37TH MIDWEST REGIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

Hosted by the University of Kansas Local Section

October 23–25, 2002

The Kansas Union
The University of Kansas
Lawrence, Kansas

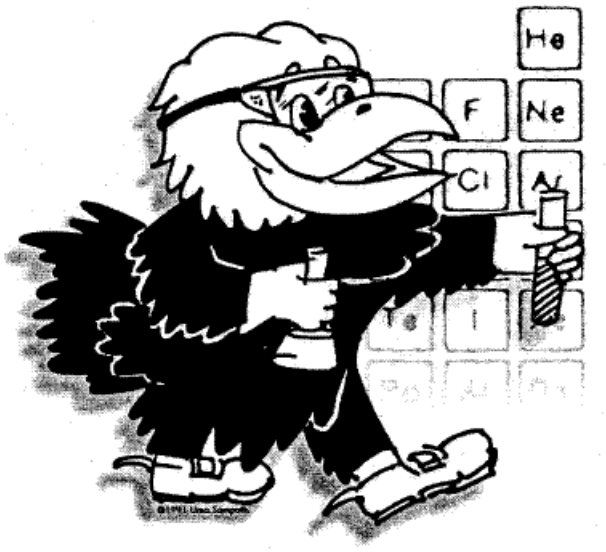
Credits

General Chair	Robert G. Carlson
Program Chairs	Cynthia K. Larive Joseph A. Heppert
General Session Chairs	
Analytical Chemistry	Heather Desaire
Chemical Education	Janet Robinson
Inorganic Chemistry	Mikhail Barybin
Organic Chemistry	Helena Malinakova
Physical Chemistry	Cindy Berrie
Symposia Chair	Paul Hanson
Exhibits Chair	Eric Munson John Stobaugh
Undergraduate Activities	Barbara Schowen Bonnie Sheriff
Treasurer	Malonne Davies
Webmaster	Kenneth Ratzlaff
University of Kansas Continuing Education	Carol Smith Heather Hoy Kristin Tate
Midwest Award	Leah O'Brien
ACS Regional Meeting Office	John Michael Sophos
Kansas Union Coordinator	Gene Wee

Welcome to the

37th Midwest Regional Meeting of the

American Chemical Society



October 23-25, 2002

The Kansas Union

The University of Kansas

Lawrence, Kansas

Hosted by the University of Kanasas Local 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

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38th Midwest Regional ACS Meeting Announcement ..... back cover

STATE OF KANSAS

BILL GRAVES, *Governor*
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Topeka, Kansas 66612-1590

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OFFICE OF THE GOVERNOR

October, 2002

University of Kansas
Section of the American Chemical Society

Greetings:

On behalf of the State of Kansas, I would like to welcome you to the 37th Annual Midwest Regional Meeting of the American Chemical Society, in Lawrence, Kansas. We are delighted to have you as our guests.

The American Chemical Society works diligently to encourage the awareness and understanding of chemistry. Through collaboration with the federal government and private industry, the American Chemical Society makes significant scientific and technological contributions in the area of chemical sciences. The continuing efforts of your members will not only benefit scientific research, but the public's health and welfare.

Best wishes for a most successful event.

Sincerely,

BILL GRAVES
Governor

BG: kg

AMERICAN CHEMICAL SOCIETY
UNIVERSITY OF KANSAS SECTION

September 12, 2002

Greetings,

The University of Kansas ACS Local Section welcomes you to the 37th Midwest Regional Meeting of the American Chemical Society.

Thanks to your participation we have been able to prepare an exciting program, including symposia on undergraduate teaching and research, applications of NMR, materials, proteomics, combinatorial chemistry, receptors and green catalysis.

The planned events include the Midwest Award, Midwest High School Award, WCC Regional Award for Contributions to Diversity, the YCC Luncheon and Employment Clearinghouse. The meeting also features a complete undergraduate program.

We would like to especially encourage you to visit Bailey Hall on our campus. In this building, in 1905, University of Kansas professors David F. McFarland and Hamilton P. Cady discovered the presence of helium in natural gas samples drawn from wells near Dexter, Kansas. Previously helium had been known to exist in the sun and in trace amounts in mineral deposits. The KU professors' discovery opened up plentiful helium supplies from the US Great Plains. To commemorate 100 years of Bailey Hall, the building has been named a National Historic Chemical Landmark by the ACS.

The MWRM and University of Kansas ACS Local Section greatly appreciate your participation in this meeting. We would also like to thank the Organizing Committee for their hard work and the exhibitors and sponsors for their financial assistance.

Krzysztof Kuczera
Chair, University of Kansas Local Section
American Chemical Society

MWRM 2002 THE MEETING AT A GLANCE

Wednesday, October 23		
6:00 PM - 10:00 PM	REGISTRATION	KANSAS UNION
7:00 PM - 10:00 PM	MIXER, POSTER SESSION AND VENDOR EXHIBITION	BALLROOM

Thursday, October 24		
7:00 AM-5:00 PM	REGISTRATION	KANSAS UNION
7:30 AM - 8:30 AM	CONTINENTAL BREAKFAST AND CONVERSATION WITH ACS GOVERNANCE	MALOTT ROOM
8:00 AM - 12:00 N	VENDOR EXHIBITION	BALLROOM
8:00 AM - 12:20 PM	NEW DEVELOPMENTS IN COMBINATORIAL CHEMISTRY	JAYHAWK ROOM
8:00 AM - 12:40 PM	INORGANIC CHEMISTRY: COORDINATION CHEMISTRY	PARLOR B/C
8:00 AM - 12:40 PM	PHYSICAL CHEMISTRY: STRUCTURE AND SPECTROSCOPY	ENGLISH ROOM
8:30 AM - 12:10 PM	ANALYTICAL CHEMISTRY: SEPARATIONS AND MASS SPECTROMETRY	CENTENNIAL ROOM
8:30 AM - 12:25 PM	GREEN CATALYSIS	ALDERSON AUDITORIUM
8:40 AM - 12:20 PM	ORGANIC CHEMISTRY: ORGANOMETALLIC METHODOLOGY	KANSAS ROOM
9:00 AM - 10:00 AM	CAREER SERVICES WORKSHOP: EMPLOYMENT TRENDS	KANSAS UNION
9:00 AM - 11:40 AM	PROBING BIOLOGICAL SURFACES	PINE ROOM
9:00 AM - 12:00 N	CHEMICAL EDUCATION: RESEARCH IN PROBLEM SOLVING	BIG 12 ROOM
10:00 AM - 11:00 AM	CAREER SERVICES WORKSHOP: RESUME PREPARATION	KANSAS UNION
11:00 AM - 12:00 N	CAREER SERVICES WORKSHOP: INTERVIEWING SKILLS	KANSAS UNION
1:00 PM - 4:00 PM	CAREER SERVICES WORKSHOP: INDIVIDUAL RESUME REVIEW	KANSAS UNION
1:00 PM - 4:20 PM	CHEMICAL EDUCATION: CHEMICAL EDUCATION RESEARCH	BIG 12 ROOM
1:00 PM - 4:35 PM	ANION RECEPTORS	JAYHAWK ROOM
1:00 PM - 4:40 PM	ORGANIC CHEMISTRY: SYNTHETIC METHODOLOGY	PARLOR B/C
1:00 PM - 4:40 PM	MEETING THE ANALYTICAL CHALLENGE OF PROTEOMICS	KANSAS ROOM
1:00 PM - 4:40 PM	APPLICATIONS OF NMR TO PROBLEMS IN MATERIAL SCIENCE	PINE ROOM
1:00 PM - 4:40 PM	CATALYSIS	ALDERSON AUDITORIUM
1:00 PM - 5:20 PM	PHYSICAL CHEMISTRY: DYNAMICS AND CHEMISTRY OF CONDENSED PHASES	ENGLISH ROOM
1:30 - 4:30 PM	ANALYTICAL CHEMISTRY: POLYMERS, MEMBRANES AND SURFACE ANALYSIS	CENTENNIAL ROOM
4:30 - 5:30 PM	MIDWEST AWARD ADDRESS	WOODRUFF AUDITORIUM
4:35 - 5:35 PM	ANION RECEPTOR POSTER SESSION	BALLROOM
6:00 PM - 8:00 PM	MIDWEST ACS AWARDS BANQUET	LAWRENCE HOLIDOME
7:00 PM - 10:00 PM	POSTER SESSION AND VENDOR EXHIBITION	BALLROOM

MWRM 2002 THE MEETING AT A GLANCE

Friday, October 25		
7:30 AM - 10:00 AM	REGISTRATION	KANSAS UNION
8:00 AM - 11:00 AM	VENDOR EXHIBITION	BALLROOM
8:00 AM - 12:20 PM	ORGANIC CHEMISTRY: PHYSICAL ORGANIC CHEMISTRY	CENTENNIAL ROOM
8:00 AM - 12:20 PM	THEORY AND SIMULATION OF CONDENSED PHASE MATERIALS	ENGLISH ROOM
8:00 AM - 12:40 PM	INORGANIC CHEMISTRY	PARLOR B/C
8:20 AM - 12:00 N	CHEMICAL EDUCATION: CLASSROOM AND LABORATORY INSTRUCTION	BIG 12 ROOM
8:30 AM - 11:45 AM	APPLICATIONS OF NMR TO PROBLEMS IN PHARMACEUTICAL CHEMISTRY	PINE ROOM
9:00 AM - 11:45 AM	ANION RECEPTORS	JAYHAWK ROOM
9:00 AM - 12:00 N	CATALYSIS	ALDERSON AUDITORIUM
12:00 N	MIDWEST REGION STEERING COMMITTEE LUNCHEON	
1:00 PM - 3:30 PM	WORKSHOP ON WRITING SUCCESSFUL RESEARCH PROPOSALS	ALDERSON AUDITORIUM
1:30 PM - 3:00 PM	UNDERGRADUATE POSTER SESSION	BALLROOM

General Information

The 37th Midwest Regional Meeting of the American Chemical Society will be held from Wednesday, October 23, to Friday, October 25, 2002, at the Kansas Union on the campus of the University of Kansas in Lawrence, Kansas. The University of Kansas Section of ACS will host the meeting.

Information and Registration

Registration will be held in the Kansas Union and will be open 6:00 - 10:00 p.m. on Wednesday, 7:00 am - 5:00 p.m. on Thursday, and 7:30 - 10:00 a.m. on Friday.

Technical Sessions

All of the tecnical sessions are in the Kansas Union as listed in the following program. A map of the union can be found on the inside back cover.

Exhibition

An exhibition featuring scientific instruments, supplies, publishers, and software will be held on Wednesday, Thursday, and Friday in the Ballroom. A number of universities will also have booths at the exhibition for anyone interested in attending graduate school.

The hours of the Exhibition are 7:00 - 10:00 p.m. on Wednesday in conjunction with the first Poster Session and the Welcoming Reception/Mixer, 8:00 a.m. - 12:00 p.m. on Thursday, and 7:00 - 10:00 p.m. on Thursday in conjunction with the second Poster Session, and 8:00 - 11:00 a.m. on Friday.

Awards

The Midwest Region Award for Outstanding Achievements in Chemistry, Sponsored by the ACS St. Louis Section, will be presented to Professor Michael Gross and the Midwest Regional High School Teaching Award will be presented to Janice P. Crowley at the Midwest Award Banquet on Thursday evening. The Midwest Award Address will be presented on Thursday at 4:30 p.m. in Woodruff Auditorium in the Kansas Union. The Midwest Award Banquet will begin at 7:00 p.m. in the Lawrence Holidome, preceded by a reception in the same location at 6:00 p.m.

The ACS Women Chemists Committee Midwest Regional Award for Contribution to Diversity will be presented to Dr. Kristin Bowman-James. This award recognizes individual who have significantly stimulated or fostered diversity in the chemical enterprises.

Special Event for Undergraduates

The undergraduate program and symposium will take place on Thursday from 5:00-10:00 p.m. and on Friday from 8:00 a.m. - 3:00 p.m.

ACS Regional Director's Breakfast

A complimentary ACS Regional Director's Breakfast will be held on Thursday from 7:30-8:30 a.m. in the Malott Room. Alll registered attendees will be welcome to attend and meet with District V Director Ann Nalley and other ACS Board Members in attendance to hear about recent Board of Directors' activities and to share ideas, questions, and concerns relating to ACS membership.

ACS Career Services/Career Resource Center

The Career Resource Center will sponsor these professional development workshops on Thursday, October 24, 2002.

- Employment Trends - 9:00 a.m.
- Resume Preparation - 10:00 a.m.
- Interviewing Skills - 11:00 a.m.

On Friday, October 25 a workshop on *Writing Research Proposals* will be offered in conjunction with the Education Division.

Individual 25-minute resume review appointments may be scheduled for Thursday, from 1:00 - 4:00PM in the main registration area. Bring a copy of your resume. Sign-up will be available in the main registration area.

For more information about any of these workshops, call: (800) 227-5558 x6076.

The Regional Employment Clearinghouse (RECH) will not be on-site at this meeting. However, ACS members and national and student affiliates interested in submitting their resume to employers, should go to http://www.chemistry.org/careers/calendar.html and follow the instructions for sign-up or call Career Services directly (800) 227-5558. Employers interested in sending job openings to job seekers should go to http://www.chemistry.org/careers/calendar.html and follow the instructions for sign-up or contact Garretta Rollins at (800) 227-5558 x6209. Job Seekers and Employers may also drop off resumes and job postings at the main meeting registration desk. The deadline for returning all forms is October 25, 2002.

58th Midwest Region Award for Outstanding Achievements in Chemistry

The St. Louis section established the ACS Midwest Regional Award in 1944 to publicly recognize outstanding achievements in chemistry made in the Midwest Region. The Award is conferred annually on a scientist who has made meritorious contributions to the advancement of pure and applied chemistry or chemical education, and the profession of chemistry. The Award consists of a Medal and a $2000 honorarium to be presented at the Midwest Regional Meeting.

This year's ACS Midwest Award winner, Professor Michael Gross, boasts a career spanning faculty appointments at the University of Nebraska-Lincoln (26 years) and, since 1994, at Washington University in St. Louis. Mike has authored over 400 scientific articles and book chapters, edited or co edited four books, and has trained over 80 graduate students, postdoctoral associates, and staff.

Mike's notable contributions to the field of mass spectrometry began early in his career and include the first observation of a gas-phase distonic ion and the discovery of “charge-remote fragmentation.” He also demonstrated the feasibility of GC/high-resolving-power MS analysis at the parts-per-trillion level, which led Mike and EPA coworkers to the discovery that a chlorinated dioxin (2378-TCDD) had accumulated in the tissue of Vietnam veterans who had handled the herbicide, Agent Orange. For this contribution Mike was awarded the “Pioneer Award—In Search of the Health Consequences of Dioxin in the Environment". Mike commissioned the first analytical three-sector tandem mass spectrometer, which was followed by his publishing of over 100 articles that serve as early demonstrations that tandem MS was to be an important tool in biology. One of these manuscripts reports the first sequencing by tandem MS of a peptide of unknown structure. Along with coworker Charles Wilkins, Mike built the second FT-ICR mass spectrometer in the late 1970s and went on to demonstrate a number of significant analytical applications such as GC/FTMS, laser desorption FTMS, high-pressure trapping in FTMS, and the algorithm for exact mass measurements. Current research has as goals the development of a low- magnetic field MALDI instrument that employs high-pressure focusing, the use of H/D exchange to understand protein/ligand interactions, and the use of mass spectrometry in cancer research.

Mike is Editor of the *Journal of the American Society of Mass Spectrometry* (since 1990), and the former editor of Mass Spectrometry Reviews (1982-1990) and was recently awarded the ACS Field and Franklin Award in Mass Spectrometry.

Midwest Award Address

Opportunities for Mass Spectrometry in Protein Biochemistry and Biophysics

Michael L. Gross
Professor of Chemistry, Washington University

Gross spent 26 years of his career at the University of Nebraska and 8 years at Washington University-St. Louis. He focused much of his attention over those years on basic ion chemistry in the gas phase, development of instruments and methods in mass spectrometry, and applications in environmental chemistry. A new focus area for mass spectrometry is proteomics, which has as one its goal to identify proteins and determine their primary structure of proteins. Gross believes that mass spectrometry can also play a role in determining higher order structure and interactions. To illustrate these relatively new opportunities, he will discuss recent work using H/D exchange on the protein calmodulin and the peptide gramicidin, showing that mass spectrometry can probe the interactions of the protein with calcium and with target peptides. Out of the measurements arises not only information on conformational changes but also equilibrium constants for the various interactions.

Previous Midwest Award Winners

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

Midwest Regional Award for

High School Chemistry Teaching

Established in 1985, the Midwest Regional Award for High School Chemistry is presented to an individual who excels in teaching chemistry to high school students and is deserving of public recognition for significant contributions in promoting chemistry at the secondary level.

Janice P. Crowley, Science Department Chair at Wichita Collegiate Upper School in Wichita, KS, has been awarded the 2002 ACS Midwest Regional Award in High School Teaching. Ms. Crowley will receive her award during the Midwest Awards Banquet at the Lawrence, KS, Holiday Inn on Thursday evening, October 24th. The Awards Banquet will be held as part of the 37th ACS Midwest Regional Meeting, hosted by the University of Kansas Local Section, October 23rd – 25th.

While still in high school, Ms. Crowley worked as a part of Dr. Gary Anderson's leukemia research team at the University of Texas/Richardson. She began her undergraduate studies in chemistry and biology at the University of Texas/Austin and was awarded her B.A. from the University of Texas/Arlington. She obtained her certificate in science education from Wichita State University and is certified in chemistry, physical science, life science and general science. Her resume indicates that she has never really been out of the classroom – first as a student and then a respected and innovative high school teacher, a university instructor and researcher, and a highly successful mentor to her peers.

Since 1986, Ms. Crowley has been Head Coach of the Science Olympiad teams wherever she has been on faculty and has taken a number of teams to the National Science Olympiad. For the past six years, she has served on the St. Thomas Aquinas School Board and is chair of the grant committee. She has taught several SEPUP workshops (Science Education for Public Understanding Program) at Wichita State University and consistently garnered accolades from her students. Other workshops at WSU have included training new chemistry teachers in methodology, teaching chemistry to minority students exploring health career opportunities and the foundations of K – 12 chemistry. For the past decade, she has taught introductory chemistry in WSU summers sessions. She has also participated in workshops preparing students for the science portion of the ACT and the Core Knowledge Chemistry presentation to K – 8 teachers at a Regional Conference in St. Paul, MN, in 2000. This is all in addition to her dedication to her students in general and AP chemistry, general science, physical

science and biology. Her AP students even do research in Gas Chromatography involving methyl esters of linoleic and linolenic acids found in French Fries!

She has received numerous awards from such varied institutions as Kansas State University, Kansas Milken, the Kansas State House of Representatives, Kansas Newman University, Southwestern Bell, the Kansas Community Foundation, the John Garvey Family Foundation, the Julie Sheppard Foundation, the Paul Wilson Foundation and the Wichita Board of Education.

One of her nominators describes her teaching as knowledgeable, approachable, friendly and organized. She has "the ability to transfer these characteristics to her students. Janice Crowley ranks with the best . . ."

Previous Midwest Region Awards for High School Chemistry Teaching

Year	Recipient	Year	Recipient
1985	Donna Jean Bogner	1994	John Oliver
1986	Mary E. Harris	1995	Robert Becke
1987	Richard K. Kavanaugh	1996	Robert Cutright
1988	Claudia K. Viehland	1997	James B. Jenkins
1990	William Harvey Nelson	1998	Andrew Dwight Shaw
1991	Dianne N. Epp	1999	Arthur J. Crum
1992	John M. Hambacker	2000	Pamela S. Abbot
1993	James E. McGahan	2001	Julie A. Larsen

The ACS Women Chemists Committee

Midwest Regional Award
for Contribution to Diversity

Dr. Kristin Bowman-James
Chemistry Department
University of Kansas

This award recognizes individuals who have significantly stimulated or fostered diversity in the chemical enterprises. For more than a quarter of a century in the Chemistry Department of the University of Kansas, and throughout her entire career, Kristin Bowman-James has pioneered gender equality in her chosen profession. She received both her B.S. and Ph.D. from Temple University in Philadelphia. At Temple, she received a number of Scholastic Awards, including the Herbert M. Winegard Memorial Award in Chemistry, the Award of the Philadelphia Section of ACS, the ASTM Student Membership Award and a FMC Corporation-American Viscose Division scholarship. Because she was heavily involved in undergraduate research with Professor Zvi Dori, she chose to remain at Temple for her graduate studies, eventually following Professior Dori to Technion in Haifa, Israel, to complete her research prior to receiving her Ph.D. in 1974.

Dr. Bowman-James arrived at the University of Kansas in 1975 as the sole female faculty member in a 21-person department – the first woman to join the KU Chemistry faculty since the 1940s. While she undertook a number of initiatives reflecting her vision for the department, her most striking achievement has been the dramatic increase in the number of women on faculty. When she arrived at KU, she attributed the gender gap to the reality that women were just beginning to follow the Ph.D. track and surmised that within a decade or two the playing field would become more level. This, however, was not to be the case, and in recent years Kristin has been extremely active in helping to promote the careers of women in the sciences, especially chemistry – primarily through her involvement with the Committee for the Advancement of Women Chemists (COACh).

In 1995, she was appointed chair of the KU Chemistry Department. By that time, three of the 27 faculty members were women. In 1999, she recruited a fourth woman and in the past two years two more women have been recruited to her

Department. She has also been instrumental in the retention of the women on the KU faculty by working with the administration to upgrade equipment and increase funding to counteract outside offers. As of this fall, seven of the 27 KU Chemistry Department faculty members are women. Under her leadership and through the sheer force of her dedication to gender equality, KU now ranks number two among this country's major Ph.D. granting chemistry departments in gender equality.

In the words of Cynthia Larive, one of her nominators and co-program chair of MWRM 2002, "In addition to the impact she has had nationally through COACh, Kristin has been an excellent role model and mentor for women faculty and students in our department at the University of Kansas. By accomplishing the impossible, Kristin has changed the research climate on our campus for the better."

BAILEY HALL: NATIONAL HISTORIC CHEMICAL LANDMARK

On Saturday, April 15, 2000, Bailey Hall was officially designated as a National Historic Chemical Landmark by the American Chemical Society during a ceremony that also celebrated the building's 100th birthday. The events that led to this designation recognized that in 1905 Professor H. P. Cady and Dr. David McFarland, members of the faculty of the Department of Chemistry, discovered helium in natural gas. This was the first demonstration that helium could be found in significant quantities on earth.

In 1868 the French astronomer Pierre Jules Cesar Janssen spoke of an element so rare that it could only be detected in the sun. Within a few years scientists found that trace amounts of that element, helium, could be obtained by heating the uranium metals but it was still considered to be the rarest of the elements. In 1903 a drilling team in Dexter, Kansas, hit upon a well which unleashed a rush of gas which could be heard for miles. The town believed that the discovery of this natural gas would lead to incredible riches and industrial growth and planned a celebration. The lighting of the escaping gas was to be the climax to a daylong celebration. To great expectations, a burning bale of hay was slowly moved into contact with the escaping gas. Instead of the expected conflagration, however, the flames of the burning bales were quickly extinguished. The process was repeated several times with the same result. Eventually samples of the gas were sent to Cady and McFarland for analysis. They found that the gas consisted of 15% methane, 72% nitrogen and 12% of an "inert residue" which they eventually showed contained helium. In 1907 Cady published their findings and commented that their work "assures that helium is no longer a rare element, but a common element, existing in goodly quantity for uses yet to be found for it."

- Based on the work of Professor Emeritus Grover W. Everett, who led the effort to secure the National Historic Chemical Landmark designation for Bailey Hall.

Undergraduate Program and Symposium

Schedule of Events

Thursday, October 24

5:00 - 7:00 p.m.	Undergraduate Social with Food, Music, and Activities No charge for registered undergraduates
7:00 - 10:00 p.m.	Sci-mix and Undergraduate Posters Present posters and keep them displayed through Friday afternoon.

Friday, October 25

8:00 - 11:45 a.m.	Undergraduate Oral Session 15- or 20-minute oral presentations
Noon - 1:30 p.m.	Undergraduate Chemistry Luncheon and Program No charge for registered undergraduates
1:30 - 3:00 p.m.	Undergraduate Poster Session Thursday night posters and posters of participants arriving Friday

SPECIAL SYMPOSIA

ANION RECEPTORS

Thursday Afternoon – Kristin Bowman-James, Presiding
Jayhawk Room

1:00 p.m. **132** DESIGN AND SYNTHESIS OF SALT BINDING RECEPTORS. **Bradley D. Smith** 130

1:50 p.m. **133** VENUS FLYTRAP PODANDS: MODULAR ASSEMBLY AND VERSATILE BINDING AND SENSING. **Jonathan Steed** 130

2:40 p.m. Break.

2:55 p.m. **134** METALLATED CALIXARENES AND CYCLOTRIVERATRYLENES AS ANION HOSTS. **Jerry L. Atwood**, K. Travis Holman 131

3:45 p.m. **135** ANION-ASSISTED TRANSPORT OF HEAVY METAL AND LANTHANIDE IONS BY POLYETHER CARBOXYLIC ACID IONOPHORES. **Richard W. Taylor**, Douglas R. Pfeiffer 131

Poster Session
Thursday Afternoon, 4:35 - 5:35 p.m.
Ballroom

136 A TOSYLATED AZACRYPTAND AS AN ANION RECEPTOR. **Kristin Bowman-James**, Paula K. Morehouse, Md. Alamgir Hossain, Jose Llinares 132

137 MIXED AMIDE-QUATERNIZED AMINE RECEPTORS FOR ANIONS. **Kristin Bowman-James**, Sung Ok Kang, Md. Alamgir Hossain 132

138 DETECTING ANIONIC CASCADE COMPLEXES INSIDE A CRYPTAND CAVITY. **Kristin Bowman-James**, Jose M. Llinares, Md. Alamgir Hossain 133

139 NEW SYNTHESIS OF N-FUNCTIONALIZED MACROCYCLES. **Kristin Bowman-James**, Jerry Kut, Md. Alamgir Hossain, Jose Miguel Llinares 133

ANION RECEPTORS (cont.)

Poster Session (cont.)

140 BINDING AND SELECTIVITY OF HALIDES IN A TINY OCTA-AZACRYPTAND. **Kristin Bowman-James**, Md. Alamgir Hossain, Jose M. Llinares 134

141 OUTER-SPHERE LIGANDS FOR URANYL CARBONATE. **Jason R. Telford** 134

Friday Morning – Kristin Bowman-James, Presiding
Jayhawk Room

9:00 a.m. **304** STRUCTURAL DESIGN CRITERIA FOR OXYANION RECEPTORS. **Ben P. Hay**, David A. Dixon, Maciej S. Gutowski, Bruce A. Moyer, Jeffrey C. Bryan 217

9:50 a.m. **305** AMIDO-PYRROLE CLEFTS. Salvatore Camiolo, Christopher P. Chapman, Korakot Navakhun, Graham J. Tizzard, **Philip A. Gale**, Michael B. Hursthouse, Mark E. Light, Andy J. Shi, Colin N. Warriner 218

10:40 a.m. Break.

10:55 a.m. **306** ANION COORDINATION CHEMISTRY. **Kristin Bowman- James** 218

APPLICATIONS OF NMR TO PROBLEMS IN MATERIALS SCIENCE

Thursday Afternoon – Dennis Hasha and Frank Blum, Presiding
Pine Room

1:00 p.m. **147** ESR SPECTROSCOPY OF UV-GENERATED RADICALS IN POLYURETHANES AND EPOXIES. Yuanyuan Huang, Ying He, Renwu Zhang, Yanching Jean, Jerry R. Richardson, **Thomas C. Sandreczki** 138

1:30 p.m. **148** DYNAMICS OF POLYMERS ADSORBED ON SILICA. **Frank D. Blum** 138

APPLICATIONS OF NMR TO PROBLEMS IN MATERIALS SCIENCE (cont.)

2:00 pm.	**149**	CHAIN PACKING IN PHENYL SUBSTITUTED POLY-CARBONATES BY $^{13}C\{^{2}H\}$ REDOR NMR. **Robert D. O'Connor**, Jeffery A. Byers, Barbara Poliks, Karen L. Wooley, Jacob Schaefer	139
2:30 p.m.		Break.	
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APPLICATIONS OF NMR TO PROBLEMS IN PHARMACEUTICAL CHEMISTRY

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MEETING THE ANALYTICAL CHALLENGES OF PROTEOMICS

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THEORY AND SIMULATION OF CONDENSED PHASE MATERIALS

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GENERAL SESSIONS

ANALYTICAL CHEMISTRY

Separations and Mass Spectrometry

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Polymers, Membranes and Surface Analysis

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INORGANIC CHEMISTRY

Coordination Chemistry

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ORGANIC CHEMISTRY

Organometallic Methodology

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Physical Organic Chemistry

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Dynamics and Chemistry of Condensed Phase

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1. IDENTIFICATION OF P542 PROTEIN INTERACTIONS USING THE YEAST TWO-HYBRID SYSTEM. **James G. McAfee**, Cyril Wehella-Gamage, Rebecca A. Smith, Stephanie L. Springer; Pittsburg State University, 1701 S. Broadway, Pittsburg, KS 66762.

Heterogeneous ribonucleoproteins (hnRNP) are very abundant proteins found in the nucleus of all eukaryotes. Over 20 hnRNPs have been identified in mammalian systems. One of the most abundant hnRNPs in vertebrates is hnRNP C. Studies on hnRNP C have shown that the protein is involved in the packaging, splicing and nuclear export of pre-mRNA. Recently, a new protein was discovered called p542 whose primary sequence was found to be highly similar to hnRNP C. Individuals infected with Ebstein Barr virus (EBV), the causative agent of infectious mononucleosis, produce auto-antibodies against a p542, and auto-antibody production results from a common epitope shared between one of the viral proteins and p542. In addition, sera isolated from individuals with certain autoimmune disorders also contain antibodies to p542. Thus, the molecular pathology of these disorders probably results from inhibition of p542 function. A primary objective of the research presented here is to gain insight into the cellular activities of p542 which we expect will share some functional overlap with hnRNP C. Specifically, in the study reported here, we have used the Yeast Two-Hybrid assay to identify cellular proteins that interact with p542. In these experiments, 5 x 106 yeast colonies harboring a human cDNA library from brain were screened for positive interactions with p542. We have currently identified 220 yeast clones that are positive for containing human cDNA specified proteins that interact with p542.

2. AN RNA PROCESSING PROTEIN MAY INFLUENCE TELOMERE ARCHITECTURE. **James McAfee**, Qian Sun, Ling-Wen Lai, Rebecca A. Smith, Irene S. Zegar; Pittsburg State University, 1701 S Broadway, Pittsburg, KS 66762.

Heterogeneous nuclear ribonucleoproteins (hnRNP) are very abundant nuclear proteins found in all eukaryotes. These proteins package pre-mRNA into ribonucleoprotein complexes, and it is in this context that nascent RNA is capped, spliced, polyadenylated and transported from the nucleus. It is evident that the hnRNP components of hnRNP complexes are not passive associates, but actually play critical roles in the pre-mRNA to mRNA transition. Of the more than 20 different hnRNP proteins that have been identified, the hnRNP C proteins, C1 and C2, are two of the more abundant. hnRNP C1 and C2 have identical primary sequences except for a 13 amino acid insert in the primary sequence of C2 which results from alternative processing of a single transcript. These two proteins exist in solution as stable homotetramers, and in addition to being effectors of RNA splicing, they reduce the conformational diversity of nascent RNA by organizing it

into stoichiometric ribonucleoprotein complexes. In addition to their roles in pre-mRNA packaging and processing, the C proteins have been shown to affect the stability of specific mRNAs through a sequence specific binding mechanism. Furthermore, recent reports suggest that the hnRNP C proteins interact specifically with uridylate rich regions found in human telomerase RNA, and may be involved with telomere maintenance. We have previously reported that the hnRNP C like protein, p542 (hRaly), is functionally equivalent to the hnRNP C proteins despite differences in this protein´s primary structure. We report here that, in addition to sharing the RNA binding properties of C1 and C2, p542 also binds to double-stranded DNA telomere repeats suggesting that it too may be involved in telomere metabolism.

3. KINETICS OF THERMALIZATION BETWEEN $^3P_1$ AND $^3P_0$ STATES OF PR^{3+} IN $CSMX_3$ CRYSTALS. **Andrew Duhaime**, Yizhe An, Stanley P. May; University of South Dakota, 414 E. Clark St., Dept. of Chemistry, Vermillion, SD 57069.

Many lanthanide ions exhibit strong luminescence. This effect is caused by the 4f electrons being shielded by the 5p and 5d electrons. This results in weak coupling between the 4f electronic states and lattice phonons, making multiphonon relaxation relatively inefficient. In some Pr^{3+} compounds, for example, emission is observed from the $^3P_1$ state, even though the next lowest electronic state ($^3P_0$) is only ~500 cm^{-1} lower in energy. This presentation compares multiphonon coupling between the $^3P_1$ and $^3P_0$ states of Pr^{3+} in three isostructural, low-phonon lattices: $CsMgCl_3$, $CsCdBr_3$ and $CsMgI_3$. In $CsCdBr_3$, we are able to optically measure the kinetics of the thermalization between $^3P_1$ and $^3P_0$ and to determine the rate constants both for multiphonon absorption and multiphonon emission.

4. INVESTIGATION OF SUBSTANCE P METABOLISM USING TWO DIFFERENT ANALYTICAL TECHNIQUES. **Joshua D. Cooper**[1], Anita L. Freed[2], Malonne I. Davies[3], Kenneth L. Audus[1], Susan M. Lunte[1]; [1]University of Kansas, 2095 Constant Ave., Lawrence, KS 66047; [2]Pfizer Global Research & Development, 2800 Plymouth Rd., Ann Arbor, MI 48105; [3]Bioanalytical Systems, Inc., Kansas Laboratory, 2095 Constant Ave., Lawrence, KS 66047.

This research compared two different analytical techniques, capillary electrophoresis with laser-induced fluorescence detection (CE-LIF) and liquid chromatography with tandem mass spectrometry (LC-MS/MS), for the investigation of substance P (SP) metabolism by bovine brain microvessel endothelial cells (BBMECs) and *in vivo* with microdialysis sampling. For the microdialysis samples, SP was perfused at a flow rate of 0.2 µL/min into the right striatum of a rat. The

samples were collected and either derivatized for analysis by CE-LIF or diluted with 0.1% formic acid for analysis by LC-MS/MS. For the BBMEC metabolism study, SP was placed into the donor chamber of the diffusion cell and 20 µL aliquots were taken from the receiver chamber at various time points. The samples were analyzed as in the microdialysis studies. For CE-LIF analysis a 50 µm ID fused silica capillary with a buffer of 100 mM TES, 80 mM NaCh and 8 mM SBE(IV)β-CD adjusted to pH 7.5, and a He/Cd laser at 442 nm was employed. The LC-MS/MS was accomplished using a gradient LC coupled to a tandem MS. The separation was performed using a C-18 column with gradient elution using 0.1% FA in water and acetonitrile. With the CE-LIF system an additional metabolite (SP 2-11) was observed in the BBMEC studies that was not observed in the microdialysis samples. The LC-MS/MS was able to detect non-lysine containing metabolites of SP (SP 5-11 and SP 6-11) in the microdialysis samples; these metabolites could not be detected by the CE-LIF method. Each of the analytical methods has advantages and disadvantages. The CE-LIF method can handle small sample volumes, but is unable to detect non-lysine containing metabolites of SP. The LC-MS/MS method is expensive to implement, but all the metabolites of SP can be determined.

5. DEVELOPMENT OF ELECTROCHEMICAL TAGS FOR DNA SEQUENCING. **Paul Weber**[1], Justin Pennington[2]; [1]Briar Cliff University, 3303 Rebecca St., Sioux City, IA 51104; [2]University of Kansas, 2095 Constant Ave., Lawrence, KS 66047.

DNA sequencing is an important analytical procedure utilized not only in research efforts, but also in routine diagnostics. Capillary electrophoresis (CE) has been successfully utilized in this area but there exists a need for the development of sequencing instrumentation that is small in size and weight. “CE on a chip” has been successful in its ability to achieve highly efficient separations in very short times. However, miniaturization of the system is not complete due to the relatively large fluorescent detection systems typically employed. Electrochemical (EC) detection is an alternative method which offers multiple advantages over fluorescence, including the feature that it can be easily miniaturized. The micro-fabrication group of Dr. Susan Lunte (University of Kansas) has been active in developing electrochemical detection for microchip capillary electrophoresis. The long-term goal of the research in our group is to develop, in conjunction with Dr. Lunte´s group, truly compact microchip CE-EC systems for the sequencing of DNA. Initial studies are aimed at labeling DNA with an electrochemical tag since DNA is not innately electrochemically active. The tags proposed are based on the electrochemical properties of the cyano[f]benzo- isoindole (CBI) group. The CBI group can be introduced into molecules containing a primary amine group by reacting the molecule with naphthalene-2,3-dicarboxaldehyde (NDA) in the

presence of cyanide. Initial results reported herein used NDA to label an aminohexyl-modified (AHM) mononucleotide. The mononucleotide contains structural features similar to those of commonly-used AHM oligonucleotides but provides a simpler structure. Additionally, the use of a mononucleotide permits the progress of the reaction to be monitored using capillary zone electrophoresis (CZE) rather than capillary gel electrophoresis (CGE), which employs expensive columns and long separation times. A CZE system with a fiber optic-based UV absorbance detector was constructed in-house to monitor the extent of labeling. CZE with electrochemical detection was then used to examine the electrochemical properties of the system and determine the limits of detection.

6. DRUG BINDING STUDY OF ALPHA 1-ACID GLYCOPROTEIN IMMOBILIZED TO HIGH PERFORMANCE LIQUID CHROMATOGRAPHY SUPPORTS. **Hai Xuan**[1], David S. Hage[2]; [1]University of Nebraska-Lincoln, Hah 731, Chemistry Department, Lincoln, NE 68508; [2]University of Nebraska-Lincoln, 738 Hamilton Hall, Lincoln, NE 68588-0304.

The oxidation of antibodies by periodate is a popular means for the site – specific modification of antibodies for coupling to solid supports. In this study, we used the periodate acid to oxidize the alpha 1-acid glycoprotein (AGP) for its immobilization within high performance liquid chromatographic columns. During the treatment of AGP with periodate, diol groups located in carbohydrate chains of AGP are cleaved to form aldehyde groups. These aldehydes then were used for attachment of AGP to supports that contain free amine or hydrazide residues. Propranolol was used as drug probe to examine the drug binding to AGP. Zonal elution studies were used to examine the binding site and determine the binding constant for propranolol binding to HAS in 0.067M, pH 7.4 phosphate buffer silane. The values at room temperature are 3.7×10^{6}M and 4.0×10^{6}M for R-propranolol and S-propranolol respectively.

7. DISSECTING FUNGAL REDUCED POLYKETIDE BIOSYNTHESIS THROUGH GENETIC REPROGRAMMING AND FUNCTIONAL COMPLEMENTATION OF A GROUP OF MYCOTOXIN PKS. Fengan Yu[1], Robert H. Proctor[2], **Liangcheng Du**[1]; [1]University of Nebraska-Lincoln, Hamilton Hall 647#, 14 R St, Lincoln, NE 68588; [2]USDA, 1815 North University St., Peoria, IL 61604.

Fungi are rich sources for polyketide natural products, synthesized by a group of very unique polyketide synthases (PKSs), many of which are valuable pharmaceuticals. Like bacterial type I modular PKSs, they have a typical domain arrangement to form a protein template. On the other hand, these domains are repeated-

ly used during the polyketide chain elongation, a feature similar to type II iterative PKSs. Since fungal PKSs only have a single set of domains, it is difficult to image how the genetic reprogramming strategies developed for bacterial PKSs could be applied to study the fungal biosynthetic mechanism. We have been studying the biosynthesis of fungal reduced polyketides by using a group of mycotoxin PKSs as a model system. These compounds have a linear carbon chain with various lengths. Their syntheses, when combined, can be regarded as a "heterogeneous multi-modular" system, which enables us to manipulate the individual domains. Upon the functional complementation and identification of new polyketids produced in the reprogrammed mutants, we wish to shed lights on the biosynthetic mechanism. To produce the mutants, we have made three DNA constructs for homologous recombination. The first is an active site mutation of the methyltransferase (MT) domain, which adds a methyl group to the polyketide carbon chain, of FUM5 from *Fusarium verticillioides*. FUM5 gene encodes a PKS catalyzing the biosynthesis of the carbon chain of fumonisins, a group of mycotoxins that impair animal health. We have obtained several MT domain mutants and are currently working on the product identification. The second is a domain swapping mutation by exchanging the FUM5 MT domain with the corresponding region on PKS1 from *Cochliobolus heterotrophus*. PKS1 gene encodes a PKS responsible for the biosynthesis of T-toxins, a family of long-chain (C35 to C41) polyketides. Unlike fumonisins, T-toxins do not have any methylation on the carbon backbone. Corresponding to this structure, no MT domain was found in PKS1. PKS1, however, has a region at the same location and with the same length as the MT domain in FUM5. We have made DNA constructs for swapping the MT domain of FUM5 with the unknown region of PKS1 and introduced the DNA into *F. verticillioides*. Finally, a gene replacement vector containing the intact 7.6 kb PKS1 has been constructed. We are working on the swapping of the whole PKS gene in *F. Verticillioides*.

8. OVEREXPRESSION OF THREE ENZYMES INVOLVED IN THE BIOSYNTHESIS OF FUMONISINS IN *E. COLI*. Yousong Ding[1], Robert H. Proctor[2], **Liangcheng Du**[2]; [1]University of Nebraska, Hamilton Hall Room 618, 13 R Street, Lincoln, Nebraska 68588; [2]USDA, 1815 North University St., Peoria, IL 61604.

