations. IUPAC and chemical textbooks should pay special attention to modern progresses to correct past errors, particularly scrutinizing those without logical reasons. It is terrible to teach misleading and wrong concepts to students. The pH glass electrode has been known as a capacitor which adsorbs charged ions to generate potentials, not misused Nernst redox, ion exchange or Harned concept. It adsorbs protons in acid and hydroxide ions in alkaline as supported by many experimental results. In acid-base calculations, the $pK_w = pH + pOH$ equation is inapplicable because of the mathematic equation =x= chemical equation. So it is proper to write the "pH/OH glass electrode" instead of "pH glass electrode" to show the electrode playing both equally different positive and negative potential functions. It may be applied to the "pAg/Cl" for the Ag/AgCl reference electrode. It is also suggested that the present pH meter should show the isoelectric point of the glass electrode and should be changed to show pH and pOH scales instead of the pH 0-14 scale. Unlike as is commonly believed that the isoelectric point of electrode glass is at pH 7.0, it is generally at pH < 7.0 due to the addition of metal oxides to the glass for increasing the electrode conductivity.

40. MICROCHIP-BASED RESISTANCE VESSEL MIMICS FOR THE DETECTION OF DEFORMATION-INDUCED ATP FROM ERYTHROCYTES. **Alexander K. Price**[1], R. Scott Martin[1] and Dana M. Spence[2]; [1]Saint Louis University, St. Louis, MO; [2]Wayne State University, Detroit, MI.

In this presentation, the fabrication of microfluidic devices for use as mimics of resistance vessels in the microcirculation will be described. Soft-lithographic methods facilitate the fabrication of poly(dimethylsiloxane)-based microchannels with dimensions similar to that of arterioles *in vivo*. When red blood cells (RBCs) are mechanically pumped through these microstructures, micromolar amounts of adenosine triphosphate (ATP) have been measured *via* luciferin/luciferase-mediated chemiluminescence. ATP is known to stimulate nitric oxide (NO) production in endothelial cells that line the lumen of vessels *in vivo*. Nitric oxide is well known for its ability to activate guanalyl cyclase, resulting in relaxation of smooth muscle cells and eventual vasodilation. With these microchip devices, we have been able to show that this deformation-induced release of ATP changes accordingly from lower to higher concentrations when the cross-sectional area of the channel is decreased. Microscopic images of RBC flow through a channel indicate that this model constitutes an adequate mimic due to the presence of a “cell-free” layer at the wall of the channel. ATP release from RBCs flowing through microchannels and microbore tubing that have similar cross-sectional areas is statistically equivalent, giving further evidence that microchip-based vessel mimics can operate just as effectively as previously identified mimics. Preliminary data involving the development of a more realistic biomimetic structure where channels scale down uniformly will also be presented.

41. INTEGRATION OF AN IMMOBILIZED PC 12 CELL REACTOR WITH A MICROCHIP-BASED FLOW ANALYSIS SYSTEM.

Michelle W. Li and R. Scott Martin; Saint Louis University, St. Louis, MO.

Recent studies have shown that nitric oxide may play a role in the degeneration of dopaminergic neurons during the development of Parkinson’s disease. Since understanding this mechanism is very difficult to achieve *in vivo*, new analytical tools involving cell culture models are needed in order to gain insight into this degeneration. It would be ideal to develop an *in vitro* cell culture system that mimics an *in vivo* system by allowing for cells to differentiate in a three-dimensional format as well as providing a means to monitor intracellular neuronal activity. As a first step towards such a model, a microchip-based approach and rat pheochromo-cytoma (PC 12) cells have been used. In this presentation, we will discuss a new method for detecting neurotransmitter release from PC12 cells using microchip-based flow analysis and amperometric detection. The cells are immobilized in poly(dimethylsiloxane)-based microchannels using a new chip-based cell culturing technique. Various coatings and coating concentrations were studied for the optimization of cell immobilization. A new method for cell introduction into the PDMS channels was also developed. This technique involved selectively coating the microchannels with collagen, followed by the pipetting the cells over the PDMS structure with the cells only being immobilized on the coated channels. The cell-coated microchannels can then be reversibly sealed to a glass plate that contains electrodes for amperometric detection. The Nafion-coated electrodes were made by micromolding carbon inks and used to measure neurotransmitter release from the cells upon stimulation with a calcium solution. Varying concentrations of PC 12 cells placed in the channels produced neurotransmitter release ranging from 20 to 160 micromolar.

42. STATUS AND DIRECTION OF THE ANALYTICAL SCIENCES DIGITAL LIBRARY. **Ted Kuwana** and Cyntha K, Larive; University of Kansas, Lawrence, KS.

The Analytical Sciences Digital Library (ASDL) went on-line in November 2002 and now has over 200 peer-reviewed websites in its library collection of www.asdlib.org. The opening page menu has five main categories: Pedagogy, Class Material, Technique and Analytical Applications. Examples of website content in each of the five categories will be shown and discussed. Recently, two new categories have been added: Online Articles and Virtual Labs. The purpose, content and implementation plan of these new categories will be discussed. Input regarding user assessment of ASDL will be sought.

43. SELF-ASSEMBLED PERYLENE-DIIMIDE/POLYELECTROLYTE COMPOSITES FOR ORGANIC THIN FILM PHOTOVOLTAICS. **Bei Liu**, Aifang Xie, Jeffrey E. Hall, Sarah L. Barron and Daniel A. Higgins; Kansas State University, Manhattan, KS.

New perylene-diimide/polyelectrolyte composite thin films with possible applications as organic photovoltaics are discussed. Asymmetric, amphiphilic, water-soluble perylene diimides have been synthesized for this purpose. These molecules serve as the photoactive component of the films. Perylene diimides in general are well-known n-type organic semiconductors. Here, cationic diimides are complexed with a negatively charged polyelectrolyte (*i.e.*, sodium polyacrylate), forming a photoactive polyelectrolyte-surfactant composite. The composite material is cast as a thin film on an indium tin oxide (ITO) substrate. For characterization of film semiconducting properties, a TPD layer is first deposited on the ITO substrate, prior to the perylene-diimide/polyelectrolyte composite. A thin film of aluminum is then deposited on top. Depending on the exact film composition and preparation conditions, the films show photovoltages ranging between a few mV and hundreds of mV. Mesoscale film morphology and perylene organization are being characterized using near-field scanning optical microscopy (NSOM) and multiphoton excited fluorescence microscopy (MPEFM). Aggregates up to a few hundred nanometers in size are observed throughout the films. Solvent vapor and thermal annealing leads to both a change in film morphology and a change in molecular order, as reflected by small angle X-ray scattering and polarized fluorescence imaging by both NSOM and MPEFM. The overall goal of these studies is to obtain uniform films incorporating long-range order. Our most recent results towards these goals will be presented.

44. DETERMINING POLYMERIZATION VOLUME CHANGE OF EPOXIDES, METHACRYLATES AND CARBOXYLATES USING MERCURY DILATOMETRY.

Greg Giese, James Code, Heather Vastlick, Jason Finley, Randall Michelson, Patrycja Wilczynska, Benjamin Iwai, Andrew Holder and Kathleen V. Kilway, University of Missouri-Kansas City, Kansas City, MO.

Within recent years, mercury amalgams have been questioned regarding their toxicity toward patients and the environment. This has caused scientists to develop synthetic composites that would replace mercury, not only due to the possible health effects of mercury, but also for aesthetic reasons. The addition of expanding monomers to dental restorative composites is an approach intended to resolve the shrinkage upon polymerization problem of these materials. In this connection, it is important to understand how and why monomers change volume upon polymerization. Furthermore, it would be extremely useful to be able to develop a computational chemistry model for the design and screening of promising monomer systems for the objective of improving their polymer properties. One thing that is required is the systematic collection of experimental data, which has been collected using the same method and conditions. A common method to measure this volume change is mercury dilatometry, which is our chosen method. Numerous polymerization volume change measurements have been taken for a variety of oxiranes and methacrylates. This standard method for sample preparation and collection is required for the development of a computational chemistry for the prediction of volume change upon polymerization. These results will be presented.

45. DETERMINATION OF SALVINORIN A IN BODY FLUIDS BY LC-MS/APCI.

Mark S. Schmidt[1], Thomas E. Prisinzano[1], Kevin Tidgewell[1], Wayne Harding[1], Eduardo R. Butelman[2], Mary J. Kreek[2] and Daryl J. Murry[1]; [1]University of Iowa, Iowa City, IA; [2]Rockefeller University, New York, NY.

Salvinorin A is the main active hallucinogenic agent extracted from the Mexican mint plant, *Salvia divinorum*. Unlike all other known hallucinogens, salvinorin A is a κ opioid receptor agonist. Other κ opioid receptor agonists have been explored as analgesics with potential for reduced dependence and tolerance, however, they exhibit dysphoria and/or psychotomimesis in humans. Currently, salvinorin A and *Salvia divinorum* are unregulated hallucinogens and are widely available over the internet. Unfortunately, the pharmacokinetics, as well as the metabolites of salvinorin A were not definitively known. Furthermore, there were no methods of detecting salvinorin A and related compounds in body fluids. A method was then developed to extract and analyze the concentration of salvinorin A in human and rhesus monkey plasma, rhesus monkey cerebrospinal fluid and human urine by negative ion LC-MS/APCI. This method has been fully validated: the LLOQ using FDA guidelines was 600 pg on column or better. Several derivatives in the salvinorin family can also be analyzed by this method using d3-salvinorin A as an internal standard. The linear range was from 150 - 75000 pg on column. The method has been used to determine plasma concentrations of salvinorins A and B in an *ex vivo* study of incubated monkey blood and an *in vivo* study in rhesus monkey. Salvinorin B was found to be the only significant metabolite and pharmacokinetic profiles were done using a single compartment model; $t_{1/2}$ was 29 minutes *in vivo*, 72 min *ex vivo*.

46. MICROCHIP-BASED BLOOD BRAIN BARRIER MIMIC FOR MONITORING THE FATE OF ENDOTHELIUM-DERIVED NITRIC OXIDE. **Matthew K. Hulvey** and R. Scott Martin; Saint Louis University, St. Louis, MO.

Red blood cells (RBCs) are known to release adenosine triphosphate (ATP) upon mechanical deformation in human circulatory vessels. It is also known that this ATP leads to the synthesis of nitric oxide (NO) in the endothelial cells that line the lumenal side of these vessels. The fate of this NO is not fully understood. It has been shown that NO participates in vasorelaxation of the surrounding smooth muscle. However, it is suspected that NO may be able to cross the blood brain barrier and lead to demyelination and axonal degeneration. It is for this reason that we have chosen to attempt the creation of a blood brain barrier (BBB) mimic. In this poster we will first discuss previous work involving the use of a novel capillary-based flow system to monitor the deformation of rabbit red blood cells. We will specifically focus on work involving diamide, which has been shown to decrease the cells relative deformability and affect the correlating ATP release. Secondly, we will discuss the creation of a microchip-based BBB mimic. The mimic will ultimately involve rabbit RBCs and bovine brain microendothelial cells (BBMECs) as well as integrated valves and electrodes. Preliminary steps of testing fully-functional valves and electrodes on a two-dimensional chip will be presented as well as data involving amperometric detection of NO released from endothelial cells following injection of ATP. The endothelial cells used to monitor NO release in these preliminary steps will be bovine pulmonary arterial endothelial cells, which are cultured and coated along the walls of the microchip flow channels. Analysis of the flow and valving channels is carried out by observing FITC-labeled fluorescent microbeads *via* an inverted microscope coupled with a CCD camera.

47. ALTERING ION TRANSPORT ACROSS NANOTUBE MEMBRANES. **Sai Sumana Penumetcha** and Erich D. Steinle; Southwest Missouri State University, Springfield, MO.

This research project examines the transport of ions through porous alumina membranes with channels of ~200 nanometers in diameter. The test molecule is the anion naphthalene disulfonate, which has absorbance in the ultraviolet range. This allows direct examination of transport by utilizing ultraviolet-visible spectroscopy. Adding subsitutents through strong alumina-silane linkages further modifies all of the surfaces of the alumina nanotube membranes. Membranes were soaked in solutions containing either octadecyltrimethoxysilane or isobutyltrimethoxysilane. Ion transport across the membrane treated with the hydrophobic octadecyltrimethoxysilane was hindered significantly, while the membranes exposed to the short alkyl-chain isobutyltrimethoxy silane demonstrated only a slight blockage of ion transport. In both cases, addition of an ionic surfactant (dodecylbenzenesulfonate) reversed these trends, allowing increased transport of the permeant anion. Additionally, fluorescence spectroscopy and reversed-phase high performance liquid chromatography were utilized to measure the influence of the cationic drug bupivacaine towards the transport of permeant anions across the nanotube membranes.

48. BORON DIPYRRIN-BORONIC ACID CHEMOSENSORS FOR BIOCHEMICAL DETECTION OF *CIS* DIOLS. **Elena Lay**, Rodrigue Tchoufong, Raghu Chitta, Francis D'Souza and Ram Singhal; Wichita State University, Wichita, KS.

Interaction of boronic acid with vicinal alcohols (*cis* diols) has been exploited to resolve and measure valuable compounds, especially glycosylated hemoglobin (HbA1c) -- marker of diabetic conditions. Earlier, we designed boronate ligands for this purpose. Presently, we describe three novel boronate ligands with fluorescence characteristics: a protected boron-dipyrromethene phenylboronic acid (BDP), boron-dipyrromethene ether phenylboronic acid (BDEP) and an ionic version 3-pyridyl boronic acid BDP (iBDP). The ligands are examined for their binding affinities with model diols, such as ribonucleosides, ribonucleotides and polyribonucleotides. Deoxyribo compounds served as controls in the experiments. Each ribo derivative exhibits a furanose (2',3' *cis* diol) capable of binding with the boronate ligand, but not deoxy nucleotides. BDP, the least polar ligand, exhibits very poor affinity for diols. While K_a for ribonucleosides (Ado, Urd) was ~ 0.25 mM^{-1}, ribonucleotides ranged between 2.8 mM^{-1} (AMP) and 25 mM^{-1} (CMP, GMP, UMP). A polyribonucleotide exhibits only one binding site at the 3' end of the molecule. Polyribouridylate showed great affinity for binding with BDP, but little for polydeoxythymidylate. The Hill's plot showed that BDP binds with all model compounds in 1:1 ratio. The BDEP, a more water-soluble ligand exhibits ten-times superior binding properties with the model compounds. The third probe iBDP is highly soluble and appears to be the best probe among three probes studied here. A very good candidate to test the probe is tRNA. It binds with $tRNA^{Asp}$ and $tRNA^{Phe}$ in 1:1 proportion and with very large K_a values. The novelty of this work lies in the nature of the probes. They are fluorescent in nature; therefore, the complex can be easily detected and measured while using very small concentrations of the affinity molecules (~nM range). These novel ligands offer great promise for clinical applications.

49. CARBON-PYROLYZED ELECTRODES FOR MICROCHIP CAPILLARY ELECTROPHORESIS WITH DUAL-ELECTRODE ELECTROCHEMICAL DETECTION. **David J. Fischer**, Walter R. Vandaveer IV and Susan M. Lunte; University of Kansas, Lawrence, KS.

Since the introduction of the “lab-on-a-chip” concept, the use of microchip CE systems has grown to include portable devices for uses such as on-site and point-of-care analysis. Electrochemical detection has become more common in a microfluidic platform because the analytical performance is not diminished when the electrodes are miniaturized, as is the case with optical modes of detection. The use of carbon electrodes is of interest in EC detection due to their low cost, large potential widow and low background noise. Carbon electrodes have previously been employed with microchip CE by inserting a carbon fiber or carbon paste into a microchannel on a polymer substrate. A disadvantage of this approach is that the electrodes are not microfabricated, which prevents the electrode from being mass produced. An improved approach for fabricating carbon electrodes involves pyrolyzing photolithographically-patterned photoresist on fused silica plates. This method of fabrication is based on well-established techniques that have been employed for the construction of microelectronics. Fabrication of PPF electrodes in this manner not only allows for high throughput production, but it also produces electrodes that are more rugged and reproducible. The capabilities and analytical performance of the integrated microchip are being evaluated using dopamine (DA), ascorbic acid (AA) and norepinephrine (NE) as model compounds. Preliminary analysis of DA shows the response of the PPF electrodes to be linear from 10 to 500 μM ($r^2 = 0.998$) while obtaining a LOD of 5 μM (S/N = 3). Further studies involving DA, AA and NE will evaluate characteristics such as ion selectivity, sensitivity, efficiency and reproducibility. Selectivity will be further enhanced by employing a dual-electrode configuration for selective detection of species exhibiting chemically-reversible redox reactions. These characteristics will be directly compared to existing techniques illustrating the abilities of PPF to perform electrochemical detection in microfluidic CE microchips.

50. DEVELOPMENT OF AN ON-LINE MICRODIALYSIS-MICROCHIP CE SYSTEM TO MONITOR NEUROTRANSMITTER RELEASE. **Pradyot Nandi**[1], Bryan Huynh[1], Barbara Fogarty[1], R. Scott Martin[2] and Susan Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Saint Louis University, St. Louis, MO.

This research is focused on the development of a microchip separation system coupled to microdialysis for near-real time monitoring applications. Advantages of coupling microchip electrophoresis to microdialysis include the small volume sample requirements of the technique and fast separation times facilitating excellent temporal resolution. In these studies, a continuous flowing sample stream was delivered into the microchip using connective fittings. Discrete samples were introduced in the separation channel by a gating injection scheme. Fluorescein, sampled directly from a syringe or recovered from a microdialysis probe, was detected every 30 seconds. Optimization studies included the investigation of different device designs, separation voltages and perfusion flow rates. Analytes of interest to this study include aspartate and glutamate, implicated in a number of neurological disorders including stroke and Alzheimer's disease. Detection of selected neurotransmitters has been achieved following offline derivatization with naphthalene-2,3-dicarboxaldehyde (NDA)/cyanide (CN). The ultimate goal of this research is the development of an online microdialysis/ microchip CE system with integration of additional functions including on-line labeling for near-real time monitoring.

51. EFFECT OF NON-POLAR SIDE CHAINS ON COLLISION-INDUCED DISSOCIATION OF CATIONIZED PEPTIDES. **Peter Hamlet**[1], Travis J. Cooper[2], Monohari Silva[2], Qun Wu[2] and Michael J. Van Stipdonk[2]; [1]Pittsburg State University, Pittsburg, KS; [2]Wichita State University, Wichita, KS.

When alanine, valine, leucine or phenylalanine replace glycine at the C-terminus of tetraglycine (GGGG), $[b_3+17+Cat]^+$ becomes the most abundant ion produced by collision-induced dissociation (CID) in an ion trap when the cation is Li^+, Na^+ or Tl^+ and the second-most abundant ion with Ag^+. The formation of $[b_3+17+Cat]^+$ involves the C-terminal residue and hydrocarbon side chains would decrease the activation energy.

For GGGX with H^+, varying the non-polar side-chain (X) has no effect. The mechanisms for CID of protonated peptides do not involve the C-terminus.

For GGXG, $[b_3-1+Cat]^+$ is already the major ion for Ag^+ and it becomes the major ion for the other cations. The formation of $[b_3-1+Cat]^+$ involves the residue next to the C-terminus and hydrocarbon side chains would decrease the activation energy.

For GXGG, the only major effect is changing from $[y_2+1+Cat]^+$ to $[b_2-1+Cat]^+$ for H^+. A hydrocarbon chain would increase the proton affinity of its fragment.

52. ELECTROCHEMICAL BEHAVIOR OF HORSE HEART CYTOCHROME C IMMOBILIZED ON FULLERENE FILM-MODIFIED ELECTRODES.

Lisa M. Rogers[1], Erin S. O'Dell[1], Agnieszka Kochman[2], Wlodzimierz Kutner[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Polish Academy of Sciences, Warsaw, Poland.

Platinum, glassy carbon and indium-tin-oxide (ITO) electrodes were modified using pristine- and pyridine-functionalized fullerenes by drop coating and/or electrochemical fullerene-palladium (C_{60}-Pd) polymer film formation. These electrodes were subsequently used for surface immobilization and electrochemical property investigation of horse heart cytochrome c (cyt c).[1] The immobilized cyt c was characterized by piezoelectric microgravimetry at a quartz crystal microbalance (QCM), optical absorption and electrochemical techniques. The UV-visible spectral studies revealed a small blue shift of both the Soret and Q band of the heme moiety of cyt c, immobilized on the C_{60}-Pd polymer film-modified ITO electrode, as compared to the bands of cyt c in solution suggesting that molecules of cyt c are densely packed onto the surface of the modified electrode. The CV studies revealed a quasi-reversible electrode behavior of the heme moiety indicating the occurrence of kinetically-hindered electron transfer. A good agreement was found between the values of cyt c electrode surface coverage determined by piezoelectric microgravimetry and cyclic voltammetry. For piezoelectric microgravimetry, these values ranged from 0.5 x 10^{-10} to 4.8 x 10^{-10} mol cm^{-2}, depending upon the amount of cyt c present in solution and the time allowed for immobilization, which compared with a value of 3.6 ± 0.4 x 10^{-10} mol cm^{-2} determined by cyclic voltammetry. The possible mechanisms of cyt c immobilization on the C_{60} film or C_{60}-Pd film modified electrodes are also discussed.

1. D'Souza, F., Rogers, L. M., O'Dell, E. S., Kochman, A. and Kutner, W. *Bioelectrochem.* 2004, 0000.

53. INFLUENCE OF SPECIFIC AMINO ACIDS ON INTRAMOLECULAR PROTON MIGRATION DURING CID. **Qun Wu**, Kellis Bulleigh and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

Knowledge of the extent to which protons migrate intramolecularly is critical to the understanding of peptide/protein fragmentation mechanisms and the accuracy of H/D exchange-mass spectrometry experiments to probe protein conformation. In this study we used an *in situ* isotope labeling method recently developed to study the influence of the site specific incorporation of amino acids such as β-alanine, γ-aminobutyric acid, 4-aminomethylbenzoic acid and sarcosine on the extent to which a proton at the carboxy terminus of a peptide will migrate to other exchangable sites during collision-induced dissociation. The specific influences of these amino acids on the proton migration during formation of key sequence ions, as well as the influence of the metal cation, will be discussed.

54. INVESTIGATION OF ION-SELECTIVE ELECTRODES BASED ON ERBIUM(III) PORPHYRINS. **Joseph K. Mbugua** and Erich D. Steinle; Southwest Missouri State University, Springfield, MO.

This research project involves the study and development of ion-selective electrodes (ISEs). In the same way that a pH electrode responds to protons in aqueous solutions, other electrodes are sensitive to anions such as chloride, fluoride and nitrate. Each ISE is dependent on a compound, known as an ionophore, to specifically bind to the target anion of choice. This work involves examining metalloporphyrins as possible anionic-selective ionophores. A plasticized PVC membrane was doped with an erbium(III) porphyrin. ISEs based on lanthanide metal complexes have not been studied previously. These membranes were mounted in electrode bodies and used to measure calibration curves of various anions over different concentration ranges and pH values. Preliminary results from the erbium(III) porphyrin-based ISEs demonstrate unique selectivity patterns that differ from commercially-available ISEs. The effect of adding lipophilic ionic sites to these membranes is also examined. Possible applications of these ISEs, especially in clinical and environmental applications, are demonstrated.

55. ION TRAP MS STUDY OF THE INFLUENCE OF SEQUENCE ON PEPTIDE FRAGMENTATION REACTION RATES. **Sammer Tekarli**, Travis Cooper and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

To gain a firmer understanding of the mechanisms that underlie the collision-induced dissociation (CID) of gas-phase peptide ions, we have undertaken a comphrensive study of peptides containing amino acids such as β-alanine, γ-aminobutyric acid, ε-amino-*n*-caproic acid and 4-aminomethylbenzoic acid, chosen because of their effect on intramolecular nucleophilic attack necessary for gas-phase cleavage. Here we report experiments in which fragment ion intensities were measured as a function of CID activation time (msec time scale). Experimentally-generated kinetic profiles were modeled using the Chemical Kinetics Simulator to produce fragmentation reaction rate constants. The time-resolved CID experiment was performed at a range of collision energies, which are related to ion effective temperature, to assess the influence of the various amino acids on relative fragmentation reaction activation energies. Results for a group of model peptides, with the alternative amino acids positioned at different sites, will be presented.

56. MEASUREMENT OF METHANOL IN AQUEOUS ALCOHOL MIXTURES BY KROMOSCOPY. **David S. Cho** and Mark A. Arnold, University of Iowa, Iowa City, IA.

Kromoscopy is a novel quantitative measurement system where white light passes through the sample and the transmitted light is analyzed by a set of discrete detector channels. Each channel is composed of a solid-state detector element coupled with a bandpass filter. The resulting four-channel outputs are related to the analyte concentration through a multi-linear regression model. Selectivity is a critical issue for this type of optical measurement, particularly for samples composed of multiple solutes with overlapping absorption spectra. In this study, the selectivity properties of Kromoscopy were investigated by establishing a set of filters for the selective measurement of methanol in aqueous solutions composed of methanol, ethanol and propanol. Measurements were made in the near infrared region of the spectrum and took advantage of differences in the near infrared absorption properties of these three alcohols. The best set of four filters was identified for the selective measurement of methanol in the presence of ethanol and propanol. These filters were selected from a set of twenty-two filters that span the spectral range from 700 to 1850 nm. The strategy used to identify the best set of four filters involved measuring the individual responses of each filter to concentration changes for each alcohol and then computationally determining the composite response expected for all possible combinations of four. Composite responses were judged by comparing relative sensitivity and selectivity for methanol over ethanol and propanol. The selected filter set is composed of filters with transmission spectra centered at 1600, 1650, 1660 and 1450nm. The analytical utility of this set of filters for selectively measuring methanol will be presented.

57. MECHANISM OF ELIMINATION OF WATER FROM GAS-PHASE METAL-CATIONIZED TRIPEPTIDE ESTERS. **Erach Talaty**, Travis Cooper, Debra Piland, David Bateman, Adeel Syed and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

In a previous study of the dissociation patterns of metal-cationized tetrapeptides of the type AcFGGX-OH, X was designed to test the importance of a five-membered intermediate in the production of the $(b_3+17+Cat)^+$ sequence ion. When this pathway was blocked (for example, by demanding a larger ring, the dominant pathway was not production of the rival $(b_3-1+Cat)^+$, but one leading to $(M-H_2O+Cat)^+$. Because this product ion persisted even with the corresponding methyl ester, a detailed study was undertaken to unravel the mechanism underlying this loss of water. The present investigation focuses on a tandem mass-spectrometric study of $(AcGGG\text{-}OMe+Li)^+$. By site specific istope labeling, it was determined that the loss of water involves the α-hydrogen atoms of the N-terminal glycine, but not those from the other two residues. This elimination of water is followed by loss of 18, 28, 59, 60 and 99 mass units. Detailed mechanisms of these fragmentations, supported by extensive labeling by ^{2}H, ^{13}C and ^{15}N will be presented.

58. MIXED REGIOSELECTIVITY IN THE ARG-177 MUTANTS OF CORYNEBACTERIUM DIPHTHERIAE HEME OXYGENASE AS A CONSEQUENCE OF IN-PLANE HEME DISORDER.

Yuhong Zeng[1], Rahul Deshmukh[2], Gregori A. Caignan[1], Richard A. Bunce[3], Angela Wilks[2] and Mario Rivera[1]; [1]The University of Kansas, Lawrence, KS; [2]School of Pharmacy, University of Maryland, Baltimore, MD; [3]Oklahoma State University, Stillwater, OK.

It has been reported that the rat-HO-1 mutants Arg-183Glu and Arg-183Asp produce approximately 30% alfa-biliverdin. A change in the pK_a for the Fe(III)-H_2O to Fe(III)-OH transition of the mutants was interpreted to be consistent with a rearrangement of the hydrogen bonding network in the distal pocket that results in altered regioselectivity [Zhou, H., *et al*. (2000) *J. Am. Chem. Soc*. **122**, 8311-8312]. We have studied the changes in regioselectivity brought about by mutating the corresponding residue (Arg-177) in heme oxygenase from *C. diphtheriae* (cd-HO). Replacing Arg-177 for Glu or Asp results in the formation of both *alpha*- and *delta*-biliverdin, whereas the Arg-177Ala mutant retains *alpha*-regioselectivity. No obvious trend in the change of pK_a values has been observed for the different cd-HO mutants, indicating that a simple rearrangement of the distal hydrogen bonding network is likely not responsible for the altered regioselectivity. NMR spectroscopic studies conducted with the Arg-177Asp and Arg-177Glu mutants of cd-HO revealed the presence of an alternative heme seating, which is related to the normal seating by about 85 degree in-plane rotation. Moreover, the two heme seatings are in dynamic exchange, which we propose is triggered by electrostatic repulsion between the side chains of Glu or Asp and heme propionate. As a consequence, the *delta*-meso-carbon in the alternative seating is placed in the same position occupied by the *alpha*-meso-carbon in the normal seating, where it is susceptible to hydroxylation. In agreement with this hypothesis, when Arg-177 is replaced by a residue with a neutral side chain (Ala), the regioselectivity remains unchanged.

59. ON THE MECHANISM AND CONSEQUENCES OF HEMIN BINDING BY APOCYTOCHROMES B5: INSIGHT FROM STUDIES OF THE S71L MUTANT OF THE BOVINE MICROSOMAL PROTEIN. **An Wang**, Adriana Altuve, Aaron B. Cowley, David R. Benson and Mario Rivera; The University of Kansas, Lawrence, KS.

All known b-heme proteins are heterogeneous because heme can occupy two orientations which differ by a 180° rotation about its a-g-meso axis. Herein we report that a small but significant excess of one orientation is formed during reconstitution of the apo forms of bovine microsomal cytochrome b5 (Mc cyt b5) and of rat outer mitochondrial membrane (OM) cyt b5 at 4 °C, due to selective binding of hemin in that orientation. NMR studies suggest that conformational heterogeneity present in the apoproteins is partially retained in the freshly reconstituted holoproteins, a result of rapid and irreversible formation of the bis-His coordination sphere and that the native folds are approached through a subsequent annealing process. Annealing of the bovine Mc cyt b5 structure appears to involve a higher activation barrier, and to be facilitated by equilibration of the two hemin orientational isomers at 24 °C. Annealing occurs without need of isomer equilibration in reconstituted rat OM cyt b5, an important consideration given that hemin is kinetically trapped in the protein under physiological conditions. The data support a conclusion that conformational heterogeneity is greater in bovine Mc apocyt b5 than in rat OM apocyt b5, consistent with the recent discovery that it exhibits a less compact fold. Increasing the compactness of bovine Mc apocyt b5 by replacing Ser-71 with Leu, the corresponding residue in rat OM apocyt b5, appears to exacerbate structural heterogeneity following reconstitution, however. We attribute this to an unfavorable steric environment at the base of the hemin binding pocket in the S71L mutant.

60. POLYMERIZATION VOLUME CHANGE IN OXIRANES AND METHACRYLATES. **Jason Finley**, Randall Michelson, Patrycja Wilczynska, Benjamin Iwai, Heather Vastlick, Greg Giese, James Code, Andrew Holder and Kathleen V. Kilway; University of Missouri-Kansas City, Kansas City, MO.

Cutting-edge research in dental reconstructive preparations over the past few decades has focused on the novel use of polymers *in lieu* of mercury amalgams. The trade-off has its graces and detriments: while polymers are strong, durable, water-insoluble and aesthetically pleasing, monomer composites are known to expand or contract during polymerization, which unduly exerts strain on teeth and necessitates further costly procedures. The present research project seeks to gain extensive, accurate, methodical data on polymerization volume change in three groups of monomers: oxiranes, spiroorthocarbonates and methacrylates. Gaining exact values for polymerization volume change is not only useful in and of it itself, but is also useful because the raw data can be used to make generalizations and predictions. The raw data will be used to make a quantum-mechanically quantitative structure activity relationship (QMQSAR) model that is able to predict polymerization shrinkages in unknown, uncreated and untested monomers in the three aforementioned classes of compounds. The QMQSAR will describe polymerization volume change in terms of independent variables called descriptors (such as hydrogen bonding, polarity and molecular weight). It will be created by looking at a group of compounds that have the same baseline structure but differ slightly in the number and type of functional groups. Because the ability of a QMQSAR to accurately predict properties increases with the number of structures included in the model, the acquisition of vast amounts of raw data is necessary before computational methods can be applied effectively. In summary, the discovery of potentially-useful monomer composites awaits the orderly, systematic collection of polymerization shrinkage data, upon which predictive computational models can be built.

61. SOL-GEL MODIFIED POLY(DIMETHYLSILOXANE) MICRO-FLUIDIC DEVICES WITH HIGH ELECTROOSMOTIC MOBILITIES AND HYDROPHILIC CHANNEL WALL CHARACTERISTICS.

Gregory T. Roman, Christopher T. Culbertson, Tyler Hlaus, Kevin Bass and Todd Seelhammer; Kansas State University, Manhattan, KS.

Using a sol-gel method we have fabricated poly(dimethylsiloxane) (PDMS) microchips with SiO_2 particles homogeneously distributed within the PDMS polymer matrix. These particles are ~ 10 nm in diameter. To fabricate such devices, PDMS (Sylgard 184) was cast against SU-8 molds. After curing, the chips were carefully removed from the mold and sealed against flat, cured pieces of PDMS to form enclosed channel manifolds. These chips were then solvated in tetraethylorthosilicate

(TEOS) causing them to expand. Subsequently, the chips were placed in an aqueous solution containing 2.8% ethylamine and heated to form nanometer-sized SiO_2 particles within the crosslinked PDMS polymer. The water contact angle for the PDMS-SiO_2 chips was ~ 90.2¢^{a} compared to a water contact angle for Sylgard 184 of ~108.5¢^{a}. More importantly, the SiO_2 modified PDMS chips showed no rhodamine B absorption after 4 hours indicating a substantially more hydrophilic and non-absorptive surface than native PDMS. Initial electroosmotic mobilities (EOM) of 8.25 ± 0.21 x 10^{-4} cm^{2}/Vs (RSD = 2.6%, n = 10) were measured. This value was approximately twice that of native Sylgard 184 PDMS chips 4.21 ± 0.093 x 10^{-4} cm^{2}/Vs (RSD = 2.2%, n =10) and 55% greater than glass chips 5.31 ± 0.41 x 10^{-4} cm^{2}/Vs (RSD = 7.7%, n = 5). After 60 days of dry storage, the EOM was 7.6 ± 0.3 x 10-4 cm2/Vs (RSD = 3.9%, n = 3), a decrease of only 8% below that of the initially measured value. Separations performed on these devices generated 80,000 to 100,000 theoretical plates in 6 to 14 s for both TAMRA and FITC derivatized AAs. The separation distance was 3.5 cm. Plots of peak variance vs. analyte migration times gave diffusion coefficients which indicate that the separation efficiencies are within 15% of the diffusion limit.

62. SPECTROSCOPIC AND ELECTROCHEMICAL INVESTIGATION OF PETUNIA PIGMENTS. James M. Chapman, Dale Harak and **Kyle Cummins**; Rockhurst University, Kansas City, MO.

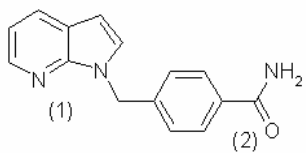
The anthocyanin pigments of Petunia Hybrida Purple Wave have been characterized by UV-visible and cyclic voltammetry. The UV-visible spectra of these pigments vary markedly with changes in pH. While the characteristic purple color of the petals is apparent at low pH, the color is absent at pH 7.0 and shifts to a green color at pH 12.0. Additionally, the pigments were further characterized at these different pHs by cyclic voltammetry in order to investigate the anti-oxidant properties previously attributed to the anthocyanins. The spectroscopic and electrochemical information was used to assign the oxidative and structural changes occurring in the pigment molecule as the pH is varied.

63. COMPLEXATION OF MONO- AND DICYANOVINYLARENES. **Cortnie Vogelsberg**[1], DeAnna Travis[1], John VanScoy[1], Douglas M. Ho[2] and Kathleen V. Kilway[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]Princeton University, Princeton, NJ.

This poster will summarize the newest results in the area of the formation of metal clusters using polynitrile building blocks. We have recently expanded our research using flexible polynitrile angular linkers to produce more directed polycyanovinyl systems. A variety of polycyano-vinylarenes were synthesized from their corresponding aldehydes using a Knoevenagel condensation. Some of the complexing agents include 4-dicyanovinyl biphenyl and 2-ferrocenyl-1,1-dicyanothene. These ligands were complexed with numerous silver salts and their structures were determined using single-crystal X-ray diffraction. Evaluation of this data revealed interesting insights into the formation and the composition of the silver complexes.

64. IF THERE WAS A FOURTH LITTLE PIG HE WOULD HAVE BUILT HIS HOUSE OUT OF THESE.....DESIGN, SYNTHESIS AND SUPRAMOLECULAR CHEMISTRY OF NEW AZAINDOLE-BASED MOLECULES. **Michelle Smith**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS.

The construction of predictable assemblies and architectures using multifunctional supramolecular reagents is presented, facilitating the assembly of extended organic molecular materials. It has been shown that it is possible to functionalize 7-azaindole (**1**) with a suitable side-arm (**2**) that can be fully utilized in this way, using a modular approach such that the two different bindings can preferentially and selectively form hydrogen bonds with two different molecules. This provides the required synthetic tools for the production of binary and ternary super-molecules.



65. METAL-ORGANIC TEMPLATES THAT DIRECT REACTIVITY IN THE SOLID STATE. **Ivan G. Georgiev**, Giannis S. Papaefstathiou and Leonard R. MacGillivray; The Univerisity of Iowa, Iowa City, IA.

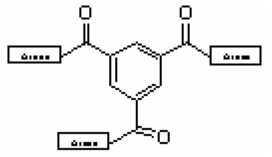
There is increasing interest in constructing rigid molecular building blocks to position olefins, supramoleculary, for reaction in the solid state. The olefins undergo [2+2] photodimerization both regio- and stereospecifical-ly, as well as in high yields. In this study our attention focuses upon the development of metal-organic templates that direct the photoreaction in the solid state. We anticipated that such templates may enable a means to combine the properties of metals (*e.g.*, optical, magnetic) with the organic solid-state reactivity for the construction of new materials with potentially unique properties. As a starting point we have synthesized a dinuclear Zn(II) complex based on the ditopic Schiff base ligand $[Zn_4L_4(OH)]^{4+}$ (LH=2,6-bis[N-(2-pyridyethyl)formimidoyl]-4-methylphenol). The complex directs the photoreaction, involving *trans*-1,2-bis(4-pyridyl)ethylene (4,4'-bpe) as a reactant in the cationic assembly $[Zn_4L_4(OH)(4,4\text{-bpe})_2]^{4+}$ by way of coordination driven self-assembly. We demonstrate that the reactivity is maintained within derivatives of such templates, which have been synthesized by attaching various functional groups to the peripheries and arms of the template ligands. We also demonstrate that such reactivity proceeds *via* a single-crystal-to-single-crystal reaction.

66. N-SUBSTITUTED PYRAZOLE…"LEGO®" FOR CHEMISTS? **Benjamin M. T. Scott**, John Desper and Christer B. Aakeroy; Kansas State University, Manhattan, KS.

Heterocyclic molecules, *e.g.* pyrazole, are readily N-functionalized *via* well-established S_N2-based reactions. If the heterocycle is appended with a sidearm that can form directional and reliable hydrogen-bond interactions we will have a versatile building block capable of forming extended frameworks *via* amide-amide interactions and nitrogen-metal interactions. In addition, these new functionalized heterocycles have the potential to form ternary co-crystals through two very different binding sites, namely the amide moiety and the nitrogen atom of the heterocycle. In this study, we report the design, synthesis and characterization of a family of benzamide-pyrazole-based ligands and some structural supramolecular chemistry that has been undertaken with these building blocks.

67. TRIAROYLBENZENE: SUPER MOLECULES IN SUPRA-MOLECULAR CHEMISTRY. **Mayuri K. Dighe**, F. Christopher Pigge and Nigam P. Rath; University of Missouri-St. Louis, St. Louis, MO.

The self-assembly of crystalline network architectures from simple building blocks is a phenomenon of great interest in supramolecular chemistry. 1,3,5- Triaroylbenzenes (TABs), which can be prepared *via* trimerization of aryl enaminones, have been found to exhibit a wide range of interesting solid state structures. Derivatives possessing arene components such as *p*-cyanophenyl, *p*-chlorophenyl, *p*-hydroxyphenyl, 2-naphthyl and 9-anthracenyl have been structurally characterized using single-crystal X-ray diffractometry. Numerous network topologies have been identified as a function of arene component. In addition certain TABs are obtained as polymorphs. Structural aspects of selected TABs will be discussed.



68. AQUEOUS MERCURY ION ADSORPTION ONTO DIFFERENT TYPES OF PLASTIC CONTAINERS. **Daniel Dorn** and James L. Robinson, U. S. Environmental Protection Agency, Kansas City, KS.

Mercury ions in the +2 valence state adsorb onto plastic containers even if preservatives are present in solution. Several types of containers were studied and several kinds of reagents were used as preservatives. Also studied were inorganic +2 mercury and a methyl mercury chloride solution. Results show some plastic containers hold onto mercury ions fairly strongly while others adsorb only a small % of the mercury ions. Chloride ions as a preservative gave interesting results for holding mercury ions in solution and the various data from this study were made into graphs that are displayed on the poster. Results show that the amount of adsorption of mercury ions onto plastic containers is not an easily predictable phenomenon.

69. RESEARCH-INTEGRATED CURRICULUM IN GEOENVIRONMENTAL ENGINEERING.

Alok Bhandari, Lakshmi N. Reddi, David R. Steward, Stacy L. Hutchinson and **Larry Erickson**; Kansas State University, Manhattan, KS.

This poster presents a curriculum framework for geoenvironmental engineering developed with support from the National Science Foundation's Combined Research-Curriculum Development (CRCD) program. The objectives of this curriculum are 1. To synthesize relevant principles and themes from a number of allied disciplines in science and engineering such as environmental engineering, geotechnical engineering/geology, water resources engineering/hydrology, chemical engineering/chemistry, biological and agricultural engineering/biological sciences and agronomy/soil sciences; 2. To incorporate rapidly evolving research on subsurface fate and transfer processes, site remediation and waste containment methods, into the curriculum; 3. To provide exposure to a multi-agency perspective such that "real world" site remediation and waste containment problems could be solved within the contraints of state and federal regulatory agencies and 4. To incorporate interactive and experiential learning-oriented education methods and inter-disciplinary team experiences into design education. Geoenvironmental engineering encompasses the application of science and engineering principles to the analysis of the fate and transport of water, contaminants and energy in geomedia and the design and implementation of processes and systems for treating, reusing and containing wastes on and in the ground.

70. SYNCHROTRON FOURIER TRANSFORM INFRARED MICROSPECTROSCOPY AS A TOOL TO MONITOR THE FATE OF ORGANIC CONTAMINANTS IN PLANTS.

Kenneth Dokken[1], Larry Erickson[1], Lawrence Davis[1] and Nebojsa Marinkovic[2]; [1]Kansas State University, Manhattan, KS; [2]Albert Einstein Center for Synchrotron Biosciences, Upton, NY.

The use of phytoremediation as a tool for cleaning sites contaminated with aromatic and heterocyclic organic compounds has gained much recognition over the past decade. It is obvious that plants are a more cost-effective, environmentally-friendly and aesthetically-pleasing alterna-tive to older, conventional methods. It is well documented that many plants can biotransform organic contaminants. However, the ultimate fate and transport of these organic compounds are unknown within most plant systems. Major issues in the field are whether transformed contaminants are still bioavailable and whether they may have greater toxicity than the parent compound. Our research focuses on using Fourier Transform Infrared (FTIR) microspectroscopy to determine the fate of aromatic and heterocylic organic compounds within the roots of plants. Currently, we are studying how benzotriazole and its derivatives are taken up and metabolized by sunflowers, maize and fescue grasses. Previously we found changes in the root structure in sunflowers treated with benzotriazole due to uptake, incorporation and/or transformation of benzotriazole. These changes were predominantly found in the lignin portion of the root, specifically in the xylem region. We were able to map out the location of benzotriazole sequestration using Synchrotron FTIR microspectroscopy at Brookhaven National Laboratories. Our working hypothesis is that the peroxidatic system responsible for lignification ultimately incorporates benzotriazole into a polymeric material that is no longer bioavailable. Studies using isotopically labeled benzotriazole have shown that a large fraction is unextractable after several days of exposure, with a significant amount remaining in the root. The technique of FTIR microspectroscopy may be used as a tool in phytoremediation to study changes of plant structure induced by the presence of organic contaminants in soil and water. This, in turn, may help in determining what plants can be used to remediate certain organic compounds when developing phytoremediation schemes.

71. ANAEROBIC BIODEGRADATION OF TETRACHLOROETHYLENE (PCE) IN SOIL AND GROUNDWATER. **Sathishkumar Santharam**, Larry Davis and Larry E. Erickson; Kansas State University, Manhattan, KS.

Dry cleaning installations operating in Manhattan, Kansas, have allowed the solvent tetrachloroethylene or perchloroethene (PCE) to seep into groundwater through soil. PCE is a dense non-aqueous phase liquid (DNAPL) and tends to settle down in groundwater; the soluble PCE moves with the groundwater, creating a contaminant plume. The public water wells are located about 1.2 miles down gradient of this site and, hence, are at risk of contamination. Earlier work has revealed that PCE and its degradation compounds such as TCE, *cis*-DCE and vinyl chloride are found significantly above their maximum contaminant levels (MCL) at many places along the plume. Remediation feasibility studies are being conducted by mesocosm experiments; a chamber is divided into six channels and filled with soil. Each channel is fed with water at the bottom and collected at the outlet, simulating the groundwater flow conditions. PCE is introduced at a concentration of about 2 mg/L in three channels, two of them with alfalfa plants and the other with grass. The concentrations of PCE at inlet and outlet are monitored and the amount of PCE disappearing in the soil zone is studied. There is evidence of PCE disappearance which may be due to mass transfer to the atmosphere and/or biodegradation. Soil samples were taken at four different depths in each channel and analyzed for PCE and its degradation products. Since no degradation products were found, the soil in channel 2 was made anaerobic by adding 100 ml of 2% glucose solution. Forty days after adding glucose solution, soil samples were taken again and analyzed for PCE and the degradation products. The headspace of soil channels was also analyzed 30 days after addition of glucose solution. Only PCE was found in the soil samples and the headspace samples. No degradation products were found.

72. ACCELERATED DEGRADATION OF HIGH EXPLOSIVES BY ZEROVALENT IRON IN THE PRESENCE OF SELECTED CARBON MATERIALS.

Jang-Eok Kim[1], Bernard J. Kronschnabel[2], Jeong Park[3], Jong-Sung Kim[2] and Patrick J. Shea[2]; [1]Kyungpook National University, Daegu, South Korea; [2]University of Nebraska-Lincoln, Lincoln, NE; [3]University of Arkansas, Fayetteville, AR.

Zerovalent iron [Fe(0)] is a promising technology for the remediation of water and soil contaminated with TNT (2,4,6-trinitrotoluene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) but treatment efficiency decreases for less water-soluble explosives such as HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine). We are exploring the potential of selected graphitic/activated carbon materials to improve this treatment process by their simultaneous action as adsorbents and redox mediators. RDX destruction by Peerless cast iron aggregates was faster than HMX but the addition of selected carbon materials increased the HMX destruction rate. A similar increase was observed when zinc metal [Zn(0)] was used with the carbon in place of Fe(0). All reaction rates were greater under anaerobic conditions than under aerobic conditions. Graphitic carbon is believed to provide sites for adsorption and chemical reduction by serving as a conduit for electrons and hydrogen from Fe(0)

oxidation. Differences among carbon materials can be attributed to their composition and the presence of impurities. Our observations and related research indicate that certain carbon materials may be used to increase the efficiency of chemical reduction treatment processes.

73. NEW INSIGHTS INTO THE MECHANISMS OF THE THERMAL FENTON REACTIONS USING DIFFERENT IRON(II)-COMPLEXES.

Stefan H. Bossmann[1], Esther Oliveros[2], Mark Kantor[2], Nabil Shahin[2], Sandra Niebler[2], Anna Bonfill[2], Michael Woerner[2] and Andre M. Braun[2]; [1]Kansas State University, Manhattan, KS; [2]University of Karlsruhe (TH), Karlsruhe, Germany.

Although the Fenton reagent (a mixture of hydrogen peroxide and an iron(II) salt) has been known for more than a century, the manifold of mechanisms occurring during the thermal Fenton reaction are still under intense discussion. Indeed, this discussion serves as a powerful driving force for the steadily increasing insight into the field of inorganic radical and electron transfer chemistry. In this work, an experimental approach towards the elucidation of the first steps taking place in the reaction between several iron(II)-complexes and hydrogen peroxide (H_2O_2) in water at pH = 3.0 is presented. 2,4-Xylidine (2,4-dimethylaniline) reacts differently with reactive intermediates via the addition or hydrogen abstraction by the hydroxyl radical (HO•) or electron transfer reactions to higher valent iron-species, such as a hydrated ferryl-complex (Fe(IV)). The chemical reactivity of the employed iron(II)-complexes with H_2O_2 differed strongly depending on the ground-state one-electron oxidation potentials. The results are interpreted in accordance with the paradigm originally developed by Goldstein *et al.* which is based on the evidence obtained from the Marcus theory that outer-sphere electron transfer reactions between metal complexes are not likely to occur because they are too slow. Therefore, most of the "Fenton-reagents" form transient metal complexes, which can be described as $[LnFe\text{-}H_2O_2]_m^+$. They form, depending on the reaction conditions, either the hydroxyl radical or higher-valent iron complex species.

74. STUDY OF ILLITE PARTICLE AGGREGATION BY COMBINED STATIC AND DYNAMIC LIGHT SCATTERING. **Ildiko K. Lini** and James A. Rice; South Dakota State University, Brookings, SD.

The aggregation of illite, 1:2 type phylosilicate, was investigated by combined static and dynamic light scattering technique. The underlying hypothesis of this study is that at the critical coagulation concentration a face-to-face type aggregation process dominates. Using the combined static and dynamic light scattering method at pH=9 and at the critical coagulation concentration, the fast coagulation rate was determined at different angles. The ratio of the hydrodynamic radius for the doublets and singlet was determined as 1.41± 0.1, which is a value characteristic of isometric particles. The light scattering experiment does show that the particles do not attach exclusively face-to-face orientation. Transmission electron micrographs show that the particles are not highly anisometric. While aggregates form in mostly face-to-face arrangement, other secondary types of aggregation are also observed.

75. *IN SITU* FTIR STUDIES OF REDUCTION OF NITRIC OXIDE EMISSIONS. **Jeremy VanAuker**, John Barriner and Dilip K. Paul; Pittsburg State University, Pittsburg, KS.

For fuel efficiency purposes, the currently used Rh-based catalyst is efficient in reducing NO under rich burn conditions; however, under lean burn conditions the catalytic activity of Rh is drastically reduced. In order to overcome this problem, the activity of an alkaline earth metal (such as Ba) is being investigated. Here the reduction of NO in presence of CO over supported Rh-Ba was carried out in an ultrahigh vacuum cell and the reactions were monitored continuously by using *in situ* FT-IR spectroscopy. It has been observed that under reducing environment, coadsorption of CO and NO at elevated temperature produces predominantly CO_2 and N_2 as desired. However, under oxidizing conditions (at 348 K) the formation of nitrites [ƒÞa(NO_2) ~1413 and ƒÞs(NO_2) ~1349 cm^{-1}] and nitrates [ƒÞa(NO_3) ~ 1616, ƒÞs(NO_3) ~1554 cm^{-1}] are observed as a result of oxidation of nitric oxide. At higher temperature (498 K) the nitrate species slowly decomposes on Rh-Ba surface forming N_2, whereas on bare Ba surface the intensity of nitrate species remained constant. That means the presence of Ba is necessary for catalytic degradation of stored nitrate species.

76. PERIODIC TABLE FOR BENZENOID HYDROCARBON ISOMER CLASSES AND BEYOND. **Jerry R. Dias**; University of Missouri, Kansas City, MO.

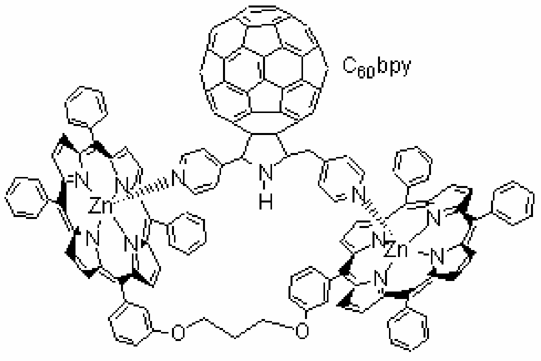
The Periodic Table of Atomic Elements is a 2-dimensional array (spreadsheet) generated according to an aufbau principle. As it will be illustrated by a Formula Periodic Table for Benzenoid Hydrocarbons, this construction turns out to be more general than heretofore realized. These Asuper spreadsheets@ have an unique structure of their own which contains chemical information in compact form. The concept of a periodic table set is like the concept of a group in mathematics. Once their respective criteria are fulfilled, one can anticipate their characteristic set properties. Thus, a periodic table set is an useful mnemonic device for organizing, studying and understanding property trends in large classes of related molecules. The Periodic Table for Benzenoid Hydrocarbons has organized this class of hydrocarbons into a systematic framework and has led to the identification of a new topological paradigm. As our benzenoid (polyhex) studies suggest, the number six is almost a magic number, for it permeates in a subtle way many aspects of mathematics, nature and science. Let n be a positive integer and ƒ¶(n) the sum of positive divisors of n. If ƒ¶(n) = 2n, then n is said to be a perfect number. Six is the smallest perfect number; *i.e*, 6 + 3 + 2 + 1 = 12. Life as we know it is based on carbon which has an atomic number of 6; its nucleus has six protons and six neutrons. The cube has six faces, the hexagon has six sides and snowflakes have hexagonal symmetry. Mud cracks are random polygonal fractures that on the average have six sides. Six equal-size billiard balls can exactly surround another of the same size. Benzene (C_6H_6, with a double six!) and Clar's aromatic sextet principle are particularly illustrative of the importance of the number six.