Fumonisins are tricarballylic esters of polyhydroxyl alkylamines and alkylamides with a 20-carbon backbone. Since their first isolation in 1988 from plant pathogenic fungus *Fusarium verticillioides*, fumonisins have been subject to extensive investigation for their chemical structures and biological activities due to their widespread occurrence on several important food crops. Biosynthetic studies are also progressing in the recent years. A gene cluster (Fum) has been cloned from the fungus, and genetic data showed that the genes are responsible for the biosynthesis of fumonisins. Biochemical data, however, are still lacking. Here, we

report the overexpression of three Fum genes in *E. coli*. Fum9 is an intron-less gene encoding a protein with 300 amino acid residues. The sequence analysis suggests that the protein might be a dioxygenase or an epoxide hydrolase, both of which are required for the biosynthesis of fumonisins. Using genomic DNA from *F. verticillioides* strain A0149 as the template, we amplified Fum9 by PCR. After DNA sequencing confirmation, the gene was cloned into expression vector pET28a and introduced to *E. coli* BL21 (DE3). Upon IPTG induction, the protein was produced with a high yield as evidenced by a strong band at the expected size (33 kD) on SDS-PAGE. The protein was purified to near homogeneity by Ni-NTA affinity column. Using chemically synthesized (±) *p*-nitrostyrene oxide as substrate, we are currently testing the enzyme´s activity. Fum7, another intron-less gene encoding a putative dehydrgogenase, has also been overexpressed in and purified from *E. coli*, using a similar approach. The 424-residue protein gave a very strong band at the size of 46 kD on SDS-PAGE. Fum8 is a 2936 bp gene containing 4 small introns and predicated to code for a protein of 839 amino acid residues with the size of 92 kD. Its sequence shows a strong similarity to amino acid-palmitoyltransferase, which is clearly the candidate for the incorporation of alanine into the fumonisin carbon backbone. We have obtained a cDNA clone of Fum8 by PCR-amplification of *F. verticillioides* cDNA. The clone has been introduced into *E. coli* for protein purification. The studies set the base for our goal of biochemically elucidating the fumonisin biosynthetic pathway.

9. THE EFFECT OF SELECTED ANALGESICS ON CATECHOLAMINE NEUROTRANSMITTER RELEASE. Sara R. Logan[1], Caren Nies[1], Kathleen E. Heppert[2], **Malonne I. Davies**[2]; [1]University of Kansas, 2095 Constant Ave., Lawrence, KS 66047; [2]BAS Kansas Research Laboratory, 2095 Constant Ave., Lawrence, KS 66047.

Changes in extracellular fluid (ECF) concentrations of catecholamine neurotransmitters (NTs) are of particular interest as a pharmacodynamic outcome of many drugs, for example Ritalin and amphetamine. The administration of post-operative analgesics, such as buprenorphine (BUP), also influences (ECF) concentrations of NTs. If the pharmacology of a particular drug is changed by an analgesic, monitoring the impact from the analgesic on the same NTs is necessary. This study used continuous microdialysis sampling in awake freely moving rats coupled on-line with micro-bore liquid chromatography-electrochemical detection to profile the effect of BUP on NTs. The animals' activity was also recorded. Doses of BUP were administered immediately post-operatively and again at 8 and 24 hr. Dopamine concentrations consistently increased with each dose administration as did 3,4-dihydroxyphenylacetic acid, 5-hydroxyindolacetic acid and homovanillic acid. The information obtained in this study will permit appropriate post-operative analgesic administration without compromising NT information or the pharmacology of different drugs.

10. MEASURING INDICATORS OF OXIDATIVE STRESS THROUGH MICRODIALYSIS AND ELECTROCHEMICAL TECHNIQUES. **Shannon S. Vandaveer**, Allyson T. Charbonnet, Craig E. Lunte; University of Kansas, Department of Chemistry, Malott Hall, Lawrence, KS 66045.

Oxidative stress is a biological indicator of cancer, strokes and myocardial infarctions. Oxidative stress can be measured from the presence of oxygen free radicals (OFR) and DNA damage and lipid peroxidation resulting from OFR formation. 8'-hydroxy-2'-deoxyguanosine (8-OHdG) has been reported as a biomarker of DNA damage. 8-OHdG is formed when OFRs damage DNA by oxidizing guanine, which is then excised. Utilizing microdialysis sampling, the levels of these compounds can be monitored in specific tissues *in vivo*. Microdialysis involves the insertion of a probe with a semi-permeable membrane to continuously monitor conscious, freely moving animals. This method is considered to be more accurate for determining local concentrations at specific tissue sites as compared to plasma and urine sampling and less destructive and more reliable than tissue homogenization. This project specifically focuses on detecting *in vivo* levels of the DNA damage biomarker, 8-OHdG, in rat brain microdialysate following oxidative stress. The oxidative stress is induced either chemically with adriamycin or physically by ischemia-reperfusion. Microdialysis probes were inserted into the cerebral cortex and into the muscle of a rat to measure basal 8-OHdG levels. The 8-OHdG levels were detected by liquid chromatography coupled to electrochemistry. Dual amperometric electrochemical detection was utilized to confirm peak identity and purity. 8-OHdG concentrations were determined in the cerebral cortex and the muscle of a rat following physical or chemical ischemia-reperfusion.

11. ANALYSIS OF OXYGEN FREE RADICAL FORMATION *IN VIVO* BY MICRODIALYSIS SAMPLING. **Allyson T. Charbonnet**, Shannon S. Vandaveer, Craig E. Lunte; University of Kansas, Department of Chemistry, 3072 Malott Hall, Lawrence, KS 66045-7582.

The overall objective of this project is to investigate the formation of oxygen free radicals (OFRs) under conditions of ischemia-reperfusion *in vivo*. Superoxide radicals and hydroxyl radicals are responsible for protein and DNA damage, decreases in activity of antioxidant enzymes and cellular membrane destruction. Although it is generally accepted that OFRs are produced in ischemic-reperfusive events and are agents of damage to cells and tissue, little is understood about the timing of their formation and how different tissues behave when experiencing ischemia-reperfusion. These free radicals are short lived and found in trace amounts in biological systems. Radical spin trapping agents, such as nitrone and nitroso compounds, have been used to form stable radical adducts for analysis. Current methods for sampling tissue and blood do not meet the analytical chal-

lenges presented for the continuous *in vivo* sampling and analysis of free radicals. It has been demonstrated that incubation of homogenized mammalian tissues results in the formation of peroxides (*PNAS*, 1985, **82**, 4798-4802). We are developing a microdialysis sampling technique using spin trapping agents to trap and sample free radicals *in vivo*. Simultaneously, we are developing a HPLC-EC method to separate the radical adduct from other components of the microdialysis sample and achieve sufficiently low limits of detection. The spin adducts of the trapping agents are both neutral and electrochemically active. They have been shown to be amenable to separation and detection by HPLC with electrochemical detection. The trapping agents 5,5-dimethyl-1-pyrroline-*n*-oxide (DMPO) and *alpha*-(4-pyridyl-1-oxide)-N-*tert*-butylnitrone (POBN) are being evaluated for recoveries of oxygen free radicals.

12. DETERMINATION OF ANALYTE RECOVERY FROM BLOOD SAMPLE BY AUTOMATED SYSTEM. Susan M. Garnick, **Malonne I. Davies**; University of Kansas, BAS Kansas Research Lab, 2095 Constant Ave., Lawrence, KS 66047.

Pharmacokinetic, metabolism and toxicology studies rely upon serial blood sampling, which can be time consuming and labor intensive. The Culex®, developed by Bioanalytical Systems Inc., automates the sampling process in awake freely moving rats. During sample collection blood is drawn into ca. 2 cm^3 reservoir containing heparinized saline. The blood displaces about 0.5 cm^3 resulting in a 0.3 cm^2 blood/saline interface. Thus, there is a potential for analytes to diffuse from the blood to the saline phase. The purpose of this study was to evaluate the recovery of analytes *in vitro*, using the Culex. Heparinized whole blood samples were spiked with three model compounds; naproxen (98% protein bound), theophylline (76% protein bound) and glucose (not bound). Samples (200 µL) were simultaneously collected by the Culex and manually every 5 min for one hour and the concentration of the three analytes were determined. Results from this study show that samples taken by the Culex reflect the actual concentration without loss of analytes to the saline phase.

13. MICROANALYTICAL TECHNIQUES FOR THE DETERMINATION OF THE RELEASE OF NITRIC OXIDE IN CELL CULTURE SYSTEMS. **Celeste Frankenfeld**, Sue Lunte, R. S. Martin, Ruri Kikura-Hanajiri; University of Kansas, 2095 Constant Ave., Lawrence, KS 66047.

Nitric oxide (NO) has been implicated in various disease states, including hypertension and neurodegenerative diseases. More recently, NO has been shown to increase the permeability of the blood brain barrier (BBB). Nitric oxide synthase (NOS) causes the release of NO *in vivo*. This enzyme can be induced by

a number of different peptides, including cytokines. An *in vitro* model of the BBB, the bovine brain microvessel endothelial cell (BBMEC) culture system, has been used to study the effects of different agents on the release of NO by the BBB. Unfortunately, NO has a short half-life and is difficult to detect directly. However, the amount of NO produced can be estimated indirectly through determination of its degradation products, nitrite and nitrate. A method to detect nitrate and nitrite using microchip capillary electrophoresis with electrochemical detection has been developed in our laboratories. Good results were obtained with simple reaction mixtures generating NO, but the determination of nitrite and nitrate in cell culture media has proven more difficult. In particular, the complexity of the BBMEC medium provides a significant challenge even for selective electrochemical detection. In addition, anti-stacking occurs due to the many salts present in the medium, leading to significant band-broadening. In this paper, the use of pH-mediated field amplification and CEEC for determination of nitrate and nitrite in BBMEC samples will be presented. The ultimate goal is to develop a "lab-on-a-chip" in which the cells are grown on the chip and sample is collected and analyzed all in one compact unit.

14. IDENTIFICATION OF COMPONENTS OF CYTOTOXIC MYXOBACTERIA CULTURE EXTRACTS. **Bridget A. Becker**[1], Cynthia K. Larive[2], Gunda I. Georg[2], Scott Crupper[3], Richard Himes[2]; [1]University of Kansas, 1251 Wescoe Hall Rd., Malott Hall Rm. B029, Lawrence, KS 66045-7582; [2]University of Kansas, Department of Chemistry, Lawrence, KS 66045; [3]Emporia State University.

LC/MS is a powerful method for the analysis of complex samples, such as those obtained from natural products. This work focuses on the epothilones, first isolated from myxobacteria strain *Sorangium cellulosum* So ce 90 and subsequently detected in extracts of cultures of other strains of myxobacteria. The goal of this research is to identify compounds, either known epothilone structures or new molecular entities, leading to the cytotoxicity of myxobacteria extracts. Preliminary results identifying components of the extracts will be presented. Also, results will be presented comparing the cytotoxicity of samples that are extracted by different methods. Progress of method development for sample fractionation and simplification by solid phase extraction will be presented. The knowledge gained from this research may help other researchers to maximize epothilone production and more efficiently isolate these compounds from myxobacteria cultures.

15. SOLID PHASE EXTRACTION METHOD FOR THE ISOLATION OF PHARMACEUTICALS FROM NATURAL WATER. **Penny M. Higginbotham**, Laurie A. Cardoza, Cynthia K. Larive; University of Kansas, Department of Chemistry, Lawrence, KS 66045.

Detection of pharmaceuticals in natural waters is a growing concern among the scientific community and the general public. The fate of pharmaceuticals in the environment and their effects on aquatic biological systems are for the most part unknown. In attempting to quantify pharmaceuticals at the low levels at which they are found in the environment, a concentration step is a necessary component of sample preparation. Additionally, separation of analyte(s) from the humic acids present in natural water is important, as humics are responsible for signal suppression in mass spectrometry and signal masking in UV-Vis spectrometry. A solid phase extraction method has been developed for the recovery of ciprofloxacin, an antibiotic, naproxen, an analgesic, propanolol, an antihypertensive, salbutamol, a bronchodilator, diltiazem, a calcium channel blocker and clofibrate, a lipid regulator, from deionized and natural waters. The analyte recoveries obtained with this method will be reported and the effectiveness for the reduction of the humic background will be discussed.

16. LC/MS/MS METHOD DEVELOPMENT OF AMLODIPINE WITH NIFEDIPINE-D6 AS THE INTERNAL STANDARD IN HUMAN PLASMA. Sparkle S. Jones[1], **Gary Clapp**[2], Richard Lucero[2]; [1]ACS Project SEED, 12400 Shawnee Mission Parkway, Shawnee, KS; [2]AAI International, 12400 Shawnee Mission Parkway, Shawnee, KS 66216.

Amlodipine (R,S)-2-[(2-aminoethoxy)methyl]-4-(2-chlorophenyl)-3-ethoxycarbonyl-5-methoxycarbonyl-6-methyl-1,2-dihydropyridine is a potent calcium channel blocker; Amlodin and Norvasc are commercially available. It is clinically used in treatment of hypertension and angina. It has the highest oral bioavailability and the longest half-life of elimination among several dihydropyridine derivatives (such as Nifedipine and Verapamil) with calcium antagonist activity. Research in published methods yielded details of a LC/MS/MS method for Amlodipine that will be evaluated in this study. Changes in the assay such as using a volatile buffer in the extraction and MTBE instead of ethyl ether as the extraction solvent, plasma instead of serum and a sample solvent appropriate to our chromatography will be evaluated to obtain the linear range of 20-5,000 pg/mL in human plasma using sodium heparin as the anticoagulant. Stability of Amlodipine in neat solution as well as ruggedness of the method for production will also be evaluated. Quantitation will be achieved on a PE-SCIEX 3000 using atmospheric pressure chemical ionization interface while monitoring the product ions (m/z 238 for Amlodipine and m/z 318 for Nidedipine-D6) of precursor ions m/z 409 and m/z 353 respectively. Nifedipine-D6 will be evaluated as a potential internal standard;

amlodipine-d4 will be obtained from our sister company AAI-International in Ne-Ulm, Germany. This research was supported by the American Chemical Society and the Project SEED endowment. Project SEED is a social action program that places economically disadvantaged high school students in academic, industrial and governmental research laboratories for 8-10 weeks during the summer.

17. DIFFERENCES IN THE CHEMICAL COMPOSITION OF DISSOLVED ORGANIC CARBON IN A PRAIRIE POTHOLE ECOSYSTEM. **Marla F. Williams**, James A. Rice; South Dakota State University, Chemistry and Biochemistry, Brookings, SD 57007.

The differences in the chemical composition of dissolved organic carbon (DOC) in surface and ground water from a prairie pothole in eastern South Dakota may be a result of sorption occurring between the surface water DOC and mineral surfaces present in the soil. Using XAD-8/XAD-4 sorption fractionation, samples of ground and surface water, and water soluble DOC from the soil were fractionated into hydrophilic and hydrophobic acids, bases and neutrals. Significant differences are seen among the fluorescence and quantitative ^{13}C solid-state NMR spectra of the three sample sets. The data suggests that the differences in composition between the surface and ground water are the result of sorption of aliphatic and aromatic components of the DOC to minerals present in subsurface materials.

18. TOXICITY OF 3-NITRO-L-TYROSINE TO CHINESE HAMSTER OVARY CELLS AND ITS POSSIBLE MECHANISM. **Wei Hu**, Nukhet Aykin-Burns, Nuran Ercal; University of Missouri-Rolla, Department of Chemistry, Rolla, MO 65409.

3-Nitro-L-tyrosine (3NT) is an oxidized amino acid that is formed by nitric oxide-derived species and has been implicated in the pathology of diverse human diseases. Although free 3NT is produced in abundant concentrations under pathological conditions, its toxic effects are unknown. In the present study, the toxicity of 3NT to Chinese hamster ovary (CHO) cells was confirmed by lactate dehydrogenase (LDH), cell proliferation (MTS) and colony formation assays. In order to investigate whether oxidative stress plays a role in the mechanism of 3NT toxicity, we determined glutathione (GSH), glutathione disulfide (GSSG), malondialdehyde (MDA) and catalase levels in CHO cells incubated with 3NT at various concentrations. Our results indicate a possible relationship between the existence of oxidative stress and the toxicity of 3NT to CHO cells.

19. CHROMATOGRAPHIC AND SPECTROSCOPIC STUDIES OF CHANGES IN WARFARIN STRUCTURE AND ITS EFFECT ON PROTEIN BINDING. **Annette C. Moser**[1], David S. Hage[2]; [1]University of Nebraska-Lincoln, 731 Hamilton Hall, Lincoln, NE 68588-0304; [2]University of Nebraska-Lincoln, 738 Hamilton Hall, Lincoln, NE 68588-0304.

The stability of warfarin in solution is significant since standards of warfarin are often stored for extended periods of time for drug-protein interaction experiments. As a result, the stability of warfarin in a buffered solution was monitored using ^{1}H NMR. From the data obtained, it was found warfarin undergoes a first order temperature dependent reaction converting the minor cyclic hemiketal to the major cyclic hemiketal. The rate constant for this process at 25 ºC was determined to be 7.9×10^{-3} hr^{-1}, with lower and higher temperatures producing slower and faster rates of conversion. Once the stability of warfarin was investigated, the effect of the conversion between diastereomers upon binding to human serum albumin (HSA) was studied by monitoring the retention factors of the major and minor cyclic hemiketal forms of (*R*)- and (*S*)-warfarin.

20. PREPARATION OF A HYDROPHOBIC PROTEIN FOR PROTEOMIC ANALYSIS OF HUMAN HEPATOMA CELLS EXPOSED TO 2,3,7,8-TETRACHLORODIBENZO-*P*-DIOXIN. Agnes M. Hindemith, **Denise K. MacMillan**; U.S. Army Corps of Engineers, 420 S. 18th Street, Omaha, NE 68102.

The cytochrome P450 superfamily of proteins, primarily found in the liver, is important for processing foreign substances. Liquid chromatography/mass spectrometry is a useful tool for studying such processes, but the hydrophobic nature of the cytochrome P450 isozymes leads to sample loss during sample preparation. To be able to study cytochrome P450 1A expression in human hepatoma cells after exposure to the environmental contaminant, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, by liquid chromatography followed by electrospray ionization and ion trap detection, specialized procedures were developed to minimize protein losses during extraction, transfer, derivitization and volume reduction. In addition, clean-up procedures were investigated to minimize ionization suppression in the mass spectrometer. Some clean-up steps gave improved phase partitioning with increased temperature and lengthened purification time. A membrane extraction kit was modified to add a chloroform extraction step that also increased yield. Incorporation of proteases when appropriate and performing meticulous cleaning steps also led to beneficial results. Details of the preparation scheme for CYP 1A isozyme samples that are compatible with determination by liquid chromatography and electrospray ionization mass spectrometry will be presented.

21. PROBING PEPTIDE/PEPTIDE INTERACTIONS USING H/D EXCHANGE, MS/MS AND ESI-MS: STRUCTURE AND METAL ION BINDING OF GRAMICIDIN DIMER. **Raghu K. Chitta**, Don L. Rempel, Michael L. Gross; Washington University in St. Louis, 1134 McMillen Labs, One Brookings Drive, St. Louis, MO 63130.

Gramicidin, a pentadecapeptide, transports metal ions up to 5 Å in diameter across the membranes by forming a channel, thus initiating the killing of bacteria. The active form is a non-covalently bound dimer. Efforts to simulate the hydrophobic environment of the cell membrane have made use of various solvents ranging from hydrophilic (water, methanol, etc.) to hydrophobic (*n*-propanol). Gramicidin is known to self-associate more in *n*-propanol than in methanol. We are interested to determine if mass spectrometry combined with H/D exchange can be used to detect self-association in solution. A solution of gramicidin was electrosprayed from methanol. A dimer was detected in the gas phase as the isotope peaks were separated by 0.5 mass units. The amount of dimer increased as the hydrophobicity of the solvent increased, suggesting that the dimer was formed in solution. To determine the structure of the dimer, H/D exchange experiments were performed by diluting the gramicidin solution in a deuterated solvent (98:1 = D:H). H/D exchange in methanol showed that all active Hs in gramicidin exchanged to Ds within ~ 5 minutes after mixing. So, H/D exchange was performed in a more hydrophobic solvent in which the equlibrium is expected to be more towards the dimer. H/D exchange experiments in *n*-propnaol showed that Gramicidin in propanol is protected from H/D exchange even after 3 h. To get more structural information and to validate a model, we embarked upon a kinetic analysis. Subtraction of the ^{13}C isotope contribution was done using Mathcad 2001, using the least squares fitting of a theoretical deuterium distribution to the experimental one and constraining all deuterium intensities to be positive. The kinetic analysis was done by fitting the time trajectory of a postulated model system to the above experimentally determined deuterium distributions. The model associates an independent first order reaction to each of the H/D exchange sites. This analysis shows that there are three classes of active Hs in the molecule with rate constants of 1.8 min^{-1} (4 Hs); 0.058 min^{-1} (10 Hs) and 0.011 min^{-1} (28 Hs) with an RMS of 0.023. Since gramicidin dimer is held together by 28 H-bonds, the 28 slow Hs are interpreted to be the active H´s in H-bonds. %D in the solvent was calculated to be 47.8. However, from proton NMR we measured %D to be 90. The discrepancy may be attributed to dilution at local sites in the peptide solution.

22. ONE TENACIOUS DISSOCIATION PATHWAY: SEQUENCE EFFECTS ON THE LOSS OF WATER FROM ALKALI METAL CATIONIZED PEPTIDES. **Michael Van Stipdonk**, Llewellyn Pike, Richard Ahrens, Victor Anbalagan, Erach Talaty; Wichita State University, Department of Chemistry, Wichita, KS 67260-0051.

The formation of $(b_n+17+Cat)^+$ products is the predominant dissociation mechanism for alkali metal cationized, gas-phase peptides. If this reaction pathway is inhibited (for example, by modifying the C-terminus to produce an ester or amide moiety), however, the predominant reaction pathway becomes the elimination of H_2O and loss of sequence diagnostic ion signal. In an effort to understand the mechanism by which H_2O is eliminated and to understand why other sequence informative products are not generated when formation of $(b_n+17+Cat)^+$ is suppressed, we have undertaken a study involving model acetylated dipeptides composed of different combinations of the amino acids glycine, deuterium labeled glycine, sarcosine and proline. When incorporated into peptides, sarcosine and proline lack amide hydrogen atoms that are suspected to be involved in the elimination of H_2O. Proline, a cyclic amino acid, tends to interfere with the formation of cyclic peptide intermediates we find necessary to many dissociation reactions. As we demonstrate here, the elimination of amide hydrogen atoms from a peptide sequence does not necessarily suppress the elimination of H_2O: Li^+ and Na^+ tend to cause the transfer of hydrogen atoms from the α-carbon position instead. The reaction pathway is minimized for the peptide sequence acetyl-proline-sarcosine methyl ester, presumably because of a combination of inhibiting cyclization and eliminating an amide hydrogen atom. The impact of our results in explaining the differences in CID patterns observed for alkali metal cationized peptides, and Ag^+ and protonated analogues, will also be presented.

23. MECHANISMS FOR THE DISSOCIATION OF GAS-PHASE, METAL CATIONIZED PEPTIDES. **Michael Van Stipdonk**, Llewellyn Pike, Richard Ahrens, Erach Talaty; Wichita State University, Department of Chemistry, Wichita, KS 67260-0051.

Collision-induced dissociation (CID) of gas-phase ions is proving invaluable to peptide/protein identification and *de novo* sequencing in proteome studies. There are several practical advantages to the CID of metal cationized peptides. The mechanisms behind the generation of structurally important products, however, remain somewhat unresolved. Here, the CID of a series of peptides, cationized by H^+, Li^+, Na^+ and Ag^+, was studied by means of multiple stage (MS^n) tandem mass spectrometry. Four product ions are generally observed, which differ dramatically in intensity depending on peptide sequence, cation and modification of the N- and C-termini. These are $(b_n+17+Cat)^+$, $(b_n-1+Cat)^+$, $(a_n-1+Cat)^+$ and $(M-H_2O+Cat)^+$. Mechanisms for the formation of each product are proposed, based in part on

careful observation of the effects of isotope labeling in model systems. Key features of the mechanisms include the nature and size of potential cyclic intermediates, the mode of transfer of protons in the gas phase and the particular hydrogen atoms involved in the transfer or in the loss of neutral species.

24. ACCURACY OF SEQUENCE DETERMINATION BY MULTI-STAGE TANDEM MS OF PROTONATED AND METAL CATIONIZED PEPTIDES. Asiri Perera, Victor Anbalagan, Ky-Diu Tran, **Michael Van Stipdonk**; Wichita State University, Department of Chemistry, Wichita, KS 67260-0051.

Multi-stage collision induced dissociation (MS^n) of gas-phase peptide ions is an alternative to Edman degradation chemistry for sequence determination. An advantage to the MS^n of metal cationized peptides offers several advantages of protonated peptides, including the fact that metal ions tend to promote the elimination of amino acids from the C-terminus, minimizing the struggle to distinguish N-terminal from C-terminal product ions and "concentrates" fragmentation for subsequent CID steps. We have initiated a systematic investigation and comparison of the MS^n of protonated and metal cationized (Li^+, Na^+ and Ag^+) peptides of varying length and sequence to determine which approach produces the most accurate and reliable sequence information. We show here that, in general, CID of metal cationized peptides is more accurate for providing sequence from the C-terminus. CID of Li^+ and Na^+ cationized peptides produces reliable sequencing only when the C-terminus is not modified: dissociation of C-terminal peptide esters or amides proceeds primarily through the elimination of H_2O and other small molecules rather than the generation of sequence ions. Ag^+ cationized peptides are less sensitive to the modification of the C-terminus, but tend to interact more strongly with amino acids that contain basic side groups. We also find that modification of the N-terminus by acetylation or benzoylation improves the efficacy of the MS^n experiment primarily by increasing the intensity of sequence ions at high CID stages. In general, we find that for most peptides, MS^n of N-acetylated peptides cationized by Li^+ provides the most reliable and accurate sequencing.

25. MASS SPECTRA-BASED FRACTION COLLECTION OF PROTEINS AND PEPTIDES CHEAP, QUICK AND DIRTY. **Scott Niemann**[1], R.J. Lindmark[2]; [1]CSS Analytical Co. Inc., 6728 Warwick Avenue, Shawnee, KS 66218; [2]Master Enterprises, 1316 Woodgate Drive, Kirkwood, MO 63122.

The isolation and purification of proteins and peptides is an integral step in compound development in the field of Proteomics. In the past, purification of products has been widely done by UV detection of the output from liquid chromatography (HPLC). The chemist would set up an HPLC run, through a semi-

preparative or preparative column and, by UV, “catch” the peaks as they come off the column. Then, each fraction is analyzed by mass spectrometer, to verify the makeup and purity. Some automation of UV fraction collection has occurred over the years by manufacturers of robotic instruments like the Foxy 200 and Foxy Jr. fraction collectors (Isco, Inc., Lincoln, NE). Using the analog signal from the UV detector, the unit was programmed to collect fractions into test tubes. Years later, mass-based fraction collection, using Atmospheric Pressure Ionization (API) techniques became available. Expensive and elaborate autosamplers using the 96 well plate format start by delivering a sample on column and by mass spectrum, were fractionated back into new wells. These systems typically cost $250,000 or more and can be quite complicated to run. A software product has developed that ties to a commercially available mass spectrometer (HPLC/MS) that can enable the chemist to take the first steps in isolation and purification at a very low cost. This software product evaluates the spectra, being collected by the mass spectrometer, and alerts the user to a specific m/z (mass, Dalton or mass to charge) being seen at the inlet. When the green light comes on the screen, flip a valve or move the end of the tubing to a clean vial. With this substantially manual process, mass-based fractionation can be accomplished without great expense. This software solution is ideally suited for graduate or undergraduate studies, and start up labs with limited budgets. This paper will discuss the total system – the software and hardware needed. This paper will show user input panels from the software, plumbing diagrams and experimental data including UV trace and Mass Spectra. Finally, information on how to semi-automate the solution will be given.

26. MICROCHIP CAPILLARY ELECTROPHORESIS SYSTEMS USING LASER-INDUCED FLUORESCENCE DETECTION FOR THE ANALYSIS OF PEPTIDES. **Nathan A. Lacher**, R. S. Martin, Susan M. Lunte; University of Kansas, Department of Pharmaceutical Chemistry, Lawrence, KS 66047.

Microfabricated fluidic chips are becoming more widespread since the initial description of the “lab-on-a-chip” concept. Automation, reduced solvent waste, increased precision and accuracy, a wide variety of chip substrates and the ability to achieve a highly efficient separation in a small amount of time are all potential advantages of microfabricated systems. Thus far, most microchip CE applications have been centered on using a glass substrate that has undergone wet etching to generate separation channels and thermal bonding to complete the fabrication of the microchip. More recently, alternative microchip substrates such as poly(di-methylsiloxane) (PDMS) have been reported for the successful separation of a wide variety of analytes. PDMS is an attractive chip substrate because it requires minimal use of clean room facilities. PDMS has been shown to be relatively simple when it comes to the chip production and electrode integration, but does have

some disadvantages that include broad peaks, severe peak tailing and an unstable surface. In this study, we will report methods to improve the performance of CE microchips based on PDMS using laser-induced fluorescence detection and electrochemical detection. PDMS is very hydrophobic, and hydrophobic compounds tend to adsorb to its surface and cannot be detected. Methods for modifying the surface of PDMS to make the surface more reproducible and applicable to a wider array of analytes are being explored. Methods of improving the performance of the detection aspect are also being explored, such as fabricating a decoupler for microchip CE-EC and the use of a "floating" potentiostat. All of the methods discussed above have led to an improved separation and detection using microchips fabricated with PDMS. PDMS has been shown to be a rugged and reliable alternative to glass for fabricating microchips.

27. THE ANALYTICAL DIGITAL SCIENCES LIBRARY (ASDL). **Theodore Kuwana**[1], Cynthia K. Larive[1], Stuart Chalk[2], Cameron Dorey[3], George Long[4]; [1]University of Kansas, 2291 Irving Hill Drive, Lawrence, Kansas 66045; [2]University of North Florida, 4567 St. Johns Bluff Road S., Jacksonville, FL 32224; [3]University of Central Arkansas, Department of Chemistry, 137 Laney, Conway, AR 72035; [4]Indiana University of Pennsylvania, Indiana, PA 15705.

The Analytical Sciences Digital Library (ASDL), a NSF-funded National Digital Sciences Library project will be described. The ASDL is an electronic library that can be accessed at www.asdlib.org that collects, catalogs and links peer reviewed web-based discovery materials pertinent to innovations in curricular development and supporting resources in the Analytical Sciences. Illustrations of the types of materials included in the collection will be presented such as innovations in teaching and learning pedagogy, resource materials for analytical sciences course and laboratory instruction, supplementary materials on analytical instrumentation and methods and a discussion forum to promote interactive discussions about teaching and learning in the analytical sciences

28. ANALYTICAL METHOD VALIDATION. **Syed B. Alam**; UMR, 5091 Clayridge Dr., Apt, 314, Saint Louis, MO 63129.

Analytical method validation is completed to ensure that methodology is accurate, specific, reproducible and rugged over the specific range where an analyte will be analyzed. A well-defined and documented validation process provides regulatory agencies with evidence that the system and method is suitable for its intended use.

29. CHARACTERIZATION OF PHOTOREFRACTIVE MATERIALS. **Jeffrey E. Hall**, Daniel A. Higgins; Kansas State University, 111 Willard Hall, Manhattan, KS 66506.

Characterization of photorefractive polymer-liquid crystal composite materials using near-field scanning optical microscopy (NSOM) and two-beam coupling (2BC) techniques is presented. Fluorescence and transmission images were taken with the NSOM, while 2BC experiments were used to measure asymmetric beam coupling in the samples. Poly(vinyl alcohol) (PVA) was used as the polymer along with dyed-doped liquid crystal commonly referred to as E7. The liquid crystal was doped with perylene as the photoexcitable electron donor and N, N´-dioctyl-2,4,8,10-naphthalene diimide (NDI) as the electron acceptor. Photorefractive materials are described as materials in which a photo-induced space-charge field changes the refractive index. These materials are of interest due to their potential industrial applications, such as optical data storage and processing, security verification applications, phase-conjugate mirrors, optic filters and some possible medical applications. Photorefractivity occurs in four steps. The first step is the generation of charges. Perylene is excited in the constructive interference regions of two coherent intersecting beams of light. The excited perylene then donates an electron to the NDI, forming a positively charged perylene and a negatively charged NDI. The charges are then separated by drift, which is aided by an applied electric field. The charges are trapped upon reaching the destructive interference regions. These trapped charges create an internal space charge field (E_{sc}). The E_{sc} leads to the modulation of the index of refraction by inducing orientational relaxation in the liquid crystal and resulting in the photorefractive effect. Our near-field studies include high resolution transmission and fluorescence imaging of these materials and studies of the local charge carrier and liquid crystal dynamics.

30. FORMATION OF BOUND RESIDUES BY NAPHTHALENE AND *CIS*-NAPHTHALENE-1,2-DIHYDRODIOL. **Gabriela Chilom**[1], Giuseppina Bestetti[2], Guido Sello[2], James A. Rice[1]; [1]South Dakota State University, Chemistry and Biochemistry, Brookings, SD 57007; [2]Universita di Milano, Genetica e Biologia dei Microorganismi, Milan, Italy.

The formation of bound residues by naphthalene and its metabolite, *cis*-naphthalene-1,2-dihydrodiol, in a sediment (1% OC), a silty loam soil (2.9% OC) and a peat (26% OC) was examined. The experiments were carried out under both sterile and nonsterile conditions. The contaminated samples were hydrolyzed at an alkaline pH and fractionated using 3000 and 500 dalton molecular weight cutoff ultrafiltration membranes operated in series. The results showed that bound residue formation is very low for naphthalene and high for the metabolite. The amount of bound residues hydrolyzed after three days was between 78-87%

for the sediment, 45-57 % for the soil and 28% for the peat. The molecular weight distribution of hydrolysis products showed binding to the high molecular weight components of the sediment organic matter and to the low molecular weight components for soil and peat organic matter.

31. MOLECULAR TRIADS COMPOSED OF FERROCENE C_{60} AND NITRO-AROMATIC ENTITIES: ELECTROCHEMICAL, COMPUTATIONAL AND PHOTOCHEMICAL INVESTIGATIONS. Phillip M. Smith[1], Melvin E. Zandler[1], **Francis D'Souza**[2], Mamoru Fujitsuka[1], Osamu Ito[1]; [1]Wichita State University, Department of Chemistry, 1845 Fairmount, Wichita, Kansas 67260-0051; [2]Tohoku University, Katahira, Sendai 980-8577, Japan.

Synthesis and physico-chemical characterization of a series of molecular triads composed of ferrocene, C_{60} and nitroaromatic entities are reported. Electro-chemical studies revealed multiple redox processes involving all three redox active, ferrocene, C_{60}, and nitrobenzene entities. Up to 8 redox couples within the accessible potential window of *o*-dichlorobenzene containing 0.1 M $(TBA)ClO_4$ are observed. A comparison between the measured redox potentials with those of the starting compounds revealed absence of any significant electronic interactions between the different redox entities. The geometric and electronic structure of the triads is elucidated by using *ab initio* B3LYP/3-21G(*) methods. In the energy optimized structures, as predicted by electrochemical studies, the first HOMO orbitals are found to be located on the ferrocene entity while the first LUMO orbitals are mainly on the C_{60} entity. The coefficients of the subsequent LUMO orbitals track the observed site of electrochemical reductions of the triads. The photochemical events of the triads are probed by both steady-state and time-resolved techniques. The steady-state emission intensities of the triads and the starting dyad, 2-(ferrocenyl)fulleropyrrolidine are found to be completely quenched compared to fulleropyrrolidine bearing no redox active substituents. The sub-picosecond and nano-second transient absorption spectral studies revealed efficient charge separation (and rapid charge recombination) in the triads and this has been attributed to the close spacing of the redox entities of the triad to one another.

32. DETERMINATION OF DIFFUSION COEFFICIENT IN ORGANICALLY MODIFIED SILICATE THIN FILMS. **Skylar A. Martin**, Daniel A. Higgins, Maryanne M. Collinson; Kansas State University, 111 Willard Hall, Manhattan, KS 66506.

Since the 1970s the development of sol-gel materials has lead to numerous applications. Sol-gel materials are being developed for use as functional coatings, chemical sensors and solid-state devices among other applications. They are

inexpensive to prepare, bench top friendly, optically transparent and chemically inert. Though much is known about the bulk properties of these materials, little is known about the nanoscale environments of sol-gel materials. In order to create effective coatings, sensors and other devices it is important to understand the local molecular environments. Since its development over a decade ago, single molecule spectroscopy and detection (SMS/D) has been invaluable in the examination of nanoscale environments. Through the use of SMD, information can be obtained about how a dye dopant interacts with a sol-gel matrix. Through the use of optical spectroscopic and single molecule detection methods, our group has observed single molecules. Recent work in our group has been directed towards a better understanding of the nanoscale properties of organically modified silicate (ORMOSIL) thin films. It has been observed that as the amount of organic precursor in the initial sol increases, the nanoscale properties of the film change dramatically. One noticeable difference is the disappearance of bright, round spots and the appearance of streaks in the fluorescent images. These streaks are believed to be dye molecules diffusing through the ORMOSIL film. In this presentation, the interaction of Nile Red with 90 mol% isobutlytrimethoxysilane/10 mol% tetraethoxysilane thin films will be examined. By using fluorescene imaging and single molecule emission time transients, the diffusion coefficient of Nile Red through the film can be determined.

33. LEACHING OF LEAD FROM CATHODE RAY TUBES (CRTS). **Ralph W. Sheets**, Tim Neterer, Richard N. Biagioni; Southwest Missouri State University, Department of Chemistry, Springfield, MO 65804.

A cathode ray tube (CRT) in a TV or computer monitor contains several kilograms of lead, and there is growing concern that if CRTs are placed in waste dumps they may leach large amounts of lead into the environment. This would require their being treated as hazardous waste and would significantly increase disposal costs. A color CRT is made of glass and consists of four parts: a neck, a funnel that is continuous with the neck, a faceplate and a frit seal which bonds the faceplate to the funnel. Musson, *et al*. have reported that although faceplates and necks of several CRTs released very little lead when subjected to the Toxicity Characteristic Leaching Procedure, funnels released more than the allowable 5 mg/L (S.E. Musson, *et al*., *Environ. Sci. Technol*., **34**, 4376-4381, 2000). It appears, however, that in this investigation the frit seals were not completely separated from the funnel glass, and that the funnel results were influenced by lead in the frit. When we isolated sections of frit seal, funnel glass, neck glass and face glass from a color TV tube and leached finely-ground gram-sized samples of each of the tube components in 20-mL portions of acetic acid/acetate solution buffered at pH 5, we found negligible leaching of lead from faceplate, neck and funnel glass (less than 0.4 mg/L). Concentrations of several thousand mg/L were leached from the frit seal, however. Furthermore, when centimeter-sized pieces of

face or funnel glass were immersed in 6 M nitric acid for six months, concentrations of lead released were less than 0.5 mg/L. It thus appears that vitrification of lead in CRT glass effectively isolates it from the environment, and that the leaching problem concerns only the frit seal. These findings, should they prove applicable to CRTs in general, suggest that if a convenient method for removing the few grams of frit seal between the faceplate and funnel could be developed, the remaining several kilograms of glass might be economically disposed of as nonhazardous waste.

34. CHARACTERIZATION OF A NEW SOLVATOCHROMIC PROBE. **Dana L. Richter-Egger**, Reanen E. Michael; University of Nebraska-Omaha, 6001 Dodge St., 365 Durham Science Center, Omaha, NE 68182.

Solvatochromic dyes are an important class of dyes because of their unique response to solvent polarity. Despite the fact that entire catalogues are devoted to molecular probes (dyes), new dyes continue to be developed each year. The demand for new dyes continues to be strong, primarily due the fact that applications continue to require increasingly specific combinations of multiple dye properties: size, polarity, pKa, absorbance wavelength, chemical reactivity, etc. Because the number of solvatochromic dyes are relatively few, discovery of a new dye of this type could prove extremely valuable to research scientists who rely on their use. Results of recent studies of a new solvatochromic dye are presented. In this fundamental research, the absorbance and steady-state fluorescence emission properties of this new, UV–visible, solvatochromic dye have been characterized in a wide range of solvents. A derivative of a known solvatochromic dye, phenol blue, this dye´s fluorescence emission properties are greatly enhanced compared to phenol blue: it has a measurable fluorescence signal in solvents ranging in polarity from *n*-heptane to water and a solvatochromic shift that spans approximately 100 nm.

35. METHODS FOR ENHANCING THE PERFORMANCE OF PDMS-BASED MICROCHIP ELECTROPHORESIS SYSTEMS. **Walter R. Vandaveer IV**[1], Nathan A. Lacher[1], R. S. Martin[1], Sabeth Verpoorte[2], Susan M. Lunte[1]; [1]University of Kansas, Department of Pharmaceutical Chemistry, McCollum Laboratories, Lawrence, KS 66047; [2]University of Neuchatel, Institute of Microtechnology, University of Neuchâtel, Neuchatel, Switzerland.

The use of microfabricated fluidic chips has become more widespread since the introduction of the “lab-on-a-chip” concept. Automation, higher throughput, faster analyses and reduced solvent waste are all potential advantages of these systems. Thus far, most microchip capillary electrophoresis (CE) applications have used glass substrates. More recently, alternative microchip substrates, such

as poly(dimethylsiloxane) (PDMS), have been successfully employed for the separation of a wide variety of analytes. PDMS is an attractive chip substrate because it requires minimal use of clean room facilities, and the electroosmotic flow (EOF) generated by this device is similar to that of fused silica. However, PDMS does have disadvantages. It is very hydrophobic, and nonpolar compounds tend to adsorb to its surface, leading to loss of analyte and/or low separation efficiencies. In addition, the PDMS surface can change over time. In this study, approaches aimed at improving the performance of both the separation and detection aspects of PDMS-based microchip CE analyses were investigated. Both electrochemical (EC) and fluorescence detection were employed. First, methods of dynamic surface modification, including the addition of bovine serum albumin (BSA) or surfactants to the run buffer, were evaluated for reducing analyte absorption. Second, covalent modification of the PDMS surface with anionic groups was explored. Lastly, methods for eliminating dead volume in the electrochemical detector were investigated. The overall performance of the microchips was measured by monitoring the EOF, peak efficiency, peak asymmetry and migration times.