77. SUPRAMOLECULAR COMPLEX COMPOSED OF A ZINC PORPHYRIN DIMER AND FULLERENE BEARING TWO AXIALLY COORDINATING PYRIDINE ENTITIES. **Suresh Gadde**[1], Melvin E. Zandler[1], Osamu Ito[2], Mitsunari Itou[2], Yasuyuki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan.

Light-induced electron transfer systems with efficient and long-lived charge separation are of great importance to develop artificial photosynthesis and molecular-level optoelectronics. A number of covalently and non-covalently linked donor-acceptor systems have been prepared to further our understanding of the controlling factors such as molecular topology and distance and orientation factors.[1] In recent years, fullerenes as electron acceptors, and porphyrins as electron donors have been realized to be important constituents owing to their rich redox, optical and photochemical properties.[1] It is now well known that in contrast with the traditionally-used two-dimensional aromatic electron acceptors, the fullerene in donor-acceptor dyads, accelerates photo-induced charge separation and slows down charge recombination. Here, we report a highly stable, self-assembled supra-molecular complex, as a photosynthetic reaction center mimic, *via* a 'two-point' axial ligand coordination approach using a covalently-linked zinc porphyrin dimer and fulleropyrrolidine functionalized with two pyridine entities.[2] The geometry and electronic structure of the triad, established from spectroscopic and *ab initio* B3LYP/3-21G(*) calculations, led to a structure shown in Scheme 1. Steady-state and time-resolved fluorescence studies revealed efficient charge separation while evidence for charge-separated state and rate of charge-recombination were obtained from nanosecond transient absorption studies.

1. El-Khouly, M. E., Ito, O., Smith, P. M. and D'Souza, F. *J. Photochem. Photobiol C: Photochem. Rev.* 2004, **5**, 79.
2. D'Souza, F., Gadde, S., Zandler, M. E., Itou, M., Araki, Y. and Ito, O. *Chem. Commun.* 2004, in press.

Scheme 1

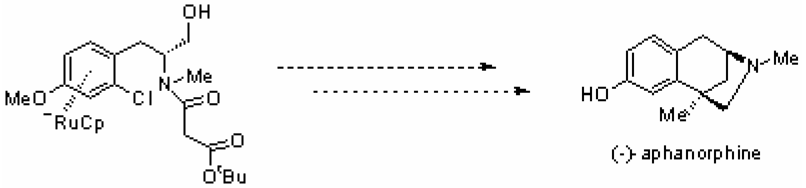


78. THREE-COMPONENT COUPLING/RING-CLOSING METATHESIS APPROACH TO THE SYNTHESIS OF FUNCTIONALIZED PHOSPHONOPYRROLES. **Shubhasish Mukherjee**, Jutta Wanner and Paul R. Hanson; University of Kansas, Lawrence, KS.

A route to the synthesis of novel *N*-substituted phosphonopyrroles is reported. Phosphonopyrroles were synthesized using a Indium(III)-mediated three-component coupling, followed by ring-closing metathesis. The fully unsaturated *P*-heterocycles were obtained *via* a DDQ-mediated oxidation. Chemo-selective reduction of the carboxylic ester moiety in the presence of a phosphonic ester was developed. Furthermore *N*-substituted pyrroles were functionalized selectively using NBS. Efforts towards implementation of library generation will be described.

79. APPLICATION OF η^6-ARENE RUTHENIUM COMPLEXES IN SYNTHESIS. **Shobha R. Malgireddy** and F. Christopher Pigge; University of Missouri - St. Louis, St. Louis, MO.

Coordination of a transition metal center to an organic ligand renders the ligand amenable to synthetic transformations not normally feasible in the absence of the metal center. η^6-Arene metal complexes exhibit an unique reactivity pattern thus acting as valuable synthetic intermediates. The metal moiety in these complexes acts as an electron-withdrawing group, stereocontrol element and also increases the acidity of aromatic and benzylic hydrogens. Thus coordinated arene rings become susceptible to reaction with nucleophiles. Synthetic manipulation of aromatic side chains involving formation of benzylic carbanions also becomes possible and has proven to be a synthetically-useful process. As part of a project aimed at developing the organic chemistry of η^6-arene ruthenium(II) complexes, we are seeking to exploit on of the reactivity patterns associated with this organometallic complex in the construction of valuable heterocyclic ring systems. This poster will center on the progress towards the total synthesis of the benzazepine based alkaloid (-)-aphanorphine *via* an organo-ruthenium approach.



80. APPLICATION OF PHOSPHATE TETHERS TO THE ASYMMETRIC SYNTHESIS OF SKIPPED POLYOL SUBUNITS. **Joshua D. Waetzig**, Alan Whitehead and Paul R. Hanson; University of Kansas, Lawrence, KS.

The development of asymmetric routes to skipped polyol subunits will be discussed. These routes rely on a terminus differentiation strategy employing ring-closing metathesis (RCM) and a temporary phosphate tether for the desymmetrization of 1,3-anti-diols. The method generates both 1,3,6- and 1,3,7-skipped polyols, which are found in a number of natural products, including tetranactin and *feigrisolide B.* Tetranactin, a hydrophobic cyclic antibiotic produced by *Streptomyces aureus*, is a member of the macrotetrolide family of ionophore antibiotics possessing antiparasitic and miticidal activity. *Feigrisolide B*, the most potent member of the *feigrisolide* family, is a hepta-lactone that has demonstrated high levels of antibacterial activity as well as medium cytotoxic and antiviral properties. The goal of this project is to extend this methodology through the incorporation of molecularly complex allylic alcohols, to the synthesis of tetranactin and *feigrisolide B*.

81. CATION STABILITY IN QUATERNARY AMMONIUM METHYLCARBONATES. **Justin G. Norberg**, Gary W. Earl and Duane E. Weisshaar; Augustana College, Sioux Falls, SD.

A new technique for quaternizing tertiary amines using the green reagent dimethylcarbonate as a methylating agent has been demonstrated. The reaction requires a 10:1 mole ratio DMC:amine at 100ºC and 100 psi. The ultimate goal of this project is to perfect this method to the point that industry will adopt it. In order to track the reaction progress, a special apparatus was assembled in which several simultaneous reactions take place in separate vessels. This was so the contents of each vessel can be analyzed at regular intervals without disturbing the other reactions. A GC-MS method was developed to analyze reaction vapors in order to look for Hofmann Elimination by-products. We have results that show the cation is stable.

82. COMPLETE TWO-DIMENSIONAL NMR ASSIGNMENT AND CHARACTERIZATION OF SULFONATED AND UNSULFONATED POLY(ETHER ETHER KETONE) (PEEK) MONOMERS. **Scott E. McKay**[1], Robert W. Lashlee III[1], Brenda D. Moul[1], Bryce A. Holthouse[1] and Robert W. Kopitzke[2]; [1]Central Missouri State University, Warrensburg, MO; [2]Winona State University, Winona, MN.

Complete assignment of 1,1'-(*p*-phenylenedioxy)bis[4-(4-fluorobenzoyl)]-benzene and sodium 2,5-bis[(*p*-fluorobenzoyl)phenoxy]benzenesulfonate were assigned using two dimensional NMR. ^{1}H, ^{13}C, DEPT-135, COSY, HMBC and HMQC were utilized in the determination of the assignments. The fluorinated poly(ether ether ketone) monomer was sulfonated once on the most activated ring with olem (20% free SO_3). The sulfonated fluoro-monomer was obtained in 44% yield as the sodium salt.

83. DESIGN AND SYNTHESIS OF AN OLIGODEOXYNUCLEOTIDE-DOTA CONJUGATE. **Samuel Sarsah** and Eric Trump; Emporia State University, Emporia, KS.

Chelates of the macrocycle DOTA and the Gd^{3+} ion serve as contrast agents for magnetic resonance imaging. The preparation of a Gd^{3+}-DOTA oligodeoxynuleotide decamer conjugate is described. The purpose is to deliver Gd^{3+} selectively into tumor cells and to, thereby, aid in the diagnosis of cancer.

84. DESYMMETRIZATION OF PSEUDO-C_2-SYMMETRIC MONOCYCLIC PHOSPHATES. **James P. McParland**, Alan Whitehead and Paul R. Hanson; University of Kansas, Lawrence, KS.

The use of cuprate addition reactions for the desymmetrization of pseudo-C_2-symmetric monocyclic phosphates is reported. Stereoselective *anti*-S_N2'-allylic cuprate displacements are used to derive non-racemic anionic phosphate building blocks. These systems are assembled *via* a phosphate tether-mediated ring-closing metathesis reaction, ultimately leading to highly functionalized products. Overall, the phosphate moiety plays a multi-faceted role as a tether, leaving group and protecting group.

85. ENZYMATICALLY-CATALYZED ALCOHOLYSIS OF SOYBEAN OIL AS THE FIRST STEP OF ALKYD RESIN SYNTHESIS. **Tomas Vlcek**; Pittsburg State University, Pittsburg, KS.

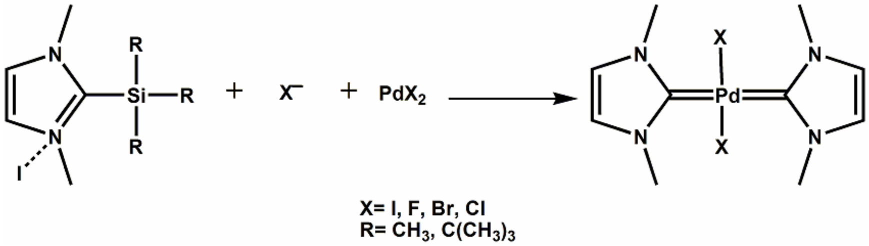
The objective of this work was to study the possibility of replacing a conventional alkyd resin alcoholysis by an enzymatically-catalyzed reaction that is suitable for the plant production. The main goal was to utilize enzymes capable of regulating selective cleavage of fatty acids from position 1- and 3- of vegetable oil triglycerides preferably leading to the formation of 2-monoglyceride (2-MG), which is responsible for air-drying of alkyd resins and for enhancing well-balanced physical-mechanical properties of coatings. Another important reason was to decrease high energy demands of conventional method of alcoholysis requiring reaction temperatures over 200º C. Mild reaction condition can make the alkyd resins' production catalyzed by enzymes more economical. The experimental work focused on comparing a) hydrolysis (soybean oil - deionized water) and b) glycerolysis (soybean oil - glycerol) reactions in the presence of commercially-available liquid lipases Lipozyme TL100L, Lipex 100L, Lipolase 100L and EX type, and immobilized lipases Novozym 435 and Lipozyme TL IM. Furthermore, the influence of raw materials' molar ratio, content of lipase catalyst, reaction time and temperature on final product composition was studied. The highest 2-MG yield approx 32% wt. was obtained in case of glycerolysis in the presence of a relatively cheap liquid Lipolase 100 L EX and 100% molar excess of glycerol to soybean oil. This procedure also reduced three times the amount of unreacted triglyceride, in comparison to the conventional method. Twelve weight percent of free fatty acids remaining in alkyd resins as a side product of lipase catalyzed alcoholysis can serve as reactive solvents. It was also found that cooling the samples after finishing of reaction to 5° C shifts significantly reaction kinetics towards higher yields of 2-MG. The degree of hydrolysis was low.

86. EXAMINATION OF THE SYNTHESIS OF NITROALCOHOLS AND NITROALKENES TO YIELD PRECURSORS FOR ISOC REACTIONS. **William D. Buchanan**, Aaron K. Graumann, Steve J. Moore and Jetty Duffy-Matzner; Augustana College, Sioux Falls, SD.

We are interested in the synthesis of a 3,4-tetrahydrafuran derivatized tetraester macrocycle that may mimic the ionophoric properties of nonactin. To this end, we have examined the production of *alpha*, *beta*-unsaturated 2H,5H-dihydrofuran ketones and carbaldehydes, which are ultimately derived from nitroalkenes. A traditional Henry reaction was compared to one based on amine-treated silica gel. The nitroalcohols were converted into nitroalkenes. The current method involves two distinct steps, while a tentative method was developed that employs only one. Propargyl alcohols and the nitroalkenes underwent Michael reactions to yield nitroethers. These can be treated under ISOC conditions to provide the novel *alpha*, *beta*-unsaturated carbonyl dihydrofurans.

87. GENERATION OF N-HETEROCYCLIC CARBENE COMPLEXES THROUGH SILYLATED IMIDAZOLIUM SALTS. **Joseph Rashad Atkins** and Stefan Kraft; Kansas State University, Manhattan, KS.

In our efforts to generate libraries of NHC-based ligands for catalysts in C-H bond activations we have recently developed a convenient method to formally transfer imidazole carbenes onto metal fragments. Key to this transformation is the *in situ* activation of silylated imidazolium precursors with fluoride or chloride. We believe that this chemistry provides a mild alternative to the commonly employed carbene transfer reaction that requires strong bases or the generation of silver-carbenes.



88. HPLC ANALYSIS IN BIOFRIENDLY QUATERNARY AMMONIUM SYNTHESIS. **Brian D. Rekken**, Gary W. Earl and Duane E. Weisshaar; Augustana College, Sioux Falls, SD.

A new technique for quaternizing tertiary amines using the green reagent dimethylcarbonate as a methylating agent has been demonstrated. The reaction requires a 10:1 mole ratio DMC:amine at 100ºC and 100 psi. The ultimate goal of this project is to perfect this method to the point that industry will adopt it. Even though HPLC had been previously used to follow the rate of the reaction, the HPLC method has now been perfected with results to be discussed.

89. IMPLEMENTATION OF ROMP-DERIVED DCC FOR LIBRARY GENERATION. **Punitha Vedantham**[1], Parul Jitendra Gor[1], Gunda I. Georg[1], Qi-Zhuang Ye[1], Daniel L. Flynn[2] and Paul R. Hanson[1]; [1]University of Kansas, Lawrence, KS; [2]Deciphera Pharmaceuticals Inc., Lawrence, KS.

The use of a high-load, soluble oligomeric DCC coupling reagent for the facile production of bromo-aryl amides and their subsequent Suzuki coupling reactions is presented. The DCC coupling reactions were performed using ROMP-derived DCC where a simple precipitation and filtration of the polymer was the sole purification method. In the Suzuki coupling reaction, a facilitated protocol has been used that employs both an Emrys microwave reactor and subsequent purification *via* a Horizon HPFC system. Overall, a 27-membered library has been generated using the above procedure.

90. INVESTIGATING ANION STABILITY IN QUATERNARY AMMONIUM METHYL CARBONATES. **Michael W. Amolins**, Gary W. Earl and Duane E. Weisshaar; Augustana College, Sioux Falls, SD.

Current methods for methylation of tertiary amines use methylating agents such as methyl chloride and dimethyl sulfate (DMS), which are known carcinogens, and cause chronic health problems in industrial workers as well as those in the surrounding communities. An alternative green synthesis was perfected utilizing dimethyl carbonate (DMC) as a methylating agent. Although methylation with DMC requires more stringent conditions (100°C, 100 psi and a 10-fold excess of DMC), the process is industrially viable. Excess DMC and methanol solvent are easily recovered and recycled in subsequent batches. IR and NMR analysis were used to show that the methyl carbonate anion is stable under a variety of conditions, but does break down in the presence of aqueous strong base and most acids.

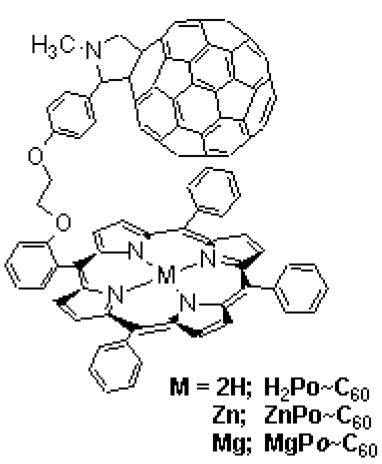
91. INVESTIGATING THE POSSIBILITY OF CHELATION BETWEEN THE OXYGEN ON THE ENYNE AND THE METAL CENTER IN THE WULFF-KAESLER [2+2] CYCLOADDITION. **Kelsie Betsch**[1], Yiqian Lian[2] and William D. Wulff[2]; [1]Augustana College, Sioux Falls, SD; [2]Michigan State University, East Lansing, MI.

It is known that chromium Fischer carbene complexes will react with 1,6-enynes to give products resulting from an intramolecular vinyl-ketene/olefin [2+2] cycloaddition. This reaction is commonly referred to as the Wulff-Kaesler [2+2] cycloaddition. Enynes with two substituents on the remote end of the olefin undergo related crossed [2+2] cycloadditions. In efforts toward the synthesis of Taxol, it was discovered that the stereoselectivity of the crossed [2+2] cycloaddition is dictated by the nature of alkoxy substituents on the enyne. One possible explanation for this selectivity is that there is chelation between the oxygen on the enyne and the metal center of the vinyl ketene intermediate. A set of isomeric enynes differing in the position and size of the alkoxy group were synthesized. Reaction of these enynes with Fischer carbene complexes should provide insight into the mechanism of the Wulff-Kaesler [2+2] cycloaddition.

92. MAGNESIUM PORPHYRIN-FULLERENE DYAD: ELECTRON TRANSFER REACTIONS. **Amy L. McCarty**[1], Suresh Gadde[1], Paul A. Kaar[1], Melvin E. Zandler[1], Osamu Ito[2], Mohamed E. El-Khouly[2], Yasuyaki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan.

Photoinduced charge separation and charge recombination in a newly synthesized, covalently-linked through a flexible ethylene dioxide bridge, magnesium porphyrin-fullerene dyad is investigated and the results have been compared to the earlier reported free-base porphyrin-fullerene and zinc porphyrin-fullerene dyads (Scheme 1). In *o*-dichlorobenzene or benzonitrile containing 0.1 M $(TBA)ClO_4$, the synthesized dyad exhibits six one-electron reversible redox reactions within the potential window of the solvent. The electrochemical HOMO-LUMO gaps were found to depend on the metal ions in the porphyrin cavity and followed the trend:

Scheme 1



$MgPo{\sim}C_{60}$ < $ZnPo{\sim}C_{60}$ < $H_2Po{\sim}C_{60}$. The geometry and electronic structures of the dyad probed using *ab initio* B3LYP/3-21G(*) methods revealed different geometry of the dyad in the presence and absence of axial coordinating pyridine ligands. The excited state emission monitored by both steady-state and time-resolved techniques revealed efficient quench-ing and that the main quenching pathway involves charge-separation from the singlet excited magnesium porphyrin to the C_{60} moiety. The charge recombination rates, k_{cr}, cal-culated from nanosecond transient absorption studies, are found to be three orders of magnitude smaller than the charge separation rates, k_{cs}. The calculated lifetime of the radical ion-pair of $MgPo{\sim}C_{60}$ is found to be up to 520 ns, which is longer than those of $ZnPo{\sim}C_{60}$ and $H_2Po{\sim}C_{60}$ in *o*-dichloro-benzene by factors of 25 – 50, indi-cating formation of relatively long-lived charge separated states in $MgPo{\sim}C_{60}$.

93. METHOXYPOLY(OXYETHYLENE)MALEIMIDES FOR SELECTIVE PROTEIN MODIFICATION. **Mary E. Hansen** and Reza S. Herati; Southwest Missouri State University, Springfield, MO.

Poly(ethylene glycol) (PEG) is widely used as a covalent modifier of biological macromolecules and surfaces as well as for low molecular weight drugs. Conjugation with PEG (PEGylation) gives a protein an impressive set of new properties, including longer circulatory life in the body, but PEGylated proteins also usually exhibit a significant decrease in activity when the mode of attachment to a protein is through amino groups. On the other hand it has been shown that, site-specific attachment of PEG to proteins through cysteine residue results in preservation of biological activity. In this work, we have investigated the Diels-Alder reactions of 3-[methoxypoly(oxyethylene)methylene]furan (1a) with dienophiles such as hexane-1,6-bismaleimide, 1,1'-(methylene-

4,1-phenylene)bismaleimide and N,N'-1,3-phenylenebismaleimide to prepare the corresponding maleimide adducts for selective modification of proteins. We also report rates for the Diels-Alder adduct of 1a and hexane-1,6-bismaleimide with ß-mercaptoethanol, N-acetylcysteine and glutathione. Syntheses and characterizations of the various Diels-Alder adducts made from 1a and the above named bismaleimides and the reactivity of adduct made from 1a and hexane-1,6-bismaleimide with various thiols and N-acetyllysine methyl ester will be presented and discussed.

94. NEW ROUTES FOR ORGANOMETALLIC-MEDIATED SYNTHESIS OF HETEROCYCLIC RING SYSTEMS. **Erik R. Hoefgen** and F. C. Pigge; University of Missouri - St. Louis, St. Louis, MO.

Wadsworth-Emmons, Figure 1, and Bayliss-Hillman type reactions, Figure 2, have both been shown to create effective nucleophiles for intramolecular attack on tethered η^6-arene-ruthenium complexes. Each reaction sequence affords ruthenium-coordinated azaspirocycles. Upon demetalation quaternary spiro-lactams or tetrahydroisoquinolines are obtained, depending on the substituents present on the arene starting material. These materials represent ver-satile building blocks potential-ly useful for the construction of heterocyclic natural products.

Figure 1

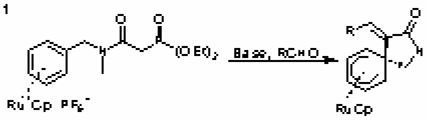
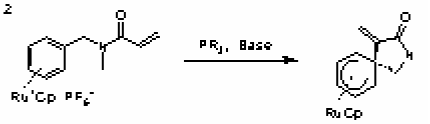


Figure 2



95. OLIGOMER-SUPPORTED BENZYLATING REAGENTS DERIVED FROM ROM POLYMERIZATION. **Mianji Zhang**[1], Joel D. Moore[1], Daniel L. Flynn[2] and Paul R. Hanson[1]; [1]University of Kansas, Lawrence, KS; [2]Deciphera Pharmaceuticals LLC, Lawrence, KS.

Several high-load soluble or insoluble oligomeric benzylating reagents were developed *via* ROM polymerization of norbornenyl–tagged monomers. These oligomers were free-flowing powders, stable at refrigerated temperatures and exploited in the benzylation of various nucleophiles. Oligomeric sulfonate esters were readily dissolved in CH_2Cl_2 and were successfully benzylated with an array of amines. Oligomeric sulfonium salts were also developed and could not only benzylate amines, but also phenols. The ionic liquid $[(b_{mim})PF_6]$ facilitated the second benzylating event and shortened the reaction time. These methods involve solution-phase or solid-phase reactions followed by precipitation/filtration of the reaction by-products to afford pure products in high yield and purity.

96. PHENO-SAFRANIN EPOXY COPOLYMERS. **Kiesha William** and Gerald Caple; University of South Dakota, Vermillion, SD.

Polyaniline has been used as a corrosion inhibitor in several different ways. Protonated polyaniline has the best properties, but this is a reversible process and polyaniline can easily lose some of its effectiveness. In our labs we have been studying the co-polymers of short polyaniline segments when polymerized with the di-epoxide DER-330. Pheno-Safranin is a compound produced from aniline and *p*-phenylenediame by a different oxidation process than we used to prepare the polyaniline segments. It has two free amino groups and has a permanent charge in it as a quatenary chloride salt. Here we report our initial studies on preparing a co-polymer of pheno-safranin and the di-epoxide DER-330. Initial studies were done in anhydrous DMSO which produced gels. These gels had a high electrical resistance and could be dried to form films on surfaces. Cyclic voltametry showed reduction of the film was an irreversible process. Preliminary studies on the oxidation potential change on iron coated with one of these co-polymers indicates potential corrosion inhibition.

97. PHOSPHATE TETHERS IN CONSTRUCTION OF ADVANCED POLYOL SUBUNITS. **William M. Sherril**[1], Joshua D. Waetzig[2] and Paul R. Hanson[2]; [1]College of the Ozarks, Point Lookout, MO; [2]University of Kansas, Lawrence, KS.

The desymmetrization of 1,3-anti-diols is achieved through the use of phosphate tethers and ring-closing metathesis (RCM). Upon removal of the phosphate tether, polyol subunits are obtained. Initial efforts toward the total synthesis of tetranactin, a potent cytotoxic natural product isolated from the fungus *Steptomyces aureus*, are reported. This natural product displays meso-symmetry and is comprised of four asymmetric monomeric subunits. Final transformation of each subunit and subsequent coupling are underway en route to the total synthesis of tetranactin.

98. PREPARATION AND PROPERTIES OF FATTY ACID-BASED POLYOLS AND POLYURETHANES. **Wei Zhang,** Zoran Petrovic, Mile Lukic and William Shirley; Pittsburg State University, Pittsburg, KS.

Soybean oil-based polyols are very valuable materials for polyurethanes. The soybean oil based polyols and the polyols-based polyurethanes have a number of perfect properties. However, the soybean oil-based polyols display relatively high viscosity due to the triglyceride structure. One possible way to decrease the viscosity is to split the triglyceride structure of soybean oil-based polyols and convert them to fatty acid-based polyols. In this study, the soybean oil-based polyols were hydrolyzed with methanol to obtain the methyl ester of fatty acids and the methyl ester of fatty acids was then transesterified with ethylene glycol to form the fatty acid-based polyols. Obtained fatty acid-based polyols were systemically analyzed. The polyurethanes based on the fatty acid-based polyols were prepared with pure MDI and polymeric MDI and the properties of the polyurethanes were tested and measured. The comparison of properties between the polyurethanes based on soybean oil-based polyols and fatty acid-based polyols was studied as well.

99. PREPARATION OF 9-(1-NITROALKYL)ACRIDINES. **Josh Taylor**[1], Melvyn W. Mosher[1] and Michael D. Mosher[2]; [1]Missouri Southern State University, Joplin, MO; [2]University of Nebraska at Kearney, Kearney, NE.

Due to our interest in the synthesis of substituted 9-hydroxyl-aminoacridines as possible antitumor agents, we have studied alternative synthetic pathways to these compounds instead of through the reaction of 9-chloroacridine with substituted hydroxylamines. One of these alternate routes to our desired compounds is from the corresponding 9-(1-nitroalkyl)acridans. The reaction of acridine with nitroalkanes in ethanol solution affords good yields of the desired 9-(1-nitroalkyl)acridans by the addition of the nitroalkane across the 9,10 position of the acridine. Mild oxidation of the acridans with lead tetraacetate gives the 9-(1-nitroalkyl)acridines. The products, yields and physical properties of the reaction products of acridine with nitroalkanes and other active methylene compounds will be presented.

100. PROGRESS TOWARDS THE SYNTHESIS OF A CLIP FOR THE BINDING OF HYDROQUINONE. **Ellen Matson**, Brian Fleharty and Somnath Sarkar; Central Missouri State University, Warrensburg, MO.

Molecular clips are noncyclic compounds which may be used as synthetic receptors to bind a neutral or ionic guest. Progress toward the synthesis of a clip for the binding of hydroquinone, a molecule of biological importance, will be described. The clip used 1,4-dioxo benzene, derived from hydroquinone, as a spacer to hold two benzophenone binding units at an optimum distance. It was expected that (1) a binding site similar in size to the guest molecule would provide an optimal space and (2) use of a rigid spacer would provide a more effective clip. A Grignard reaction of benzaldehyde and 3-bromotoluene produced 3-methylbenzhydrol, which was oxidized by Silica Gel-supported Jones Oxidation to yield 3-methylbenzophenone. The methyl group was brominated in the third step to give 3-bromomethyl benzophenone. Model substitution reactions of hydroquinone were performed with commercially available benzyl bromide, which provided 1,4-dibenzyloxybenzene in moderate yield. In the reaction of hydroquinone with 2-bromomethyl naphthalene (prepared from commercially available methylnaphthalene), formation of the naphthalene clip in low yield was evidenced in preliminary proton NMR spectrum. The experiments, thus far, suggest that the reaction condition used to carry out the two model reactions could be suitable to prepare the benzophenone clip.

101. REGIOSELECTIVITY OF REACTIONS INVOLVING APIGENIN. **Eric Trump**[1] and Gunda Georg[2]; [1]Emporia State University, Emporia, KS; [2]University of Kansas, Lawrence, KS.

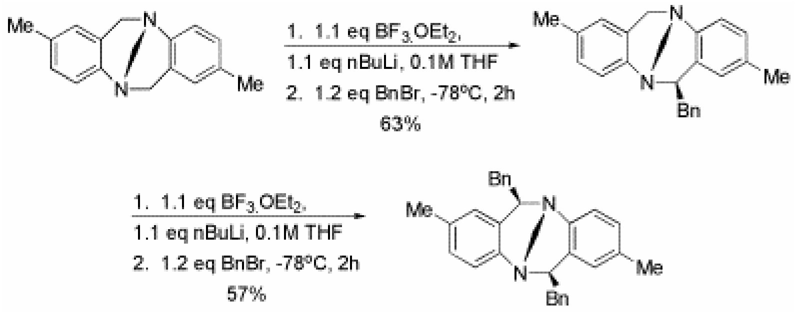
The flavone apigenin is a natural product that has shown promise in cancer prevention. Apigenin contains three phenolic groups of differing reactivities. Apigenin underwent esterifications first with one equivalent and then with two equivalents of various acyl chlorides. Similarly, a series of carbonate monoesters (a single isomer of each) and diesters were prepared from one and two equivalents of equivalents of the corresponding chlorofomates, respectively. Finally, the reaction of peracetylated glucopyranosyl bromide with apigenin was completely regioselective, yielding a single isomer of glucopyranosyl apigenin.

102. REINVESTIGATION OF THE ACI-NITRO/NITROALKANE TAUTOMERIZATION. **Douglas Miller** and Melvyn W. Mosher; Missouri Southern State University, Joplin, MO.

The aci-nitro-nitroalkane tautermization has been reinvestigated using the method of NMR spectroscopy. This tautomerization has been reported in the literature to be important and the aci-nitroalkane form of nitromethane has been estimated at over 10%. Based upon these NMR studies, this tautermization is much less important and the aci-nitoalkane constitutes less than 1% for nitromethane.

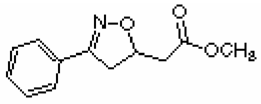
103. SEQUENTIAL ALKYLATION OF TRÖGER'S BASE. AN APPROACH TO NEW CHIRAL LIGANDS. Michael Harmata and **Kanok-On Rayanil**; University of Missouri-Columbia, Columbia, MO.

The sequential alkylation of Tröger's base has been carried out in a regio- and stereoselective fashion. Complexation of Tröger's base with boron trifluoride followed by reaction with an alkyllithium reagent produced a species that could be alkylated with complete stereoselectivity. This process could be repeated to afforded analogues of Tröger's base in which both methylene groups had been alkylated. The development of this methodology and future prospects for the use of the method as a route to chiral ligands will be presented.


Me
Me
N
N
1. 1.1 eq BF3.OEt2,
1.1 eq nBuLi, 0.1M THF
2. 1.2 eq BnBr, -78ºC, 2h
63%
Bn
1. 1.1 eq BF3.OEt2,
1.1 eq nBuLi, 0.1M THF
2. 1.2 eq BnBr, -78ºC, 2h
57%
Bn
Bn

104. SPECTROSCOPY OF 3,5-DISUBSTITUTED ISOXAZOLINES. **Laura G. Emmerich**, Katherine S. Frost and Michael D. Mosher; University of Nebraska at Kearney, Kearney, NE.

Spectroscopic analysis, using high-field NMR techniques, of 3,5-disubstituted isoxazolines has provided insight into their three-dimensional structure. The effects of substitution at C-5 of the isoxazoline ring can be observed as chemical shift changes for the remaining atoms. These shifts, and their associated coupling constants, translate into conformational changes in the average structure of the molecule. Specific chemical shifts, confor-mational analysis and complete correlations for these isoxazolines will be reported.



105 STUDIES DIRECTED TOWARD DIMERIZATION OF LITHOCHOLIC ESTER DERIVATIVES USING GRUBB'S REAGENT. **Christopher G. Dallstream** and Jerry R. Dias; University of Missouri-Kansas City, Kansas City, MO.

The bile acids, such as lithocholic acid, have been well documented in their binding properties with other components. Their unique features in terms of chirality, rigid framework and chemically-different hydroxyl groups have made them components for supramolecular chemistry. Therefore, with the recently gained prominence olefin metathesis in synthetic organic chemistry, there is an interest in the development of selective cross-metathesis of olefins using Grubb's reagent. With the high activity of the ruthenium-based catalyst we decided to investigate potential applications in cross-metathesis. We are first to report herein, to our knowledge, the addition of unsaturated acids to the methyl ester, and cross-metathesis between terminal olefins to generate a linear bile acid dimer (head to head).

106. SYNTHESIS AND CHARACTERIZATION OF POLYMER NETWORKS *VIA* HYDROSILYLATION OF TRIGLYCERIDES. **Alisa Zlatanic** and Zoran Petrovic; Pittsburg State University, Pittsburg, KS.

Two types of polymer networks were successfully prepared reacting silicon hydride species with double bonds of triglycerides. Unsaturated substrates used were 1) high-oleic safflower oil modified by metathesis reaction containing both terminal and internal double bonds, and 2) soybean oil of RBD grade. As a crosslinker, tetrakis(dimethylsiloxy)silane bearing four Si-H groups per molecule was used. Hydrosilylation reaction was catalyzed by Karstedt's catalyst: bis(divinyltetramethyldisiloxane)Pto in vinylsilicone (PtO $[(CH_2{=}CH(Me)_2Si)_2O]_{1.5}$). A molar ratio of silicon hydride to double bonds varied from the typical 2 to 1 to 0.5 to 1 in order to obtain polymer networks of different crosslinking densities. The thermal and oxidative stability of polymer networks was tested by thermogravimetry. In inert atmosphere (N_2), degradation occurred at 4400C, while in the presence of oxygen, networks degraded at a 200C lower temperature. The temperature of glass transition, determined by the use of a differential scanning calorimetry (DSC), varied from -56 to -420C for networks based on soy oil. All hydrosilylation networks were very brittle, pointing at very short network chains and the need to either further decrease the fraction of crosslinker in the formulation or to use a different crosslinker of lower silicon hydride functionality, preferably 2.

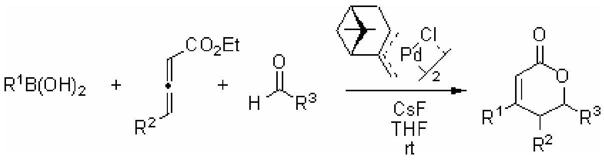
107. SYNTHESIS OF α,β-UNSATURATED-δ-LACTONES *VIA* PALLADIUM-CATALYZED COUPLING OF ALLENYL ESTERS, BORONIC ACIDS AND ALDEHYDES. **Chad D. Hopkins**[1], Lisa Guan[2] and Helena C. Malinakova[1]; [1]University of Kansas, Lawrence, KS; [2]Independence Community College, Independence, KS.

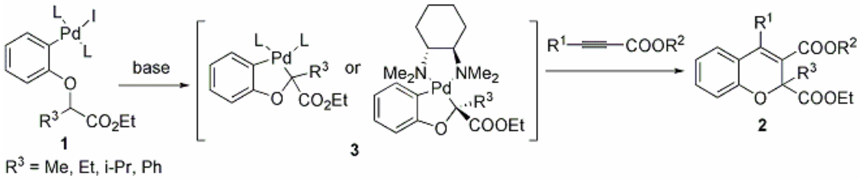
Development of new modular and convergent synthetic methodologies constitutes an important goal of modern synthetic chemistry. Transition metal-catalyzed multi-component coupling reactions emerged as a particularly valuable synthetic tool. Recently, we have described a new palladium-catalyzed three-component coupling reaction between boronic acids, allenes and aldehydes providing highly substituted branched homoallylic alcohols. The reaction is catalyzed by a β-pinene-derived allylpalladium(II) dimer (10 mol% Pd) and the process is believed to involve an unsymmetrical bis-π-allylpalladium intermediate that operates as a nucleophilic allyl-transfer reagent. Our recent studies revealed that the use of allenyl esters resulted in the reversal of the allylation regiochemistry, providing γ, β-unsaturated-δ-lactones. Herein we describe the synthesis of structurally diverse lactones including the optimization of the catalyst load, reaction yield and the scope and limitation studies. Experiments aimed at clarifying the mechanistic reasons for the divergent regioselectivity as well as approaches to asymmetric syn-thesis of lactones will be presented.

108. SYNTHESIS OF 2,2,3,4-TETRASUBSTITUTED ^{2}H-1-BENZOPYRANS *VIA* A PALLADIUM-MEDIATED ANNULATION OF UNSYMMETRICAL ALKYNES.

Genliang Lu, John C. Hershberger and Helena C. Malinakova; University of Kansas, Lawrence, KS.

Palladium-catalyzed annulation reactions of alkynes involving an attack of internal nucleophiles on organopalladium intermediates provide a powerful tool for the synthesis of heterocycles. However, the protocols remain limited to the use of heteroatoms or highly stabilized malonate carbanions as nucleophiles. We have been exploring the possibility to incorporate sp^3-hybridized tertiary palladium-bonded stereogenic carbons into the heterocyclic products exploiting novel palladacycles as intermediates. Herein we report the preparation of racemic highly-substituted benzopyrans **2** by a regiocontrolled reaction of stable organopalladium complexes **1** with unsymmetrical alkynes. The steric hindrance arising from the attachment of tertiary carbons to palladium in the *in situ* generated palladacycles **3** required a systematic optimization of the auxiliary ligands L. Approaches to asymmetric synthesis of benzopyrans **2** relying on the asymmetry transfer from chiral nonracemic diamine ligands will also be described.





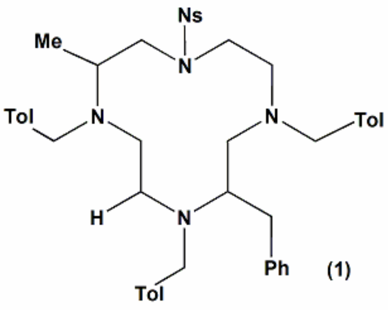
R^3 = Me, Et, i-Pr, Ph

L = PPh_3, PPh_2Me, $PPhMe_2$, PMe_3

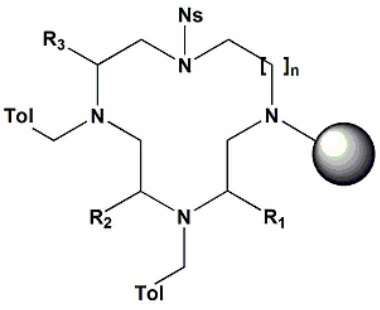
109. SYNTHESIS OF A TETRAAZAMACROCYCLE FOR A HYDRODEHALOGENATION CATALYST.

James A. Townsend, Christopher Culbertson and Stefan Kraft; Kansas State University, Manhattan, KS.

Nickel(I)-tetraazamacrocycles constitute an important class of hydrodehalogenation catalysts. Studies on structure-activity relationships of these catalysts are rare mainly due to impediments in the synthesis of larger ligand libraries. The synthesis of ligand **1** as a general template for the solid phase synthesis of tetraazamacrocycles will be discussed. Synthesis is accomplished through a series of amide bond formations and reductions to form straight chain polyamines. Ring formation via the Mitsunobu reaction is the key step of the sequence.



(1)



n= 1 or 2

R1=R2=R3= Peptide group side chain

110. SYNTHESIS OF ARYL ETHERS THROUGH THE THERMAL DECOMPOSITION OF ARYLDIAZONIUM TETRAFLUOROBORATE SALTS.

James A. Shriver and Daniel P. Flaherty; Central College, Pella, IA.

The synthesis of aryl ethers is commonly achieved through the O-alkylation of various phenols with alkyl halides. However, synthesis of the parent phenols as well as the alkyl halides can often be difficult to achieve and time consuming. Our research is geared towards making this connection in a single step through a diazonium tetrafluoroborate salt. While aryldiazonium salts are typically used for copper-mediated free-radical-type reactions such as the Sandmeyer reaction, it is also known that they can thermally decompose to form, what is suggested, as an aryl cation. Building upon this, reaction of this proposed cation with even weakly nucleophilic species such as alcohols should lead to the targeted product. Early results indicate that the reaction does indeed occur with yields ranging from 30-55% for the parent benzenediazonium tetrafluoroborate salt under optimized conditions in neat alcoholic solvent. Reactions carried out in other solvents as opposed to neat alcohol give rise to intriguing side products where typically “non-nucleophilic” solvents react with aryldiazonium salt leading to some interesting side products. More complex benzenediazonium salts also react to give the desired product in various yields depending on the nature of the substrate. However, in these cases, we also isolate other side products that lead insight into why moderate yields are seen for the parent compound. While this process is general, careful control of the reaction must be established to inhibit formation of these other products. We are continuing to explore the electronic and steric effects of this system as well as looking toward reaction of this system with atypical nucleophiles.

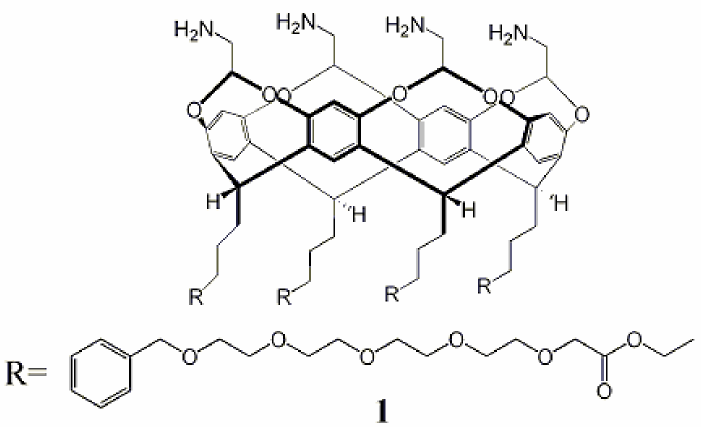
111. SYNTHESIS OF GLYCOSIDE AND THIOGLYCOSIDE DENDRIMERS AND EVALUATION AS METAL CHELATORS. **Michael J. Panigot**, Mark Draganjac, Audra Bowman, Randi Sebourn, Justin Yancey, Angela Buckman, Andrea Hausman and Bryanna Lies; Arkansas State University, State University, AR.

This project involves the preparation of glycoside and thioglycoside containing dendrimers. These compounds may be useful in removing heavy metals in the environment, such as lead-based paint and those found in tobacco. The carbohydrate provides water solubility and possibly biological recognition. The synthetic goal is the first generation dendri-mer. It can be prepared by reaction of 1,3,5-tristhiomethylbenzene with a carbohydrate peracetate in the presence of BF_3 etherate. 1,3,5-Tristhio-methylbenzene can be prepared from benzylic bromination of mesitylene and reaction of the tribromide with thiourea followed by base hydrolysis. After formation of the thioglycoside, hydrolysis of the acetate groups will provide the desired product. Additionally the glycosides of phloroglucinol and possibly 1,3,5-tris(hydroxymethyl)benzene will be prepared from the glycosyl halide *via* Koenigs-Knorr synthesis. The ability of these com-pounds to act as metal chelators will also be investigated.

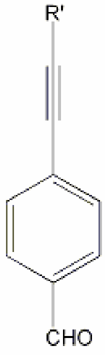
112. SYNTHESIS OF NOVEL WATER SOLUBLE CAVITANT.

Xiaoxuan Liu and Stefan Kraft; Kansas State University, Manhattan, KS.

In an effort to study water-soluble resorcarene receptors that are able to bind rod-like guests, we have recently embarked on the synthesis of glyme-substituted resorcarene **1**. Preliminary studies of dynamic combinatorial libraries containing **1**, suitable aldehydes **2** and steroid guests will be presented.



1



2

113. SYNTHESIS OF ORGANIC THIOSULFATES TAILORED FOR THE ELECTROCHEMICAL DEPOSITION OF “SELF-ASSEMBLED MONOLAYERS” AT GOLD SURFACES.

Stefan H. Bossmann[1], Eliso Gogritchiani[2], Sandra Niebler[2], Michael Woerner[2] and Andre M. Braun[2]; [1]Kansas State University, Manhattan, KS; [2]University of Karlsruhe, Karlsruhe, Germany.

The reconstitution of various channel proteins within artificially generated mono- and bilayers is of greatly increasing importance in the strongly growing field of bioelectronics. Typical goals of these investigations are the design of functional nanostructured electrodes and the creation of porin transport assays. The art of biomimicry is of special importance for these applications because the natural biophysical properties of the hosting membrane systems have to be mimicked in order to facilitate a successful application of pore-forming proteins. The synthesis of very long-chained organic thiosulfates was accomplished in order to design artificial monolayers, which are suitable hosts of the channel porin isolated from *Mycobacterium smegmatis* (MspA). MspA forms the longest hydrophilic protein channel known to date (length: 10 nm, diameter: 3 nm). Its natural environment is the outer mycobacterial membrane of *Mycobacterium smegmatis*. It should be noted that the mycolic acids (> C90), which are responsible for the biophysical properties of this extremely thick and hydrophobic membrane, are chemically linked to the biopolymer arabinogalactane, which is situated underneath the outer mycolic acid membrane. The synthesis of organic thiosulfates started from 3-(4-hydroxy-phenyl)-acrylic acid-methylester, decane-1,10-diol and 1,10-dibromo-decane. A combination of nucleophilic substitutions led to the synthesis of 3-[4-(10-bromo-decyloxy)-phenyl]-acrylic acid-methyl-ester and its homologous w-bromo-"surfactants". Their only difference in structure is their number of decyloxy-groups within the surfactant's linear chain (n=1,3,7). The introduction of the organic thiosulfate-group can also be achieved by nucleophilic substitution employing sodium thiosulfate ($Na_2S_3O_3$) as nucleophilic reagent. Finally, the methyl ester protection group was removed by basic hydrolysis. These so-called "Bunte-salts" are versatile reagents for the electro-oxidative deposition of very long-chain monolayers on gold-surfaces which allow the subsequent reconsti-tution of MspA. To achieve this goal, a complete coverage of the gold-surface must be avoided. Otherwise the covered surface becomes repulsive for the channel protein.

114. SYNTHETIC EFFORTS TOWARD CYCLIPOSTINS AND THEIR ANALOGS. **Maria del Sol Jimenez**, Kevin Poon, Shubhasish Mukherjee and Paul R. Hanson; University of Kansas, Lawrence, KS.

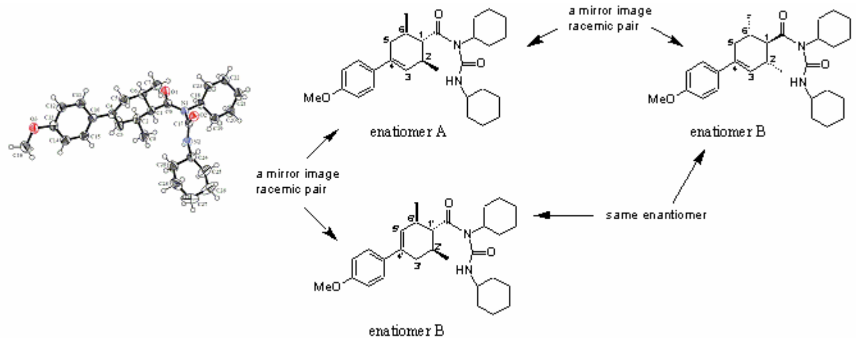
Efforts focusing on the development of synthetic routes toward the diastereoselective synthesis of cyclipostins and their analogs are reported. An approach involving the use of rhodium (II)-mediated intramolecular C-H insertion to obtain a γ-lactone advanced intermediate is described. The cyclipostins are a novel class of natural products that were isolated from cultures of *Streptomyces sp.* These compounds are phosphorus heterocycles that possess inhibitory activity against hormone-sensitive lipase (HSL), with IC_{50} in the nanomolar range. Their mechanism of action is unknown.

115. SYNTHETIC ROUTES TO DIVERSE CYCLIC SULFAMIDES. **Jung Ho Jun**, Maria del Sol Jiménez, Paul R. Hanson and Johnathan Evans; University of Kansas, Lawrence, KS.

Synthetic routes to a diverse set of cyclic N-hydroxy sulfamides and sulfamoyl carbamates are reported. These routes rely on pathways employing ring-closing metathesis, Mitsunobu alkylation and EDC coupling to achieve the synthesis of the target S-heterocylic compounds. Diversity is obtained on the periphery of the cyclic sulfamide scaffold by applying several *alpha*-hydroxy acids and amino acids in both the Mitsunobu alkylation and EDC coupling steps, respectively.

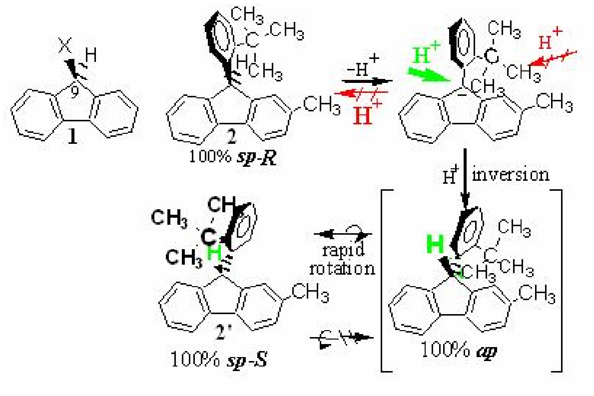
116. UNUSUAL ENANTIOMERS THAT DIFFER ONLY IN THE POSITION OF THEIR DOUBLE BOND AND WHOSE CRYSTALLINE FORMS APPEAR TO BE SUPERIMPOSED ONTO EACH OTHER. **Songwen Xie**, Cal Y. Meyers and Paul D. Robinson; [1]Southern Illinois University, Carbondale, IL.

During the resolution of our small estrogenic cyclohexenecarboxylic acids, a carbonyl urea by-product was made. Its X-ray crystal structure indicated larger than normal thermal displacements for several atoms and the 3-cyclohexene ring also exhibited a shorter than normal C4-C5 bond length. These combined observations suggested a superimposition of the two enantiomers, one having the double bond at C3-C4 and the other at C4'-C5'. The X-ray instrument could not resolve the two structures and showed an average bond length between carbons 3, 4 and 5. Such superimposition and unresolved structure is indeed unusual. The chirality of this compound is engendered solely by the presence of the double bond; a simple “1-2 shift” of the double bond is tantamount to inversion. This phenomenon applies to linear as well as cyclic systems. We intend to expand our studies of this type of asymmetry.



117. WHEN ARE EXPERIMENTALLY DETERMINED pK_a VALUES NOT "REAL pK_a" VALUES? **Aaron W. McLean**[1], Cal Y. Meyers[1], Yuqing Hou[1] and Paul D. Robinson[2]; [1]Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry; Southern Illinois University Carbondale, Carbondale, IL; [2]Southern Illinois University Carbondale, Carbondale, IL.

Our earlier studies of fluorenes having a 9-X substituent (**1**) indicated that their respective pK_a values (for 9-H, determined in the standard way in DMSO, 25°C) were quite unexpected in several instances and did not reflect the "standard" σ_I or σ_R values reported for the X substituents, relative to $\sigma = 0$ for X = H. For example, the pK_a of **1** when X = phenyl is **17.9**, when X = *o*-methylphenyl, it is **18.8**, when X = 2,4,6-trimethylphenyl, it is **18.6** and the pK_a when X = *o-tert*-butylphenyl, is **20.2**. Since the σ_I values for these substituents in the these acidity determinations are virtually the same, *i.e. 0.10*, why is the *ortho-tert*-butylphenyl compound *140-times* **less acidic** than the simple *ortho*-methylphenyl analog? Our recent study of the stereochemistry of deprotonation-reprotonation of optically active **2** provides the answer.



118. KIRKWOOD-BUFF DERIVED FORCE FIELD FOR AMIDES.

Myungshim Kang and Paul E. Smith; Kansas State University, Manhattan, KS.

A force field for the computer simulation of aqueous solutions of amides is presented. The force field is designed to reproduce the experimentally-observed density and Kirkwood-Buff integrals for N-methylacetamide (NMA), allowing for an accurate description of the NMA activity. Other properties such as the diffusion constants and heat of mixing are also well reproduced. The force field is extended to include N,N'-dimethylacetamide and acetamide with good success. The model provides a basis for an accurate force field for peptides and proteins.

119. *AB INITIO* STUDIES OF THE ALKYLATION OF BENZENE.

Dustin S. Hillman, Shenmin Li and Ward H. Thompson; University of Kansas, Lawrence, KS.

We have studied the Friedel-Crafts alkylation of methyl chloride with benzene to investigate the mechanism, the role of an aluminum chloride catalyst and solvent effects. The pathways between products and reactants are examined considering both a single, concerted transition state and a complex, multi-transition state route. *Ab initio* calculations at the HF/6-31G* level were used for optimization and frequency calculations of the local minima and transition states; MP2/6-31G* calculations of the single point energies at the transition states were carried out following intrinsic reaction coordinate calculations. The energies obtained in these *ab initio* calculations show high reaction barriers in the absence of a catalyst. Equilibrium solvent effects lower the energy barriers significantly.

120. ANGULAR DEPENDENCE OF SINGLE IONIZATION OF HYDROGEN MOLECULES BY PROTON IMPACT. **Nora G. Johnson**[1], K. D. Carnes[2], Heather D. Baxter[1], I. Ben-Itzhak[2] and E. Wells[1]; [1]Augustana College, Sioux Falls, SD; [2]Kansas State University, Manhattan, KS.

A cold beam of hydrogen molecules was ionized by 4 MeV protons. A small fraction of the single ionization events reaches the vibrational continuum of the electronic ground state of H_2^+. A three-dimensional momentum imaging technique allows isolation of these ground-state dissociation fragments and determination of the molecular orientation at the time of the collision. There are at least three different, contradictory theoretical predictions for the angular distribution of the fragments relative to the ion beam. Our preliminary results show a relatively isotropic angular dependence for the single ionization cross-section.

This work was supported by the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy. N. G. J., H. D. B. and E. W. received additional support *via* the NASA/South Dakota Space Grant Consortium through Cooperative Agreement NGT5-40095 and the Augustana Research/Artist Fund.

121. CHARACTERIZATION OF ISOCYANOAZULENE SELF-ASSEMBLED MONOLAYERS ON GOLD. **David R. Moody**[1], Cindy L. Berrie[2], Mikhail V. Barybin[2], Randall Robinson[2] and Edward Weintrob[2]; [1]Creighton University, Omaha, NE; [2]University of Kansas, Lawrence, KS.

Self-assembled monolayers (SAMs) of various isocyanoazulene molecules on gold substrates have been successfully prepared. These SAMs were characterized by FT-IR and contact angle measurement techniques. Using these techniques it has been shown that isocyanoazulene will bond to gold and form monolayers. FT-IR grazing angle spectroscopy of most isocyanoazulene SAMs absorb in the infrared at expected frequencies of C-N bonded to gold stretching at around 2170 wavenumbers. When deposited from dichloromethane, 2,6-diisocyano-1,3-ethylesterazulene exhibits two distinct bands in the IR which appear at around 2163 and 2117 wavenumbers. However, when deposited from ethanol, the bands shift to around 2100 and 2120 wavenumbers which may indicate physisorption or polymerization of the molecules. The structure and packing of these monolayers will be further investigated using AFM and ellipsometry.

122. DERIVATIVES OF THE POLARIZATION PROPAGATOR INCLUDING ORBITAL RELAXATION EFFECTS.

Edmund L. Tisko[1] and Katharine C. Hunt[2]; [1]University of Nebraska at Omaha, Omaha, NE; [2]Michigan State University, East Lansing, MI.

In this note, we relate derivatives of the polarization propagator $\Pi_{ij}^{kl}(\omega)$ used in many-body theory to the nonlinear polarization propagator $\Pi_{ijk}^{\ell mn}(\omega_1,\omega_2)$, and we relate derivatives of $\Pi_{ijk}^{\ell mn}(\omega_1,\omega_2)$ to the nonlinear propagator of the next higher order $\Pi_{ijk\ell}^{mnpq}(\omega_1,\omega_2,\omega_3)$. We restrict the analysis to differentiation with respect to parameters η for which the derivative of the Hamiltonian $\partial H/\partial\eta$ can be written as a sum of one-electron operators. Geometrical derivatives are obtained by specializing to $\eta = R_\alpha^I$, the α coordinate of nucleus I. We treat orbital relaxation explicitly, by allowing for the η-dependence of creation and annihilation operators in $\Pi_{ij}^{kl}(\omega)$ and in the nonlinear polarization propagators. This treatment entails an extension of the geometrical derivative relations among response functions proven by Olsen and Jørgensen, because the propagator derivatives may involve changes in the one-electron orbitals that do not appear in the susceptibility derivatives. These results underlie the relations between Raman intensities and electric-field shielding tensors, which we have explained in terms of nonlocal polarizability and hyperpolarizability densities. The results suggest an alternative computational route to geometrical or other derivatives of both linear and nonlinear response functions: these derivatives can be evaluated without numerical differentiation, directly from the propagator of the next higher order.

123. FLUORESCENCE MICROSCOPY INVESTIGATION OF PHOSPHOLIPID/SPHINGOMYELIN/CHOLESTEROL DERIVATIVES IN MIXED LANGMUIR MONOLAYERS. **Rose Rowden** and Alexa B. Serfis; Saint Louis University, St. Louis, MO.

Cholesterol and sphingolipids form ordered domains in membranes while cholesterol incorporation allows for tight packing of membrane lipids. These membrane “rafts” participate in numerous biochemical processes including membrane transport and cell signaling. It has been reported that dehydrocholesterol promotes raft formation as well as cholesterol in natural membrane systems, while its role in the Smith-Lemli-Opitz syndrome (SLOS) remains unclear. This work investigates how cholesterol derivatives promote raft formation. Langmuir monolayers were used as model membranes to study phospholipids (PC), desmosterol (DES), dehydrocholesterol (DHC) and sphingomyelin (SM) packing. With the aid of fluorescence microscopy, the interactions among the lipids and sterols in binary and ternary mixtures were studied. Cholesterol and desmosterol promoted phase separation and domain formation in PC and SM monolayers. DHC did not promote domain formation in lipid monolayers to the same extent. This may have important implications for raft formation in natural membranes and in the occurrence of SLOS.

124. *IN SITU* NMR OF COMBUSTION USING OPTICALLY PUMPED ^{129}Xe. **Rachel L. Parris**[1] and Thomas Meersmann[2]; [1]Emporia State University, Emporia, KS; [2]Colorado State University, Fort Collins, CO.

The primary goal is the *in situ* study of a catalyzed combustion process using a PdO catalyst. By using hyperpolarized ^{129}Xe, images of gas flow, gas concentration and gas diffusion may be taken of the catalyst under *in situ* conditions. The reason for using optically pumped ^{129}Xe is that it is a good probe of void space.

This all has potential application as an analytical tool for the determination of the gas flow, dynamics and temperature distribution of catalyzed reactions within an opaque media, which would be difficult to investigate by other techniques.

125. INVESTIGATIONS OF THE CONDUCTIVITY OF ORGANIC THIN FILMS USING CONDUCTIVE ATOMIC FORCE MICROSCOPY.

David Du Bose, Cindy Berrie and Cornelius Kristalyn; University of Kansas, Lawrence, KS.

Conductive atomic force microscopy (CAFM) and scanning tunneling microscopy (STM) studies have been performed on self-assembled monolayers of conjugated thiols to investigate electron transport mechanisms in these films. Monolayers of 4-aminothiophenol and subsequent adlayers of terephthaldicaboxaldehyde and 1,4- phenylene-diamine have been deposited on gold substrates and characterized using contact angle, AFM, ellipsometry and Fourier transform infrared spectroscopy. Conductive AFM has been used to make measurements of the current versus voltage (I-V curves). The shape of these I-V curves provides insight into the conductivity of the molecules as well as the mechanism of charge transport in these films.

126. MOLECULAR DYNAMICS OF LIQUID CLUSTERS: METHODS AND RESULTS.

John M. Schneiderman and Brian G. Moore; Augustana College, Sioux Falls, SD.

We have used molecular dynamics to study the liquid state of small ($N \approx$ 30-500 atom) atomic clusters, specifically with interactions defined by a pair-wise Lennard-Jones potential energy. We present results for several structural measures, including the familiar radial distribution function and new measures such as the radial potential energy histogram. This histogram is distinctly bimodal, reflecting the two qualitatively different regions--surface and bulk. We have also developed an object-oriented approach to the simulations, using C++. To this end several classes were developed; for example, an atom class and a cluster class. A graphical user interface was also developed to display the atoms while the simulation is in progress.

127. MONTE CARLO SIMULATION OF ABSORPTION AND FLUORES-CENCE SPECTRA AND TWO-DIMENSIONAL FREE-ENERGY CALCULATIONS IN NANO-CONFINED SOLVENTS.

J. A. Gomez and Ward H. Thompson; University of Kansas, Lawrence, KS.

We have simulated the absorption and fluorescence spectra of a model solute molecule (AB) with a charge-transfer electronic transition dissolved in CH_3I confined solvent. The calculations of two-dimensional free energy surfaces have been performed as a function of the coordinates of the solute molecule. Solutions are confined in smooth hydrophobic spherical and ellipsoidal cavities of varying sizes. Monte Carlo simulations have also been performed for a 1,2-dichloroethane molecule dissolved in methanol solvent confined in spherical cavities. Free energy surfaces for 1,2-dichloroethane molecule are calculated as a function of the radial position of the center of mass and the CH_3-Cl-Cl-CH_3 dihedral angle. For the calculation of two-dimensional free energy surface of solute molecules, the umbrella sampling approach combined with the weighted histogram analysis methods (WHAM) has been employed. We also present the solute and solvent probability density distributions for interpreting the spectra. In order to study the effect on the solvent properties due to roughness on cavity wall one shell atomic cavity with approximate spherical symmetry has also been modeled.

128. NANOARRAY-SURFACES BY RECONSTITUTION OF THE MSPA PORIN INTO STABILIZED LONG-CHAIN-LIPID-MONOLAYERS AT A GOLD-SURFACE.

Stefan H. Bossmann[1], Katharine E. Janik[1], Sandra Niebler[2], Eliso Gogritchiani[2], Michael Woerner[2], Andre M. Braun[2] and Michael Niederweis[3]; [1]Kansas State University, Manhattan, KS; [2]University of Karlsruhe, Karlsruhe, Germany; [3]University of Erlangen-Nürnberg, Erlangen, Germany.

A novel electrochemical method for the oxidative deposition of organic thiosulfates on (polycrystalline) gold-layers was developed. In contrast to the classic thermal methods of SAM deposition on gold, this unusual electrochemical method permits, for the first time, the deposition of specific amounts of “surfactants” on the electrode's surface. These “surfactants”, which belong to the group of organic thiosulfates (Bunte-salts), were synthesized by a “molecular LEGO” - approach. This synthetic strategy allows the preparation of variable chain lengths ranging from 2 to 10 nm as well as the deposition of highly dense “organic islands” on gold, without the necessity of a complete surface coverage. These (partially covered) polycrystalline gold electrodes and the kinetics of electro-initiated surfactant deposition were studied by cyclic voltammography and electrical impedance spectroscopy (EIS).

Complementary REM-measurements, combined with computer-aided image analysis (IMAGE/NIH) confirmed the existence of heterogeneously-covered polycrystalline gold surfaces. These surfaces can be especially designed to host channel-forming proteins (porins), which naturally reconstitute in monolayer-type outer cell membranes of *Mycobacteria*. The value of this novel concept was proven by the reconstitution of the channel porin isolated from *Mycobacterium smegmatis* (MspA). This process of reconstitution produced distinct porin channels possessing defined nanospaces at the bottom of the goblet-like porin structures allowing access of bulk-electrolyte. The presence of these distinct structures was verified using a combination of the various analytical methods described above.

129. ULTRAFAST MODE-SELECTIVE STUDIES OF INTRAMOLECULAR ENERGY TRANSFER. Abhijit Chakraborty, Benjamin D. Prince, Beth M. Denk and **Hans U. Stauffer**; Iowa State University, Ames, IA.

The inevitable process of intramolecular vibrational energy redistribution (IVR) has long presented a challenge to the selective and exclusive excitation of vibrational motions in even small isolated molecular systems. As part of an experimental effort directed toward the use of controlled coherent excitation to direct vibrational energy flow in gas phase and condensed phase systems, we describe experiments using frequency- and time-resolved coherent anti-Stokes Raman scattering (CARS) as probes of frequencies in the ‘fingerprint' region of the vibrational spectrum (800 – 1800 cm^{-1}). Following initial excitation of selected vibrational overtones (*e.g.*, two quanta of C H stretch in pyridine or toluene) with ultrafast pulses, this type of probe allows, on an ultrafast (<100 fs) timescale, observation of the flow of vibrational excitation into low-frequency modes that play an important role in the IVR process. When used in conjunction with ultrafast pulse shaping techniques and feedback-controlled learning algorithms, this frequency-resolved probe of IVR will allow directed control over the flow of vibrational energy from the initial mode into other vibrational modes in the molecule.

130. SINGLE-MOLECULE SPECTROSCOPY STUDIES OF LOCAL MATRIX ACIDITY IN SOL-GEL DERIVED FILMS. **Yi Fu**, Maryanne M. Collinson and Daniel A. Higgins; Kansas State University, Manhattan, KS.

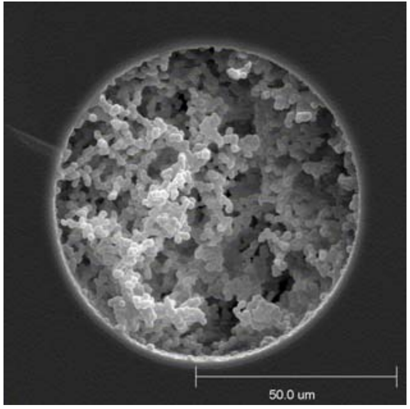
The surface of all silicate-based films incorporate a significant number of acidic sites. Single molecule (SM) spectroscopic methods were employed to study single site variations in the acidity characteristics of sol-gel-derived silicate films. Silica sols were prepared by the acid-catalyzed hydrolysis and condensation of tetraethoxysilane (TEOS). Aluminosilica sols were prepared from the double Si-Al precursor $(BuO)_2Al\text{-}O\text{-}Si(OEt)_3$ in alcoholic solution. The pH-sensitive dye Carboxy SNARF-1 (C.SNARF-1) was doped into the sols and used as a means to sense matrix acidity in spin cast films. The ratio of C.SNARF-1 fluorescence emission at 580 nm (protonated form) and 640 nm (deprotonated form) was used to characterize the pH in local film microenvironments. Histograms constructed from the SM results represent dramatic variations in film acidity properties as a function of treatment conditions. The results prove that spectral variability observed for C.SNARF-1 SMs is dominated by variations in the local matrix acidity.

131. CONTROLLING DIFFUSION IN HYDRATED SOL-GEL DERIVED GLASSES. **Mandakini Kanungo** and Maryanne M. Collinson; Kansas State University, Manhattan, KS.

Understanding the molecular diffusion of encapsulated guest species in sol-gel host matrix is very important for its application in solid-state electrochemical devices and chemical sensors. Intermolecular interactions, coupled with constrained environments, play a significant role in understanding the diffusion of species in hydrated sol-gel matrices. In the present work, the diffusion rate of the encapsulated guest species was controlled by altering the charge of the pore wall of the silicate matrixes. This was done by judiciously choosing the functional group immobilized in the silicate matrix. Ultramicroelectrodes embedded into the sol-gel host matrix were used to evaluate the diffusion of encapsulated species during the sol-gel-xerogel formation. Slow scan cyclic voltammetry, coupled with potential step chronoamperometry, was used to measure the diffusion coefficient (Dapp) of the guest probe during the drying of the gel. It was observed that at one extreme, the encapsulated probed diffused at rates similar to that in solution whereas at other extremes, Dapp dropped more than one order of magnitudes.

132. MONOLITHIC PROTEIN STATIONARY PHASES PREPARED BY THE SOL-GEL METHOD FOR USE IN AFFINITY CAPILLARY LIQUID CHROMATOGRAPHY. **Jeffrey A. Crank** and Nenad M. Kostic; Iowa State University, Ames, IA.

Capillary monolithic silica columns used for normal and reversed phase separations offer the advantage of lower back pressure compared to packed columns. However, capillary monolithic columns have not been applied to affinity or immunoaffinity chromatography. We used the sol-gel method to encapsulate proteins in a silica matrix for capillary affinity chromatography. A monolithic protein stationary phase was prepared by the tetramethyl orthosilicate procedure. The protein-containing sol was injected into a 75 micro-meter i.d. capillary that had been pretreated with sodium hydroxide. The sol gelled into a rigid micro-porous and macro-porous stationary phase. The porosity of the gel was characterized by scanning electron microscopy and Brunauer-Emmett-Teller adsorption/ desorption isotherms. The figure below shows an SEM image of a monolithic column containing 10mg/mL BSA at 1000x magnification. Ubiquitin, bovine serum albumin (BSA) and catalase at different loadings were used in preliminary tests to determine the effects of protein size and concentration on the stationary phase properties. Prelimi-nary separations were performed using the pumps from a capillary electrophoresis instrument with BSA-doped monolithic columns. Future separations will be performed with antibody-doped monolithic columns.



133. PROGRESS TOWARDS A SEPARATION-BASED SENSOR FOR PEROXYNITRITE AND ITS METABOLITES.

Celeste Frankenfeld[1], Matthew R. Rosebraugh[2] and Susan Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Drake University, Des Moines, IA.

Peroxynitrite ($ONOO^-$), a reaction product of nitric oxide (NO) and superoxide ($O_2^{\cdot -}$), is a very short-lived, highly-reactive anion that causes oxidative damage. When stressed, cells produce $O_2^{\cdot -}$, a radical anion, which combines with NO to form $ONOO^-$. $ONOO^-$ then proceeds to break down cell membranes through lipid peroxidation, destroy DNA, interfere with cellular energy production and oxidize LDL, leading to the formation of fatty streaks and atherosclerosis.

Determination of levels of $ONOO^-$ produced under varying cellular environments will permit a better understanding of the role that $ONOO^-$ plays in healthy and diseased individuals. Clinical testing of $ONOO^-$ levels would give doctors a way to monitor the progress and health of heart disease patients. However, $ONOO^-$ is difficult to detect directly because of its short half-life.

Capillary electrophoresis (CE) is a technique that is useful for sensitive and selective study of this short-lived molecule because it allows analysis at high pH. Although $ONOO^-$ has a half-life of around one second under physiological conditions, at pH 12 it can be detected for over an hour. Also, CE can be used in conjunction with various forms of detection, including UV and electrochemical (EC). A diode array UV detector allows multiple wavelengths to be monitored at once; in this case $ONOO^-$ is separated from degradation products nitrite and nitrate, and each is monitored at the wavelength of its optimum absorbance. $ONOO^-$ is electrochemically active, thus much lower concentrations of $ONOO^-$ may be detected with the increased sensitivity EC offers. In this report, detection of $ONOO^-$ by microchip CE with electrochemical detection will also be discussed.

134. CLINICAL APPLICATIONS OF HOMOCYSTEINE USING MICROCHIP CAPILLARY ELECTROPHORESIS WITH ELECTROCHEMICAL DETECTION.

Leslie D. Wagner[1], **Walter R. Vandaveer IV**[2], Stephanie Pasas-Farmer[2] and Susan M. Lunte[2]; [1]Northern Arizona University, Flagstaff, AZ; [2]University of Kansas, Lawrence, KS.

Recent studies have identified elevated levels of homocysteine (Hcy), a sulfur-containing amino acid, as an independent risk factor for cardiovascular disease. Hcy exists in plasma in several forms, mainly protein-bound and disulfide. Total homocysteine (tHcy) is generally reported to encompass all forms of Hcy. Normal levels of tHcy for healthy individuals range from 5–15 micromolar; at higher concentrations, there is an increased risk for cardiovascular disease. These findings suggest a need for sensitive and selective methodologies to determine tHcy levels in plasma samples. Current clinical assays for tHcy are generally performed at a central laboratory on expensive automated instruments that run hundreds of samples a day. The purpose of this study is to further efforts to create a feasible microchip system employing capillary electrophoresis with electrochemical detection (CEEC) for the clinical analysis of tHcy in human plasma. The advantages of CEEC are numerous and include the capability for high-throughput of small volume samples with sensitive and selective detection. Additionally, such systems in the microchip format would permit rapid point-of-care or near-patient testing on inexpensive and disposable devices. Using this system, Hcy was successfully separated from other interfering thiols known to exist in human plasma, such as cysteine and glutathione, in approxi-mately 120 s. These samples were detected at a cobalt phthalocyanine (CoPC) carbon paste electrode on a poly(dimethylsiloxane) (PDMS) microchip. In addition, an internal standard that can be used to quantitate tHcy levels was identified. Finally, work toward analyzing tHcy in plasma samples on a microchip CEEC system will also be presented.

135. NEUROCHEMICAL APPLICATIONS OF PDMS MICROCHIPS FABRICATED USING CO_2 LASER ABLATION. **Barbara A. Fogarty**[1], Kathleen Heppert[1], Theodore Cory[2], Kalonie Hulbutta[3], R. Scott Martin[4] and Susan M. Lunte[1]; [1]University of Kansas, Lawrence, KS; [2]Drake University, Des Moines, IA; [3]Haskell Indian Nations University, Lawrence, KS; [4]Saint Louis University, St. Louis, MO.

The separation and detection of fluorescently-labeled amino acids and peptides on polymer microchip devices fabricated using CO_2 laser ablation is described. Advantages of miniaturized analytical devices include small sample and reagent requirements, fast analysis times and the ability to integrate sample preparation steps onto planar platforms. The use of inexpensive polymer substrates such as poly(dimethyl-siloxane) (PDMS) facilitates the production of portable, disposable devices for 'point-of-care' diagnostic systems. PDMS devices are typically created using patterned templates with positive relief of the microchip design. The master, produced using photolithography, can take up to a day to manufacture in a cleanroom environment. Transfer of the design is achieved by casting PDMS against the master template. By contrast, direct ablation of PDMS with a low-cost commercial laser can allow rapid patterning of microchannels. Using pre-cured PDMS, the entire device is patterned and assembled within a few minutes without the need for master production or the use of cleanroom facilities. The effects of laser focusing, power and speed on the resulting channel dimensions were investigated. Using optimized settings, the smallest channels that could be produced averaged 35 μm in depth and 115 μm in width. Devices were used for the separation of amino acids and peptides pre-labeled with naphthalene 2,3-dicarboxaldehyde and cyanide (NDA-CN). Advan-tages to the use of NDA-CN labeling as opposed to fluorescein-isothiocyanate include speed of derivatization reaction (minutes), relative stability of derivatives (hours) and high quantum efficiencies of resulting derivatives independent of solvent type and pH. The ultimate goal includes integration of the sample derivatization steps towards the development of an on-chip labeling protocol.

136. NITRILE PRODUCT FROM THE CID OF $(b_3\text{-}1\text{+Cat})^+$ SEQUENCE IONS. Travis J. Cooper and **Michael J. Van Stipdonk**; Wichita State University, Wichita, KS.

While investigating the influence of several "alternative" amino acids on the general fragmentation patterns of a series of model tetrapeptides we observed an unusual reaction pathway for the dissociation of certain $(b_3\text{-}1\text{+Cat})^+$ sequence ions. Instead of the characteristic ring-opening reaction for $(b_n\text{-}1\text{+Cat})^+$ products, in which CO is eliminated to generate the $(a_n\text{-}1\text{+Cat})^+$ species, the dissociation of the $(b_3\text{-}1\text{+Cat})^+$ species derived from the model peptide AXAG when X = β-alanine, γ-aminobutyric acid, ε-aminocaproic acid or 4-aminomethylbenzoic acid instead caused the elimination of 72 mass units. The neutral loss is 1 mass unit greater than the residue mass of the alanine residue adjacent to the C-terminus. As we show here, by altering the amino to the C-terminal side of the amino acid X and by labeling specific residues with ^{15}N, we conclude that the novel dissociation pathway leads to a metal cationized nitrile. With respect to the various amino acids at position X, the nitrile product becomes more prominent in the order β -alanine < γ-aminobutyric acid < ε-aminocaproic acid < 4-aminomethylbenzoic acid. The pathway is not observed for peptides with α-amino acids at position X. The nitrile product is observed most prominently during the CID of Li^+ and Na^+ cationized peptides, only to a small extent for Ag^+ cationized peptides and not at all from protonated analogues.

137. INFLUENCE OF "ALTERNATIVE" AMINO ACIDS ON FORMATION OF $(B)_N$ AND $(Y)_N$ SEQUENCE IONS DURING PEPTIDE CID. **Travis J. Cooper** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

Intramolecular nucleophilic attack and the formation of 5-member ring intermediates are proposed to play a major role in the generation of sequence ions by the collisional activation of gas-phase peptide ions. Within the context of improving the understanding of the mechanisms that underlie peptide fragmentation, the goal of this study was to determine the influence of "alternative" amino acids, such as β-alanine, γ-aminobutyric acid and 4-aminomethylbenzoic acid, selected because they either require larger cyclic intermediates, or block cyclization, on the appearance of the collision-induced dissociation of a series of protonated tetrapeptides. We report here that the site-specific incorporation of these amino acid profoundly influences the relative intensities of $(b_n)^+$ and $(y_n)^+$ product ions and, most dramatically, when the amino acid is directly involved in the formation of the cyclic intermediate required for the intramolecular attack. We also found that the relative proton affinities of the alternative amino acids influences the competition between formation of product ions that contain the carboxy terminus and those that contain the amino terminus.

138. MEASURING CLINICAL SALICYLATE LEVELS WITH LUTETIUM(III) PORPHYRIN-BASED ION-SELECTIVE ELECTRODES.

Erich D. Steinle, Stacy W. Scranton, Monica N. Kinde and James M. Hastings; Southwest Missouri State University, Springfield, MO.

Ion-selective electrodes (ISEs) are often utilized in clinical laboratories to measure the levels of specific ions in a variety of media (blood, serum, urine). Traditionally, arrays of these ISEs are incorporated into a clinical analyzer to allow simultaneous determinations. However, measurements of salicylate (the natural by-product of the common drug aspirin) are performed using the colorimetric Trinder method. In this work, new ISEs comprised of a lutetium(III) porphyrin are developed to provide direct measurements of salicylate.

Initial studies focused on optimizing membrane composition to enhance selectivity and sensitivity towards salicylate. Lipophilic ionic sites were added to these plasticized PVC membranes to further improve response. Calibration curves in a synthetic urine solution towards salicylate demonstrated the utility of the lutetium(III) porphyrin-based ISEs. The accuracy of the ISEs was compared using the classical Trinder test. And the effect of the drug promethazine on the response of the ISEs was examined.

139. SEPARATION AND QUANTIFICATION OF N-ACETYL-L-CYSTEINE (NAC) AND N-ACETYL-CYSTEINE-AMIDE (AD4) BY HPLC WITH FLUORESCENCE DETECTION.

Wei Wu and Nuran Ercal; University of Missouri-Rolla, Rolla, MO.

N-acetyl-L-cysteine (NAC) is a well-known antioxidant which is capable of facilitating glutathione (GSH) biosynthesis and replenishing intracellular GSH under oxidatively challenging circumstances. N-acetylcysteine-amide (AD4), the amide form of NAC, is a newly designed and synthesized thiol-containing compound which is believed to be more lipophilic and able to more easily cross cell membrane than NAC. The metabolic mechanism and antioxidant effects of these compounds on cells and animals have previously been investigated. However, an analytical method that can separate and determine both of these compounds and GSH simultaneously is lacking to date. Because of the structural similarities between these two compounds, it is difficult to separate and quantify them by using the existing reversed-phase high-performance liquid chromatography (HPLC) method for NAC that we had published previously. Therefore, we developed a HPLC method with fluorescence detection (λ_{ex}=330nm, λ_{em}=376nm) by using N-(1-pyrenyl) maleimide (NPM) as the derivatizing agent. Biological thiols such as glutathione (GSH) and cysteine (CYS) can also be determined simultaneously using this method. Our preliminary results show that this new technique separates two similar compounds (NAC and AD4) along with other biological thiols. Moreover, it has proved to be a sensitive technique and the complete assay takes less than 20 minutes.

140. ASSESSMENT OF SOME HEAVY METALS IN MUSHROOM SAMPLES FROM ONDO STATE, AKURE, NIGERIA. **Francis Olawale Abulude**; Federal College of Agriculture, Akure, Ondo State, Nigeria.

Mushrooms are economically important fungi that live under the ground or inside wood; only by fruiting, they reveal their presence. The levels of Zn, Mn, Co, Cd, Pb and Cu were determined in seven different types of mushrooms obtained in Akure, Ondo State, Nigeria, by a flame atomic absorption spectrophotometer. Preliminary analytical results indicated significant correlations between metal concentrations in the samples. The levels of metals in the mushroom samples under study were not considered to be toxic to man and animal.

141. INFLUENCE OF NEEM LEAF EXTRACT ON THE *IN VITRO* NET PROTEIN VALUE OF HULLED AND DEHULLED COWPEA (*VIGNA UNGUICULATA L. WALP*) FLOUR.

Francis Olawale Abulude; Federal College of Agriculture, Akure, Ondo State, Nigeria.

The effect of neem leaf extracts on the *in vitro* digestibility of cowpea protein (*Vigna unguiculata L. Walp*) has been evaluated. Four different concentrations of neem leaf extracts and karate E 25 (control) were applied on the samples. Hulled and dehulled samples were processed for the study. The proximate composition of the dehulled seeds was as follows: Crude protein (22.83 - 24.90%), ether extract (6.88 - 8.08%), crude fibre (4.01 - 5.25%), moisture (3.62 - 4.25%) and carbohydrate (55.28 - 58.58%) while the corresponding hulled seeds contained: crude protein (19.98 - 20.72%), ether extract (9.25 - 10.25%), crude fibre (7.25 - 8.28%), moisture (5.68 - 6.35%) and carbohydrate-1 (51.29 - 55.52%). The highest digestibility value was 59.10% for dehulled seeds and the least was 54.10% for hulled seeds. Dehulled samples had higher values for biological value (BV), net protein utilization and net protein value than the hulled samples. It was found that result of the sample and the control were similar.

142. MOLECULAR CHARACTERIZATION OF DIGESTIVE PROTEINASES OF THE YELLOW MEALWORM, *TENEBRIO MOLITOR L.*

Sheila Prabhakar[1], Mingshun Chen[1], Youping Deng[1], Yoonseong Park[1], C. Michael Smith[1], Elena N. Elpidina[2], Konstantin S. Vinokurov[2] and Brenda Oppert[3]; [1]Kansas State University, Manhattan, KS; [2]Moscow State University, Moscow, Russia; [3]Grain Marketing & Production Research Center, Manhattan, KS.

Proteases are enzymes that hydrolyze peptide bonds and insect digestive proteases have been a major target to control pests. To evaluate the potential of a proteinase inhibitor to disrupt the normal metabolic function and physiology of insect digestion, information on digestive proteolytic activity in a target pest must be obtained. Insects provide excellent models for studying gut function as they are adapted to many habitats and feeding habits. Plants produce defense molecules, such as protease inhibitors, to prevent insect damage. The coevolution of insect-plant compensatory responses to digestive enzyme inhibitors is the subject of our study. We are characterizing the major digestive

proteinases and the genes encoding them in a storage pest, the yellow mealworm, *Tenebrio molitor*. Serine and cysteine proteinases from *T. molitor* have been isolated and analyzed using class-specific substrates and inhibitors. cDNA sequences for proteinases have been obtained from a midgut cDNA library. Studies that utilize biochemical and genetic information to probe the response of *T. molitor* larvae to dietary proteinase inhibitors will be discussed. This research is supported by a Civilian Research Defense Fund Grant RB2-2396-MO-02.

143. SEQUENCE FOR THE LOW MOLECULAR WEIGHT CR(III)-BINDING PEPTIDE? IMPLICATIONS FOR Cr BIOCHEMISTRY. **J. David Van Horn**, Deendayal Dinakarpandian and Vincent Morrissette; University of Missouri-Kansas City, Kansas City, MO.

The amino acid composition of a low molecular weight chromium-binding peptide (LMWCr), isolated from bovine liver, is reportedly E:G:C:D::4:2:2:2, though its sequence has not been discovered. The biochemical form and action of Cr(III) has been the subject of many experimental reports and continues to be investigated. Clarification of Cr-protein interactions should provide a basis for novel therapies based on metallocomplexes or small molecules. A genomic search of the non-redundant database for all possible decapeptides of the reported composition yields three exact matches: EDGEECDCGE, DGEECDCGEE and CEGGCEEDDE. The first two are found in ADAM 19 (A Disintegrin and Metalloproteinase domain 19) and the last in a protein kinase in rice (*Oryza sativa*). A broader search for pentameric sequences (and assuming a disulfide dimer) corresponding to the stoichiometric ratio E:D:G:C::2:1:1:1, within all human proteins and those proteins in the insulin signaling pathway, yields a single match at an acidic region in the a-subunit of the insulin receptor (-EECGD-, residues 175-184). A synthetic peptide derived from this sequence binds chromium and forms a metal-peptide complex that has properties matching those reported for isolated LMWCr. The search for an acidic decameric sequence indicates that LMWCr may not be a contiguous sequence. The localization of a pentameric sequence in a significant insulin-signaling pathway protein suggests a possible identity for the LMWCr peptide. This identification clarifies directions for further investigation of LMWCr peptide fractions, chromium bio-coordination chemistry and insulin signaling. Implications for models of chromium action in the insulin-signaling pathway are discussed.

144. DETERMINING THE FUNCTION OF HYPOTHETICAL PROTEIN SAV1430 FROM STAPHYLOCOCCUS AUREUS USING NMR SPECTROSCOPY.

Kelly A. Mercier[1], **Michael Baran**[2], Rong Xiao[2], Robert Powers[1] and Gaetano T. Montelione[2]; [1]University of Nebraska-Lincoln, Lincoln, NE; [2]Rutgers University, Piscataway, NJ.

From the Human Genomic Project and similar studies, more than 45,000 novel proteins have been identified that need to be characterized structurally and functionally. To determine the function of a novel protein, we have developed a high throughput NMR screening method to determine the function of hypothetical protein SAV1430 from *Staphylococcus aureus* through small molecule binding studies. Using a multi-step NMR protocol and a continually growing compound library of small molecules that have well-documented functions and co-structures in the PDB, we have identified 14 compounds of similar structure that exhibit binding to SAV1430. To support this method, we have determined that our experimental results correlate with theoretical SAV1430-ligand co-structures calculated using AutoDock. From these studies, we have been able to annotate a possible function for SAV1430. Continuing efforts will include validating this method using proteins of known function with well-characterized small molecule binders.

145. TETRACHLOROETHENE (PCE) DEGRADATION IN CONTAMINATED SOIL AND GROUNDWATER.

Jwan H. Ibbini, Larry Davis and Larry Erickson, Kansas State University, Manhattan, KS.

Tetrachloroethene (Perchloroethylene PCE) is widely used in dry cleaning fabrics and metal degreasing operations. Because of leakage and poor disposal practices, PCE and its degradation products are now among the most common groundwater contaminants. EPA considers PCE a possible human carcinogen. In Manhattan, Kansas, PCE was used as a solvent in a former dry cleaning facility, contaminating soil and ground water in the area. PCE and its degradation products such as trichloroethene (TCE), *cis*-dichloroethene (*cis*-DCE) and vinyl chloride (VC) were also detected in the ground water plume. A laboratory microcosm study was conducted to evaluate biostimulation and bioaugmentation to dechlorinate PCE to ethene. Microcosms from soil and groundwater from the site were amended with different nutrient combinations. Lactate and yeast extract stimulated partial dechlorination of PCE to give TCE, DCE and VC. Another study was performed using nutrients and the KB-1 microbial enrichment cultures. Faster degradation rates (within few days) were observed when KB-1 was introduced to the system compared to those without the bacterial consortium. Some ethene and much methane were produced.

Keywords: Biostimulation, Bioaugmentation, PCE, groundwater, microcosms.

146. PROLINE CATABOLIC ENZYMES: STRUCTURE, MECHANISM AND SCHIZOPHRENIA. **John J. Tanner**; University of Missouri-Columbia, Columbia, MO.

Abnormalities in proline metabolism are important in several human diseases including cancer and schizophrenia. The enzymes proline dehydrogenase (PRODH) and pyrroline-5-carboxylate dehydrogenase (P5CDH) play central roles in proline metabolism by catalyzing the two-step oxidation of proline to glutamate. In humans, PRODH and P5CDH are separate enzymes encoded by separate genes. Interestingly, in some bacteria, these two enzymes are combined into a single, large protein known as PutA (Proline Utilization A). In enteric bacteria, PutA also serves as a transcriptional repressor of its own gene. While PutA proteins have been studied since the 1960s, they have remained enigmatic due to a complete lack of three-dimensional structural information. In this seminar, I will present crystal structures of truncated and full-length PutA proteins and describe the insights they provide for understanding catalytic mechanism and the role of proline catabolism in human disease.

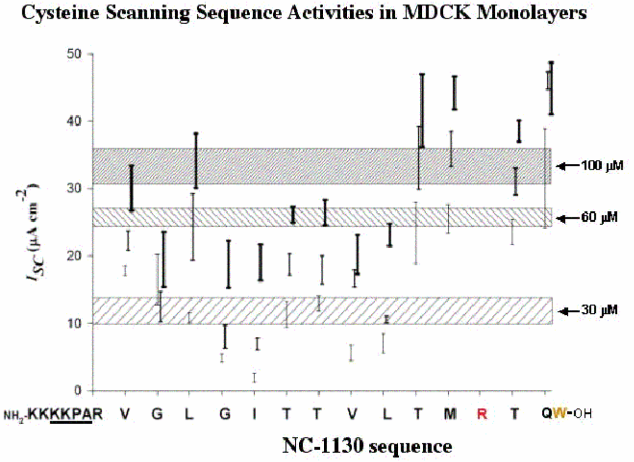
147. DESIGN OF CHANNEL-FORMING PEPTIDES WITH ALTERED TRANSPORT FUNCTION. **Maria A.B.L. Seabra**, Gabriel Cook, Robert Brandt, Bruce Schultz, Takeo Iwamoto and John Tommich; Kansas State University, Manhattan, KS.

The peptide-based channel replacement therapy is a very powerful technique which is designed for potential use as a novel treatment for patients having Cystic Fibrosis (CF), who show severe impairments of epithelial salt and fluid secretion as well as reabsorption. One of our goals was mapping the pore-lining residues of a high conductance channel-forming peptide (KKKKPARVGLGITTVLTMRTQW) derived from the second transmembrane segment of the a-1-subunit of the glycine receptor (M2GlyR). Residues 3-6, 8-18, 20 and 21 were individually replaced by cysteine to allow for scanning of the channel pore with charged thiol reagents.

The substituted peptides were synthesized based on F-moc chemistry and purified using HPLC. The channel formation was verified by ion transport assessment across MDCK epithelial monolayers. The peptide secondary structure was obtained by using circular dichroism (CD) in 10mM SDS micelles.

The non-cysteine substituted control peptide concentration dependently supports transmural ion flux (11.8±2.0 and 33.38±2.6mcA/cm^2 at 60 and 200mcM respectively). Cysteine-substituted peptides exhibited a wide range of maximal flux values when employed at 60mM (1.95±0.7 mcA/cm^2 for Ile 12 Cys to 31.5±7.4mcA/cm^2 for Gln 21 Cys). Greatest maximal transmural flux was observed for Gln 21 Cys at 200mcM (44.85± 3.9mcA/cm^2), the greatest maximal value of any M2GlyR-derived peptide observed to date (see Figure 1). Analysis of the secondary structures for these substituted peptides revealed a direct correlation between the amount of helical content and increased net flux.

We can conclude from these studies that there is considerable plasticity in channel-forming sequences and, through the systematic design and testing of pore forming sequences, new designs with optimized permeation and ion selectivities can be generated.



148. USE OF LIGAND-MODIFIED COLLOID-ENHANCED ULTRAFILTRATION TO SELECTIVELY REMOVE HEAVY METALS FROM WATER. **Richard W. Taylor**, Kay K. Bjornen and John F. Scamehorn; University of Oklahoma, Norman, OK.

Ligand-modified colloid-enhanced ultrafiltration (LM-CEUF) is a separation technique where a ligand and soluble colloid are added to an aqueous solution containing a mixture of cations. The ligands are selected or designed to complex the target cation (Cd, Pb, Hg) selectively and to solubilize extensively into the colloid. The colloidal phase may consist of surfactant micelles with hydrophobic chelating ligands or cationic polyelectrolyte polymers with polyanionic chelating agents. Separation is achieved by ultrafiltration using a membrane with pore sizes small enough to reject the colloid and the associated metal-ligand complex. The fraction of target ion retained by the ligand-modified colloid is expressed as a rejection coefficient. Recent studies using thiourea and nitrilotriacetic acid derivatives as ligands, gave rejection coefficients > 99% for Hg^{2+} and Pb^{2+}, respectively[1,2]. 7-Undecyl-8-hydroxyquinoline has been investigated as a ligand for cadmium using the cationic surfactant cetylpyridinium nitrate (CPN) or the neutral surfactant *n*-dodecylhexa-(ethyleneglycol)ether ($DD(EO)_6$) as the colloid. Protonation equilibria, Cd^{2+} complexation stoichiometry and separation behavior have been investigated in CPN and $DD(EO)_6$. In each surfactant the neutral form of the uncomplexed ligand is predominate from pH 3 to 9. At pH 8.0 the ligand:metal stoichiometry is 2:1 in $DD(EO)_6$ and 3:1 in CPN solutions. The effects of pH, Cd^{2+} concentration and added electrolyte (NaCl) on metal ion separation were investigated and show that Cd^{2+} rejection exceeds 99% at pH 8.0-9.0 in CPN and $DD(EO)_6$ in the presence a ten-fold excess of ligand. At pH < 6.5, Cd^{2+} is released, allowing the colloid-ligand mixture to be recycled after a second ultrafiltration step to remove free Cd^{2+}.

1. J. D. Roach, S. D. Christian, E. E. Tucker, R. W. Taylor and J. F. Scamehorn, *Sep. Sci. Technol.*, **38**, 1925 (2003)
2. J. Rouse, K. K. Bjornen, R. W. Taylor and B. J. Schiau, *Environmental Practice*, **6**, 157 (2004)

149. OCCURRENCE AND FATE OF ANTIMICROBIALS IN MUNICIPAL WASTEWATER TREATMENT PLANTS: A NORTHEAST KANSAS PERSPECTIVE. **Alok Bhandari**, Larry Close, David Koch and Robert Hunter; Kansas State University, Manhattan, KS.

Municipal wastewater treatment plants (WWTPs) act as point sources for the introduction of pharmaceutical agents such as antibiotics and antimicrobials into the environment. The discharge of these compounds into receiving streams has the potential to perturb microbial ecology, increase the proliferation of antibiotic-resistant pathogens and pose serious threat to human health. The development of solutions to control the release of pharmaceutical agents into the environment necessitates an estimation of the amounts of these chemicals entering and exiting municipal WWTPs. In this paper, we report the occurrence of four widely prescribed antibiotics – ciprofloxacin sulfamethoxazole and azithromycin – in four northeast Kansas WWTPs and estimate the mass loading of these antibiotics into the Kansas River. Results from this research provide critical and timely information on the mass flow of these antimicrobials through municipal WWTPs in the lower Kansas River basin.

150. DISTRIBUTION OF POLYCYCLIC AROMATIC HYDROCARBONS IN URBAN STREAMS, THE KANSAS CITY AREA. **Jing Tao**[1], Gary Welker[2], Donald Huggins[3], Jerry Dias[1] and James Murowchick[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]U.S. Environmental Protection Agency, Region 7, Kansas City, KS; [3]Kansas Biological Survey, Lawrence, KS.

Investigations continue to indicate that urban streams are among the most contaminated aquatic ecosystems with regard to both new and old organic compounds that are frequently detected in stream sediments. A study was conducted to identify and quantify the extent, distribution pattern and severity of organic contamination in bed sediment of five streams whose watersheds drain various portions of the Metropolitan Kansas City area. Samples were taken from more than 100 depositional zones occurring within 29 study sites (*i.e.*, stream segments) along the upper, middle and lower reaches of these streams. Sediment samples from multi-depositional zones were composited into a single sample for each site and analyzed for a number of physical, chemical and toxicological parameters. This presentation will focus on the spatial patterns of PAHs in the study streams. Land use and socioeconomic conditions associated with various sediment contaminants will be discussed. Our findings indicate that PAH contamination in bed sediment is closely related to the extent of urbanization within individual watersheds. Specifically, Brush, Indian and Turkey Creeks with relatively high human populations and house densities all showed significant levels of PAHs while Tomahawk Creek and Cedar Creek of lesser urbanization had low levels of contamination. Additionally, the types of PAHs and their concentrations varied within individual watersheds.

151. ENVIRONMENTAL KNOWLEDGE AND ASSESSMENT TOOL (EKAT). **Ryan M. Green** and Terrie Boguski; Kansas State University, Manhattan, KS.

The Environmental Knowledge and Assessment Tool (EKAT) is an automated tool to identify, research and evaluate environmental and safety-related issues for materials. Originally a concept of the Marine Corps System Command (MARCORSYSCOM) in order to better integrate their environmental requirements into their systems acquisition program, the tool’s design makes it useful to other federal and state agencies, communities, industry and small businesses.

EKAT automatically evaluates chemicals for federal environmental compliance issues and highlights key health and safety concerns for those chemicals. The Web-based tool also allows multiple users to centrally organize and reliably document environmental solutions while working collaboratively to generate reports and make decisions.

EKAT presents basic information on technical and regulatory requirements and serves as a resource center linking to other references, tools and databases to assist in research efforts to minimize any unintentional safety and environmental effects associated with a material’s use. Information resource pages within EKAT provide overviews of chosen subject areas, including answers to frequently asked questions and links to other Web sites for further research. The software program also provides quick access to environmental tools, allowing the user to research material properties, investigate environmental issues and find pollution prevention alternatives.

Assessment tools within EKAT calculate pollutant emissions associated with the program user’s process activities using EPA-approved air pollution factors as well as evaluate the environmental impact of chemical emissions over the multiple stages of the life of a product. EKAT can also evaluate chemicals for state-specific air and hazardous waste compli-ance issues associated with solvent cleaning operations in selected states.

152. COOKING PROCESS' RELATIONSHIP TO AIR QUALITY. **Julia A. Keen**; Kansas State University, Manhattan, KS.

The focus of this paper is how the air contaminants created in the cooking process impact both the outdoor environment and indoor air quality. The types of contaminates and how they directly affected the facility, the facility occupants and the surrounding environment are all addressed in detail. In addition to the problems caused by the cooking process, this paper addresses the measures that can be taken to reduce the amount of negative impact that occurs from the cooking process and the different legislation being passed to limit the emissions of commercial kitchens.

153. LEAD, ZINC AND CADMIUM LEVELS IN PLASTER AND MORTAR FROM STRUCTURES IN JASPER AND NEWTON COUNTIES, MISSOURI. **Jeffrey W. Pavlik**, Richard N. Biagioni, Phyllis Perry and Ralph W. Sheets; Southwest Missouri State University, Springfield, MO.

Local legends claim that it was once common practice in the Jasper and Newton counties of Missouri to use mine tailings to mix with cement for concrete, plaster and mortar. The purpose of this study is to obtain valid concentration measurements for the samples, provide further evidence that mine tailings are present in these samples and to disprove alternative theories. Approximately 200 samples were taken from sites in southwest Missouri. Samples were analyzed for the metals by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Levels were 100 to 500 ppm Pb, 50 to 200ppm Cd and 500 to 20,000ppm Zn. Samples from the Springfield area did not show significant amounts of the metals. Depth studies were conducted which showed uniform composition throughout the samples. Concentration of heavier components of the samples allowed for X-ray diffraction crystallography which confirmed the presence of sphalerite, hemimorphite and other ore components. Gallium was also detected in samples, ranging from 0.6 to 12ppm. The sphalerite portion of a piece of ore from the area had 113ppm gallium. Further studies will include an investigation of typical river sand Zn, Pb and Cd levels to evaluate the existent metal's content in conventional sources of construction materials.

154. OXIDATION KINETICS OF AQUEOUS ANTHRAQUINONE DYE IN AN *IN SITU* OZONE REACTOR AND CONVENTIONAL GAS-LIQUID CONTACTOR.

Kishora K. Panda and Alexander P. Mathews; Kansas State University, Manhattan, KS.

Textile dyes are very resistant to biodegradation and impart color to receiving waters at extremely low dye concentrations. Ozone oxidation of dyes in wastewaters has been shown to produce decomposition products that are more readily amenable to biodegradation. In this study, a novel *in situ* ozonator was studied for the oxidation of Reactive Blue 19 (RB 19) dye and its performance is compared with that of a conventional ozone generator and gas-liquid contactor system. The *in situ* ozone generator utilizes a concentric tubular arrangement wherein the inner tube is a porous ceramic electrode. The aqueous solution is passed through the inner tube, while the ozone generated from high voltage discharge in the annular space diffuses through the ceramic electrode into the solution. This can enhance dye decomposition through direct contact with the corona discharge at the gas-liquid interface, as well as by reaction with the molecular ozone that diffuses through the porous electrode. Experimental investigations were conducted for the oxidation of RB 19 at varying feed ozone and dye concentrations, gas flow rates and pH values. Mathematical models have been developed to simulate the mass transfer and oxidation processes and to estimate mass transfer and oxidation rates in the *in situ* ozonator. The mass transfer of molecular ozone in this reactor has been found to be about 130% higher than reported for bubble column reactors. Results on dye oxidation rates and the effects of direct corona discharge on the quality of treated wastewater will be presented. Comparative results will be provided for the oxidation of RB 19 in a conventional gas-liquid reactor.

155. SAFETY OF GLYCOL, DIESEL FUEL OR COMBUSTION SMOKES IN THE PRESENCE OF MAGNESIUM OR TITANIUM DIOXIDE CLEARING AGENTS. **John Pickrell**[1], Gunjan Gakhar[1], Ravi S. Mulukutla[2], Ronaldo Maghirang[1], John S. Klabunde[2], Paul S. Malchesky[2], Ryan Green[1], Frederick Oehme[1] and Larry Erickson[1]; [1]Kansas State University, Manhattan, KS; [2]NanoScale Materials Inc., Manhattan, KS.

Health risks from exposure to glycol, diesel fuel or combustion smokes and the ability of NanoActiveTM TiO_2 or NanoActiveTM MgO to clear each smoke were investigated. Glycol smoke (~ 2 microns aerodynamic diameter; AD), diesel fuel (1 microns AD) and combustion smoke (~0.3 microns AD) are small enough to deposit deep in lung. Glycol smokes were not toxic (10-fold lower than the ACGIH-TLV limit for triethylene glycol, propylene glycol). Diesel fuel smoke EEGL allowed single exposures that obscured at 50 m for 6 hours and training exposure to REGL levels that obscured visibility at 200 m. We are examining guidance factors for combustion smoke and investigating TiO_2 or MgO nanoparticles (marketed as NanoActive^{TM} materials) to clear these smokes. Soldiers may be exposed to TiO_2 at clearing levels with masks (air purifying factor [APF] > 5) for ¼ hour. Repeated training exposures to these smokes required masks with APF > 2500. Bulk MgO was not toxic, with smaller MgO mists (~0.3 microns), 1 hour exposures, required no respiratory protection. Repeated exposures required respiratory masks (APF> 100) for training. At Kansas State University with future work we will measure the solubility of NanoActive^{TM} MgO and NanoActive^{TM} TiO_2 in water and lung simulant fluid. We will also measure the solubility of collected smoke particles of glycol, diesel fuel and combustion smokes. The solubility of combinations of smoke and lung clearing agents will be evaluated to determine environmental and lung persistence. The relation of increased surface area and enhanced lung fluid solubility will be factored in recommendations of smokes and clearing agents for single and repeated exposures.

1. Committee on Toxicology, National Research Council, Toxicity of Military Smokes and Obscurants. Washington, D.C., National Academy Press Vol 2, (1999) pp 68-96.

156. HALOGENATED METAL-OXIDE NANOPARTICLES FOR BACTERICIDAL AND SPORICIDAL USE.

Johanna A. Haggstrom, Kenneth J. Klabunde and George L. Marchin; Kansas State University, Manhattan, KS.

Nanoparticles have many corners, edges and defect sites which make them good candidates for adsorption. Adducts with halogens/ interhalogens adsorbed on various metal oxides and other high surface area materials have been prepared *via* activation under vacuum, or in oxygen, followed by halogenation under vacuum. The adducts formed have been analyzed by Raman Spectroscopy and the amount of halogen adsorbed has been determined by Thermo Gravimetric Analysis (TGA). For a comparison, commercially available samples (μm) have also been studied for adsorption capabilities. The prepared adducts have been tested for bactericidal and sporicidal activity.

157. WATER-SOLUBLE CONJUGATED POLYMERS: SYNTHESIS AND OPTICAL PROPERTIES.

Baohan Xie, Meng Lu, Jeonghee Kang, Ruiyun Guo, Vikalp Thakor and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO.

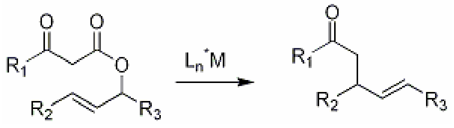
Two sets of water-soluble poly(phenylene vinylene)s (PPVs) were synthesized and their optical properties were studied. The aqueous solubility of all these polymers is rendered by pendant sulphonate ionic functional groups. One set of polymers (polymer I series) contains, in addition to the sulphonate pendants, dimethoxy substituents, while the other (polymer II series) contains oligo(ethylene oxide) side chains. Within each set, polymers containing lithium (Ia and IIa), sodium (Ib and IIb) and potassium (Ic and IIc) counter ions were prepared. For polymer I series, the maximum absorption wavelengths slightly bathochromically shift when the size of the counter ion increases. Polymer II series, however, do not show the same trend. Instead, the polymer with Na^+ (polymer IIb) exhibits a maximum absorption wavelength about 18 nm lower than those of polymers with Li^+ and K^+. The fluorescence emissions of polymer I series show strong solvent dependence as the maximum emission wavelengths red-shift significantly (~20 nm) when the solvent is changed from methanol to water. The fluorescence emissions of the three series II polymers in water, on the other hand, are very close to those of polymers in methanol (< 10 nm red-shift). These results indicate that series I polymers in water exhibit much stronger aggregation than the three series II polymers, which also accounts for the much lower fluorescence quantum yields observed for series I polymers. Fluorescence quenching studies of the polymers with methyl viologen (MV_2^+) in dilute aqueous solutions show that series II polymers exhibit higher quenching efficiencies than those of series I polymers, reflecting again less polymer aggregation of series II polymers. The high fluorescence quantum yields and high fluorescence quenching efficiencies of the other two series II polymers indicate that they are the choices of polymers for biosensor applications.

158. SELENIUM CATALYZED HALOLACTONIZATION: NUCLEOPHILIC ACTIVATION OF ELECTROPHILIC HALOGENATING REAGENTS. **Shelli R. Mellegaard** and Jon A. Tunge; The University of Kansas, Lawrence, KS.

Halolactonization is catalyzed by selenium reagents, such as diphenyl diselenide, in the presence of N-halosuccinimides. In some cases, the increased reaction rates are also supplemented by an increase in selectivity for the γ-lactone products. Due to the existing evidence, this regiocontrol is attributed to kinetic rather than thermodynamic control.

159. ALLYLATION OF NONSTABILIZED KETONE ENOLATES *VIA* THE TRANSITION METAL-CATALYZED CARROLL REARRANGEMENT. **Erin C. Burger** and Jon A. Tunge; University of Kansas, Lawrence, KS.

Palladium and ruthenium have been shown to be selective catalysts for the Carroll rearrangement. This methodology provides a route for the allylation of nonstabilized ketone enolates. Chiral, nonracemic ligands have been used to provide products with high yields and enantiomeric excesses. The scope of this catalytic rearrangement will be discussed as well as ongoing mechanistic work.

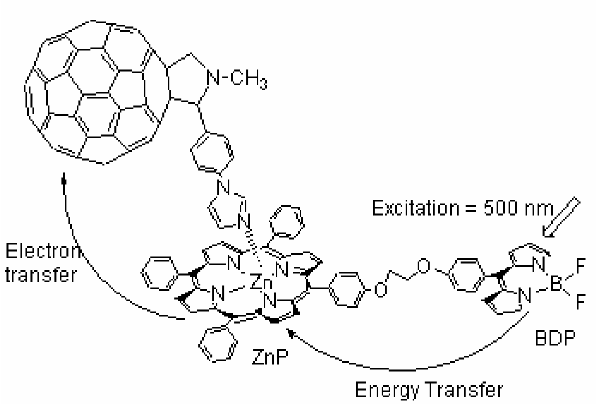


160. MODELING 'ANTENNA-REACTION CENTER' FUNCTIONALITY OF PHOTOSYNTHESIS: ENERGY TRANSFER FOLLOWED BY ELECTRON TRANSFER IN SUPRAMOLECULAR TRIADS COMPOSED OF BORON DIPYRRIN, ZINC PORPHYRIN AND FULLERENE.