36. CHEMCHAR GASIFICATION OF SEWAGE SLUDGE AS A SOURCE OF CARBON FOR WASTE TREATMENT. **Stanley E. Manahan**, Brendan P. McAuley; University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211.

Dried sewage sludge works very well as a raw material for the ChemChar gasification process, which is designed to maximize production of carbon with minimum generation of waste products. A scheme is presented in which a granular carbonaceous solid is produced from gasification of dried sludge and used for additional drying and gasification of sludge. The characteristics and uses of char produced by gasification of sewage sludge and the use of sewage sludge as a binder for the gasification of biomass, such as waste grain, are also discussed.

37. STRONG CATION EXCHANGE MONOLITH FOR FAST SEPARATION OF BIOMOLECULES. **Jason Kraska**, Shaofeng Xie, Lan Xu, Tao Jiang, Baburaj Kunnummal, Robert Allington; Isco Inc., 4700 Superior Street, Lincoln, NE 68504.

Porous monolithic separation media are prepared *in situ* by polymerization of a mixture of functional monomer, crosslinking monomer and inert porogenic solvents directly within chromatographic columns. The desired surface chemistry is obtained *in situ* by copolymerization of monomers with desired functionality and/or by surface modification. The polymerization conditions, monomers and

porogenic solvents control the resulting pore structure of the monolith. Compared to more traditional columns, such as packed beads, monolithic columns exhibit much lower backpressure even at high flow rates while achieving better resolution. A number of various monolithic columns have been developed and marketed by ISCO Inc. for rapid separation of biomolecules in reversed-phase and ion exchange modes. This presentation will introduce the SWIFT™ strong cation exchange column. The column's utility and durability will be demonstrated through chromatographic data such as fast separation of proteins and peptides, dynamic loading capacity, stability, batch reproducibility and protein recovery.

38. REPRODUCIBILITIES OF SEPARATIONS WITH SWIFT™ MONOLITHIC COLUMNS. **Lan Xu**, Shaofeng Xie, Tao Jiang, Baburaj Kunnumal, Jason Kraska, Robert W. Allington; Isco, Inc., 4700 Superior Street, Lincoln, NE 68504.

Polymeric Swift™ monolithic separation media have been produced by *in situ* polymerization of functional monomers at the presence of free-radical initiator and inert porogenic solvents directly within a column. The preparation processes only involve one polymerization step, and a second modification step for some columns. Unlike the column packed with particles, whose column reproducibility is controlled by multiple preparation steps and by the “Black Art” of packing, the reproducibility of monolithic columns are determined only by the reaction conditions, which can easily be controlled precisely. Thus, monolithic columns have great potential in high reproducibility. Different types of Swift™ monolithic separation media including reverse-phase, cation and anion exchangers have been developed. This poster will present our studies on column-to-column and batch-to-batch reproducibility of these Swift™ columns in resolution, retention factor, capacity and backpressure as well as their chemical stabilities, run stabilities and shelf lives.

39. APPLICATIONS OF MONOLITHIC COLUMNS IN HIGH SPEED PROTEIN SEPARATION. **Baburaj Kunnummal**, Shaofeng Xie, Robert W. Allington; ISCO INC., 4700 Superior Street, Lincoln, NE 68504.

With the increase in workload from a variety of *in vivo* and *in vitro* screening procedures, new analytical methodologies to perform bio-separation in an accurate and high-throughput manner are in great demand. In this study, monolithic columns were used instead of conventional particulate HPLC columns to perform high speed chromatographic separations. Because the pressure drop on a monolithic column was considerably lower than that on a particulate column, high flow rate can be used for most of the separations. The advantage of using a regular column length at high flow rates, combined with extremely small depen-

dency of separation efficiency on linear flow velocity, allowed for the generation of sufficient chromatographic resolving power in a significantly reduced run time. One- and two-dimensional separation applications will be presented to show the power of this separation media for fast protein analysis in the field of proteome research.

40. INVESTIGATION OF THE MECHANISM OF pH-MEDIATED STACKING OF ANIONS FOR ON-LINE SAMPLE PRECONCENTRATION IN CAPILLARY ELECTROPHORESIS. **Stacy D. Arnett**, Craig E. Lunte; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

Capillary electrophoresis (CE) has become a powerful analytical technique for the analysis of physiological samples such as plasma and microdialysate. However, sample destacking can occur during the analysis of these high-ionic strength samples, resulting in poor separation efficiency and reduced sensitivity. A technique termed pH-mediated stacking has previously been developed to analyze microdialysate samples and achieve on-line preconcentration of analytes. For analysis of anions with this technique, or "base stacking," the background electrolyte (BGE) consists of the salt of a weak base. During electrokinetic injection of the sample, cations from the BGE displace sample cations. During the subsequent electrokinetic injection of base, hydroxide ions neutralize BGE cations to create a low conductivity zone. Anionic analytes are then electro- focused at the front of the titrated zone and separation continues in the BGE. pH-mediated stacking has been successfully used to analyze compounds in microdialysate samples. However, the mechanism has not been fully investigated. To elucidate this mechanism, six anions in a matrix of Ringer's solution were analyzed by CE-UV with base stacking. Peak efficiency was shown to increase with decreasing sample ionic strength and increasing BGE ionic strength. Substantial differences in efficiency and the optimal injection time ratio of sample to base were observed with different BGEs. The peak efficiency for one anion, 8-hydroxy-2'-deoxyguanosine, was more than 4 million plates. Other nucleosides were also investigated for analysis with stacking. Resolution was shown to degrade with increasing injection times, however when resolution was not an issue, sample injection time could be increased to 6 minutes. A linear relationship between peak area and sample injection time was demonstrated and sub-micromolar detection limits were achieved. In each BGE, the minimum length of base injection required to stack each analyte increased as a function of analyte mobility. It appears that in order for the titrated zone to overtake anions with higher mobilities, a greater length of capillary must be titrated, and thus a longer injection of hydroxide ions is required. Information gained in this study will prove valuable for method development when pH-mediated stacking is used for physiological sample analysis by CE.

41. ON-LINE SAMPLING PORT DEVELOPMENT FOR MICROFLUIDIC DEVICES. **Bryan H. Huynh**[1], Susan M. Lunte[2], R. S. Martin[3]; [1]University of Kansas, 2095 Constant Ave., Lawrence, KS 66047; [2]University of Kansas, Department of Pharmaceutical Chemistry, Lawrence, KS 66047; [3]University of Iowa, Iowa City, IA.

In order to couple microdialysis to microchip electrophoresis for use as a separation-based sensor, sampling port designs and geometries that will enable nanoliter aliquots to be discretely sampled from a continuously flowing stream are being explored. An important requirement of the sampling port is that it can accommodate low flow rates (microliter/min) and fast sampling times while not perturbing the contents of a separation system. Work done by Attiya *et al*. showed that mL/min flow rates can be discretely sampled by increasing the resistance to flow in the separation channels relative to the sampling port. While this work showed promise, the flow rates and sampling times were too large for most biological applications. In this work, we investigated the use of a tapered sampling port with an outlet port cross-sectional area that is much greater than that of the sampling port inlet or separation channels. This tapering is designed to enable low flow rates, minimal in-channel mixing and increased temporal resolution of the sampler. In preliminary studies it was found that the resistance to flow of the sampling port outlet must be at least 5 orders of magnitude lower than that of the separation channels. Results and further optimization of these sampling port geometries will be presented. In addition, studies to test the performance of the sampling port by coupling it to a CE-based separation system using a home-built LIF system and fluorescence-labeled amino acids will be described.

42. AMPEROMETRIC DETECTION FOR MICROCHIP SEPARATION DEVICES. **Damon M. Osbourn**, Craig E. Lunte; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

One of the benefits of using electrochemical detection (EC) with the microfabrication of separation systems is the ability to maintain good detection limits after miniaturization. There are two primary concerns in coupling EC with capillary electrophoresis (CE). The first is the separation of the electrophoretic current through the capillary from the faradaic current at the working electrode. Due to the increased collection efficiencies of on-column detection, ideally one would want to use a decoupler to achieve lower detection limits. Unfortunately, decouplers are often fragile and difficult to manufacture. The benefit of using microchip CEEC is the ability to produce more robust decouplers and electrodes. The decouplers can be designed to provide more stability in a format that could be mass-produced. The second major obstacle in CEEC is the reproducible alignment of the electrode with respect to the capillary. In the planar format, electrodes can be permanently aligned with the separation channel. This work describes the development of a

microfabricated CEEC device employing on- column detection with carbon paste microelectrodes. The system consists of a poly(dimethylsiloxane) substrate. Electrodes are made by packing carbon paste into one end of a glass capillary and threading tungsten wire to make electrical contact through the other end. Holes matching the outer diameter of the capillary are then drilled through a cover plate. This provides a robust design for reproducible alignment of electrodes with the separation channel, while allowing the removal of electrodes for polishing. The decoupler is produced by drilling a hole through the cover plate and casting a cellulose acetate film inside the hole. The cathodic reservoir of the separation circuit is positioned above the cellulose acetate decoupler. Decoupler performance and electrode positioning are eval- uated.

43. ON-COLUMN PRECONCENTRATION OF GLUTATHIONE IN MICRODIALYSIS SAMPLES FOR CAPILLARY ELECTROPHORESIS. **Mohammed E. Hoque**, Craig E. Lunte; University of Kansas, Department of Chemistry, 3072 Malott Hall, Lawrence, KS 66045.

Capillary electrophoresis (CE) is a useful separation method for the analysis of biological samples. Analysis of high-ionic strength biological samples in CE results in poor resolution and poor detection limit as band broadening occurs. To overcome this limitation, an on-column sample concentration technique, pH-mediated stacking, can be employed. This preconcentration technique enhances the sensitivity for high-ionic strength samples in CE. Glutathione is present in various body fluids and tissues in micromolar concentration. It is a tripeptide, composed of glycine, glutamic acid and cysteine and is found in the body in two forms: reduced glutathione (GSH) and glutathione disulfide (GSSG). GSH plays an important role in the defense against oxidative stress such as ischemia-reperfusion. GSH reacts with oxygen free radicals during oxidative process resulting in its oxidation to GSSG. Therefore, monitoring of the ratio of GSH to GSSG levels in biological samples during and after oxidative events will provide an indication of oxidative stress and the mechanism of glutathione´s function as a radical scavenger. The purposes of this investigation are to optimize a pH-mediated CE-UV method for the analysis of microdialysis samples and to understand the glutathione activity during ischemic and reperfusion events. The developed CE-UV method will provide low detection limits to determine both forms of glutathione simultaneously. The preliminary data of a CE-UV study with pH-mediated stacking shows an increase in sensitivity of 66-fold for the detection of GSSG in Ringer´s solution relative to normal sample injection without stacking. In this study, GSSG has been detected in the microdialysis samples of the liver of both anesthetized and sacrificed rats.

44. ELECTROCHEMICAL INVESTIGATIONS OF FULLERENE NANO-CLUSTER MODIFIED ELECTRODES. **Francis D'Souza**, Amy Lea Schumacher; Wichita State University, Department of Chemistry, 1845 Fairmount, Wichita, KS 67260-0051.

Formation and characterization of stable fullerene modified electrodes with well-defined surface morphology are useful for developing electrochemical and photochemical nano devices. In the present study, we have modified platinum and ITO electrodes by electrophoretically depositing nanoclusters of pristine fullerenes (C_{60} and C_{70}) and ferrocene-C_{60}, donor-acceptor type dyads. These electrodes have been characterized by simultaneous cyclic voltammetry and piezoelectric microgravimetry at an electrochemical quartz crystal nanobalance. Properties of the films with respect to the structural changes, stability with respect to the different redox states and the nature of counter cation are reported.

45. MIXED MONOLAYERS OF N-PALMITOYL-D-*ERTHYRO*-SPHINGO-MYELIN WITH DIHYDROCHOLESTEROL, EPIDIHYDROCHOLESTEROL AND CHOLESTEROL METHYL ETHER. **Keith J. Stine**, Donna M. Andrauskas, David B. Sauer; University of Missouri - St. Louis, 8001 Natural Bridge Road, Saint Louis, MO 63121.

Sphingolipids are membrane components present in smaller amounts than the more widely recognized phospholipids; however, there is an increasing interest in these lipids and their role in membrane biochemistry. Sphingolipids, together with cholesterol, form small microdomains known as rafts that host and organize cellular signaling proteins. For this reason, the interaction between sphingolipids and cholesterol is especially interesting. Monolayers of a representative sphingo-lipid, N-palmitoyl-D-*erthyro*-sphingomyelin and epidihydrocholesterol were com-pared with those formed with dihydrocholesterol to probe the effect of changing the configuration of the hydroxyl group. Monolayers of the sphingolipid mixed with cholesterol methyl ether were studied to probe the effect of hydrogen-bonding. All of these systems were studied as a function of steroid mole fraction and show differing behavior. The techniques used are Π-A isotherms, Brewster angle microscopy and fluorescence microscopy.

46. A COMPUTATIONAL STUDY OF THE EFFECT OF THE IMIDAZOLE RING ORIENTATION ON THE EPR PARAMETERS FOR VANADYL-IMIDAZOLE COMPLEXES. **Alexander C. Saladino**, Sarah C. Larsen; University of Iowa, 433 Chemistry Building, Iowa City, IA 52242.

The vanadium hyperfine coupling constant for vanadyl-imidazole complexes depends on the orientation of the imidazole ring with respect to the vanadyl bond as illustrated by a recent EPR study of vanadyl-imidazole model complexes

(Pecoraro *et al*. *J. Am. Chem. Soc.* 2000, **122**, 767). In the study reported here, density functional theory (DFT) calculations of EPR hyperfine and quadrupole coupling constants for a model complex, $[VO(imid)(H_2O)_4]^{2+}$, were used to elucidate the orientation dependence of the vanadium and nitrogen hyperfine coupling constants for an equatorially coordinated imidazole ligand. The computational results for the orientation dependence of the vanadium hyperfine coupling constant reproduces the functional dependence ($A_{II}(imidazole)=A + Bsin(2\theta(-90))$) observed in the experimental EPR data. The computational results predict a similar orientation dependence for the vanadium quadrupole coupling constant and for the nitrogen hyperfine coupling constant for the coordinated nitrogen of the imidazole ligand. These results have important implications for EPR and pulsed EPR studies of vanadoproteins.

47. *A PRIORI* ELIMINATION OF CONFIGURATIONAL DEADWOOD FROM CI WAVEFUNCTIONS. **Laimutis Bytautas**, Joseph Ivanic, Klaus Ruedenberg; Iowa State University and Ames Laboratory, 307 Wilhelm Hall, Department of Chemistry, Ames, IA 50011.

The main disadvantage in dealing with the ordinary CI-type wavefunctions is the necessity to deal with excessive numbers of configurations that make up the CI-expansion in order to recover the correlation energy within the "chemical accuracy". It is well known that they usually contain large amounts of configurations that are ineffectual, so-called "dead-wood". Thus, one of the main objectives in dealing with CI-based methods consists of finding efficient ways to eliminate "dead-wood-type" configurations in a systematic fashion. We find that the use of split-localized molecular orbitals, *i.e*. orbitals that have been localized in SCF-HF occupied and SCF-HF virtual space, respectively are useful in this context. Very few physically well-motivated arguments based on localized MOs yield a rather simple scheme for generating accurate and compact CI-wavefunctions. For the chosen active space size (N electrons in M orbitals) the truncated CI-expansion can be deduced *a priori* within "chemical accuracy" requirement. The results are presented for HNO, CO_2 and NCCN molecules at the SDTQ-CI level. *E.g*., for the case of N electrons in N orbitals it is found that for CO_2 and NCCN 11% and 7% respectively of all SDTQ-CI determinants are sufficient to yield 1 milihartree accuracy. The truncation efficiency of localized MOs is superior to that of natural orbitals and it increases with the size of the molecule. This circumstance extends the applicability of CI-based methods to the larger systems of chemical interest.

48. COMPARISON OF CHOLESTEROL, DESMOSTEROL AND 7-DEHYDRO-CHOLESTEROL IN PHOSPHOLIPID MODEL MEMBRANES USING LANGMUIR MONOLAYERS AND FLUORESCENCE MICROSCOPY. **Erin E. Berring**, Alexa Serfis; Saint Louis University, Department of Chemistry, Monsanto Hall, St. Louis, MO 63103.

It is known that the composition and concentration of sterols are important to the proper functioning of cellular membranes. Specifically, a debilitating disease called the Smith-Lemli-Opitz syndrome is caused, in part, by a cholesterol deficiency and an increase in the concentration of the cholesterol precursor 7-dehydrocholesterol. In studies of this syndrome, it was found that some membranes are adversely affected by changes in sterol composition and concentrations, while others appear to function normally. In this study, the interactions of cholesterol (CHOL) and structurally similar sterols, desmosterol (DES), and 7-dehydrocholesterol (DHC), with L-α-dipalmitoylphosphatidylcholine (DPPC) monolayers were compared in order to better understand how changes in sterol structure affect the physical properties of DPPC-sterol model membranes. Pressure-area isotherms and fluorescence microscopy techniques were used to study the Langmuir films containing DPPC and 10, 20 or 30 mol percent sterol. Similar isotherm behavior was noted for the CHOL, DES and DHC mixed isotherms at all concentrations. Fluorescence microscopy images of lipid and sterol domains verified the similarity of CHOL and DES in the model membranes. However, DHC appeared to interact differently with the DPPC monolayer, indicating that DHC causes changes in membrane structure that are slightly different from cholesterol.

49. MOLECULAR DYNAMICS SIMULATIONS OF A COMPLEX OF CALMODULIN WITH A BINDING PEPTIDE OF THE CALCIUM PUMP IN SOLUTION. **Cheng Yang**, Krzysztof Kuczera; University of Kansas, 1251 Wescoe Hall Drive, 2010 Malott Hall, Lawrence, Kansas KS 66045.

In order to study the unusual binding mode of only the c-terminal half of calmodulin binding to the target peptide, we have performed an 4 ns MD simulation of calmodulin complexed with a peptide of the calcium pump in explicit water, under realistic conditions of constant temperature and pressure, in the presence of a physiological concentration of counterions and using Ewald summation to avoid truncation of long-range electrostatic forces. During the simulation the system tended to perform small fluctuations around the starting NMR structure with the RMS deviations of 1.7Å for the C-terminal domain and 1.8Å for the bound peptide. Thus the complex of the peptide only bound to the C-terminal half of CaM is stable. The hydrophobic, electrostatic, van der Waals interactions are supposed to

contribute to the unusual binding mode through calculating buried surface areas, CHARMM interaction energies and continuum model interaction free energies.

50. STUDIES ON COVALENTLY LINKED PORPHYRIN-C_{60} DYADS: STABILIZATION OF CHARGE SEPARATED STATES BY AXIAL COORDINATION. Gadde Suresh[1], Melvin E. Zandler[1], Mohamed E. El-Khouly[2], Mamoru Fujitsuka[2], Osamu Ito[2], **Francis D'Souza**[1]; [1]Wichita State University, Department of Chemistry, 1845, Fairmount, Wichita, KS 67260-0051; [2]Tohoku University, Katahira, Sendai 980-8577, Japan.

The effect of axial ligation on the photoinduced charge separation and charge recombination of a series of covalently linked porphyrin-C_{60} dyads is investigated. Towards this, *meso*-tetraphenylporphyrin and its zinc(II) derivative are functionalized at the *ortho* or *para* positions of one of the aryl groups to bear a fulleropyrrolidine entity through a flexible ethylene dioxide bridge to probe the effect of intramolecular electron-transfer phenomena. In *o*-dichlorobenzene, 0.1 M $(TBA)ClO_4$, the synthesized dyads exhibit seven one-electron reversible redox reactions within in the potential window of the solvent and the measured redox potentials and UV-visible absorption spectra reveal charge-transfer interactions between the electron donor, porphyrin and electron acceptor, fullerene entities. The geometric and electronic structures of the dyads probed by *ab initio* B3LYP/3-21G(*) methods also revealed the existence of charge transfer interactions. The excited state photochemical events are monitored by both steady-state and time-resolved emission as well as transient absorption techniques. In *o*-dichlorobenzene or in benzonitrile, the main quenching pathway involves charge-separation from the excited porphyrin to the C_{60} moiety. The k_{cs} and k_{cr} are found to depend on the type of substitution (*ortho* or *para*) and the metal ion in the porphyrin cavity. Relatively long-lived charge separated states are observed upon coordinating pyridine axial ligands to the central metal ion of the zinc porphyrin-C_{60} dyads, and this has been attributed to the delocalization of the zinc(II) tetraphenylporphyrin *pi*-cation radical to the axial coordinated ligand.

51. INTRACAVITY LASER SPECTROSCOPY AND FOURIER TRANSFORM SPECTROSCOPY OF NICKEL CHLORIDE: SYSTEM F. **James J. O'Brien**[1], Leah C. O'Brien[2]; [1]University of Missouri-St. Louis, Department of Chemistry and Biochemistry, 8001 Natural Bridge Rd, St. Louis, MO 63121-4499; [2]Southern Illinois University, Department of Chemistry, Southern Illinois University-Edwardsville, Edwardsville, IL 62026-1652.

Several vibronic bands associated with the [15.0] $^2\Delta_{5/2}$ - ***A*** $^2\Delta_{5/2}$ transition of NiCl have been observed. Results of the analysis and molecular parameters of both electronic states will be presented.

52. PRESSURES OF OXYGEN IN EQUILIBRIUM WITH ERBIUM BARIUM COPPER OXIDE AT ELEVATED TEMPERATURES. **Dwight L. Myers**, Richard Walkup, M. S. Pennington; East Central University, 1400 E. 12th Street, Ada, OK 74820.

Vaporization studies of the erbium barium copper oxide superconductor have been performed over the temperature range of 566K to 873K utilizing the transpiration method of vapor pressure measurement. The erbium barium copper oxide sample used was synthesized by high temperature solid state reaction. Initial oxygen content was determined by iodometric titration. Vaporization experiments were performed using high purity nitrogen as the carrier gas in the transpiration apparatus. Oxygen stoichiometry after each experiment was calculated from the observed mass loss of oxygen. Preliminary results for pressures of oxygen will be presented. Comparison will be made to results previously obtained for the yttrium barium copper oxide superconductor.

53. AN EXPERIMENTAL PROCEDURE TO DETERMINE THE K_{SP} OF CALCIUM DODECYL SULFATE. **Seth Vernon**, Jim D. Roach; Emporia State University, 1200 Commercial St., Box 4030, Emporia, KS 66801.

Chemistry concepts that are tied to common occurrences or daily life can be more easily retained and recalled. The study of soap scum for example provides fascinating avenues into many areas of chemistry. This work provides an experimental procedure whereby the K_{sp} of calcium dodecyl sulfate (CaDS) can be determined and concepts such as water hardness, surface tension, solubility and equilibrium can be reinforced. The experiment is designed for use in introductory/ freshman level chemistry laboratory courses. Calcium dodecyl sulfate precipitate is produced from a solution of calcium chloride and sodium dodecyl sulfate (SDS). Data for a surface tension isotherm is obtained through titration of a concentrated SDS solution into water using an Eppendorf pipette. This isotherm can then be used to determine the concentration of dodecyl sulfate (below its critical micelle concentration) in equilibrium with CaDS. With preparation of the CaDS solution during a preceding week's laboratory session, the remainder of the experiment can be completed in about two hours.

54. $GE_4X_{10}^{4-}$ (X = S, SE) ADAMANTANOID CLUSTER IDENTIFICATION USING *AB INITIO* VIBRATIONAL CALCULATIONS AND FT-RAMAN SPECTROSCOPY. **Scott J. Kirkby**; University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65409.

The synthesis of tetrahedrally coordinated building blocks is an important starting point in the formation of three-dimensional microporous and open-framework

materials. One family of materials that has developed significant interest is the $T_4X_{10}^{4-}$ (T = group IV element and X = chalcogenide) adamantanoid clusters. The goal is to use these clusters as inorganic monomers in the construction of new open-framework phases. A significant difficulty, however, is the identification of the clusters after initial synthesis. This results from the one-step hydrothermal synthesis route and the nonstoichiometric reagent compositions required for formation. Adding to the difficulty is that the products are often amorphous. A simple spectroscopic identification would allow the concentration of purification efforts on only those methods yielding the desired clusters. Identification of the clusters from functional group analysis is of limited value because of the chemical similarity among the possible products. *Ab initio* vibrational calculations allow the fingerprinting of the clusters using FT-Raman spectroscopy. This route led to the identification of a $Ge_4Se_{10}^{4-}$ cluster. This result was latter verified by single crystal x-ray diffraction.

55. IDENTIFICATION OF SE SUBSTITUTION LOCATION IN $Ge_4S_gSe_1^{4-}$ CLUSTERS USING *AB INITIO* VIBRATIONAL CALCULATIONS AND FT-RAMAN SPECTROSCOPY. **Scott J. Kirkby**; University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65409.

Optimization of the synthesis of mixed chalcogenide $Ge_4S_{10-x}Se_x^{4-}$ adamantanoid clusters is complicated by the nonstoichiometric one-step hydrothermal method used. The products are often amorphous and before purification, contain significant amounts of unreacted Ge, S/Se and potentially various side-products. Rapid and easy identification of the clusters in the product is required to aid the synthetic efforts. However, functional group analysis using FT-IR and FT-Raman spectroscopy was not successful because of the high degree of chemical similarity for various types of clusters and side products. A successful method was found by using *ab initio* vibrational calculations to fingerprint the FT-Raman spectra. Using these calculations, a product composed of $Ge_4S_gSe_1^{4-}$ with the Se in one of the terminal positions was identified. The structure was subsequently confirmed using single crystal x-ray diffraction on a crystal from an optimized preparation.

56. CHANGES IN THE HYPERFINE CONSTANT OF HEXAMETHYLBENZENE RADICAL CATIONS STABILIZED ON THE SURFACE OF SULFATED ALUMINA. Olga Y. Ovsyannikova[1], Alina V. Timoshok[1], Alexander F. Bedilo[2], **Alexander M. Volodin**[1]; [1]Boreskov Institute of Catalysis, Prospekt Lavrentieva, 5, Novosibirsk, Russia 630090, Russia; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506.

Sulfated alumina catalysts are known to possess strong one-electron acceptor sites capable of forming hexamethylbenzene (HMB) radical cations after HMB

adsorption from different organic solvents. In this study we observed the values of the hyperfine constant in the HMB radical cations to depend on the choice of solvent, temperature and catalyst pretreatment. At any fixed temperature, the hyperfine constant increases following an increase in the solvent ionization potential. For example, at 223 K the constant goes from 5.91 for *p*-xylene (I.P. = 8.44 eV) to 6.53 for *n*-hexane (I.P. = 10.13 eV) with intermediate values obtained for toluene, benzene and chlorobenzene. We believe that this is caused by fast electron exchange between HMB radical cations and the solvent molecules, which becomes more and more significant as the ionization potential of the solvent goes down and approaches that of HMB. While for aliphatic solvents the constant does not seem to depend on temperature, in solvents with lower ionization potentials it steadily increases as temperature goes up in the range of 183-293 K. Slight dependence of the constant on the catalyst pretreatment conditions has also been observed. Its decrease when the catalyst activation temperature is increased from 523 to 873 K seems to reflect strengthening of the acceptor sites on the catalyst surface. This technique appears to offer a useful tool for probing relative strengths of surface acceptor sites in different catalysts or after different treatments.

57. $^5D_1$ AND $^5D_2$ EU^{3+}-EU^{3+} CROSS RELAXATION IN $CSMGCL_3$. Clarissa G. Barnes, **Lisa M. Tilkens**, Stanley May; University of South Dakota, 414 E. Clark, Vermillion, SD 57069.

The $CsMgCl_3$ crystal matrix provides an ideal environment for studying $^5D_1$ and $^5D_2$ cross relaxation between EU^{3+} ions, because these ions enter the lattice as ion pairs. A EU^{3+} ion in either the $^5D_1$ or $^5D_2$ excited state can transfer electronic energy transfer to the other EU^{3+} ion in the pair. Our goal was to determine the relationship between the spectral overlap of donor and acceptor transitions to the rates of energy transfer in EU^{3+}-EU^{3+} pairs. The resonant transitions are $^5D_1 \rightarrow {}^7F_3$ / $^7F_1 \rightarrow {}^5D_0$ and $^5D_2 \rightarrow {}^7F_4$ / $^7F_1 \rightarrow {}^5D_1$. The resonant excitation and emission spectra were measured at temperatures from 100 to 300K, from which the donor-acceptor overlap integrals were calculated. We compared the experimentally determined overlap integrals with the corresponding observed energy transfer rates, correcting for the Boltzmann populations of the initial levels of the transitions. This data indicate that temperature dependence for $^5D_1$ cross relaxation results from the temperature dependence of the Boltzmann population of $^7F_1$. The temperature dependence of $^5D_2$ cross relaxation is also strongly effected by the temperature dependence of the overlap integral.

58. IDENTIFICATION OF A NEW [9.0] $^2\Pi_{3/2}$ STATE IN GAS PHASE NICKEL CHLORIDE. Sinan Tumturk, **Leah C. O'Brien**; Southern Illinois University, Department of Chemistry, Edwardsville, IL 62026-1652.

A new electronic transition in NiCl has been observed near 9000 cm^{-1} for the first time and identified as [9.0] $^2\Pi_{3/2}$ - ***X*** $^2\Pi_{3/2}$. Results of the analysis and molecular parameters for the newly identified $^2\Pi_{3/2}$ state will be presented.

59. GLASS TRANSITION OF POLYMERS NEAR SURFACES PROBED BY POSITRON ANNIHILATION SPECTROSCOPY. Junjie Zhang, **Y. C. Jean**; University of Missouri-Kansas City, 5009 Rockhill Rd., Kansas City, MO 64110.

Glass transition temperature (T_g) as a function of depth and interfacial effect in polymers can be studied by using positron annihilation spectroscopy (PAS) by controlling positron incident energy. Existing studies by conventional methods show that T_g changes at different depth of films and at different levels of substrate-polymer interactions. We will report the results of Doppler broadening of energy spectra as a function of temperature across T_g in polystyrene with different thickness, molecular weight and different levels of interfacial interactions. The use of PAS to study surface and interfacial effect on polymeric properties will be discussed.

60. PHOTODEGRADATION OF POLYMERIC COATINGS STUDIED BY POSITRON ANNIHILATION SPECTROSCOPY. Renwu Zhang, **Y. C. Jean**, Hongmin Chen, T.C. Sandreczki; University of Missouri-Kansas City, 5009 Rockhill RD., Kansas City, MO 64110.

Polymeric coatings, polyurethane, acrylic, epoxy and sulfonate-based, were prepared and exposed to Florida natural weathering and UV accelerated conditions. The Doppler broadening energy spectra and positron lifetime were measured as a function of incident positron energy at different periods of weatherings. A significant decrease in the S parameter and positronium formation fraction is interpreted as loss of free volume as result of environmental deterioration. The observed decrease of free-volume parameters among these coatings is used as an indicator to test coating durability in micro-scale and at the early stage of photodegradation. Relationships between atomic scale properties by positron spectroscopy and macroscopic physical and mechanical properties by conventional methods will be discussed in terms of coating durability.

61. MOLECULAR DYNAMICS STUDY OF NATIVE CYTOCHROME B5 AND ITS MUTANTS. **Qinyi Cheng**; University of Kansas, Department of Chemistry and Molecular Biosciences, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Cytochrome b5 (Cytb5) is a small ubiquitous protein involved in electron transfer reactions. Two distinct forms of cytb5 have been identified in rat liver cells: one is associated with the membrane of the endoplasmic reticulum (microsomal, or Mc, cytb5) and the other anchored in the outer membrane of mitochondria (OM cytbt5). The physical properties of these two proteins are markedly different. The OM form has a more negative reduction potential and is more stable toward chemical and thermal denaturation. Moreover, hemin is kinetically trapped in rat OM cytb5 but not in the Mc proteins. Two hydrophobic networks were identified to be present in OM proteins as a result of previous experimental studies, which may contribute to the stability of OM cytb5. One encompasses the side chains of Ala18, Ile32, Leu36 and Leu47, while the other encompasses the side chains of Ile25, Phe58, Leu71 and the heme. Thus two mutant proteins were subject to molecular dynamics simulation, a triple mutant of OM (A18S/I32L/L47R) and a quintuple mutant of OM (A18S/I25L/I32L/L47R/L71S). By substituting residues in the hydrophobic networks in the OM from cytb5 with corresponding residues present in the Mc form, we aimed to find the effect of gradual and complete elimination of the two extended hydrophobic networks. The average distance between the hydrophobic cores observed in the trajectories may be correlated with the protein stability. This distance is 9.4 Å in the rat OM protein, 10.3 Å in the triple mutant, 11.2 Å in the rat Mc and 14.4 Å in the bovine Mc form. We have also simulated apo-cytochrome b5 in order to analyze the effect of the heme on cytochrome b5 structure and mobility.

62. COMPLEX DYNAMICS DRIVEN BY SULFUR(-II) OXIDATION. **Glen A. Frerichs**[1], Qingyu Gao[2], Richard C. Thompson[3]; [1]Westminster College, 501 Westminster Ave., Fulton, MO 65251; [2]China University of Mining and Technology, Xuzhou, P.R. China 221008, P.R. China; [3]University of Missouri-Columbia, 125 Chemistry, Columbia, MO 65211.

A general model for the nonlinear pH dynamics in the oxidation of sulfur(-II) species has been proposed previously. This model is based upon changes in the oxidation state of sulfur in the presence of a generic oxidant, so that any nonlinear behavior arising from the chemistry of the oxidant is omitted. The proposed model successfully simulates the general kinetic feature (fingerprint) that is observed experimentally in batch, and predicts pH oscillations in a continuous flow stirred tank reactor (CSTR). In the present study we report that further analysis and simulations based on the general model yield a wide variety of complex phenomena, including mixed-mode oscillations, period-doubling bifurcations leading to chaos, quasiperiodicity and quasiperiodic chaos. Further, compound

oscillations and chemical bursting can be observed under suitable conditions. The existence of quasiperiodicity suggests the possibility of chemical coupling. Core oscillators have been devised involving subsystems that are capable of independent oscillations. A comparison will be made to experimental results showing similar complex behavior, especially for those systems involving oxidation of S(-II) species such as thiosulfate, thiocyanate and thiourea.

63. PROBING MOLECULAR-SCALE ADHESION FORCES WITH CHEMICAL FORCE MICROSCOPY. **Jill E. Headrick**, Cindy L. Berrie; University of Kansas, 2010 Malott Hall, 1251 Wescoe Hall Dr., Lawrence, KS 66045- 7582.

Atomic force microscopy (AFM) is a powerful imaging technique in which an atomically-sharp probe tip is scanned over a sample in order to investigate surface topography, measure local chemical and mechanical properties and study interfacial phenomena. Chemical force microscopy is a modified version of AFM that allows for specific chemical characterization of a system. The adhesion force between a probe tip and a sample depends strongly on the nature of the functional groups exposed at the surface of the substrate and the tip, as well as the nature of the surrounding medium. Because of this, chemical sensitivity can be achieved by chemically derivatizing AFM probe tips with substances having specific terminal functional groups. The adhesion force measured over surfaces or regions of different chemical functionality can vary by over two orders of magnitude. Unfortunately, many of the established chemical-functionalization methods lead to a significant increase in the size and radius of curvature of the tip, which effectively sacrifices resolution. Commercially-available microfabricated Si_3N_4 probe tips have been modified with a variety of self-assembled alkylsilane monolayers having distinct terminal functionalities, such as $–CH_3$, $-CH_2Br$ and -COOH, using a fabrication process that minimizes undesirable resolution-loss due to tip growth. This technique involves etching the Si_3N_4 tip with concentrated HF to remove the native oxide layer and reacting the HF-treated tips with alkylsilanes, which covalently bond to the silicon nitride surface and form well-ordered, self-assembled monolayers. The adhesion forces between these functionalized tips and various substrates have been measured in air and liquid environments. These modified probe tips have also been used to perform preliminary chemical sensing experiments on nanostructured surfaces.

64. DEUTERIUM NMR STUDIES OF DNA BASE PAIRS. Jamie Mraz, Xingang Zhao, **Gerard S. Harbison;** University of Nebraska, 517 Hamilton Hall, University of Nebraska-Lincoln, Lincoln, NE 68588-0304.

Despite their importance to biophysics and to life itself, until now nucleic acid base pairing has received little attention from the solid-state NMR community. We have, therefore, prepared a series of DNA base pairs deuterium labeled at the positions of the inter-base hydrogen bonds and studied them by deuterium NMR. We find that DNA and RNA bases in general have unusually long longitudinal relaxation times, of the order of several minutes at room temperature, which indicate systems in which thermally-activated dynamics are non-existent. The quadrupole coupling constants measured are, in general, consistent with the strength of the hydrogen bonds, and show no evidence of dynamic tautomerism, local motion or low barrier hydrogen bonds. We are currently using high-level *ab initio* methods to calculate vibrationally averaged electric field gradients at the deuterium site, to establish the computational and experimental requirements for measuring and interpreting deuterium NMR spectra of intact DNA and RNA oligomers.

65. DETERMINATION OF THE SURFACE AREAS OF THE INDIVIDUAL COMPONENTS IN NANOCRYSTALLINE C/MGO COMPOSITES. **Maxim S. Mel'gunov**[1], Alexander F. Bedilo[2], Kenneth J. Klabunde[2]; [1]Boreskov Institute of Catalysis, 5 Lavrentieva, Novosibirsk, Russia 630090, Russia; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506.

A recently developed method for measuring the surface area of individual components in composite materials (Mel´gunov et al., *React. Kinet. Catal. Lett*. **64** (1998) 153; *Colloid & Surf*. A, **186** (2001) 203) has been applied to studies of carbon deposited over nanocrystalline MgO. The technique is based on a considerable difference observed between the amounts of CO_2 physically adsorbed per unit surface area of carbon vs MgO. The results obtained will be compared with those calculated from CO_2 chemisorption data. It will be shown that the latter have higher uncertainty due to specificity of CO_2 chemisorption over active surface sites of nanocrystalline MgO. Meanwhile, physisorption mostly takes place on a regular surface of carbon and MgO, thus allowing one to obtain reliable information on the surface coverage with carbon that does not depend on the MgO particle size and concentration of defects on its surface.

66. NONTRADITIONAL SOLVENTS FOR SUSTAINABLE CHEMICAL PROCESSES I. **Charles L. Liotta**, Charles Eckert; Georgia Institute of Technology, Schools of Chemistry and Biochemistry and Chemical Engineering, Atlanta, Georgia 30332-0400.

We show the synergism between chemistry and engineering in developing novel solvent systems for reactions and subsequent separations. Our goal is to achieve sustainable technology, which means both more benign processes as well as economic advantages. Thus we take a systems approach to the synthesis problem, using tunable solvents to achieve homogeneous reactions and heterogeneous separations. In Part I we take as examples supercritical fluid solutions, especially for phase transfer catalyzed reactions, where the use of benign CO_2 permits both improved mass transfer and facile recycle of catalysts. Another example is nearcritical (250-300ºC) water, which dissolves both ions and nonpolar organics, and which dissociates readily to promote both acid and base catalysis. A third example is ionic liquids, where the separation challenges are met by stripping product out with benign CO_2.

67. NONTRADITIONAL SOLVENTS FOR SUSTAINABLE CHEMICAL PROCESSES II. **Charles Eckert**, Charles L. Liotta; Georgia Institute of Technology, Schools of Chemistry and Biochemistry and Chemical Engineering, Atlanta, Georgia 30332-0100.

We show the synergism between chemistry and engineering in developing novel solvent systems for reactions and subsequent separations. Our goal is to achieve sustainable technology, which means both more benign processes as well as economic advantages. Thus we take a systems approach to the synthesis problem, using tunable solvents to achieve homogeneous reactions and heterogeneous separations. In Part II we continue with examples of systems where the addition of CO_2 to an organic is used to tune or alter phase behavior. We show separation of isomers or of chiral compounds by crystallization from gas-expanded liquids (GELs). We show techniques of making biphasic reactions monophasic for reaction and biphasic for catalyst recycle. Further we demonstrate the application of GELs to recycle phase transfer catalysts by CO_2 assisted aqueous extraction. Finally we show the use of organic-aqueous tunable solvents for biocatalyzed reactions.

68. PRESSURIZED CO_2: A VERSATILE TOOL FOR HOMOGENEOUSLY-CATALYZED GREEN CHEMISTRY. **Philip G. Jessop**[1], Christopher D. Ablan[1], Chih-Cheng Tai[1], David J. Heldebrant[1], Roy R. Stanley[1], Jason P. Hallett[2], Charles A. Eckert[2], Charles L. Liotta[2]; [1]University of California-Davis, Department of Chemistry, Davis, CA 95616; [2]Georgia Institute of Technology, Atlanta, GA 30332-0325.

While the use of supercritical CO_2 as a solvent for catalysis is now well-known and intensively studied, there are many other ways in which compressed CO_2 can promote green homogeneous catalysis.