Phillip M. Smith[1], Melvin E. Zandler[1], Amy L. McCarty[1], Osamu Ito[2], Mitsunari Itou[2], Yasuyuki Araki[2] and Francis D'Souza[1]; [1]Wichita State University, Wichita, KS; [2]Tohoku University, Sendai, Japan.

Photosynthetic 'antenna-reaction center' models have been constructed and photoinduced energy and electron transfer reactions are investigated. These supramolecular models consist of axially-coordinated imidazole appended fulleropyrrolidine to the zinc porphyrin covalently linked to either one (Scheme 1) or four boron dipyrrin entities. Selective excitation of the boron dipyrrin moiety in the boron dipyrrin-zinc porphyrin dyad in Scheme 1 resulted in efficient energy transfer generating singlet excited zinc porphyrin.[1] Upon forming the supramolecular triad, the excited zinc porphyrin resulted in efficient electron transfer to the coordinated fullerene resulting in a charge-separated state. The observed energy transfer followed by electron transfer in the present supra-molecular triad mimics the events of natural photosynthesis. Here, the boron dipyrrin acts as antenna chlorophyll that absorbs light energy and transports spatially to the photosynthetic reaction center, while the electron transfer from the excited zinc porphyrin to fullerene mimics the primary events of the reaction center where conversion of the electronic excitation energy to chemical energy in the form of charge separation takes place.

Scheme 1



1. D'Souza, F., Smith, P. M., Zandler, M. E., McCarty, A. L., Itoi, M., Araki, Y. and Ito, O. *J. Am. Chem. Soc.* 2004, **126**, 7898.

161. HALOGEN KINETIC ELEMENT EFFECT IN NUCLEOPHILIC AROMATIC PHOTOSUBSTITUTIONS. **Gene G. Wubbels**[1], Bryan Coughlin[2], Carol Peterson[2], Laura Flynn[3] and Heather A. Scholtz[3]; [1]University of Nebraska at Kearney, Kearney, NE; [2]Grinnell College, Grinnell, IA; [3]Washington College, Chestertown, MD.

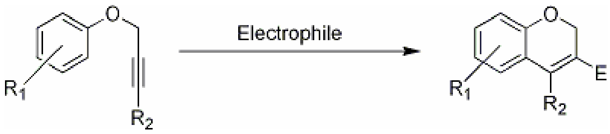
Ultraviolet irradiation of 2-halo-4-nitroanisoles (halogen = F, Cl, Br, I) in aqueous sodium hydroxide solution causes mainly displacement of halogen by hydroxide ion and minor amounts of displacement of methoxy in three cases. Sensitization and quenching experiments reveal that the reactions occur from the triplet state. Determination of the kinetic dependencies of the reactions on the hydroxide ion concentration and independent measurement of efficiencies of intersystem crossing and triplet decay allow calculation of the rate constants for attack by hydroxide ion on the triplet to make *sigma*-complex intermediates. The rate constant for attack on the fluorine-bearing carbon is 1.5 x 10^9 M^{-1} se^{c-1}. The relative rates for attack by hydroxide ion on the halogen-bearing carbon are 93:15:11:1 for F, Cl, Br and I, respectively. The relative rates of photodisplacement of halogens are inverse to halogen leaving group abilities and are similar to the halogen kinetic element effects for ground state nucleophilic aromatic substitutions by comparable nucleophiles, despite rate differences for the thermal and photochemical reactions on the order of 10^{12}. This implies that the transition state involved in the *meta*-to-nitro photosubstitution on nitrophenyl ethers is a simple heterolytic bond formation between the nucleophile and the photoexcited triplet.

162. PRELIMINARY STUDIES ON THE DEOXYGENATION OF FATTY ACIDS TO HYDROCARBON FEEDSTOCKS. **Amol A. More**, Keith Hohn and John R. Schlup; Kansas State University, Manhattan, KS.

One of the most important technological challenges of this century is to find suitable replacements for petroleum for the production of fuels and chemicals. Deoxygenation of fatty acids could provide a source for long chain alkanes and alkenes. Pyrolysis and catalysis of oleic acid was investigated over ZSM-5 and ZnO catalysts by means of Robinson-Mahoney stationary basket reactor. The reactor was operated at atmospheric pressure and at two temperatures, 200°C and 250°C. Conversion was monitored *via* disappearance of –COOH in the oleic acid. Light hydrocarbon gases, CO and CO_2, were the major products. Pyrolysis of oleic acid resulted in very low conversions, while cracking was observed with ZSM-5 catalyst. ZnO resulted in formation of a metallic soap *via* the fusion reaction; however, CO and CO_2 were also formed in an oxygen-free atmosphere, indicating deoxygenation had occurred.

163. SYNTHESIS OF 2-H BENZOPYRANS THROUGH C-C BOND FORMATION *VIA* IODOCYCLIZATION. **Shilpa A. Worlikar** and Richard C. Larock; Iowa State University, Ames, IA.

The iodocyclization of substituted propargylic aryl ethers produces iodobenzopyrans in excellent yields. This methodology results in vinylic iodides which can be subjected to Suzuki cross-coupling with arylboronic acids to provide an efficient route to synthesize a class of compounds known to have potent anti-estrogenic activity. Sonogashira coupling affords useful precursors to additional polycyclic compounds. The scope of this reaction on various substrates will be discussed.



164. DEVELOPMENT OF CYCLIC ENOL PHOSPHONAMIDATES USING RING-CLOSING METATHESIS. **Stephen R. Sieck**, Matthew D. McReynolds and Paul R. Hanson; University of Kansas, Lawrence, KS.

The development of cyclic, six-membered enol phosphonamidates utilizing the ring-closing metathesis reaction (RCM) will be discussed. The strategy allows for the generation of various phosphonamidic monochloridates that can be further functionalized to an array of acyclic, enol phosphonamidates. Subsequent treatment with a variety of metathesis catalyst affords both the desired RCM product and a dimer produced from cross-metathesis (XMET). Efforts have been made to optimize the formation of the desired RCM product and minimize XMET.

This strategy allows for the generation of cyclic enol phosphonamidates, which can be derivatized into C-6 substituted analogs of cyclophosphamide, a powerful anti-cancer agent.

165. FUNCTIONALLY-ACTIVE PHOSPHATE TETHERS IN SYNTHESIS. **Alan Whitehead** and Paul R. Hanson; University of Kansas, Lawrence, KS.

Historically, the use of phosphate triesters in complex syntheses has primarily focused on nucleophilic displacement reactions of allylic phosphates and cross-coupling/reduction reactions with enolphosphates, both of which exploit the leaving group ability of the phosphate monoanion. The additional use of phosphate triesters in iodophosphonylation procedures pioneered by Bartlett and their obvious role in oligonucleotide synthesis further highlight both nucleophilic properties and facile coupling characteristics, innate to phosphates. This reactivity profile is over-shadowed by the vast extent to which nature employs their anionic counterparts, organophosphate mono- and dianions, which play a dominant role in key biological processes employing their unique chemical properties. We now report a fundamentally new role of phosphate triesters in synthesis, which embodies two relatively-unexplored areas of phosphate chemistry, namely their dual use as removable, functionally-active tethers for tripodal coupling of alcohol subunits and subsequent role as latent leaving groups in selective cleavage reactions.

166. FUNCTIONALLY-ACTIVE PHOSPHATE TETHERS: HARNESSING LATENT LEAVING GROUP ABILITY IN BICYCLIC PHOSPHATE TRIESTERS. **Alan Whitehead** and Paul R. Hanson; University of Kansas, Lawrence, KS.

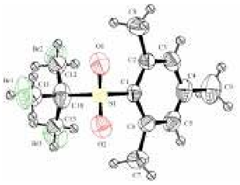
The development of functionall-active phosphate tethers (P-tethers) for the tripodal coupling of allylic alcohols with subsequent selective cleavage processes is described. This study focuses on using latent leaving group ability within the phosphate tether to dictate selective cleavage processes en route to the asymmetric generation of differentiated building blocks for use in natural product synthesis. Several features of phosphate chemistry are exploited including (i) tripodal coupling (ii) the stability of phosphate monoanions and (iii) latent

S_N2 and S_N2' leaving group properties of both alkyl and allylic phosphates.

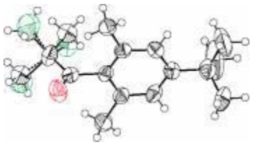
167. SOME UNUSUAL CHARACTERISTICS OF CRYSTALLINE ORGANIC COMPOUNDS UNCOVERED BY X-RAY STUDIES, *e.g.*, ROTATIONAL DISORDER AND H-BONDING VS. "MP (DEC.)".

Cal Y. Meyers, Paul B. Sandrock, Aaron W. McLean and Paul D. Robinson; Meyers Institute for Interdisciplinary Research in Organic and Medicinal Chemistry, Southern Illinois University Carbondale, Carbondale, IL.

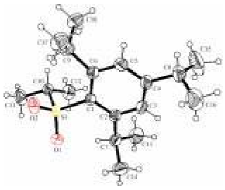
Our long-term studies of the comparative reactivity and physical characteristics of a series of ketones and related sulfones have provided exciting results…some expected and others quite unexpected. The solid compounds were purified by several crystallizations, and vacuum-oven drying and identified unequivocally by X-ray crystal analysis. Some, but not all, of the crystalline sulfones displayed various degrees of "rotational disorder" whereby several rotameric conformations involving the a-R substituents attached group were well-defined in the crystalline structure (*e.g.* **I**) and that of related ketones (*e.g.* **II**), but not in all the sulfones or ketones that we simply deemed would be rotationally restricted (*e.g.* **III**).



I a-Br-*i*-Pr mesityl sulfone



II a-Br-*i*-Pr 2-(5-*t*-Bu-1,3-xylyl) ketone

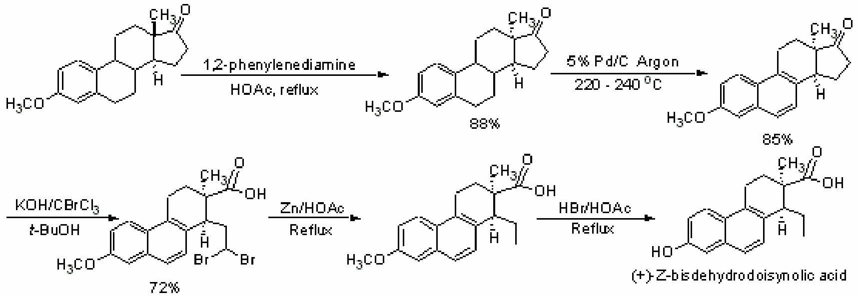


III *i*-Pr 2,4,6-tri-*i*-Pr phenyl sulfone

We have also questioned the common belief that when the melt of a sharply melting crystalline compound **fails** to recrystallize when cooled and re-melt sharply at the same temperature, it has melted "with decomposition" [often stated as "mp XXº (dec.)"]. Our in-depth X-ray crystallographic studies of a series of compounds indicate strongly that, to a large extent, these are intermolecular H-bonded crystalline compounds, the melts of which **do** crystallize over a period of minutes, hours or longer, or however long it takes for the required intermolecular hydrogen bonds to be re-formed, leading to the respective crystalline states. In most instances we have ascertained that the melts of such compounds have NMR spectra and sharp melting points identical, respectively, to those of the original pre-melted crystals. In such cases it is **not** the **molecule** *per se* that has "decomposed" on melting, but the intermolecular **H-bonded packing structure** required for the crystallization, which, in the absence of solvent, is re-formed slowly.

168. ENANTIOSPECIFIC SYNTHESIS OF (+)-Z-BISDEHYDRODOISYNOLIC ACID. **Yuqing Hou**; Southern Illinois University, Carbondale, IL.

(+)- and (-)-*Z*-Bisdehydrodoisynolic acids have exhibited paradoxical Selective Estrogen Receptor Modulator (SERM) properties in various receptor-binding, cell line and animal-model studies. More interestingly, (+)-*Z*-bisdehydrodoisynolic acid showed potential as a chemotherapeutic agent for prostate cancer and benign prostate hypertrophy, while exhibiting little feminizing effect. However, (+)-*Z*-bisdehydrodoisynolic acid has been obtained through a laborious resolution of the enantiomers. In this study, an enantiospecific synthesis of (+)-*Z*-bisdehydrodoisynolic acid has been carried out successfully from estrone in five steps in good overall yield. Thus, C-13 of estrone was epimerized with 1,2-phenylenediamine in refluxing HOAc, followed by the aromatization of the B-ring with 5% Pd/C ca. 230 °C to give isoequilenin, which sequentially went through a D-ring cleavage with KOH/$CBrCl_3$/*t*-BuOH, reduction with Zn/HOAc and demethylation to provide the desired product.



169. ELUCIDATION OF CONDUCTIVITY IN A HIGHLY-CONJUGATED POLYMER USING ESR AND CONDUCTIVITY. **T.C. Sandreczki**[1], J. Park[1], J. Guthrie[2], F. Badrun[1], K. Rogers[1] and J. Bowen[1]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]University of Missouri-Columbia, Columbia, MO.

ESR spectroscopy and electrical conductance have been used to elucidate the nature of conductivity in a highly-conjugated benzimidazo-benzophenanthroline-type polymer. The maximum conductance and maximum electron spin concentration occur at different doping levels and support a site-to-site hopping model.

170. INFLUENCE OF LIGAND VIBRATIONAL ENERGIES ON HYDRATION BEHAVIOR OF Ag(I) COMPLEXES IN THE GAS PHASE. **Dorothy A. Hanna**[1] and Michael Van Stipdonk[2]; [1]Kansas Wesleyan University, Salina, KS; [2]Wichita State University, Wichita, KS.

Modern ion trap mass spectrometry has been shown to be an effective tool for investigating the reactivity of ionic species in the absence of solvent effects, thus providing access to information on ligand influences upon the metal ion's intrinsic reactivity. When isolated within the ion trap, coordinately-unsaturated complexes are subject to ligand addition reactions through collisions with neutral molecules present in the spray solution and the coolant gas. Interpretation of kinetic data obtained by ITMS studies in terms of ligand electronic effects upon the metal requires an understanding of the extent to which transfer of excess energy from reactive collisions into the ligand's internal vibrational modes influences the observed kinetics of the complexes. The change in hydration behavior of Ag(I) complexes upon isotopic substitution of the ligand is examined in order to investigate the influence of ligand vibrational energies upon the complexes' reactivity toward addition reactions in the environment of the ion trap.

171. EQUILIBRIUM STRUCTURE OF *ORTHO*-BENZYNE. **Peter Groner**[1] and Stephen G. Kukolich[2]; [1]University of Missouri - Kansas City, Kansas City, MO; [2]University of Arizona, Tucson, AZ.

Approximate equilibrium rotational constants were obtained for seven isotopomers of *ortho*-benzyne from the experimental ground-state rotational constants and theoretical vibration-rotation constants derived from *ab initio* force fields (MP2(full)/6-31G(d)). They were used to determine an approximate equilibrium structure of *ortho*-benzyne in the gas phase. The distances of the C-C bonds were, beginning with the formal triple bond, 1.255(3), 1.383(2), 1.403(2), 1.405(3) Å. The bond angles agreed to 1° or better with earlier CCSD(T)/6-31G(d,p) *ab initio* predictions.

172. ENERGY TRANSFER AT A GAS-LIQUID INTERFACE. **Tamas Szabo**, Ali Siavosh-Haghighi and John E. Adams; University of Missouri-Columbia, Columbia, MO.

When a solid energetic material burns, a thin liquid layer forms on the surface of the solid, with the evaporation of this liquid leading then to gasification of the material. One of the processes contributing to the establishment of a steady-state temperature of this liquid layer is collisional energy feedback occuring when hot combustion products strike the liquid surface. To characterize this energy exchange, we have carried out molecular dynamics simulations of gas-liquid surface energy transfer, with a special emphasis being placed on how the extent of the energy transfer depends on the surface temperature. Our initial results confirm previous experimental probes of these systems, indicating that as the surface temperature increases, the percentage of the incident species that are trapped at (and subsequently equilibrated with) the surface increases.

173. CHEMILUMINESCENCE FROM SURFACE REACTION ON METAL-OXIDE NANOCRYSTALS. Hohn Keith and **Chien-Chang Huang**; Kansas State University, Manhattan, KS.

Chemiluminescence from liquid-phase reactions are well known. The reaction of tetrakis demethyl amino ethylene (TDE) is unique because it requires only a protonic source and oxygen. Much less well known are chemiluminescent surface reactions. These are interesting because they could provide a means for characterizing surface properties through detection of light. In addition, modification of particle sizes and pore sizes can control the rate of oxygen transport to TDE, thereby controlling the lifetime and intensity of chemiluminescence. The reaction of TDE was studied on metal oxide nanocrystals with an eye on practical applications as a portable light source.

The reaction of TDE and oxygen has been studied in the presence of metal oxide nanocrystals purchased from Nanoscale Materials and conventional metal oxides. The intensity and lifetime of light emissions for eight metal oxides has been measured with a fiber optic spectrometer. Commercial MgO gave the highest intensity and largest total light emission, while Nanoactive MgOplus produced weak light emissions that persisted for only fifteen minutes.

It is proposed that isolated surface hydroxyls play a role in surface-initiated chemiluminescence. Infrared spectroscopy provides support for this hypothesis, as Nanoactive MgOplus has only a weak peak represent-tative of isolated hydroxyls while all other samples had intense peaks. Furthermore, exposing Nanoactive MgOplus to a moist environment led to an increase in intensity of the IR peak for isolated hydroxyls and also an order-of-magnitude increase in the intensity emitted from reaction with TDE.

This paper will describe the effectiveness of different metal oxides in the TDE reaction and will discuss how different pretreatment conditions affect reaction. The role of surface hydroxyls in the reaction mechanism will be discussed. Finally, changing the metal oxide particle size will be discussed as a means for controlling reaction lifetime.

174. *IN SITU* INFRARED STUDY OF THE CATALYTIC IGNITION OF METHANE ON Pt/Al_2O_3.

Chundi Cao, Abdennour Bourane, John R. Schlup and Keith L. Hohn; Kansas State University, Manhattan, KS.

Catalytic partial oxidation (CPO) of alkanes at millisecond contact times has been found to be an efficient means for producing syngas. In a millisecond contact time reactor, a pre-mixed fuel and oxygen mixture is flowed at high flow rates through a noble metal catalyst. The catalyst is heated until catalytic ignition occurs, at which time autothermal operation is possible. CPO could also be considered as a means for producing hydrogen in mobile applications for powering a fuel cell. The process by which the catalyst is ignited is of special interest, since a fast light off would be required so that the automobile could be powered as soon as the ignition key was turned. Most studies on the catalytic ignition have focused on accurately measuring the temperature at which either surface or surface-initiated gas phase ignition occurs. There is a lack of information about how the surface species change as the temperature is raised towards the ignition temperature. This work uses DRIFT spectroscopy coupled with mass spectrometry to study the mechanism of the CPO of methane on Pt/Al_2O_3 as the catalyst is ignited. Light-off experiments were conducted on fresh, aged and on oxidized platinum catalysts. The catalytic ignition temperature changed dramatically with catalyst state. It was measured at 597 K for the fresh catalyst, but was only 567 K for the aged catalyst. The oxidized catalyst had the highest ignition temperature of 623 K. The DRIFTS results showed that during catalytic ignition, the surface is mainly oxygen-covered. Catalytic ignition then occurs when the temperature is high enough that the oxygen surface coverage is decreased leaving sites available for chemisorption of the fuel. Finally, upon ignition adsorbed CO is formed as the oxygen coverage decreases and methane can interact with the surface. The reaction mechanism for catalytic ignition is discussed.

175. DFT MO CALCULATIONS ON PORPHYRIN-QUINHYDRONE DYADS: PREDICTION OF STABLE STACKED QUINONE-HYDROQUINONE ENTITIES WITH B3LYP/3-21G(*). Francis D'Souza[1], Paul A. Karr[2], **Melvin E. Zandler**[1] and Michael Beck[2]; [1]Wichita State University, Wichita, KS; [2]Wayne State College, Wayne, NE.

DFT calculations at the B3LYP/3-21G(*) level were performed on quinhydrone (a 1:1 quinone-hydroquinone complex) paired self-assembled supramolecular porphyrin-quinone porphyrin-hydroquinone dyads. In the B3LYP/3-21G(*) optimized structures, the quinone-hydroquinone entities were stacked on one another with an inter-planar distance of about 3 Å. The calculated O–H–O distances revealed the presence of the anticipated two hydrogen bonds. The computed association energies varied with substituents, but the negative values suggest quinhydrone as a viable self-assembly mechanism to form stable supramolecular complexes. Such self-assembled donor-acceptor systems with attached tetraphenylporphyrin entities have potential to mimic the early events of bacterial photosynthesis and may have promise for advances in solar energy conversion and in building molecular optoelectronics such as switches and photonic wires. The computed HOMO-LUMO energy gaps followed the electrochemically-measured values and the HOMO and LUMO orbitals were found to track the electrochemically and spectroelectrochemically determined site of electron transfer (porphyrin, quinone or hydroquinone sites). The simple quinone-hydroquinone complex was studied by several DFT procedures with higher basis sets to determine the reason for the surprisingly high quality prediction of quinhydrone characteristics by the B3LYP/3-21G(*) method. Basis sets including 3-21G(*), 6-31G*, 6-31+G*, 6-31++G*, 6-311G(d,p) and 6-311G(2df,dp) with the HF, BLYP, B3LYP, B3PW91 and MPW1PW91 methods were employed to determine Basis Set Superposition Error (BSSE) and correlation energy effects.

176. MOLECULAR DYNAMICS SIMULATIONS OF THE EFFECT OF PHOSPHORYLATION ON STRUCTURE AND DYNAMICS OF PHOSPHOLAMBAN IN MEMBRANE BILAYER.

Yao A. Houndonougbo, Krzysztof Kuczera and Gouri S. Jas; University of Kansas, Lawrence, KS.

Phospholamban (PLB) is a transmembrane protein that regulates calcium ATPase in the cardiac sarcoplasmic reticulum. PLB is phosphorylated at Ser-16 by a cAMP-dependent phosphokinase and at Thr-17 by a calcium/calmodulin-dependent phosphokinase. The phosphorylation/dephosphorylation of phospholamban removes and restores, respectively, its inhibitory activity on cardiac sarcoplasmic reticulum calcium ATPase. Using results of 5 ns molecular dynamics simulations of phosphorylated phospholamban in di-palmitoyl phosphatidylcholine (DPPC) bilayer membrane, we present a microscopic description of the structure and dynamics of phospholamban phosphorylated either at Ser-16 or Thr-17 in a membrane environment. Phospholamban phosphorylated maintains its "L" shape, with two well-defined helical domains at the N- and C-termini. In the case of PLB phosphorylation at Ser-16, the average interhelix angle is 110 +/- 22 degree, whereas for PLB phosphorylation at Thr-17 the value is 85 +/- 10 degree. In our previous simulations of unphosphorylated phospholamban [Y. Houndonougbo, K. Kuczera and G. Jas, submitted to *Biochemistry*], we have found the average interhelical angle of 120 +/- 21 degree. Thus, we conclude that PLB phosphorylation does not affect the "L" shape structure of phospholamban but results in a more compact structure, consistent with experimental data.

177. FT-IR STUDIES OF PHOTOCHEMICAL OXIDATION OF ORGANIC COMPOUNDS OVER TiO_2-SiO_2. **Dilip K. Paul**[1], D. A. Panayotov[2] and J. T. Yates[2]; [1]Pittsburg State University, Pittsburg, KS; [2]University of Pittsburgh, Pittsburgh.

The photocatalytic oxidation of 2-chloroethyl ethyl sulfide (2-CEES, a simulant for mustard gas) on high area TiO_2-SiO_2 pwder has been studied by transmission FTIR spectroscopy. It has been found that the photocatalytic oxidation of 2-CEES occurs on the surface at 200 K with an appreciable rate. In addition to 2-CEES, we have also studied the photooxidation of diethyl sulfide (DES), as a comparison, to test the role of Cl substitution in the 2-CEES molecule. With both 2-CEES and DES partially- and fully-oxidized products are observed. By comparison of the spectral developments during the photooxidation of 2-CEES and DES, it appears that the presence of chlorine substituent in 2-CEES is not strongly influential in the photooxidation sequences for this molecule.The 2-CEES molecule is hydrogen-bonded to the Si-OH groups by both Cl and S moieties and photooxidation leads to loss of the spectral features caused by H-bonding as the 2-CEES molecule is destroyed.

178. ELECTRONIC STRUCTURE FOR POLYTYPES OF SEMI-CONDUCTING BORON CARBIDE. **Petru Lunca-Popa**, Snjezana Balaz, Carolina Ilie and Jennifer I. Brand; University of Nebraska, Lincoln, NE.

Semiconducting boron carbide is a complex new material with applications ranging from low-powered neutron detectors for homeland security to direct power conversion devices. Many polytypes can be produced from plasma-enhanced chemical vapor deposition using closo-carborane isomers as precursors. Investigating the electronic structures of these precursors and polytypes helps to explain the production of both p-type and n-type materials, the tunable bandgaps and the self-doping capability due to isomeric variations[1,2]. In this work, direct and indirect optical bandgaps of films of various polytypes were determined by UV-VIS spectroscopy and correlated with macroscopic electrical properties, such as the temperature dependence of the resistivity. Bandgaps of 1.5 eV were found for films derived from *ortho*- and *meta*-carboranes, even though these two species produce p-type and n-type semiconductors, respectively. For *para*-carborane-derived films, the bandgap was 2.8 eV. These experimental results are compared to theoretical calculations in initial efforts to understand the complexities in the electronic structure and bonding of semiconducting boron carbide. Ground state levels were calculated for the three isomeric carboranes using a HyperChem package using PM3-NDO calculations with the PM3 basis set[3]. These calculations predict the n- and p-type behaviors correctly for *ortho*- and *meta*-carboranes, but showed much less difference in the ground-state HOMO-LUMO gaps for all three species (10.1, 10.7 and 10.0eV for *o*-, *m*- and *p*-carborane respectively), similar to previous results from MNDO[1,4].

1. A. N. Caruso, R. B. Billa, S. Balaz, J. I. Brand and P. A. Dowben, *J. Phys: Cond. Matter* **16** (2004) L139-L146.
2. P. Lunca-Popa, J. I. Brand, S. Balaz, L. G. Rosa, N. M. Boag, M. Bai, B. W. Robertson and P.A. Dowben. In review. Appl. Phys. Let.
3. J. J. P. Stewart, *J. Comput. Chem*. **10**, 221 (1989)
4. A. N. Caruso, L. Bernard, Bo Xu and P. A. Dowben, *J. Phys. Chem. B* **107**, 9620-9623 (2003).

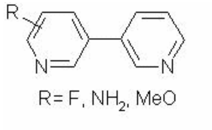
179. PERSPECTIVES IN MOLECULAR TECTONICS. **Mir Wais Hosseini**; Universite Louis Pasteur, Strasbourg, France.

Molecular crystals are compact and periodic entities. They are defined by the nature of their molecular components and interactions between them in the solid state. Although single crystals are described by translation of the unit cell into all three directions of space; however, by considering crystals as supramolecular entities, one may describe them in terms of networks by analyzing the intermolecular interactions and their geometrical features. Such analysis is based on specific recognition patterns within the crystalline material. This way of analyzing molecular crystals in terms of networks is called molecular tectonics. This approach leads to the definition of tectons or construction units which are structurally- and energetically-defined active molecular building blocks bearing within their backbone an assembling program based on molecular recognition processes. The molecular programming leading to the formation of molecular networks with predefined dimensionality and connectivity is ensured by the nature and localization of recognition sites within the structure of tectons. The strength of molecular tectonics is related to the fact that it not only allows one to describe a given crystal in terms of networks but, also and more interestingly, this approach allows one to conceive predefined molecular networks through the specific design of tectons. A variety of tecons and molecular networks based on diverse intermolecular interactions will be presented.

180. TRIPLE PLAY: TERNARY SUPERMOLECULES BASED ON ASYMMETRIC BIPYRIDINES.

Brock D. Levin, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS.

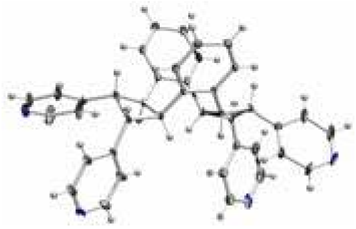
As we work toward a better understanding of intermolecular interactions and an improved ability to predict which types of these interactions work well in concert, it becomes important to be able to rationalize and anticipate how very similar molecules will react when introduced to polytopic receptors. In this case, the supramolecular target is a set of discrete ternary co-crystals containing carboxylic acids of different strengths assembled with the aid of asymmetric, ditopic hydrogen-bond acceptors. Here we present the synthesis and characterization of some of these ligands as well as a study of their effectiveness as selective supramolecular reagents.



181. SYNTHESIS OF MOLECULAR TARGETS IN THE SOLID STATE *VIA* TEMPLATE-CONTROLLED REACTIVITY.

Tomislav Friscic, Xiuchun Gao and Leonard R. MacGillivray; University of Iowa, Iowa City, IA.

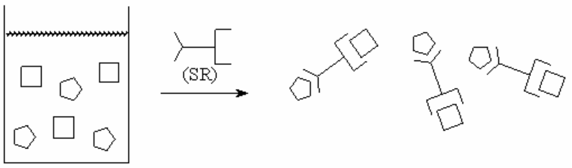
The solid state is a promising medium to conduct organic syntheses. The molecular order and the absence of large-scale molecular movements in the solid provide an environment that allows reaction products to be obtained stereospecifically and in quantitative yield. However, reactivity in the solid state is to a great extent controlled by crystal packing and, is consequently, difficult to control or predict. The difficulties of controlling solid-state reactivity, which arise from the effects of crystal packing, may be circumvented by employing molecules that act as templates to control the organization of reactants. Specifically, we have demonstrated that resorcinol and derivatives function as linear templates to organize double bonds of olefins for the [2+2] photodimerization, according to topochemical postulates given by Schmidt. We regard such template-controlled solid-state approach to be a general method to conduct synthesis in the solid state. In that sense, the linear templates are expected to be adaptable to changes introduced to reactant molecules, such as size, shape and functional groups. In order to establish such generality, we have undertaken the syntheses of molecular targets based on ladderane and [2.2]-cyclophane frameworks, that allowed us to focus on changes in molecular size and shape. Specifically, the targets were linear ([3]-ladderane, [5]-ladderane and a *para*-cyclophane), as well as bent (*ortho*- and *meta*-cyclophane) molecules. All targets were obtained regioospecifically and in quantitative yield, demonstrating the generality of the method for con-structing molecules of different sizes and shapes.



182. FROM MOLECULAR FUNCTION TO SUPRAMOLECULAR SYNTHESIS. **Christer Aakeröy**; Kansas State University, Manhattan, KS.

Chemistry is the science of communication and change and these interrelated processes are primarily initiated and controlled by reversible interactions between molecules. Our ability to design and synthesize discrete molecular species has been developed and refined for over a century and today we are capable of making extraordinary molecules that rival some of nature's best efforts when it comes to structural complexity and chemical reactivity. However, the synthesis of supramolecular assemblies composed of many different molecular fragments held together by non-covalent forces is far less advanced and our understanding of how groups of molecules communicate, bind, organize and function is still incomplete.

This presentation is intended to demonstrate how the use of suitable supramolecular reagents (SRs) can allow for directed assembly of small molecules into architectures of considerable complexity. The general synthetic approach is based upon a hierarchical view of intermolecular forces that allows for a modular high-yielding assembly process of ternary co-crystals (see below).



183. SUPRAMOLECULAR CHEMISTRY OF BORONIC ACIDS: A CARBOXYLIC ACID-AMIDE HYBRID?

Debra J. Salmon, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS.

Boronic acids are receiving much attention for their usage as starting material for cross-coupling reactions, such as Suzuki or Sonogashira reactions. In fact, the chemical manufacturer Aldrich reports 365 entries containing “boronic acid.” With the increasing interest has come a desire to know how this functional group interacts with other molecules (Figure 1). The supramolecular chemistry of boronic acids has not been investigated to the same extent that other functional groups have been studied[1,2,3]. What makes the study of boronic acids interesting is that, in addition to having straightforward syntheses[4], they also contain both hydrogen-bond donors and acceptors. The goal of this work is to understand how boronic acids behave in the solid state. Do boronic acids always form B-O-H dimers similar to carboxylic acids or would they rather form the hydrogen-bonding ribbons shown by amide-amide interactions? With what type of substrate would boronic acids best interact and, finally, can boronic acids be used as supramolecular reagents for building binary and ternary co-crystals?

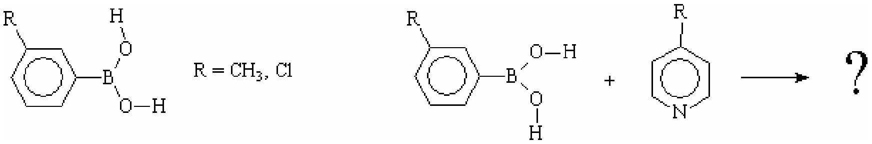


Figure 1. General scheme of boronic acid; boronic acid plus heterocycle.

184. LINEAR TEMPLATES: TOOLS FOR ASSEMBLING AND CONSTRUCTING MOLECULES IN CRYSTALLINE SOLIDS.

Leonard R. MacGillivray, Tomislav Friscic, Dushyant B. Varshney, Tamara D. Hamilton, Qianli Chu and Giannis S. Papaefstathiou; University of Iowa, Iowa City, IA.

Molecules that assemble and juxtapose molecules to react to form covalent bonds could have widespread applications in chemical synthesis and materials science. In this context, we are developing a supramolecular approach to molecular synthesis that permits ditopic molecules, in the form of linear templates, to assemble and position olefins within hydrogen-bonded molecular assemblies in the solid state for chemical reaction to form covalent bonds. The templates juxapose olefins *via* hydrogen bonds for single and multiple [2+2] photodimerizations. In this presentation, we demonstrate how linear templates can be used to conduct target-oriented molecular synthesis. The targets include linear and bent molecules, as well as molecular ladders. The ability of the templates to facilitate the construction of molecular targets lies in the ability of the templates to adapt to changes in size and shape of the reactants. We will also discuss how such template molecules enable reactivity of members of a homologous series of olefins.

185. RECIPE FOR MAKING TERNARY SUPERMOLECULES. **Joaquin F. Urbina**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS.

Traditional organic synthesis has all but conquered the covalent bond. Supramolecular synthesis and crystal engineering, however, are still in their developing stages in formulating strategies for reliable supramolecular synthons. The carboxylic acid…pyridine synthon has proven to consist of robust intermolecular interactions and has been employed in the deliberate construction of binary, or two-component, supermolecules. The quest for ternary, or three-component, supermolecules demands more sophisticated protocols that can only be applied through a hierarchy of supramolecular synthons. Deliberate ternary systems have been achieved using isonicotinamide as the centerpiece linking a strong and a weak carboxylic acid *via* the carboxylic acid…pyridine and carboxylic acid…carboxamide synthons. We have utilized a very similar approach except that our supramolecular reagent, 3-(benzimidazol-1-yl)methyl-pyridine, consists of two distinct heterocycles. The benzimidazol-1-yl nitrogen atom is more basic than the pyridyl nitrogen atom and according to the best donor-best acceptor strategy would accept the stronger carboxylic acid, thereby leaving the pyridyl site to accept the weaker carboxylic acid, Fig. 1. Consequently, we will examine the scope of our supramolecular reagent based on co-crystallizations with carboxylic acids of different pK_as.

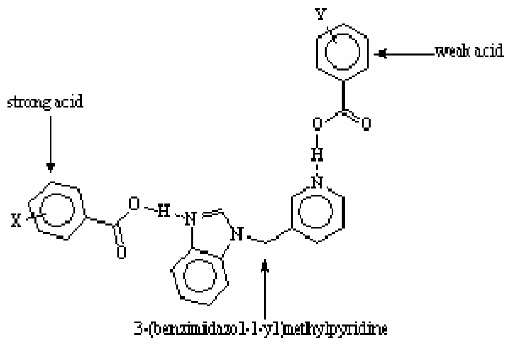


Fig. 1 Ternary supermolecule based on a strong acid, 3-(benzimidazol-1-yl)methylpyridine, and a weak acid.

186. TARGETED SOLID-STATE SUPRAMOLECULAR ASSEMBLIES INVOLVING ANTHRACENE DERIVATIVES. **Tony N. Sokolov**, Tomislav Friscic and Leonard R. MacGillivray; University of Iowa, Iowa City, IA.

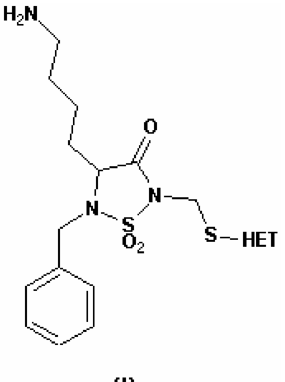
Control of molecular packing in the solid state has important ramifications in synthetic chemistry and material science. Template-directed solid-state synthesis involving linear templates that operate *via* hydrogen bonds has allowed for the modification of molecular packing in the solid state so as to reliably achieve [2+2] photoreactivity in olefinic systems. This approach has permitted access to molecular targets as a [2.2]-*p*-cyclophane and [n]-ladderanes in 100% yield. To extend this approach to olefins of increasing complexity, we now target polycyclic molecules with hydrogen bond acceptor groups. Such targeted assemblies, specifically based on anthracene, could extend the method to properties of polycyclic aromatics (*e.g.*, fluorescence, cycloadditions). We anticipated that linear templates could induce face-to-face arrangements of polycyclic aromatic systems. Our initial results demonstrate the formation of discrete three- and four-component assemblies with 1,8-napthalenedicarboxylic acid and resorcinol-based templates. In these assemblies, we observe anthracenes that adopt both co-planar and twisted arrangements which are based on the choice of hydrogen bond acceptor groups, or “handles”.

187. IMPROVED LOADING AND CLEAVAGE METHODS FOR SOLID-PHASE SYNTHESIS USING CHLOROTRITYL RESINS: SYNTHESIS AND TESTING OF A LIBRARY OF 144 DISCRETE CHEMICALS AS POTENTIAL FARNESYLTRANSFERASE INHIBITORS. **Kevin J. Langenwalter**[1], Jewn Giew Park[1], Yuan-Ping Pang[1], Patrick J. Casey[2] and Carolyn A. Weinbaum[2]; [1]Mayo Clinic College of Medicine, Rochester, MN; [2]Duke University Medical Center, Durham, NC.

The use of chlorotrityl resins for the immobilization of amines is sometimes deterred by the lengthy process of loading the reactants on the resins and product decomposition caused by the reactive chlorotrityl group in the presence of 1% TFA as a cleavage agent. Here, we report improved methods developed for selective and efficient loading of aminobenzoic acid derivatives on chlorotrityl resins and for cleavage of aniline-containing products from the resins without decomposition. These methods led to the synthesis of a library of 144 discrete chemicals as potential farnesyltransferase inhibitors (FTIs) using IRORI's radio-frequency-encoded sorting technique and to the study of the applicability of the bivalence approach to the development of FTIs.

188. INHIBITION OF HUMAN TRYPTASE BY 1,2,5-THIADIAZOLIDIN-3-ONE-1,1-DIOXIDE-BASED HETEROCYCLIC SULFIDES. **Swathi Mohan**[1], Tzutshin Wong[1], Christopher S. Groutas[1], Zhong Lai[1], Kevin R. Alliston[1], Nga Vu[1], Norman M. Schechter[2] and William C. Groutas[1]; [1]Wichita State University, Department of Chemistry, Wichita, KS; [2]University of Pennsylvania, Department of Dermatology, Philadelphia, PA.

Human tryptase (EC 3.4.21.59) is a trypsin-like serine protease that is stored in the cytoplasmic granules of mast cells. Like trypsin, the primary specificity site (S1) of tryptase prefers a basic P1 residue. However, unlike trypsin, tryptase is a tetrameric glycoprotein that is composed of four identical subunits and is only active when complexed to heparin. Upon activation by various stimuli, the mast cells undergo degranulation releasing tryptase, histamine and other secretory products into the extracellular space. The release of tryptase is associated with a range of acute inflammatory processes which include the activation of pre-kallikrein, protease-activated receptor-2 (PAR-2) and tissue remodeling. Tryptase has been implicated in the pathophysiology of asthma and other inflammatory diseases characterized by the recruitment and degranulation of mast cells; consequently, it is a validated target for the development of therapeutic agents for these diseases. We describe herein the results of exploratory studies related to the mechanism-based inhibition of human tryptase by 1,2,5-thiadiazolidin-3-one-1,1-dioxide-based hetero-cyclic sulfide derivatives (**I**). (Financial support of this work by the National Institutes of Health (HL 57788 and AI 45075) is greatly acknowledged).



(I)

189. ISOINDOLIN-1-ONE: A POWERFUL SCAFFOLD FOR THE DESIGN OF POTENT NON-COVALENT INHIBITORS OF SERINE PROTEASES. **Tzu Tshin Wong**[1], Christopher S. Groutas[1], Xiangdong Gan[1], Kevin R. Alliston[1], Laura S. Stevenson[1], William C. Groutas[1] and John R. Hoidal[2]; [1]Wichita State University, Wichita, KS; [2]University of Utah Health Sciences Center, Salt Lake City, UT.

Chronic obstructive pulmonary disease (COPD) is the fourth leading cause of death in the U.S. The symptoms of COPD include a broad range of abnormalities in the lungs, particularly the destruction of lung tissue and other components of the extracellular matrix. The breakdown of lung elastic fibers is effected by a host of proteolytic enzymes that includes neutrophil elastase (HLE), proteinase 3 (PR 3), cathepsin G, cathepsin S and macrophage metalloelastase (MMP-12). Amongst these enzymes, HLE and PR3 share many similarities in terms of their active site topography and primary specificity pocket, hence they have been the most difficult to differentiate with synthetic small molecules and/or peptidyl substrates. The ability to selectively inhibit these enzymes is a crucial issue and may lead to a clear definition of the precise roles HLE and PR3 play in the pathogenesis of COPD. The design, synthesis and *in vitro* biochemical evaluation of selective, noncovalent inhibitors of HLE and PR3 based on the isoindolin-1-one scaffold that exploit the subtle differences in the S' subsites of the two enzymes will be described.

(Financial support of this work by the National Institutes of Health (HL57788, HL 66543 and HL 72903) is gratefully acknowledged).

190. MECHANISM-BASED INACTIVATION OF HUMAN LEUKOCYTE ELASTASE *VIA* AN ENZYME-INDUCED SULFONAMIDE FRAGMENTATION PROCESS. **Xiangdong Gan**, Liuqing Wei, Zhong Lai, Kevin R. Alliston, Jiaying Zhong, Jeff B. Epp, Juan Tu, Asiri B. Perera, Michael Van Stipdonk and William C. Groutas; Wichita State University, Wichita, KS.

We describe herein the design, synthesis and *in vitro* biochemical evaluation of two novel classes of mechanism-based inhibitors of human leukocyte elastase (HLE) that inactivate the enzyme *via* an unprecedented enzyme-induced sulfonamide fragmentation cascade. The inhibitors incorporate in their structure either an appropriately-functionalized saccharin scaffold, or a 1,2,5-thiadiazolidin-3-one-1,1-dioxide scaffold. The inactivation of the enzyme by these inhibitors was found to be efficient, time-dependent and to involve the active site. Biochemical, HPLC and mass spectrometric studies show that the interaction of these inhibitors with HLE results in the initial formation of a Michaelis-Menten complex and subsequent formation of a tetrahedral intermediate with the active site serine (Ser-195). Collapse of the tetrahedral intermediate with tandem fragmentation results in the formation of a highly reactive conjugated sulfonyl imine which can either react with water to form a relatively stable acyl enzyme and/or undergo a Michael addition reaction with an active site nucleophilic residue (His-57). The results also demonstrate convincingly the superiority of the 1,2,5-thiadiazolidin-3-one-1,1-dioxide scaffold over the saccharin scaffold in the design of inhibitors of (chymo)trypsin-like serine proteases. Financial support of this work by the National Institutes of Health (HL 57788) is gratefully acknowledged.

191. MOLECULAR MODELING ON THE ACUTE TOXICITY OF THE ORGANOPHOSPHORUS COMPOUNDS ON THE ACETYLCHOLINESTERASE ENZYME. **Jianxin Guo**[1], Gerald Lushington[1], Margaret M. Hurley[2] and Jeffrey B. Wright[3]; [1]University of Kansas, Lawrence, KS; [2]U.S. Army Research Laboratory, Aberdeen Proving Ground, MD; [3]U.S. Army SBCCOM/Natick Soldier Center, Natick, MA.

The acute toxicity of the organophosphorus compounds (OPs) is derived mainly from the competitive inhibition of the acetylcholinesterase enzyme (AChE) irreversibly by the OPs. Such inhibition causes the accumulation of the acetylcholine and, thus, prevents the nervous system to function properly. The Absorption, Delivery, Metabolism, Excretion (ADME) of the OPs is also important in modeling such toxicity besides the interaction and reaction of the OPs with AChE in the active site. A set of 38 OPs with known acute toxicity data has been used to analysis the factors controlling the process. A good correlation has been found by taking account for the following factors: 1) The metabolism product of the OPs usually has a much more potent inhibition on AChE than their parent compounds unless the OPs interact directly with AChE. An effort has been taken to consider both the parent compounds and the metabolism product as part of the toxicity mechanism. 2) The surface area of OPs is important to the absorption and delivery process; they should be also taken into account. 3) The inhibition of the enzyme mainly by forming the chemical bond between Serine 203 of the enzyme with the Ops; the energy barrier of the reaction is the major factor to be considered for the acute toxicity.

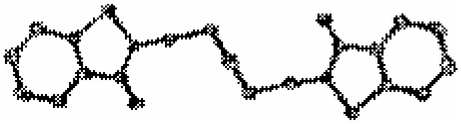
192. SERENDIPITOUS DISCOVERY OF AN UNEXPECTED REARRANGEMENT LEADS TO TWO NEW CLASSES OF POTENTIAL PROTEASE INHIBITORS. **Zhong Lai**[1], Jiaying Zhong[1], Christopher S. Groutas[1], Tzutshin Wong[1], Xiangdong Gan[1], Kevin R. Alliston[1], David Eichhorn[1], John R. Hoidal[2] and William C. Groutas[1]; [1]Wichita State University, Wichita, KS; [2]University of Utah Health Sciences Center, Salt Lake City, UT.

The pathogenesis of a range of human diseases arises from the aberrant activity of proteolytic enzymes. For example, chronic obstructive pulmonary disease (COPD) is a characterized by an influx of macrophages, neutrophils and T lymphocytes to the lungs. Likewise, in asthma, an inflammatory disease of the airways, mast cells, eosinophils and neutrophils are the major effector cells. The recruitment of these cells is accompanied by the extracellular release of pro-inflammatory mediators, including a range of serine, cysteine and metallo- proteases. While many questions remain regarding the precise role that each protease plays in a particular disease state, it is generally believed that selective inhibition of protease associated with inflammatory disease such as COPD (neutrophil elastase, proteinase 3) and asthma (tryptase) may not only lead to new therapeutic agents, but also shed light on the molecular mechanism underlying the pathophysiology of the inflammatory disease. Agents capable of selectively modulating the activity of these enzymes are of potential therapeutic value. Thus, there is a continuing need for the design of scaffolds that can be used in the development of new classes of protease inhibitors. The results of studies related to the serendipitous discovery of two novel templates that can be used in the design of protease inhibitors will be described. Financial support of this work by the National Institutes of Health (HL 57788 to WCG and HL 66543 and HL 72903 to JRH) and Supergen, Inc. is gratefully acknowledged.

193. AMIDE-CONTAINING MODELS FOR NITRILE HYDRATASE.

David M. Eichhorn and **Curtis E. Moore**; Wichita State University, Wichita, KS.

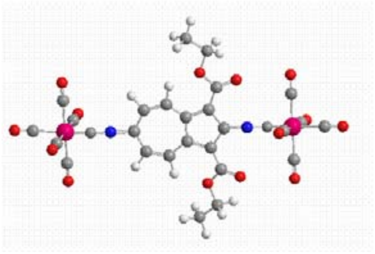
The enzyme nitrile hydratase (NHase), which catalyzes the hydrolysis of organic nitriles to amides, contains a trivalent Fe or Co at its active site with a coordination environment consisting of two amide Ns, three cysteine Ss, two of which have been post-translationally oxidized to sulfinic and sulfenic acid groups and one water ligand. Expanding on our recently reported use of 2,2'-dithiodibenzaldehyde for syntheses of metal complexes containing mixed thiolate/imine coordination environments, we are exploring the use of derivatives of 2,2'-dithiodisalicylic acid for the synthesis of complexes containing mixed thiolate/amide coordination environments as models for the active site of NHase.



194. AZULENE AS A STRUCTURAL AND ELECTRONIC BRIDGE IN ELECTRON-RICH ORGANOMETALLICS.

Edward Weintob[1], Randall E. Robinson[2], Thomas C. Holovics[2], Stephan F. Deplazes[2] and Mikhail V. Barybin[2]; [1]Columbia University, New York, NY; [2]University of Kansas, Lawrence, KS.

An efficient, five-step synthesis of air- and thermally-stable 2,6-diisocyano-1,3-ethoxycarbonyl-azulene from 2-amino-1,3-ethoxycarbonyl-azulene has been established. The ability of this linear, fully conjugated, nonbenzenoid spacer to form a structural and electronic bridge between low-valent transition metal fragments has been demonstrated. Synthetic work as well as spectroscopic and electrochemical data supporting the feasibility of assembling organometallic, multi-stage "molecular batteries" of a novel type will be presented.



195. BIOACTINIDE CHEMISTRY-URANYL INTERACTIONS WITH -DAHK- AND DERIVATIVES. **Huan Huang**, Shveta Chaudhary and J. David Van Horn; University of Missouri-Kansas City, Kansas City, MO.

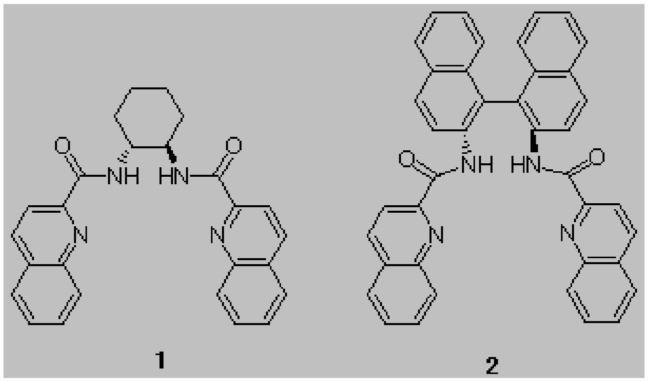
While the adverse effects associated with uranium nephrotoxicity have been well established, researchers have not pinpointed the specific molecular species involved with uranyl(UO_2^{2+}) transport and chemical toxicity *in vivo*. Our laboratory is studying the interaction of the uranyl cation with peptides and proteins. In gas phase, uranyl cation forms 1:1 complexes with peptides, DAHK-$CONH_2$ or GGH. Solution state studies with the same peptides and variants, DGHG, AcDGHG and DAHKSE-$CONH_2$, indicate that peptide-carboxylato donors can coordinate to the uranyl bis-carbonato complex. IR results are consistent with peptide-carboxylato coordination. UV-visible and fluorescence spectra of uranyl carbonate exhibit significant changes or quenching upon addition of peptide. Uranyl carbonate fluorescence quenching experiments show that small amounts of protein (0.1 eq.) can effectively quench the uranyl fluorescence emission.

196. BONDING AND ELECTRONIC PROPERTIES IN THE ZINTL PHASES: THEORETICAL STUDIES OF $EuGe_2$, EuGaGe AND EuZnGe. **Tae-soo You** and Gordon J. Miller; Iowa State University, Ames, IA.

$EuGe_2$ is a so-called Zintl phase compound that shows metallic character instead of typical semiconducting character. To understand the origin of this electronic behavior substituted compounds, EuZnGe and EuGaGe, have been studied in comparison with $EuGe_2$. The electronic structures of $EuGe_2$ and EuZnGe have been conducted using the non-spin-polarized and spin-polarized TB-LMTO (tight-binding, linear muffin-tin orbital) method to find out the relationship between chemical bonding and physical properties. Calculations for EuGaGe are in process. This study focuses on the differences in orbital interactions between the Ge-Ge bond in $EuGe_2$ and the Zn-Ge bond in EuZnGe using DOS (densities of states) and COHP (crystal orbital Hamilton populations). Results from spin-polarized calculation analysis are also shown.

197. CHIRAL BIS(QUINALDINECARBOXAMIDE) LIGANDS FOR HELICAL COMPLEXES. **Dipesh Prema**; Kansas State University, Manhattan, KS.

New nis(quinaldinecarboxamide) ligands have been synthesized by the condensation of quinaldic acid with (1R,2R)-diaminocyclohexane or (S)-2,2'-diamino-1,1'-binapthalene in the presence of triphenylphosphite. The resulting ligands, **1** and **2**, can be metallated with iron(II) trifalte and chloride salts with or without base to give air sensitive paramagnetic complexes. Work is being done to elucidate crystal structures of these compounds.



198. CHROMIUM(III) BIOCOORDINATION CHEMISTRY: MODELS AND REACTIONS. **J. David Van Horn**[1], Shveta Chaudhary[1], Vincent Morrissette[1], Deendayal Dinakarpandian[1] and Brian Bennett[2]; [1]University of Missouri-Kansas City, Kansas City, MO; [2]Medical College of Wisconsin, Milwaukee, WI.

While Cr(III) is generally considered to be a trace essential nutrient, researchers have yet to elucidate a molecular level action for this transition metal[1]. Because of the potential importance of Cr to human health and disease in areas such as Type 2 Diabetes and obesity, good working models of *in vivo* Cr action are of critical importance and concern. Recent efforts have pointed to Cr peptide complexes (glutathione or a "Low molecular weight Cr" binding peptide, LMWCr) as potential species for transport and interaction with components of the insulin signaling pathway[1,2]. Here, we present a new model for the role of chromium in the insulin signaling pathway[3] based on insulin pathway mapping, a genomic database search and the synthesis of Cr-peptide complexes. Further, the kinetic stability of trinuclear Cr clusters (thought to play a role in Cr(III) biochemistry) has been studied as well as other Cr(III) biocoordination chemistry.