- Supercritical CO_2 can be used, in combination with ionic liquids or other more benign nonvolatile liquids, as a biphasic medium for catalysis.
- Gaseous CO_2 can soften or melt solids to allow for solventless reactions.
- CO_2 dissolved in liquid solvents can make them temporarily and reversibly fluorophilic. This phenomenon has been used in the development of a method for homogeneous catalyst recovery and recycling and a method for the recrystallization of highly fluorinated compounds.
- CO_2 dissolved in ionic liquids reduces their viscosity; reactions such as asymmetric hydrogenation that are affected by mass transport effects can thus be favorably or unfavorably influenced by the CO_2.
- Finally, CO_2 can serve as a reagent itself; recent explorations of CO_2 fixation will be summarized, including a simple method for high pressure combinatorial catalyst discovery.

69. CATALYTIC ACTIVATION OF HYDROGEN PEROXIDE FOR GREEN CHEMICAL PROCESSES. **Terrence J. Collins**; Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213-2683.

By developing new technologies to move the elemental balance of technology closer to that of biochemistry, chemists can eliminate much of the pollution attributable to chemical technology. In the large area of oxidation chemistry, this primarily means replacing technologies based upon toxic metals or chlorine-based oxidants with alternatives based upon nontoxic metals and oxygen-based oxidants. Hydrogen peroxide is a key reagent in numerous enzymatic oxidations. With an annual production of more than 1.3 million tonnes, hydrogen peroxide is also an important commodity chemical for industrial oxidations. However, in contrast with biochemical processes, catalysis has been largely absent from peroxide technologies. Over the last two decades, my group/institute has been developing oxidatively and hydrolytically robust catalysts for peroxide activation via an iterative design process. Subtle changes in the structure and composition of the ligand systems on which the design work is focused can greatly enhance the robustness of their complexes towards oxidative and hydrolytic degradation in the

presence of peroxide. This work has led to useful applications in numerous fields. The design history, nature, properties and behavior of the resulting so-called TAML® catalysts and the research aspects of their reduction to practice for selected technologies will be briefly sketched.

70. CHALLENGES AND OPPORTUNITIES IN THE USE OF IONIC LIQUIDS: SEPARATIONS, EXTRACTIONS AND THE CHOICE OF IONIC LIQUID. **Robin D. Rogers**, John D. Holbrey; University of Alabama, Box 870336, Department of Chemistry, Tuscaloosa, AL 35401.

Techniques and approaches to clean separations and product isolation with regard to chemical reactions and processing in, or using, ionic liquid (IL) systems include precipitation, secondary extraction, sc-CO_2, pH switching, distillation, IL gas separations, membrane separations and dissolution and washing of ionic liquids. The use of ILs provides routes to minimize catalyst leaching and to facilitate catalyst recovery and reuse with no loss of activity. Developments in these fields come from an understanding of ILs and their solvation and solvent properties. This presentation will discuss the challenges and opportunities presented by the use of ILs as solvents in chemical transformations.

71. RECENT ADVANCES IN CATALYSIS USING DENSE CARBON DIOXIDE AS A PROCESSING MEDIUM. **Bala Subramaniam**; University of Kansas, 4006 Learned Hall, Lawrence, KS 66045.

The pressure tunable density and transport properties of supercritical fluids are well suited for performing catalytic reactions. During the last decade, supercritical fluids (mainly carbon dioxide and water) have been increasingly explored for performing a variety of catalytic reactions such as selective oxidations, hydrogenations, hydroformylations and alkylations. Ways in which near-critical media, particularly dense phase carbon dioxide, lend themselves for exploitation in homogeneous and heterogeneous catalysis will be presented. In homogeneous catalysis, the emphasis will be on recent developments on selective oxidation catalysis and hydroformylations. Specifically, the use of mixed solvents (carbon dioxide, water and organic media) as reaction media will be highlighted. In heterogeneous catalysis, hydrogenations on supported catalysts and solid-acid catalysis will be emphasized. Barriers and challenges confronting commercialization of CO_2-based processes in industrial chemicals processing and recent advances in overcoming these barriers will be discussed.

72. THE EFFECTS OF INQUIRY INSTRUCTION ON STUDENT LEARNING IN TECHNOLOGY-BASED UNDERGRADUATE CHEMISTRY LABORATORIES. **Karen M. Meade**; University of Iowa, 227 CB, Department of Chemistry, Iowa City, IA 52242-1294.

The purpose of this study was to identify conceptual and attitudinal effects of inquiry learning in technology-based undergraduate chemistry laboratories. There were 428 participants who were registered in general chemistry laboratory at the University of Iowa in the Spring of 2002. Conceptual and attitudinal pre-test and post-test results were quantitative in nature. Qualitative results were collected from questionnaires and focus groups. Quantitative data were analyzed using a repeated measures analysis of variance to identify differences between treatment groups. A high-inquiry treatment group was open-ended and required student decisions regarding data collection, data representation and interpretation. The low-inquiry treatment involved collaboration and traditional learning strategies. Major findings of this study were: 1) Pre-test to post-test conceptual gains were significant for both treatment groups. Low-inquiry students performed significantly better on exploration questions than high-inquiry students. 2) Process skills developed at higher levels for high-inquiry students than low-inquiry students. 3) Positive attitudes decreased significantly for all students from pre-test to post-test. More favorable attitudes toward Science Enjoyment and the Ability to Do Well in Science were found for high-inquiry students. More favorable attitudes toward Science Enjoyment and the Ability to Do Well in Science were found for low-inquiry males and high-inquiry females. 4) More favorable attitudes toward the nature of science caused by use of the learning cycle were reported by high-inquiry students. 5) Low-inquiry students reported more favorable attitudes toward technologies in the laboratory than did high-inquiry students. Favorable attitudes toward the use of infrared spectrometers and unfavorable attitudes toward the use of pH meters were reported by both treatment groups. 6) More formal reasoning skills were reported by high-inquiry students. Both groups reported that looking for patterns was a common theme in the laboratories. Hypotheses were reported as rarely used by both treatment groups. These findings are significant because they indicate that inquiry activities positively affect attitudes toward science, gender equality and contribute to the development of formal reasoning skills and process skills.

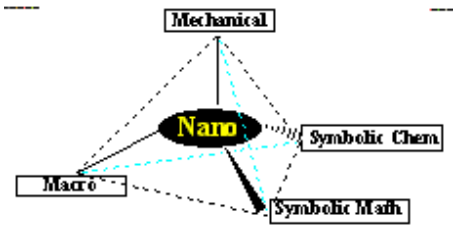
73. REPRESENTATIONAL COMPETENCE AND CHEMICAL UNDERSTANDING AS A BASIS FOR PROBLEM SOLVING. **Patty Kreikemeier**; SRI, Center for Technology in Learning, Menlo Park, CA 94025.

Growing evidence suggests that the use of visual representations supports the development of understanding in science. The role of visual representations has been of particular import to researchers exploring chemistry education. A key

reason that visual representations matter as they do in chemistry is because the primary phenomena investigated in the discipline—molecules and their interactions—are, for all practical purposes, unobservable. The job of the chemist, and likewise that of the chemistry student, is to understand molecular-level phenomena as they are mediated through a variety of representational forms. These representational forms include non-linguistic or visual forms—such as molecular diagrams and graphs—in addition to verbal descriptions, notational symbols and the like. Although a number of studies have shown positive correlations between student use of visualization tools and measures of conceptual learning in chemistry classrooms, it is not yet clear what the mechanisms are by which visual representations influence this development. We investigate some basic aspects of students' conceptual development in chemistry within the context of a computer-based, representational knowledge-building environment called the ChemSense KBE. We posit that students develop both greater competence in using representations and greater depth of chemical understanding as a result of working in this environment, and that these two forms of development mutually support each other in the process of learning chemistry.

74. CHEMICAL PROBLEM SOLVING: MULTIPLE REPRESENTATIONS IN RESEARCH AND IN TEACHING. **Janet Bond-Robinson**; University of Kansas, 2010 Malott, Chemistry Department, Lawrence, KS 66045.

Chemical knowledge is expressed in five forms that can be interrelated as corners of a tetrahedron. All of these knowledge forms are used in problem solving: (1) the macro and tangible: what can be seen, touched and smelled, (2) the submacro: atoms, molecules, ions and structures, (3) the chemical symbols and representations, (4) mathematical symbols and representations and (5) mechanical knowledge of systems. All of these forms can be thought of as types of mental representations easily activated by an expert chemist and showing interconnections of relevant concepts. Rather than lump the symbolic representations we pull apart the mathematical from the chemical—since their origins and symbol systems are entirely dissimilar—even though they are combined in chemical proportional relationships and graphs, for example. The fifth way of knowing chemistry concerns the knowledge expression in mechanical systems—at the macro and nano levels—and has been little discussed, we argue, because of the lack of focus on studying the day-to-day work of chemists. Explanations involving multiple representations are provided of problem solving in chemical research as well as in teaching chemistry so that students learn well.



Forms of Chemical Knowledge

75. A DEMONSTRATION LIBRARY OF PRIVILEDGED MOLECULES. **Les Mitscher**, Sanjay Menon, Segaran Pillai; University of Kansas, Malott Hall, Lawrence, KS 66047.

Drug seeking is a complex enterprise whose success rate is heavily dependent upon selecting the most promising structures as early as possible. Starting with drug-like substances having attractive ADMET properties from the outset is particularly useful. These considerations are illustrated by synthesis and testing of a library of indazoles.

76. STRATEGIES FOR THE DESIGN AND DEVELOPMENT OF EXPLORATORY COMBINATORIAL LIBRARIES. **Gary L. Bolton**; Pfizer Global Research and Development, 2800 Plymouth Road, Ann Arbor, MI 48105.

Application of combinatorial chemistry techniques has become an important component in the search for new structural classes of drug-like compounds. Fundamental considerations such as synthetic chemistry requirements and available library production and purification technology often determine whether a solution or solid phase approach would be most efficient. Complementary utilization of these basic elements can allow the design and construction of compound libraries which may not otherwise be readily accessible. Recent examples will be presented where encoded split-mix solid phase methods and parallel solution synthesis have been effectively exploited as part of a general strategy for the development and production of exploratory libraries comprising some unique cyclic scaffolds.

77. TAKING ADVANTAGE OF SPOC. **Philip B. Cox**; Pharmacia Corp., 4901 Searle Parkway, Skokie, IL 60077.

The age of combinatorial chemistry can be considered, in many ways, a synthesis revolution. Up until the early 1990s, organic chemists were trained using techniques that, although tried and trusted, had not changed in decades. Although many innovations have transpired in synthetic methodology and analysis, the techniques employed by bench organic chemists has remained essentially the same. Combinatorial chemistry has forced organic chemists to re-invent the wheel and integrate other technologies such as automation and polymer chemistry into the fold. One particular technique that underwent a renaissance in this revolution is solid phase organic chemistry (SPOC). Since the pioneering work of Merrifield in the 1960s, this technology remained confined to peptide synthesis until the emergence of combinatorial chemistry. Indeed we have arrived at a point were SPOC can be used for the synthesis of a whole host of diverse organic molecules. This presentation will look at where we are today with SPOC, with particular

reference to how we have taken advantage of this technology to assemble libraries of interesting heterocycles and phosphinic acids.

78. PROMISING COMBINATORIAL APPROACHES TO CARBOCYCLES AND HETEROCYCLES USING PALLADIUM- AND IODINE-PROMOTED CYCLIZATIONS. **Richard C. Larock**; Iowa State University, Department of Chemistry, Ames, IA 50011.

A wide variety of carbocycles and heterocycles can be efficiently prepared by the palladium-catalyzed annulation of internal and terminal alkynes by functionally substituted aromatic and vinylic halides. Novel palladium rearrangements expand the scope of this methodology. The iodocyclization of functionally substituted alkynes also provides a promising new approach to iodoheterocycles and carbocycles useful in organic synthesis. Potential combinatorial applications of this chemistry will be discussed.

79. FLUOROUS TECHNOLOGY FOR SOLUTION PHASE PARALLEL SYNTHESIS. **Craig W. Lindsley**, Zhijian Zhao, William H. Leister; Merck Research Laboratories, WP14-1 P.O. Box 4 Sumneytown Pike, West Point, PA 19486.

Solution phase parallel synthesis was once dominated by the application of resin-bound reagents and scavengers. With the introduction of fluorous technologies by Curran, this emerging field is having a profound impact on the way High Throughput Medicinal chemistry groups are approaching solution phase parallel synthesis. Fluorous materials are commercially available from a number of sources, simple to derivatize and can be readily separated from non-fluorous components by rapid FluoroFlash SPE affording pure materials which have in effect been purified by silica gel chromatography. Novel applications of fluorous-tethered materials as quenching reagents, to facilitate chemistries where resin-based technology fails, as well as the scope and limitations of fluorous-tethered amine bases will be disclosed.

80. NORBORNENYL TAGS: APPLICATIONS IN COMBINATORIAL CHEMISTRY. **Daniel L. Flynn**[1], Paul R. Hanson[2]; [1]Deciphera Pharmaceuticals Inc, 3 Great Rock Circle, Natick, MA 01760; [2]University of Kansas, Lawrence, KS 66045.

Norbornenyl and oxanorbornenyl ring systems are well-known to be excellent substrates for metal-carbene catalyzed Ring Opening Metathesis Polymerization (ROMP) reactions at room temperature. Furthermore, the isolated double bond is

pragmatically orthogonal to most medicinal small molecule functionalities and therefore, offers the opportunity for selective chemical tagging of reactants, reagents, catalysts and sequestering enabling reagents. This lecture will discuss applications of norbornenyl tagging for general use in phase-trafficking, scavenging and soluble supported synthesis.

81. THE CONFORMATIONS OF ADSORBED BIOMOLECULES: THE EFFECT OF SURFACE CHEMISTRY. **Cindy Berrie**, Katherine L. Marchin; University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

Biomolecule-surface interactions have been studied by using atomic force microscopy (AFM) to probe the conformations of surface-adsorbed biomolecules at the single-molecule level. Well-characterized model substrates have been used to investigate the effect of surface chemistry and structure on the adsorption of biomolecules. In one example, dramatic differences in the average size and shape of fibrinogen molecules adsorbed to hydrophobic and hydrophilic substrates have been observed. These changes can be readily seen in AFM images of individual molecules with sub-molecular resolution.

82. FLUORESCENT POLYMER/LIQUID-CRYSTAL COMPOSITES STUDIED BY NEAR-FIELD OPTICAL AND ATOMIC FORCE MICROSCOPIES. **Daniel Higgins**; Kansas State University, Dept. of Chemistry, Manhattan, KS 66506.

Near-field scanning optical microscopy (NSOM) and atomic force microscopy (AFM) are used to study polymer/liquid-crystal composites prepared by the complexation of polyelectrolytes and ionic surfactants. These polyelectrolyte-surfactant complexes (PSCs) form highly mesostructured thin films. Fluorescent materials prepared by complexation of poly(vinyl sulfate) (PVS) and a cationic indocarbocyanine surfactant dye (DiI) are investigated. The results are compared to those obtained from more common PSC films prepared using PVS and alkyltrimethylammonium bromide (CnTAB). The latter samples were doped with a hydrophobic dye (nile red) for NSOM fluorescence imaging and spectroscopy. In both systems, local film morphology and chemical composition were studied as a function of surfactant:anionic-site stoichiometry. In the PVS-CnTAB system, film characteristics were also investigated as a function of surfactant alkane chain length (for n=12, 14, 16, 18). AFM and NSOM images obtained from these samples show a clear evolution of PSC film morphology with surfactant content and chain length. PVS alone forms a "porous" film containing polymer "network" structures. Pore formation is attributed to film shrinkage and substrate dewetting during drying. At low surfactant content (*i.e.*, 1:100 stoichiometry), the films become much more uniform, despite the fact that the surfactant concentrations in each solution employed were all above the critical aggregation concentration

(CAC). At moderate surfactant loading (≤ 10:100 stoichiometry), small topographic protrusions (10-40 nm in height) appear across the films. Fluorescence NSOM images show these protrusions incorporate both dye and surfactant. Fluorescence spectroscopy on the PVS-DiI system shows the dye is present in an aggregated form. As a result, the protrusions are concluded to be polymer-surfactant micelles and/or micelles aggregates. At highest surfactant loading (25:100 and 50:100 stoichiometries), clear evidence for lamellar polymer-surfactant bilayer formation is obtained. The bilayers exhibit heights on the order of 4-5 nm. Surfactant-dependent dewetting of the glass substrate surface is also observed at these high loadings. Finally, AFM images of the lamellar structures for 50:100 films show the presence of interesting, defected bilayer regions. The possible origins of these defected regions and their associated bilayer height variations are discussed.

83. PROBING BIOLOGICAL FUNCTION AT THE SINGLE MOLECULE LEVEL. **Robert C. Dunn**, David Moore-Nichols; University of Kansas, 224 Strong Hall, Lawrence, KS 66045.

Technology has progressed to the point where it is now possible to not only detect the fluorescence from a single molecule, but also carry out spectroscopic measurements at the single molecule level. This has opened new opportunities for using single molecule measurements as probes of their local environment and structure. Moreover, the ability to detect single molecule emission allows one to study dynamics that might normally be hidden in bulk measurements on large ensembles of molecules. In our laboratory, we are developing both far-field and near-field single molecule optical techniques for applications in the biological sciences. The development of these techniques and their application to the study of nuclear pore complexes in the nuclear envelope will be discussed.

84. TIME-RESOLVED SINGLE MOLECULE STUDIES ON THE BINDING DYNAMICS OF CALMODULIN TO PLASMA MEMBRANE CALCIUM ATPASE. Manoj K. Singh, Kenneth D. Osborn, **Carey K. Johnson**; University of Kansas, Malott Hall, Lawrence, KS 66045.

Calmodulin (CaM), a calcium signaling protein, is known to interact with a number of proteins and enzymes in presence of calcium. Binding of CaM to plasma membrane calcium ATPase (PMCA) activates the enzyme which is critical to the maintenance of intracellular calcium level. Time-resolved single molecule spectroscopy has been used to investigate the binding dynamics of CaM to PMCA. The N-domain of CaM has been labeled by a dye, tetramethylrhodamine (TMR). Fluorescence lifetime of TMR is sensitive to the surrounding environment. At saturating level of calcium (mM), CaM binds PMCA tightly with both the N- and

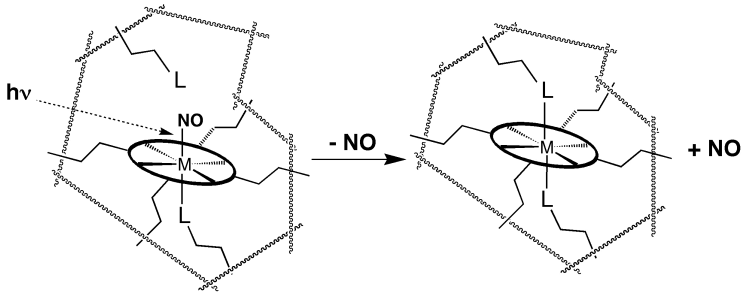
C-domains wrapped around it. At lower levels of calcium (microM) the CaM C-domain remains bound to the target but the N-domain dissociates. Sensitivity to environment may lead to sensitivity of fluorescence properties to the binding of the N-domain. These states can be identified by monitoring changes in the lifetime of TMR at single molecule level. It is also possible that at an intermediate level of calcium, there could be a dynamic equilibrium between bound and the free state. Therefore, efforts have been made to investigate the dynamic aspect of CaM binding to PMCA at single molecule level. Results obtained during these investigations will be presented.

85. INVESTIGATING MOVEMENT OF *SPODOPTERA FRUGIPERDA* INSECT CELLS DURING OPTICAL TRAPPING. **Jennifer J. Winkenwerder**, Mark A. Arnold, Jonathon T. Olesberg; The University of Iowa and Optical Science and Technology Center, 296 IATL, Iowa City, IA 52242.

We have previously used a dual-trap laser tweezers system to measure pico-newton scale forces for cell-to-cell interactions between two *Sf9* insect cells (*Spodoptera frugiperda*-Fall Armyworm). During these experiments, we observed that when a *Sf9* cell is trapped in the laser, cells in the surrounding region move toward the trapped cell. Since the cells move over distances of hundreds of microns and are directed toward the trapped cell, the phenomenon cannot be explained by Brownian motion. Experiments were conducted to characterize this phenomenon in an attempt to establish the physical or biological origin of the cell movement under these conditions. Studies were conducted with various cell-sized objects, including polystyrene beads (PSB), red blood cells (RBC), *Sf9* cells and mixtures of these objects. Various matrices were evaluated, including isotonic buffer at pH 6.0 and serum-containing growth medium. The influence of the optical power being applied to the trapped object with respect to movement of the other objects was also evaluated. The laser tweezers system is based on two 200 mW, single-mode 830 nm laser diodes coupled to a Zeiss inverted microscope. Results indicate no statistical difference (99.5% confidence level) between data collected for the movement of *Sf9* cells, PSB or RBC in isotonic buffer when a corresponding object is trapped. The net velocities toward the trap are less than 0.2 μm/min. Likewise, no cell movement toward the trap is observed when the trap is on, but no cell is trapped. There is substantial movement, however, of *Sf9* cells in the serum-containing growth medium. In growth medium, the average *Sf9* cell velocity toward the trapped cell is 2.18 ± 1.46 μm/min (n=29). There is some net motion of the PSB toward the trapped PSC, but the net velocity is significantly smaller (0.37 ± 0.35 μm/min, n=20). The migration velocity of the ***Sf9*** cells depends on the magnitude of the laser trap power. This dependence on optical power is not seen for the PSB. From these experiments, we conclude that the environment of the matrix surrounding the ***Sf9*** cells plays a significant role in the interaction between trapped and non-trapped ***Sf9*** insect cells.

86. DEVELOPMENT OF POLYMERIC MATERIALS FOR THE PHOTO-RELEASE/DELIVERY OF NITRIC OXIDE. **Jeremy T. Koch**, Karen M. Padden, A. S. Borovik; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

The biological effects of nitric oxide (NO) can be protective (antioxidant), regulatory (controls vascular tone) and deleterious (enzyme inhibition, DNA damage), thus, the controlled and targeted release of this molecule would be useful. Template copolymerization can be used to immobilize metal complexes that bind NO in porous organic hosts. One approach for delivery is through the release of NO from these materials by photolytic cleavage of the M-NO bond. This paper reports the synthesis, characterization and function of bioinspired metalloporphyrin complexes immobilized in a methacrylate host. EPR spectroscopy is used to probe the binding and release of NO.



87. RAPID PREPARATIVE BIOSEPARATIONS BY LARGE MONOLITHIC COLUMNS. **Tao Jiang**, Shaofeng Xie, Lan Xu, Jason Kraska, Baburaj Kunnummal, Robert W. Allington; Isco, Inc., 4700 Superior Street, Lincoln, NE 68504.

Monoliths, the fourth generation of separation media, were prepared by *in situ* copolymerization of monomers in the presence of porogenic solvents. Compared with beaded media, monoliths can be run at much higher flow rates with low back pressure and high resolution. Monoliths offer rapid separations. However, so far, there is no large-volume monolithic column prepared by *in situ* polymerization due to the difficulties to get a homogenous pore structure. This paper will present the preparation of large-volume monolithic columns (100 x 35 mm ID) with a bed volume of up to 60mL by *in situ* polymerization, on the basis of strong anion exchange (SAX), weak cation exchange (WCX) and reversed phases (RP). These columns were used on the separations of peptides, proteins and nucleotides. They showed similar resolution and unit binding capacity with the small volume monoliths (100 x 10 mm ID) and the column efficiency and binding capacity are

flow-independent. These large-volume monolithic columns have great potential on the fast preparative bioseparation.

88. ELECTROENCAPSULATION OF REAGENTS WITHIN SOL-GEL DERIVED FILMS. **Deepa P. Nambiar**, Maryanne M. Collinson; Kansas State University, 111 Willard Hall, Department of Chemistry, Manhattan, KS 66506.

The sol-gel approach has been used extensively for the development of materials for analytical applications. In a typical procedure an alkoxysilane is mixed with water in a mutual solvent in the presence of an acid or base. The sol-gel is formed by hydrolysis and condensation reactions of silane. Generally sol-gel derived films are obtained by dip coating or spin coating procedures. In this work, we report a new method to prepare stable silicate films that involves the electrochemical generation of OH^-. In this procedure a negative potential is applied to an electrode surface placed in a solution containing tetramethoxysilane and water. The condensation of the sol is enhanced by the electrogenerated OH^- and the gel is formed as a thin layer on the surface of the working electrode. In this work we will describe this procedure and show how it can be used to trap redox probes and pH dyes for electrochemical and optical characterization.

89. THE DEVELOPMENT OF ION-SELECTIVE POLYMER MEMBRANE ELECTRODES BASED ON LUTETIUM(III) PORPHYRINS. **Erich D. Steinle**, Stacy W. Scranton; Southwest Missouri State University, Department of Chemistry, 901 S. National Ave., Springfield, MO 65804.

During the last 15 years, many different metalloporphyrins have been utilized as ionophores in liquid/polymer membrane ion-selective electrodes (ISEs). These sensors respond to anions with selectivity patterns that significantly deviate from the traditional Hofmeister series (ClO_4^- > SCN^- > salicylate$^-$ > I^- > NO_3^- > Br^- > NO_2^- > Cl^- > HCO_3^- > F^-). Mn(III), Co(II), Sn(IV), In(III) and Ga(III) porphyrin-based ISEs have been shown to exhibit enhanced selectivity towards thiocyanate, nitrite, salicylate, chloride and fluoride, respectively. Indeed, previous research has been directed primarily on metals that reside within the transition to post-transition sections of the periodic table. In this work, a metalloporphyrin containing the lanthanide-series metal lutetium(III) is introduced as a new ionophore. Lutetium(III) tetraphenylporphyrin, Ln(III)[TPP]Cl, is doped directly into a plasticized PVC membrane and the potentiometric behavior of the resulting sensor is evaluated. The emf response slopes of the ISE containing this metalloporphyrin towards anions are slightly sub-Nernstian, but the selectivity pattern demonstrates a preference for salicylate. Furthermore, the result of adding either lipophilic cationic (tetraalkylammonium) or anionic (tetraphenylborate) sites to the membrane will be assessed. The effects of dielectric constant of the plasticizer

and sample pH on the response characteristics of this membrane electrode will also be reported. The improved selectivity of the Ln(III) porphyrin-based ISE towards salicylate over other common lipophilic ions such as perchlorate and thiocyanate may lead to new possibilities for salicylate sensing. The feasibility of applying this ISE as a detector of aspirin in clinical applications will be discussed.

90. SINGLE MOLECULE FLUORESCENCE INVESTIGATION OF CALMODULIN FUNCTION. **Michael W. Allen**, Brian D. Slaughter, Ramona J. Urbauer, Carey K. Johnson; University of Kansas, 1251 Wescoe Hall Drive, Department of Chemistry, Lawrence, Kansas 66047.

The prototypical calcium ion sensor calmodulin (CaM) is responsible for many intracellular processes. Although it binds over 40 diverse protein and peptide targets showing little or no structural homology, the binding dynamics of CaM are not well understood. Mutation of calmodulin and attachment of fluorescence dye(s) to the N- or (and) C-terminus allows the use of single-molecule fluorescence spectroscopy to probe the dynamics associated with target recognition and binding. During binding, the globular domains of the N- and C-terminus, which are initially separated in an extended geometry, form a compact structure after binding to a peptide target. By monitoring the intensity of a single fluorescent probe attached to CaM, the dynamics of the protein in the absence and presence of a peptide target (CaM binding domain of PMCA) have been studied. The intensity of the fluorescence trajectories of single CaM molecules have been analyzed by autocorrelation methods. Addition of a peptide target leads to a change in the intensity autocorrelations of the fluorescently labeled CaM. Attachment of donor and acceptor fluorescent dyes on the N- and C-terminus affords the opportunity to probe the dynamics and kinetics of CaM via FRET.

91. NEAR-IR-FLUORESCENT LABELED PHENYTOIN FOR ANALYTICAL APPLICATIONS IN DRUG MONITORING. **Corey M. Ohnmacht**[1], David S. Hage[2]; [1]University of Nebraska-Lincoln, 741 Hamilton Hall, University of Nebraska-Lincoln, Lincoln, NE 68588-0304; [2]University of Nebraska-Lincoln, 738 Hamilton Hall, University of Nebraska-Lincoln, Lincoln, NE 68588-0304.

Continuing work with the anti-epileptic drug, phenytoin (5,5-diphenyl-hydantoin) has led to the development of phenytoin being conjugated to a near-IR-fluorescent dye. The first stage in development was to produce a primary amine-containing analog of phenytoin, which could then undergo the N-hydroxysuccinimide (NHS) ester reaction to form an amide-linked derivative. Two methods were examined to produce the amine-containing derivative of phenytoin. Method 1 proceeded by preparing 3-(chloroethyl)-5,5-diphenylhydantoin that then underwent amination by direct displacement of the chlorine by an excess of ammonia

gas. This method produced a compound with a MH^+ ion at 296.0 m/z by ESI/MS/MS, which was also identifiable by proton NMR. Method 2 was a one-step reaction that involved reacting 5,5-diphenyl-hydantoin with hydrazine hydrate to produce 3-N-amino-5,5-diphenylhydantoin. This product was also identifiable by ESI/MS/MS and proton NMR. Because of its ease of preparation and cost benefits, method 2 was the preferred choice for the preparation of the amine-containing derivative. The second stage in development involved attaching the product from method 2 to the near-IR-fluorescent dye. This was accomplished by preparing a saturated solution of 3-N-amino-5,5-diphenylhydantoin in sodium bicarbonate buffer and then slowly adding a solution of the NHS-containing dye while mixing on ice for two hours. The labeled phenytoin development will be used along with an in-house detector made by Li-Cor (Lincoln, NE) for studies where low limits of detection and low background from biological samples are required.

92. SKIN PENETRATION STUDIES USING MICRODIALYSIS. **Sarah F. McDonald**, Craig E. Lunte; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Esterom® is composed of the hydrolytic/solvolytic products of cocaine formulated in propylene glycol. When applied topically, it has shown to increase the range of motion in patients. The major components of Esterom® are known; however, the active components have not been identified. Following topical administration, the components of Esterom® are not detected in the blood. The purpose of this research is to develop a method to determine which components of Esterom® are able to penetrate the skin to better evaluate the active components. Dermal microdialysis is becoming accepted as a tool for evaluating skin penetration of topically applied drugs. Microdialysis probes were implanted into rat dermis. A concentrated solution of each component of Esterom® in propylene glycol was applied separately to the dermis directly above the microdialysis probe. Compounds were also applied simultaneously to the dermis to determine if synergism was present. Synergism could aid in the skin penetration of compounds that do not penetrate by themselves. Ringer's solution was perfused through the probe. Samples were collected and analyzed using an on-line microdialysis HPLC-UV system. The skin penetration of each component of Esterom® was evaluated. It was found that benzoic acid penetrated the skin. Hydroxypropyl benzoate hydrolyzes to benzoic acid upon skin penetration. Very little skin penetration is seen when benzoylecgonine or hydroxypropyl benzoylecgonine is applied to the skin. Some hydrolysis of hydroxypropyl benzoylecgonine to benzoylecgonine is observed. Almost no penetration is seen when ecgonidine, methylecgonidine or hydroxypropyl ecgonidine are applied to the skin. Skin penetration kinetics were evaluated for each component of Esterom®. This research shows that implantation of microdialysis probes into rat dermis is an effective way

to monitor skin penetration. Future studies include looking at the ability of the components of Esterom® to reach the underlying muscle.

93. TISSUE PHANTOM AND ANIMAL MODELS FOR NEAR INFRARED SPECTROSCOPY OF HUMAN SKIN. **Jun Chen**, Benjamin C. Armitage, Jonathon T. Olesberg, Mark A. Arnold; University of Iowa, 296 IATL, Iowa City, IA 52242.

Noninvasive blood glucose sensing involves transmitting near infrared light through the human body and analyzing the resulting spectrum for the concentration of glucose. Human skin is one potential site for such a measurement. The impact of the skin matrix on near infrared spectra must be characterized to ascertain the utility of this approach. This presentation will focus on the evaluation of a tissue phantom and animal model for near infrared spectra of human skin. An analysis of near infrared spectra collected across human tissue indicates that water, protein and fat are the primary absorbing species over the combination spectral range (5000 – 4000 cm^{-1}). As a result, the tissue phantom is constructed by combining individual layers of these substances. The relative thickness of each layer can be adjusted to match the relative amounts of these components within the skin. Spectra collected across such tissue phantoms accurately match those collected across human skin in terms of the position and magnitude of the major absorption features. In addition, three putative animal models have been evaluated by comparing skin spectra collected from various locations on the body of laboratory mice, rats and rabbits to human skin spectra. Regression analysis of these *in vivo* spectra is used to estimate the effective amount of each major chemical component (water, protein and fat). Both the tissue phantom and animal model experiments are evaluated relative to spectra collected from the thin skin on the back of the hand. The tissue phantom analysis indicates that these human spectra are best modeled by combining layers of phosphate buffer, collagen protein, elastin protein, keratin protein, proteoglycans and a small amount of fatty tissue. Regression analysis of spectra obtained from human volunteers provides an estimate of the effective thickness of each component. The ranges of thickness are: 0.75 – 1.41 mm for water, 0.30 – 2.64 mm for collagen, 0.05 – 2.32 mm for elastin, 0.22 – 0.87 mm for keratin, 0.01 – 0.10mm for proteoglycans and 0.03 - 0.05 mm for fat. Furthermore, the animal model work indicates that spectra collected on the upper back region of the laboratory rats best match human hand skin spectra.

94. AN APPLICATION OF QM-QSAR METHOD TO LIPOPHILICITY. Lin Ye[1], **Andrew J. Holder**[2], Jason Morrill[3]; [1]University of Missouri-Kansas City, 5000 Oak Street 511#, Kansas City, MO 64112; [2]University of Missouri-Kansas City, Department of Chemistry, 5110 Rockhill Rd., Kansas City, MO 64110; [3]Atchison, KS 66002.

The addition of expanding monomer to dental composites is a promising approach to resolve the shrinkage problem in such matrix resins. For the expanding monomers, a list of specific properties needs to be evaluated to determine feasibility for use as a dental composite. As a value to indicate the molecular lipophilicity and thus the ability of the molecule to be transported across biological membranes, logPo/w is a key indicator. This paper describes an approach to develop a predictive model for logPo/w of members of the class of expanding monomers termed spiroorthocarbonates (SOCs), which undergo double ring opening upon cationic polymerization. The approach is based on the semiempirical quantum mechanical technique AM1, which is used to provide data for subsequent development of a multilinear equation describing the property of interest in terms of chemically meaningful quantitative structure activity relationship (QSAR) descriptors. A linear regression model with R_2 = 0.945 is derived from an extensive training set of molecules. Other statistical measures indicate that the model is acceptable as a predictive tool and extensible beyond the training set. The three selected descriptors for the prediction of logPo/w are the molecular surface area, total dipole of the molecule and the FPSA-3 (Fractional atom charge weighted partial positive surface area). The model will be rationalized and described in detail.

95. APPLICATION OF MOLECULAR ORBITAL DFT METHODS TO PROBE THE SEQUENCE OF ELECTRON TRANSFER IN SYSTEMS BEARING MULTIREDOX ENTITIES. **Melvin E. Zandler**, Francis D'Souza, Frank A. Provenzano; Wichita State University, 1845 Fairmount, Wichita, KS 67260-0051.

Evaluation of the sequence of the sites of electron transfer in molecular systems bearing one or more redox active groups [for example, molecular dyads, triads, tetrads, etc., designed for photochemical energy conversion and optical devices] by spectroelectrochemical methods is often difficult especially when the redox potentials are closely located. Knowledge of the redox potential based sequence of electron transfers is an important property needed to arrive at the electron transfer pathways in supramolecular systems. In the present study we have explored the utilization of computational methods to predict the sequence of the site of electron transfer in β-substituted porphyrins, as well as supramolecular dyads and triads comprised of porphyrin, quinone, fullerene (C_{60}), ferrocene and dinitrobenzene groups (Scheme 1) and the results have been compared to

experimental studies. Both semi-empirical (AM1 and PM3) and moderate level *ab initio* (Hartree Fock and Density Functional) methods have been utilized to explore the geometric and electronic properties of these molecular systems. While semi-empirical AM1 and PM3 as well as Hartree Fock *ab initio* methods usually produce a plausible geometry, an incorrect electronic structure, based on the location of the HOMO and LUMO orbitals, is often obtained by these methods. However, *ab initio* methods at B3LYP/3-21G(*) level accurately predict both the geometry and the electronic structure in most of the studied molecular systems.

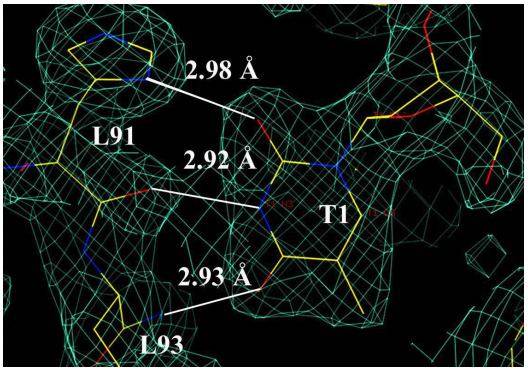
96. *IN SITU* FT-IR STUDY OF THE ACID FREE NITRATION OF BENZENE AND TOLUENE IN NA-ZSM-5. **Scott J. Kirkby**; University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65409.

The reaction of benzene/toluene and NO_2 adsorbed into an initially acid free Na-ZSM-5 pellet has been studied by *in situ* FT-IR spectroscopy. The resulting products are consistent with an electrophilic substitution reaction with a partially charged $NO_2^{\delta+}$ associated with the charge balancing Na^+ cations. Under the reaction conditions, only benzene or toluene molecules adsorbed in proximity to cations in the zeolite react. In addition, for toluene, the substitution product is exclusively 4-nitrotoluene. This is in marked contrast to traditional industrial methods for the nitration of aromatic rings using NO_2. These involve strong acids to generate NO_2^+, which is the active entity in an electrophilic substitution of the ring. The enhanced selectivity of using Na-ZSM-5 results from the reaction occurring on the internal void space of the zeolite. This limits the reaction volume to favor formation of the 1,4-substituted aromatic ring.

97. STRUCTURAL STUDIES OF AN ANTIBODY FRAGMENT (FAB) COMPLEXED WITH SINGLE-STRANDED DNA. **Season P. Prewitt**[1], Jonathan P. Schuermann[1], Susan L. Deutscher[2], John J. Tanner[1]; [1]University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211; [2]University of Missouri-Columbia, M121 Medical Sciences Bldg, Columbia, MO 65212.

Anti-DNA antibodies are important because they are part of the natural human immune response to foreign antigen and they are present at high levels in certain autoimmune disorders such as systemic lupus erythematosus. They also afford a unique opportunity to examine protein-DNA recognition by a set of six protein loops linked to a conserved beta sheet framework. This presentation will focus on X-ray crystallographic studies of an anti-ssDNA antigen-binding fragment (Fab) isolated from an autoimmune, lupus-prone mouse. Crystallization and structure determination results for this Fab complexed with dT_3, dT_5, dT_{10}, and dT_{15} will be presented. These structures reveal a novel ssDNA binding motif that we have termed the "D-ARM" (ssDNA-Antibody Recognition Module). The D-ARM consists

of two aromatic side chains from LCDR1 and HCDR3 that stack above and below the DNA base, and a third residue from LCDR3 that hydrogen bonds to the base. In our structures, for example, the D-ARM consists of Tyr L32, Tyr H101 and His L91. This constellation of protein-DNA interactions is also observed in other anti-DNA Fab structures, thus we hypothesize that the D-ARM is a fundamental antibody-ssDNA recognition motif.



Hydrogen bonding in the D-ARM of the DNA-1/dT$_3$ structure

98. PROPAGATOR THEORIES OF CHEMICAL BONDING. **Joseph V. Ortiz**; Kansas State University, Department of Chemistry, Manhattan, KS 66506-3701.

Students of chemistry typically learn a variety of qualitative theories of chemical bonding which are presented in terms of molecular orbital concepts. Thus, the behavior of orbitals and their energies is used to explain trends in molecular shapes, chemical reactivity and electronic properties, especially spectra. Contemporary computational chemistry, however, emphasizes the calculation of observables through treatment of many-electron wavefunctions and energies or through the employment of density functionals. Simple orbital notions, therefore, may appear to have only qualitative validity in accounting for chemical phenomena. Propagator theory offers a way to rigorously and quantitatively predict molecular properties while retaining the conceptual clarity and simplicity of theories based on orbital concepts. In electron propagator theory, correlated electron binding energies, Dyson orbitals and correlation potentials are the rigorous generalizations of familiar qualitative notions. The success of *ab initio*, electron propagator calculations in the accurate prediction of ionization energies and electron affinities will be illustrated with several examples. Opportunities for the application of propagator methods to challenging problems in chemical bonding theory and for the extension of this approach to ground and excited state properties will be discussed.

99. A NEW pH OSCILLATOR: THE FORMALDEHYDE-HYDROGEN PEROXIDE-SULFITE SYSTEM IN A CSTR. **Glen A. Frerichs**[1], Richard C. Thompson[2]; [1]Westminster College, 501 Westminster Ave., Fulton, MO 65251; [2]University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211.

Oscillations both in pH and in the potential of a Pt electrode have been observed for the homogeneous system of HCHO-H_2O_2-Na_2SO_3-H_2SO_4 in a continuous-flow stirred tank reactor (CSTR). Autocatalytic oxidation of HSO_3^- by H_2O_2 is the main source of positive feedback in H^+, while negative feedback is provided by the reaction of HCHO with SO_3^{2-}. The latter reaction is the basis for a clock reaction that has been used in demonstrations and in physical chemistry laboratory experiments. A proposed model for simulating this oscillating system will be presented. The possible significance of the HCHO-H_2O_2 reaction in this chemical oscillator will be discussed.