1. A. Levina, R. Codd, C. T. Dillon and P. A. Lay, *Prog. Inorg. Chem.* 2002, **51**, 145-250.
2. J. B. Vincent, *Acc. Chem. Res.* 2000, **33**, 503-510.
3. P. De Meyts and J. Whittaker, *Nature Rev.* 2002, **1**, 769-783.

199. CLUSTERS FORMED FROM THE REACTIONS OF GLYCOLIC ACID WITH COMBINATIONS OF SODIUM MOLYBDATE, SODIUM TUNGSTATE AND SODIUM HYDROGEN PHOSPHATE: CRYSTAL STRUCTURES AND ORGANIC PRODUCT ANALYSIS. **T. Adrian George**, David N. Kirk, Charles R. Ross II, Tom J. Brett, Patrick J. D. Kennedy and John J. Stezowski; University of Nebraska-Lincoln, Lincoln, NE.

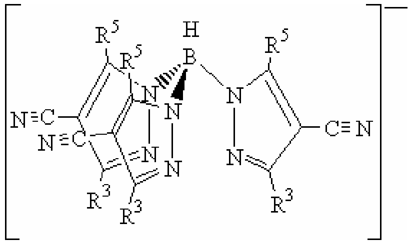
Heating an intimate 1:2 molar mixture of Na_2MoO_4 and glycolic acid gave a red tar that is water soluble. Addition of $[n\text{-}Bu_4N]Br$ afforded red crystals of $[n\text{-}Bu_4N]_4\{Mo_4O_8(C_2H_2O_3)_2[MoO_3(C_2H_2O_3)]_2\}$, **1**. The anion structure is based on the well-known compact $[Mo_4O_8]$ framework. All four dianionic glycolate ligands are multidentate: two are tridentate and are part of the framework and two are bidentate and are coordinated to the six-coordinate terminal Mo(VI) atoms. In this reaction, glycolic acid is acting as a ligand and a reducing agent; the oxidation product glyoxalic was determined quantitatively. No oxalic acid or CO_2 were detected. Occasionally, from this reaction yellow-orange crystals of $[n\text{-}Bu_4N]_4[Mo_4O_8(C_2H_2O_3)_2(MoO_4)_2]$, **2**, were obtained. The anion structure is based on the same $[Mo_4O_8]$ framework but differs from the anion of **1** in having terminal bidentate MoO_4 in place of $[MoO_3(C_2H_2O_3)]$. Although no reaction occurred between glycolic acid and Na_2WO_4, a reaction did occur with a mixture of Na_2MoO_4 and Na_2WO_4. Red crystals of $[n\text{-}Bu_4N]_4\{Mo_4O_8(C_2H_2O_3)_2[WO_3(C_2H_2O_3)]_2\}$, **3**, were obtained and studied by electrospray mass spectrometry and X-ray diffraction. Within each single crystal of **3** are cocrystallized $[n\text{-}Bu_4N]_4\{Mo_4O_8(C_2H_2O_3)_2[WO_3(C_2H_2O_3)]_2\}$, $[n\text{-}Bu_4N]_4\{Mo_4O_8(C_2H_2O_3)_2[MoO_3(C_2H_2O_3)][WO_3(C_2H_2O_3)]\}$ and **1**. In all the mixed-metal complexes, only Mo is found in the $[M_4O_8]$ framework. From the reaction of glycolic acid with a mixture of Na_2MoO_4 and Na_2HPO_4, crystals of the hydrated sodium salt of $[Mo_6P_4O_{24}(OH)_7]^{5-}$ were obtained. Within the crystal structure sodium ions adopt a number of unusual arrangements, including linear chains of four sodium ions. Structural interrelationships will be discussed.

200. COMPUTATIONAL AND SPECTROSCOPIC STUDIES OF Re(I) BIPYRIDYL COMPLEXES CONTAINING 2,6-DIMETHYLPHENYLISOCYANIDE LIGAND. Stanislav R. Stoyanov, John M. Villegas and **D. Paul Rillema**; Wichita State University, Wichita, KS.

Density Functional Theory (DFT) calculations produce optimized geometries of the complexes $[Re(CO)_3(bpy)Cl]$ (**1**), $[Re(CO)_3(bpy)(py)](CF_3SO_3)$ (**2**), $[Re(CO)_3(bpy)(CN_x)](CF_3SO_3)$ (**3**) and $[Re(CO)(bpy)(CN_x)_3](CF_3SO_3)$ (**4**), where bpy = 2,2'-bipyridine, py = pyridine and CN_x = 2,6-dimethylphenylisocyanide in their ground and lowest-lying triplet-states. The complexes exhibit emission both at room temperature and at 77 K except **4** which is only emissive at 77 K. The 77 K emission lifetimes range from 3.9 μs for **1** to 8.8 μs for **3**. The emissive lowest-lying triplet-state is a triplet metal-ligand-to-ligand charge transfer (^{3}MLLCT) state for complexes **1**, **2** and **3** but a ^{3}LMCT state for complex **4**. The electronic, electrochemical, thermodynamic, HOMO-LUMO and emitting state energy gaps as well as the emission lifetimes increase in the order **1** < **2** < **3**. A ^{3}d-d excited state, located above the ^{3}LMCT state, accounts for the loss of room temperature emission for complex **4**.

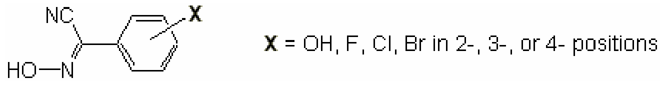
201. CYANOSCORPIONATE LIGANDS AND METAL COMPLEXES. David M. Eichhorn and **Peter Zhao**; Wichita State University, Wichita, KS.

Scorpionate ligands have been used for almost 40 years as monoanionic chelating ligands for transition metals. We recently reported the syntheses and metal complexation of scorpionate ligands containing CN substitution at the 4-position of the pyrazole ring. We are exploring these complexes as precursors for the synthesis of organic/inorganic polymeric materials which may display interesting electronic or magnetic properties. We report herein our progress in this area.



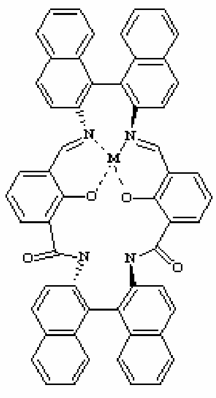
202. DESIGN OF NEW TYPES OF METAL-ORGANIC NETWORKS FOR ONE-DIMENSIONAL MIXED-VALENCE COORDINATION POLYMERS. **Daniel Robertson**[1], Nikolay Gerasimchuk[1], John F. Cannon[2] and Charles Barnes[3]; [1]Southwest Missouri State University, Springfield, MO; [2]Brigham Young University, Provo, UT; [3]University of Missouri-Columbia, Columbia, MO.

A series of 12 monosubstituted arylcyanoxime ligands shown below has been synthesized using nitrosation of respective substituted phenylacetonitriles by freshly prepared alkylnitrites at basic conditions (Meyer reaction) in *n*-propanol at room temperature and under an inert gas protection. Obtained organic compounds represent weak organic acids that were characterized by means of IR, UV-visible and NMR ^{1}H, ^{13}C spectroscopy, mass-spectrometry and x-ray analysis (four ligands). Reaction of hot aqueous solutions of Thallium(I) carbonate with protonated solid cyanoximes HL quantitatively leads to a formation of yellow-orange needles of TlL. Identity of formed coordination complexes was established by elemental analyses and spectroscopic methods. Crystal structures of several Tl(I) complexes were determined and it was found that they represent centrosymmetric dimeric compounds having general formulas Tl_2L_2. Dimeric units connected with each other *via* oxygen atom of the NO-forming ruffled Tl_2O_2 one-dimensional coordination polymers that comprised of rhombic sheets. Metal-metal distances in complexes are close to that in metallic thallium. Interactions between aqueous solutions of silver(I) nitrate and Na-salts of the above cyanoximes also resulted in quantitative precipitation of AgL complexes. Complexes of AgL composition represent three-dimentional coordination polymers of different complexity also with bridging acidoligands. Cyanoxime anions in Tl(I) complexes are in the oxime-form, while in Ag(I) complexes ligands are in the nitroso form and are planar contrary to their structures in protonated oximes HL. Synthesis of mixed valence Tl(I)/Tl(III) coordination polymers is discussed.

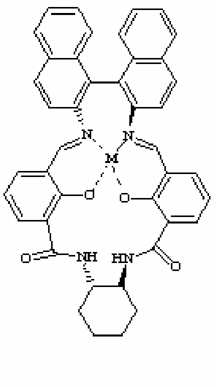


203. DESIGN OF “TWISTED” MACROCYCLES. **Azadeh Lalehzari** and Christopher J. Levy; Kansas State University, Manhattan, KS.

Asymmetric macrocyclic complexes have lately been of a great interest due to their potentials of catalyzing asymmetric oxidation reactions. By insertion of four chiral centers in these systems, well-defined macrocyclic complexes with high barriers to conformational flipping can be achieved. This conformational “locking” can be the key to a better, cleaner and more applicable asymmetric oxidation. Presented here are the synthesis of the two highly-twisted, chiral complexes **1** and **2**. The diamide precursors are easily synthesized by condensing 3-formylsalicylic acid with (R,R)-bi(2-naphthylamine) and (1R,2R)-diaminocyclohexane, respectively. After diamide formation, a simple Schiff-base condensation with (R,R)-bi(2-naphthylamine) will form the chiral macrocycle. Metalation gives the final twisted complex.



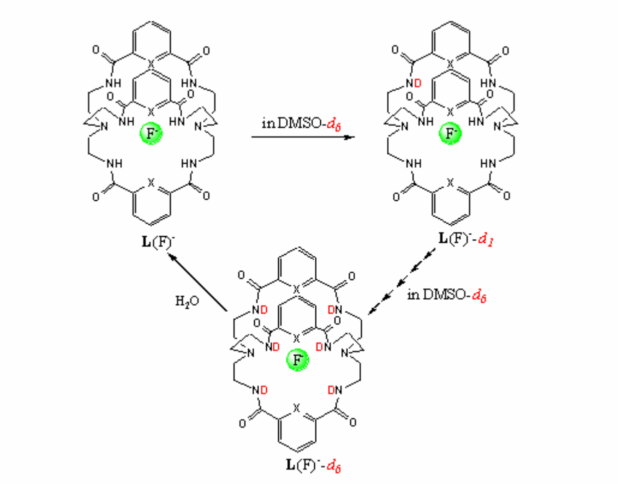
1



2

204. DEUTERIUM EXCHANGE FROM DMSO-d_6 TO POLYAMIDE CRYPTANDS. **Sung Ok Kang**, David VanderVelde, Douglas Powell and Kristin Bowman-James; University of Kansas, Lawrence, KS.

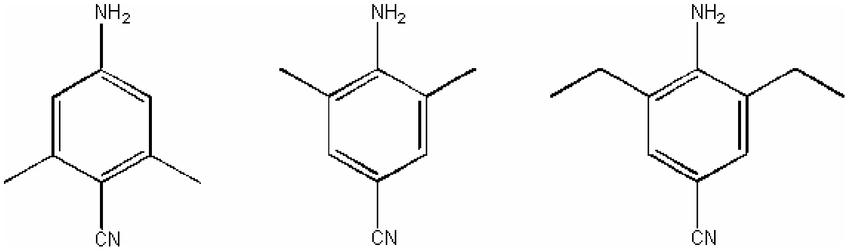
Recently we have been reporting the new class of anion receptors probing the effects of dimensionality and preorganization in pursuit of strong and selective binding receptors of anions in supramolecular chemistry. ^{19}F NMR of these anion receptors with fluoride anions display interesting binding behavior in DMSO-d_6. Both crystal structures of solid state and ^{19}F NMR studies of solution structures with these polyamide cryptands will be discussed.



205 ELECTROCHEMICAL STUDIES AND FUNCTIONALIZATION OF POLYOXOMETALATES. **Kristopher Mijares** and Eric A. Maatta, Kansas State University, Manhattan, KS.

It is now possible to synthesize many modified polyoxometalates in which their terminal oxo $[O]^{2-}$ ligands have been replaced with electronically similar entities such as hydrazido $[NNR_2]^{2-}$, organoimido $[NR]^{2-}$ and diazoalkane $[NNCR_2]^{2-}$ ligands. The close resemblance between oxo and nitrido $[N]^{3-}$ ligands, in terms of bonding to a metal site *via* one *sigma* and two *pi*-type orbitals makes nitrido-substituted polyoxometalates attractive targets. We will present recent results from our synthetic and electrochemical studies of modified Keggin-type heteropolyanions incorporating $[Os(VI)N]^{3+}$ units.

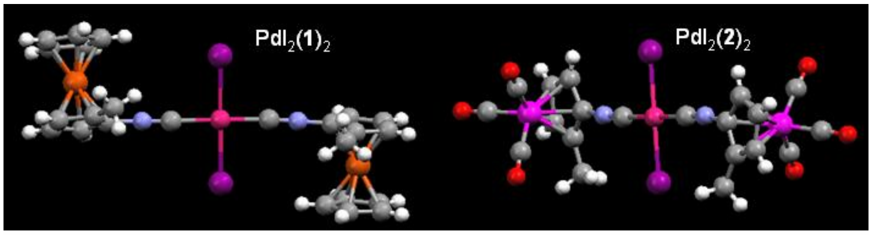
We will also present results on the syntheses of various substituted cyano-anilines, such as those shown below. We intend to use these species to prepare new types of organoimido-functionalized polyoxometalates by metathetical reactions of their phosphine-imine derivatives.



206. FIRST PLANAR-CHIRAL ISOCYANIDES. **Stephan F. Deplazes**, Thomas C. Holovics and Mikhail V. Barybin; University of Kansas, Lawrence, KS.

Recently, we reported on the chemistry of isocyanoferrocene, $(CNC_5H_4)Fe(C_5H_5)$, and isocyanocymantrene, $(CNC_5H_4)Mn(CO)_3$ and demonstrated that electronic properties (especially π-acidity) of the isocyanocyclopentadienide ligand can be tuned to a substantial extent by varying the nature of the metal fragment bound to its ring.[1] This presentation will describe syntheses and properties of $({}_{p}S)$-1-isocyano-2-methyl-ferrocene (**1**) and $({}_{p}S)$-1-isocyano-2-methyl-cymantrene (**2**), which represent the only examples of planar-chiral isocyanides isolated to date. The Figure below illustrates X-ray crystal structures of the adducts of **1** and **2** with PdI_2. Various applications of planar-chiral isocyanides in organometallic chemistry will be discussed.

1. Barybin *et al. Organometallics* 2004, **23**, 2927-2938.



207. HIGHLY PHOSPHORESCENT IRIDIUM COMPLEXES: SYNTHESIS AND USE IN ORGANIC LIGHT-EMITTING DIODES. **Betty Marie Jennifer Paulose** and Chien-Hong Cheng; National Tsing Hua University, Hsinchu 300, Taiwan.

Organic light-emitting diodes (OLEDs) are currently an active area of research due to their potential application in flat panel displays. Electroluminescent materials incorporating complexes of heavy metals are particularly interesting due to their extremely high efficiencies as electroluminescent emitters. Our interest in the design of new organic ligands for iridium complexes to achieve great efficiency and color purity for OLEDs has led us to the synthesis of a series of 2-alkenylpyridines. The synthesis of these new ligands, the preparation of the corresponding iridium complexes and the application of these complexes in OLEDs will be discussed.

208. HYBRID MOLECULAR DUMBBELLS OF TWO POLYOXOMETALATE CLUSTERS BRIDGED WITH AN ORGANIC CONJUGATED ROD. **Meng Lu**, Baohan Xie, Jeonghee Kang and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO.

Recently, attention has been paid to hybrid materials of covalently-linked polyoxometalates (POMs) and conjugated organic components. It would be interesting to investigate the electron interactions between the POMs and organic moiety of these materials. Here we report the first hybrid dumbbells in which two different clusters (one $[Mo_6O_{19}]^{2-}$ and one $[MoW_5O_{19}]^{2-}$) are covalently bridged with a rigid, π-conjugated organic rod. The redox properties of this hybrid dumbbell were studied by cyclic voltammetry, indicating that electrons could transfer from one cluster to the other through the conjugated organic bridge. It has also been characterized using ^{1}H-NMR, FT-IR, UV-Visible and Mass spectroscopy (ESI-APCI).

209. INVESTIGATION OF THE ELECTRONIC STRUCTURE OF PENTA- AND HEXACOORDINATED FERRIC HIGH SPIN (S=5/2) HEME PROTEINS BY ^{13}C NMR. **Aileen Y. Alontaga** and Mario Rivera; University of Kansas, Lawrence, KS.

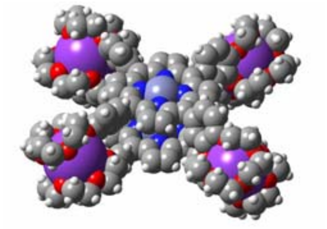
The electronic structure and coordination state of the iron center of high spin (S=5/2) ferric heme proteins has been investigated by ^{13}C NMR spectroscopy. Sperm whale H64V mutant, and the wild type forms of sperm whale and horse heart metmyoglobin, have been used as penta- and hexacoordinate heme proteins, respectively. To overcome the low natural abundance of ^{13}C, heme selectively labeled with ^{13}C was reconstituted into the appropriate apomyoglobin. For both high spin (S=5/2) penta- and hexa-coordinated metmyoglobins, where all the d-orbitals are half-occupied, α and β delocalization is expected. The NMR spectra revealed that the ^{13}C chemical shifts of the pyrrole carbon *alpha* and *beta* of both penta- and hexa-coordinate metmyoglobins experience direct *sigma* spin delocalization, which results in downfield resonances (960 - 1500 ppm) due to the $d_{x}2_{-y}2$ orbital being half-filled. Interestingly, the meso ^{13}C chemical shifts are important indicators of the coordination state of the iron. The meso ^{13}C chemical shifts of the mutant are found between 230 and 312 ppm. In contrast, the hexacoordinate metmyoglobins exhibit high field shifts between -90 and -40 ppm. The change in sign of the meso ^{13}C revealed that there is a positive and negative β spin density at the meso carbons of penta- and hexacoordinate heme proteins, respectively, due to the unpaired electrons in the β orbitals. In addition, the ^{13}C methyl shifts of the penta- and hexacoordinate heme proteins are almost identical, suggesting that these carbons are not affected by β-bonding interactions.

210 INVESTIGATIONS ON METALLOPORPHYRIN DIMERS FORMED BY CATION COMPLEXATION OF CROWN ETHER CAVITIES.

Raghu Chitta, Lisa M. Rogers, Amber Wanklyn, Paul A. Karr, Pawan K. Kahol, Melvin E. Zandler and Francis D'Souza; Wichita State University, Wichita, KS.

The effect on the electrochemical oxidation and reduction potentials of 5,10,15,20-tetrakis(benzo-15-crown-5) porphyrin (TCP) and its metal derivatives (MTCP; M = Mg(II), VO(IV), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Ag(II)) upon potassium ion-induced dimerization of the porphyrins was systematically performed in benzonitrile containing 0.1 M (TBA)ClO_4 by differential pulse voltammetry technique. The HOMO-LUMO energy level diagram constructed from the electrochemical data revealed destabilization of the HOMO level and stabilization of the LUMO level upon dimer formation while such a perturbation was larger for the HOMO level than the LUMO level.[1] The geometry and electronic structure of a representative ZnTCP and its dimer, $K_4(ZnTCP)_2$ were evaluated by the *ab initio* B3LYP method utilizing a mixed basis set of 3-21G(*) for Zn, K, O, N and STO-3G for C and H. The inter-porphyrin ring distance of the dimer calculated from the optimized geometry agreed with the spectroscopically determined one and the calculated HOMO and LUMO frontier orbitals revealed delocalization on both of the porphyrins rings. The metal-metal distances calculated from the triplet ESR spectra of the porphyrins bearing paramagnetic metal ions in the cavity followed the trend: Cu-Cu < VO-VO < Ag-Ag. However, the spectral shifts resulting from the exciton coupling of the interacting porphyrin *pi*-systems revealed no specific trend with respect to the metal ion in the porphyrin cavity. Additionally, linear trends in the electrochemically-measured HOMO-LUMO gap and the energy corresponding to the most intense visible band of both MCP and $K_4(MCP)_2$ were observed. A reduced HOMO-LUMO gap predicted for the dimer by B3LYP/(3-21G(*), STO-3G) calculations was confirmed by the results of optical absorption and electrochemical studies.

1. Chitta, R., Rogers, L. M., Wanklyn, A., Karr, P. A., Kahol, P. K., Zandler, M. E. and D'Souza, F. *Inorg. Chem.* 2004, in press.

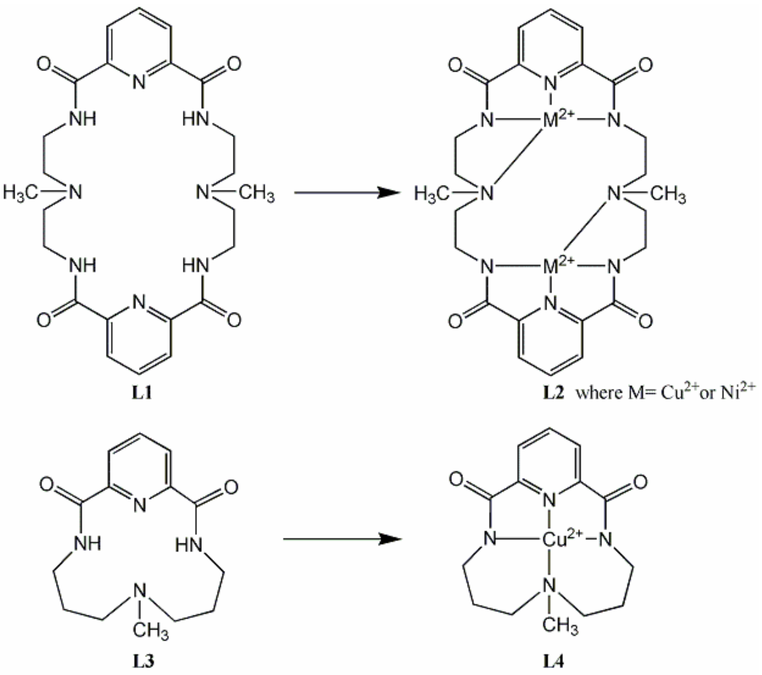


211. MODEL COMPLEXES FOR THE A-CLUSTER OF CODH/ACS. David M. Eichhorn and **Joshua Zimmerman**; Wichita State University, Wichita, KS.

The A-cluster of the enzyme CO Dehydrogenase/Acetyl CoA Synthase is responsible for catalyzing the assembly of Acetyl CoA from CoA, CO and a methyl group delivered by a corrinoid Fe/S protein. The A-cluster contains an Fe-S cubane bridged by a cysteine thiolate to a dinuclear M(μ-S)$_2$M' cluster in which M' is Ni and M is believed to be either Ni or Cu. We are using 2,2'-dithiodibenzaldehyde to synthesize model complexes for the dinuclear portion of this cluster.

212. NEW VERSATILE ANIONIC AND CATIONIC MACROCYCLIC RECEPTORS. **Jerry A. Kut**, Rowshan A. Begum, Sung-Ok Kang, Douglas R. Powell and Kristin Bowman-James; University of Kansas, Lawrence, KS.

Bowman-James and co-workers have recently reported the synthesis and anion binding studies of a pyridine mixed amine/amide macrocyclic receptor, **L1**. Although the area of anion recognition is an important area of chemistry, there is a growing interest in our group in utilizing these types of macrocycles to study the formation of metal complexes for potential catalytic applications. We have performed exploratory studies with the 2+2 pyridine macrocyclic tetraamide **L1** and a 1+1 pyridine macrocyclic diamide **L3**. **L1** has been shown to form both dimeric copper and nickel complexes, **L2**, whereas **L3** forms a monomeric copper complex, **L4**. Synthesis, X-ray crystallographic structures, UV-vis, EPR and magnetic susceptibility will be reported for this new family of macrocyclic metal complexes.



L1

L2 where M= Cu^{2+} or Ni^{2+}

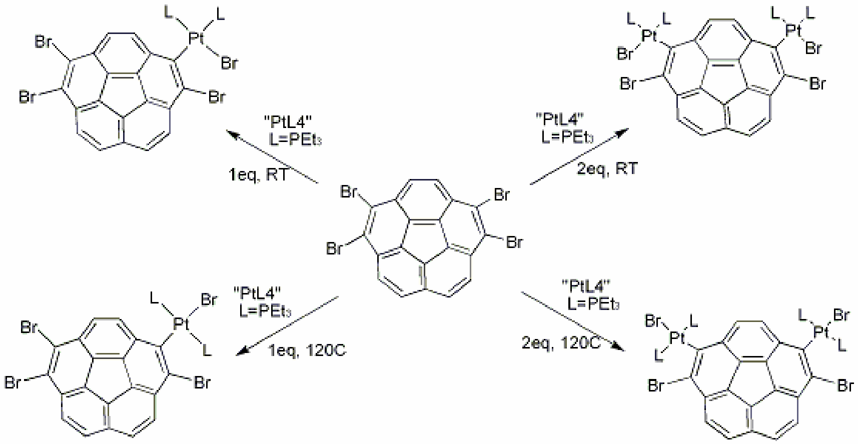
L3

L4

213. NICKEL AND PLATINUM CORANNULENE DERIVATIVES. **Han Baek Lee** and Paul R. Sharp; University of Missouri, Columbia, MO.

Corannulene ($C_{20}H_{10}$), polycyclic aromatic hydrocarbons (PAHs) is a bowl-shaped fullerene fragments. Recently much effort has been into the synthesis of metal-complexed fullerene and the related carbon clusters. In this fashion, transition metal chemistry of corannulene has aroused a great deal of interests due to improvements in the synthesis of corannulene. A variety of metal (Ru, Ir, Rh, Re) derivatives of corannulene have been prepared[1]; all these cases were coordinated to the surface through the π-bonding. However, corannulene derivatives with a transition metal complexed in a σ-fashion are rare. Here, we report the first complexes with transition metal directly bonded to the edge of corannulene derivatives.

1. (a) Seider, T. J., Baldridge, K. K., O'connor, J. M. and Siegel J. S. J. *Am. Chem. Soc.* 1997, **119**, 4781-4782 (b) Alvarez, C. M., Angelici, R. J., Sygula A., Sygula, R. and Rabideau, P. W. *Organometallics*, 2003, **22**, 624-626 (c) Petrukhina, M. A., Andreini, K. W., Mack J. and Scott, L. T. *Angew. Chem. Int. Ed.* 2003, **42**, 3375-3379 (d) Chin, R. M., Baird, B., Jarosh, M., Rassman, S., Barry, B. and Jones, W. D. *Organometallics*, 2003, **22**, 4829-4832



Scheme 1

214. NITRIDO FUNCTIONALIZED POLYOXOMETALATES. **Louis M. Wojcinski II**[1], Sean Tomlinson[1], Christopher G. Hamaker[2] and Eric A. Maatta[1]; [1]Kansas State University, Manhattan, KS; [2]Illinois State University, Normal, IL.

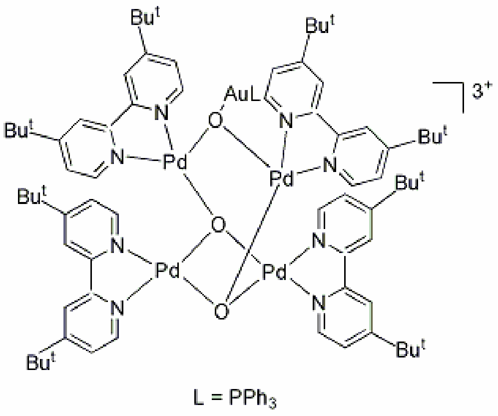
The nitrido and imido derivatives of several high valent transition metals, especially Cr(V) and Mn(V), have shown promise as intermediates in nitrene transfer reactions. We have begun studies focused on the synthesis of Mn(V) nitrido and imido functionalized Wells-Dawson and Keggin lacunary polyoxotungates. These Mn(V) substituted polyoxometallates are prepared *via* the photolytic oxidation of the corresponding Mn(III) azido and imido polyoxoanions. This paper discusses the synthetic methodologies used to prepare these materials and the spectroscopic studies of the products.

215. Pd AND Pt OXO CHEMISTRY SUPPORTED BY DI-*TERT*-BUTYLBIPYRIDINE.

Anupam Singh and Paul R. Sharp; University of Missouri-Columbia, Columbia, MO.

During the past two decades, much attention has been devoted towards late transition metal complexes containing metal oxygen bonds, which play an important role in the development of various catalytic processes and in biological systems[1]. Oxygen and nitrogen species bound to metals are usually involved in these reactions[2]. Because of the high reactivity of M-O bonds, our current efforts are in studying the syntheses and reactivity of these complexes. Herein, we describe the syntheses and characterization of binuclear and tetranuclear palladium and platinum oxo complexes (**1**, **2** & **3**) obtained by the reation of di-*tert*-butylbipyridine palladium dichloride with $[(AuL)_3O]^+$(L = PPh_3) in 1:1 and 4:3 ratio in CH_2Cl_2 respectively. We have successfully isolated first tetranuclear Palladium (II) oxo complex (**3**) bearing di-*tert*-butylbipyridine ligand.

1. R. H. Holm and E. L. Solomon, *Chem. Rev.* 2004, **104**, 347.
2. (a) J. R. Monnier, J. L. Stavinoha and G. W. Hartley, *Journal of Cataly-sis* 2004, **226**, 321. (b) J. Kim, H. Zhao, C. Panja, A. Olivas and B. E. Koel, *Surface Science* 2004, **564**, 53.(c) X.-C.Guo and R. J. Madix, *Surface Science* 2004, **564**, 21.



216. $RE_{2-x}Fe_4Si_{14-y}$ (RE = Y, Gd, Er, Tm, Yb) INTERGROWTH STRUCTURES: STRUCTURAL MODELS, PROPERTIES AND ELECTRONIC STRUCTURE.

Mi-kyung Han and Gordon J. Miller; Iowa State University, Ames, IA.

New ternary rare-earth iron silicides $RE_{2-x}Fe_4Si_{14-y}$ (RE = Y, Gd, Er, Yb, Tm) were synthesized by arc-melting the elemental components and high temperature annealing. These compounds crystallize in the hexagonal system with *a* ≈ 0.39 nm, *c* ≈ 1.53 nm. The structures are built up of rare-earth silicide planes with approximate compositions ‘”$E_{1.2}Si_{1.9}$” alternating with β-$FeSi_2$-derived slabs. Figure 1 shows the structure viewed along the *b* axis. The rare-earth silicide sheets show intrinsic disorder of RE and Si atoms due to interatomic distance constraints. Investigation by transition electron microscopy reveals a superstructure in the crystallographic *ab*-plane. Magnetic susceptibility suggests no magnetic coupling between rare-earth elements and resistivity measurements indicate poor metallic behavior with a large residual resistivity at low temperatures (consistent with disorder). TB-LMTO-ASA electronic structure calculations show the Fermi level falls at a pseudogap in the densities of states.

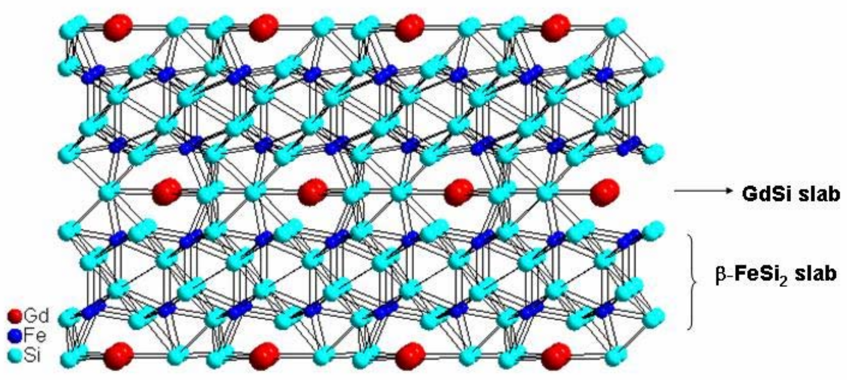


Figure 1. View of $RE_{2-x}Fe_4Si_{14-y}$ along the b axis.

217. REDUCTION OF THE FERROUS α-VERDOHEME-CYTOCHROME *B*$_5$ COMPLEX. **Christopher O. Damaso**[1], Nick D. Rubie[2], Pierre Moënne Loccoz[2] and Mario Rivera[1]; [1]The University of Kansas, Lawrence, KS; [2]OGI School of Science and Engineering at OHSU, Beaverton, OR.

α-Verdoheme is an important intermediate in the degradation of heme carried out by the enzyme heme oxygenase (HO) in mammals and in most pathogenic bacteria. Despite its physiological importance, the chemistry of verdoheme has received little attention. To explore its properties, ferrous-α-verdoheme-cytochrome b_5 complex, $[Fe^{II}$(verdoheme)$]^+$, has been prepared and characterized spectroscopically. Anaerobic reduction of excess dithionite to $[Fe^{II}$(verdoheme)$]^+$ at pH 10 produces a one-electron-reduced species suggested spectroscopically as ferrous hexacoordinated verdoheme π radical which is best represented as $[Fe^{II}$(verdoheme•)] ↔ $[Fe^{I}$(verdoheme)] resonance hydrid. At lower pH values (7.0 and 8.0), the one-electron-reduced species disproportionates to produce the resting state complex, $[Fe^{II}$(verdoheme)$]^+$ and the two-electron-reduced anion which may exist as $[Fe^{II}$(verdoheme:)$]^-$ ↔ $[Fe^{I}$(verdoheme•)$]^-$. The disproportionation reaction becomes very slow as the pH is raised above 9.0. Exposure of the one-electron-reduced and two-electron-reduced complexes of cytochrome b_5 to dioxygen results in fast and quantitative reoxidation to the resting state $[Fe^{II}$(verdoheme)$]^+$ complex.

218. STRUCTURAL REINVESTIGATION ON BINARY Ga-Mn AND CRYSTALLOGRAPHIC AND MAGNETIC STRUCTURAL INVESTI-GATIONS ON TERNARY Ga-Cr-Fe COMPOUNDS. **Hyunjin Ko**; Iowa State University of Science and Technology, Ames, IA.

Transition metal gallides were prepared by a high-temperature solid-state reaction in evacuated sealed silica tubes and their crystalline structures were characterized. From the X-ray single crystal and powder diffraction experiments, a trigonal distortion of the cubic γ-brass structure is observed for Ga_xMn_{1-x} compounds in the range of $0.36 \leq x \leq 0.375$ (a = 12.7082 Å, c = 15.6105 Å). Also, an isoelectronic compound, $GaFe_{0.5}Cr_{0.5}$, was prepared and studied to have a similar structure as the binary Ga-Mn compound (a = 12.5504 Å, c = 7.8637 Å). For better understanding of the site preference of the transition metals, possible magnetic model structures with different spin orientations were investigated from a theoretical perspective.

219. SYNTHESIS AND CHARACTERIZATION OF Au-Ge COMPLEXES. **Anandhi Upendran** and Paul R. Sharp; University of Missouri, Columbia, MO.

Au clusters supported on electropositive element (EP) oxide surfaces are known to be highly-catalytically active. Further, molecular species with discrete gold-germanium bonds are a new class of bimetallic compounds relevant for a variety of devices with interfaces between gold conductors and germanium-based semiconductors. The synthesis and characterization of simple model complexes will provide a fundamental understanding of gold cluster bonding to oxygen centers and electropositive elements. Studies on compounds containing direct metal-metal bonds between gold and heavier group 14 elements are rare in literature. Herein we report a series of Au-Ge complexes formed by the reaction of LAuCl with $GeNR_2$ (L = PPh_3, $P(Cy)_3$, PEt_3) with $GeNR_2$ (R = $SiMe_3$). The synthesis, characterization and reaction chemistry of the new complexes will be described in detail.

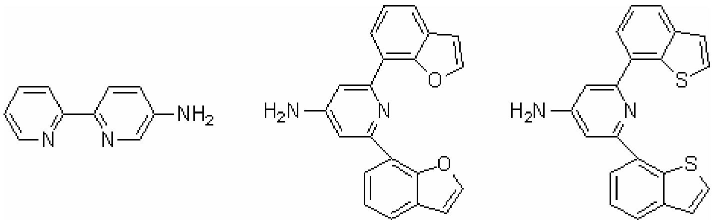
$$\text{LAuCl} + \text{GeN(SiMe}_3)_2 \xrightarrow{\text{Toluene, R.T.}} \text{LAuGe(Cl)N(SiMe}_3)_2$$

$$\text{L} = \text{PPh}_3, \text{P(Cy)}_3, \text{P(Et)}_3$$

220. SYNTHESIS OF NEW FUNCTIONALIZED POLYOXOMETALATES. **Jeffery D. Karcher** and Eric A. Maatta; Kansas State University, Manhattan, KS.

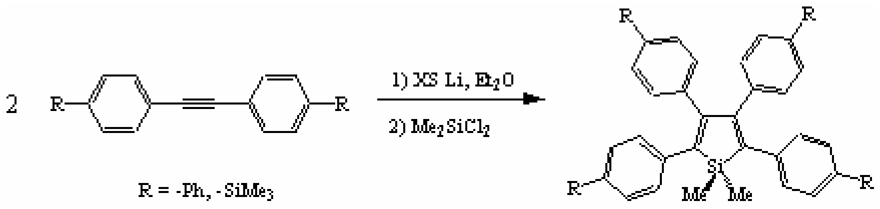
Several new classes of polyoxometalates (POMs) have emerged in which one or more terminal oxo $[O]^{2-}$ ligands have been replaced by isoelectronic entities, including organoimido $[N\text{-}R]^{2-}$, diazoalkane $[NNCR_2]^{2-}$, and nitrido $[N]^{3-}$ ligands. In the case of the hexamolybdate ion $[Mo_6O_{19}]^{2-}$, one convenient method for the systematic introduction of a variety of organoimido ligands involves metathetical oxo/imido exchange using a phosphineimine $R_3P{=}NR'$ as the organoimido delivery reagent; such reactions produce an imido-hexamolybdate $[Mo_6O_{18}(NR')]^{2-}$ and a phosphine oxide $R_3P{=}O$.

We are interested in expanding the range of functionality capable of being incorporated into these organoimido-POMs to include new types of multi-dentate metal-binding sites. We will present results of our synthetic studies on a variety of new phosphineimines and their amino precursors such as the systems shown below.



221. TOWARD THE SYNTHESIS OF NOVEL 2,3,4,5-TETRAARYL-SILOLES. **Barrett E. Eichler**, Amy E. Brown, Jill A. Webster, Christopher D. Thomas and M. Steven McClain; Northwest Missouri State University, Maryville, MO.

Siloles (1-*sila*-cyclopenta-2,4-dienes) have received much interest recently as potential conducting and light-emitting materials. 2,3,4,5-Tetraphenylsilole has been extensively studied in recent years because of the ease of synthesis from readily available diphenylacetylene. A series of symmetric diarylacetylenes have been synthesized and reduced with lithium metal as per the tetraphenylsilole synthesis.



222. FIRST-PRINCIPLES OPTICAL CROSS-SECTIONS FOR SINGLE-WALLED CARBON NANOTUBES. **S. L. Elizondo**[1], Shagoto Nandi[2] and J. W. Mintmire[1]; [1]Oklahoma State University, Stillwater, OK; [2]Boston University, Boston, MA.

Using a first-principles local-density functional (LDF) method, theoretical calculations for the optical absorption properties of single-walled carbon nanotubes are carried out. Our motivation is influenced by recent interests in utilizing optical absorption and Raman data to characterize the structure of individual carbon nanotubes. Bachilo, *et. al*. report results from a spectrofluorimetric study, in which first and second van Hove optical transitions are measured for various nanotube species and then assigned to specific (n,m) nanotube structures[1]. In interpreting the data, the ratio of optical excitation to emission energies is plotted for each peak versus the peak's excitation wavelength and they state that the result qualitatively resembles findings from an extended tight-binding model calculation[2]. It is from this comparison, along with supplementary Raman spectra analysis, that the particular assignments are made. It is essential to note that the extended tight-binding model neglects polarization effects. Previous work revealed that the optical response for polarizations parallel to the nanotube axis differs from the optical response for polarizations transverse to the nanotube axis[3]. In this work, first-principles LDF calculations are implemented to examine the optical cross-sections of specific nanotubes, taking into account the effect of polarization. In conclusion, we demonstrate that mapping optical data to individual (n,m) nanotube structures is more complex than initially believed, predominantly due to polarization effects.

This work was supported by the ONR, the DoD HPCMO CHSSI program and the NSF Oklahoma EPSCoR NanoNet, NSF REU and NSF IGERT programs at OSU.

1. S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, R. E. Smalley and R. B. Weisman, *Science* **298**, 2361 (2002).
2. S. Reich, J. Maultzsch, C. Thomsen and P. Ordegon, *Phys. Rev. B* **66**, 035412 (2002).
3. J. W. Mintmire and C. T. White, *Synthetic Metals* **77**, 231 (1996).

223. ELECTRON PROPAGATOR CALCULATIONS ON SEVERAL PROPERTIES OF CH_3 AND CH_3^+. **Koevi A. Agbemehin** and J. V. Ortiz; Kansas State University, Manhattan, KS.

Methyl radical CH_3 and cation CH_3^+ have been investigated with the electron propagator method where several approximations, including OVGF and Koopman's theorem, were employed. Geometry optimization of the molecules was successively performed at the Hartree-Fock, MP2 and CCSD(T) levels. A use of diffuse functions allowed the system's orbitals to occupy larger regions of spaces, thereby offering a reliable study of Rydberg states of CH_3. This presentation will show some of the unique advantages that the propagator method procures through an evaluation of properties such as electron affinities, transition energies, ionization energies and corresponding Dyson orbitals. Examination of the Dyson orbitals enables assignments of Rydberg states based on angular dependence and radial nodes of the Dyson orbitals.

224. INTERPRETATION OF THE PHOTOELECTRON SPECTRUM OF $ScC_6H_6^-$. **Srikanth Kambalapalli** and J. V. Ortiz; Kansas State University, Manhattan, KS.

Ab initio, many-body methods are used to determine structures, relative energies and vertical electron-detachment energies of $ScC_6H_6^-$. The two lowest anionic structures are singlets that display boat and inverse-boat conformations of the C_6H_6 ligand and have energies that are within 0.1 eV of each other. The principal peaks in a recently reported anion photoelectron spectrum are assigned to Dyson orbitals that are dominated by Sc 4s or $3d_{x}2_{-y}2$ contributions in the boat form or by Sc 4s or $3d_{xy}$ contributions in the inverse-boat form. A triplet with C_{6v} symmetry is the third most stable state of the anion.

225. DENSITY FUNCTIONAL SIMULATION OF METALLIC CARBON NANOWIRES. **Ravi K. Vadapalli** and J. W. Mintmire; Oklahoma State University, Stillwater, OK.

Zhao *et. al*[1] have reported the experimental production of metallic carbon nanowires (CNW) as well as model simulations using armchair (5,5) and zigzag (9,0) single-walled carbon nanotubes (SWNT). Carbon nanowires can be visualized as a SWNT with a linear carbon chain inserted in the interior and parallel to the SWNT axis. Both these CNWs had interlayer spacings of about 0.35 nm, corresponding to the experimental interlayer spacings observed in graphite and multiwalled carbon nanotubes (MWNT). Their simulations indicate that the inserted carbon chain results in increased density-of-states (DOS) at the Fermi level in the CNWs, potentially improving the conducting properties. We will present results for extended simulations for CNWs using a first-principles local density functional (LDF) approach. We carried out simulations for CNWs with armchair SWNTs with indices ranging from five to ten. For the (5,5) CNW, our calculations also indicate an increase in the density-of-states at the Fermi level. Our results indicate that the central coaxial location for the inner carbon chain would be energetically unstable with respect to off-axis positions for nanowires with outside diameters greater than the (5,5) SWNT. Simulations using a linear chain off-axis but parallel to the SWNT axis with commensurate periodic boundary conditions indicates that the minimum energy position for the inner chain remains roughly 0.35 nm from the outer SWNT wall.

This work was supported by ONR and the DoD HPCMO CHSSI program through the Naval Research Laboratory.

1. X. Zhao, Y. Ando, Y. Liu, M. Jinno and T. Suzuki, *Phys. Rev. Lett.* **90**, 187401 (2003).

226. INDIVIDUAL CONTRIBUTIONS TO ELECTRON PROPAGATOR SELF-ENERGY AND THEIR COMPUTATIONAL COST.

V. G. Zakrzewski, Olga Dolgounitcheva and J. V. Ortiz; Kansas State University, Manhattan, KS.

Electron propagator methods proved to be reliable tools in predicting ionization energies and electron affinities for a large number of organic molecules. The most successfull approximations are the Outer Valence Green's Function (OVGF) and Partial Third Order (P3). The P3 has definite computational advantages over the OVGF because in the case of ionization energies, especially, it needs appreciably less computational efforts as not every type of molecular integrals in molecular basis set contributes to the effective self-energy part. The OVGF approximation contains contributions from every possible type of transformed molecular integrals and, in cases of large molecules, becomes prohibitively slow. The most time-consuming step is a computation of contributions from molecular integrals with four virtual integrals. These contributions are not present in the P3 approximation for the case of ionizations. Therefore, a natural idea was to test the importance of these terms for accuracy of the OVGF calculations. Preliminary conclusion is that dropping the contri-bution from integrals with four virtual integrals does not lead to dramatic changes in ionization energies. However, savings in computational time are rather significant.

227. STABILIZATION OF ZWITTERIONIC GLYCINE BY SOLVATING EFFECTS.

Mark R. Sterling, Olga Dolgounitcheva, V. G. Zakrzewski and J. V. Ortiz; Kansas State University, Manhattan, KS.

Aminoacids are known to exist as neutral, aminocarboxylic entities in the gas phase while zwitterionic forms are dominating in condensed media. The question of the minimum number of the solvent molecules sufficient to keep the zwitterionic forms of aminoacids from collapsing to more stable aminocarboxylic isomers is still open.

In this work, we apply different computational methods to find stable configurations of zwitterionic form of the simplest aminoacid, glycine, solvated with water. Zwitterionic structure was optimized with DFT and MP2 methods in water as the solvent (cavity model). The structure proved to be stable unlike the case of isolated zwitterion which collapsed to the aminocarboxylic form with no barrier on the way.

Different orientations of 1:1 complexes of Zwitterionic Glycine:water were then optimized with the starting geometry of solvated zwitterion. None of these hold and the structures optimized to 1:1 aminocarboxylic form:water complexes.

Optimizations of complexes of Zwitterion with two water molecules led to two dramatically different results: nonsymmetrically solvated zwitterions collapsed to aminocarboxylic forms while one symmetric complex held. This complex (called a "bike") proved to be a true, local minimum irrespective of the method used (DFT, MP2, or CCSD). We thus conclude that two molecules of water are sufficient to stabilize the zwitterionic structure of glycine.

Ionization energies and electron affinities of each stable complex were also calculated with electron propagator methods.

228. ELECTRON PROPAGATOR APPROACH TO IONIZATION ENERGIES OF PORPHYNE AND PORPHYRINS. **Olga Dolgounitcheva**, V. G. Zakrzewski and J. V. Ortiz; Kansas State University, Manhattan, KS.

Porphyrins and related macrocycles are crucial elements in many life processes. Chemical reactivity of porphyrins in such events as electron transfer, oxidation and reduction and others is directly related to their ionization energies and electron affinities. Gas phase UV photoelectron spectra (PES) of porphyrins are very scarce and available only for porphine itself and a number of heavily substituted porphyrins and metal porphyrins. In many cases, PES are rather complicated and their assignments controversial. Under these circumstances, reliable theoretic-cal ionization energies are highly desirable. Electron propagator methods seem to be ideal for the cause as they were proved to give excellent agreement between theoretical and experimental ionization energies for quite a number of organic compounds.

In the current work, we present the ionization energies and assignments for porphine, octamethylporphyrin and a number of metalloporphyrins, including vanadyl porphyrin, obtained with different electron propagator methods. In cases of closed--shell porphyrins, the splitting of the two upper levels is rather small for all molecules under consideration. In cases of open-shell porphyrins, the non-Aufbau behavior is typical.

229. STRUCTURE AND ENERGETICS OF [B, N, O, H_2]: QUANTUM MECHANICS SHOWS MULTIPLE MINIMA. **Aaron K. Corum**[1], Carol A. Deakyne[1] and Joel F. Liebman[2]; [1]University of Missouri - Columbia, Columbia, MO; [2]University of Maryland, Baltimore County, Baltimore, MD.

High level quantum chemical calculations have been performed to study [B, N, O, H_2], which is isoelectronically related to the well-known ketene H_2CCO and to [B, C, F, H_2]. Cyclic and acyclic systems with both BĐN and BĐO connectivities have been examined for the singlet state and a variety of isomeric forms have been identified. As chemical intuition suggests the most stable structure is H_2NBO. However, thus far, fourteen additional minima have been disclosed on the potential energy surface, including classical chain structures, ring structures and hydrogen-bonded structures. AIM and NBO analyses have been carried out to gain an understanding of the bonding in the various isomeric forms of [B, N, O, H_2].

230. EFFECTS OF NANOPARTICLE SIZE ON NEAR-IR REFLECTANCE. **Ravi S. Mulukutla**[1], Jeevanandam Pethaiyan[2], Mendy Phillips[2], Sambhudas Chaudhari[2], Paul S. Malchesky[1] and Kenneth J. Klabunde[2]; [1]NanoScale Materials Inc., Manhattan, KS; [2]Kansas State University, Manhattan, KS.

The IR reflectance of a material increases as the particle size decreases (at constant absorption coefficient), according to Kubelka-Munk theory. On this basis, one would expect nanocrystalline materials to have higher reflectance owing to their smaller particle size compared to microcrystalline materials. Nanoparticles are available in a variety of shapes and they also possess high surface areas and nanocrystallinity. Several nanoparticles of metal oxides (marketed as NanoActive^{TM} materials) and natural materials and their physically-or chemically-modified analogs were accessed for their reflective/absorptive properties in near IR region (NIR, 750-2500nm). The near IR spectroscopy measurements concluded that several NanoActive^{TM} materials were more reflective than natural materials; however, some natural materials and NanoActive^{TM} materials were found to be the most absorptive. The study also concluded that NIR reflectance depends on the particle size and has a threshold value at which the reflectance drops. This phenomenon was validated by physically modifying the aggregates.

231. METAL-OXIDE NANOPARTICLES FOR SMOKE CLEARING. John S. Klabunde[1], **Ravi S. Mulukutla**[1], Ronaldo G. Maghirang[2], Bernardo Predicala[2], Paul S. Malchesky[1] and Kenneth J. Klabunde[2]; [1]NanoScale Materials Inc., Manhattan, KS; [2]Kansas State University, Manhattan, KS.

Smoke is an aerosol of particulate matter and causes visual obscuration in indoor environments no matter from which source it has been generated. Fast clearing of smoke is a challenge and no technologies for this purpose are available, to our knowledge, except adequate ventilation or dilution. Metal oxide nanoparticles possess unique morphology, particle size and high surface reactivity and are marketed as NanoActive^{TM} materials by NanoScale. When some of the NanoActive^{TM} materials were disseminated into an airspace filled with smokes like glycol (theatrical), atomized diesel fog or combustion smoke, a rapid clearance was observed when compared to the rate at which smoke alone can clear. The rate of smoke clearing was monitored by a visible light transmission method in which the %transmission increased over time after the deployment of nanoparticles. In addition to surface area and surface chemical properties, the study revealed that particle size distribution, density and settling velocity of the nanoparticles are very important in order to rapidly clear the representative smoke. Further research on utilizing nanoparticles to reduce smoke can lead to promising applications.

232. REACTION OF Pb NANOPARTICLES WITH 1-DODECANETHIOL. Zhiqiang Yang, **K. J. Klabunde** and Christopher M. Sorensen; Kansas State University, Manhattan, KS.

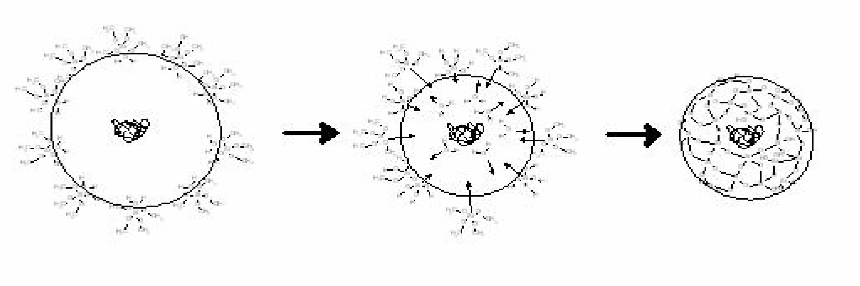
Here we report the reaction of Pb nanoparticles with 1-dodecanethiol at high temperature. When boiling in 4-*tert*-butyltoluene(190°C), Pb nanoparticles obtained from the solvated metal atom dispersion(SMAD) method react readily with 1-dodecanethiol to produce Pb(II) dodecanethiolate, which is not thermally stable and further decomposes to lead sulfide. Under certain conditions, monodisperse PbS nanorods can be obtained according to transmission electron microscopy and the nanorods show the tendency to self-assemble to linear strands. These results give another example where nanoparticles of a substance are much more chemically reactive than normal polycrystalline, bulk samples.

233. BIOTEMPLATING OF SILICA THIN FILMS WITH *E. COLI*. **Andrew Chambers**; Truman State University, Kirksville, MO.

The use of biological templates to engineer porosity in thin films of silica created by the sol-gel process was explored. The sol was prepared by the acid-catalyzed hydrolysis and condensation of tetramethoxysilane. *Escherichia coli* (*E. coli*) were directly combined with the sol prior being spin cast onto a surface. Once the films were cured in a low humidity environment, the *E. coli* were removed by either calcination or chemical treatments. The films were characterized before and after template removal using an atomic force microscope (AFM) operated in tapping mode. AFM images show that there is considerable variation in the dimensions of the cavities and that these cavities might not fully expose the substrate on which the films were spun. These materials have potential applications in chemical sensors, growth of nanoparticles and molecular recognition.