100. THEORETICAL STUDY OF THE ELECTRONIC TRANSITIONS OF INDOLINE AND INDOLINE-2-CARBOXYLIC ACID AND CONFORMATIONS OF INDOLINE IN A BLOCKED PEPTIDE. **Brian Slaughter**, G. H. Lushington, Michael W. Allen, Carey K. Johnson; University of Kansas, 1251 Wescoe Hall Dr., Chemistry Department, Lawrence, KS 66045.

Indoline, a proline derivative, has been introduced into peptides as a fluorescent probe. The substitution of indoline into peptides aids in determination of rotational properties of peptides in solution by time-correlated-single photon counting (TCSPC). Unlike tryptophan, tyrosine and phenyalanine, indoline is rigidly attached to the peptide backbone, thus removing side-chain rotational components of the anisotropy decay that are present for the natural amino acids. In this study, time-dependent density functional theory, configuration interaction and spectroscopic intermediate neglect of differential overlap are used to classify spectroscopic properties of indoline and indoline-2-carboxylic acid. L_a and L_b states in indoline and indoline-2-carboxylic acid are assigned. Excitation energies and oscillator strengths were calculated and compared to experiment. Dipole moments, transition dipoles and transition densities were also obtained. In addition, Hartree Fock, denstiy funtional theory and MP2 optimizations were performed on N-acetyl-N'-ethylprolineamide and N-acetyl-N´–ethylindolineamide to compare the conformations of proline and indoline in a peptide backbone. NMR experiments on Gly-Pro-Gly and Gly-Ind-Gly were compared to results of the conformational calculations.

101. RAMAN INVESTIGATION OF SULFURIC ACID TO 513 ºC. **George Walrafen**, Wen-Huang Yang, Y. C. Chu; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Road, Lawrence, KS 66045.

Raman intensities (from 42 and 87 mol % acid) yielded ΔH´s of 3.2-3.5 k_{cal}/mol for H-bond rupture and H_2SO_4 and H_2O formation between H_3O^+ and HSO_4^-, and 5.7-5.9 k_{cal}/mol between $H_5O_2^+$ and HSO_4^-, consistent with ΔH_{mixing}.

102. DIFFUSION OF ORGANIC SOLUTES IN THE N-ALKANES. **Bruce A. Kowert**, Chantel F. Fuqua, Courtney L. Mapes, Jared B. Jones, Jacob A. Zahm, Kurtis T. Sobush; St. Louis University, Department of Chemistry, St. Louis, MO 63103-2010.

The translational diffusion constants, D, of a series of conjugated hydrocarbons (including triptycene, *p*-cyclophane, tetraphenylbutadiene, diphenylbutadiene and diphenylhexatriene) have been determined in the *n*-alkanes using capillary flow techniques. The solutes showed varying degrees of deviation from the Stokes-Einstein (SE) relation. The data can be fitted to log(D/T) = logA – p*log (viscosity) with $p < 1$ ($p = 1$ for the SE relation). The D values will be included with those for other solutes in the *n*-alkanes ($0.50 < p < 0.94$) in a discussion of the deviations from SE behavior based on the relative sizes of the solutes and solvents.

103. $[(CH_3)_4N]_2FeGe_4S_{10}$ AND $Cs_2FeGe_4S_{10}$: A SOLID-STATE EXAMPLE OF MOLECUAR ORBITAL THEORY. **Scott J. Kirkby**; University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65409.

$[(CH_3)_4N]_2FeGe_4S_{10}$ and $Cs_2FeGe_4S_{10}$ are a pair of isostructural open-framework materials differing only in the charge balancing species occupying the void spaces of the three-dimensional $FeGe_4S_{10}^{2-}$ lattice. These materials have sufficient local flexibility to distort around the void space cations to minimize the energy of the entire structure. The result is two materials containing S_4 symmetry site Fe^{2+} bonded to four chemically identical sulfur atoms. The bond lengths for the sulfur are essentially identical between the two phases but with significantly different bond angles. As a result, the near-IR *d-d* spectroscopy of these materials is qualitatively different. These differences may be readily explained by a simple model using molecular orbital theory. The Angular Overlap Model makes use of the separation of the *d* orbital wavefunctions into radial and angular components. The relative energies of the five *d* orbitals may then be determined as functions of the bond angles of the Fe^{2+} center and the four coordinated sulfurs. This model provides an explanation, not only for the relative energies of the *d-d* transitions observed in the near-IR, but also for their relative intensities as well.

104. LOCAL MINIMA ON THE S_{12} RING POTENTIAL SURFACE: 21, SO FAR. **Robert E. Harris;** Department of Chemistry, University of Missouri-Columbia, 125 Chemistry, Columbia, MO 65211.

Structures of S_{12} rings were optimized using the Gaussian94® suite of programs at the RHF level with the 6-31G* basis set. A variety of initial structures led to 21 distinct local minima on the S_{12} potential surface. Energies of the optimized structures were calculated at the MP(2)(FC) level. The crystallographically-known form is lowest in energy. (This form is a planar hexagonal ring of S atoms, with the other six atoms alternating above and below the ring between the ring atoms, nearer the axis of the ring than the ring atoms.) A few of the forms are only a little higher in energy than this form and may contribute a small fraction of the small total amount of S_{12} in equilibrium sulfur vapor. Vibrational analyses were carried out and enthalpies and entropies were calculated. The equilibrium constant for $1.5S_8 = S_{12}$ for the lowest energy forms of S_8 and of S_{12} is estimated as 1.3×10^{-4} $atm^{-0.5}$ at 25° and about 5×10^{-5} at the boiling point (n.b.p. = 742.8K.) A rough estimate of the liquid phase composition at the n.b.p. suggests that S_{12} may be a volume fraction of about 10^{-3} of the liquid.

105. THE MODELING OF ROTATIONAL SPECTRA OF MOLECULES WITH TWO METHYL INTERNAL ROTORS. **Peter Groner**; University of Missouri-Kansas City, Department of Chemistry, 5100 Rockhill Rd, Kansas City, MO 64110.

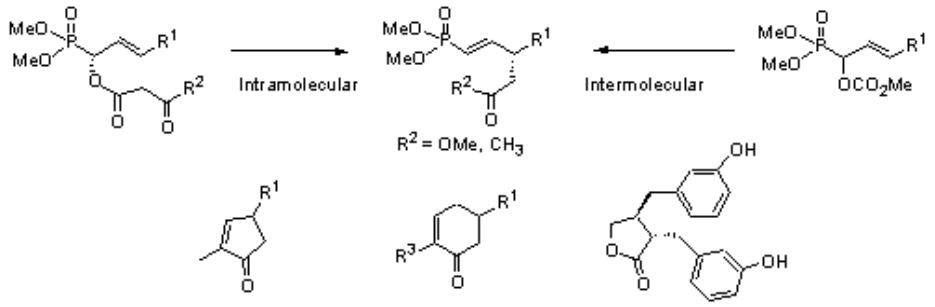
The rotational spectra of molecules with two methyl internal rotors are complicated by the interactions between overall and internal rotations. As a con- sequence, each rotational line is split into four or five components. A computer program based on a general method published earlier has been developed that is able to treat many of the different cases. Dimethyl ether, acetone, 2-methyl-propene (isobutene) and 3-methyl-1,2-butadiene (dimethylallene) have equilibrium structures with C_{2v} symmetry. Other molecules with equivalent methyl groups have C_2 symmetry (dimethyl disulfide) or C_s symmetry (2-fluoropropane). Molecules with inequivalent methyl groups have C_s symmetry (*anti* conformation of ethyl methyl ether) or C_1 symmetry (^{34}S mono-substituted dimethyl disulfide). The program has been used to fit the rotational spectra observed for these molecules to experimental precision and to make reliable predictions of spectral lines for some of these molecules for astronomical observations.

106. TIME-RESOLVED SINGLE MOLECULE STUDIES ON THE BINDING DYNAMICS OF CALMODULIN TO PLASMA MEMBRANE CALCIUM ATPASE. **Manoj K. Singh**, Kenneth D. Osborn, Carey K. Johnson; University of Kansas, Department of Chemistry, Lawrence, KS 66045.

Calmodulin (CaM), a calcium signaling protein, is known to interact with a number of proteins and enzymes in presence of calcium. Binding of CaM to plasma membrane calcium ATPase (PMCA) activates the enzyme which is critical to the maintenance of intracellular calcium level. Time-resolved single molecule spectroscopy has been used to investigate the binding dynamics of CaM to PMCA. The N-domain of CaM has been labeled by a dye, tetramethylrhodamine (TMR). Fluorescence lifetime of TMR is sensitive to the surrounding environment. At saturating level of calcium (mM), CaM binds PMCA tightly with both the N- and C-domains wrapped around it. At lower levels of calcium (microM) the CaM C-domain remains bound to the target but the N-domain dissociates. Sensitivity to environment may lead to sensitivity of fluorescence properties to the binding of the N-domain. These states can be identified by monitoring changes in the lifetime of TMR at single molecule level. It is also possible that at an intermediate level of calcium, there could be a dynamic equilibrium between bound and the free state. Therefore, efforts have been made to investigate the dynamic aspect of CaM binding to PMCA at single molecule level. Results obtained during these investigations will be presented.

107. PALLADIUM CATALYZED REACTIONS OF ALLYLIC HYDROXY PHOSPHONATES: A CONCISE SYNTHESIS OF ENTEROLACTONE. Bingli Yan, **Christopher D. Spilling**; University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121.

New methods for the synthesis of chiral, non-racemic cyclopentenones, cyclohexenones and lactones starting from allylic hydroxy phosphonates will be presented. Treatment of an allylic hydroxyphosphonate with diketene followed by palladium-catalyzed Carroll rearrangement and Wacker oxidation afforded the *beta*,eps-diketophosphonates. Wadsworth-Emmons reaction of the diketophosphonates yields cyclopentenones. The rearrangement and the oxidation steps display high regioselectivity and complete retention of chirality. Attempts to synthesize cyclohexenones via hydroboration of vinyl phosphonate and tandem base-catalyzed retro Pudovik and aldol reactions failed. An alternative approach to the cyclohexenones via palladium-catalyzed rearrangement of the malonate ester derivatives of allylic hydroxyphosphonates will be described. A concise synthesis of enterolactone will also be presented. The synthesis utilizes a Grubb's metathesis followed by palladium catalyzed malonate addition to form the key carbon-carbon bonds.



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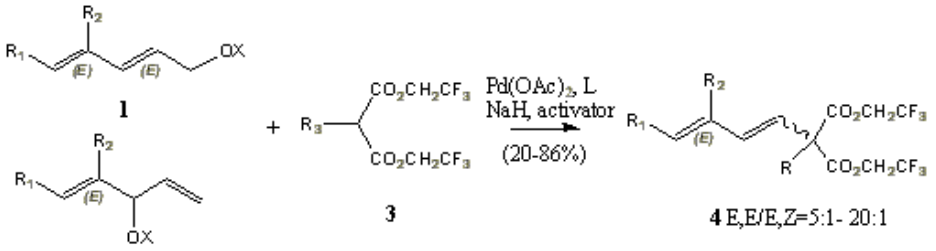
108. PALLADIUM CATALYZED REGIOSELECTIVE AND STEREOSELECTIVE ALKYLATION OF DIENYL ACETATES AND ALCOHOLS WITH BIS(TRI-FLUOROETHYL) MALONATES. James M. Takacs, **Xuntian Jiang**, Alexei P. Leonov; University of Nebraska-Lincoln, Hamilton Hall, Lincoln, NE 68588.

Palladium-catalyzed alkylation of dienyl substrates with malonate esters can yield three regioisomeric products and controlling both the regioselectivity and the stereoselectivity can be problematic. We have been exploring the use of bis(tri-fluoroethyl)malonates in palladium-catalyzed dienylations and find that good to excellent regio- and stereoselectivity is observed with these nucleophiles in the reaction of both dienyl acetates and alcohols. The predominant product is that of substitution at the unsubstituted terminus of the pentadienyl intermediate so as to give the (E,E)-isomer.



1 + **3** → **4** E,E/E,Z=5:1- 20:1

2

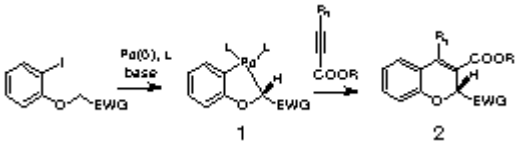
R_1, R_2=H, Me, Ph, p-MeO(C_6H_4) and p-MeO_2C(C_6H_4),
R_3=H, Me, CH_2:CHCH:CH(CH_2)n, n=1,2,3
X=Ac, H
R=H, Me, (E,E)-R_1CH:C(R_2)CH:$CHCH_2$, CH_2:CHCH:CH(CH_2)n, n=1,2,3

109. PALLADIUM-CATALYZED REACTIONS OF ALLYLIC PHOSPHONATES: STUDIES DIRECTED TOWARD THE SYNTHESIS OF SPHINGOMYELIN PHOSPHONATE ANALOGS. Anchalee Thanavaro, **Christopher D. Spilling**; University of Missouri-St. Louis, Department of Chemistry, 8001 Natural Bridge Rd., St. Louis, MO 63121.

We have recently studied the palladium-catalyzed reactions of allylic phosphonates. Under palladium(0) catalysis, allylic phosphonate undergoes rearrangement cleanly and results in allylic transposition. However, palladium(II) catalyzed reaction undergoes cyclization to give N-substituted oxazolidinone. Both intermediates were designed to be precursors to isosteric and non-isosteric phosphonate analogs of sphingomyelin.

110. REGIOSELECTIVE SYNTHESIS OF 2*H*-1-BENZOPYRANS VIA PALLADACYCLES WITH A METAL-BONDED STEREOGENIC CARBON. Janelle L. Portscheller, **Helena C. Malinakova**; University of Kansas, Department of Chemistry, 2010 Malott Hall, Lawrence, KS 66045.

Cascade reactions mediated by palladium complexes constitute a powerful synthetic tool. Recently, new pathways for these transformations have been observed and rationalized by proposing palladacycles as reactive intermediates. In this context, systematic exploration of the chemistry of stable palladacycles holds a great synthetic promise. We have prepared a series of novel stable oxapalladacycles (**1**) featuring a palladium-bonded stereogenic sp^3-hybridized carbon. Palladacycles (**1**) were found to participate in a remarkably regioselective insertion of activated unsymmetrical alkynes yielding highly functionalized 2*H*-1-benzopyrans (**2**). Detailed studies on the roles played by the EWG-group, nature of the ligands (L) and substituents R_1 in this transformation will be presented. Progress towards the development of a catalytic and asymmetric method will also be described.



111. RUTHENIUM MEDIATED SPIROCYCLIZATION. John J. Coniglio, **F. Christopher Pigge**; University of Missouri-St. Louis, Department of Chemistry and Biochemistry, St. Louis, MO 63121-4499.

Cyclohexadienyl ruthenium(II) complexes containing an azaspirocyclic ring system have been prepared from (η^6-N-benzyl acetoacetamide)CpRu(II) precursors via sequential intramolecular nucleophilic addition and enolate trapping. This spirocyclization reaction is applicable to N-benzyl acetoacetamide ligands pos-

sessing alkyl, alkoxy or chloro substituents, with isolated yields ranging from 44% to 86%. Arene ruthenium complexes prepared from phenethyl acetoacetamide failed to undergo spirocyclization, but instead participated in an intramolecular S_NAr reaction yielding a benzeazapine ring system. Exposure of the methoxy- or chloro-substituted complexes to $CuCl_2$ have yielded metal-free azaspirocylic compounds or isoquinoline derivatives (via rearrangement) in yields ranging from 22% to 91%. Treating the 4-methoxy- or 2-methoxy-substituted complexes with BF_3 etherate and a chloride source furnishes either a spirolactamdienone or spirolactamenone/epoxide product depending on reaction conditions.

112. PARALLEL OPTIMIZATION OF PALLADIUM-CATALYZED CARBOCYCLIZATIONS: BISDIENES AND ANILINES. **Jianxin Han**, James Takacs; University of Nebraska-Lincoln, 754 Hamilton Hall, Lincoln, NE 68588-0304.

The Takacs group has been interested in developing palladium-catalyzed carbocyclization reactions for use in synthesizing biologically active natural products. Currently, the reactions under investigation involve bisdiene substrates that cyclize with incorporation of a trapping agent, in this case, anilines. The efficiency of the cyclization/trapping reaction depends upon a number of variables including the substrate, trapping agent, catalyst precursor, ligand and solvent. In an attempt to find the most suitable reaction conditions, trapping by a series of substituted anilines has been studied using parallel reaction optimization, primarily varying the catalyst precursors and ligands. The steric effects of alkyl substituents on the aniline nitrogen and the electronic effects of *para* substituents on the aromatic ring will be discussed.

113. DEVELOPMENT OF OXIDATION CATALYSTS IMMOBILIZED WITHIN POROUS ORGANIC AND INORGANIC HOSTS. **Leilani L. Welbes**, A. S. Borovik; University of Kansas, 1251 Wescoe Dr., Lawrence, KS 66045.

Immobilization of metal complexes in porous hosts has proven to be an effective method for generating new materials with beneficial properties. Recent advances in this area have included the fabrication of materials for separation and sensor applications. One continuing challenge in this field is to develop catalytic porous materials, where the active sites contain coordinatively unsaturated metal centers. Interest in creating catalytic polymeric hosts has grown in recent years because of their potential for reuse, long storage life and potential for enhanced stereoselectivity. We are using template copolymerization methods to immobilize metal complexes in porous organic and inorganic hosts for use as heterogeneous oxidation catalysts. Reported in this paper are synthetic methods and characterization of monomeric cobalt complexes, which serve as templates for the formation of immobilized sites. In addition, template copolymerization methods and

properties of the immobilized metal sites will be described. Application of these materials to the kinetic resolution of several epoxides will also be described.

114. ENGINEERED METALLOPROTEINS: BUILDING A SEQUENCE SELECTIVE NUCLEASE. **Sonya J. Franklin**; University of Iowa, Iowa City, IA 52242.

Our objective is the development of small metalloproteins as DNA-binding and cleavage agents, by *de novo* protein design. We are designing and cloning hybrid helix-turn-helix (HTH) DNA-binding protein, in which the architecturally equivalent consensus Ca-binding loop of an EF-Hand motif has replaced the turn. These constructs bind lanthanides, and thus deliver the hydrolytically active metal for cleavage with sequence preference. By exploiting conserved geometric features, we can rationally design artificial repressors and restriction enzymes, which could target the transcription mechanism of cells for both site-specific chemotherapeutic and antibiotic applications. We are characterizing the protein fold, structure, metal-affinity, DNA-binding affinity and sequence-selectivity of these chimeric proteins.

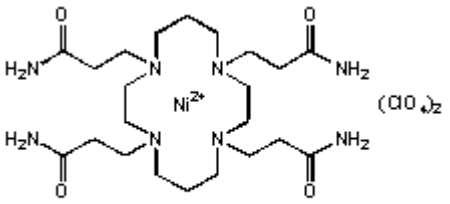
115. HYDROGEN BONDING MOTIFS ABOUT METAL IONS: STABILIZATION OF A $Co^{III}_2(\mu\text{-}O)_2$ CORE. **Peter Larsen**, A. Borovik; University of Kansas, 1251 Wescoe Dr., Lawrence, KS 66045.

Hydrogen bomnds (H-Bonds have been shown to contribute to the structure and stability of metalloproteins. In particular, H-bonds have been shown to help stabilize activated species in metalloprotein reaction pathways. To assist in modeling these species and pathways an H-bond donating ligand: Bis[(*tert*-butyl)aminocarbonyl]-1,2-diaminoethane ($[H_2L]^{2-}$) was employed. We prepared complexes $K_2[M^{II}(H_2L)_2]$ where M = Mn, Fe, Co and Ni. $[Co^{II}(H_2L)_2]^{2-}$ reacts with dioxygen to yield $[Co^{III}(H_2L)(\mu\text{-}O)]_2^{2-}$ which contains a $M(\mu\text{-}O)_2M$ core. Such cores are proposed as intermediates in some metalloproteins. This talk will feature the synthesis and characterization of this $Co^{III}_2(\mu\text{-}O)_2$ complex.

116. MOLECULARLY IMPRINTED POLYMERS FOR THE SPECIFIC REBINDING OF MACROCYCLIC NICKEL(II) COMPLEXES VIA HYDROGEN BONDING. **Xiaobin Zuo**, Daryle H. Busch; University of Kansas, Department of Chemistry, 2010 Malott Hall, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

A series of macroporous polymers imprinted with the nickel(II) perchlorate complex of a tetraamide-substituted cyclam (**1**) were investigated. The imprinting was based on the hydrogen bond interactions between the templating complex

and the functional monomer acrylamide during the copolymerization with ethylene glycol dimethacrylate. In these systems thermally initiated polymers exhibit higher surface areas and rebinding capacity than photochemically initiated ones. The re-uptake of the complex (**1**) by the polymer prepared at 50°C using azobis-(isobutyronitrile) as the initiator was found to be 26.8%, a very high value compared to those previously reported for non-covalently imprinted polymers. The polymer can be reused several times without loss of rebinding activity.



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117. TEMPLATE-DIRECTED SYNTHESIS OF A POLYHEDRAL HOST. Tamara D. Hamilton, Giannis S. Papaefstathiou, **Leonard R. MacGillivray**; University of Iowa, Department of Chemistry, Iowa City, IA 52242.

The self-assembly approach to building metal-organic hosts offers an alternative to classical synthetic routes. Metal-ligand bonds are more kinetically labile than covalent bonds and, therefore, can lead to defect-free architectures because of the thermodynamic equilibrium that exists in solution between the architecture and its components. The building blocks of such hosts can be designed to contain all the information needed to self-assemble in fewer steps and with higher yields than typically accomplished using other methods. The inspiration for such an approach comes from nature where DNA, acting as a linear template, directs the synthesis of subunits that self-assemble to form large hosts such as viruses. With this in mind, we have used template-directed solid-state synthesis to generate an unsymmetrical tetrapyridylcyclobutane. Co-crystallization of this molecule with copper(II) salts yields a self-assembled, discrete, hexanuclear polyhedral host that approaches nanoscale dimensions. The assembly carries a positive charge and encapsulates two polyatomic anions as guests.

118. THE CONSTRUCTION OF METALLAMACROCYCLES USING THE SELF-ASSEMBLY APPROACH. **Gordon K. Anderson**, Mesfin Janka, Nigam P. Rath; University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121.

It is evident that self-assembly strategies offer certain advantages over classical, linear covalent syntheses in the formation of complex supramolecular entities. Their present applications involve molecular recognition, host-guest chemistry and catalysis, while long-term goals are focused on the design of new materials with desirable properties and the manufacturing of nanoscale devices. We have used

the directional bonding self-assembly approach to construct two- and three-dimensional polygons and polyhedra. The synthesis and characterization of metallamacrocycles prepared from 1,3-bis(3- or 4-pyridyl)benzene or 1,3,5-tris(3- or 4-pyridyl)benzene and appropriate diphosphinemetal-containing angular units will be presented.

119. SYNTHESIS OF DIARYLPYRAZINES AND THE FORMATION OF SILVER-PYRAZINE COORDINATION POLYMERS. Nate Schultheiss, **Eric Bosch**; Southwest Missouri State University, 901 S. National Ave., Springfield, MO 65804.

The self-assembly of transition metal cations with polydentate organic ligands is a powerful means to generate one-, two- or three-dimensional supramolecular coordination networks. We have successfully synthesized and characterized 2,6-, 2,3- and 2,5-diaryl-1,4-pyrazine ligands. We will be closely examining the effects of steric crowding and solvents on the formation of silver containing coordination networks. Crystal structures will be shown to explain how the above effects and π-stacking in the crystal play a role in the nature of the solid-state complexes. We will also present preliminary results of the self-assembly of silver salts with pyrazine ligands containing carboxylic acids and oximes.

120. INVERTED METAL ORGANIC FRAMEWORKS INVOLVING ORGANIC BUILDING UNITS DERIVED FROM THE SOLID STATE. Giannis S. Papaefstathiou, **Leonard R. MacGillivray**; University of Iowa, Department of Chemistry, Iowa City, IA 52242.

The synthesis and characterization of open 2D and 3D metal-organic frameworks (MOFs) has been an area of rapid growth. The motivation has been the prospect of generating a wide range of materials with predetermined structures and useful properties (*e.g*. electronic, magnetic). The most common strategy used to build such materials is to propagate the coordination environment of a transition-metal-ion with a linear bifunctional ligand. Using this method, the metal ion acts as a node and the organic ligand serves as a spacer. As a result, the cavities of such MOFs are decorated by the organic spacer and usually are filled with counter ions. In this presentation, we will demonstrate how organic molecules derived from reactions conducted in the solid-state using linear templates may be used as organic building units for the construction of porous MOFs. In these frameworks the function of the metal ion and organic ligand have been inverted (IMOFs) such that the organic ligand serves as a node and the metal ion acts as a spacer. The resulting IMOFs possess cavities with walls decorated with organic anions. This approach results in materials with cavities that approach nanometer-scale dimensions and enables us to readily modify the surface of the cavities by changing the

anions. The synthesis, characterization and stability of such IMOFs will be discussed. This contribution outlines a novel application of a solid-state organic synthesis.

121. SYNTHESES AND CHARACTERIZATION OF MULTIDENTATE Cu(II) INORGANIC-ORGANIC HYBRID ARRAYS. Carter M. Silvernail[1], Victor W. Day[1], Roger D. Sommer[2], Arnold L. Rheingold[2], **John A. Belot**[1]; [1]University of Nebraska-Lincoln, Hamilton Hall, Room 754, Lincoln, NE 68588-0304; [2]University of Delaware, Newark, DE 19716.

Inorganic-organic hybrid materials have become an area of intense investigation due to existence as functional materials for the design of molecular electronics, magnetic materials and catalytic systems. The inorganic constituents of these materials often define physical and structural properties using metal ions coordinated to electronically tunable, multidentate ligands supporting secondary interactions. The syntheses, isolation, crystal chemistry and transport properties of multidentate Cu(II) inorganic and inorganic-organic hybrids will be presented.

122. FIRST HOMOLEPTIC COMPLEXES OF ISOCYANOFERROCENE: PROBING SPIN DELOCALIZATION WITHIN A NONBENZOID AROMATIC Π-SYSTEM BY MULTINUCLEAR NMR. Thomas C. Holovics, Stephan F. Deplazes, Douglas R. Powell, Gerald H. Lushington, **Mikhail V. Barybin**; University of Kansas, Malott Hall, Department of Chemistry, Lawrence, KS 66045.

An efficient synthesis of air- and thermally robust, peach-colored isocyanoferrocene (CNFc) was accomplished via formylation of aminoferrocene followed by dehydration of the resulting formamide. Combining 6 equiv. of CNFc with bis(naphthalene)chromium(0) afforded orange-red $Cr(CNFc)_6$. Sequential one-electron oxidations of the latter produced high yields of saddle-brown $[Cr(CNFc)_6]^+$ and forest-green $[Cr(CNFc)_6]^{2+}$. Spectroscopic, magnetic, structural and electrochemical properties of the above compounds will be discussed. Analysis of unpaired spin delocalization within nonalternant aromatic π-systems of paramagnetic $[Cr(CNFc)_6]^+$ and $[Cr(CNFc)_6]^{2+}$ will be presented. Comparison of the Frontier orbitals of CNFc with those of aryl isocyanides will be reported as well.

123. ESTIMATION OF MO—H BOND STRENGTH IN MONOMERIC MANGANESE AND IRON COMPLEXES: A COMPARATIVE STUDY. **Rajeev Gupta**, A. S. Borovik; University of Kansas, 1251 Wescoe Hall Drive, Department of Chemistry, Lawrence, KS 66046.

Manganese and iron complexes with terminal hydroxo and oxo ligands are proposed intermediates in a variety of metalloproteins including oxygen evolving complex of Photosystem II and Lipoxygenase. Activation of the MO—H bond has been considered an implicit key step at the active site of such metalloproteins. Implication of such unique reactivity in synthetic systems, which contain M—O(H) units, is often difficult due to lack of their stability. Urea derived tripodal ligand capable of providing intramolecular hydrogen bonds, has been used to synthesize M(II/III)—OH and M(III)—O complexes. Their stability is derived in part by the incorporation of hydrogen bonds, which surrounds the M—O(H) units. This talk will discuss the syntheses and properties for a series of manganese and iron complexes with M—O(H) units. Estimation of the MO—H bond dissociation energies for these complexes will also be discussed and compared to that of different metalloproteins.

124. EXPLORING NEW COORDINATION ENVIRONMENTS IN URANIUM OXO CHEMISTRY. **Paul Duval**, Leah M. Arrigo, Levi J. Banks; University of Missouri-Columbia, 601 S. College Ave., Columbia, MO 65211.

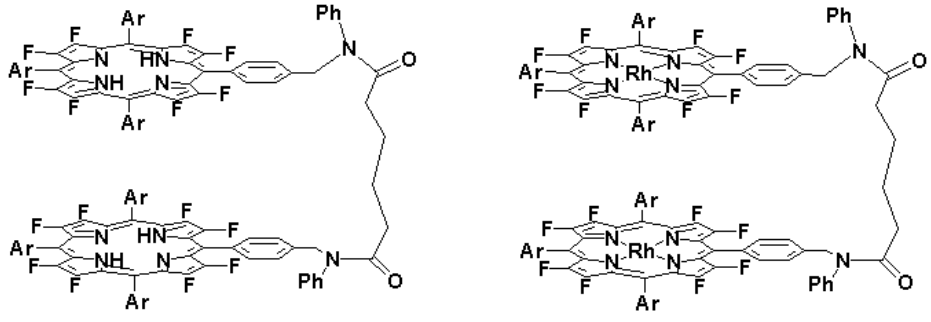
The coordination chemistry of the uranyl ion in aqueous media is dominated by strong covalent bonding along the axial O=U=O unit, which contrasts dramatically with the weaker electrostatic interactions observed for the ligands (typically 4-6) that coordinate in the equatorial plane. We are currently examining new coordination environments for the uranyl ion in non-aqueous media, particularly employing strong-donor amide and alkoxide ligands in the equatorial plane. These ligands effectively compete with the axial dioxo unit for bonding to the high-valent uranium center, generating a subtle electronic balance that labilizes the normally inert U=O bonds. Chelating tripodal ligand sets have been utilized in attempts to direct the linear uranyl moiety to a *cis* geometry. Another possible synthetic route to uranium *cis*-dioxo complexes would entail the sequential introduction of oxo groups to an organometallic precursor in which a *cis* geometry is already enforced by the ancillary ligands. Various uranium(V) oxo complexes have been isolated from these studies, including a series of oxo clusters and mixed-valent uranium species.

125. ANHYDROUS LANTHANIDE SCHIFF BASE COMPLEXES PRODUCED VIA TRIFLATE DERIVED AMIDES. Steven A. Schuetz[1], Victor W. Day[1], Joanna L. Clark[1], Roger D. Sommer[2], Arnold L. Rheingold[2], **John A. Belot**[1]; [1]University of Nebraska-Lincoln, Hamilton Hall, Lincoln, NE 68588-0304; [2]University of Delaware, Newark, DE 19716.

Anhydrous, Schiff base lanthanide complexes have been isolated from the reaction between $Ln(OTf)_3$-derived $Ln[N(TMS)_2]_3$ and tetradentate ketoiminates exhibiting various steric and electronic factors. Final product stoichiometry (*i.e.*, monomer, dimer or tetramer) is selectively controlled by exploiting ligand substituents, reaction conditions and/or lanthanide radii. These compounds can react further with Brönsted acids to yield various rare earth complexes. All examples are active catalysts for numerous small molecule transformations and polar monomer polymerizations, the details of which will also be presented.

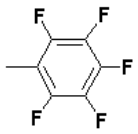
126. SYNTHESIS AND REACTIVITY OF A HEAVILY FLUORINATED PORPHYRIN DIMER AND ITS DIRHODIUM COMPLEX. **Andrew P. Nelson**, Haoran Sun, Stephen G. DiMagno; University of Nebraska, Hamilton Hall, Lincoln, NE 68588.

As a step towards the design of a more efficient catalyst for alkane functionalization, we synthesized a new heavily fluorinated porphyrin dimer **1** and its corresponding dirhodium complex **2**. The dimeric free base ligand **1** was synthesized from the trispentafluorophenyl-β-ocatufluoroporphyrin derivatives 5-(4-α-phenylaminotolyl)-10,15,20-trispentafluorophenyl-2,3,7,8,12,13,17,18-octafluoroporphyrin, and adipoyl chloride as the linker. The reactivity of **2** versus our previously re-



1 **2**

Ar =



ported monomeric system will be discussed. These studies have shown a dramatic increase in the magnitude of the rate constant for C-H activation. In addition, the thermodynamic driving force for H_2 activation also increases dramatically.

127. THE DEVELOPMENT OF NOVEL CATALYTIC ASYMMETRIC CARBON-CARBON BOND FORMING REACTIONS. **Tomislav Rovis**; Colorado State University, Department of Chemistry, Fort Collins, CO 80523.

Asymmetric carbon-carbon bond forming reactions are an invaluable tool in organic synthesis. The development of new reaction manifolds and increasing the scope of current techniques is mandated by a lack of generality among many established methods. This talk will explore both transition-metal and organo catalyzed approaches at controlling stereochemistry in conjunction with the creation of new C-C bonds ultimately leading to 1,4 and 1,5 dicarbonyl compounds.

128. THIAZOLIUM CATALYZED SYNTHESIS OF KETOAMIDES: APPLICATION TO THE SYNTHESIS OF TETRASUBSTITUTED IMIDAZOLES. **Jerry A. Murry**; Merck Research Laboratories, P.O. Box 2000, Rahway, NJ 07065.

Amido ketones are an important class of biologically relevant molecules. Efforts to prepare diverse arrays of these compounds as enzyme inhibitors are current and extensive. In addition, these substrates represent a subclass of building blocks that may be used to make stereochemically complex targets as well as valuable heterocycles. We have been interested in designing non-metal, organo-catalytic processes towards biologically interesting molecules. In this context, we have developed a general, practical method for the synthesis of ketoamides which utilizes a thiazolium salt to catalyze a cross-coupling reaction of various aldehydes with acyl imines. The scope of this reaction as well as mechanistic information will be presented. In addition, application of this methodolgy to the the synthesis of several tetrasubstituted imidazole p38 kinase inhibitors will also be presented.

129. IAN-AMINES: EXPLORING NEW STRATEGIES IN CATALYSIS WITH AXIALLY CHIRAL β-DIKETIMINES. **Jeffrey N. Johnston**; Indiana University-Bloomington, Department of Chemistry, 800 East Kirkwood Avenue, Bloomington, IN 47405.

Axially chiral β-diketimines derived from isoquinoline and 2-aminonaphthalene provide a variety of opportunities in catalysis. Details pertaining to their atropiso-

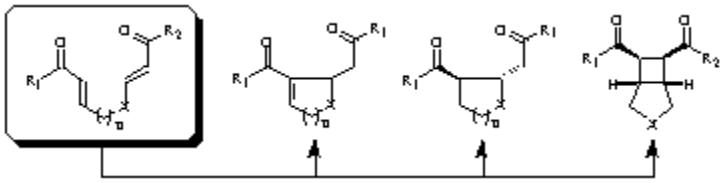
meric stability, coordination chemistry and availability in optically enriched form will be described. Progress in asymmetric reaction development will also be detailed.

130. PARALLEL AND "RATIONAL" APPROACHES TO ASYMMETRIC CATALYSIS. **Scott R. Gilbertson**; Washington University in St. Louis, Campus Box 1134, St. Louis, MO 63130.

Combinatorial chemistry has recently burst on the scene as a valuable tool for the discovery of new drug candidates. There are many similarities between the design of new therapeutic agents and the development of new asymmetric ligands, the most important of which is the limitation of a rational design strategy. For this reason we have embarked on a program that will allow the use of combinatorial technology in the development of new ligands for transition metal catalyzed asymmetric reactions. Through the synthesis of a series of phosphine containing amino acids, we have developed a system that allows for the synthesis and screening of libraries of phosphine transition metal complexes by combinatorial methods. This is accomplished through the synthesis of a variety of phosphine containing building blocks that are compatible with known peptide chemistry and combinatorial technology. These building blocks are then used in the synthesis of libraries of phosphine ligands that also take advantage of the secondary structure of peptides. We are beginning to use this technology in the discovery of new transition metal complexes that catalyze a number of novel organic transformations. Select examples of these ligands and reactions will be discussed. Some of the reactions we are currently working on are palladium catalyzed allylation, the Heck reaction and rhodium catalyzed cycloisomerizations. Additionally our work with simple chiral phosphine-oxazoline ligands will be discussed.

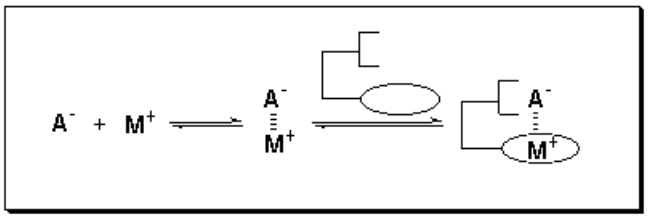
131. CATALYTIC CYCLOREDUCTIONS, CYCLOADDITIONS AND CYCLOISOMERIZATIONS. **Michael J. Krische**; University of Texas at Austin, Department of Chemistry and Biochemistry (A5300), Austin, TX 78712.

The use of enones as latent enolates enables regioselective C-C bond formation, while avoiding the prefabrication of chemically labile enols and enolates. Through the use of a (diketonato)cobalt/silane catalyst system, we have devised highly diastereoselective aldol and Michael cycloreductions (*J. Am. Chem. Soc*. 2001, **123**, 5112). Modulation of the catalyst system has enabled the first intramolecular metal catalyzed alkene [2+2]cycloaddition (*J. Am. Chem. Soc*. 2001, **123**, 6716). Finally, exposure of bis(enones) to nucleophilic organic catalysts provides a simple and effective method for the cycloisomerization of electron deficient 1,5- and 1,6-dienes (*J. Am. Chem. Soc*. 2001, **123**, 2402).



132. DESIGN AND SYNTHESIS OF SALT BINDING RECEPTORS. **Bradley D. Smith**; University of Notre Dame, Notre Dame, IN 46556.

There is currently an active effort to develop synthetic receptors for anions. We have recently shown that if both of the counter-ions in a target salt have localized charges (a likely situation in many anion separation problems) then the consequent ion-pairing of the salt can dramatically lower receptor/anion binding affinities and alter binding selectivities. One way to counter this problem is to develop ditopic receptors that can simultaneously bind both of the salt counter-ions. We are investigating the salt binding properties of various synthetic receptors using NMR and X-ray crystallography. We have synthesized a receptor that binds NaCl as a solvent separated ion-pair. We have also developed a receptor that binds many types of salts as their contact ion-pairs. An important feature with these salt binding systems is the ability of the cation to substantially enhance anion binding constants.



133. VENUS FLYTRAP PODANDS: MODULAR ASSEMBLY AND VERSATILE BINDING AND SENSING. **Jonathan Steed**; King's College, WC2R, London, Strand 2LS, United Kingdom.

Using a series of simple but highly modular and versatile procedures we have prepared a plethora of highly effective anion binding units based on both organic and inorganic cores. These moieties have been coupled to redox-active and fluorescent reporter groups to give molecular sensors. They also form the basis for anion-binding amphiphiles for use in optical waveguide sensing. Anion binding in these systems is slow on the ^{1}H NMR time scale and complexation induces remarkable conformational changes in the host geometry reminiscent of the trapping of an insect by the infamous Venus Flytrap.

134. METALLATED CALIXARENES AND CYCLOTRIVERATRYLENES AS ANION HOSTS. **Jerry L. Atwood**, K. Travis Holman; University of Missouri-Columbia, 125, Chemistry, Columbia, MO 65211.

Some years ago our group initiated a study directed at the synthesis of *p*-metallated calixarenes and related macrocycles. Studies focused on cationic fragments of the second and third row late transition metals (*i.e*. Ru, Rh, Ir), as there is ample literature precedence for the facile synthesis of such η^6-arene compounds. Much of our recent effort has been involved with the elaboration of the cavity by prudent choice of the R^1 groups. Quite selective anion binding hosts have been discovered.

135. ANION-ASSISTED TRANSPORT OF HEAVY METAL AND LANTHANIDE IONS BY POLYETHER CARBOXYLIC ACID IONOPHORES. **Richard W. Taylor**[1], Douglas R. Pfeiffer[2]; [1]University of Oklahoma, 620 Parrington Oval, Norman, OK 73019; [2]Ohio State University, Columbus, OH 43210-1218.

Polyether antibiotics are naturally occurring carboxylic acid ionophores that can transport metal ions across biological and synthetic membranes. Monensin, A23187 (calcimycin) and 4-BrA23187 are members of this group that have been widely used as research tools to manipulate transmembrane concentration gradients of physiological ions (Na^+, K^+, Mg^{2+}, Ca^{2+}) to study the roles of these cations in biochemical processes. The anionic form of the ionophore (L) reacts with a metal ion (M) to form a neutral hydrophobic complex that is transported across the non-polar interior region of the membrane. Generally, monensin transports Na^+ or K^+ as the 1:1 ML complex, whereas A23187 and 4-BrA23187 transport Ca^{2+} and Mg^{2+} as the 1:2 ML_2 complexes. Thus, for alkali and alkaline-earth ions the predominant transport mechanism involves electroneutral exchange of the target ion for H^+ or some other metal ion. However, with divalent post-transition metal ions and lanthanide ions, anion-assisted electroneutral transport is also possible. This additional pathway involves formation of neutral, ternary complexes of the form $ML_{(n-1)}A$ (n = 2,3). In cases where the free or complexed metal ion is subject to hydrolysis in neutral or slightly basic media, the anion (A) is hydroxide and the transported species is formed according to the reaction; $M^{n+} + \boldsymbol{(n-1)}L^- + OH^- \leftrightarrow ML_{(n-1)}OH$. For 0.1 micromolar monensin at pH 7.0 the transport selectivity ($S_{Pb/Ca}$) for Pb^{2+} over Ca^{2+} is 3,400, where $S_{Pb/Ca}$ is the ratio of individual initial transport rates. Under these conditions the predominant forms of the complexed ionophore are PbLOH and CaL^+ for the respective metal ions. In this case, hydroxide binding to PbL^+ gives rise to a membrane permeant species while no corresponding reaction occurs for CaL^+. With 4-BrA23187, an analogous hydroxide-assisted transport process gives $S_{Zn/Ca}$ ~ 500 at pH 7.0. The relationships between transport selectivity and properties of the metal ion (charge,

coordination number, hydrolysis, pKa), the ionophore (charge, number of donor atoms) and the anion (charge, metal ion affinity) will be discussed.