234. ENCAPSULATION OF LACTATE DEHYDROGENASE IN SILICA BY ITS DIRECT REACTION WITH TETRAMETHOXYSILANE. **Igor I. Slowing** and Nenad M. Kostic; Iowa State University, Ames, IA.

Enzymes encapsulated in silica matrices are stable and active catalysts for reactions. Traditionally the encapsulation is performed by mixing of an enzyme solution either with an orthosilicic acid sol while it is in the process of gelation or with preformed silica glass, product of a sol-gel process. In this study, following the observation that some natural peptides can promote silica precipitation, encapsulation of lactate dehydrogenase (LDH) in silica has been achieved by direct reaction of buffered solutions of the enzyme with tetramethoxysilane (TMOS). The buffered enzyme solutions are the promoters of *in situ* hydrolysis of TMOS and of polymerization of the resulting orthosilicic acid, so the enzyme gets trapped in the solid silica matrix as the water molecules of its solution are being consumed and replaced by silica. The process yields solid particles that display enzymatic activity. The degree of activity of the resulting LDH-containing silica particles depends on their sizes, the time of their formation and the pH of the enzyme solution.



235. SINGLE MOLECULE STUDIES OF DYE-DOPED MESOPOROUS SILICATE FILMS. **William Sanders**, Daniel A. Higgins and Maryanne M. Collinson; Kansas State University, Manhattan, KS.

Single molecule imaging and spectroscopy were used to characterize the local chemical environments of Nile Red encapsulated within a thin mesoporous silicate film. The film was prepared by spin casting a dye doped sol formed by hydrolyzing and condensing tetraethoxysilane (TEOS) in the presence of the surfactant, cetyltrimethylammonium bromide (CTAB). The mesoporous structure of the film was characterized using X-ray diffraction, which showed one strong reflection (d = 3.4 nm) and two smaller reflections (d = 2.9 nm and 1.2 nm) consistent with a cubic phase. Fluorescence images of as-prepared mesoporous films doped with Nile Red showed dramatic line-by-line variations in single molecule emission indicative of translational diffusion. These results suggest that Nile Red is located in the surfactant-like regions of the films.

236. *FUM13* AND *FUM14*: TWO GENES INVOLVED IN THE BIOSYNTHESIS OF MYCOTOXIN FUMONISINS IN *FUSARIUM VERTICILLIOIDES.* **Kathia Zaleta-Rivera**, Ravi S. Bojja, Han Yi, Chunping Xu, Patrick H. Dussault and Liangcheng Du; University of Nebraska-Lincoln, Lincoln, NE.

Fumonisins are mycotoxins produced by filamentous fungus *Fusarium verticillioides*, which is a widespread pathogen of corn. Fumonisins cause several fatal diseases in animals and impose cancer risk to humans. In order to control the toxin contamination in agriculture and food industry, it is essential to have an understanding on the biosynthetic mechanism. Here, we report the biochemical characterization of two genes, *FUM13* and *FUM14*, involved in the biosynthesis of fumonisins. Both genes have been heterologously expressed in *E. coli* and the produced proteins, Fum13p and Fum14p, have been purified for *in vitro* activity assays. The preliminary data confirmed that Fum13p catalyzes the 3-keto reduction of fumonisins and this activity is dependent on NADPH. Fum14p showed an acyltransferase activity when it was incubated with HFB1 (hydrolyzed fumonisin B1) and N-acetylcysteamine monothioester or thiophenyl monothioester of tricarballylic acid. The results provide directly evidence for the role of these two genes in the biosynthesis of fumonisins.

237. BIOLOGICALLY IMPORTANT THIOLS IN VARIOUS VEGETABLES AND FRUITS. **Omca Demirkol** and Nuran Ercal; University of Missouri-Rolla, Rolla, MO.

Biological thiols are important antioxidants and recent studies showed that their contents vary depending on the groups of foodstuffs. Therefore, we investigated the levels of some biological thiols in various vegetables and fruits by using a sensitive HPLC technique. Biological thiols measured in some vegetables and fruits include glutathione (L-glutamyl-L-cysteinly-glycine, GSH), N-acetylcysteine (NAC), captopril [CAP ($C_9H_{15}NO_3S$)], homocysteine (HCYS), cysteine (CYS) and γ-glutamyl cysteine (GGC). Our results show that biological thiol contents are between 3-349 nM/g wet weight in vegetables and 4-136 nM/g wet weight in fruits. CAP is only found in asparagus (28 nM/g wet weight). Furthermore, none of the biological thiols analyzed were found in cabbages, red grapes, blackberries, apples and peaches. Therefore, various vegetables and fruits differ significantly in their thiol contents. Oxidation of these important thiols may occur and result in production of toxic by-products if they are exposed to radiation and ozone treatment for sterilization purposes. Further studies should be performed to monitor the levels of these biological thiols.

238. CHARACTERIZATION OF LOVASTATIN DIKETIDE SYNTHASE FROM *ASPERGILLUS TERRUS.* **Han Yi**, Xiangcheng Zhu, Yousong Ding and Liangcheng Du; University of Nebraska-Lincoln, Lincoln, NE.

An elevated level of blood cholesterol is the primary risk factor for coronary heart disease. Statins are potent inhibitors of the biosynthesis of cholesterol and can dramatically lower cholesterol levels, thus reducing the risk of cardiovascular disease. We are interesting in the mechanism by which the statins are synthesized in fungi. Lovastatin is isolated from filamentous fungus *Aspergillus terreus*, and its biosynthetic genes have previously been cloned. Here, we report the initial efforts toward the characterization of a gene, LovF, which encodes lovastatin diketide synthase (LDKS), a key enzyme in the formation of the 2-methylbutyryl side-chain of lovastatin. LDKS contains seven domains and is unique among fungal modular polyketide synthases (PKSs) because it catalyzes only one cycle (non-iterative) of polyketide chain elongation. (1) The intact LDKS as well as its ketosynthase domain, acyltransferase domain and acyl carrier protein domain have been heterologously expressed in *A. nidulans* or *E. coli* and the produced proteins successfully purified. Using radioactively-labeled acetyl CoA or malonyl CoA as substrate, we are *in vitro* characterizing the substrate specificity of the enzyme and domains. (2) The ketosynthase domain and acyltransferase domain of LDKS have been studied by the *in vivo* domain-replacement approach. The domain of fumonisin polyketide synthase, Fum1p, was replaced with the corresponding LDKS domain. Fumonisins are a group of mycotoxins produced by several *Fusarium* species and Fum1p is a modular PKS also consisting of seven domains. In contrast to LDKS, however, Fum1p catalyzes seven cycles (iterative) of polyketide chain elongation. Two mutant strains of *F. verticillioides* containing the chimeric PKS gene have been generated for the understanding of the domain properties of these two distinct fungal PKSs. The results will help understand the biosynthetic mechanism of fungal polyketides and could lead to the development of new statins with improved biological activities.

239. COMPARATIVE EVALUATION OF N-ACETYLCYSTEINE AND N-ACETYLCYSTEINE AMIDE IN LEAD-EXPOSED C57BL/6 MICE.

Suman Penugonda, Micheal F. Webb and Nuran Ercal; University of Missouri - Rolla, Rolla, MO.

Lead, a toxic heavy metal, is well-known for disrupting the prooxidant/antioxidant balance of tissues and inducing physiological and behavioral dysfunctions. Despite the availability of several chelating and antioxidant combination therapies, lead poisoning remains a pervasive health problem. Even low exposure of lead can cause permanent damage to the central nervous system in infants and young children. Several studies have been reported comparing different antioxidants and chelating agents in the treatment of lead poisoning; however, there are certain limitations in the use of these agents. In our previous studies although N-acetylcysteine (NAC) was shown to have a potential for exhibiting antioxidant action in lead poisoning, it was not effective in chelating lead from target tissues. An Israeli company has recently synthesized a new compound called AD4 (N-acetyl cysteine amide). AD4 is a modified form of NAC. The carboxyl terminus is modified to an amide, which has been shown in Cu toxicity studies to cross the blood brain barrier. It has also been reported that AD4 is a potential agent in the therapy of multiple sclerosis (MS) and other neurodegenerative disorders. Preliminary HPLC results (taken from standard curves of NAC and AD4 (0-25000nM) that reacted with 30000nM Pb) showed that AD4 may be more effective in combating Pb toxicity than NAC. In this study, we plan to compare the efficacy of NAC and AD4 in C57BL/6 mice by examining the lead levels in target tissues as well as the alterations in lead-induced oxidative stress indices.

240. CRYSTALLIZATION AND PRELIMINARY ANALYSIS OF A RESPI-RATORY BURST-INHIBITING ACID PHOSPHATASE FROM *FRANCISELLA TULARENSIS.*

Richard Levi Felts; University of Missouri, Columbia, MO.

Francisilla tularensis is a class A pathogen found in many parts of the world predominantly in North America and Europe. As a potential bioterrorism bacterium it is of great importance to understand the mechanism of how this bacteria infects the host. It has been suggested that an acid phosphatase enzyme from this bacteria is responsible for suppressing the respiratory burst and allowing the bacteria to replicate inside of the host's phagocytic cells. Recently this acid phosphatase has been expressed, purified and crystallized allowing for preliminary analysis of the protein.

241. CYTOTOXICITY OF *META*-TYROSINE: A MECHANISTIC APPROACH. **Suneetha Mare** and Nuran Ercal; University of Missouri-Rolla, Rolla, MO.

In vitro studies demonstrate that hydroxyl radical converts L-phenylalanine to meta-tyrosine, an unnatural isomer of L-tyrosine. Quantification of *meta*-tyrosine has been widely used as an index of oxidative damage in tissue proteins. However, the possibility that *meta*-tyrosine might be generated oxidatively from free L-phenylalanine, could subsequently be incorporated into proteins as a L-tyrosine analog and might cause those proteins to malfunction has received little attention. In the present study, we demonstrated that free *meta*-tyrosine is toxic to cultured Chinese hamster ovary (CHO) cells by MTS assay. In the same experiment we also verified that L-phenylalanine and L-tyrosine did not have significant impact on the toxicity of *meta*-tyrosine (0.2mM). We have shown the morphological changes in CHO cells to indicate the cytotoxic effects of *meta*-tyrosine. The mechanism for cell death was defined by caspase-3 assay (apoptosis). This preliminary data from our study provides the mechanism for *meta*-tyrosine cytotoxicity on CHO cells.

242. FUNGAL CITRIC ACID PRODUCTION BY *ASPERGILLUS NIGER* ATCC 26550. **Gang Xie** and Thomas P. West; South Dakota State University, Brookings, SD.

Citric acid is an important additive used by the food industry. In this study, the ability of the fungus *Aspergillus niger* ATCC 26550 to utilize corn distillers' grains with solubles or grains hydrolyzed under mild acid condition as a substrate to produce citric acid was studied. In addition, the effect of 3% methanol with or without hydrolyzing the grains on fungal citric acid production was perused. Under sterile conditions, 5 g of corn distillers' grains with solubles was inoculated with about 4000 fungal cells and incubated in a flask for 10 days at 25°C. After 10 days, the grains were extracted with water to remove the citric acid present. The concentration of citric acid produced was analyzed using a coupled enzyme assay. It was found that the citric acid level was highest in untreated grains with 3% methanol. Moreover, biomass production was influenced by acid hydrolysis of the grains. The 1% sulfuric acid-hydrolyzed grains supported the highest biomass production by the fungus while the 2% and 2.5% sulfuric acid-hydrolyzed grains supported its lowest biomass production. In summary, enhanced fungal citric acid production by *A. niger* ATCC 26550 was noted after fungal growth on 0.5% and 1% sulfuric acid-hydrolyzed corn distillers' grains with solubles while methanol addition stimulated citric acid synthesis on untreated grains.

243. HELIX-COIL EQUILIBRIUM OF A MODEL PEPTIDE. **Krzysztof Kuczera** and Gouri S. Jas; University of Kansas, Lawrence, KS.

We have performed experimental measurements and computer simulations of the equilibrium structure and folding of a 21-residue *alpha*-helical heteropeptide. Far UV circular dichroism spectroscopy identified the presence of helical structure and determined the observed melting temperature of 296 K, the folding enthalpy of -11.6 kcal/mol and folding entropy of -39.6 cal/(mol K). Our simulations involve 45 ns of replica exchange molecular dynamics of the peptide, using 8 replicas at temperatures between 280 and 450 K and the program CHARMM with a continuum solvent model. In a 30 ns simulation started from a helical structure, conformational equilibrium at all temperatures was reached after 15 ns. This simulation was used to calculate the peptide melting curve, predicting folding transition with a melting temperature of 330-350 K, enthalpy change of -10 kcal/mol and entropy change of -30 cal/(mol K). The simulation results were also used to analyze the peptide structural fluctuations and the free energy surface of helix unfolding. In a separate 15 ns replica exchange molecular dynamics simulation started from the extended structure, the helical conformation was first attained after about 2.8 ns and equilibrium was reached after 10 ns of simulation. These results showed a sequential folding process with a systematic increase in the number of hydrogen bonds until the helical state is reached and confirmed that the *alpha*-helical state is the global free energy minimum for the peptide at low temperatures.

244. MELTING BEHAVIOR OF DNA COMPLEXES CONTAINING JOINED TRIPLEX AND HAIRPIN LOOP MOTIFS.

Sarah E. Betzold[1] and Luis A. Marky[2]; [1]University of Nebraska Lincoln, Lincoln, NE; [2]University of Nebraska Medical Center, Omaha, NE.

Our laboratory is interested in predicting the thermal stability and melting behavior of nucleic acids from knowledge of its sequence. The main objective is to estimate the binding energetics of proteins, and other cofactors, involved in the opening of the DNA double helix during replication and transcription. In this work, we use a combination of temperature-dependent UV spectroscopy and differential scanning calorimetry (DSC) techniques to determine complete thermodynamic profiles for the unfolding of two DNA intramolecular complexes. The sequence of each complex was designed to yield a triplex connected to a hairpin loop through their duplex stem. The UV melting curves of each complex are biphasic with transition temperatures, T_M, and shapes that remained constant with increasing strand concentration, confirming their intramolecular formation. Furthermore, the increase in salt concentration and water activity both increased the T_M of each transition; thus, salt and water stabilize their helical structures. However, the DSC unfolding curves show three sequential transitions. Deconvolution of these curves allowed us to determine standard thermodynamic profiles for each of their three transitions. Each profile shows that the favorable formation of a particular structure in a given complex results from the typical compensation of a favorable enthalpy (due to the formation of base pairs and base-pair stacks) with an unfavorable entropy (due to the ordering of the oligonucleotide and the uptake of both counterions and water molecules). The magnitude of the thermodynamic parameters (and associated T_Ms) allowed us to conclude that the observed three transitions correspond to the initial disruption of the triplex motif (removal of TTTTTT or TTTTTTC$^+$), followed by the partial melting of the duplex (disruption of 5-6 A·T base pairs) and the final melting of the hairpin motif (disruption of its stem of 4 G·C base pairs). Supported by Grant MCB-0315746 from NSF.

245. MODELING AND SIMULATION OF THE HUMAN DELTA OPIOID RECEPTOR. **Mahalaxmi Aburi** and Paul E. Smith; Kansas State University, Manhattan, KS.

A model for the human *delta* opioid receptor has been generated *via* sequence alignment, structure building using the crystal structure of bovine rhodopsin as a template and refinement by molecular dynamics simulation. The model building suggested that, in addition to the previously postulated interaction between D128-Y308, an internal salt bridge also exists between residues D128 and R192, both of which are conserved in all the opioid receptors. The model and salt bridge were then shown to be stable during a 20 ns simulation in a lipid bilayer. It is therefore proposed that both of these interactions play a role in stabilizing the inactive state of the receptor. The model is also used in an effort to rationalize many of the mutational studies performed on *delta* opioid receptors and to suggest a plausible explanation for the differences between known *delta* opioid agonists and antagonists.

246. PROTEIN KINASE C AND ANNEXIN VI IN THE ROLE OF CELL ADHESION. **Heather E. Shinogle**, David S. Moore and Robert C. Dunn; University of Kansas, Lawrence, KS.

Cell adhesion is an important factor for cell growth and development. A lack of cell adhesion can lead to cell death caused by cell detachment, also known as *anoikis*. This is caused by the inability of the cell to reattach itself to a different, appropriate site of adhesion within a given duration. Protein kinase C (PKC) is vital in the regulation of these focal adhesion sites when it is bound to syndecan 4. PKC modifies proteins and changes the interactions between other proteins. Previous studies have been unable to determine the exact physiological function of annexin VI. It will be determined, through the use of confocal microscopy and Förster resonance energy transfer (FRET) how annexin VI interacts with PKC, potentially modifying its kinase activity in cultured human vascular smooth muscle cells.

247. PURIFICATION AND CHARACTERIZATION OF PHYTOCHROME FROM OAT SEEDLINGS. James M. Chapman[1], **Peter Simone**[1], Kyle Cummins[1], D. Philip Colombo, Jr.[1], Sheher Mohsin[2] and M. A. Lee[1]; [1]Rockhurst University, Kansas City, MO; [2]Agilent Technologies, Schaumburg, IL.

Phytochrome, a photoactivated protein, can trigger plant growth and seed germination. Classic experiments show that successive exposures to red and far-red light can reversibly turn germination on and off. To date, we have tried variations of published purification techniques. Currently, we are working on a simple and rapid purification technique that we hope will yield greater quantities of the protein. This work describes a novel isolation of the protein and characterization with time-of-flight mass spectrometry (TOF-MS), atomic force microscopy (AFM), gel techniques and LC-MS. Successful confirmation of protein isolation will be followed by AFM imaging of the phytochrome and analysis of the light-dependent conformational changes of phytochrome after exposure to red and far-red light.

248. ROSIGLITAZONE AMELIORATES ABNORMAL ACTIVITY OF PTP1B IN SKELETAL MUSCLE OF FAT-FED, STREPTOZOTOCIN-TREATED DIABETIC RATS. **Wu Yong**[1], Jingping Ou Yang[1], Ke Wu[1], Yunfeng Zhou[1] and Wen Chongyuan[2]; [1]Wuhan University, Wuhan, China; [2]Renmin Hospital, Wuhan University, Wuhan, China.

Protein tyrosine phosphatase 1B (PTP1B) acts as a physiological negative regulator of insulin signaling by dephosphorylating the activated insulin receptor (IR) thereby limiting the insulin signal. We examined the effect of Rosiglitazone, a PPAR-selective agonist, on PTP1B and its possible role in the amelioration of insulin resistance. Ten weeks old fat-fed, Streptozotocin (STZ)-treated rats, an animal model of non-insulin dependent diabetes mellitus (NIDDM), were treated orally once daily with rosiglitazone (3.0μmol/kg/day) for two weeks along with age matched non-diabetic rats controls. The diabetic rats responded to rosiglitazone with a significant decrease in plasma glucose and improved insulin sensitivity, which was shown by insulin tolerance test using KITT as an index. The activity and expression of PTP1B in skeletal muscle, myocardial tissue and liver in NIDDM rats have been shown to increase, thus diminishing insulin signaling in the target tissues. Hence, PTP1B is an important target for anti-diabetic drug research. We found that rosiglitazone could restrain both PTP1B protein levels and activities in skeletal muscle but not in liver in NIDDM rats. According with this change, insulin-induced tyrosine phosphorylation of insulin receptor (IR) β-subunits and insulin receptor substrate-1 (IRS-1) in muscles but not in liver in rosiglitazone-treated NIDDM rats were improved. There was no significant change in the activity and expression of PTP1B in the rosiglitazone-treated normal rats and blood insulin levels could not be changed by treatment with rosiglitazone in NIDDM rats. These results suggest that rosiglitazone has insulin-sensitizing and hypoglycemic activity and decreases elevated expressions and activities of PTP1B in the skeletal muscle of NIDDM rats. Although it remains unknown whether such effects of rosiglitazone are mediated by peroxisome proliferator-activated receptor, these data provide useful information for under-standing the significance of PTP1B in insulin-resistant rats and the molecular mechanism of rosiglitazone action.

249. SENSITIVE PROCEDURE FOR MEASURING NAD^+ AND NADH IN SERUM: THEIR CONCENTRATIONS IN HUMANS OF DIFFER-ENT AGE GROUPS. **Junqian Zhang**, D. Paul Rillema and Ram Singhal; Wichita State University, Wichita, KS.

The reducing elements furnish energy in the biological systems. NADH is the major contributor of the biological energy in the form of ATP. We have developed sensitive analytical methods to measure NADH. A pre-column treatment of the serum samples followed by separation of the major components by high performance liquid chromatography is established after examining several analytical methods. This procedure offers excellent separations of NAD^+ and NADH from other metabolites of the serum. The recovery of the two adenine compounds is quantitative. We observed instability of the NADH both in freshly-drawn serum samples and also during separation on the column. A loss in NADH results in parallel gain in NAD^+. These metabolites are measured in humans of varying age groups to discover the role of NADH in senescence. Serum NADH contents are examined in individuals of different ages (20 years to 80 years old) by enzymatic methods. The serum NADH concentration is very small (50 nM to 1.2 μM). Serum NADH undergoes oxidation *in vitro* irrespective of the storage conditions employed. Several antioxidants to prevent oxidation of NADH in the serum were thoroughly examined. Serum NADH contents cannot be stabilized *in vitro*. Serum enzymes and dissolved oxygen appear to oxidize NADH, making it impossible to measure the NADH contents with confidence. The concentration of NAD^+ in human erythrocytes is studied. The ratio of erythrocyte-NAD^+ to serum-fluorescence appears to increase with age. The female subjects tend to have higher NAD^+ concentration than the male subjects do. The serum NAD^+ concentration in female subjects (46 yr. to 78 yr.) was found to be 2.8 μM.

250. ACTIVITY COEFFICIENTS OF DIRTY DISTILLED WATER AND BEYOND. **Charles M. Greenlief**; Emporia State University, Emporia, KS.

For three decades Pitzer's ion-interaction model has been utilized to correlate activity and osmotic coefficients of electrolytes over a wide range of concentrations. In most cases the model correlates the data to within experimental accuracy. The success of this model still has not been included in undergraduate textbooks. Data for single electrolytes in aqueous and methanolic solutions are analyzed for literature data for these thermodynamic properties at 25°C.

251. OLD TITRATION WITH A NEW TWIST: REINFORCING THE RELATIONSHIP BETWEEN TECHNICAL SKILL AND PRECISION IN QUANTITATIVE ANALYSIS. **Shauna L. Hiley**; Missouri Western State College, St. Joseph, MO.

The importance of consistent technical skill in quantitative measurement can be an elusive concept in practical application for Quantitative Analysis students. In order to reinforce the meaning and relevance of standard deviation and precision, students in the Missouri Western State College CHE 321 Quantitative Analysis course perform a common standardization of aqueous NaOH with primary standard KHP, using 10 to 15 trials. The students then analyze their results by graphing relative standard deviation versus the number of trials, describing any trend present and relating it to their experimental procedure if possible. Then they are required to perform a propagation of error on their results and defend whether or not they deserve all of the “precision points” for the experiment. This reflective exercise really drives home the importance of good lab technique and brings out the competitive nature of the students.

The ease of the procedure allows the students to concentrate on their technique and consistency. Student results offer opportunities to discuss a variety of lab pitfalls, including equipment problems. In a subsequent experiment students are asked to determine the % KHP in an unknown sample using the same procedure. Student scores show an increase in the performance on this lab since the addition of the new standardization exercise.

252. CHARACTERIZATION AND ANALYSIS OF A PRODUCT (CAP): A SEMESTER LONG GUIDED INQUIRY LABORATORY SEQUENCE FOR USE IN GENERAL CHEMISTRY. **Michael W. Ducey, Jr.**, Shauna L. Hiley, Benjamin D. Caldwell and Gerald L. Zweerink; Missouri Western State College, St. Joseph, MO.

Missouri Western State College (MWSC) students enrolled in the first semester of General Chemistry complete a series of guided inquiry laboratory experiments with a common theme. The Characterization and Analysis of a Product (CAP) sequence is a series of five instrument intensive experiments begun during the first laboratory period and completed in the second to last laboratory period. The purpose of the CAP sequence is to provide connectivity between laboratory experiments and to relate chemistry to products that students are familiar with. During their first laboratory period students are organized into groups and are provided with a commercial product such as a brewed tea, energy drink or cough syrup to examine over the course of the semester. Experiments involving the products include an introduction to the scientific method, characterization of a methylene chloride extract of the product by GC-MS and melting point analysis, spectroscopic characterization of the product by FT-IR and AA/AE and through student planned experiments. Both “on-campus” students as well as students enrolled in High School College Credit sections complete the laboratory sequence. Experimental descriptions, examples of student planned experiments and feedback from both students and instructors will be presented.

253. DETERMINATION OF THE FAT CONTENT OF PROCESSED MEATS BY NMR. **James M. Chapman** and **Matthew J. Francoeur**; Rockhurst University, Kansas City, MO.

Our purpose for creating this experiment was to use nuclear magnetic resonance spectroscopy (NMR) as a quantitative analytical tool to determine a relationship between labeled fat percent and spectrum integrated fat area in processed meat (hotdogs). We developed a sampling method utilizing juice straws that permits insertion of the sample material into the NMR tube with minimum effort. As part of the experiment students will have to construct a standard plot with integrated area versus known fat content of the hotdogs. Once constructed the plot can be utilized to determine the fat content of other hotdogs for which the fat content is unknown to the student. The method could be utilized for the determination of fat in other processed meats and foodstuffs.

254. WHERE'S THE HEAT? A SURVEY OF HOT PEPPERS TO DETERMINE THE LOCATION OF THE CAPSAICIN WITHIN THE FRUIT. James M. Chapman and **Matthew J. Sullivan**; Rockhurst University, Kansas City, MO.

Hot peppers are used for a variety of purposes with the most common being as a food additive to give dishes that hot, spicy flavor. Anecdotally, people say to avoid the seeds when eating the uncooked peppers because that is where the heat is located. Our purpose for creating this experiment was to have students determine the differences in capsaicin/dihydrocapsaicin content between pepper varieties and to find where the capsaicinoids are located within the structures of the pepper. To accomplish this, students will have to research the literature to determine an appropriate HPLC mobile phase for separating the capsaicinoids, decide how to divide the pepper (we decided to split the pepper into three sections for analysis: the skin, the seeds and the core (placenta)) and perform their own extractions.

255. SOLID-STATE REACTIONS WITHIN A SELF-ASSEMBLED DISCRETE CAGE. **Makoto Fujita**; The University of Tokyo, Tokyo, Japan.

In this paper, we discuss solid state (-like) reactions within a self-assembled coordination cage. The cage assembles from six metal ions (Pd(II)) and four exo-tridentate ligands (1,3,5-tris(4-pyridyl)triazine). It has a nanometer-sized hydrophobic cavity and binds a family of neutral organic substrates in the cavity. The substrates do not feel the environment of the cage if once enclathrated. Thus, [2+2] photodimerization of olefins in the cage proceeds quite efficiently both in solid and solution. Crystallographic analysis reveals that the substrates are not restricted in the cage and behave like in solution. Photo-dissociation of CO from $CpMn(CO)_3$ in the cage also takes place smoothly in solid state, in contrast to the photo inertness of the crystal of $CpMn(CO)_3$ itself. The carbonyl complex has conformational freedom and gives coordinatively unsaturated $CpMn(CO)_2$ without further oligomerization, as revealed by crystallographic analysis. The formation of "a molecular ice" (an adamantanoid $(H_2O)_{10}$ cluster) in the cage, which is revealed by X-ray and neutron diffraction studies, is also discussed.

256. DUAL RESPONSIBILITIES; MULTI-TASKING MOLECULES. **Nate C. Schultheiss**, Christer B. Aakeröy and John Desper; Kansas State University, Manhattan, KS.

The ability to direct the assembly of discrete coordination complexes into extended one-dimensional architectures is an important supramolecular synthetic goal. One approach that provides synthetic and structural flexibility takes advantage of building blocks that contain both a hydrogen-bonding moiety and a binding site for the metal ion. In order to expand current strategies for inorganic crystal engineering we have designed and synthesized two asymmetric pyridyl-pyrimidine (py-pym) ligands, Fig. 1, with the desired functionalities, through a Pd-catalyzed Suzuki cross-coupling reaction in good yields. These ditopic ligands are suitable for binding a metal center through the py-moiety whereas the pym-moiety provides a self-complementary hydrogen-bonding functionality capable of organizing metal ions into an extended linear 1-D network. The successful implementation of our synthetic approach will be demonstrated through a structural analysis of several different copper(II) salts interconnected *via* these py-pym ligands resulting in extended architectures with desired connectivities.

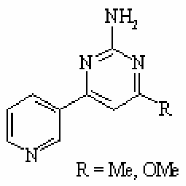


Figure 1.

257. "BLOCKING" LIGANDS FOR MOLECULAR TECTONICS. **Jesús Valdés-Martínez**; Universidad Nacional Autónoma de México, México, D.F., Mexico.

There are numerous reasons for incorporating metal ions into supramolecular networks. Metal ions give access to physical and chemical properties that are less common in organic solids: magnetic properties, conductivity and catalytic activity, for example. In addition, metal ions display a range of coordination geometries that impart structural elements not usually present in organic compounds. Thus, through metal ions it is possible to acquire greater flexibility in constructing materials with specific dimensions and topologies. But, on the other side, materials synthesis and crystal engineering require control at molecular and supramolecular levels and the geometric versatility of metal ions introduces problems to the already complicated problem of controlling the organization of molecules in a crystal lattice.

One way to get control at a molecular level is the use of ligands that block specific positions in the coordination sphere and direct the coordination of bridging ligands in the desired positions. In this talk we will show how these ligands can be used to do more than blocking positions and, in fact, be used to modulate the properties of the tecton and/or affect the supramolecular structure of the material.

258. HOW SOLID IS THE ORGANIC SOLID STATE? **Jerry L. Atwood** and Leonard J. Barbour; University of Missouri-Columbia, Columbia, MO.

More than 800 papers have been published on *p*-*tert*-butylcalix[4]arene. However, we have recently discovered that this well-known macrocycle undergoes single-crystal-to-single-crystal phase transitions upon guest uptake and release. The calixarene does not possess pores or channels in the solid state. However, despite a lack of porosity of the material, guest transport through the solid occurs readily until a thermodynamically stable structure is achieved. In order to actively facilitate this dynamic process, the host molecules undergo significant positional and/or orientational rearrangement. This transformation of the host lattice is triggered by weak van der Waals interaction between the molecular components. In order for the material to maintain its macroscopic integrity, extensive cooperativity must exist between molecules throughout the crystal, such that rearrangement can occur in a well-orchestrated fashion. Implications of this discovery for gas separation and gas storage will be discussed.

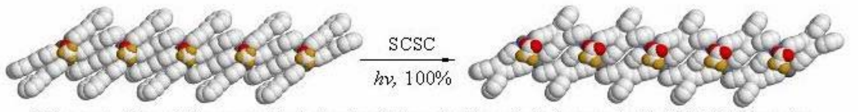
1. Atwood, Barbour, Jerga and Schottel, (2002) *Science*, **298**, 1000.
2. Atwood, Barbour, Jerga, (2004) *Angew. Chem. Int. Ed. Engl.*, **43**, 2948.

259. CALIX[4]RESORCINARENES AS TEMPLATES FOR SOLID STATE REACTIONS. **Heba Abourahma** and Leonard R. MacGillivray; University of Iowa, Iowa City, IA.

The use of directional supramolecular interactions to align molecules, subsequently affecting reactivity in the solid state has been successfully employed. More specifically, we have previously demonstrated the ability of resorcinol and its derivatives to act as linear templates for directing olefin alignment in the solid state to undergo [2+2] photoreaction in 100% yield and with stereo- and regio-specificity. Calix[4]resorcinarenes, which have been widely studied for their host-guest properties, can be envisioned as “collections” of four linear resorcinol templates and, in turn, have the capability to act as templates. This contribution will demonstrate that this is indeed the case. The reaction of C-alkylcalix[4]resorcinarene (alkyl = methyl, ethyl or propyl) with a number of stilbazoles in the presence of different guests will be presented. The effect of the templates and guest molecules on the reactivity of stilbazoles will also be presented.

260. TOWARDS GENERALITY IN TEMPLATE-CONTROLLED REACTIVITY: 'TEMPLATE SWITCHING' IN METAL-ORGANIC SOLIDS. **Qianli Chu** and Leonard R. MacGillivray; University of Iowa, Iowa City, IA.

The solid state is a promising medium for regio- and stereo-selective reactions. We have introduced silver triflate as a linear template for controlling the [2+2] photodimerization of monofunctional reactants based on stilbazole and its derivatives in the solid state. In this presentation, we will demonstrate generality of the supramolecular approach by switching the anions. Specifically, the discrete assembly and its reactivity are maintained after changing anions of our silver templates from triflate to trifluoroacetate, pentafluoropropionate and heptafluorobutyrate, as well as free anions (*e.g.*, hexafluoro-phosphate). Applications of template-switching to seek the design of materials that combine the properties of metals with reactivity are now being investigated.



Scheme 1. Silver trifluoroacetate is the template and stilbazole is the reactant in this SCSC reaction. (SCSC: single-crystal-to-single-crystal)

261. TRANSIENT PEPTIDE-INDUCED TRANSPORT OF DRUGS ACROSS BARRIER MEMBRANES. **John M. Tomich**; Kansas State University, Manhattan, KS.

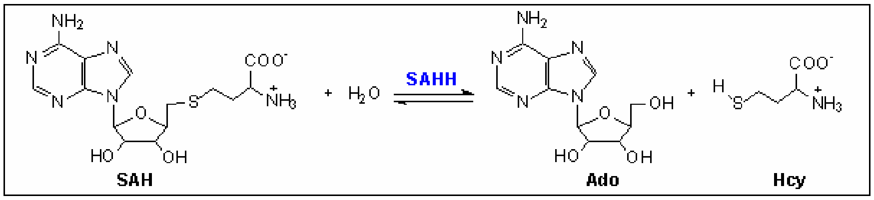
In developing a lead compound for use in the clinic as a channel replacement therapeutic, we discovered a palindromic channel-forming peptide (NC-1059) that transiently facilitates the paracellular movement of larger hydrophilic compounds to the basolateral compartment in epithelial monolayers. Within 20 minutes of peptide application to the apical surface of confluent cell monolayers, transepithelial resistance (R_{TE}) drops to about 10% of initial level. By six hours, either with a short or continual exposure to the peptide, resistance begins to recover. After 24 hr, R_{TE} returns to pretreatment levels. Subsequent exposure of the cells to the peptide repeats the cycle of (R_{TE}) reduction followed restoration of R_{TE}. Repeated applications were carried out over a four-week period. Application of the peptide to the basolateral surface has no effect on R_{TE}. *In vitro* transport activity was tested after exposure to the peptide in a variety of epithelial membranes with different basal R_{TE} values. A series of fluorescently labeled molecular weight standards were employed. All of the different cell types responded to the peptide in a concentration dependent manner. Compounds with molecular weights of 20 kDa were transported in all tested cell lines, with several lines allowing transport of molecules with mass of 40 kDa.

We are currently exploring *in vitro* and *in vivo* applications of this peptide as a short-acting modulator of epithelial barriers in the eye. It has long been recognized that delivery of instilled hydrophilic or larger molecular weight drugs into the corneal stroma as well as interior portions of the eye is difficult due in part to the highly resistive outer epithelial layer(s). For example, the drug vancomycin is extremely hydrophilic and must be administered to the eye by injection. We hypothesize that inclusion of NC-1059 with this or other hydrophilic antibiotics should greatly enhance ophthalmic drug delivery.

262. INHIBITION OF S-ADENOSYLHOMOCYSTEINE HYDROLASE BY D-ERITADENINE ANALOGUES.

Fusao Takusagawa[1] and Duy H. Hua[2]; [1]University of Kansas, Lawrence, KS; [2]Kansas State University, Manhattan, KS.

S-Adenosylhomocysteine hydrolase (SAHH) catalyzes the hydrolysis of S-adenosylhomocysteine (SAH) to form Ado and Hcy.



Because SAH inhibits severely S-adenosylmethionine(SAM)-dependent methyltransferases, action of SAHH regulates a number of SAM-dependent transmethylation reactions. SAHHs from all sources are oligomeric proteins with subunits of Mr 45,000 to 50,000. Each subunit contains one mole of tightly bound NAD^+. The reaction is reversible and the equilibrium lies far in the direction of SAH synthesis. Under physiological conditions, however, the removal of both Ado and Hcy is sufficiently rapid that the net reaction proceeds in the direction of hydrolysis. We have determined several crystal structures of the rat liver enzyme and found that the enzyme undergoes a large conformational change upon substrate binding. Through site-directed mutagenesis and kinetic measurements, the amino acid residues that are involved in the catalytic mechanism have been identified and a detailed catalytic mechanism has been proposed. A number of inhibitors of SAHH have been identified. One group includes Ado analogues with carbocyclic ribose moieties which are mechanism-based inhibitors. The other group contains Ado analogues with "acyclic sugar" moieties which are relatively weak reversible inhibitors, except for D-eritadenine (DEA) which is a potent inhibitor and has a hypocholesterolemic activity. On the basis of the crystal structure of SAHH complexed with DEA, we have modified DEA and synthesized the DEA analogues. The SAHH inhibitory activities and hypocholesterolemic activities of the DEA analogues will be presented.

263. BLENDING PARALLEL SYNTHESES INTO MEDICINAL CHEMISTRY: DISCOVERY OF POTENT TIE-2 INHIBITORS. **Jinshan Chen**; Pfizer Global Research & Development, Groton, CT.

This presentation describes the progression of Tie-2 project, from HTS to the identification of a potent lead series, with an emphasis on the role of parallel synthesis strategy throughout the program. No *in vivo* data for this project will be disclosed.

264. EFFECT OF MOLECULAR PROPERTIES ON THE SELECTIVE ACCUMULATION OF CHEMICALS IN TUMOR CELLS. **Stefan Trapp**[1] and Richard W. Horobin[2]; [1]Technical University of Denmark, Kongens Lyngby, Denmark; [2]University of Glasgow, Glasgow, United Kingdom.

Cationic lipophilic dyes can accumulate in mitochondria and especially in mitochondria of tumor cells. We investigated the chemical properties and the processes allowing selective uptake into tumor cells using the Fick-Nernst-Planck equation. The model simulates uptake into cytoplasm and mitochondria and is valid for neutral molecules and ions and, thus, also for weak electrolytes. The differential equation system was analytically solved for the steady-state and the dynamic case. The parameterization was for a generic human cell, with a –60 mV more negative potential at the inner mitochondria membrane of generic tumor cells. Chemical input data are lipophilicity (log K_{OW}), acid/base dissociation constant (pKa) and electric charge (z). Accumulation in mitochondria occurred for polar acids with pKa between 5 and < 9 due to the ion trap and for lipophilic bases with pKa > 11 or permanent cations due to electrical attraction. Selective accumulation in tumor cells was found for monovalent cations or strong bases with log K_{OW} of the cation between > -2 and < +2, optimum near 0. The results are in agreement with experimental results for rhodamine 123, a series of cationic triarylmethane dyes and MKT-077, an anticancer drug targeting tumor mitochondria.

265. STUDIES TOWARD A TOTAL SYNTHESIS OF (+)-MYRICERIC ACID A. **Angelo Aguilar**, Bernard Wiredu, Keil J. Regehr, Philine Wangemann and Duy H. Hua; Kansas State University, Manhattan, KS.

Pentacyclic triterpenes are widely found in more than 90% of *Diospyros* (Syn: Persimmon, ebony) plants. The genus *Diospyros* consists of tropical trees and shrubs and has been known for its medicinal use for many years. Many important biological activities have been associated with pentacyclic triterpenes, *e.g.*, endothelin A receptor antagonist, anticancer, anti-inflammatory, antimicrobial, antiobesity, kinase inhibition and anti-HIV activities, to name a few. In search of an efficient total synthesis of biologically-active pentacyclic triterpenes, such as (+)-myriceric acid A, we investigated a convergent coupling of ring fragment A-B-C and a precursor of fragment E. Here, we report a new coupling reaction involving α-selenyl ketones and conjugated ynones in the construction of the A-B-C-D ring fragment of (+)-myriceric acid A. The conversion of this key intermediate leading to the total synthesis of (+)-myriceric acid A is being studied. Inhibition of vasoconstriction of (+)-myriceric acid A in the isolated *in vitro* superfused spiral modiolar artery of gerbil was evaluated.

266. COMPUTATIONAL MODELS FOR NANOTUBES AND NANO-WIRES. **J. W. Mintmire**; Oklahoma State University, Stillwater, OK.

One-dimensional nanostructures such as inorganic nanowires and nanotubes represent potential materials for key components of future electronic, optoelectronic and nanoelectromechanical systems. They will also serve as important model systems to demonstrate quantum-size effects in nanostructured materials. Understanding the properties of these nanostructures is essential to the development of devices based on their use and substantial progress has been made in the synthesis of Si, Ge, GaAs, InP semiconductor nanowires as well as with a range of metal oxides. Typical semiconductor nanowires are synthesized with diameters ranging from 10-50 nm, although recent experiments report the synthesis of silicon nanowires with diameters as small as 1 nm.

We are currently developing a scalable and portable suite of programs for calculating the first-principles' electronic structure, total energy and energy derivatives of quasi-one-dimensional nanostructures with screw symmetry, allowing us to treat carbon nanotubes, silicon and silica nanowires as well as a range of biomolecular materials such as DNA, etc. This approach considers the helical symmetry of these particular materials and calculates the electronic structure using local Gaussian-type orbitals within a one-dimensional local-density functional band-structure approach. A nanowire can be described by a unit cell containing a finite number of atoms and a screw operation acting on that unit cell. We discuss how this approach has been adapted to a parallel environment and present some results for double-walled carbon nanotubes and semiconductor nanowires.

This work was supported by the U.S. Office of Naval Research, the DoD HPCMO CHSSI program through the Naval Research Laboratory and the Oklahoma NASA EPSCoR program.

267. ENDOHEDRAL SILICON FULLERENES. **Xiao Cheng Zeng**[1], Soohaeng Yoo[1], Jijun Zhao[2] and Jinlan Wang[3]; [1]University of Nebraska-Lincoln, Lincoln, NE, [2]University of North Carolina, Chapel Hill, NC; [3]Argonne National Laboratory, Argonne, IL.

We have performed an unbiased search for the lowest-energy geometric structures of medium-sized silicon clusters SiN ($27 < N < 39$) using a genetic algorithm and nonorthogonal-tight-binding method, followed by a refining and biased search using basin-hopping method coupled with density-functional theory. We show that the carbon fullerene cages are most likely generic cage motifs (“magic cages”) to form low-lying stuffed-cage silicon clusters (beyond the size $N \geq 27$). An empirical rule of the optimal “stuffing/cage” combination is given for constructing low-lying endohedral silicon fullerenes.

268. FIRST PRINCIPLES STUDY OF SCN/GAN AND SCN/INN SUPERLATTICES. **V. Ranjan**, Saad-Bin Omran and L. Bellaiche; University of Arkansas, Fayetteville, AR.

First principles calculations are performed to predict the structural, optical, piezoelectric, dielectric and dynamic properties of ScN_n/Ga_m (respectively, ScN_n/In_m) systems that consist of n layers of hexagonal ScN alternating with m layers of hexagonal GaN (respectively, InN) along the [0001] direction. All these properties dramatically depend on the n/m ratio, implying that various physical quantities can be optimized in the studied systems.The main reason for such dramatic dependence is that the ground-state structure is found to be a 5-time coordinated (non-polar) layered phase for n/m larger than 1, while it resembles the 4-time coordinated (pyroelectric) wurtzite phase for n/m lower than 1. Our first-principles calculations also reveal the microscopic mechanisms leading to the evolution from one ground-state to the other around n/m=1 and the precise role played by Sc, Ga, In and N atoms in these mechanisms.

269. TOWARD PRACTICAL ORGANIC POLYMER MAGNETS: LESSONS LEARNED FROM POLYARYLMETHYL POLYRADICALS. **Andrzej Rajca**; University of Nebraska-Lincoln, Lincoln, NE.

Recently, magnetic ordering at temperature of about 10 K was reported for organic conjugated polymer based upon organic spin clusters of the relatively reactive triarylmethyl radical. This result demonstrated feasibility of obtaining purely organic magnetic polymers (with no metals).[1,2] Two major benchmarks must be attained before such polymer magnets can be made into practical materials: (1) stability at ambient conditions and (2) magnetic ordering above room temperature.

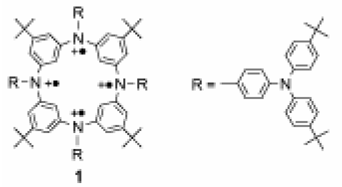
This presentation summarizes the design principles for organic polymers with magnetic ordering and discusses the problems of the electronic structure that impact the prospects for obtaining practical polymer magnets.

1. A. Rajca, J. Wongsriratanakul and S. Rajca, ″Magnetic Ordering in an Organic Polymer,″ *Science* 2001, **294**, 1503–1505.
2. S. Rajca, A. Rajca, J. Wongsriratanakul, P. Butler and S. Choi, ″Organic Spin Clusters. Dendritic-Macrocyclic Polyarylmethyl Polyradical with Very High-Spin of S = 10 and its Derivatives: Synthesis, Magnetic Studies and Small Angle Neutron Scattering.″ *J. Am. Chem. Soc.* 2004, **126**, 6972–6986.

270. SYNTHESIS AND MAGNETIC STUDY OF MACROCYCLIC TETRARADICAL TETRACATION. **Kouichi Shiraishi**, Andrzej

Rajca and Suchada Rajca; University Nebraska-Lincoln, Lincoln, NE.

High-spin molecules have been widely investigated for organic ferromagnet. Recently, we reported the first organic conjugated polymer with magnetic ordering at temperature of about 10 K.[1] However, the polymer is based on relatively reactive triarylmethyl radicals and it has to be handled below 170 K. Radicals that are stable at ambient conditions are desired for building blocks for high-spin molecules and polymers. One such radical may be aminium radical cation of *p*-phenylenediamine, which is readily prepared *via* oxidation of the corresponding diamine. Our conceptual approach to high-spin states is to link the redox active *p*-phenylenediamine units with *m*-phenylenes, leading to macrocyclic cross-conjugated π-systems. Synthesis of macrocyclic tetraradical tetracation **1** and its magnetic study will be reported.



1

1. A. Rajca, J. Wongsriratanakul and S. Rajca, *Science* 2001, **294**, 1503.

271. SOLVENT EFFECTS ON THE ADSORPTION AND REACTION OF 2-CHLOROETHYLETHYL SULFIDE AND OTHER CWA MIMICS. **Richard M. Narske**[1], Robert Zimmanck[1] and Kenneth J. Klabunde[2]; [1]Augustana College, Rock Island, IL; [2]Kansas State University, Manhattan, KS.

The adsorption and reactions of 2-chloroethylethyl sulfide (2-CEES) and 2-chloroethylphenyl sulfide, mimics of bis-(2,2'-dichloro)ethyl sulfide ("HD" or Mustard Gas), and dimethylmethyl phosphonate, on nanocrystalline aluminum oxide, Al_2O_3, titanium oxide, TiO_2 and mixed oxides of aluminum and magnesium were studied in pentane and nonafluorobutylmethyl butyl ether. The decomposition reactions were followed by gas chromatography. Reactions of these oxides showed a greater reactivity than studies involving AP-MgO reported earlier. Reaction rates in the polyfluoroether proceeded at rates comparable to the reactions in pentane. Solid state, MAS ^{13}C, and ^{27}Al NMR studies were done on these nanocrystalline oxides before and after the reaction to determine the crystal structure change in the case of aluminum oxide and also to determine the presence of the bonded alkoxide on the surface of the nanocrystalline oxides.

272. NANOPARTICLES IN NATURAL AND ENGINEERED SYSTEMS. **Vicki H. Grassian**; University of Iowa, Iowa City, IA.

The study of nanoparticles in natural and engineered systems is important as these particles can impact air quality. For example, particulates can alter the chemical balance of the atmosphere by providing a reactive substrate or medium on and in which reactions can occur. Atmospheric nanoparticles may perhaps be the most important particles in the Earth's atmosphere as they provide the greatest surface area for these reactions. In the case of engineered systems, newly synthesized nanocrystalline zeolites can be used in the environmental remediation of NO_x and VOCs. This talk will highlight some of our recent studies on nanoparticles in these natural and engineered systems.

273. NANOMACHINING OF METAL PARTICLES BY DIGESTIVE RIPENING USING THIOL LIGANDS. SYNTHESIS AND CHARACTERIZATION OF GOLD AND SILVER ALLOY NANOPARTICLES, AND THEIR FORMATION. **Alexander B. Smetana**, Kenneth J. Klabunde and Christopher M. Sorensen; Kansas State University, Manhattan, KS.

Our previous method of refining polydisperse metal nanoparticle colloids, termed digestive ripening, has been shown to facilitate an alloying process where the product is a uniform monodisperse colloid with an average particle diameter of 5.3nm +/- 0.4nm. The synthesis is simple and amenable to large quantities of materials. These particles display a surface plasmon absorption in the UV-Vis spectrum that is dependent on the concentrations of the gold and silver precursor colloids. Through this procedure we can tailor the position of the absorption peak anywhere in the range of the gold and silver reagent colloids. The alloy particles have displayed an excellent capability to form beautiful self-assembled superlattice architectures. This reaction has supplied us an invaluable tool to investigate the mechanism of digestive ripening for it is easily followed *via* the UV-Vis spectra. This investigation and the characterization of the particles will be described.

274. SYNTHESIS, CHARACTERIZATION, PHOTOCATALYTIC AND DIELECTRIC PROPERTIES OF NANOSIZED STRONTIUM AND BARIUM TITANATES. **Dmytro Demydov** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS.

The application of mixed oxides as photocatalytic and dielectric materials is currently an area of tremendous promise in research. A new approach to synthesize nanocrystals of strontium titanate ($SrTiO_3$) and barium titanate ($BaTiO_3$) has been developed. Nanosized mixed metal oxides were synthesized by a modified aerogel procedure from alkoxides. Crystallite size of aerogel prepared powders can be varied by the use of different solvents. A mixture of ethanol and toluene was found to be the best binary solvent for supercritical drying, which produced a $SrTiO_3$ sample with a surface area of 159±9 m^2/g and an average crystallite size of 8±2 nm and a $BaTiO_3$ sample with a surface area of 175±15 m^2/g and an average crystallite size of 6±2 nm. The structural and surface characteristic properties were studied by nitrogen BET analysis, transmission electron microscopy and powder XRD. Comparison with commercial samples was also made. Strontium titanate has been studied for photocatalytic oxidation of volatile organic compounds. Barium titanate has been studied as a dielectric material. Results on syntheses, structural aspects and application of $SrTiO_3$ as a photocatalyst and $BaTiO_3$ as a dialectic material will be presented and discussed.

275. SYNTHESIS AND ELECTROCHEMICAL STUDIES OF METAL-OXIDE NANOPARTICLES. **Duane Bartak** and Adam Carlson; University of Northern Iowa, Cedar Falls, IA.

Nanoparticles of selected metal oxides including cobalt oxide, nickel oxide and vanadium pentoxide were prepared, characterized and their electrochemical properties studied. The syntheses of metal hydroxide gels were carried out by sol gel techniques. The conversion of the hydroxides to oxide was accomplished by a variety of approaches including high temperature super critical drying of the gels in an autoclave and carbon dioxide critical point drying. Characterization of the metal oxides included surface areas, total pore volumes and XRD measurements. Electrochemical studies of metal oxides were accomplished in ethylene carbonate:dimethyl carbonate solvent mixtures using lithium perchlorate or lithium hexafluorophosphate electrolytes.

Slow-scan cyclic voltammetric experiments of the metal oxides were carried out by coating the oxide nanoparticles on an aluminum substrate and sticky carbon techniques. The metal oxide nanoparticles were tested as cathode materials in lithium-ion secondary batteries. Discharge/charge measurements of V_2O_5 cathodes in these lithium-ion batteries indicated capacities of over 300 mAh/g at discharge rates of C/40.

276. DIELECTROPHORETIC INTERCONNECTS COMPOSED OF SEMICONDUCTOR NANOPARTICLES. **Bret Flanders** and Birol Ozturk; Oklahoma State University, Stillwater, OK.

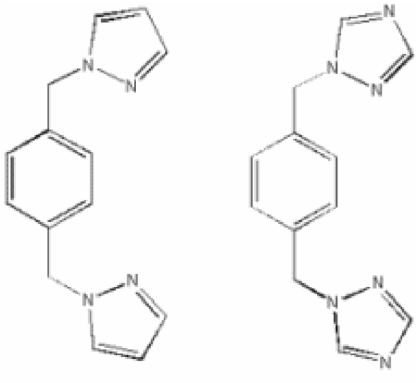
The dielectrophoretic manipulation of nanoscopic materials is a promising approach to the large scale fabrication of electronic devices. Here we use dielectrophoresis to form individual submicron wires from CdS nanoparticles and to interface them with macroscopic electrodes at targeted locations, all in one step. In order to fabricate the CdS interconnects, it was necessary to dilute the nanoparticle solutions to extremely low concentrations. Current-voltage measurements of these wires exhibited a broad range of behaviors, including non-ohmic current flow. Furthermore, many electronic devices consist of semiconducting interconnects that bridge source and drain terminals, as do these CdS wires. Hence, these structures are promising candidates for photo-conductive switches and field effect transistors.

277. TO BE ANNOUNCED. **Richard Colton**; Naval Research Laboratory, Washington, DC.

Richard Colton's latest research will be described.

278. RELIABLE RECIPE FOR MAKING BINARY COCRYSTALS. **Meg E. Fasulo**, Christer B. Aakeroy and John Desper; Kansas State University, Manhattan, KS.

Hydrogen bonds are important players in supramolecular chemistry. Carboxylic acids, oximes and amides by themselves network into crystals *via* hydrogen bonds. By introducing different competing hydrogen bond acceptors into solutions of these chemical moieties, we intend to develop reliable strategies for the preparation of binary co-crystals which is the first essential step in supramolecular solid-state chemistry. We have designed two ditopic ligands as intermolecular probes for this purpose, 1,4-bis[(pyrazol-1-yl)methyl]benzene (**1**) and 1,4-bis[(triazol-1-yl)methyl]-benzene (**2**) (Scheme 1) and this presentation will outline some of their supramolecular structural chemistry.



1 2

279. CAPILLARY ELECTROPHORETIC ANALYSIS OF FORENSIC SAMPLES. **Robert A. Heegel**; Augustana College, Sioux Falls, SD.

Current analytical methods for the analysis of clandestine laboratory evidence primarily focus on the analysis of the organic species using gas chromatography/mass spectrometry and infrared spectrophotometry. However, analytical techniques used to analyze inorganic species in samples collected from clandestine laboratory cases need to be able to provide relevant information concerning the process and materials involved. Capillary electrophoresis allows for the separation and analysis of the inorganic species including phosphorus species which can, in turn, determine the method of manufacture. In addition, CE can be utilized in the examination of other forensic evidence including explosives, gun shot residue, poisoning, DNA and drug identification.

Sponsors: Dr. David M. Northrop, Dr. Eric C. Person, Ms. Lori A. Knops-Washington State Patrol Crime Lab-Marysville

280. CHARACTERIZING REACTIVITY OF BENZYL ESTERS IN SODIUM DODECYL SULFATE MICELLES. Tram B. Hoang[1], Melissa Odorzynski[1], Alex Bulochnik[1], Gholam Mirafzal[2] and **Hassan Almoazen**[1]; [1]College of Pharmacy and Health Sciences, Drake University, Des Moines, IA; [2]Department of Chemistry, Drake University, Des Moines, IA.

Research to study the effect of changing the hydrophobicity of the alkyl group of benzyl esters on its hydrolysis in sodium dodecyl sulfate micelles at pH 9 and 40ºC. Hydrolysis reactions of benzyl esters were studied in borate buffer at pH of 9. Reaction products, benzyl alcohol, acetic acid and acetoacetic acid were separated using HPLC and detected using UV at 254nm and conductivity detectors. Different concentrations of sodium dodecyl sulfate were added to each reaction vessel. Vessel temperature was kept constant at 40ºC using a water bath. Hydrolysis reaction of benzyl acetate and benzyl acetoacetate followed pseudo-first-order kinetics; experimental rate constants were determined. Rate constants in the micelles as well as partition coefficients were mathematically evaluated using pseudo-phase model by nonlinear curve fitting. The keto group on the acid side of benzyl acetoacetate renders the ester more susceptible for hydrolysis. A plot of experimental rate constants of benzyl acetate and benzyl acetoacetate as a function of surfactant concentrations showed that the critical micelle concentration CMC is at a range of 0.00138-0.00243 mole/L which is consistent with previous surface tension measurements. The rate constant of benzyl acetate in micelles was half its value for benzyl acetoacetate while the partition coefficient was doubled. Comparing rate constants as well as partition coefficients in micelles suggests that the benzyl acetoacetate is closer to the surface region of the micelle than benzyl acetate and that the concentration of benzyl acetate is double the concentration of benzyl acetoacetate in micelles. This is probable due to the repelling effect of the keto group with the sulfate at the surface of micelles. A number of benzyl esters with different alkyl side chain have been synthesized and are currently being studied in our laboratory. This project was funded by Iowa Space Grant Consortium ISGC and National Aeronautics Space Agency NASA.

281. CHEMILUMINESCENCE FROM REACTION OF LUMINOL WITH SUPERBASIC SOLIDS.

Sean R. Tomlinson, Chien-Chang Huang and Keith L. Hohn; Kansas State University, Manhattan, KS.

The chemiluminescence of luminol when reacted with oxygen and a strong base is well known. All reactions heretofore performed with luminol have been liquid phase. The purpose of this research is to determine the viability of reaction of luminol with solid bases. Nanocrystalline metal oxides, such as MgO and CaO, have been used because of their unique physical and chemical properties; for instance, increased basicity. However, it has been found that neither MgO nor CaO were sufficiently strong bases to produce luminol chemiluminescence. UV-VIS measurements suggested that the nanocrystals react with luminol to produce the monoanionic form of luminol, but do not produce the dianion, the form that reacts with O_2 and produces light. This suggests that more basic solid catalysts are needed. Therefore, MgO has been doped with sodium to produce a superbasic material.

The reaction of luminol with sodium-doped MgO has been studied for a range of sodium weight percentages. The intensity of the chemiluminescence has been measured for each Na/MgO sample. The strength of the basic sites of a 5 wt% Na/MgO sample has been measured to be of strength between pKb = 17 and 27. Future experiments will further refine the base strength measurement and determine the number of basic sites for a given sample. Correlating the indicator data to the chemiluminescence spectroscopy data will aid in achieving the ultimate goal of this research: developing a chemiluminscent technique for measuring the concentration of basic sites on solid catalysts.

282. DETECTION OF ENDOGENOUS THIOLS USING A CHEMICALLY-MODIFIED CARBON INK MICROELECTRODE.

Courtney D. Kuhnline and R. Scott Martin; Saint Louis University, St. Louis, MO.

The detection of thiols, such as homocysteine, cysteine and glutathione, is necessary to monitor various disease states. In particular, the American Heart Association recommends at-risk patients be tested for elevated levels of homocysteine as an indicator of heart disease.

Cysteine deficiencies are associated with liver damage and slowed growth. Glutathione is an important antioxidant that contributes to diabetes and hypertension. These biological associations generate the need for miniaturized detection systems allowing portable monitoring as well as more quantitative and timely results. Microchip-based methods can provide these types of systems. Micromolding of carbon ink microelectrodes with poly(dimethylsiloxane) (PDMS) microchannels generates a solidified carbon microelectrode on a glass plate. By sealing a PDMS flow channel across the electrode, flow injection analysis with amperometric detection is possible. The detection of thiols at unmodified carbon microelectrodes, occurs at very high potentials where many possible interferants are also detected. Cobalt phthalocyanine (CoPC) is a compound that acts as an electrocatalyst and lowers the potential needed for the oxidation of thiols. In this work we will describe the development of carbon ink microelectrodes modified with CoPC. The amount of thinner, the amount of CoPC and the CoPC transfer method were evaluated to optimize the ink compositon. Discrete injections of cysteine showed a hydrodynamic voltammogram with a maximum response at 500mV. Flow analysis at this potential produced a linear response between 50 mM -750 mM and a 15 mM limit of detection. These microelectrodes can potentially be integrated with microchip capillary electrophoresis in order to separate complex mixtures of these thiols in biological samples. Progress is also being made towards detecting glutathione levels in erythrocytes as well as homocysteine levels in human blood plasma.

283. DETECTION OF SUBSTANCE P IN BIOLOGICAL SAMPLES.

Brooke Shellaine Barrett, Walter R. Vandaveer IV and Susan M. Lunte; University of Kansas, Lawrence, KS.

The purpose of this research is to develop a method for the detection of substance P in biological samples using a bioaffinity assay performed on a miniaturized electrophoretic device. Substance P is a neuropeptide that is present throughout the body in the range of subpicomoles-to-low nanomoles per gram of tissue and is involved in a great number of neurochemical activities including pain transmission, depression, stimulation of smooth muscle, learning and memory. Immunoassay has been used previously as a tool for the detection and quantitation of physiological molecules at low concentrations. Enzyme immunoassay is based on labeling antigen with enzyme that catalyzes production of a detectable product. The selectivity of antigen/antibody binding and the chemical amplification feature of an enzyme label enable high specificity and low detection levels. A capillary electrophoresis (CE) method with ultraviolet-visible (UV) detection was developed for quantitation of substance P in biological samples. In this assay, enzyme-labeled substance P competes with unlabeled substance P for binding to a limited amount of antibodies. A substrate is added and the enzyme, alkaline phosphatase, catalyzes its hydrolysis, forming a product whose concentration is inversely proportional to unbound substance P. The concentration of substance P was indirectly determined by monitoring the absorbance of the substrate, *p*-nitrophenyl phosphate, and the product, *p*-nitrophenol, individually after CE separation. The limitation of the UV approach was poor sensitivity, with detection limits in the micromolar range. Therefore, the assay was transferred to a CE system with electrochemical detection (EC) and the detection limits were reduced to the low picomolar ranges. In this method, an electrochemically active substrate and product, *p*-aminophenyl phosphate and *p*-aminophenol, were utilized to indirectly determine the concentration of substance P. The ultimate goal of this research is to perform the immunoassay on a miniaturized capillary electrophoresis device for fast analysis and high throughput.

284. EFFECT OF ACIDITY ON THE NONLINEAR BEHAVIOR OF THE CHLORITE-SULFITE pH OSCILLATOR IN A CSTR.

Rizia Bardhan, Varun Talwar and Glen A. Frerichs; Westminster College, Fulton, MO.

Chlorite-based oscillators involving various sulfur-containing species have been known for some time. A recently discovered minimal or prototype pH oscillator is based on the $NaClO_2$-Na_2SO_3-H_2SO_4 system in a continuous-flow stirred tank reactor (CSTR). A model has been proposed that allows simulation of the general features of the oscillations in a CSTR. Previously, a phase diagram was obtained characterizing the nonlinear behavior of the chlorite-sulfite pH oscillator over a wide range of $[ClO_2^-]_0$ and $[SO_3^{2-}]_0$. In the present study, we attempt to characterize the nonlinear behavior of this pH oscillator as a function of $[H^+]_0$ and k_0, the reciprocal residence time, while holding $[ClO_2^-]_0$ and $[SO_3^{2-}]_0$ constant. The system is found to be very sensitive to $[H^+]_0$, giving a variety of dynamical behavior including periodic and aperiodic oscillations, bistability between steady states and bistability between steady state and oscillatory state. Surprisingly, small-amplitude oscillations were observed in a CSTR at low k_0, even with no net H^+ added. The proposed model will be revisited in light of recent results.

285. EXPERIMENTAL AND COMPUTATIONAL INVESTIGATION OF INFLUENCE OF ETHER, KETONE AND ESTER LIGANDS ON INTRINSIC HYDRATION BEHAVIOR OF Ag(I) IN THE GAS PHASE. **Julie D. Becker**[1], Dorothy A. Hanna[1] and Michael J. Van Stipdonk[2]; [1]Kansas Wesleyan University, Salina, KS; [2]Wichita State University, Wichita, KS.

Ion trap mass spectrometry provides a means of examining the reactivity of coordinately unsaturated complexes in the absence of solvent, thus allowing an investigation of ligand influences upon the metal ion's intrinsic reactivity without the complications of solvent effects. The relative tendency of ether, ester and ketone complexes of Ag(I) to undergo hydration by ambient water molecules when held without collisional activation in the ion trap was observed and rationalized in terms of the complexes' lowest energy structures obtained through molecular modeling.

286. IMIDAZOLIDES AS ENVIRONMENTALLY-FRIENDLY ACYLATING AGENTS IN UNDERGRADUATE LABORATORIES. **Mark Cradduck**, Rebecca Lacy and Anne D. George; Nebraska Wesleyan University, Lincoln, NE.

N,N'-Carbonyldiimidazole reacts rapidly at room temperature with equimolar carboxylic acid to form imidazolide. We will describe a mini-scale preparation of DEET. Initial results will also be presented of competitive rate studies of acylations using imidazolides prepared *in situ*.

287. INTERACTION OF WILD AND MUTANT FORMS OF PHOSPHOLIPASE A2 FROM *YERSINIA ENTEROCOLITICA*. **Julia Lutovich** and Alexa Serfis; Saint Louis University, St. Louis, MO.

Yersinia enterocolitica is a bacterial pathogen that causes gastroenteritis in humans and the pathogen is typically ingested when contaminated water or improperly sanitized food is consumed. *Y. enterocolitica* secretes a phospholipase with A2 activity (YPLA) and it is believed that enzymatic cleavage of colonic epithelial membrane phospholipids causes membrane destabilization, resulting in pathogen entrance into the cell. In order to more fully understand the role of YPLA in pathogenesis, interactions of YPLA and a mutant form with liposomal bilayers has been studied with fluorescence spectroscopy. Calcein release from liposomes was monitored upon addition of YPLA. It was found that YPLA caused steady release of entrapped calcein, with the mutant form being more effective. A lag in the kinetics of the wild form indicates that the N terminus may mediate the initial contact with the membrane.

288. INVESTIGATION OF K^+, Ag^+ AND Tl^+ COMPLEXES WITH THYMINE BY ESI-TANDEM MS. **Rema Amawi**, Junqian Zhang and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

Human telomeres are a focus of research because of their role in genome integrity, cellular aging and cancer. Recent studies have shown that electrospray ionization (ESI) can be used to generate metal cationized quartets of nucleobases reminiscent of the guanine quartet structures within oligonucleotides that assemble *in vitro*. The goal of this study was to determine whether the combination of ESI and ion-trap mass spectrometry could be used to investigate the relative stability of metal ion-nucleobase complexes in the gas phase. Because of its higher solubility in aqueous solution relative to guanine, thymine was chosen as the test base. The metal ions selected were K^+, Ag^+ and Tl^+: cations with similar ionic radius but significant differences in hard/soft acid properties. As we show here, ESI was used to generate complexes containing the metal ion coordinated by up to five thymine molecules in the case of K^+ and Tl^+, but only four for Ag^+. Energy-resolved collision-induced dissociation (CID) showed that the collision energy required to eliminate a single thymine ligand was lowest for complexes containing four or five thymine ligands and highest for those containing two. The CID profiles, ion peak shapes and chemical mass shifts reveal significant differences in complex stability and indicate that the species are predominantly hydrogen-bonded structures. The most-probable complex geomtries were investigated using computational chemistry.

289. LC-EC ANALYSIS OF AMINO ACIDS ON DIAMOND ELECTRODES. **Claire Long** and Miles D. Koppang; University of South Dakota, Vermillion, SD.

All but three of the twenty amino acids found in proteins can be considered electroinactive on conventional carbon-based electrodes such as glassy carbon. Derivatization of the amino acids is usually necessary to produce an electrochemical signal. On boron-doped diamond thin-film electrodes, these electroinactive amino acids produce well-resolved oxidation waves using cyclic voltammetry in aqueous carbonate buffer, pH 10 (CBpH10). Diamond electrodes have been used in flow injection analysis to detect submicromolar concentrations of amino acids. Our goal is to develop a liquid chromatographic (LC) analysis scheme for amino acids using electrochemical (EC) detection with diamond electrodes. We have observed well-defined oxidation waves for nonderivatized amino acids in CBpH10 in the presence of up to 50 % acetonitrile by volume, solvent mixtures typically used in LC applications. On a mixed-mode anion exchange column with an ion-pairing cation (tetrabutylammonium cation) in a basic mobile phase (pH10), phenylalanine and arginine were separated and detected electrochemically without derivatization.

290. LIGAND EXCHANGE REACTIONS OF CHROMIUM(V). **Sheila Barnard**, Javier Chacon and Surendra N. Mahapatro, Regis University; Denver, CO.

The pH and ionic strength dependence of the decomposition of pyridinium bis[citrato(2-)oxochromate(V) and chromium(V)-glutathione complex have been studied by spectrophotometry and electron paramagnetic resonance (EPR) specroscopy. Preliminary results of the ligand exchange reactions with hydroxy carboxylic acids, pyridine-carboxylates, selen (Schiff bases) and malatol will be presented.

291. PHASE ONE OF THE SYNTHESIS OF THE TETRAAZAMACROTRICYCLE [4^6]ADAMANZANE: SYNTHESIS OF *N*-(*p*-TOLUENESULFONYL)-1,6,11-TRIAZACYCLOPENTADECANE AND *N*,*N*-BIS(CHLOROCARBONYLPROPYL)-*p*-TOLUENESULFONAMIDE.

Patrick R. Porubsky and Shaun E. Schmidt; Washburn University, Topeka, KS.

The long term goal of this research is the synthesis of [4^6]adamanzane. This cage compound is being synthesized to investigate its coordination properties and possible medical applications. In this initial phase, two parts of the cage are being constructed using a modified Richman-Atkins approach: the singly protected triazamacrocycle, *N*-*p*-toluenesulfonyl)-1,6,11-triazacyclopentadecane, and the diacid chloride, *N*,*N*-bis(chlorocarbonylpropyl)-*p*-toluenesulfonamide. IR and ^{1}H-NMR spectroscopy are used in the identification of the molecules isolated.

292. PHENOLIC ACID CONSTITUENT ANALYSIS OF *ECHINACEA SPP.* USING *µ*CE-EC.

Ryan J. Grigsby[1], Walter R. Vandaveer IV[2] and Susan M. Lunte[2]; [1]Haskell Indian Nations University, Lawrence, KS; [2]University of Kansas, Lawrence, KS.

Echinacea is a genus of flowering plants, native to the southeastern United States, that has been used to treat viral and bacterial infections. It is now cultivated world-wide and is a top seller in the herbal supplement industry. Several methods have been developed to determine the concentrations of pharmacologically-active constituents (phenolic acids and alkylamides) in certain *Echinacea* species. These methods include gas chromatography with mass spectrometric detection (GC-MS), liquid chromatography with electrochemical detection (LC-EC) and capillary electrophoresis with ultraviolet light detection (CE-UV). Unfortunately, these modes of analysis, while proven reliable, require expensive equipment, are time-consuming to run and are not usually located near the point-of-cultivation. Therefore, to overcome these constraints, the goal of this project is to develop a reliable and portable analytical system using microchip capillary electrophoresis with electrochemical detection (*µ*CE-EC). While *µ*CE-EC is useful only for the detection of *Echinacea*'s phenolic acid constituents, it has several advantages, including relatively inexpensive equipment, smaller sample requirements and faster analysis time. This system can be for the analysis of not only crude plant-material but also nutraceuticals. The microchip devices for this project were fabricated in-house and employed an integrated carbon-fiber electrode for the detection of *Echinacea* phenolic acid constituent standards.

293. PRODUCTION AND COLLISION-INDUCED DISSOCIATION OF GAS-PHASE, WATER AND ALCOHOL COORDINATED URANYL COMPLEXES CONTAINING HALIDE OR PERCHLORATE ANIONS. **Winnie Chien**, Victor Anbalagan and Michael Van Stipdonk; Wichita State University, Wichita, KS.

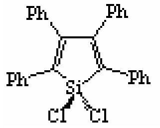
In this work, electrospray ionization was used to generate mono-positive gas-phase complexes of general formula $[UO_2A(S)_n]^+$ where A = OH, Cl, Br, I or ClO_4, S = H_2O, CH_3OH or CH_3CH_2OH and n=1-3. The multiple stage dissociation pathways of the complexes were then studied using ion-trap mass spectrometry. For H_2O-coordinated cations, the dissociation reactions observed included the elimination of H_2O ligands and the loss of HA (where A = Cl, Br or I). Only for the Br and ClO_4 versions did CID of the hydrated species generate the bare, uranyl-anion complexes. CID of the chloride and iodide versions led instead to the production of uranyl-hydroxide and hydrated UO_2^+. Replacement of H_2O ligands by alcohol increased the tendency to eliminate HA, consistent with the higher intrinsic acidity of the alcohols compared to water and potentially stronger UO_2-O interactions within the alkoxide complexes compared to the hydroxide version.

294. PROGRESS TOWARD THE SYNTHESIS OF AN EXPANDED OXOPHLORIN. **Philip O. Suchi** and Sam H. Leung; Washburn University, Topeka, KS.

Porphyrins and related compounds are photosensitizers potentially useful for photodynamic therapy (PDT). This project involves the synthesis of an expanded oxophlorin, a porphyrin derivative. We hoped that the extended conjugation in this molecule would bring about absorption at a longer wavelength in the visible region suitable for PDT. We planned to construct the target molecule by a "2 + 2" approach (the top half of the molecule combining with the bottom half). Currently we are able to synthesize the precursor (a 1,5-dipyrrolyl-1,4-pentadien-3-one) to the top half of the expanded oxophlorin.

295. REACTIVITY OF 1,1,-DICHLORO-2,3,4,5-TETRAPHENYLSILOLE. **Christopher D. Thomas**[1], Barrett E. Eichler[1], Jill A. Webster[1], M. Steven McClain[1], Amy E. Brown[1] and Douglas R. Powell[2]; [1]Northwest Missouri State University, Maryville, MO; [2]University of Kansas, Lawrence, KS.

Siloles (1-sila-cyclopenta-2,4-dienes) have received much interest recently as potential conducting and light-emitting materials. Studies of the reactivity of a 1,1-dichlorosilole (DCS) are currently underway. Two silole rings have been added to anthracene and investigations into the reduction of this molecule with alkali metals have been performed. Other research involves salt-elimination reactions of DCS with various amines and lithium amides.



DCS

296. REMOTE CONTROL UV-VIS SPECTROSCOPY FOR SECONDARY SCHOOLS. **Daniel K. Unruh**, Gary Histand and Richard Zerger; Bethel College, North Newton, KS.

Using LabView, National Instruments interface hardware and a UV-Vis spectrometer secondary school students are provided with Web-based control of a series of equilibrium experiments. This project makes an inquiry=based learning experience typically not available to secondary school students. This project generated the LabView source code to operate the spectrometer, the temperature conrol mechanism, the reagent pumps, and provided a live camera feed of the experiment. An appropriate experiment was found that allows for the change of color based on modifications in product and reactant concentration and temperature. These changes can then be detected either visually or spectroscopicly.

297. SELECTIVE INHIBITION OF HEME OXYGENASE OF *PSEUDOMONAS AERUGINOSA*. **Matthew A. Siemer**[1] and Mario Rivera[2]; [1]University of Kansas, Bushton, KS; [2]University of Kansas, Lawrence, KS.

The body uses the protein heme oxygenase to catalyze the oxidation of heme and the recycling of iron. Pathogenic bacteria also use this enzyme to obtain the iron needed for infection from their host's heme.

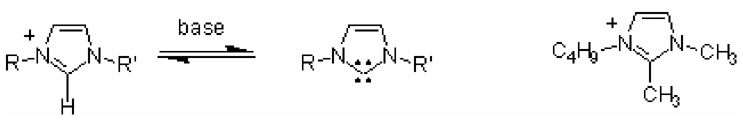
The heme oxygenase in *Pseudomonas aeruginosa* is unique in that it breaks the heme macrocycle at the δ-meso-carbon rather than at the more common α-meso position. This observation was used as a starting point to test the possible selective inhibition of the heme oxygenase from *Pseudomonas aeruginosa*. The inhibitory effects of several compounds were tested. The results will be discussed in the context of the structure of these compounds and the structure of bacterial and mammalian heme oxygenase enzymes.

298. SEPARATION OF NITRATE, NITRITE, AND PEROXYNITRITE USING CAPILLARY ELECTROPHORESIS. Matthew R. Rosebraugh[1], **Celeste Frankenfeld**[2], Barbara A. Fogarty[2] and Susan M. Lunte[2]; [1]Drake University, Des Moines, IA; [2]University of Kansas, Lawrence, KS.

Peroxynitrite has been implicated in many diseases including diabetes, atherosclerosis, ischemia-reperfusions injury and Alzheimer's. In biological systems, peroxynitrite is formed by the reaction of nitric oxide and superoxide. At physiological pH, peroxynitrite has a half-life of less than 1 second, reportedly increasing to 1 hour at pH 12. There are currently several methods for the detection of peroxynitrite including the use of electrochemical sensors, reaction with fluorescent/ chemiluminescent probes and indirect detection by monitoring nitration of other chemical species. Limitations of current approaches include the need for derivatization and possible interferences due to lack of separation. This research is focused on the development of a capillary electrophoresis (CE)-based method for the separation of peroxynitrite from its degradation products, nitrite and nitrate. Advantages of CE for this application include limited sample and reagent consumption, automated analysis and the ability to perform a multi-component separation at pH 12. Method optimization included investigation of the effects of buffer pH and concentration, separation voltage and injection conditions. The optimized method was used to monitor the stability of a commercial sample of peroxynitrite at pH 12 over time. Peroxynitrite was detected at 240 nm for ~3.5 hours before disappearance of the analyte peak. This is the first report of a separations-based analytical method for the simultaneous determination of peroxynitrite, nitrite and nitrate.

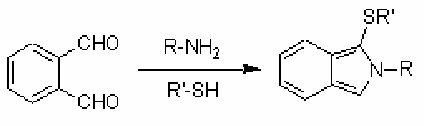
299. STUDIES OF THE ROBINSON ANNULATION REACTION IN IONIC LIQUIDS. David C. Hawkinson and **Keith B. McCollister**; University of South Dakota, Vermillion, SD.

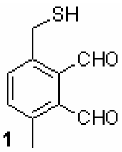
In a recent report of hydroxide ion-promoted Robinson annulation reaction of 1,3-diphenyl-2-propen-1-one with ethyl acetoacetate in 1-hexyl-3-methylimidazolium hexafluorophosphate ([6-mim]PF_6; (Morrison, *et. al.*, *Tetrahedron Lett.* 2001, 6053) it was suggested that the imidazolidene carbene, the conjugate base of the imidazolium cation formed by deprotonation at C2, was likely the active base in the reaction. To test this proposition, we have prepared 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([bdmim]PF_6), which cannot form the corresponding imidazolidene carbene; in this solvent the Robinson annulation does not occur as was observed with [6-mim]PF_6 or [bmim]PF_6. The acid-catalyzed Robinson annulation reaction of 2-methyl cyclohexanone with methyl vinyl ketone has also been examined. While this reaction yields the expected product, the ionic liquid undergoes severe decomposition in the process.



300. SYNTHESIS OF A THIOL-SUBSTITUTED *ortho*-PHTHALALDEHYDE FOR THE DERIVATIZATION OF AMINO ACIDS. David C. Hawkinson, Miles D. Koppang and **Andy Mueting**, University of South Dakota, Vermillion, SD.

ortho-Phthalaldehyde (OPA) is widely used for the derivatization of amino acids for chromatographic analysis as the resulting 2-alkylisoindoles can be detected by spectrophotometric or electrochemical methods. As shown below, primary amines react with OPA in the presence of one equivalent of thiol to form 1-alkylthio-2-alkylisoindoles. We have recently begun the synthesis of a thiol-substituted OPA derivative (**1**) for potential use in amino acid analysis. Key steps in the synthesis of compound **1** include cycloaddition of dimethyl butynedioate to 2,4-hexadienol and subsequent aromatization of the Diels-Alder adduct. Progress on the synthesis of this compound to date will be presented.





1

301. TERTIARY TO TERTIARY CARBOCATION REARRANGEMENTS.

Robert Pavlis, Katie Lemmon and Todd Francis; Pittsburg State University, Pittsburg, KS.

It is not generally appreciated that isoenergetic hydride shifts occur nearly as rapidly as those that release energy. Thus when 3-pentanol is refluxed with concentrated aqueous HCL, there is produced a statistical mixture of 2- and 3-chloropentane. The literature is replete with discussions of secondary to secondary rearrangements of this sort, but seems quite sparce on the subject of tertiary to tertiary ones. Because tertiary cations are much more stable than secondary, it might seem that they would be far less prone to rearrange. This is indicated by *ab initio* calculations.

2,3-Dimethylpentan-2-ol and 2,3-dimethylpentan-3-ol can easily be obtained using Grignard reagents. These molecules react rapidly with concentrated aqueous HCl. The products exhibit rearrangement, though less than statistical.

This poster will discuss these results and their implications.

302. MECHANISM OF AMINO ACID OXIDATION AT DIAMOND ELECTRODES: FLUORESCENCE IMAGING OF THE OXIDATION SITES.

Amanda Bakke and Miles D. Koppang; University of South Dakota, Vermillion, SD.

On conventional carbon-based electrodes, only three of the twenty amino acids found in proteins are electroactive or can be oxidized at a constant applied potential. On boron-doped diamond thin-film electrodes, all twenty amino acids yield well-resolved oxidation waves in aqueous carbonate buffer, pH 10. A mechanism for oxidation, consistent with various electrochemical data, has been proposed and is based on underpotential oxidation of water or hydroxide ions to surface-bound hydroxyl radicals at non-diamond carbon located or concentrated at the grain boundaries of the diamond films. Oxidation occurs through oxygen transfer by the bound hydroxyl radicals to the amine functionality which is complexed to surface boron. We have attempted to image or “visualize” the hydroxyl intermediate through electrogenerated chemiluminescence imaging with luminol and fluorescence imaging with quinine. Details and results from these imaging experiments will be presented.

303. STIMULI-RESPONSIVE ORGANOSILICA SOL-GELS: SYNTHESIS, CHARACTERIZATION, PROPERTIES, AND APPLICATIONS.

Bakul C. Dave; Southern Illinois University, Carbondale, Carbondale, IL.

This presentation will focus on organosilica sol-gels that act as environmentally-responsive materials. These sol-gels—prepared from precursors which contain both hydrophilic and hydrophobic groups—exhibit bulk volume changes with respect to different stimuli such as pH, temperature, salt, solvents, etc. These volume changes result in altered porosity of the gel matrix which can be utilized as a means for externally regulated separation, release and delivery of encapsulated molecular entities. Recent results on use of organosilica sol-gels as smart materials whose properties can be tuned by external stimuli will be presented. The applications of these glasses as smart or intelligent materials, which can interact with their environment and generate an active response, will be discussed in this presentation.

304. MECHANICALLY STRONG LIGHTWEIGHT POROUS MATERIALS (X-AEROGELS).

Nicholas Leventis; NASA Glenn Research Center, Cleveland, OH.

We have invented a new class of strong lightweight materials obtained by reacting the mesoporous surfaces of fractal networks of inorganic nanoparticles with polymeric crosslinking agents. Since the amounts of the inorganic material and the polymer are comparable, the new material can be viewed either as an aerogel modified by templated accumulation and polymerization of polymer precursors on the mesoporous surfaces of the inorganic network or as a nanoporous polymer made by casting a polymeric precursor on a nanostructured inorganic template. The most striking feature of the new material is that for a nominal increase in density by a factor of three, its mechanical strength can be up to 300 times higher than the strength of the underlying inorganic framework. The specific compressive strength of these materials is ~10x that of steel, while their thermal conductivity is low: in the range of 20-40 mW/mK. We have synthesized polymer crosslinked aerogels (nicknamed X-Aerogels) using ~35 different metal and semimetal oxides, while we have also demonstrated crosslinking with several different polymers such as polyurethanes/polyureas, epoxies and polyolefins. We anticipate that X-Aerogels will find use in applications where they will play the dual role of the thermal insulator and a structural material. Such applications may range from spacecraft components to packaging of sensitive electronic devices.

305. ENZYMATIC CATALYSIS, PHOTOISOMERIZATION AND ELECTRON-TRANSFER RELAY REACTIONS IN NANOPOROUS SILICA. Jovica D. Badjic, Ekaterina V. Pletneva and **Nenad M. Kostic**; Iowa State University, Ames, IA.

Sol-gel silica is a little-understood medium for chemical reactions. Before doped glasses can be used as biosensors, catalysts, optical probes or biomaterials, effects of encapsulation on structure and reactivity of dopants must be understood. We studied how reactivity of proteins and organic compounds encapsulated in silica depends on electrostatic and hydrogen-bonding interactions between the guest molecules and silica matrix. The glass matrix constrains carbonic anhydrase and prevents both its full unfolding and its refolding. The encapsulated enzyme acts as an esterase and obeys the Michaelis-Menten law. The turnover number and specific activity are low because the substrate reaches only the enzyme located near the monolith surfaces.[1] We trigger photochemical reactions of the encapsulated species and study their kinetics without interference of the macroscopic, slow diffusion of the reactant through the porous matrix. Uptake, release and photoisomerization of aza-benzene and its derivatives depends on hydrogen bonding between these guests and the polar groups lining the pore walls.[2] When the same guest molecules are held inside micelles embedded in silica, photoisomerization kinetics depends on electrostatic interactions which can be tuned by adjusting pH and ionic strength.[3] We mimic biological electron-transport chain by immobilizing metalloproteins in silica glass and letting mobile metal complex shuttle electrons between them. The electron donor is a zinc derivative of cytochrome c; the acceptor is either plastocyanin or native, iron-containing cytochrome c; the mobile carriers are complexes of iron or ruthenium and the reactions are triggered by laser flash.[4]

1. J. D. Badjic and N. M. Kostic, *Chem. Mater*. 1999, **11**, 3671-3679.
2. J. D. Badjic and N. M. Kostic, *J. Mater. Chem*. 2001, **11**, 408-418.
3. J. D. Badjic and N. M. Kostic, *J. Phys. Chem*. B 2001, **105**, 7482-7489.
4. E. V. Pletneva, M. M. Crnogorac, and N. M. Kostic, *J. Am. Chem. Soc*. 2002, **124**, 14342-14354.

306. TEMPLATED DIRECTED FORMATION OF HEMISPHERICAL CAVITIES IN A SILICATE FILM AND THE CONTROLLED GROWTH OF CONDUCTING NANOPARTICLES. **Maryanne Collinson** and Mandakini Kanungo; Kansas State University, Manhattan, KS.

Polystyrene latex spheres have been used as templates to create a 2-D ordered array of hemispherical cavities in a silicate thin film. Latex spheres were doped into a silica sol prepared by the sol-gel process and the resultant solution spin cast on a conducting surface. The spheres were removed by soaking the film in chloroform. The depth and the diameter of the resultant cavities were changed from nms to *μ*ms by varying the size of the sphere and the composition of the sol. Scanning electron microscopy and atomic force microscopy (AFM) were used to image the films. Nanosized copper and polyaniline were electrodeposited in the cavities after pinholes between cavities were "capped" to create an ordered array of conducting nanostructures in a silica host.

307. SINGLE-MOLECULE SPECTROSCOPY STUDIES OF DIFFUSION BY SILICATE-BOUND DYES IN SOL-GEL-DERIVED THIN FILMS. **Daniel Higgins**, Skylar Martin, Maryanne Collinson and Saroja Ginagunta; Kansas State University, Manhattan, KS.

Single molecule fluorescence spectroscopy is used to study dye diffusion within organically-modified silicate (ORMOSIL) films. ORMOSIL films are prepared from sols containing tetraethoxysilane (TEOS) and isobutyltrimethoxysilane (BTMOS). Nile red and a new silanized form of nile red that can be covalently attached to the silicate matrix are used as probe molecules. The number and rate of single molecules diffusing through the films increases with increasing film organic content. Autocorrelation of the fluorescence images yields a quantitative measure of the relative populations of fixed and diffusing species. Surprisingly, both “free” and silicate-bound nile red exhibit relatively facile motions. Single-molecule/single-point fluorescence correlation spectroscopy is used to measure the dye diffusion coefficients in sub-micrometer film regions. Histograms depicting the distribution of diffusion coefficients are reported. The diffusion coefficient for matrix bound nile red appears to be only a factor of three smaller than for the “free” dye, yielding values of 1.6×10^{-10} cm^2/s and 3.9×10^{-10} cm^2/s respectively. The unexpectedly rapid diffusion of matrix-bound nile red is attributed to the presence of liquid-like silicate oligomers in the films. Comparison of the results derived from experimental and simulated time transients indicates heterogeneity in these films occurs on sub-hundred-nanometer length scales.

308. PARALLELIZATION OF THE GAMESS ELECTRONIC STRUCTURE CODE. **Mike Schmidt**, Iowa State University, Ames, IA.

This talk will describe the long running effort, dating from 1992, to parallelize the GAMESS electronic structure code developed in the Gordon research group. This program contains many different computational kernels, with data storage ranging from O(N^2) to O(N^4), and with computational costs of O(N^3) to O(N^7). The project reflects the nature of the constantly changing hardware, including the interconnection, and the available support software, in addition to the nature of the quantum chemistry calculation itself. A number of students and postdocs in the Gordon group have contributed to this project, starting with a replicated memory parallel SCF program in 1993. Distributed memory programming was introduced in 1999 to support a parallel MP2 gradient code, through a library called the Distributed Data Interface. The latest enhancement of our DDI support software was introduced in 2004 to optimize distributed memory programming on the ubiquitous SMP nodes. The goal, of course, is to allow efficient, scalable computation of molecular wavefunctions, not only for large molecules, but also for more complex and accurate ansaetze.

309. CONTROLLED CORRELATION ENERGY EXTRAPOLATION BY INTRINSIC SCALING. **Klaus Ruedenberg** and Laimutis Bytautas; Iowa State University, Ames, IA.

Remarkably accurate scaling relations have been shown to exist between the correlation energy contributions from various excitation levels of the variational configuration interaction approach, considered as functions of the size of the correlating orbital space. These relationships have been used to develop a new method for extrapolating sequences of smaller CI calculations to the full CI energy. Applications to the ground states of the systems Ne, F_2, O_2, N_2, C_2, H_2O with cc-pVTZ and cc-pVQZ basis sets have demonstrated the ability of the method to yield benchmark quality results with a comparatively moderate computational effort. The method is called "Controlled Extrapolation by Intrinsic Scaling". Further extrapolations to the complete basis set limits have recovered the binding energies of F_2, O_2, N_2, C_2 with an accuracy of 0.5 millihartree or better. The information gained in the context of this extrapolation process has moreover been used to truncate the full configurational expansions without compromising their chemical accuracy. This deletion of configure-tional deadwood is accomplished by judiciously limiting the participation of the ranges of predetermined approximate natural orbital sets in the various excitation categories.

310. EFFECTIVE FRAGMENT POTENTIAL: THEORY AND APPLICATIONS. **Mark S. Gordon**; Iowa State University, Ames, IA.

The effective fragment potential (EFP) method, developed directly from quantum mechanics, is a sophisticated method that is capable of simulating cluster behavior, solvent effects and properties of bulk liquids. After an introduction to the theory, several applications of the method, drawn from both cluster and bulk studies, will be discussed.

311. RECENT ADVENTURES IN POLYMORPHISM. **Joel Bernstein**; Ben-Gurion University of the Negev, Beer Sheva, Israel.

Polymorphism is a phenomenon first recognized in1821, widely studied during the latter half of the 19th and beginning of the 20th century. After a period of relative dormancy, the last quarter century has shown a renewed interest in the phenomenon in part due to the potential significant economic ramifications of the existence of multiple crystal forms of a substance. Different crystal forms (polymorphs and solvates) of a substance can and do exhibit different physical, chemical and biological properties; hence the knowledge of the existence of different crystal forms and the ability to control the production of that crystal form can be crucial in the development and marketing of a substance. For pharmaceutical products in particular, the existence of multiple crystal forms can have important implications in the manufacturing, storage, use and intellectual property considerations of the product. The current state of knowledge about the polymorphism in particular, and different crystal forms in general, can be assessed addressing three main questions: 1. What is the frequency of occurrence of polymorphism and/or different crystal forms? Given a molecular structural formula, can we predict the existence of different polymorphs and/or solvates? 2. How do we prepare different crystal forms in a controlled and reproducible manner? 3. What are the similarities and differences of properties of the different crystal forms? Given that a particular substance does exist in different crystal forms, and that properties may differ among those forms, how can we best characterize the different polymorphs and utilize the phenomenon of polymorphism to investigate structure-property relations? We will present a general overview of the current situation in polymorphism in molecular with suitable examples from recent studies from both the literature and our own laboratories.

312. CRYSTAL ENGINEERING OF SOME PHARMACEUTICALLY-ACTIVE CO-CRYSTALS. **Keith R. Lorimer**, Scott Childs and Lenard Chyall; SSCI Inc., West Lafayette, IN.

Many of the common problems encountered with drug research and development stem from the physical properties of the solid, active pharmaceutical ingredients (API) and include stability, polymorphism, bioavailability, morphology and non-crystallinity. The molecular properties of APIs can also provide challenges, as they tend to be large in size (due to their biological nature) and can exhibit high degrees of flexibility and functionality.

In order to address these issues, there must be an understanding and control of the chemistry between molecules and, therefore, represents an emerging area of research with great potential within the field crystal engineering. Although much progress has been made in recent years on the engineering of co-crystals, there has been little development of co-crystals in pharmaceutics. One of the approaches undertaken at SSCI Inc. has been to develop co-crystals of APIs with small molecules with complimentary functional groups.

Several examples of co-crystals will be presented containing both molecular and ionic components, linked *via* hydrogen-bonding to the API. The ionic co-crystals comprise three component systems (one molecular and one salt) and have been termed neutral salts. Their structures and properties have been investigated and will be discussed in comparison with the parent API molecules.

313. PHARMACEUTICAL CO-CRYSTALS: SYNTHESIS, SCALE-UP AND PROPERTIES. **Matthew Peterson**, Magali B. Hickey, Julius F. Remenar, Sherry L. Morissette, Hector R. Guzman, J. Michael MacPhee and Örn Almarsson, TransForm Pharmaceuticals, Lexington, MA.

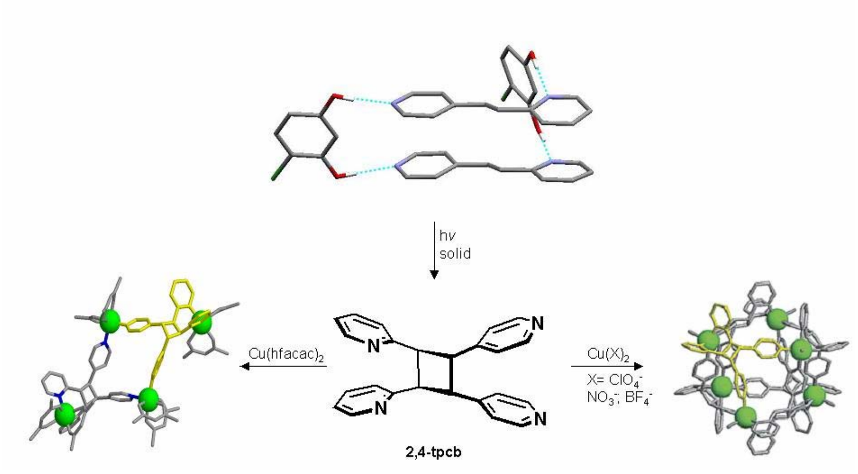
Co-crystals present an interesting opportunity to improve the materials' properties of pharmaceutical compounds. In this presentation the formation and physico-chemical performance of several co-crystals will be discussed. For example, the improved solubility of itraconazole co-crystals relative to the free base will be discussed, as will be the parsimony of carbamazepine:saccharin and its physical performance. Other examples will also be highlighted.

314. DESIGN AND SYNTHESIS OF N-BASED LIGANDS FOR COORDINATION AND HYDROGEN-BONDED NETWORKS. **Eric Bosch**, Nate Schultheiss, Joseph Ellsworth and Ivan Georgiev; Southwest Missouri State University, Springfield, MO.

We describe the design and synthesis of polytopic ligands based on pyridine, pyrimidine and pyrazine. The application of these ligands to crystal engineering using coordination chemistry and hydrogen bonding will be presented. Thus the self-assembly of tetrapyridyl, dipyridyl and bispyrazyl ligands with silver(I) and copper(II) salts results in the formation of a variety of one-, two- and three-dimensional coordination polymers and hexagonal coordination complexes. In contrast the self-assembly of bis-pyrimidine ligands with C-methyl calix[4]resorcinarene results in the formation of chain-link hydrogen-bonded capsules.

315. SOLID-STATE SYNTHESIS ENABLES CONSTRUCTION OF A POLYFUNCTIONAL LIGAND THAT GIVES RISE TO METAL-ORGANIC POLYGONS AND POLYHEDRA. **Tamara D. Hamilton**, Giannis S. Papaefstathiou, Qianli Chu and Leonard R. MacGillivray; University of Iowa, Iowa City, IA.

Self-assembly of metals with bridging organic ligands to form discrete and infinite architectures is an important branch of coordination chemistry. Congruous design of the ligand is imperative to metal-mediated self-assembly, as the organic unit must contain appropriate functionalities to recognize the metal and form the desired assembly. Template-directed synthesis in the solid state has enabled regiocontrol of [2 + 2] photodimerization of olefins, so that an unsymmetrical tetra-pyridylcyclobutane with two 2-pyridyl groups and two 4-pyridyl groups (2,4-tpcb) was isolated in 100% yield and gram quantities (*J. Am. Chem. Soc*. 2002, **124**, 11606). The novelty of 2,4-tpcb lies in its polyfunctionality: possession of both a chelating site and two monodentate coordination sites. Most metal-mediated self-assembly to date has been based on polytopic monofunctional ligands – those possessing multiple copies of identical coordination sites. Since 2,4-tpcb is polyfunctional, the ability of one set of pyridines to participate in forming a metal-organic architecture can be selectively “turned off” during the self-assembly process, allowing the ligand to give rise to assemblies of differing geometry (*e.g*., polygons, polyhedra) when exposed to different metals or different anions. Discrete polygons, polyhedra and a 2D infinite 4.82 net arising from 2,4-tpcb have been characterized by single-crystal X-ray crystallography. To our knowledge, the ability to form polygonal (2D) and polyhedral (3D) assemblies using the same organic ligand is unprecedented in the field of metal-mediated self-assembly and opens doors to applications in molecular information processing and anionic guest release.



316. INVERTED METAL ORGANIC FRAMEWORKS CONSTRUCTED USING ORGANIC BUILDING UNITS DERIVED FROM THE ORGANIC SOLID STATE. **Claude L. Mertzenich**[1], Giannis S. Papaefstathiou[2], Tomislav Friscic[2], Dale C. Swenson[2] and Leonard R. MacGillivray[2]; [1]Luther College, Decorah, IA; [2]University of Iowa, Iowa City, IA.

Porous and/or cavity-containing 2D and 3D crystalline extended frameworks can be constructed from metal ions and organic ligands that typically act as nodes and spacers, respectively, to yield metal-organic frameworks (MOFs). As a consequence, functionalization of MOF cavities usually relies on covalent modification of the organic spacer. An inverted metal-organic framework (IMOF) is a MOF that consists of a single metal ion or cluster that serves as a linear spacer and an organic ligand that serves as a node. Organic functionalization of cavity-containing IMOFs can be achieved using a supramolecular approach, wherein organic anions are attached to the linear metallic bridge, thus avoiding a tedious organic synthesis. The results of experiments designed to systematically decorate the interior spaces of IMOFs with a growing number and diversity of carboxylate anions will be presented. The structural integrity of the framework of composition $[(Cu_4(O_2CR)_8\text{-}(4,4'\text{-tpcb}))\cdot X(\text{guest solvent(s)})]_\infty$ {R = organic group coordinatively bonded to the dicopper paddle wheel complex; 4,4'-tpcb = *rctt*-tetrakis(4-

pyridyl)cyclobutane; X = number of included guest molecules of crystallization} can be maintained across a series, demonstrating that the IMOFs are tolerant to supramolecular organic functionalization. Resulting detailed physical thermal and spectroscopic properties and the consistently convergent nature of the anions into the IMOF interior spaces across the series will be discussed.

317. HYDROGEN-BONDED INORGANIC-ORGANIC LAMELLAR SOLIDS AND THEIR POTENTIAL AS CLAY MIMICS. **Brian Helfrich**; Mississippi State University, Mississippi State, MS.

Naturally-occurring clays are known for their ability to absorb and release guest molecules and/or ions under well-studied conditions. But unlike porous materials, clays do not have pre-defined open spaces where guests may reside. Instead, clays have the ability to ‘swell' as layers in the solid separate from one another due to the fact that the forces in the layer are stronger than those between the layers. Guest species then have an affinity to the area - hydrophilic or hydrophobic – between the layers. Our desire is to develop an inorganic-organic hybrid material in which the layer is held together by charge-assisted hydrogen bonds and between the layers there exists a hydrophobic region. Once achieved, we wish to study the thermal properties of this solid and test the material's ability to absorb guest species.

318. FROM FERROELASTICS TO FERROELECTRICS. **Mark D. Hollingsworth**, Matthew L. Peterson, Jeremy R. Rush, Mark J. Abel, Alexis A. Black, David A. Kesselring, Amanda G. Butenhoff, Kevin L. Pate and Julie A. Cooper; Kansas State University, Manhattan, KS.

In our efforts to better understand cooperative processes in crystalline solids, we have sought general strategies for developing a series of ferroelastic and ferroelectric crystals, in which external anisotropic stresses or electric fields can be used to switch between orientation states. By using a variety of crystal engineering techniques to tailor the distortion from high symmetry in series of organic inclusion compounds, we have succeeded in preparing over forty new ferroelastic materials. A small fraction of these are also ferroelectric, as shown by video-microscopy and electric field dependent NLO effects. Although we have had great success in our efforts to generate new ferroelastic materials, developing general strategies for making new ferroelectrics is much more difficult; the requirements for ferroelectricity are much more stringent since the crystal should have a macroscopic dipole moment that can be reoriented in an electric field. This talk outlines our strategies for generating, aligning and optimizing the polar ordering of guests in ferroelastic inclusion compounds, thereby making them ferroelectric. The design and properties of organic salts exhibiting electrooptical effects will also be discussed.

319. NOVEL DESIGN AND SYNTHESIS OF NONPEPTIDE AVP RECEPTOR ANTAGONISTS AND AGONISTS. **Kazumi Kondo**; Otsuka Pharmaceutical Co., Ltd., Tokushima, Japan.

The cyclic nonpeptide arginine vasopressin (AVP) is a well-known hormone whose actions are mediated by stimulation of specific G protein-coupled receptors (GPCRs) currently classified into three well-defined receptor subtypes: V_{1a}, V_{1b} and V_2 receptors. AVP is involved in numerous physiological functions including the regulation of blood volume, body fluid osmolality and blood pressure.

Although several potent peptide AVP V_2 receptor antagonists have been synthesized, the evaluation of their therapeutic utility has been severely hampered due to the lack of oral bioavailability, species differences and agonist effects in humans.

We initiated attempts to discover some structurally-diverse nonpeptides having an affinity for the AVP receptors to overcome these problems. After some modifications of a lead structure from the compound library of Otsuka, OPC-21268 was found to be a nonpeptide compound that shows potent affinity to the AVP V_{1a} receptor and has potent antagonist activity by oral administration. Some continuous efforts to improve the potencies and biological properties produced OPC-31260 and OPC-41061 (tolvaptan) as selective V_2 receptor antagonists. These compounds strongly induced water excretion in the collecting ducts of the kidney and did not alter solute excretion (urine Na^+ and/or K^+ loss). Such agents could be of high therapeutic value for the treatment of several water retaining disorders such as SIADH, liver cirrhosis, certain stages of congestive heart failure and hypertension, nephritic syndrome and edema.

On the basis of the discovery of these nonpeptide antagonists, we designed a V_2 receptor agonist by monitoring the accumulation of the cAMP production using the human receptor expressed HeLa cells. After consideration of SAR and the structural requirements for an agonist, we selected OPC-51803 as the orally active compound for further evaluation.

320. DISCOVERY OF A SELECTIVE ITK INHIBITOR THAT BLOCKS T-CELL ACTIVATION AND REDUCES MURINE LUNG INFLAMMATION. **Jagabandhu Das**, John Wityak, Chunjian Liu, Robert V. Moquin, Joseph A. Furch, James Lin, Steven H. Spergel, Arthur Doweyko, Amrita Kamath, Hongjian Zhang, Kathleen D. O'Day, Becky Penhallow, Chen-Yi Hung, Steven Kanner, Tai-An Lin, John H. Dodd and Joel C. Barrish; Bristol-Myers Squibb Co., Princeton, NJ.

Itk (Emt, Tsk), a member of the Tec family of non-receptor tyrosine kinases is expressed mainly on CD4+ T-cells. Mice deficient in Itk exhibit defects in T-cell signaling and development leading to reduced IL-2 production. Selective Itk inhibitors may, therefore, have utilities as an immunosuppressive agent in the treatment of rheumatoid arthritis, graft rejection and other T-cell mediated immunological disorders. Synthesis and SAR studies leading to a novel and selective Itk inhibitor will be presented. The inhibitor is efficacious in reducing lung inflammation in a mouse model of ovalbumin induced allergy/asthma.

321. DESIGN, SYNTHESIS AND EVALUATION OF INHIBITORS OF PYRIDOXAL PHOSPHATE DEPENDENT ENZYMES. **David B. Berkowitz**; University of Nebraska, Lincoln, NE.

Physiological amino acid chemistry often involves enzymes that rely upon the pyridoxal phosphate (PLP) cofactor, derived from vitamin B6. PLP provides chemical functionality that is well suited for the stepwise cleavage/formation of bonds to the α-, β- or γ- carbons of amino acids. This presentation will describe our efforts to divert this chemistry toward 'suicide inhibition' or 'Trojan horse inhibition' avenues with suitably designed unnatural amino acids. For the amino acid decarboxylase (AADC) enzymatic class, the use of quaternary amino acids bearing β,γ-unsaturation is particularly attractive, as this both introduces a potential suicide trigger and renders the AA inert to PLP enzymes that require an α-proton (*i.e.*, transaminases, racemases and β- or γ-eliminase or replacement enzymes). Synthetic advances in the enantioselective synthesis of β,γ-unsaturated AAs will be presented, as will data on their application to PLP enzyme inactivation.

322. 3D MODEL OF A SUBSTRATE-BOUND LIGHT-CHAIN DOMAIN OF BOTOX PREDICTED BY MULTIPLE MOLECULAR DYNAMICS SIMULATION DOCKING: NEW APPROACH TO DOCKING FLEXIBLE MOLECULES WITH CONSIDERATION OF SOLVATION. **Yuan-Ping Pang**; Mayo Clinic, Rochester, MN.

Botulinum neurotoxin serotype A (Botox), a widely used cosmetic, is a toxic by-product of a naturally occurring bacterium. Currently there is no antidote to Botox. The light-chain domain of Botox is a zinc endopeptidase that can be used as a target for developing small-molecule antidotes to Botox. The 3D structure of this endopeptidase complexed with its substrate is still unavailable. This article reports a 3D model of the endopeptidase in complex with a heptapeptide substrate predicted by performing 200 different molecular dynamics simulations (2.0 ns for each simulation with a 1.0-fs time step). This model explains the results of mutagenesis studies of the endopeptidase and the structure-activity relationship of known inhibitors of the endopeptidase. It also provides guidance for developing small-molecule antidotes targeting the endopeptidase and suggests that the use of multiple molecular dynamics simulations is a means to dock flexible molecules stochastically into their protein targets with consideration of solvation.

323. TOTAL SYNTHESIS OF (±)-OVALICIN AND ITS ANALOGS. **Srinivas Battina,** Kaiyan Lou, Ana Jimenez and Duy H. Hua; Kansas State University, Manhattan, KS.