136. A TOSYLATED AZACRYPTAND AS AN ANION RECEPTOR. **Kristin Bowman-James**, Paula K. Morehouse, Md. Alamgir Hossain, Jose Llinares; University of Kansas, 1017 Malott, Lawrence, KS 66045.

In 1968 Park and Simmons reported that bridgehead protons on katapinands, diazabicyclic molecules, could have either an 'in' or 'out' conformation, with an 'in-in' conformation being the most stable. Once protonated, the katapinands contain cavities of high positive charge density that have affinity for anions. Chemists investigating anion binding have expanded on these bicylic systems to introduce more amine sites in the bicycles, resulting in what are now known as azacryptands. Often these systems are synthesized by protecting (or tosylating) the bridging amine sites to prevent them from undesirable interactions. Only after detosylation, to retrieve the secondary amines, are the anion binding properties investigated. During the course of our studies, we found that the protected (tosylated) azacryptands are also readily capable of protonation at the bridge-head amines as in the katapinands. Consequently, they are also capable of binding anions. Results from these studies will be presented including the binding of bromide with a tosylated azacryptand, and the crystallographic findings for both the bromide and neutral receptor. Park, C.H.; Simmons, H.E. *J. Am. Chem. Soc*. 1968, **90**, 2428-2429. Park, C.H.; Simmons, H.E. *J. Am. Chem. Soc*. 1968, **90**, 2431-2432.

137. MIXED AMIDE-QUATERNIZED AMINE RECEPTORS FOR ANIONS. **Kristin Bowman-James**, Sung Ok Kang, Md. Alamgir Hossain; University of Kansas, 1017 Malott, Lawrence, KS 66045.

Synthetic receptors employed for the selective binding of anion usually consist of either positively charged ammonium, *i.e*., protonated polyamines and/or quaternized ammonium salts, or neutral species such as amides, sulfonamides, pyrroles, ureas and thioureas, as well as Lewis acids[1]. We have been exploring a series of mixed amide/amine macrocyclic receptors because of their promise in a variety of applications. In a further design modification, made in order to add charge complementarity to the binding, we have combined the two binding concepts of quaternized ammonium ions with neutral amide/amine receptor species. The resulting receptors are potentially superior in that they eliminate the need for other extraneous counterions. Synthesis, anion binding properties and structural studies will be reported for both the neutral amide/amine anion receptors as well as on the new class of mixed amide/quaternized amine receptors.

[1]Supramolecular Chemistry of Anions; A. Bianchi, K. Bowman-James, E. García-España, Eds.; Wiley-VCH: New York, 1997.

138. DETECTING ANIONIC CASCADE COMPLEXES INSIDE A CRYPTAND CAVITY. **Kristin Bowman-James**, Jose M. Llinares, Md. Alamgir Hossain; University of Kansas, 1017 Malott Hall, Lawrence, KS 66045.

Certain monocyclic and bicyclic polyamine ligands (the latter also known as azacryptands) have been found to bind two transition metal cations which are then connected by an anion bridge (cascade). Recently an example of ditopic binding between the fluorides makes this an analogy to transition metal "cascade" complexes. This structure serves to increase the analogies between cation and anion coordination chemistry. The protonation and binding constants were determinated by potentiometric methods and binding constants were also calculated by ^{1}H NMR. Although the system is very complex, potentiometric studies indicate a binuclear species at low pH. Only mononuclear species are seen at pH 5.0 and NMR binding studies confirm the results. ^{19}F NMR at pH 5.0 indicates two kinds of fluorides, which are assigned as fluoride inside and outside the azacryptand.

139. NEW SYNTHESIS OF N-FUNCTIONALIZED MACROCYCLES. **Kristin Bowman-James**, Jerry Kut, Md. Alamgir Hossain, Jose Miguel Llinares; University of Kansas, 1017 Malott Hall, Lawrence, KS 66045.

The synthesis of polyaza macrocyclic ligands is accomplished by various strategies. Many routes involve tedious protection/deprotection and high dilution techniques. Likewise, similar methods often need to be employed for functionalization of the amines in these systems. Herein is described a facile route for the functionalization of selected amines in a macrocyclic ligand. It is now well established that macrocyclic ligands can be synthesized in good yield, by a one-step Schiff base dipodal (2 + 2) aldehyde condensation, with a variety of amines to produce macrocyclic polyimines. These can also be readily reduced to yield the corresponding amines. We have extended the utility of this methodology by taking advantage of the imine functionality as a “protecting group” in order to functionalize the central amines of the macrocycle. The result is a series of new macrocycles in which the central amine is functionalized, including the dual azamacrocycle/crown ether host system. The synthesis and chemistry of these and related systems will be discussed.

140. BINDING AND SELECTIVITY OF HALIDES IN A TINY OCTAAZACRYPTAND. **Kristin Bowman-James**, Md. Alamgir Hossain, Jose M. Llinares; University of Kansas, 224 Strong Hall, Lawrence, KS 66045.

The tiny 'octaazacryptand', 1,4,7,10,13,16,21,24-octaazabicyclo[8.8.8]hexacosane, has long been considered as a selective receptor for fluoride[1]. Recently, however, we obtained crystallographic findings that revealed a chloride ion inside the cavity.[2] ^{1}H NMR findings in water indicate that the ligand binds fluoride very strongly in the pH range 5.5 – 2.5 while a dramatic increase in the affinity for chloride occurs under very acidic condition at pH 2.5 or less. Upon further investigation using NMR methods, we uncovered that this unanticipated pH sensitivity to chloride binding occurs only for that ion, *i.e*., there is no significant binding for bromide, iodide or nitrate at any pH. These results will be reported along with several crystal structures of the tiny octaazacryptand.

[1]B. Dietrich, J.-M. Lehn, J. Guilhem and C. Pascard, *Tetrahedron Lett*., 1989, **30**, 4125.
[2]M. A. Hossain, J. M. Linares, C. A. Miller, L. Seib and K. Bowman-James, *Chem. Commum*., 2000, 2269.

141. OUTER-SPHERE LIGANDS FOR URANYL CARBONATE. **Jason R. Telford**; University of Iowa, Iowa City, IA 52242.

Using a biomimetic approach to the problem of anion monitoring and remediation, we have designed novel supramolecular hosts for the uranyl tris(carbonato) anion. Guest recognition is tailored to the unique geometric features of the uranyl complex and modulated by topography, hydrogen bonding and coulombic interactions. Cyclodextrins and calix[n]arenes are used as architectural scaffolding. The synthesis, structures and solution thermodynamics of these ligands will be described.

142. CHARACTERIZATION OF POST-TRANSLATIONAL MODIFICATIONS IN LARGE MEMBRANE PROTEINS AND PROTEIN AGGREGATES OF LOW SOLUBILITY. **Christian Schöneich**[1], V. S. Sharov[1], J. Laszewski[1], Nadia Galeva[2], Todd Williams[2]; [1]University of Kansas, 404 Settlers Drive, Lawrence, KS 66049; [2]University of Kansas, Lawrence, KS 66045.

Tyrosine nitration alters protein function and structure and is a hallmark of biological aging associated with oxidative stress. For a clear correlation of the extent of post-translational modifications with age-associated dysfunction, nitration yields and sites need to be characterized. Ideally, such studies require 100% sequence coverage and experimental strategies are developed especially for membrane proteins like SERCA and large insoluble protein aggregates, as ob-

tained with glycogen phosphorylase B (PhosB). We optimized a method where, subsequent to isolation from biological samples or *in vitro* nitration, proteins are solubilized in TFA and resolved on a C4 reversed-phase column with an EtOH gradient, dried, resolubilized and purified by SDS-PAGE. After in-gel digestion with various combinations of cyanogen bromide and protease, peptides are ex- tracted with various aqueous detergents and analyzed by MALDI-TOF MS and HPLC-ESI MS/MS. So far, MALDI and ESI-MS/MS analysis yields ca. 66% sequence coverage, identifying nitration at Tyr281, Tyr405, Tyr204, Tyr473 and Tyr525 (in order of reactivity) on PhosB, and Tyr122 on the SERCA1 isoform. *In vitro* nitration of PhosB occurs on 11 of 25 resolved Tyr residues, with Tyr281 being most reactive. *In vitro*, Tyr122 of SERCA1 is most reactive; however, this modification is less abundant *in vivo*, potentially reflecting accelerated protein turnover.

143. PROTEOMICS: WHAT IS IT AND WHAT ARE THE CURRENT CHALLENGES?. **Dawn R. Dufield**; Pharmacia, 700 Chesterfield Pkwy. N, Mail Zone: AA1F, St. Louis, MO 63198.

Over the last few years, proteomics has been a very rapidly emerging technology. The improvements in mass spectrometry have directly contributed to the advances in this field. As a result of the extremely fast growth in this field, the term “Proteomics” adopted an abundance of meanings. This presentation will attempt to address some of these, in particular, the two-dimensional gel electrophoresis and mass spectrometric approaches. The advantages and disadvantages of “traditional” versus more “novel” proteomics will be addressed, including the typical 2D-PAGE to LC/MS/MS as well as the ICAT technology. The recent technological advances in mass spectrometric hardware and software which enable nanoscale LC/MS/MS will be discussed as well as current analytical challenges. This increased interest in proteomics has necessitated the develop- ment of highly automated systems. There is also a strong need for increased software development to support this highly automated acquisition throughput. The current bottleneck is now in the data reduction. The ability of this continually developing technology to identify potential biomarkers in various biological fluids has led the field in various directions. As a result, there has been a need for better fractionation methods and on-line two-dimensional chromatographic methods such as the MUDPIT approach. Furthermore, the need for better or more diverse search engines has emerged. Many biological fluids may contain disease specific, clinically relevant endogenous peptides which have termini not produced by typical enzymatic digestion such as the traditional trypsin digestion. This non-specificity places a large demand on the search engines, requiring the evaluation of every possible amino acid cleavage. Search engines are an integral part of the proteomics process. Some approaches to optimizing the search strategy as well as limitations associated with various search engines such as MASCOT will also

be presented. Lastly, the need for good bioinformatics will be addressed. As more and more data are collected, there is an increasing need for data reduction programs and an ability to capture all the information in an automated fashion.

144. NMR SPECTROSCOPIC STUDY OF *PSEUDOMONAS AERUGINOSA* HEME OXYGENASE: THE FORMATION OF β- AND δ-BILIVERDIN IS A CONSEQUENCE OF AN UNUSUAL HEME SEATING. **Mario Rivera**[1], Gregori A. Caignan[1], Rahul Deshmukh[2], Angela Wilks[2]; [1]Oklahoma State University, Department of Chemistry, Stillwater, OK 74078-3071; [2]University of Maryland, Department of Pharmaceutical Sciences, School of Pharmacy, Baltimore, MD 21201-1180.

Mammalian heme oxygenase (HO) maintains heme homeostasis by oxidatively cleaving heme to α-biliverdin. The reaction consumes three molecules of oxygen and a total of seven electron equivalents in order to release one molecule of α-biliverdin, one molecule of CO and one iron ion. Recently, bacterial HOs have been identified in *Neisseria meningitidis* (nm-HO), *Corynebacterium diphtheriae* (cd-HO) and *Pseudomonas aeruginosa* (pa-HO). The role of bacterial HOs entails the breakdown of heme in order to provide the bacterium with the ability to use heme as a source of iron. The reactions catalyzed by nm-HO and cd-HO are similar to those carried out by human and rat HO-1 in that the heme is hydroxylated and cleaved exclusively at the α-meso carbon. In contrast, the reaction catalyzed by pa-HO produces β-biliverdin (30%) and δ-biliverdin (70%). The origin of this unusual regioselectivity has been studied by ^{1}H, and ^{13}C NMR spectroscopies. These studies suggest that the heme in pa-HO is seated in a manner that is distinct from that observed for all other α-hydroxylating heme oxygenases. In pa-HO the heme is rotated in-plane ~110°, so that the δ-meso carbon of the major orientational isomer is located within the HO-fold in the place where the α-hydroxylating enzymes typically place the α-meso carbon. This unusual heme seating originates from the absence of stabilizing interactions between the polypeptide and the heme propionates that are typically found in α-hydroxylating heme oxygenase enzymes. These interactions typically involve Lys-16 and Tyr-112 in nm-HO, and Lys-16 and Tyr-134 in human and rat HO-1. The corresponding residues in pa-HO are Asn-19 and Phe-117, respectively. In agreement with this hypothesis, NMR spectroscopic studies of the Asn-19 Lys/Phe-117 Tyr double mutant of pa-HO demonstrate that the latter exists in solution as a mixture of molecules exhibiting two distinct heme seatings; one is identical to that exhibited by wild type pa-HO and the alternative seating is similar to that exhibited by á-hydroxylating HOs. Each of the these heme seatings gives rise to a subset of two heme orientational isomers related to each other by 180° rotation about the α-δ-meso axis. The coexistence of these molecules, in the

proportions suggested by their corresponding ^{1}H NMR signals, explains the unusual regioselectivity exhibited by the double mutant, which we found produces α-biliverdin (55%), β-biliverdin (10%) and δ-biliverdin (35%).

145. MICROFLUIDIC DEVICES FOR PROTEOMICS. **Christopher T. Culbertson**[1], J. M. Ramsey[2], Maxine A. McClain[3], Jeremy D. Ramsey[2]; [1]Kansas State University, 111 Willard Hall, Manhattan, KS 66506; [2]Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6142; [3]The Georgia Institute of Technology, Atlanta, GA.

Proteomics is concerned with identifying the protein complement of a cell. The types and kinds of proteins expressed, however, vary with time as a cell goes through its growth cycle, differentiates or is subjected to external stimuli. To quantitate these changes, cells need to be examined individually at known time points in their growth cycle or under conditions where known stimuli are applied. Microfluidic devices are well suited for the analysis of proteins in single cells. These devices are capable of transporting cells automatically through a series of processing steps which can include exposing the cell to an external stimulus, lysing the cell and adding reagents to label the proteins within each cell. Separations on these devices can be performed rapidly and with high efficiency. The separation speed and power come from the ability 1) to make injection plugs of very short spatial extent using non-mechanical fluidic valving techniques and 2) to apply high electric field strengths without generating significant Joule heating. The fluidic valve also has essentially no dead volume so little analyte dilution occurs after cell lysis. Given that many of the interesting proteins in a cell will be in the nanomolar range, control of dilution is critical. Such separation power and speed, along with the ability to use ultrasensitive detection methods like laser-induced fluorescence on-chip, should allow the detection and quantitation of a significant number of proteins in each individual cell. We will demonstrate and discuss the transport, manipulation and lysis of cells on microfabricated devices along with methods for analyzing the cellular contents.

146. THE USE OF ANALYTICAL CHEMISTRY IN THE DISCOVERY AND DEVELOPMENT OF GENOMICS-BASED HUMAN PROTEIN DRUGS. **Melissa D. Perkins**; Human Genome Sciences, Inc., 9410 Key West Ave., Rockville, MD 20850.

Understanding how gene products, proteins, work together to create and maintain complex biological systems involves the various protein production processes within cells. Proteomics is the study of protein expression by biological systems, including relative abundance, post-translational modifications, stability within the cell and fluctuations as a response to environment and altered cellular needs. In

contrast to genomic sequence, which captures DNA information that is stable throughout the lifetime of an organism, proteomics summarizes protein-expression patterns of a biological system at different times. Through an understanding of what proteins the human body needs and how proteins are used to function and combat disease, new protein pharmaceuticals can be developed. Human Genome Sciences, Inc., is a pioneer in genomics for the discovery and development of new pharmaceutical products. The goal of the company is to become a global biopharmaceutical company that discovers, develops, manufactures and sells their own gene-based drugs. A portion of Human Genome Sciences´ current pipeline is comprised of novel human protein and antibody drugs arising from genomics-based research. Through discovery to market, analytical chemistry is used. Here, we will follow the progression of a genomics-based drug from discovery to clinical trials and discuss the analytical challenges that arise along the way.

147. ESR SPECTROSCOPY OF UV-GENERATED RADICALS IN POLYURETHANES AND EPOXIES. Yuanyuan Huang, Ying He, Renwu Zhang, Yanching Jean, Jerry R. Richardson, **Thomas C. Sandreczki**; University of Missouri-Kansas City, 5100 Rockhill Road, Kansas City, MO 64110-2446.

Ultraviolet light was used to generate free radicals in aliphatic polyurethanes and in glycidyl bisphenol-A type epoxies. UV sources included narrow-band 340 and 313 nm fluorescent lamps and a broadband Xe-arc lamp. Early stage radicals were detected by generating them in the ESR cavity at 77 K. At this temperature, a typical urethane signal was a 5-line spectrum having 2.5 mT hyperfine splittings. A typical epoxy signal was multi-lined and bore resemblance a cumyl radical signal. Identification of the radicals responsible for these signals involves looking at separate components of the urethane and epoxy in an attempt to isolate the relevant moieties. The effect of TiO_2 was examined in polyurethane samples. Under ambient conditions, free radical production was markedly different between a clearcoat sample and one filled with 15% TiO_2. It appears that the presence or absence of this pigment significantly affects long-term stability of the coating. Support by AFOSR and NSF is gratefully acknowledged.

148. DYNAMICS OF POLYMERS ADSORBED ON SILICA. **Frank D. Blum**; University of Missouri-Rolla, 142 Schrenk Hall, Rolla, MO 65409-0010.

An overview of the study of dynamics of polymers at surfaces will be given with an emphasis on the behavior of poly(vinyl acetate) and poly(methyl acrylate). Both of these polymers, when adsorbed on silica, form layers that are graded in terms of mobility. We review nuclear magnetic resonance, modulated differential scanning

calorimetry and adhesion studies on these thin polymer layers. We find that the role of the molecular motion in the polymers is apparent in each type of study.

149. CHAIN PACKING IN PHENYL SUBSTITUTED POLYCARBONATES BY $^{13}C\{^{2}H\}$ REDOR NMR. **Robert D. O'Connor**[1], Jeffery A. Byers[1], Barbara Poliks[2], Karen L. Wooley[1], Jacob Schaefer[1]; [1]Washington University in St. Louis, One Brookings Drive, Chemistry Department, St. Louis, MO 63130; [2]Binghamton University, Physics Department, Binghamton.

Rotational-echo double-resonance $^{13}C\{^{2}H\}$ NMR has been used to characterize the chain packing in ^{13}C-carbonyl, ^{2}H-labeled phenol-substituted and ethoxy-phenyl-substituted bisphenol A polycarbonates. For both polymers, the REDOR dephasing showed that the distance between the phenol-*d* or ethoxy-d_3 labels of one chain is between 4-5 Å from the carbonyl-^{13}C label of another chain. Additionally, differences between the REDOR dephasing rates of the centerband and spinning sidebands proved the presence of local interchain orientational order in both polymers. For phenol-polycarbonate, further analysis showed that 66% the interchain ^{2}H-^{13}C dipolar vectors have an orientation of approximately 30° (azimuthal) and 70° (polar) in the carbonyl-carbon chemical-shift tensor reference frame. Similarly, for ethoxyphenyl-polycarbonate 36% have an orientation of 60° (azimuthal) and 70° (polar).

150. MATERIALS SCIENCE: NMR RELAXATION STUDIES AND MOLECULAR MODELING OF CONDENSED PHASE IONIC LIQUIDS. **Robert Carper**[1], Zhizhong Meng[1], Andreas Doelle[2], Peter Wasserscheid[2]; [1]Wichita State University, Chemistry Dept., 1845 Fairmount, Wichita, KS 67260-0051; [2]RWTH, Aachen, Germany.

The solution microdynamics of [BMIM][PF_6] has been studied by ^{13}C NMR spectroscopy. The ^{13}C relaxation times and nuclear Overhauser enhancement (NOE) measurements are used to determine rotational correlation times. The continuous distribution of correlation times defined by Cole and Davidson that has been used to interpret the relaxation data of viscous liquids and glassy solids is used to model the [BMIM][PF_6] system. The Cole Davidson model is combined with the model-free approach of Lipari and Szabo (LS). The combination of the Cole-Davidson and Lipari-Szabo models successfully represents the imidazolium ring carbons. The Bloembergen, Purcell and Pound (BPP) method is combined with the LS method to represent the flexible side chains in [BMIM][PF_6]. The results of semi-empirical (AM1 and PM3) and *ab initio* (Hartree-Fock and Density Functional Theory) calculations are compared for the [BMIM][PF_6] ionic liquid. The *ab initio* calculations include fully optimized structures at the RHF/3-21G(*), RHF/6-31G*, RHF/6-31G**, MP2/6-31G*, B3LYP/6-31G* and B3LYP/6-31G**

levels. In addition to the gas phase calculations of these ion pairs, semi-empirical modeling of the formation of multiple ion pair dimers also provides insight into their possible aggregation in the liquid state.

151. ALKYL REDISTRIBUTION IN DISTANNOXANES: THE $[ME_2SNCL]_2O$/ $[^nBU_2SNCL]_2O$ BINARY SYSTEM. **Dennis L. Hasha**[1], David L. Tierney[2], Peter J. Moehs[3]; [1]University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65409-0010; [2]University of New Mexico, Department of Chemistry, Albuquerque, NM 87131; [3]Saginaw Valley University, University Center, Michigan 48710.

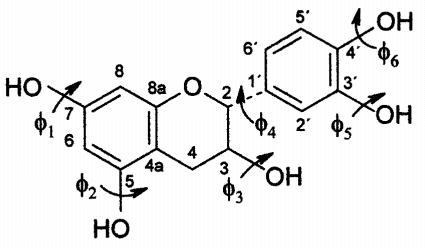
The alkyl redistribution reaction in the binary $[Me_2SnCl]_2O/[^nBu_2SnCl]_2O$ mixture is examined using ^{119}Sn NMR spectroscopy. Binary mixtures of $[Me_2SnCl]_2O$ and $[^nBu_2SnCl]_2O$ reach equilibrium slowly at room temperature. The reactant dimers are found to be in equilibrium with all seven mixed alkyl dimers. These mixed dimers differ in the ratio of the methyl and *n*-butyl groups as well as their relative positions. The equilibrium concentrations of the binary mixtures reveal that the bulkier *n*-butyl group is sterically directed towards the exocyclic sites. However, the statistically favored 2:2 mixed alkyl dimer, in which the two *n*-butyl groups occupy an endo- and exocyclic site, is the most abundant dimer in the equilibrated equimolar $[Me_2SnCl]_2O/[^nBu_2SnCl]_2O$ mixture. The mixed alkyl distannoxanes are produced via two coupled processes. At 298 K the dominant redistribution mechanism involves the dissociation of the distannoxane dimers, $\{[R_2SnCl]_2O\}_2$, into R_2SnCl_2 and the trinuclear tin species, $[R_2SnCl_2][R_2SnO]_2$ with the subsequent coupling of dissimilar fragments. This mechanism is incapable of producing mixed distannoxanes which possess different alkyl groups attached to the two endocyclic tins. These products appear to be formed by a fluxional process resulting in the exchange of the endo- and exocyclic tin sites of the trinuclear tin species, followed by the association with a R_2SnCl_2 fragment.

152. CARBON-13 CP-MAS NUCLEAR MAGNETIC RESONANCE STUDIES OF TEAS. **Antonio Martínez-Richa[1]**, Pedro Joseph-Nathan[2]; **[1]**Universidad de Guanajuato, Noria alta s/n, Guanajuato, Gto 36050, Mexico; **[2]**Centro de Investigación y de Estudios Avanzados del IPN, Apartado 14-740, Mexico City, Mexico.

^{13}C CP-MAS NMR spectra of green tea, black tea and other teas were obtained and assigned based on the solution and solid-state NMR spectra of tropolone, (+)-catechin hydrate, gallic acid and flavone derivatives. Conformational analysis and molecular modeling was used to explain differences between NMR spectra in solution and in the solid-state for (+)-catechin.The minimum-energy conformation geometry of (+)-catechin indicates that torsional angles for H-O-C phenolic groups

are close to planarity (see Figure 1). This indicates that conjugation of the phenolic oxygens to the aromatic rings is more important in the solid and explains the differences observed in the chemical shifts. Other important feature is the fact that carbon 6 orients toward the ether oxygen of the six-membered ring; being the bond distance between them being 2.9Å. The peak shape and chemical shifts observed for carbonyl carbons in CP-MAS spectra of black and green teas indicate the existence of different chemical species, mainly free phenolic acids

ferences between teas. Finally, CP-spectra of extracted black tea were obtained. A detailed comparison of the black tea ^{13}C CP-MAS spectrum and the frame left after extraction reveals that flavonoids were almost completely solubilized by hot water.



Definition of torsion angles for (+)-catechin

153. MAGNETIC ALIGNMENT IN NOMINALLY NON-MAGNETIC HEXAGONAL METAL HYDRIDES: NMR. Vikram D. Kodibagkar[1], **Caleb D. Browning[1]**, Xiaoping Tang[2], Yue Wu[2], Robert C. Bowman, Jr.[3], Mark S. Conradi[1]; [1]Washington University, Physics Department, One Brookings Dr., St. Louis, MO 63130; [2]University of North Carolina, Department of Physics and Astronomy, Chapel Hill, NC 27599; [3]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.

Powders of three hexagonal metal-hydrides are found to align in 4.4-8.3 T magnetic fields used for NMR. The field-alignment is unexpected, since all three systems have very small susceptibilities, as demonstrated by narrow NMR lines. The extent of alignment runs from nearly complete to barely detectable in $ZrBe_2(H,D)_x$, LuD_3 and YD_3, respectively. The preferred alignment in $ZrBe_2(H,D)_x$ is with the crystallites' *c*-axes perpendicular to B, while the *c*-axes and B tend to be parallel in LuD_3 and YD_3. The alignment must be considered for proper analysis of NMR spectra in these and related materials.

154. MOLECULAR WEIGHT AND DYNAMICS IN PMA-D_3 IN THE GLASS TRANSITION REGION. **Burak Metin**, Frank D. Blum; University of Missouri-Rolla, Department of Chemistry, 142 Schrenk Hall, Rolla, MO 65401.

The effect of molecular weight on the dynamics of poly(methyl acrylate)-d_3 (PMA-d_3) in the glass transition region was studied using the deuterium quad-

rupole echo NMR. The ^{2}H NMR spectra of the methyl groups were observed in order to understand the dynamics around the glass transition (T_g) region. For high molecular weight samples, segmental motions were found to be quite homogenous, while for lower molecular mass samples, they were found to be heterogeneous with respect to the behavior of different segments (*e.g*. chain ends and middles) in the glass transition region. The transition was found to occur at lower temperatures as the molecular weight decreased. The appearance of a mobile component due to chain ends was more prominent for lower molecular mass samples at lower temperatures in the glass transition region.

155. DOES MULTIMEDIA IMPROVE STUDENT ACHIEVEMENT IN CHEMISTRY?. **Elizabeth Hansen**, Harold H. Harris; University of Missouri-St. Louis, 8001 Natural Bridge Road, 315 Benton Hall, St. Louis, MO 63121.

We have examined the effects of adding significant amounts of computer technology to an otherwise traditional general chemistry course for science majors. Innovative components added to the conventional curriculum were video demonstrations during lecture and the Blackboard® computer program, which allows the instructor to post announcements, graded quizzes, practice problems and exams, tutorials, student grades and many other supplemental resources on-line. Examining the effects these added elements had on student achievement was done by assessing student surveys, student interviews, exam grades, final course grades and monitoring the students' use of Blackboard®. Some surprising results will be presented.

156. TEAM LEARNING WORKSHOPS AND ON-LINE QUIZZES: IS THE LECTURER NEEDED? **David L. Garin**; University of Missouri-St. Louis, 8001 Natural Bridge Rd., St. Louis, MO 63121.

Some textbook publishers have provided computer programs that allow students to take on-line quizzes. In the 2001-2 AY, on-line quizzes and team-learning workshops were utilized for our introductory chemistry course, in addition to the traditional three hours of lecture. The workshops were led by a student facilitator responsible for a class of 10-20 students working in groups of 2-4. The facilitators were both undergraduate and graduate students. On-line multiple choice quizzes were required for each text chapter covered (11). The on-line quiz (open text, no time limit) could be continuously repeated to replace the previous score and counted for less than 7% of the final point total. Two-hour workshops met weekly, attendance was mandatory and workshop grades constituted 13% of the final point total. Attending lecture was not required. Evaluations at the end of the semester revealed that students overwhelmingly approved of the workshops when facilitators were performing adequately and found the workshops to be their most

useful learning tool. Videotapes of each of the workshops during W2002 will be available which will accurately depict the activities of workshop sessions. Can the course be successfully offered by utilizing workshops and on-line quizzes, without a lecturer? One experienced lecturer's opinion will be offered.

157. TEACHING EXPERIMENTAL DESIGN THROUGH PROJECT-BASED ORGANIC CHEMISTRY LABORATORY. **Somnath Sarkar**; Central Missouri State University, 420 WCM, Warrensburg, MO 64093.

Students in the second semester sophomore organic chemistry class conducted a six-week project during spring 2002 at Central Missouri State University. The objective of the project was to help them learn rational experimental design and fundamental research methods used in organic chemistry. Students in teams of two selected one of the four compounds, namely Vanillin, cinnamaldehyde, butyric acid and 4-hydroxy acetophenone. Students were responsible for making small changes in the molecule in a rational manner and studing the effect of these changes on smell. Each team designed their experiment, studied literature, conducted their experiment to make three new compounds and characterized them using NMR and IR spectroscopy. The types of projects undertaken by the students, the types of challenges involved in supervising such a project-based laboratory and the student attitude regarding this experience will be discussed.

158. MORE THAN JUST PROTECTING THE ENVIRONMENT: TEACHING ABOUT THE ENVIRONMENT. **Margaret E. Wickham St. Germain**[1], Mary Ann Figuly[2], Dawn Schwartz[2]; [1]U.S. Environmental Protection Agency, Region 7, 901 North Fifth Street, Kansas City, KS 66101; [2]Northwest Science and Technology Middle School, 2400 North 18th Street, Kansas City, KS 66101.

EPA Region 7's relationship with the Kansas City, Kansas Unified School District 500 began more than five years ago–when the District needed additional expertise with revising its math and science curricula of three schools in efforts to increase student motivation and achievement. Northwest Science and Technology Middle School (NWMS) was among three of the chosen schools EPA has helped to develop and deliver innovative science concepts focusing on environmental themes and stewardship. The first curriculum was developed in 1998-1999, called the *Water Cycle and Related Treatment Processes*. This curriculum, presented to 80 sixth-graders, taught students the basics about the water cycle in fun, creative ways, such as games, rap songs, experiments, table-top demonstrations and field trips to local water and waste water treatment plants. The second curriculum was developed for the next three school years, called *Stream Ecology as Impacted by Urban Development*. This curriculum, presented to 120 sixth through eighth-graders, presented entertaining, thought-provoking topics, and included lectures, class activities, games, experiments, demonstrations and two

field trips per year. Students, accompanied by EPA employees, actually participated in field sampling activities at the East Fork of Line Creek in Kansas City, Missouri. Students learned about reading maps, urban development and environmental topics, such as water quality, botany, macro invertebrates, hydrology, data collection and field skills. This project has sparked involvement by several parents. Thus, students and parents learned techniques used by scientists to evaluate the diversity of life in a natural stream setting and how streams are impacted by surrounding areas. This presentation will share the successes and challenges of developing a technical curriculum for inner-city, middle school students, in partnership with teachers and parents.

159. BECOMING SCIENTISTS: COGNITIVE, AFFECTIVE AND MOTIVATIONAL STRETCHES OF NOVICE SCIENTISTS DURING A COGNITIVE APPRENTICESHIP. **Amy Preece**, Janet Bond-Robinson; University of Kansas, 2010 Malott Hall, Lawrence, KS 66045.

This study of the nature of science with undergraduate researchers in chemistry investigates the nature of scientific practice on an everyday basis to build a template for designing inquiry based curricula. Particular attention is paid to the development of integrated disciplinary knowledge with the procedural knowledge of laboratory practice entitled empirical chemical knowledge. Results reveal that novice researchers find frustration caused by little overlap between course experiences and the work in research, making the gain of empirical chemical knowledge difficult even for very good students. Growth occurs by sustained efforts to solve a series of everyday problems within a large project rather than devising an entire study on their own. The social culture of mentors, practice on techniques and instruments, concrete work connected with vocabulary and guidance in interpreting representations are the features of a cognitive apprenticeship in an intelligent research environment that lead to growth in expertise.

160. MAKING CONNECTIONS: A PROGRAM TO ENCOURAGE HIGH SCHOOL STUDENTS TO STUDY CHEMISTRY. **Jesse C. Moore**, Kathryn Boyle, Sarah Evans, Kena Chapman; Friends University, 2100 University, Wichita, KS 67213.

A report from the National Science Teachers Association (NSTA Reports, May 1999) points out that U.S. high school students are well below the international average in science knowledge. Science teachers surveyed said that for reform efforts to be successful, the entire community must support the effort and that: "...programs having scientists work with students provide the student with positive images of scientists and engineers; aroused their interest in science; gave them useful information about science careers; and helped them better understand science content." This program's goal was to encourage young people to study

science and to choose chemistry as a career by building bridges between them, their teachers, their parents and institutions of higher education. The program was targeted to students in their early high school years as that is when they make choices that affect their later coursework and career options. Over the past two summers, sixty high school students have spent a week on the Friends University campus involved in hands-on chemistry workshops which gave them a chance to become acquainted with peers who have similar interests and with chemistry faculty, college students and chemists who can serve as role models and resource people. The workshops introduced the students to chemical concepts and methods such as separation methods, compound identification, quantitative methods and computer methods that they can later use to carry out their own project. Each student was assigned a mentor and, with the help of their mentor, developed a plan for an independent project to be done over the next year using community resources. Most important, the workshop were designed to be interesting and fun. Student evaluations of the program were favorable and 87% of the students surveyed reported they were more likely to choose a career in chemistry because of their participation in the program.

161. IMPACT AND EFFECTIVENESS OF TRAINING NEW CHEMISTRY GRADUATE TEACHING ASSISTANTS. **Romola Rodriques**, Janet Bond Robinson; University of Kansas, Department of Chemistry, 2010 Malott Hall, Lawrence, KS 66045.

An instrumental case study of a recent graduate of our Graduate Training Programme for Teaching Assistants is undertaken the semester following his/her completion of the course. This phenomenological study was tended to (1) gain insights into the development of the metacognitive strategies employed by GTAs in their preparation and execution of their duties and (2) evaluate and develop the curriculum design of the course to aid GTAs' pedagogical content knowledge development of the Chemistry Department. Complementary methods of observation, self-reporting and guided approach interviews were conducted by one of the researchers to address these objectives. Our preliminary results indicate that there are six key areas of considerable difficulty for new GTAs: (a) giving appropriate instructions at the beginning and during the laboratory session; (b) organizing and managing an inquiry-oriented chemistry laboratory; (c) effectively explaining chemistry concepts to students; (d) competently linking laboratory experiments to the underlying concepts; (e) challenging students' thinking and their capacity to effectually communicate their knowledge; and (f) developing competency teaching with chemical instruments and technology. As a result of our findings, we propose to (1) design and implement a guided-inquiry oriented curriculum to train new Chemistry GTAs and (2) investigate the effectiveness of this training on GTAs' ability to (a) organize and manage guided-inquiry Chemistry laboratories, (b)

competently connect and explain underlying Chemis- try concepts and (c) challenge students´ thinking and understanding of these Chemistry concepts.

162. DO CURRICULUM REFORMS AFFECT STUDENT ACHIEVEMENT IN CHEMISTRY? **Elizabeth Hansen**, Harold Harris; University of Missouri-St. Louis, 8001 Natural Bridge Road, 315 Benton Hall, St. Louis, MO 63121.

Both before and after curriculum reforms of our first-semester, general chemistry course for science majors, we analyzed the effects on student achievement. To our very established, traditional general chemistry course many reforms were introduced. The reforms affected nearly every part of the course, from lecture to recitation sessions, and from labs to homework. This quasi-experimental design was examined through the results of scores on the ACS First-Term General Chemistry Standardized Exam, final grades, student attitudes towards studying and learning science, student surveys, student interviews and online monitoring. However, this presentation will focus on both the expected and unexpected results on the ACS exam.

163. THE IMPACT OF COOPERATIVE LEARNING AND SCAFFOLDED HOMEWORK IN AN UNDERGRADUATE ORGANIC CHEMISTRY COURSE. **Robert A. Doyle**[1], Janet Bond Robinson[2]; [1]Creighton University, 2500 California Plaza, Omaha, NE 68178-0104; [2]University of Kansas, Lawrence, KS 66045.

Eighty students in the first semester of the one-year organic chemistry sequence for science majors and pre-health professionals were randomly assigned to scaffolded homework or traditional homework. Scaffolded homework problems contained distinct problem representation, solution and verification phases. Students assigned either type of homework were offered optional problem solving sessions emphasizing cooperative learning. Statistically significant results, related data and implications for instruction will be presented.

164. THE ANALYTICAL DIGITAL SCIENCES LIBRARY (ASDL). **Theodore Kuwana**[1], Cynthia K. Larive[1], Stuart Chalk[2], Cameron Dorey[3], George Long[4]; [1]University of Kansas, 2291 Irving Hill Drive, Lawrence, KS 66045; [2]University of North Florida, 4567 St. Johns Bluff Road S., Jacksonville, FL 32224; [3]University of Central Arkansas, Department of Chemistry, 137 Laney, Conway, AR 72035; [4]Indiana University of Pennsylvania, Indiana, PA 15705.

The Analytical Sciences Digital Library (ASDL), a NSF-funded National Digital Sciences Library project will be described. The ASDL is an electronic library that can be accessed at www.asdlib.org that collects, catalogs and links peer reviewed web-based discovery materials pertinent to innovations in curricular development and supporting resources in the Analytical Sciences. Illustrations of the types of materials included in the collection will be presented such as innovations in teaching and learning pedagogy, resource materials for analytical sciences course and laboratory instruction, supplementary materials on analytical instrumentation and methods and a discussion forum to promote interactive discussions about teaching and learning in the analytical sciences.

165. INFLUENCE OF "ALTERNATIVE" AMINO ACIDS ON THE DISSOCIATION PATTERNS GENERATED BY CID OF GAS-PHASE PEPTIDE IONS. **Michael Van Stipdonk**, Manohari Silva, Marcus Barber, Victor Anbalagan, Erach Talaty; Wichita State University, Department of Chemistry, Wichita, Kansas 67260-0051.

Ring intermediates are thought to play a major role in the dissociation of gas phase peptide ions. The production of $(b_n+17+Cat)^+$ and $(b_n-1+Cat)^+$ ions from metal cationized peptides is proposed to involve intramolecular nucleophilic attack by carbonyl oxygen atoms, either from the C-terminal or N-terminal side of the cleavage site, including the generation of key 5-member ring intermediates. In this study, we examined the CID of metal cationized (Li^+, Na^+ and Ag^+) synthetic peptides of sequence AcFGGX and AcFFXA, with several “alternative” amino acids at position X. Our aim is to understand the effect of forcing the intervention of larger ring intermediates (*i.e*. 6, 7 or 9 member), or blocking cyclization altogether, on the intensity of the sequence ions such as $(b_3+17+Cat)^+$ and $(b_n-1+Cat)^+$. Assuming that ring formation occurs, peptides with the amino acids α-alanine, γã-aminobutyric acid or ε-amino-*n*-caproic acid at the C-terminus proceed to $(b_3+17+Cat)^+$ via 6, 7 and 9 member ring intermediates, respectively, which are kinetically less favorable than 5 member rings. Significant differences in the energetics of ring-opening and in the stability of the neutral species eliminated are also expected. While amino acids such as *para*-aminobenzoic acid and 4-aminocyclohexanecarboxylic acid will prevent cyclization at the C-terminus, proline and *ortho*-aminobenzoic acid should permit ring formation, albeit through

bicyclic intermediates. We present here the results of this study and demonstrate that forcing the intervention of larger ring intermediates, or blocking cyclization, has a profound influence of the dissociation patterns generated from peptide ions. The appearance of the CID spectrum is also highly dependent on the choice of cation.

166. MULTIPLE STAGE TANDEM MASS SPECTROMETRY FOR PEPTIDE SEQUENCING IN PROTEOME STUDIES. **Michael Van Stipdonk**; Wichita State University, Department of Chemistry, Wichita, KS 67260-0051.

Proteomics relies on the separation and identification of the multitude of proteins expressed by an organism in a given physiological state. Accurate sequencing of peptides and proteins, with high throughput and good detection limits, is therefore crucial to proteome studies. Mass spectrometric methods such as peptide mass-mapping and sequence tagging are "workhorse" methods for indirect (*i.e.* involving library and database searching) protein sequencing and/or identification. We have initiated a comprehensive study of the parameters that affect the practicality and accuracy of direct or *de novo* peptide sequence determination using multi-stage or MS^n tandem mass spectrometry. Presented here are important issues such as the use of metal ions as cationizing agents and chemical modification of the N-terminus, and their influence on the accuracy of peptide sequencing by mass spectrometry.