The potent antibiotic, antiangiogenetic and immunosuppressive properties of sesquiterpenes ovalicin and fumagillin have attracted a great number of investigative studies in the biological field. Our studies on the inhibition of methionine aminopeptidase 2 have led us to synthesize new analogs of ovalicin and fumagillin. Three total syntheses of ovalicin were reported starting from the core six-membered rings, 2-hydroxymethyl-5-methoxyphenol, L-quebrachitol, and (-)-quinic acid, respectively. We utilized an intramolecular Heck reaction in the construction of an appropriately functionalized methylidenecyclohexene, which upon selective epoxidation and dihydroxylation gave the key intermediate, 6-trialkylsilyloxy-1-oxaspiro[2.5]octan-4,5-diol. The diol was converted into ovalicin in six steps. The starting methylidenecyclohexene was synthesized in four steps from ethyl propriolate.

324. TRICYCLIC PYRONES THAT BLOCK *BETA*-SHEET FORMATION AND AGGREGATION OF ALZHEIMER'S AMYLOID BETA-40 PEPTIDE. Hui-Chuan Wu[1], Erik Pettersson[1], Srinivas Battina[1], Ana Jimenez[1], Bernard Wiredu[1], Takeo Iwamoto[1], Gary A. Radke[1], Qianqian Li[2], Chao Xu[2], Jianjun Wang[2], Lee-Way Jin[3] and **Duy H. Hua**[1]; [1]Kansas State University, Manhattan, KS; [2]Southern Illinois University at Carbondale, Carbondale, IL; [3]University of Washington, Seattle, WA.

The pathogenic events leading to Alzheimer's disease (AD) may reside in the production and deposition of amyloid-*beta* (A*beta*) peptides (fibril formation). A*beta* peptides, hydrophobic polypeptides containing 39-42-amino acids, are derived from a transmembrane glycoprotein, amyloid *beta* precursor protein (APP). In search of compounds that ameliorate the toxicity of A*beta* peptides, we synthesized a new class of derivatives of tricyclic pyrones (TP) and evaluated their counteraction of amyloid toxicity. We found that several TP structures prevent the death of human neuroblastoma MC65 cells that conditionally express a S*beta*C gene (this gene produces a partial APP fusion protein; amino-17 residues plus C99). We also found that the death of MC65 is intimately related to intracellular accumulation of non-soluble, homo- or hetero-polymeric A*beta* complexes. The end result of this accumulation is a cytoplasmic aggregate, reminiscent of the intraneuronal A*beta*-positive inclusions seen in the hippocampus of the early stage AD and in young APP transgenic mice. Using surface plasmon resonance (SPR) spectroscopy, we found that active TPs bind to residues A*beta*(1-40) and A*beta*(16-20). Moreover, we also found that these TPs inhibit aggregation (*beta*-sheet formation) of A*beta*(1-28) and A*beta*(1-40) in Tris-buffered saline (TBS) solution at pH 7.4, in 1,1,1-trifluoroethanol (25%) and in phosphate buffer solution using HPLC-MS, CD and 2D NMR spectroscopies. These results suggest that TPs block *beta*-sheet formation and consequently prevent fibril formation of A*beta* peptides and prevent neuron-cell death second-ary to A*beta* toxicity.

325. CHROMIUM CLUSTER BREAKDOWN KINETICS. **Shveta Chaudhary** and J. David Van Horn; University of Missouri-Kansas City, Kansas City, MO.

A trinuclear chromium(III) cluster {Cr_3O} in a peptide environment is proposed to be a significant biological form of chromium. As part of our research clarifying the biological role of Cr(III), we assessed the hypothesis that the kinetics of trinuclear chromium cluster breakdown must be slow for this moiety to be a viable biological entity. The study of reaction kinetics of this form of Cr will further the understanding of Cr transport, mechanism of action and fate in biological systems. The kinetics of breakdown of trinuclear "basic chromium(III) acetate" were determined *in vitro* using competing ligands (Glu, Ser, Asp, His, Gly, malonic acid, etc.) under *pseudo*-first-order conditions. Reactions were monitored by visible spectroscopy at temperatures 40-60°C. Observed rates (k_{obs}) were determined from least square regression analysis of each experiment by plotting $\log(A_\infty - A_0)/(A_\infty - A_t)$ vs. time (t). Activation parameters for reactions were calculated using the Eyring equation. Observed rates at 60 °C and thermodynamic parameters for the reaction of chromium acetate with different ligands are as follows:

Glycine, $k_{obs} = 10 \times 10^{-4}$ min^{-1}, $\Delta H^\ddagger = 31.2 \pm 5.4$ kJ mol^{-1}, $\Delta S^\ddagger = -218 \pm 37$ J K^{-1} mol^{-1}

D,L-Lactic acid, $k_{obs} = 16 \times 10^{-4}$ min^{-1}, $\Delta H^\ddagger = 66.1 \pm 6.4$ kJ mol^{-1}, $\Delta S^\ddagger = -121 \pm 12$ J K^{-1} mol^{-1}

Aspartic acid, $k_{obs} = 17 \times 10^{-4}$ min^{-1}, $\Delta H^\ddagger = 92.5 \pm 3.7$ kJ mol^{-1}, $\Delta S^\ddagger = -35.8 \pm 1.5$ J K^{-1} mol^{-1}

Histidine, $k_{obs} = 50 \times 10^{-4}$ min^{-1}, $\Delta H^\ddagger = 74.6 \pm 7.5$ kJ mol^{-1}, $\Delta S^\ddagger = -83.8 \pm 8.4$ J K^{-1} mol^{-1}

326. ADSORPTION OF THIOPHENES OUT OF HYDROCARBONS USING SILVER-IMPREGNATED NANOCRYSTALLINE ALUMINUM OXIDE. **Jeevanandam Pethaiyan** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS.

Organosulfur compounds such as thiophene and related molecules present in the commercial fuels pose serious environmental problems and a considerable effort is being made to remove these molecules to obtain sulfur-free or ultra-low-sulfur fuel. The hydrodesulfurization (HDS) process which has been used traditionally is ineffective for the removal of thiophenes and alternative technologies are of immense interest to obtain sulfur-free fuels. One of these approaches is based on adsorption under milder conditions and this process might be a cost-effective and economical one. In the present study, adsorption of thiophene and its derivatives was carried out from a pentane solution using silver-impregnated nanocrystalline metal oxides, with a particular emphasis on aluminum oxide. The modified nanocrystalline aluminum oxide was prepared by an impregnation method and characterized. The adsorption experiments were carried out for thiophene, benzothiophene, dibenzothiophene and 4,6-dimethyl dibenzothiophene. It was found that the incorporation of soft Lewis acid sites such as silver ions is necessary for the adsorption of thiophene related molecules. The modified adsorbent was found to retain its adsorption properties even after compaction and it can be reused for adsorption after regeneration by heating at moderate temperatures. The adsorption properties of the silver-impregnated aluminum oxide (Ag-AP-Al_2O_3) were compared with several other high surface area materials. Detailed characterization studies indicated that the active site in Ag-AP-Al_2O_3 is the Ag^+ ion coordinated to carbonate and metallic silver nanoparticles do not appear to be effective in thiophene adsorption.

327. PHOTOCATALYTIC OXIDATION OF 2-CEES (A CHEMICAL WARFARE AGENT SIMULANT) OVER NANOSTRUCTURED TiO_2-SiO_2 UNDER UV LIGHT. **Shalini Rodrigues**, S. Uma, I. N. Martyanov and K. J. Klabunde; Kansas State University, Manhattan, KS.

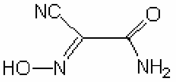
Photocatalytic oxidation of 2-chloroethyl ethyl sulfide (CEES), a simulant of mustard gas was studied on nanostructured TiO_2-SiO_2 by means of GC-MS at room temperature. The photooxidation resulted in the formation of CH_2CH_2, $ClCHCH_2$, CO_2, H_2O and SO_2. Extraction of the solid with acetonitrile showed the absence of disulfides, sulfones or sulfoxides. On the other hand, photocatalytic oxidation of 2-CEES over degussa P25 TiO_2 resulted in formation of a number of primary gaseous intermediates including $CH_3C(O)H$, $ClCH_2C(O)H$, CH_2CH_2, $ClCHCH_2$, $CH_3CH_2S_2CH_2CH_3$, $ClCH_2CH_2S_2CH_2CH_3$ and $ClCH_2CH_2S_2CH_2CH_3$. Also, the products of extraction showed disulfides and sulfones. Prolonged illumination led to their disappearance and eventually to the formation of CO_2, H_2O and SO_2. However, the most interesting aspect of this study is that the photocatalytic oxidation of 2CEES over the TiO_2-SiO_2 catalyst yields no disulfides as compared to Degussa P25 TiO_2 under similar experimental conditions, thus, making it a better catalyst.

328. LAYERED PEROVSKITE PHOTOCATALYSTS. **S. Uma**, Shalini Rodrigues and Kenneth J. Klabunde; Kansas State University, Manhattan, KS.

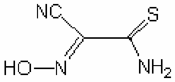
Photocatalysts decompose harmful volatile organics and also are useful in splitting water for cleaner hydrogen production. Currently, TiO_2 is the most widely used photocatalyst fulfilling the above mentioned goals. However, TiO_2 with its band gap energy of 3.2 eV is only active for UV light irradiation (λ<380 nm). Many research efforts are concentrated in discovering new photocatalysts (i) that are active under visible light irradiation and (ii) that are more active than TiO_2 under UV irradiation. Layered perovskites having Ti(IV) and/or Nb(V) offer an interesting class of oxides that can be envisaged as potential photocatalysts. Herein, we report the synthesis, characterization and photocatalytic activities of a series of oxides of the general formula, $A[M_{n-1}(Nb/Ti)_nO_{3n+1}]$(A = Rb; M = Pb, Cd, Bi; n=3) for the decomposition of acetaldehyde. These oxides were found to be excellent photocatalysts comparable to P25 TiO_2 for the decomposition of acetaldehyde under UV light radiation. The effect of loading cocatalysts such as Ni in these layered perovskites for attaining visible light activities will also be presented.

329. FIRST BIOLOGICALLY-ACTIVE Pd(II) AND Pt(II) CYANOXIMATES. **Nikolay Gerasimchuk**, Paul Durham and Daniel Eddings; Southwest Missouri State University, Springfield, MO.

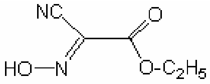
Some of the platinum and palladium compounds are established anticancer inorganic pharmaceuticals. Substantial biological activity (growth regulating, antimicrobial, pesticide detoxifying) was also found during the last two decades' investigations of the cyanoximes. An attempt has been made to combine useful properties of both classes of compounds in order to create a new group of potential antitumor agents. A series of previously unknown bivalent Pd and Pt complexes with cyanoxime ligands shown below has been prepared and characterized using spectroscopic and structural methods. Crystal structures of two Pd(II) complexes based on AACO and MCO ligands revealed that anionic cyanoximes exhibit bidentate chelate coordination to transition metal *via* oxygen atoms of carboxylic group and nitrogen atoms of the nitroso groups forming either *cis*-complexes. Both free ligands and their metal complexes were studied *in vitro* on anticancer activity using HeLa cervical cancer and WiDR colon cancer human cancer cell lines and cisplatin as a positive control. Results indicated significant antiproliferating activity for both Pd(II) and Pt(II) MCO-containing complexes causing 28% and 16% HeLa cells death, respectively, comparing to that of 55% for cisplatin at the same conditions. These two compounds were selected for further investigations.



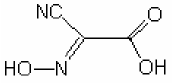
HACO



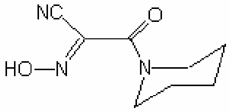
HTCO



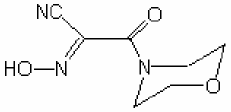
HECO



HAACO



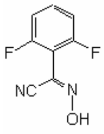
HPiPCO



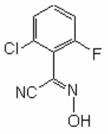
HMCO

330. PREPARATION AND STUDIES OF DISUBSTITUTED ARYLCYANOXIMES AND THEIR BIVALENT PLATINUM AND PALLADIUM COMPLEXES. **Leon Goeden**[1], Nikolay Gerasimchuk[1], Charles Barnes[2] and John F. Cannon[3]; [1]Southwest Missouri State University, Springfield, MO; [2]University of Missouri-Columbia, Columbia, MO; [3]Brigham Young University, Provo, UT.

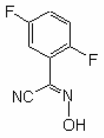
A series of 6 new cyanoxime ligands displayed below was synthesized using nitrosation of respective disubstituted phenylacetonitriles by freshly obtained alkylnitrites at basic conditions (Meyer reaction) in propanol at room temperature and under an inert gas protection. Conditions of these reactions were investigated and thoroughly developed in order to avoid formation of products of several side reactions such as the Thorp reaction and oxidative decyanation. Ligands 1, 2 and 4 being heated undergo nucleophilic defluorination and form usual benzizoxazoles. Stoichiometric ML_2 nH_2O (n=0-3) complexes of Pd(II) and Pt(II) with all 6 disubstituted arylcyanoximes were obtained from aqueous solutions and characterized using spectroscopic methods. Structures, properties and biological activity of some of the synthesized cyanoxime ligands and their transition metal coordination compounds are discussed.



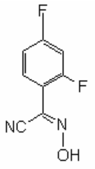
1



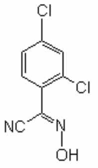
2



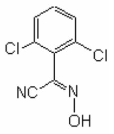
3



4



5



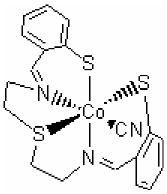
6

331. SYNTHESIS AND CHARACTERIZATIONS OF CHARGE TRANSFER HYBRIDS. **Jeonghee Kang**, James Nelson, Meng Lu, Degang Wang, Sheng Ye, Arindam Ganguly and Zhonghua Peng; University of Missouri-Kansas City, Kansas City, MO.

Hybrid materials based on covalently linked polyoxometalates (POMs) and organic conjugated units have drawn increasing attention not only because of their appealing structural features, but also due to the prospect of generating a whole new class of electrically active materials. In particular, hybrids based on covalently linked organic η-systems as the electron donor and POM clusters as the electron acceptor represent a novel new class of charge transfer hybrids with promising applications in photovoltaic cells. Herein we report the synthesis and characterizations of a number of such hybrids; some of them have ferroence as the electron donor and others have transition metal complexes. Both structural characterization, including NMR, FTIR, and X-ray analysis, and physical properties characterizations including electrochemistry will be presented.

332. MODEL COMPLEXES FOR NITRILE HYDRATASE. **David M. Eichhorn** and Bradley W. Smucker; Wichita State University, Wichita, KS.

The enzyme Nitrile Hydratase (NHase), which catalyzes the hydrolysis of organic nitriles to amides, contains a trivalent Fe or Co at its active site with a coordination environment consisting of two amide Ns, three cysteine Ss, two of which have been post-translationally oxidized to sulfinic and sulfenic acid groups and one water ligand. Using the disulfide synthon 2,2'-dithiodibenzaldehyde, we have synthesized the



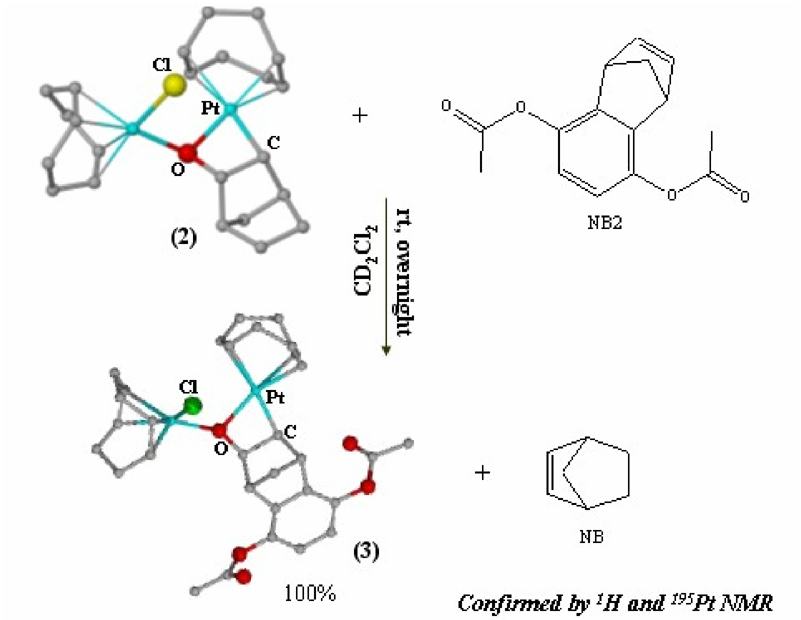
first model complex for Co NHase with a coordination environment containing two N and three S ligands.

333. SYNTHESIS OF NEW CHELATING DICARBENE LIGANDS AND THEIR APPLICATION IN SUZUKI-MIYAURA CROSS-COUPLING REACTIONS. **Adriana I. Moncada** and LeGrande M. Slaughter; Oklahoma State University, Stillwater, OK.

Since the recent discovery of stable N-heterocyclic carbenes, there has been intense interest in using these compounds as ancillary ligands for a number of late transition metal catalyzed reactions. Commonly, chelating N-heterocyclic carbene ligands are synthesized from imidazoles. Here we present a flexible synthetic route to synthesize novel chelating carbene ligands, based on a long known reaction, the nucleophilic addition of amines and hydrazines to coordinated isocyanides. Several palladium complexes of chelating dicarbene ligands have been synthesized and structurally characterized. These complexes have been used to catalyze the Suzuki-Miyaura cross-coupling reaction and present high activity in many cases, even in the presence of air and moisture. The stability of the catalysts in the presence of bases as well as at the high temperatures used in the reaction has been tested in order to identify structural features in the catalysts responsible of their activity.

334. REVERSIBLE ALKENE COUPLING TO Pt(II) OXO-COMPLEXES. **Endre Szuromi** and Paul R. Sharp; University of Missouri-Columbia, Columbia, MO.

We have found that the Pt(II) oxo-complex $[(1,5\text{-COD})_4Pt_4(\mu^3\text{-}O)_2Cl_2][BF_4]_2$ (**1**) readily reacts with alkenes. The reaction with ethylene results in the formation of acetaldehyde, a Pt(II)-allyl complex and CODPt(Cl)Et. Reaction with norbornylene gives a quantitative yield of a platinaoxetane (**2**)(*J. Am. Chem. Soc.*; 2003; **125**(35); 10522-10523). Platinaoxetane **2** was found to react with a benzonorbornylene derivative (NB2) to give free norbornylene (NB) and a new platinaoxetane (**3**) quantitatively. Metallaoxetanes **2** and **3** give the same ethylene reaction products as oxo-complex **1**. Our results indicate that alkene oxidations by our Pt(II) oxo-complexes follow a similar pathway, which most likely involves the coupling of the alkene to the Pt(II) complex to give a reactive platinaoxetane.

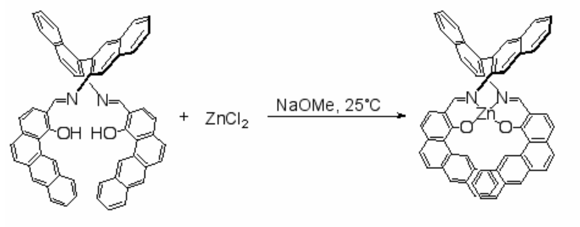


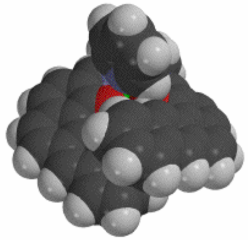
Confirmed by ^1H and ^{195}Pt NMR

335. NEW MONOHELICAL TRANSITION METAL COMPLEXES.

Christopher J. Levy, Alexander Wiznycia and Hellen Dyer, Kansas State University, Manhattan, KS.

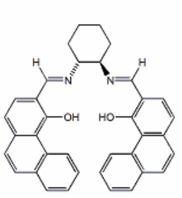
New chiral salen and bis(iminoquinaldine) ligands have been designed with rigid polyaromatic sidearms so that monohelical complexes are formed upon coordination to transition metal ions. (R, R)-1,2-diaminocyclohexane and (R)-1,1'-binaphthyl-2,2'-diamine have been used as chiral ligand backbones, with the latter being highly reliable for generating monohelical complexes of a single handedness. Iron(II) and zinc(II) complexes for a number of ligands have been structurally characterized. Initial VT-NMR studies have not identified interconversions between helical forms, although the crystallographic evidence appears to indicate that this does occur in several cases where the (R,R)-1,2-diaminocyclohexane backbone is present.



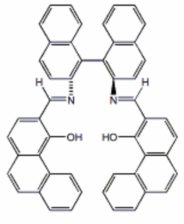


336. HELICAL IRON AND ZINC COMPLEXES DERIVED FROM TETRADENTATE SCHIFF BASE LIGANDS. **Alexander Wiznycia** and Christopher J. Levy; Kansas State University, Manhattan, KS.

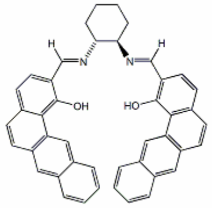
The synthesis and characterization of a series of helical zinc and iron complexes is reported. The aldehydes 4-hydroxyphenanthrene-3-carboxaldehyde and 1-hydroxybenz[a]anthracene-2-carboxaldehyde were prepared and reacted with (1R,2R)-diaminocyclohexane and (R)-1,1'-binaphthyl-2,2'-diamine to give tetradentate ligands **1-4**. Metallation with zinc and iron salts gave the corresponding complexes. These were characterized spectroscopically.



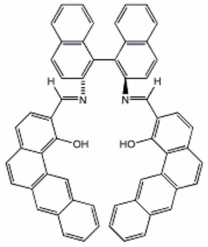
1



2



3



4

337. SIXTEEN VALENCE-ELECTRON SPECIES CONTAINING BORON: STRUCTURAL DIVERSITY ABOUNDS.

Carol A. Deakyne[1], Aaron K. Corum[1] and Joel F. Liebman[2]; [1]University of Missouri - Columbia, Columbia, MO; [2]University of Maryland, Baltimore County, Baltimore, MD.

In order to gain new insight into the structure and bonding of boron-containing molecules, we have recently been investigating fundamental sixteen valence-electron species with the general formulas [B, X, Y, H_2] and [B, X, Y, H_3]$^+$. Here X, Y = C, F or N, O. Intuition suggests that the ion [B, C, F, H_3]$^+$ has the structure [CH_3BF]$^+$, isoelectronically related to the well-known CH_3CN and [CH_3CO]$^+$. Similarly, CH_2BF and NH_2BO are boron analogs of the well-known cumulenes H_2CCCH_2 and H_2CCO. However, high level quantum chemical calculations disclose multiple minima on the singlet potential energy surfaces of [B, C, F, H_2], [B, C, F, H_3]$^+$ and [B, N, O, H_2]. The calculations yield a variety of possible structures for these species, including both cyclic and the expected acyclic, hydrogen-bonded and fluorine-bridged. Barriers to the rearrange-ments between isomers have also been evaluated. Although all three of the above species will be discussed, the intriguing structural and bonding properties of [B, C, F, H_2] will be the main focus of this talk.

338. ELECTRON PROPAGATOR THEORY CALCULATIONS OF PHOTOELECTRON CROSS-SECTIONS: BEYOND THE DIPOLE APPROXIMATION.

Gustavo Seabra[1], I. Kaplan[2], V. G. Zakrzewski[1] and J. V. Ortiz[1]; [1]Kansas State University, Manhattan, KS; [2]Universidad Nacional Autonoma de Mexico, Mexico, D.F., Mexico.

In calculations of photoelectron cross-sections (PE-XS), as well as in the interpretation of experimental data, one usually makes the so-called *dipole approximation* (DA) for the radiation-matter interaction Hamiltonian:

$$V = -\frac{eA_0}{m_e c} e^{i(\mathbf{k}\cdot\mathbf{r}_i)}\, \hat{\mathbf{n}} \cdot \mathbf{p}_i \overset{\text{(DA)}}{\approx} -\frac{eA_0}{m_e c}\, \hat{\mathbf{n}} \cdot \mathbf{p}_i\,,$$

where e, $\boldsymbol{m_e}$, $\boldsymbol{r_i}$ and $\boldsymbol{p_i}$ are the electron charge, mass, position and momentum, **k** and $\hat{n}$ are the photon wavenumber and polarization, $\boldsymbol{c}$ is the speed of light and $\boldsymbol{A_0}$ is related to the energy density of the radiation.

This approximation is supposed to be appropriate when the wavelength of the ionizing radiation is much larger than the size of the target.

However, more detailed studies have shown nondipole effects to be important for ionizing radiation of energy as low as ~400eV. We have developed a scheme to calculate the PE-XS using the full exponential operator, equivalent to including all multipole terms in the transition operator expansion. According to

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi}\left[1 - \frac{\beta}{4}(3\cos^2\theta - 1) + (\delta + \frac{\gamma}{2}\sin^2\theta)\cos\theta\right]$$

where σ is the total cross section, β, γ and δ are angular parameters and the angle $\boldsymbol{\theta}$ is between the incident radiation and outgoing electron, comparison of calculations with and without the DA at different angles between incident radiation and photoelectron allow for an estimate of the importance of the higher order terms. Calculations for small molecules, using the Plane Wave (PW) representation for the photoelectron indicate that the first correction to the DA, which introduces electric quadrupole and magnetic dipole terms, is in the order of 10-30% in the range of 1-5 keV, while higher order corrections are about an order of magnitude smaller.

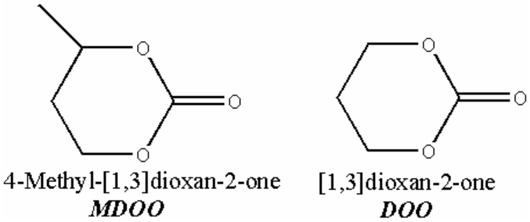
339. POTENTIAL ENERGY SURFACE OF 1-METHYL-8-NITRONAPHTHALENE EXPLORED WITH HYBRID HARTREE-FOCK-DENSITY FUNCTIONAL THEORY METHODS.

Yuri V. Il'ichev; Wichita State University, Wichita, KS.

The potential energy surface of 1-methyl-8-nitronaphthalene (**1**) in the singlet and triplet state was mapped by using four different hybrid models (B3LYP, BH&HLYP, PBE1PBE, MPW1K). Reaction paths leading from **1** either to a nitrite (**2**) or to the *aci*-form (**3**) and further to different tricyclic intermediates were characterized. Overall, 27 minima and 24 transition structures were located at the B3LYP/6-31G(d) level for singlet-state molecules of composition $C_{11}H_9NO_2$. The restricted singlet wavefunctions (both closed- and open-shell) for **3** were found to be either unstable or identical to those of other isomers. However, seven stereoisomers of **3** could be located when the unrestricted formalism was used. For the triplet state, 31 stationary points, of which 18 were minima, were found at the same level of theory. Geometries of **3** and diradical transition structures were also optimized at the UPBE1PBE and UMPW1K levels with the 6-31+G(d,p) basis set. Single-point energies were calculated with the 6-311++G(3df,2p) basis set. For singlet diradicals **3**, the unrestricted wavefunctions obtained with the different functionals were heavily contaminated by higher spin states, while the triplet wavefunctions were practically free of contamination. All hybrid models provided qualitatively consistent pictures for the potential energy landscape. The triplet ground state has been predicted for all isomers of **3**. Interconversion of the *aci*-form stereoisomers was characterized by very low barriers both in the singlet and triplet state. The activation barrier for cyclization of the singlet diradical **3** to a derivative of naphthoxazine was found to be lower than that for the reaction yielding a benz[cd]indole derivative. In the triplet state, tautomerization of **1** was predicted to effectively compete with the isomerization to **2**. These results are discussed in respect to atmospheric reactions of nitronaphthalenes and to development of novel photolabile protecting groups based on *peri*-substituted naphthalenes.

340. SEMIEMPIRICAL QUANTUM MECHANICAL STUDY OF THE CATIONIC HOMOPOLYMERIZATION OF 4-METHYL-[1,3]-DIOXAN-2-ONE (MDOO). Andrew J. Holder and **Yi Liu**; UMKC, Kansas City, MO.

The title molecule exhibited substantial expansion on polymerization observed by mercury dilatometry experiments performed here. In order to elucidate this observation and hopefully shed light on the underlying phenomenon of low-shrink or expanding monomers, mechanistic pathways involving the polymerization reaction were studied using semiempirical quantum mechanical methods.



The mechanism was investigated in detail and compared to previous work on [1,3]dioxan-2-one (DOO). The reaction path of the MDOO is analogous to DOO, involving three steps: 1. cyclic carbonate oxygen protonation, 2. nucleophilic monomer attack at the carbon α to one of the ring oxygens and 3. a new C-O bond forms and subsequent ring-opening occurs. When optimizing the conformations two reactant minima were located, the energies of which varied by the position of the proton with respect to the attacked carbon on the polymerization step. While the energy difference was negligible, these two conformations lead to different transition states and different products.

341. WHERE ARE THE ELECTRONS IN A DOUBLE RYDBERG ANION? A THEORETICAL STUDY WITH THE ELECTRON LOCALIZATION FUNCTION. **Junia Melin** and J. V. Ortiz; Kansas State University, Manhattan, KS.

A double Rydberg anion consists of a cationic core and two electrons distributed peripherally in a Rydberg-like orbital. Low energy features of photoelectron spectra on anion-molecule complexes have been successfully explained by theoretical descriptions of Rydberg structures. Moreover, theory predicts the existence of other double Rydberg anions which have not yet been studied experimentally. Because of the unusual nature of these systems, alternative methods of analysis of their electronic structure may be useful for understanding the behavior of the two diffuse electrons. In this work, we apply the Electron Localization Function (*ELF*) to double Rydberg anions which have been previously described in our group. The *ELF* function, which is based on a topological analysis of the electron density, performs a partition of the molecular space into chemically meaningful regions and has been used widely to describe electron localization in molecules and solids. The diffuse Rydberg electrons are not involved in formal bonds nor do they constitute lone pairs. Through the *ELF* analysis, we can identify the spatial distribution of the diffuse electrons and describe how they respond to chemical substitutions or to interactions with other molecules.

342. SCALING FACTORS FOR HARMONIC VIBRATIONAL FREQUEN-CIES CALCULATED BY USING CORRELATION-CONSISTENT BASIS SETS. **Ralph A. Wheeler**[1], Scott E. Boesch[1], Changming Gu[1], Pankaj Sinha[2] and Angela K. Wilson[2]; [1]University of Oklahoma, Norman, OK; [2]University of North Texas, Denton, TX.

Multiplicative scaling factors are frequently used to bring calculated vibrational frequencies into closer agreement with experimentally measured frequencies. Values of the scaling factors depend not only on the quantum chemical method, but also on the specific basis set used. Although correlation-consistent basis sets are widely used, a systematic study of vibrational scaling factors for correlation-consistent basis sets has not been published. A least-squares approach has been used to determine multiplicative scaling factors for harmonic vibrational frequencies. The harmonic frequencies were calculated using several of the most popular quantum chemical methods and the correlation consistent family of basis sets cc-pVxZ and aug-cc-pVxZ (where x=D(2), T(3), Q(4)). Scaling factors were similarly determined for the enthalpy of formation and entropy of formation and an additional set of molecules was used to calculate scaling factors for the zero-point vibrational energy.

343. ON THE MECHANISMS OF PROMOTION AND POISONING OF THE REACTIVITY OF METAL SURFACES. **Talat Rahman** and Sergei Stolbov; Kansas State University, Manhattan, KS.

Alkali metals are known as efficient promoters in heterogeneous catalysis, while adsorbed S is considered to be a poison. The exact nature of the phenomenon responsible for promotion or poison appear to be not yet understood. Of the several theoretical models that have been presented, one emphasizes the significance of the "isoelectronic reactivity index"as a measure of surface reactivity. We will present results of first principles calculations of the surface electronic structure of Cu and Pd surfaces with chemisorbed C, S, K, and Na which examine the implications of the various proposed measures of surface reactivity. We will show in particular that there is a dramatic increase and delocalization of the isoelectronic reactivity index of Cu and Pd surfaces on alkali adsorption on which can be traced to an unusual feature in the surface potential barrier produced by the adsorbate. We also find that the low-energy electronic excitations associated with the high reactivity index causes a significant decrease in the vibrational frequency and dissocia-tion barrier of an oxygen molecule approaching the surface. This suggests that the revealed phenomenon is a driving force for the "promotion effect". Our results also provide clues to some of the unusual optical properties of quantum wells formed when alkali adsorb on Cu surfaces. Finally we will compare the changes in the local surface electronic and the nature of the adsorbate-substrate bonding for the various systems considered.

344. MOLECULAR-SCALE AND COARSE-GRAINED MODELING OF XEROGELS AND AEROGELS. **Lev D. Gelb**, Niny Z. Rao and Rafael Salazar; Washington University, St. Louis, MO.

A multiscale approach is taken to generating and studying realistic molecular models of silicate materials produced by sol-gel processing. We have performed molecular dynamics simulations of the polymerize-tion of silicic acid in aqueous solution using the potential developed by Fueston and Garofalini [*J. Phys. Chem*. 1990, **94**, 5351]. Simulations have been run at different temperatures and at many different concentrations. Water clearly acts as a catalyst in these simulations. When the water-to-silicon ratio is large, we find that the initial stages of the polymerization process are dominated by the conversion of monomers to dimers and addition of monomers to small clusters, while at longer times cluster-cluster aggregation is observed. Using data from simulations at different temperatures, the activation energies and absolute rates of condensation between silicic acid monomers were calculated at different water-to-silicon ratios and found to compare favorably with experimental results.

For the simulation of larger-scale gel structures and gel drying, a coarse-grained particulate model is proposed. The model consists of simplified "gel particles" which interact *via* short-ranged, sticky potentials. We have used this model and a simple lattice-based description of an adsorbing gas to probe the relationship between meso-scale gel structure and adsorption isotherms.

345. EFFECT OF COULOMBIC INTERACTIONS ON THE MOBILITY OF GUEST MOLECULES. James W. Gilliland[1], Kazushige Yokoyama[2] and **Wai Tak Yip**[1]; [1]University of Oklahoma, Norman, OK; [2]SUNY Geneseo, Geneseo, NY.

The mobility of rhodamine 6G (R6G), Nile Red (NR) sulforhodamine B (SRB) and Oregon Green 514 (ORG) in sol-gel silicate films prepared by the spin-coating method are determined by single molecule fluorescence polarization measurement. In this work, we focus on examining the effect of coulombic interactions on the rotational mobility of encapsulated molecules in sol-gel silicates. Positively charged R6G, neutral NR and Zwitterion SRB exhibit similar mobility in dry films whereas a slightly higher mobility was observed from the negatively-charged ORG. This indicates that coulombic interactions only have a moderate effect on the mobility of sol-gel encapsulated guest molecules in dry films. Upon equilibration with water and different pH buffers, the effect of coulombic repulsion on enhancing ORG mobility became more pronounced while coulombic attraction remained an unimportant factor to the mobility of R6G, NR and SRB. The potential implications of these observations will be discussed under the context of the immobilization mechanism of organic molecules in sol-gel silicates.

346. HIERARCHICALLY-IMPRINTED NANOPOROUS SOL-GEL MATERIALS. **Sheng Dai**; Oak Ridge National Laboratory, Oak Ridge, TN.

Molecular imprinting involves arranging monomers of polymerization synthesis around a template molecule so that complexes between the monomer and template molecules are formed. Subsequent polymerization of the monomer molecules results in trapping template molecules in a highly cross-linked amorphous polymer matrix. Extraction of the imprint molecules leaves a predetermined arrangement of ligands and a tailored binding pocket. Thus far, the organization of precursor monomers has been achieved mainly in inhomogeneous organic polymer matrices, with little control over structural parameters, such as pore sizes and surface areas. Here, we report the synthesis of imprinted materials with precise control of not only adsorption sites but also pore structures. The concepts behind our multilevel imprinting are as follows. Surfactant micelles and target metal ions both act as templates in these hierarchically imprinted materials. The removal of the templates results in the formation of different sized imprints within the silica matrix, each with a specific function. On the microporous level, the removal of the metal ion from the complex leaves cavities (0.1-0.3 nm) that exhibit ionic recognition. These pores give the sol-gel materials enhanced selectivity for the given ion. On the mesoporous level, the removal of the surfactant micelles results in the formation of relatively large, cylindrical pores (diameter 2.5-4.0 nm) which give the gel an overall porosity which includes large surface areas and excellent metal ion transport kinetics. This combination of high capacity and selectivity, coupled with fast kinetics, makes these materials ideal candidates for many applications. Because the whole process utilizes template or imprinting synthesis twice and on different length scales, it can be viewed as a hierarchical double-imprinting process.

347. SENSOR FOR NERVE AGENTS USING SOL-GEL CHEMISTRY.

John C. DiCesare, Starr N. Horne, Jennifer L. Parker, Sireesh Boya and Christopher J. Peeples; The University of Tulsa, Tulsa, OK.

Development of a sensor capable of selective detection of specific nerve agents is imperative in today's atmosphere of terrorism. The sensor needs to be inexpensive, portable, reliable, absent of false positives and available to all military and first responders. By utilizing the techniques of molecular imprinting, combinatorial chemistry, silica sol-gel synthesis and lanthanide luminescence, a sensor for the detection of non-persistent nerve agents (Sarin) and persistent nerve agents (VX) are being developed. There are many parameters that require investigation in order for the sensor to become a reality. These parameters include 1) the selection of a chelate that can bind to the lanthanide and anchor the nerve agent simulant during the formation of the molecularly imprinted polymer, 2) the determination of the environment best suited for this complex formation, 3) the formation as well as modification of the silica sol-gel for molecular imprinting to take place and 4) the proper quantity and ratios of monomers used to create the three-dimensional imprint. Key to the success of optimizing these parameters is the development of a combinatorial assay that allows for the synthesis and testing of tens of thousands of combinations of parameters. Work on the development of the combinatorial assay has led to a method of preparing thin film polymers capable of analyzing the presence of nerve agent simulants.

348. ENCAPSULATED SOL-GEL SYSTEM FOR THE COLORIMETRIC DETERMINATION OF CHROMIUM(VI). **David L. McCurdy**, Niba Nchotu, Andrew Chambers, William Hodgson and Jon Johanning; Truman State University, Kirksville, MO.

Most methods for the quantitative determination of trace level chromium measure only total chromium and will not allow measurement of chromium(VI) which is toxic and carcinogenic but, generally, is only a small fraction of the total chromium in natural samples. Of the methods that are applied to measure chromium(VI), the detection limits are generally too high for routine use or are complex and expensive.

This presentation will describe our efforts to develop a simple colorimetric approach for measuring trace level chromium(VI) using sol-gel encapsu-lated crystal violet. The approach uses a modified iodometric reaction scheme initiated with chromium(VI) in aqueous samples and ultimately results in the oxidation of leuco crystal violet (LCV) into crystal violet (CV+) directly within a small volume sol-gel monolith. The purple CV+ is measured directly in the sol-gel matrix using a simple spectrophotometer. This reaction scheme has been shown to be capable of detecting chromium(VI) as low as 9 ng/mL when performed in solution phase. It is anticipated that this sol-gel encapsulation approach, which facilitates preconcentration, will eventually allow detection of chromium(VI) at the sub-ppb level.

349. LASER WRITING OF METAL NANOPARTICLES AND SEMICONDUCTOR QUANTUM DOTS. **Massimo F. Bertino**[1], R. Gadipalli[1], A. T. Tokuhiro[1], J. G. Story[1] and Nicholas Leventis[2]; [1]University of Missouri-Rolla, Rolla, MO; [2]NASA Glenn Research Center, Cleveland, OH.

Silica aerogels were patterned with CdS using a photolithographic technique based on local heating with infrared (IR) light. The solvent of silica hydrogels was exchanged with an aqueous solution of the precursors $CdNO_3$ and NH_4OH, all pre-cooled to a temperature of 5C. Half of the bathing solution was then replaced by a thiourea solution. After thiourea diffused into the hydrogels, the samples were exposed to a focused IR beam from a continuous wave, Nd-YAG laser. The precursors reacted in the spots heated by the IR beam to form CdS nanoparticles. We successfully lithographed features with a diameter of about 40 μm, which extended inside the monoliths for up to 4 mm. Samples were characterized with transmission electron microscopy and optical absorption, photoluminescence and Raman spectroscopies. Spots illumi-nated by the IR beam were made up by CdS nanoparticles dispersed in a silica matrix. The CdS nanoparticles had a diameter in the 4-6 nm range in samples exposed for four minutes to the IR beam and of up to 100 nm in samples exposed for ten minutes.

350. PREPARATION OF HIGH SURFACE AREA $VOHPO_4 \cdot 0.5H_2O$ WITH THE ALKOXIDE METHOD. **Juan M. Salazar** and Keith L. Hohn; Kansas State University, Manhattan, KS.

Vanadium phosphorous oxides (VPO) catalyze the partial oxidation of butane to maleic anhydride. These catalysts are commercially manufactured by refluxing V_2O_5 with organic compounds to reduce the metal to the +4 oxidation state followed by reaction with phosphoric acid to obtain the precursor phase ($VOHPO_4 \cdot 0.5H_2O$). The precursor is then dehy-drated and calcined at a high temperature to produce the active phase comprising vanadyl pyrophosphate ($(VO)_2P_2O_7$). The purpose of the present work is to use an alkoxide method to synthesize the precursor ($VOHPO_4 \cdot 0.5H_2O$) with an increased surface area, thus enhancing its characteristics as the raw material for the synthesis of $(VO)_2P_2O_7$. The alkoxide method has been frequently adopted to obtain metal oxides with high surface areas. The method resorts to wet preparation, proceeding through hydrolysis and condensation reactions of the liquid metal alkoxides with water or another acidic hydrolyzing agent to yield metal oxides. In this work, the precursor phase has been synthesized by reacting vanadium (V) alkoxides with orthophosphoric acid in different solvents. This led to formation of a $VOPO_4$ gel. This gel was then dried under atmospheric conditions or in an autoclave. It was found that autoclave drying was effective in producing a high surface area VPO phase when an appropriate amount of solvent was used. Too little solvent led to vaporization of the solvent, collapsing the gel structure and leading to a low surface area. However, it was also found that the high tempera-ture and presence of alcohols (formed during hydrolysis reaction) in the autoclave led to reduction of $VOPO_4$ to $VOHPO_4 \cdot 0.5H_2O$. Through this method the precursor phase was produced with surface areas double that of the best reported literature procedures. The resultant oxides were characterized by diffuse reflectance infrared

Fourier transform spec-trometry (DRIFTS) and X-ray diffraction (XRD). Moreover, their surface areas were measured with BET analysis.

351. SOLVENT EFFECTS IN THE HYDROLYSIS OF MAGNESIUM METHOXIDE AND THE PRODUCTION OF NANOCRYSTALLINE MAGNESIUM HYDROXIDE: AN AID IN UNDERSTANDING THE FORMATION OF POROUS INORGANIC MATERIALS. **Ranjit T. Koodali** and Kenneth J. Klabunde; Kansas State University, Manhattan, KS.

The hydrolysis of magnesium methoxide in various solvent-methanol mixtures with water to methoxide ratio of two has been studied. Solvents having low dielectric constants such as toluene, benzene and anisole were found to accelerate the gelation process while solvents having high dielectric constants such as acetonitrile, N,N-dimethylformamide and dimethyl sulfoxide did not have a significant effect in the gelation process. A correlation between the gelation time and the dielectric constant of the solvents employed was found, which suggests that the solvation of the alcohol-alkoxide mixture is an important parameter which influences the gelation time and, hence, the resulting properties of the dry gel. The partial-charge model was invoked to explain the hydrolysis of metal alkoxides in the presence of toluene. Also, the study demonstrates that with appropriate choice of solvents (such as toluene, benzene or anisole), high surface area porous inorganic oxides can be obtained. High temper-ature hypercritical procedure does not seem to be necessary for the preparation of nanoscale $Mg(OH)_2$. This has important implications in the synthesis of porous oxide materials with high surface area.

352. ARENEDIAZONIUM SALTS: CYCLIC VOLTAMMETRY AND NON-BONDED ELECTRON TRANSFER REACTION WITH CYTO-CHROME C. **Surendra N. Mahapatro**, Hong T. Le, Nhan V. Pham and Rhiannon C. ReVello; Regis University, Denver, CO.

We report cyclic voltammetry studies on a series of substituted arenediazonium tetrafluoroborate salts in acetonitrile and aqueous acetonitrile. In aqueous acetonitrile (CH_3CN:0.1 M phosphate buffer, pH 7; 50:50 v/v), the observed one-electron quasi-reversible wave for *p*-nitrobenzenediazonium tetrafluoroborate implicates the diazohydroxide as the electro-active species. The diazonium salts undergo facile electron transfer reactions with ferrocytochrome c.

353. LEWIS STRUCTURES OF SO_2, SO_3 AND SO_4^{2-} USING *AB INITIO* CALCULATIONS. **Zeb C. Kramer** and Stephen A. Angel; Washburn University, Topeka, KS.

Lewis structures of SO_2, SO_3 and SO_4^{2-} are inconsistently presented in elementary chemistry textbooks. These texts and several articles published in the *Journal of Chemical Education* either favor structures generated using the octet rule or those that reduce the formal charges on the constituent atoms. It is the purpose of this study to elucidate the most relevant Lewis structure of each molecule using *ab initio* quantum chemical calculations. Justification of the model chemistries are asessed by comparing experimental values to calculated vibrational frequencies, force constants, heats of formation and dipoles. Using the empirically-valid basis set and method the relevant Lewis structure may be presented by analyzing bond lengths, population analysis methods and additional output available in the software packages *Guassian '03* and *Spartan '04*.

354. EFFECTS OF BASES, ALDEHYDE STRUCTURES AND WATER IN SOLID-STATE WITTIG REACTIONS. **Kevin Patrick Kent** and Stephen Angel; Washburn University, Topeka, KS.

Traditionally, the Wittig reaction requires the use of a strong base in an organic solvent for the synthesis of alkenes from ketones and aldehydes. Following a recent report of solid-state Wittig reactions, using a ball-milling machine, parameters affecting solid state yields are reported, using alternate milling techniques. Trends of alkali- and alkaline-earth carbonates and phosphates were studied. Some effects of water on the reaction were also observed. Progress towards studying the effects of aldehyde structures on the reaction is being made.

355. INTRINSIC HYDRATION TENDENCIES OF LANTHANUM (III) COMPLEXES. **Jennifer Morrison** and Michael J. Van Stipdonk; Wichita State University, Wichita, KS.

Complexes containing lanthanide ions such as gadolinium are commonly used as MRI contrast agents. The complexes are useful because of their influence on proton relaxation times. We present here experiments designed to explore the use of electrospray ionization and ion trap mass spectrometry to explore the intrinsic interactions between water and model lanthanum complexes. ESI was used to generate singly- and doubly-charged complexes containing lanthanum (III) and ligands such as acetylacetonate and acetone. The complexes were then isolated and stored in an ion trap to react with ca. 10^{-6} torr of water for varying periods of time (1-10,000 msec). A chemical kinetics simulator was then used to model the hydration reactions and generate relative reaction rate constants. These experiments demonstrate that the combination of ESI and ITMS can be used effectively to study the influences of ligands and complex coordination number on intrinsic hydration reactions.

356. SMILES-A REPLACEMENT FOR IUPAC NOMENCLATURE. **Robert Pavlis**; Pittsburg State University, Pittsburg, KS.

The IUPAC system of nomenclature is supposed to provide a system whereby an organic chemical structure can be represented by a name that allows this structure to be recreated from the name. The name is also supposed to be pronounceable.

The unfortunate reality is that, except for very simple molecules, it fails on BOTH counts. SMILES (Simplified Molecular Input Line Entry Specifica-tion) allows molecules to be represented by standard alpha numeric characters and it provides complete connectivity and stereochemical information. Computer programs are available that convert SMILES strings into both two and three dimensional structures. SMILES fails even worse than IUPAC, however, on being pronouncable!

This paper will discuss whether the SMILES system should be made a part of organic chemistry courses and it will also discuss using SMILES to generate images of molecules for course work.

357. PERIODIC TABLE BY STUDENTS: CONNECTING LEARNING WITH STUDENTS' INTERESTS. **Jung R. Oh**; Kansas State University-Salina, Salina, KS.

‘Periodic Table' project is assigned in the General Chemistry course to foster creative expression of students and to connect students' learning to their personal areas of interest, academic major programs and daily lives. Students are to research a chemical element, to design concise representations for a collective display and to present informative, creative projects using media of their own choice. In course portfolios and an end-of-semester survey, students indicated that these assignments become enjoyable course work and learning projects they are attached to in a personal way. This project is one of my teaching strategy tools to respect a variety of learning styles, to connect chemistry into our daily lives and to engage students learning with their own talents and insights.

358. ORGANIC CHEMISTRY MISCONCEPTIONS REVEALED BY TALK-ALOUD PROTOCOLS. **Robert A. Doyle**[1], Janet Bond-Robinson[2] and Randall Robinson[2]; [1]Creighton University, Omaha, NE; [2]University of Kansas, Lawrence, KS.

Eight first-semester organic chemistry students at a midwestern research university were audiotaped while solving organic chemistry problems. Transcripts of the interviews were analyzed to identify specific misconceptions. The following were frequent misconceptions: misidentify-cation of the reactive site(s) of a molecule, seeing a molecule as the sum of its component atoms or parts rather than as a whole (for example, seeing ozone as merely three oxygen atoms), misconceptions about acid-base theory and problems with the terminology of organic chemistry. An additional finding was that students could often predict the product(s) of a reaction without knowing the reaction mechanism.

359. GENERAL CHEMISTRY "LATE SHOW": LECTURE VIDEOS IN LARGE-ENROLLMENT COURSES. **Brian D. Huesgen** and John E. Adams; University of Missouri-Columbia, Columbia, MO.

In large-enrollment courses, students often find it difficult to absorb all the information presented in lecture. Furthermore, although instructors would like to believe that such is not the case, the students often are not giving their full attention to the subject matter being discussed. We have begun video taping in-class lectures in some general chemistry courses and posting the digitized videos on web, so that students may review the lectures at their own pace and at a time of their own choosing. Student response to this initiative thusfar has been overwhelmingly positive--even students who do not use the videos tend to appreciate their availability. To date, the ability to access the lectures outside of the classroom has not adversely impacted lecture attendance.

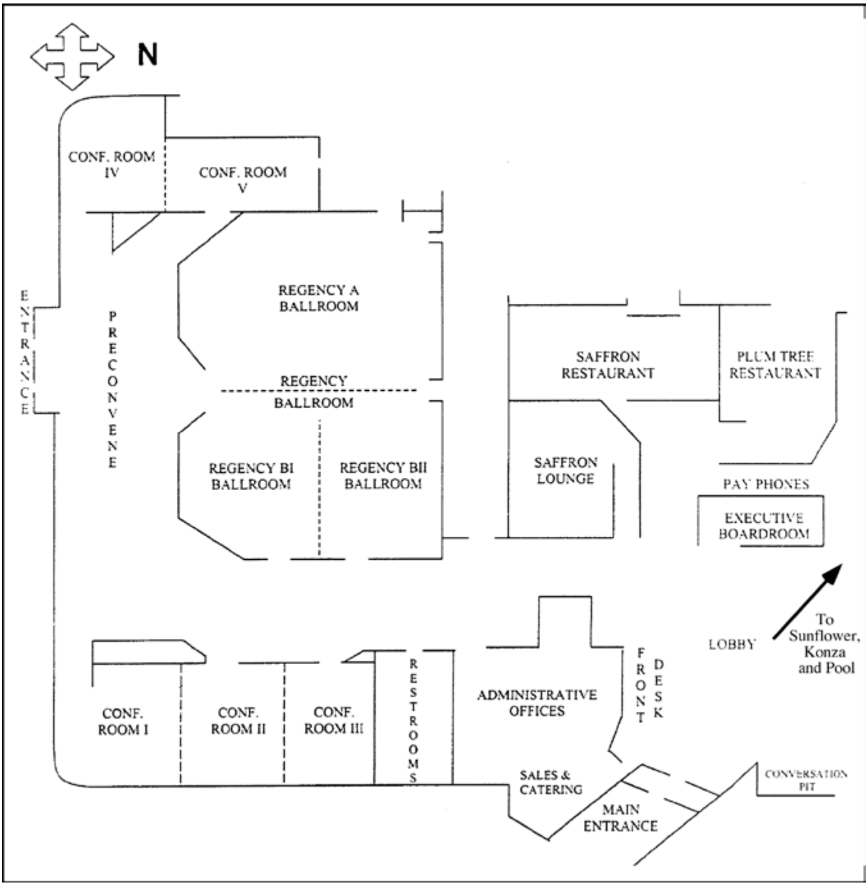
360. INTERACTIVE DEMONSTRATIONS FOR MOLE RATIOS AND LIMITING REAGENTS.

Bryan E. Breyfogle and Crystal Wood; Southwest Missouri State University, Springfield, MO.

The objective of this study was to develop interactive lecture demonstrations (ILD) based on conceptual change learning theory. Experimental instruction was designed for an introductory chemistry course for nonmajors to address misconceptions related to mole ratios and limiting reagents. Students were asked a series of questions related to two chemical demonstrations *via* an electronic keypad system. Questions asked during the demonstrations included conceptual items, particulate items and traditional textbook style calculations. Results indicate that use of the ILDs decreased students' misconceptions and that they were a positive addition to the course. Students' understanding was determined *via* a pretest and posttest that included multiple choice and free response questions. Students showed significant improvement on the multiple choice items after instruction. Evaluation of free response items *via* a rubric indicated that participants' understanding of stoichiometry increased. A large majority of student evaluations suggested that the interactive system had a positive effect on their learning.

AUTHOR INDEX (Presenting authors denoted in bold)

Manhattan Holiday Inn Holidome Map



40th MIDWEST REGIONAL MEETING

AMERICAN CHEMICAL SOCIETY
Joplin, Missouri
October 26-28 2005
www.mwrm2005.org

Featured Symposia

- *Science Education K through 12*
- *Smaller is Better: Miniaturization in Analytical Chemistry*
- *Interaction of Organic and Inorganic Substances with Clay Minerals*
- *Green Chemistry*
- *Heterocycles*
- *Innovations in Chemistry Education*
- *Chemical Ethics*

General Sessions

- *Analytical*
- *Biochemical and Medicinal*
- *Chemistry Education*
- *Inorganic*
- *Organic and Polymer*
- *Physical*

Holiday Inn Hotel and Convention Center
Joplin, Missouri

Mel Mosher, General Chair (417-625-9733) mosher-m@mssu.edu
Michael Garoutte, Program Chair (417-625-9579) garoutte-m@mssu.edu
Department of Chemistry
Missouri Southern State University
Joplin, MO 64801

Celebrating our 65th Anniversary in 2005