167. LC/MS AND ISOTOPE LABELING TO EVALUATE CHANGES TO CYTOCHROME P450 1A EXPRESSION AFTER EXPOSURE TO 2,3,7,8-TETRACHLORODIBENZO-***P***-DIOXIN. **Denise K. MacMillan**, Agnes M. Hindemith, Martha G. Rhoades; U.S. Army Corps of Engineers, 420 S. 18th Street, Omaha, NE 68102.

The cytochrome P450 1A subfamily of isozymes found in the liver is known to respond to xenobiotic substances such as drugs and environmental contaminants, such as 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). Enzyme response is often measured by monitoring substrate disappearance or metabolite production, or through mRNA expression. These methods do not identify all the proteins influenced by exposure. Also, the measurements may not directly correlate to the extent of change in the target protein. Direct evaluation of relative changes to protein concentrations can be made through use of isotope labeling and LC/MS. Direct measurement may enable future development of sensitive bioassays for determination of environmental contamination. To better understand the potential for a bioassay, cytochrome P450 isozyme expression in control human hepatoma HepG2 cells is compared in this study to expression in TCDD-exposed cells by

using isotope labeling and LC/MS. The focus of this study is the use of LC/MS to identify and quantitate proteins from HepG2 cell lysates. Optimization of the sample preparation steps will be discussed in detail elsewhere. Briefly, membrane proteins were isolated from HepG2 cells after exposure to TCDD. After further purification and concentration, the protein cysteines were labeled with a biotinylated iodoacetamide derivative by using the ICAT™ Kit for Protein Labeling from Applied Biosystems. The labeled proteins were then digested and the labeled peptides were isolated by avidin affinity chromatography. Peptides were separated with reverse phase liquid chromatography and determined by using data dependent scanning on a Finnigan LCQ™ DECA ion trap mass spectrometer with electrospray ionization. Relative protein concentrations are obtained from abundance ratios of the differentially labeled peptides. Other studies have noted a sixteen-fold induction of CYP 1A from HepG2 cells exposed to TCDD, but we have not observed such a significant change with our system. In addition to quantitation of the CYP 1A isozymes, other HepG2 proteins affected by exposure to TCDD can be identified simultaneously from the cell lysates.

168. ANALYSIS OF ACIDIC PHARMACEUTICALS IN ENVIRONMENTAL SAMPLES USING LC/MS/MS. **Amy S. Lillquist**, Craig E. Lunte, Todd D. Williams; University of Kansas, 1251 Wescoe Hall Dr., Chemistry Dept., Lawrence, KS 66045.

Recently, concern has arisen over the possible contamination of water sources by popularly prescribed and over-the-counter pharmaceuticals and their possible metabolites posing unknown health effects on living populations coming in contact with these water sources. A wide variety of pharmaceutical compounds have been detected at ng/L levels in aquifers, sewage treatment plant effluent and rivers in Europe [*J. Chromatogr. A* 2001, **910**, 69-78]. Pharmaceuticals have also been detected in the United States at ng/L levels [*Environ. Sci. Technol.* 2002, **36**, 1202-1211]. Human consumption of drugs introduces these com- pounds into water sources from raw or treated sewage. While sewage treatment plants are effective at eliminating bacteria and treating sewage prior to reintroduction into the surface water supply, there is no set protocol for the elimination of pharmaceutical compounds. Hence, many drugs have the potential to appear in drinking water supplies through the reintroduction of treated wastewater back into the environment. An analytical method was devised to detect five popular acidic antibiotics and analgesics. LC/MS/MS was used as the separation and detection technique, respectively. A SPE method was included prior to analysis for sample cleanup and preconcentration. Two different MS techniques were used for the analysis of the compounds. MS/MS was used for confirmation of pharamaceuticals in water, while MRM was the method for quantitation of pharmaceuticals in the water samples. Identification of diclofenac, ketoprofen,

naproxen and sulfamethoxazole was made in influent and effluent water samples from the Lawrence, KS, wastewater treatment plant. Ketoprofen, naproxen and sulfamethoxazole were detected in the Kansas River.

169. ANALYSIS OF BASIC PHARMACEUTICAL COMPOUNDS IN THE AQUATIC ENVIRONMENT BY LC/MS/MS. **Kimberly D. Bratton**[1], Todd D. Williams[2], Craig E. Lunte[1]; [1]University of Kansas, Department of Chemistry, Lawrence, KS 66045; [2]University of Kansas, Mass Spectrometry Laboratory, Lawrence, KS 66045.

Many analytical methods have focused on the detection of agricultural compounds such as herbicides, pesticides and animal antibiotics in the environment. These compounds could pose an immediate or long-term threat to humans and other organisms. However, pharmaceutical compounds appearing in wastewater streams resulting from human uptake and subsequent excretion could also prove to be a potential threat to living organisms. Pharmacokinetics studies have shown that more than half of all compounds consumed are excreted from the body unchanged. These substances can potentially survive sewage treatment systems because of their high stability against biological degradation. In several European countries researchers have identified pharmaceutical compounds such as diclofenac, clofibric acid and ibuprofen at µg/L concentrations in surface and ground water as well as in drinking water [*Acta Hydrochim. Hydrobiol.* 1998, **26**, 272-278]. In the U.S., researchers at the United States Geological Survey (USGS) have detected several pharmaceuticals, hormones and other organic wastewater contaminants in streams across 30 states [*Environ. Sci. Technol.* 2002, **36**, 1202-1211]. An analytical method was developed to detect several common basic pharmaceutical compounds including antihypertensives and anti- depressants in wastewater. The method includes a solid phase extraction (SPE) that acts to cleanup and concentrate the sample a thousand fold. The samples were analyzed by LC/MS/MS using two mass spectrometry techniques, MS/MS to confirm the presence of the pharmaceuticals in the samples and MRM to quantitate. Identification of albuterol, atenolol, metoprolol, propranolol and fluoxetine were found in both the city of Lawrence, KS, influent and effluent wastewater samples. Kansas River water showed the presence of all five pharmaceuticals as well. Tentative identification of the pharmaceuticals in tap water has been made.

170. DETERMINATION OF SOLUBILITY AND STABILITY OF THE THREE DEGRADATION PRODUCTS OF HEXAHYDRO-1,3,5-TRINITRO-1,3,5-TRIAZINE (RDX). **Martha G. Rhoades**[1], Denise K. MacMillan[2]; [1]Analytical Services, Inc., 420 S. 18th St., Omaha, NE 68102; [2]U.S. Army Corps of Engineers Environmental Chemistry Branch, 420 S. 18th St., Omaha, NE 68102.

Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) is one of the most important military explosives used today. RDX in soil is known to decompose into three nitroso products: TNX (hexahydro-1,3,5-trinitroso-1,3,5-triazine), DNX (hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine) and MNX (hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine). Many such nitrosamines are known or suspected carcinogens. The toxicity and mobility of RDX are well studied and understood but there is little information available regarding the three breakdown products. Seizures and convulsions have been observed in rats exposed to RDX. Studies have also shown RDX to accumulate in the liver and kidneys of rats. Due to the similarity in structure, it is possible that the nitroso degradation products exhibit toxicity and reactivity properties similar to those of RDX. The U.S. Army Corps of Engineers Environmental Chemistry Branch is investigating the potential health and environmental risks associated with the degradation of RDX and subsequent production of TNX, DNX and MNX. If the degradation products themselves are environmental hazards, the Army could be faced with the need to take additional precautions at sites where there is significant RDX contamination. We are investigating the stability and solubility of TNX, DNX and MNX in our initial steps towards understanding environmental activity of these degradation products. To determine solubility and stability over time, TNX, DNX and MNX were each added to water at five different temperatures and three different pH conditions. Aliquots were taken over 72 hours. Initial analyte concentration and stability results determined by LC/MS indicate that the breakdown products are less soluble in water than RDX.

171. ON-COLUMN PRECONCENTRATION OF PHARMACEUTICAL CATIONS FOR CAPILLARY ELECTROPHORESIS. **Julie A. Gillogly**, Craig E. Lunte; University of Kansas, Department of Chemistry, 3072 Malott Hall, Lawrence, KS 66045.

When using capillary electrophoresis (CE) for the analysis of biological samples, it is often necessary to employ techniques to overcome peak-broadening that results from having a high conductivity sample matrix. To improve the concentration detection limits and peak efficiency of pharmaceutical cations in CE, pH-mediated acid stacking was performed. In pH-mediated acid stacking, a high conductivity buffer such as acetate is titrated to acetic acid by the injection of acid into the capillary. Cationic analytes then migrate to the front of the titrated sample zone

due to electrofocusing of the sample, improving peak sensitivity greater than 100-fold. One problem encountered with pH-mediated stacking is that a significant portion of the capillary is used in the preconcentration step and only a short length of capillary is left for separation. The use of a longer capillary, however, would increase experimental time and require a higher separation voltage. To overcome this problem, the titrated zone can be removed prior to the separation step by applying reverse pressure. This pressure forces the low conductivity titrated zone out of the inlet end of the capillary. Employing this technique allows for a larger sample volume to be injected. This method was used for detection and quantitation of pharmaceutical compounds prepared in Ringer's solution, which simulates microdialysis sample conditions.

172. CHARACTERIZATION OF CARBAMAZEPINE BINDING ON HUMAN SERUM ALBUMIN USING HIGH PERFORMANCE AFFINITY CHROMATOGRAPHY. **Heeseung Kim**[1], David S. Hage[2]; [1]University of Nebraska-Lincoln, 731 Hamilton Hall, Lincoln, NE 68588-0304; [2]University of Nebraska-Lincoln, 738 Hamilton Hall, Lincoln, NE 68588-0304.

This study characterizes the binding of carbamazepine (CBZ) on human serum albumin (HSA) immobilized high performance affinity chromatography. Frontal analysis is used to determine binding strength (association equilibrium constant) and the binding capacity. The association constant for the binding of CBZ to HSA was found to be 5.3×10^3 M^{-1} at pH 7.4 and 37 °C. The binding capacity was found to be increased as temperature increases from 4 °C to 45 °C. Zonal elution technique is also used to examine the binding of CBZ at the warfarin and indole sites of HSA. The results of zonal elution indicated there is no direct competition between CBZ and R-warfarin or L-tryptophan. Changes in retention of R-warfarin and L-tryptophan occur when CBZ was used as a competing agent in mobile phase. R-warfarin and L-tryptophan, however, as competing agents have no effect on retention of CBZ. This indicated that the displacement of R-warfarin and L-tryptophan is caused by allosteric effect of CBZ binding on HSA.

173. STUDIES OF PHENYTOIN BINDING TO HUMAN SERUM ALBUMIN BY HIGH-PERFORMANCE AFFINITY CHROMATOGRAPHY. **Jianzhong Chen**[1], Corey Ohnmacht Ohnmacht[1], David S. Hage[2]; [1]University of Nebraska-Lincoln, HAH741, Lincoln, NE 68588; [2]University of Nebraska-Lincoln, 738 Hamilton Hall, Lincoln, NE 68588-0304.

High-performance affinity chromatography was used for studying the binding of phenytoin to an immobilized human serum albumin (HSA) column. Zonal analysis using four different compounds for the four binding sites as the probes and different concentration phenytoin solutions as the mobile phase was performed.

The results showed that phenytoin can bind to warfarin, tamoxifen and digitoxin site of HSA. The binding of phenytoin to digitoxin site of HSA was determined as 6.47x103 M^{-1}. Due to the mutual interaction of warfarin site and tamoxifen site, the binding constant can't be obtained; the effect of phenytoin on R-warfarin appeared to increase the binding of R-warfarin at low concentrations and decrease the binding of R-warfarin at high concentrations. As for the binding of *cis*-clomiphene to HSA, for the concentration range studied, phenytoin essentially increases it. Zonal analysis with tryptophan or warfarin as the competing agent while phenytoin as the probe was also performed. This complexity of drug-drug interaction further suggests the importance of monitoring free drug concentration in human body for drug dose instruction.

174. ADSORPTION AND REACTION OF AMINES ON GERMANIUM AND SILICON SURFACES. Pornpimol Prayongpan, **C. M. Greenlief**; University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211.

The adsorption and reaction of allyl- and ethyl-amine with the Ge(100) and Si(100) surfaces is examined. These processes are followed by a variety of surface sensitive techniques including ultraviolet photoelectron spectroscopy and temperature programmed desorption. Possible adsorption structures are also examined by theoretical methods. Density functional theory calculations are used to help interpret the photoelectron spectroscopy data. The calculated molecular orbital energies (within Koopmans' approximation) are used to help identify adsorbed molecular species as well as reaction intermediates. The interaction of these nitrogen-containing molecules with surface dimer bonds and ordering of the resulting surface layers will be discussed.

175. ENERGY TRANSFER IN Tb(III)-Tb(III) PAIRS IN $CsMX_3$ COMPOUNDS. **Stanley May**, Katherine Murra, Tricia Lawrence; University of South Dakota, 414 East Clark Street, Department of Chemistry, Vermillion, SD 57069.

Microscopic rate constants for Tb($^5D_3$) cross relaxation have been determined as a function of temperature in symmetrical Tb^{3+}-Tb^{3+} pairs in $CsCdBr_3$, $CsMgBr_3$ and $CsMgCl_3$. The temperature dependence and maximum efficiency of cross relaxation is very different in the three hosts, despite the fact that the energy-level structures and luminescence spectra of Tb^{3+} are all quite similar. The difference in cross relaxation behavior in the three systems is due to resonance considerations being the dominant factor in determining transfer efficiencies, easily outweighing the influences of general transition strengths and donor-acceptor separations. Cross relaxation in these systems is due to 'resonant' processes, in the sense that only donor and acceptor transitions with significant overlap of the zero-phonon spectral lines participate in active transfer mechanisms. All transitions in

resonance involve a 'hot' crystal-field transition, either on the donor, or on the acceptor, or on both. The temperature dependence of cross relaxation is due to the changing thermal populations of the initial crystal-field levels of resonant donor and acceptor transitions. Although phonon-assisted processes cannot be discounted, they do not appear to have a significant impact on the temperature dependence of cross relaxation.

176. VARIABLE TEMPERATURE DEUTERIUM NMR AND *AB INITIO* STUDIES ON STRONGLY HYDROGEN BONDED SYSTEMS. Xingang Zhao, Carter Silvernail, John A. Belot, **Gerard S. Harbison**; University of Nebraska-Lincoln, 517 Hamilton Hall, Lincoln, Nebraska 68588-0304.

Strong hydrogen bonds have been a subject of intense research interest for many years; however, quantitative characterization of the proton probability distribution function has so far eluded investigators. X-ray diffraction does not reliably locate hydrogen atoms, while neutron diffraction requires large crystals and a neutron source. Although vibrational spectroscopy is very sensitive to the shape of the potential, it is hindered by the fact that interesting hydrogen bond vibrations are frequently broadened in the solid state by coupling of their large electrostatic moments to the crystal lattice. In this work, a series of enolized 2,4 diketones were studied by solid state deuterium NMR. The deuterium quadrupole coupling constants and asymmetry parameters were measured as a function of temperature. It is found that a characteristic property of short, low barrier hydrogen bonds (LBHBs) is a positively temperature-dependent QCC value. These phenomena are explained quantitatively using a theoretical model which employs vibrationally averaged electric field gradient tensors calculated by *ab initio* methods, using large basis sets and electron correlation via multi-reference perturbation theory methods, followed by variational solution of the three-dimensional vibrational Hamiltonian.

177. TEXTURAL EVOLUTION OF NANOCRYSTALLINE $Mg(OH)_2$ TO MgO AND $MgCl_2$. **Maxim S. Mel'gunov**[1], Alexander F. Bedilo[2], Kenneth J. Klabunde[2]; [1]Boreskov Institute of Catalysis, 5 Lavrentieva, Novosibirsk, Novosibirsk 630090, Russia; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506.

Transformation of nanocrystalline aerogel-prepared $Mg(OH)_2$ to MgO under dynamic vacuum has been studied in a temperature range of 570-770K. Release of chemisorbed compounds accompanies the hydroxide-to-oxide transformation that is almost complete after prolonged treatment at 570K. Fragmentation of nanoparticles occurs below 670K. At higher temperatures the transformation results in re-crystallization and sintering of nanoparticles, whose mean size in-

creases and relative number decreases rapidly with temperature. Shrinkage of mesoporous aggregates increases with temperature, so no extra pore volume appears. Moreover, the pore volume already present in as-prepared $Mg(OH)_2$ decreases as well. Topochemical conversion of the obtained nanocrystalline MgO to $MgCl_2$ was performed by the interaction with 1-chlorobutane at 470-620K. At early stages the transformation results in the formation of an impermeable chloride coating over MgO nanoparticles, followed by accretion of primary nanoparticles at higher topochemical conversion. The size of the nanoparticle aggregates does not depend on the conversion degree and remains the same. At the maximum degree of transformation starting porous MgO aggregates are trans- formed to almost nonporous $MgCl_2$ particles.

178. THE USE OF FATS AND OILS AS A PHAGE CHANGE MATERIAL TO STORE AND RELEASE ENERGY. **William R. Sutterlin**; University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211.

As industrialized nations seek to improve energy efficiency, alleviate energy shortages associated with peak power demand and reduce dependence on petroleum-based products, PCMs are increasingly in demand as ultra energy efficient insulation materials for residential and commercial climate control. Many currently available PCMs, however, are themselves petroleum-based. The successful use of a PCM involves repeatedly adding and removing heat from the PCM. The latent heats of PCMs can absorb and release hundreds of more times the energy of sensible heat alternatives. Our research represents a particularly promising green chemistry technology in that underutilized bio-based products - namely beef tallow and soybean oil - will be converted into PCMs and marketed to replace non-renewable petroleum products (*i.e*., paraffins) for use in reducing the energy consumed to heat and cool residential and commercial buildings.

179. CAN H/D EXCHANGE AND ESI-MS BE USED TO DETERMINE FOLDING AND AFFINITY IN PROTEIN INTERACTIONS? **Mei M. Zhu**, Don L. Rempel, Michael L. Gross; Washington University in St. Louis, Chemistry Department, St. Louis, MO 63130.

Nature frequently uses the protein-ligand binding and the resulting induced conformational changes to control the activity of regulatory proteins and to interconvert mechanical work and physicochemical free energy. H/D exchange and ESI-MS are a promising combination to probe protein-ligand interactions. In this presentation, we describe implementation of a H/D exchange titration method and a protein-ligand fractional species model to examine the conformational changes, stoichiometry and binding constants in the interactions of a small, acidic protein, calmodulin with Ca^{2+} and peptides. In forward H/D exchange kinetics,

Ca-saturated porcine calmodulin (holo-CaM) showed a slower rate and lower extent of H/D exchange than its apo form. When binding with melittin (ML), more amide hydrogens were protected than for the holo-CaM. The H/D exchange data were fitted with a three-group kinetics model. The apo-CaM, holo-CaM and holo-CaM:ML complexes showed different numbers of fast, medium and slow exchanging amide hydrogens. In equilibrium titrations, we found a 1:4 CaM:Ca complex in CaM by titrating apo-CaM with Ca^{2+}, a 1:1 CaM:peptide complex in holo-CaM by titrating with melittin or mastoparan. Assuming that the conformational change as shown in H/D exchange peptide titration was proportional to ligand binding, the binding constants for holoCaM:melittin and holoCaM: mastoparan are determined. The simulation showed that the conformational change of CaM that occurs upon interaction with Ca is mainly due to the formation of the CaM-4Ca species. A six-parameter fitting model was built for CaM-Ca titrations. The macroscopic binding constants K_3, K_4 and the contribution of each CaM-xCa fractional species to the conformational change in CaM-Ca interactions were measured. The Ca-binding affinities at different ionic strength were calculated. Our observation on the decrease in Ca-binding affinity with the increase in ionic strength agrees with the previous literature reports.

180. SINGLE-MOLECULE SPECTROSCOPY OF CALMODULIN AND ITS INTERACTIONS WITH THE PLASMA-MEMBRANE Ca^{2+}-ATPASE. **Kenneth D. Osborn**, Manoj K. Singh, Asma Zaidi, Carey K. Johnson; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

Calmodulin (CaM) is a small calcium signaling protein that is known to bind and activate a large number of targets, yet the mechanism by which this occurs is still poorly understood. Recent results from single-molecule spectroscopy of CaM have revealed interesting aspects in target recognition and binding to the plasma-membrane Ca^{2+}-ATPase (PMCA). The structure of the PMCA includes an autoinhibitory domain that binds CaM and an ATP-binding site which drives the pump. We have imaged fluorescently labeled CaM bound to PMCA in native erythrocyte membranes as well as purified and reconstituted into mixed micelles. Current dynamics studies have tracked environmentally sensitive dyes during protein motion. Certain dyes are known to change their fluorescence intensity upon sampling different environments as the protein functions. FRET labeling sites have been chosen to probe binding dynamics of CaM to the target along with motion between CaM and the nucleotide-binding site of the PMCA. Polarization modulation methods with a maximum-likelihood analysis have also been used to probe rotational dynamics of the CaM/PMCA complex.

181. DETERIORATION OF POLYMERIC COATINGS STUDIED BY POSITRON ANNIHILATION SPECTROSCOPY. Hongmin Chen, **Y. C. Jean**, Renwu Zhang, Q. Peng, J. R. Richardson, T. C. Sandreczki; University of Missouri-Kansas City, 5009 Rockhill Rd., Kansas City, MO 64110.

A series of commercial coatings, based on polyurethane, acrylic, epoxy and sulfonate, were prepared according to the industrial specifications and were exposed to Florida natural weathering and UV accelerated conditions. The Doppler broadening energy spectra were measured as a function of incident positron energy at different periods of weatherings. A significant decrease in the S parameter is interpreted as loss of free volume as result of environmental deterioration. The observed decrease of S parameter among these coatings is used as an indicator to test coating durability in micro-scale and at the early stage of photo-degradation. Atomic force microscopy and glossimetry were also applied to study the surface morphology and gloss respectively. Relationship between atomic scale properties by positron spectroscopy and macroscopic physical and mechanical properties by conventional methods will be discussed in terms of coating durability.

182. LIGAND AND ALKYL CHAIN LENGTH EFFECTS ON THE DIGESTIVE RIPENING PROCESS FOR MONODISPERSE GOLD NANOPARTICLES. **Prasad L. Bhagavatula**, Savka I. Stoeva, Kenneth J. Klabunde, Christopher Sorensen; Kansas State University, 111 Willard Hall, Department of Chemistry, Manhattan, KS 66506.

A systematic study for the effectiveness of several ligands as digestive ripening agents was undertaken. The digestive ripening process involves the refluxing of polydisperse gold nanoparticles with a surface active ligand at the solvent boiling temperature (usually toluene) to produce monodisperse gold nanoparticles. In this study thiols, phosphines, amines, silanes, alcohols, bromides, iodides and simple alkanes were employed as digestive ripening agents. It was established that in addition to thiols, phosphines, amines and silanes are also effective digestive ripening agents converting the polydisperse particles into nearly monodisperse ones. Initially, gold nanoparticles with a broad size distribution were prepared through the inverse micelle method. The important steps in the digestive ripening process are identified to be i) the breaking of these large, prismatic, as-prepared gold particles to nearly spherical small particles by the addition of ligand, ii) the separation of these ligand stabilized particles from the initial reaction side products by precipitation from polar solvents and finally iii) heating this isolated colloid in the presence of the ligand resulting in monodisperse particles. Most of the ligands (except simple alkanes) like alcohols and halides work well in the first step but fail in the second step. The failure of the ligands in the second step is directly related to the ligand-Au binding strengths where weaker ligands fail to stick to the gold

particle surfaces in the presence of polar solvents. A qualitative description of the ligand-Au binding strengths can be found in the hard and soft acid base theory. Au^0 which is described as soft acid likes soft bases like thiols and phosphines as ligands compared to alcohols which are hard bases. In the successful digestive ripening cases it was also observed that the usage of different ligands stabilizes different sizes of gold nanoparticles. Varying the alkyl chain length of the same ligand, on the other hand, crucially controls the self assembling nature of these nanoparticles. For example, shorter chain length ligands like octanethiols favor 3D ordering of the particles while particles stabilized by longer chain length ligands (hexadecanethiol) lead to separate particles which form 2D layers on substrates. These effects are qualitatively explained by the decreasing van der Waal attractions between gold nanoparticles as the alkyl chain length of the capping agent is increased.

183. PROBING THE CONFORMATIONAL DYNAMICS OF LEUCINE ENKEPHALIN IN SOLUTION USING TIME-RESOLVED FLUORESCENCE SPECTROSCOPY. **Jay R. Unruh**, Carey K. Johnson; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66046.

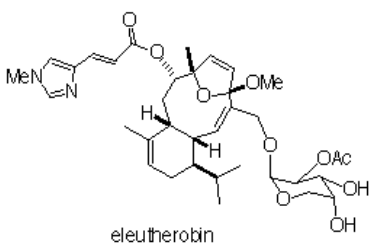
Despite the large amount of attention that leucine enkephalin (Tyr-Gly-Gly-Phe-Leu) has received in the last twenty-five years, the nature of its structure in aqueous solution and its dynamics continue to be debated. We have probed the conformational dynamics of this peptide through time-domain fluorescence anisotropy of the tyrosine residue. Previous studies have shown a temperature dependent conformational change allowing the coupling of tyrosine motions to the solvent at higher temperature [Harms, G.S.; Freund, W.L.; Johnson, C.K. *J. Phys. Chem. B* 1998, **102**, 5004-5010]. We have undertaken studies to determine the effect of hydrophobicity in this peptide by site-directed mutation. Initial results indicate that tyrosine experiences a greater amount of reorientational freedom in peptides with decreased hydrophobicity. We are also undertaking experiments to investigate the relationship between the first and fourth position using fluorescence resonance energy transfer.

184. FREE VOLUME PROPERTIES OF DRUG-DELIVERY POLYMERS. Ying Li, **Y. C. Jean**; University of Missouri-Kansas City, 5009 Rockhill Rd., Kansas City, MO 64110.

Positron annihilation spectroscopy has been used to measure free-volume properties in a series of polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG) systems as a function of chemical composition, temperature, covalent bonding and hydrogen bonding. Applications of positron spectroscopy to investigate drug-delivery mechanisms will be discussed.

185. APPROACHES TO THE SYNTHESIS OF THE EUNICELLIN DITERPENES. **Matthias McIntosh**; University of Arkansas, 101 CHBC, Dept. of Chemistry and Biochemistry, Fayetteville, AR 72701.

The eunicellin diterpenes are a large family of 2,11-cyclized cembranoids of marine origin. Their challenging structures and, in some cases, potent biological activity make them attractive targets for total synthesis. In this paper we will describe approaches to the eunicellin diterpenes via cycloaldolization and Ireland-Claisen rearrangement.



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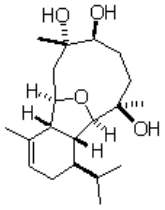

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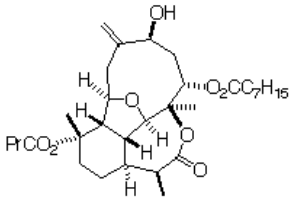

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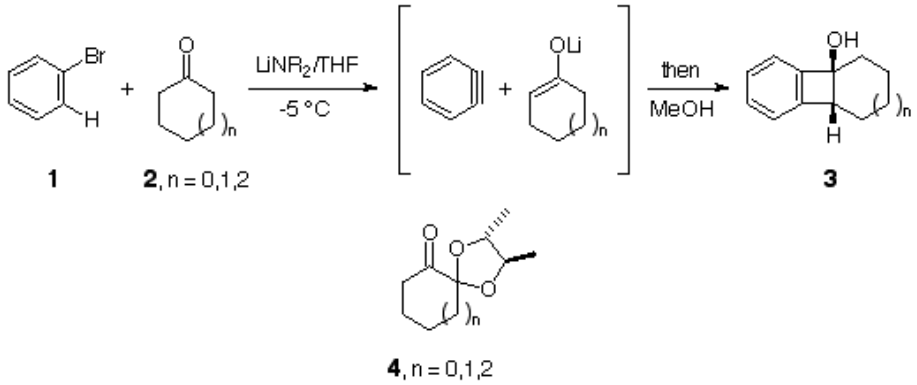
186. DIASTEREOSELECTIVE ADDITION OF KETONE ENOLATES TO BENZYNE: ASYMMETRIC SYNTHESIS OF BENZOCYCLOBUTENOLS. **Olivier Nicaise**, Daniel J. Mans, Robert J. Otto, Emilio Villa Hefti, Alison L. Maddeford; Saint Louis University, 202 Monsanto Hall, Department of Chemistry, St. Louis, MO 63103-2010.

We have recently initiated a research project directed toward the development of asymmetric aromatic elimination/addition reactions mediated by lithium dialkyl amide bases. This type of transformation with substrates **1** and **2** is a one-pot reaction that involves benzyne and a lithium ketone enolate as reactive intermediates, and forms the chiral, *cis*-fused benzocyclobutenol **3**; the benzocyclobutenol motif is responsible for the biological activity of this type of compound (*e.g.*, anticonvulsive, bronchorelaxing, and β-blocking). Developing an asymmetric variant of this reaction amounts to investigating the asymmetric addition of enolates to benzyne. We will first describe our preliminary work that consisted of determining the optimal reaction conditions for the formation of racemic **3** (n = 2) in high yield, and the use of a 2-ketal ketone as substrate will also be presented. Finally, the results obtained in the reactions of optically pure 2-ketal ketones **4** with **1** will be disclosed, showing that a high level of diastereoselectivity can be reached in these reactions.



187. OZONOLYSIS OF ALKENES: A SAFER, CLEANER APPROACH. Kyle C. Mott[1], Joseph Raible[2], **Patrick H. Dussault**[2]; [1]University of Nebraska-Lincoln, 838 Hamilton, Department of Chemistry, Lincoln, NE 68588-0304; [2]University of Nebraska-Lincoln, 840 Hamilton, Lincoln, NE 68588-0304.

Ozonolysis is one of the most widely used methods for the oxidative cleavage of alkenes to carbonyl compounds. Although ozonolysis of simple alkenes rapidly produces high yields of the corresponding ozonide (1,2,4 trioxolane), reduction of the ozonide to form the carbonyl group often requires long reaction times. Worse, workup following incomplete reduction can result in concentrated solutions of ozonide prone to dangerously exothermic decomposition. To circumvent these problems, we have been investigating new methods for trapping the carbonyl oxide intermediates in ozonolysis. One method produces good to moderate yields of the corresponding carbonyl compounds without the need for a reductive workup.

188. DEOXIMATION REACTION WITH SILICA GEL SUPPORTED AMMONIUM PEROXYDISULFATE IN METHYLENE CHLORIDE MEDIA. **Mohammed Ali**, Brian Spence; Southeast Missouri State University, Chemistry Department, Rhodes 201, Cape Girardeau, MO 63701.

As a part of our continued interest in developing solid supported reagents for organic transformations, we have investigated conversion of oximes to the corresponding carbonyl compounds in methylene chloride utilizing a reagent prepared by supporting ammonium peroxydisulfate on silica gel. Silica gel supported ammonium peroxydisulfate reagent is easy to prepare. The reagent is highly chemoselective for the above transformation and produces high yield of carbonyl products. The reaction medium is very mild and can tolerate a number of functional groups. The results of our investigation will be presented at the meeting.

189. DEHYDRATION OF ALDOXIMES TO NITRILES UTILIZING 2-CHLORO-N-METHYLPYRIDINIUM IODIDE, MUKAYAMA'S REAGENT. **Mohammed Ali**, Lucy Thurston; Southeast Missouri State University, Chemistry Department, Rhodes 201, Cape Girardeau, MO 63701.

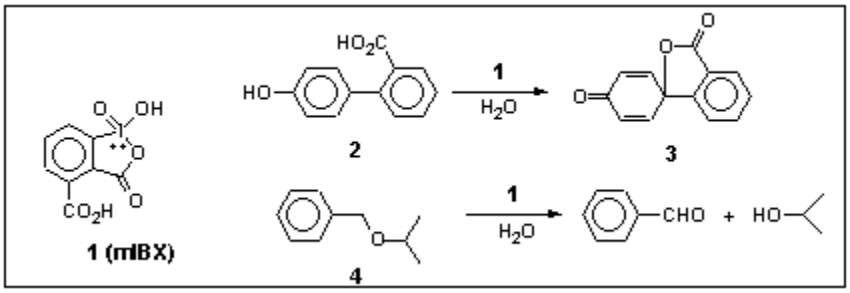
We wish to report a facile dehydration of aldoximes to the corresponding nitriles using 2-chloro-N-methylpyridinium iodide, known as Mukayama reagent, in the presence of triethyl amine. Refluxing a mixture of an aldoxime, Mukayama reagent, and triethyl amine in methylene chloride for several hours furnishes nitriles in excellent yield. This procedure is applicable to a wide variety of aldoximes.

190. OXIDATION OF SULFIDES WITH SILICA GEL SUPPORTED PERIODIC ACID IN NON-AQUEOUS MEDIA. **Mohammed H. Ali**, Courtney Maguire; Southeast Missouri State University, One University Plaza, Rhodes 201, Cape Girardeau, MO 63701.

A reagent prepared by supporting periodic acid on silica gel has been used for oxidation of sulfides to sulfoxides utilizing non-aqueous media. We have found that this reagent can be used to oxidize sulfides to either sulfoxides or to sulfones by controlling the amount of the reagent utilized in the reaction. Two or slightly higher equivalents of silica gel supported periodic acid produces good yield of sulfoxides whereas large excess of this reagent produces sulfones. We have been able to oxidize a wide variety of sulfides to sulfoxides in excellent yields utilizing silica gel supported periodic acid employing methylene chloride as the solvent. Utilization of solid support makes product isolation easy. Also, this procedure is simple, safer to carry out and produces smaller amounts of solid waste.

191. OXIDATIVE TRANSFORMATIONS USING A NOVEL WATER-SOLUBLE DERIVATIVE OF *O*-IODOXYBENZOIC ACID. Arun P. Thottumkara[1], **Thottumkara Vinod**[2]; [1]Macomb High School, 1525 S. Johnson Rd., Macomb, IL 61455; [2]Western Illinois University, One University Circle, Macomb, IL 61455.

Hypervalent iodine reagents have attracted considerable attention lately as mild and selective oxidizing agents in organic chemistry. We have recently reported the synthesis of **1**, a water-soluble derivative of the well-known *o*-iodoxybenzoic acid (IBX). The structurally modified IBX, **1**, which we call mIBX, oxidizes phenols to corresponding quinones and oxidatively cleaves benzyl ethers in water and other eco-friendly solvents. Representative examples of the conversions are shown in the box. These and other synthetically useful oxidative transformations using mIBX will be discussed.



192. MOLECULAR ASSOCIATION AND SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS. **Kathleen V. Kilway**, Gerardo Marquez, Shiping Deng, Sarah Burkhardt, Robert Clevenger, Joseph Vincent, Robert Ingalls; University of Missouri-Kansas City, 205 Spencer Chemistry Building, 5100 Rockhill Road, Kansas City, MO 64110-2499.

Molecular-assembly research often uses simple building blocks and connectivity principles to construct diverse new materials. Van der Waals interactions, hydrogen bonding and dative bonding have been used for the spontaneous self-assembly of nanomaterials. This talk will cover new results in the areas of the synthesis of unusual aromatic compounds and the formation of metal clusters using polynitrile building blocks. In the former area, we have used acenaphthene units as building blocks for the construction of unusual, large, nonplanar, aromatic compounds. In latter area, we use polynitrile angular linkers to chelate silver in a variety of complexes. We have systematically used di-, tri- and tetratopic polynitriles to investigate the influence of the angular ligand, solvent and metal in molecular assembly.

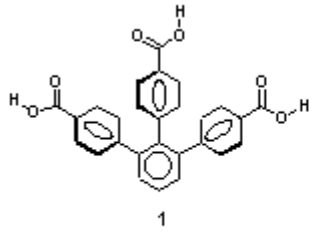
193. TEMPLATE-DIRECTED SOLID-STATE ORGANIC SYNTHESIS. **Leonard R. MacGillivray**, Giannis S. Papaefstathiou, Dushyant Varshney, Tamara D. Hamilton, Tomislav Friscic; University of Iowa, 423B Chemistry Building, Department of Chemistry, Iowa City, IA 52242-1294.

Molecules that function as linear templates provide a means to juxtapose (supramolecularly) two molecules for a bimolecular reaction. Such an ability to deliberately orient and position two molecules to react affords chemists an opportunity to engineer molecules that may be difficult to achieve via a more classical approach to synthesis. In this presentation, we describe progress towards a general method for controlling chemical reactivity using linear templates. The approach relies upon utilizing templates that operate via hydrogen bonds in the organized environment of the solid state. Applications of products

derived from the linear templates to the field of metallosupramolecular chemistry will also be discussed.

194. NOVEL META-TERPHENYL DERIVATIVES AS TECTONS FOR THE CONSTRUCTION OF MOLECULAR SOLIDS. **Thottumkara Vinod**, Ryan S. Wright; Western Illinois University, One University Circle, Macomb, IL 61455.

The supramolecular assembly of organic and inorganic molecules into functional solids with tunable properties, for example, pores of defined size and shape have recently attracted the attention of chemists and materials scientists with an interest in crystal engineering. Dimensions and structural motifs of H-bonded networks in molecular solids depend primarily on the topology and robustness of the tectons (building blocks) and an understanding of these parameters can potentially provide molecular-level control of solid-state structures. The near orthogonality of the H-bonding functional groups and the molecular rigidity of the *m*-terphenyl derivatives, **1- 4** are expected to generate lattices with voids. The synthesis and structures of these building blocks will be discussed.



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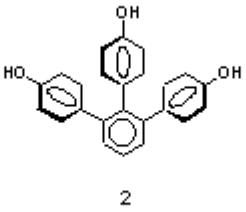

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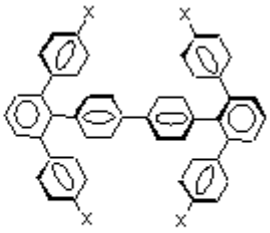


3 X = OH
4 X = CO_2H

195. THE METAL BINDING AFFINITY AND SOLUTION STRUCTURE OF AN ENGRAILED HOMEODOMAIN AND EF-HAND CHIMERA. **Joel T. Welch**, Sonya J. Franklin; University of Iowa, 371 Chemistry Building, Iowa City, IA 52242.

By exploiting a near super-imposable turn of two similar yet unrelated protein folds, we have designed a new class of DNA nucleases. The combination of the recognition helices of the engrailed homeodomain with the metal binding loop of calmodulin has generated chimeric peptides that possess both affinity for DNA and the ability to bind hydrolytically active metal ions. In the presence of either Ca (II) or Ln (III), this helix-loop-helix design has a metal dependent structure which shares elements of both parent folds. Binding studies which utilize both isothermal titration calorimetry and fluorescence measurements will be presented. An NMR model based upon NOE constraints demonstrates the feasibility of design-

ing a metal binding loop into the helix-turn-helix motif. Finally, the progress of incorporating ^{15}N into these systems to derive further structural information will be discussed.

196. COMPARING SPECTROSCOPIC AND LIGAND BINDING PROPERTIES OF N-ACETYLMICROPEROXIDASE-8 AND A DESIGNED HEME PROTEIN MODEL. Aaron B. Cowley[1], Svetlana Silchenko[1], Kenton R. Rodgers[2], **David R. Benson**[1]; [1]University of Kansas, Department of Chemistry, 1251 Wescoe Hall Dr., Lawrence, KS; [2]North Dakota State University, Department of Chemistry, Fargo, ND.

Treatment of cytochrome *c* with pepsin and trypsin followed by acetylation yields N-acetylmicroperoxidase-8 (AcMP8), a heme-peptide which retains the native histidine axial ligand of the parent protein but is missing the native methionine ligand. As a means of exploring how the mode of attachment of an intramolecular histidine axial ligand influences heme properties, we designed and synthesized **1**, comprising a single peptide covalently attached to a propionate group of iron mesoporphyrin IX. Spectroscopic data show that ferrous **1** is pentacoordinated and high spin at neutral pH, while AcMP8 exists as a mixture of pentacoordinated and hexacoordinated (water ligated) species and therefore exhibits high spin/low spin equilibrium. In contrast, the ferric complexes of **1** and AcMP8 are both hexacoordinated with a water molecule occupying the sixth coordination site, but ferric **1** is almost completely high spin while ferric AcMP8 exhibits a spin equilibrium. In these respects, **1** is more similar to myoglobin and hemoglobin than is AcMP8. However, spectrophotometric titrations reveal that exogenous thioether ligands coordinate considerably more strongly to AcMP8 than to **1** in both the Fe(III) and Fe(II) oxidation states. The results of these studies suggest that the rigid linkage between the histidine ligand and heme in cytochrome *c* is essential for maintaining strong coordination of the axial methionine ligand.

197. PRODUCTION OF ^{149}Pm: A HIGH SPECIFIC ACTIVITY RADIOISOTOPE FOR THERAPY. Mary F. Embree, Gary J. Ehrhardt, Alan R. Ketring, James A. Gawenis, Tammy T. Tyler, Keith D. Bailey, **Cathy S. Cutler**; University of Missouri-Columbia, MURR, Research Park Drive, Columbia, MO 65211.

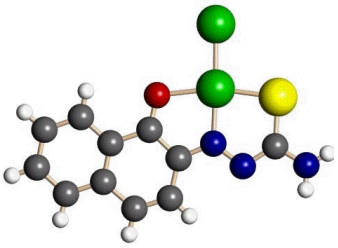
Tumors have been successfully imaged with targeting peptides labeled with diagnostic radionuclides. Therapeutic agents, which use these receptor-seeking peptides radiolabeled with beta emitting nuclides, are under investigation. Since tumor cell receptor sites are limited, high specific activity radionuclides are essential. ^{149}Pm is produced with high specific activity. Its nuclear properties (β^- = 1.1 MeV, $t_{1/2}$ = 2.21 d, γ = 286 keV) make it desirable for use in radiotherapy. Desired levels of radioactivity are achieved with small masses of Pm. This low number of

atoms further necessitates excluding contaminants during processing. The purpose of this study is to define a method that will reliably produce high specific activity ^{149}Pm in amounts and purities, which make it viable for use in radiotherapy. ^{149}Pm is produced by indirect neutron capture. Nd nitrate (92% enriched with ^{148}Nd) is irradiated to produce Nd-149 ($t_{1/2}$ = 1.73 h). ^{149}Nd β^- decays to ^{149}Pm. ^{149}Pm is then chemically separated from the Nd by ion-exchange chromatography. A column of Eichrom Ln resin is loaded with a 1 - 2.5 mg Nd target (with up to 200 mCi of ^{149}Pm) dissolved in nitric acid. Nd is first eluted with 0.15 M nitric acid. ^{149}Pm is then flushed off the column with 0.5 M nitric acid. All acids are optima grade. Tests are currently underway to optimize the process. It may be possible to increase the speed and resolution of the Pm separation by heating the chromatographic column. Alternate column preparation techniques are also being tested to improve final product purity. Finally, a remote system allowing higher activity production of ^{149}Pm, is under development. The radionuclidic purity of ^{149}Pm is tested by gamma spectroscopy. The viability of Pm-149 as a radionuclide for radiotherapy is examined by testing the efficiency and stability of its labeling onto DOTA. DOTA and its analogs are commonly use as bifunctional chelates for attaching radioisotopes to peptides being evaluated for radiotherapy. High specific activity ^{149}Pm can be reliably produced. ^{149}Pm shows excellent radionuclidic purity and readily forms complexes with ligands, such as DOTA. These complexes are stable over time under various conditions. ^{149}Pm is a promising radionuclide for cancer therapy.

198. COMPLEXES OF NAPHTHAQUINONE THIOSEMICARBAZONE AND THEIR BIOLOGICAL ACTIVITY. Zahra Afrasiabi[1], **Ekkehard Sinn**[1], Subhash Padhye[2], Lev N. Zakharov[3], Arnold L. Rheingold[3], [1]University of Missouri-Rolla, Chemistry Department, Rolla, MO 65401; [2]Chemistry Department, University of Pune, Pune, India; [3]Chemistry Department, University of Delaware, Newark, DE.

Thiosemicarbazones (TSCs) containing the active =NN(H)C(S) chromophore possess a wide range of biological activity. The mechanism of action is due to the ability of TSCs to inhibit the biosynthesis of DNA, possibly by blocking the enzyme ribonucleotide diphosphate reductase, binding to the nitrogen base of DNA, blocking base replication and creation of lesions in DNA strands by oxidative ruptures. In most cases the highest activity is associated with a metal atom. We are therefore examining the effect of metal binding on these TSCs. In this regard metal complexes of 1,2-naphthaquinone thiosemicarbazone (NQTS) have been prepared and characterized. The crystal structures of the NQTS and its palladium complex (PdNQTS.DMSO) have been solved by single-crystal X-ray diffraction. NQTS shows a planar structure with E isomeric form. The change in the ligand configuration from E (in NQTS) to Z (in PdNQTS.DMSO) is found to affect charge

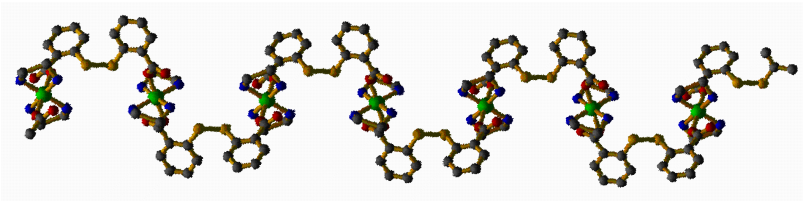
delocalization within the ligand moiety as well as the deprotonation of the hydrazinic nitrogen, where the greatest changes are observed along the thiocarbonyl C=S and C-N=N linkages.



PdNQTS.DMSO

199. A POLYMERIC NICKEL COMPLEX WITH ORGANIC DISULFIDE BRIDGES. Curtis Moore, **David M. Eichhorn**; Wichita State University, Department of Chemistry, 1845 Fairmount, Wichita, KS 67260-0051.

We have been exploring a novel method for incorporating thiolate coordination to transition metal complexes using 2,2'-dithiodibenzaldehyde as the thiolate source. This results in metal complexes containing imine and thiolate donors. An attempt to use similar methodology to synthesize complexes with amide and thiolate donors resulted, instead, in an infinite-chain polymer with nickel(II) centers bridged by 2,2'-dithiodibenzoate moieties.

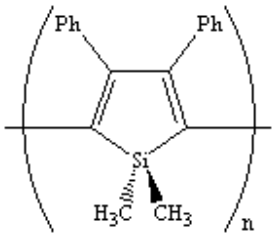


200. METAL COMPLEXATION OF BIIMIDAZOLE DIESTER DERIVATIVES. **Shelonda Finch**[1], Harvest Collier[2]; [1]University of Missouri-Rolla, Chemistry Department, 142 Schrenk Hall, Rolla, MO 65409; [2]University of Missouri-Rolla, Chemistry Department, 142 Schrenk Hall, Rolla, MO 65409.

Incorporation of metals into multiple binding sites of macromolecular species has been shown to significantly modify their reactivity, solubility and thermal properties. Two routes can be taken to incorporate metal ions into a polymer, either through polymerization of the monomer before metal complexation or metal binding of the monomer followed by polymerization of the monomer complex. The possible conditions that affect the selection of the synthetic method that provides the desired product will be influenced by monomer polymerization, steric and electronic factors of the monomer as well as binding site geometry and metal binding affinity. This report will convey the initial findings for an investigation of the preparation and characterization of new polymerizable monomer metal ion coordinating diester derivatives of 2,2´-biimidazole.

201. SILOLE-BASED LUMINESCENT MATERIALS. **Barrett E. Eichler**, Brian J. Oxley; Northwest Missouri State University, 800 University Drive, Maryville, MO 64468.

Pi-electron conjugated polymers have received much interest recently as potential conducting and light-emitting materials. Siloles (1-sila-cyclopenta-2,4-dienes) have also been recently studied as light-emitting materials because of a small HOMO-LUMO gap. Synthesis, characterization and the properties of polymers that include siloles and other *pi*-electron conjugated moieties, is the focus of this research.



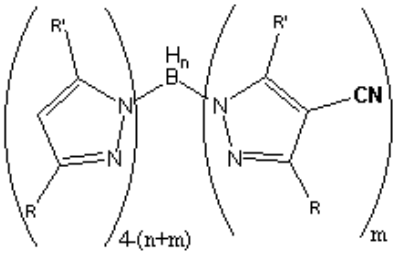
Silole Polymer

202. *IN SITU* FOURIER TRANSFORM ANALYSIS OF A NOVEL AEROGEL SILVER CATALYST. **Emily S. Babusa**, Lynell J. Gilbert, Thomas P. Schuman, Scott J. Kirkby; University of Missouri-Rolla, 142 Schrenk Hall, 1870 Miner Circle, Rolla, MO 65409-0001.

Silver-supported catalysts have long been employed for the partial oxidation of ethylene to ethylene oxide. A novel catalyst has been synthesized such that silver nanoclusters are deposited in the pores of an aerogel framework via radiolysis. The resultant increase in the surface area of silver, over that of traditional silver-supported silicates, should result in a greater ethylene oxide yield. Product composition and reaction rates are determined from analysis of the infrared spectra of the reaction products taken progressively during the reaction. The efficacy of the catalyst is compared to that of a traditional Ag-supported catalyst in terms of the conversion rate of ethylene and the selectivity to the oxidation product, ethylene oxide, rather than the competitive combustion reaction.

203. CYANO-SUBSTITUTED POLYPYRAZOLYLBORATES. Peter Zhao, **David M. Eichhorn**; Wichita State University, Department of Chemistry, 1845 Fairmount, Wichita, KS 67260-0051.

We have been developing the chemistry of polypyrazolylborate, or scorpionate, ligands containing cyano substituents on the pyrazole rings. We will present recent progress in this field, including ligands with phenyl, *t*-butyl and methyl substituents, as well as heteroscorpionate ligands which contain both cyano-substituted and non-cyano-substituted pyrazole rings.



204. OXIDATIVE DEHYDROGENATION OF BUTANE ON NANOCRYSTALLINE MgO, Al_2O_3 AND V/MgO CATALYSTS IN THE PRESENCE OF SMALL AMOUNTS OF IODINE. Vladimir V. Chesnokov[1], **Alexander F. Bedilo**[2], David S. Heroux[2], Kenneth J. Klabunde[2]; [1]Boreskov Institute of Catalysis, Prospekt Lavrentieva 5, Novosibirsk, Russia; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506.

The possibility of one-step selective oxidative dehydrogenation of butane to butadiene in the presence of oxygen and iodine has been investigated. High surface area nanocrystalline MgO, Al_2O_3 and MgO-Al_2O_3, commercial MgO and a series of 10% V/MgO samples have been used as catalysts. The key reagent in this process is molecular iodine that reacts with butane and butenes at 550°C to form butadiene and HI. The use of an acceptor that reacts with HI easily and completely shifts the equilibrium of the dehydrogenation reactions to the right and makes it possible to achieve high butane conversion with high selectivity to butadiene. When excess oxygen is present in the feed, molecular iodine is successfully regenerated and can be recycled. Very high butadiene selectivity (up to 80%) has been achieved in the presence of small amounts of iodine (0.25 vol. %) over a vanadia-magnesia catalyst. The results obtained for iodine-mediated oxidative dehydrogenation of butane are very promising for future practical applications of this approach. Besides butadiene, this method can be applied for synthesis of many other olefins, *e.g*. propene, isobutene or isoprene.

205. THE CHEMISTRY OF PYRIDINE-CONTAINING RUTHENIUM CARBIDE COMPLEXES. **Joseph A. Heppert**, Joseph M. Vilain, Melanie A. Gile, Mark H. Mason, Susan L. Mason, Douglas R. Powell; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Bis-pyridine substituted Grubbs ruthenium alkylidene complexes react with the dimethyl ester of Feist's acid, producing products consistent with the generation of a terminal ruthenium carbide derivative. The resulting carbide has not, however, been isolated and characterized. The pyridine ligands may be too labile to stabilize this highly reactive functional group. The reaction produces a new ruthenium vinylidene complex that may result from the Michael addition of the carbide with free olefin, or may be produced through base-catalyzed rearrange- ment of an intermediate in the decomposition of a ruthenium cyclopropylidene intermediate.

206. STRUCTURES OF RUTHENIUM CARBIDE DERIVATIVES. **Joseph A. Heppert**, Melanie Gile, Joseph Vilain, Mark H. Mason, Susan L. Mason, Douglas Powell; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Mononuclear ruthenium carbide derivatives can be prepared from reactions between a range of Grubbs alkylidene metathesis catalysts and the dimethyl ester of Feist's acid. The structures of these complexes, which are quite homologous, will be compared with the structures of the parent Grubbs alkylidene complexes and other mononuclear carbides in order to rationalize observations about the electronic structure and reactivity of the complexes. The structure of a bimetallic copper/ruthenium carbide derived from the carbide precursor will also be compared with the structures of other complexes having square Cu2X2 core units.

207. TIME DEPENDENT DENSITY FUNCTIONAL THEORY CALCULATIONS OF PT(II) COMPLEXES FOR INTERPRETATION OF EMISSION BEHAVIOR. **Paul Rillema**, Stanislav R. Stoyanov, John M. Villegas; Wichita State University, Department of Chemistry, 1845 Fairmount, Wichita, KS 67260.

Time-dependent Density Functional Theory (TDDFT) calculations on singlet and triplet monomers, dimers and trimers of stacked square planar complexes of Pt(II) with diimine and biphenyl ligands were performed to bring a better understanding of the nature of the excited states in these compounds. An attempt has been made to link the changes in molecular geometry upon light excitation to formation of self-trapped excited states. The relaxation patterns of excited states have been interpreted using exciton theory.

208. DESIGN AND SYNTHESIS OF SUPRAMOLECULAR HOSTS FOR METAL COMPLEXES. Farzad Fani-Pakdel, **Jason R. Telford**; University of Iowa, Department of Chemistry, Iowa City, IA 52242.

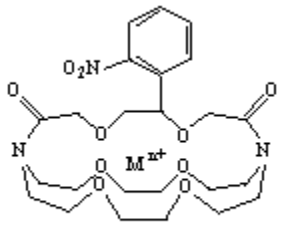
Supramolecular hosts have been constructed from cyclodextrin and calixarene templates. These hosts recognize guests such as metal complexes through symmetric hydrogen bonding and van der Waals interactions. In our research we have engineered specific hydrogen bonding topologies onto derivatives of Calix[8]arene, Calix[4]arene, *alpha*- and *beta*-cyclodextrin. The syntheses and characterization of these compounds are presented.

209. COORDINATION NETWORKS WITH COPPER(I) AND 1,3-DITHIANE. **Jacqueline M. Knaust**, Steven W. Keller; University of Missouri-Columbia, Department of Chemistry, Columbia, MO 65211.

1,3-Dithiane has been used as a pyrimidine analogue in the synthesis of several new one-dimensional Cu(I) coordination networks. The saturated nature of the thiane ring leading to the chair conformation as opposed to the flat aromatic nature of pyrimidine and the possible donation of two electron pairs from each S-atom leads to fifteen different bonding modes possible for this one ligand. Reaction of $[Cu(MeCN)_4]BF_4$with 1,3-dithiane results in the formation of four novel coordination networks depending on metal to ligand ratio and solvent conditions used. **1** and **2**, both $[Cu(1,3\text{-dithiane})(MeCN)_2]^{+3}$, and **3**, $[Cu(1,3\text{-dithiane})_2(MeCN)]^{+3}$, are similar one-dimensional chains, but due to the different bonding modes of the dithiane sulfur atoms all three networks are unique. In 4, $[Cu(1,3\text{-dithiane})(MeCN)]^{+3}$, one–dimensional ribbons are formed where each dithiane is bonding to three copper(I) centers; one of the S-atoms on each ligand acts as a μ_2 4-electron donor.

210. MANAGING TIGHT BINDING RECEPTORS FOR NEW SEPARATIONS TECHNOLOGIES 1: NEW APPLICATIONS OF THE PHOTOLABILE POLY-ETHER CRYPTAND. **Jong-Ill Lee**, Richard S. Givens, Daryle H. Busch, Chi Zhang; University of Kansas, Department of Chemistry, Lawrence, KS 66045.

The *o*-nitrobenzyl group was introduced into one of the bridges of a [2.2.2] cryptand, where the rate constant for binding metal ions exceeds $10^6 – 10^9$. The release of the metal ion is much slower, however. To accelerate the dissociation rate, photoinduced fracture of one of the bridges opens the cryptate to a sample macrocycle. This approach permits the use of cryptates to sequester selected metal ion, then separating and releasing them under controlled environments. The capture of metal ions K^+, Ca^{2+} and Mn^{2+} has been achieved and further studies on capturing other metal ions such as Co^{2+} and Ni^{2+} as well as the photo-release of these ions from their cryptates are in progress.



Cryptate NC222-M^{n+} (M = K, Ca, Mn, etc.)

211. SCHIFF BASE RING CLOSURE MECHANISMS IN MULTI-METAL BINDING MACROCYCLIC RING SYSTEMS. **Johnathan P. Harper**, Harvest Collier; University of Missouri-Rolla, 10 King Drive, Rolla, MO 65401.

For many years there has been interest in the redox characteristics of multinuclear binding moities found in nature. The goal of this research is to generate macrocyclic rings which are capable of simultaneously binding more than one metal center. Due to the synthetic flexibility of these systems, it should be possible to tailor the electronic and steric environments around metal centers while adjusting the size of the ligand 'pocket.' In this investigation, emphasis will be placed on Schiff base mechanisms of ring closure which incorporate 2,2´-biimidazole as a cooperating dinuclear metal ion binding ring component. Reaction pathways for the necessary precursors and ring formation will be reported.

212. ANHYDROUS LANTHANIDE SCHIFF BASE COMPLEXES PRODUCED VIA TRIFLATE DERIVED AMIDES. **John A. Belot**[1], Steven A. Schuetz[1], Victor W. Day[1], Joanna L. Clark[1], Roger D. Sommer[2], Arnold L. Rheingold[2]; [1]University of Nebraska-Lincoln, Hamilton Hall, Room 746, Lincoln, NE 68588-0304; [2]University of Delaware, Newark, DE 19716.

Anhydrous lanthanide Schiff base chemistry remains an “unfulfilled promise” in f-element chemistry. This contribution will describe new anhydrous, Schiff base lanthanide complexes produced via the 'silylamide route'. However, the $Ln[N(TMS)_2]_3$ used was not derived from $LnCl_3$, but instead utilized $Ln(OTf)_3$. The products form tetradentate ketoiminates which exhibit various steric and electronic factors. Final product stoichiometry (*i.e.*, monomer, dimer or tetramer) can be selectively controlled by exploiting ligand substituents, reaction conditions and/or lanthanide radii. These complexes also undergo various substitution reactions in almost quantitative yields. All compounds are active catalysts for numerous small molecule transformations and polar monomer polymerizations, the details of which will also be presented in this contribution.

213. ACID WASHING OF EICHROM LN RESIN AND LAB-WARE FOR DETERMINING TRACE METAL CONTAMINANTS. Keith D. Bailey, Barry Higgins, Alan R. Ketring, **Cathy S. Cutler**; University of Missouri-Columbia, 1513 S. Providence Rd., Columbia, MO 65211.

To determine and quantify possible trace metal contaminants leached from Eichrom LN Resin, Kontes glass flex column, 20-mL LDPE (low-density polyethylene) scintillation vials, HDPE (high-density polyethylene) columns and glass/ HDPE flasks during chromatographic separation and production of high specific activity radioisotopes. Elimination or reduction of potential contaminants will allow us to achieve higher radiolabeling yields. We investigated whether

washing the resin and lab-ware, with Ascorbic acid and varying concentrations of HNO_3, would reduce potential contaminants in the final product solution resulting in higher radiolabeling yields. Five concentrations of HNO_3 (7M, 5M, 2.5M, 1M, 0.1M) and 1M Ascorbic acid were passed through the column, resin, tubing, plastic scintillation vials and reservoir in the following order. First: 250-mL of 1M Ascorbic acid followed by 500mL MilliQ water. Second: 250-mL each of the five concentrations of HNO_3 in descending order from 7M were passed through the column. Fractions were collected in 10-mL vials and analyzed on an ICP-MS to quantify metal contaminants. Metals analyzed for include: Al, Ca, Ce, Co, Cr, Cu, Fe, Ni, Pb, Zn and Zr. Results show significant amounts of Al, Ca, Fe and Zn were leached from both the glass and plastic lab-ware: glass: Al = 2800ppb, Ca = 6500ppb, Fe = 1500ppb, Zn = 4800ppb, plastic: Al = 500ppb, Ca = 30000ppb, Fe = 1600ppb, Zn = 650ppb. Significant amounts of trace metal contaminants are leached from glass and HDPE lab-ware. To reduce trace metal contaminates from the chromatographic process, lab-ware constructed of metal free materials are being evaluated.

214. GROUP 6 TRANSITION METAL COMPLEXES FORMED WITHIN NAX ZEOLITE. **William M. Shirley**, Stanley P. Scoville; Chemistry Department, Pittsburg State University, Pittsburg, KS 66762.

The major reasons for studying group 6 metal carbonyl complexes within a zeolite is that they may be catalyst precursors and precursors of materials for electronic or optical devices. Solid-state ^{13}C NMR and diffuse reflectance IR have been used to observe supported chromium hexacarbonyl and (arene)tricarbonylchromium complexes within the NaX zeolite. The arenes benzene, aniline, mesitylene, anisole and aniline all form hexahapto tricarbonyl complexes physisorbed within the zeolite supercage under the proper conditions. The (benzene)tricarbonylchromium complex is physisorbed at two sites in the zeolite supercage and produces two carbonyl resonances at 300 K. Variable temperature MAS NMR shows these two resonances coalescing near 360 K with an activation energy of 48 kJ/mol. The physisorbed complex $Cr(CO)_3(C_5H_5N)_3$ forms when pyridine reacts with partially decomposed $Cr(CO)_6$/NaX. The temperature programmed decomposition of $W(CO)_5(CS)$ adsorbed on NaX zeolite shows that the loss of CO occurs in two main stages with peaks at 345 and 425 K. The surface complex $W(CO)_2(CS)$/NaX is probably forming during the peak at 345 K while decomposition of this surface complex is indicated by the 425 K peak.

215. STUDY OF THE PREFERENTIAL SOLVATION OF TRANSITION METAL COMPLEXES BY H-NMR. **Michael D. Mosher**, Christopher L. Exstrom; University of Nebraska at Kearney, Department of Chemistry, Kearney, NE 68849-1150.

An understanding of solvation models for transition metal complexes can aid in the development of solvatochromic sensor materials. However, many of the literature methods that study these solute-solvent interactions rely on the relative chemical shift of the X-nucleus. Given the more intimate interaction between ligand and solvent, we have been interested in the use of H-NMR to develop these solvation models. A series of first row transition metal complexes ($M(acac)_3$) in various solvent mixtures were studied by H-NMR. The results of this study, and the distinction between the specific and non-specific solute-solvent interactions, will be discussed.

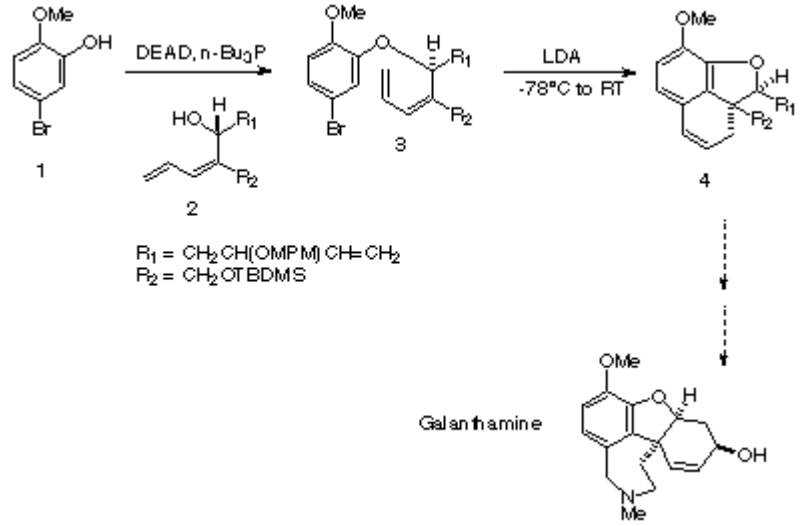
216. DESIGN, SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF PD(II) AND PT(II) AND THEIR CATALYTIC REACTIVITY TOWARDS PEPTIDES. Victor Anbalagan, Winnie Chien, **Michael Van Stipdonk**; Wichita State University, Department of Chemistry, Wichita, KS 67260-0051.

Enzymatic cleavage is an important tool in the identification and sequencing of proteins, analysis of protein domains, studies of protein association and synthesis of new drugs etc. Transition metal complexes are beginning to be applied for hydrolytic cleavage of unactivated amide bonds by hydrolysis. We are interested in the application of novel transition metal complexes to the selective hydrolysis of proteins and peptides. It is reported that Pd(II) complexes efficiently cleave amide bond next to amino acids such as histidine and methionine in peptides and proteins. Hence we have decided to synthesize complexes of palladium(II) and platinum(II) and to study them as a cleaving agents for peptides/proteins. The mechanism of hydrolytic reactivity of these complexes will be studied by the interaction of these complexes with peptides. Here we report the synthesis, characterization and stereo-specific reactivity of these complexes towards peptides/proteins. We will also report the study of collision-induced dissociation of model peptides containing amino acids such as histidine or tryptophan or methionine with these metal complexes.

217. TANDEM [2+2] ARYNE CYCLOADDITION-REARRANGEMENT APPROACH TO (-)-GALANTHAMINE. **Keith R. Buszek**; Kansas State University, 111 Willard Hall, Department of Chemistry, Manhattan, KS 66506.

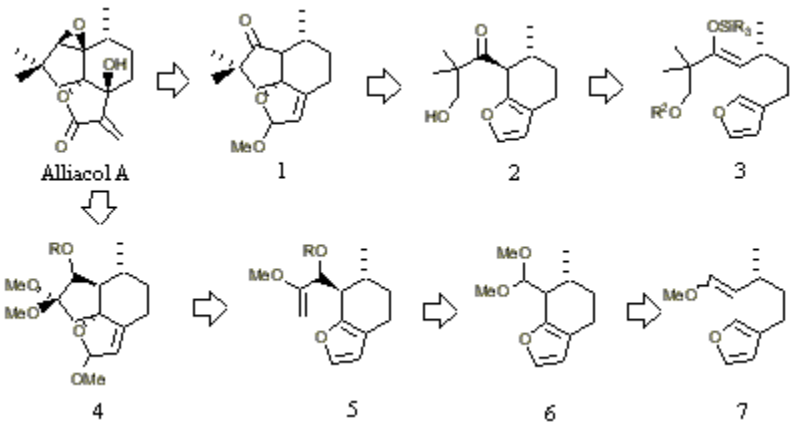
Efforts toward the total synthesis of the acetylcholinesterase inhibitor galanthamine will be described. The key step in our approach involves the application of

our tandem [2+2] aryne cycloaddition-rearrangement strategy to form the tri-cyclic intermediate **4**.



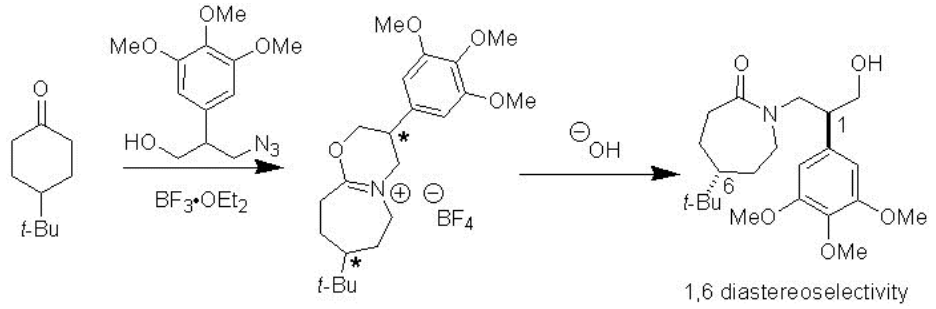
218. STUDIES TOWARD ALLIACOL A VIA RADICAL CATION CYCLIZATION REACTIONS. **John M. Mihelcic**, Kevin D. Moeller; Washington University in St. Louis, One Brookings Drive, St. Louis, MO 63130.

Previously we have shown that radical cations are facile participants in intra-molecular cyclization reactions. Investigations into the synthetic utility of these reactive intermediates currently focus on Alliacol A, a naturally occuring sesquiterpene with a unique angurally fused tricyclic core. Two approaches have been studied and both generate radical cations via electrochemical oxida- tion. In the first route, a highly functionalized substrate (**3**) would lead to the target in a rapid fashion. An alternate approach would use two oxidative cyclizations (**7**→**6**) and (**5**→**4**), the second of which suggests a 5-endo trig closure, a process limited by orbital overlap contraints. Is the radical cation reactive enough to overcome such barriers?



219. 1,6 ASYMMETRIC INDUCTION IN THE LEWIS ACID-PROMOTED REACTION OF HYDROXYALKYL AZIDES. **Christopher Katz**, Jeffery Aube; The University of Kansas, Malott Hall, Lawrence, KS 66045.

The Lewis acid-promoted reaction between phenyl substituted hydroxy azides and *tert*-butyl cyclohexanone has been examined. The reaction proceeds through an iminium ether that is reacted with hydroxide to provide diastereomeric N-alkylated lactams. The overall reaction provides product with modest to excellent 1,6 diastereoselection. The compass of this methodology will be discussed.



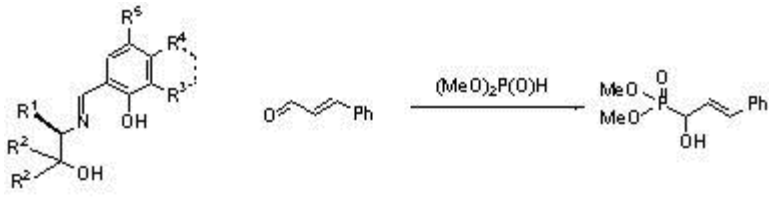
220. DESYMMETRIZATION VIA INTRAMOLECULAR CYCLOPROPANATION: APPLICATIONS ON PHOSPHORUS TEMPLATES. Joel D. Moore, Kevin T. Sprott, Aaron D. Wrobleski, **Paul R. Hanson**; University of Kansas, 1251 Wescoe Hall Dr., Department of Chemistry, Lawrence, KS 66045-7582.

Diastereotopic differentiation strategies on a variety of allylic phosphonoacetates are described. The approach utilizes $Rh_2(OAc)_4$-catalyzed intramolecular cyclopropanation (ICP) employing the *(R)*-pantolactone auxilliary in the ester func-

tionality of the phosphonoacetate. The olefinic diastereofacial selectivity is governed by inherent electronic and steric interactions in the reacting carbene intermediate, while the group selectivity is dictated by the chiral auxilliary. This approach is being developed as an effective method to access bicyclic *P*-chiral phosphonates.

221. PREPARATION AND USE OF NEW CHIRAL SCHIFF´S BASE LIGANDS IN ENANTIOSELECTIVE PUDOVIK REACTION. Anyu He, **Christopher D. Spilling**; University of Missouri-St. Louis, Department of Chemistry and Biochemistry, St. Louis, MO 63121.

Chiral Schiff bases are easily prepared from 3,5-di-*tert*-butyl-2-hydroxy-benzaldehyde, 2-hydroxy-naphthaldehyde and a series of chiral, non-racemic amino alcohols. Application of the Schiff´s base ligands to the asymmetric Pudovik reaction was studied. Complexes, formed *in situ*, between the ligands and $Ti(OiPr)_4$ or ($AlMe_3$), catalyze the reaction of cinnamaldehyde with dimethyl-phosphite. This poster will present the results of these studies.

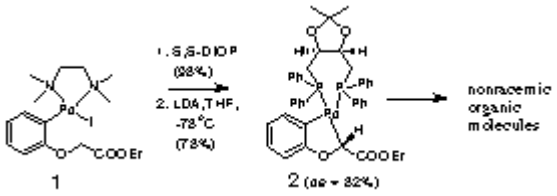


Figure

222. DIASTEREOSELECTIVE SYNTHESIS OF PALLADACYCLES WITH AN ASYMMETRIC METAL-BONDED CARBON AND THEIR USE IN ORGANIC SYNTHESIS. Sara E. Lilley[1], Janelle L. Portscheller[2], N'vida E. Houndonougbo[2], **Helena C. Malinakova**[2]; [1]College of the Ozarks, Department of Chemistry, Point Lookout, MO 65726; [2]University of Kansas, Department of Chemistry, 2010 Malott Hall, Lawrence, KS 66045.

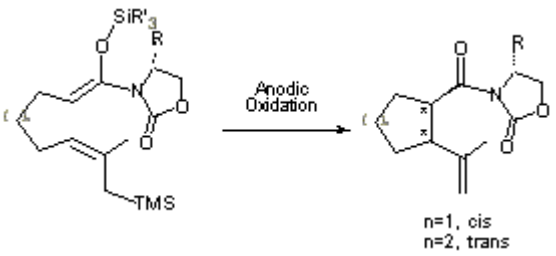
In the past, fundamental studies on the reactivity of transition metal complexes led to the development of new general synthetic methods. We have envisioned that palladacycles could be prepared from achiral substrates with concomitant generation of a metal-bonded stereogenic carbon, and subsequently serve as templates for asymmetric synthesis of valuable organic products. As a first step towards this goal, we have demonstrated that chirality of the ligands can be used to effect asymmetric induction at the metal-bonded stereogenic carbon. Thus, exchange of the TMEDA ligand for (S,S-DIOP) in complex **1** followed by treatment with LDA, afforded the palladacycle **2** in a high diastereomeric excess. Detailed studies on the effect of reaction conditions and the nature of ligands on

the diastereomeric purity of palladacycles will be presented. Preparation of additional palladacycles with diverse structures and their application to the synthesis of nonracemic organic products will also be described.



223. REVERSING THE POLARITY OF ENOLATE EQUIVALENTS: THE USE OF N,O-KETENE ACETALS IN INTRAMOLECULAR ANODIC OLEFIN COUPLING REACTIONS. **Yung-tzung Huang**, Kevin D. Moeller; Washington University in St. Louis, Campus Box 1134, St. Louis, MO 63130.

While intramolecular anodic olefin coupling reactions have proven to be useful tools for generating new C-C bonds, asymmetric variants on the reactions have not been studied. Are such reactions feasible? In an effort to address this question, we have begun to study the compatibility of the reactions with ketene acetal equivalents. In this way, we hope to take advantage of chiral auxiliaries that have already been developed in connection with the asymmetric aldol reaction. In this paper, the utility of oxazolidinone derived ketene acetal equivalents as initiating groups for the anodic olefin coupling reaction will be discussed.



224. NEW SYNTHESES TOWARD CYCLIC ENOL PHOSPHATES AND RELATED COMPOUNDS: A RING-CLOSING METATHESIS APPROACH. Alan Whitehead, Stephen R. Sieck, Joel D. Moore, Matthew D. McReynolds, **Paul Hanson**; University of Kansas, 5030 Malott Hall, Lawrence, KS 66045-7582.

A ring-closing metathesis (RCM) strategy employing the second generation Grubbs catalyst for the formation of cyclic enol phosphates and their related compounds is described. We are currently utilizing the RCM reaction towards a variety of cyclic enol phosphate type compounds. In addition, we have further developed the methodology to access a novel class of cyclophosphamide derivatives. The reported cases represent the first examples of RCM on enol phosphates, ketene acetal phosphates and enol phosphonamidates.

225. PARALLEL OPTIMIZATION OF PALLADIUM-CATALYZED CARBOCYCLIZATIONS: BISDIENES AND N-HYDROXY PHTHALIMIDE. **Margaret E. Gifford**, Scott D. Schroeder, James M. Takacs; University of Nebraska, Department of Chemistry, Hamilton Hall, Lincoln, NE 68588-3501.

The Takacs group has been interested in discovering and developing palladium-catalyzed carbocyclization reactions for use in synthesizing biologically active natural products. Currently, the reactions under investigation involve bisdiene substrates that cyclize with incorporation of a trapping agent (pronucleophile). The efficiency of the cyclization/trapping reaction depends upon a number of variables including the substrate, trapping agent, catalyst precursor, ligand and solvent. In an attempt to find the most suitable reaction conditions, a series of parallel reactions, primarily involving the variation of catalyst precursors and ligands have been carried out. From these experiments, several catalyst systems that exhibit high efficiency have been uncovered.

226. PHOSPHORUS TEMPORARY TETHERS: APPLICATION TO THE SYNTHESIS OF 7-MEMBERED HETEROCYCLES. Matthew D. McReynolds, Kevin T. Sprott, **Paul R. Hanson**; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045-7582.

The functionalization of 1,4-diamines to the synthesis of 7-membered heterocycles as analogs of potent HIV protease inhibitors DMP-323 and DMP-450 is described. We have recently reported a highly efficient method using a phosphorus tether/ring-closing metathesis (RCM)/hydrolysis sequence to derive 1,4-diamines containing the (*Z*)-1,4-diaminobut-2-ene subunit. We now report the utility of the 1,4-diamine synthon in the rapid assembly of structurally diverse 7-membered heterocycles, including cyclic ureas, phosphonamides, sulfamides and sulfurous acid diamides. Stereoselective dihydroxylation studies, investigations of RCM to 7-membered cyclic ureas and preliminary HIV protease inhibition results will also be discussed.

227. ROM POLYMERIZATION TO OLIGOMERIC DICHLOROTRIAZINE: SYNTHESIS AND UTILITY. Donald A. Probst[1], Paul R. Hanson[2], **Daniel L. Flynn**[3]; [1]University of Kansas, 5030 Malott Hall, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582; [2]University of Kansas, 5030 Malott Hall, Department of Chemistry, Lawrence, KS 66045-7582; [3]Neogenesis Pharmaceuticals, Inc., 840 Memorial Drive, Cambridge, MA 02139.

Efforts towards the synthesis and use of norbornenyl-tagged dichlorotriazine are reported. Subsequent ring-opening metathesis polymerization results in an oligomer that exhibits selective solubility. This allows the use of the oligomeric reagent in solution phase chemistry, followed by precipitation and filtration of the oligomer.

228. TEMPO-MEDIATED COPOLYMERIZATION OF 4-[METHOXYPOLY-(ETHYLENE OXIDE)]-METHYLENESTYRENE WITH VINYL MONOMERS. **Tip Jungsriyawongse**, Reza Herati; Southwest Missouri State University, 901 S. National, Springfield, MO 65804.

Controlled free radical polymerization (CFRP) has gained in importance in recent years because it enables one to synthesize polymers with controlled molecular weight, narrow molecular weight distribution and well defined architectures. In this work we have synthesized 4-[methoxypoly(ethylene oxide)]-methylenestyrene, **I**, and have studied its CFRP with monomers such as styrene, *p*-vinylbenzyl chloride and phthalimide methylenestyrene using 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) in combination with benzoyl peroxide as the initiating system. It is shown that the copolymerization of **I** with the above vinyl monomers is controllable and the molecular weight of the copolymers increases with polymerization time, and the molecular weight distribution of the resulting polymers is narrow. Synthesis and characterization of the copolymers and their further modifications to obtain functional amino copolymers will be presented and discussed.

229. SYNTHESIS OF POLYCYCLIC, AROMATIC HYDROCARBONS USING DIELS-ALDER ADDITION TO A SUBSTITUTED THIOPHENE. Joseph Vincent, Amy Rice, Robert Ingalls, Robert Clevenger, **Kathleen V. Kilway**; University of Missouri-Kansas City, 205 Spencer Chemistry Building, 5100 Rockhill Road, Kansas City, MO 64110-2499.

One of our group's research interests is the use of a substituted acenaphthene as a building block for larger polycyclic, aromatic hydrocarbons. A double Diels-Alder reaction of 1,4-benzoquinone with 2,5,7,10-tetra(*t*-butyl)diacenaphtho[1,2-b:1',2'-d]thiophene followed by dehydrogenation produced a twisted anthraquinone. Further substitution at central carbonyl groups of our resulting anthroquinone utilizing either Grignard or Wittig reactions is underway. Other reactions under investigation are Diels-Alder additions of maleimide and maleic anhydride to our substituted thiophene. These results will be presented.

230. A SULFUR LYNCHPIN/RCM STRATEGY TO NOVEL *S*-HETEROCYCLES. Jung Ho Jun[1], María d. Jiménez[1], Joseph M. Dougherty[1], **Paul R. Hanson**[2]; [1]University of Kansas, 5024 Malott Hall, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrene, KS 66045-7582; [2]University of Kansas, 5029 Malott Hall, Department of Chemistry, Lawrence, KS 66045-7582.

New synthetic routes employing sulfamide, sulfonamide, sulfamoyl carbamate, and sulfamoyl urea lynchpins for the construction of novel *S*-heterocycles are described. These routes utilize the ring-closing metathesis (RCM) reaction in conjunction with the inherent chemistry of each sulfur-containing lynchpin to generate

novel *S*-heterocycles. Synthetic pathways leading to new sulfamide analogs of DMP-323 and several peptide-like *S*-heterocycles will highlight the method.

231. GEM-DIFLUORINATION OF DIARYLTHIOLANES BY SELECTFLUOR AND PYRIDINIUM POLYHYDROGEN FLUORIDE. Ramesh Alleti[1], **R. V. Prakash**[1], G. K. Surya Prakash[2], Meher K. Perambuduru[1]; [1]University of Missouri-Rolla, 142 Schrenk Hall, #340, Rolla, MO 65401; [2]University of Southern California, University Park, Los Angeles, CA 90089-1661.

Diaryl dithiolanes were readily transformed into the corresponding gem-difluoro compounds using Selectfluor™ and pyridinium polyhydrogen fluoride (PPHF) under mild conditions. This reaction is applicable to substrates which can generate stable carbocation intermediates. The dithiolanes derived from the aromatic aldehydes or acetophenone derivatives consistently gave the corresponding carbonyl compounds almost exclusively. The reaction is very convenient and efficient for the preparation of the 1,1-diaryldifluoromethanes and complements other existing methods.

232. ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS IN IONIC LIQUIDS. Zahra Afrasiabi, **V. Prakash Reddy**, Ekkehard Sinn; University of Missouri-Rolla, Chemistry Department, Rolla, MO 65401.

Room temperature ionic liquids (RTILs) have essentially no vapor to contaminate the environment, yet they are frequently excellent solvents for organic and inorganic reagents. Therefore they are solvents of choice for large scale commercial reactions, potentially displacing conventional organic solvents in such applications. Electrophilic aromatic substitution reactions, such as halogenation and nitration are important industrial processes. These reactions can be con0 ventionally carried out using the corresponding electrophiles generated *in situ* through the Selectfluor™-mediated oxidative processes in RTILs as “green” solvents. In many cases we have observed enhanced rates of reactions in RTILs compared to the conventional solvents. The resulting substitution products are, in most cases, isolable as pure compounds by distillation from the reaction mixture. In these cases not only is the polluting solvent eliminated, but the reaction is more economic.

233. APPLICATIONS OF CAPTURE-ROMP-RELEASE STRATEGIES IN SYNTHESIS. Shubhasish Mukherjee[1], Andrew M. Harned[2], Kevin W. Poon[1], Daniel L. Flynn[3], **Paul R. Hanson**[2]; [1]University of Kansas, 5031 Malott Hall, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045; [2]University of Kansas, 5030 Malott Hall, Department of Chemistry, Lawrence, KS 66045-7582; [3]Neogenesis Pharmaceuticals Inc., 840 Memorial Drive, Cambridge, MA 02139.

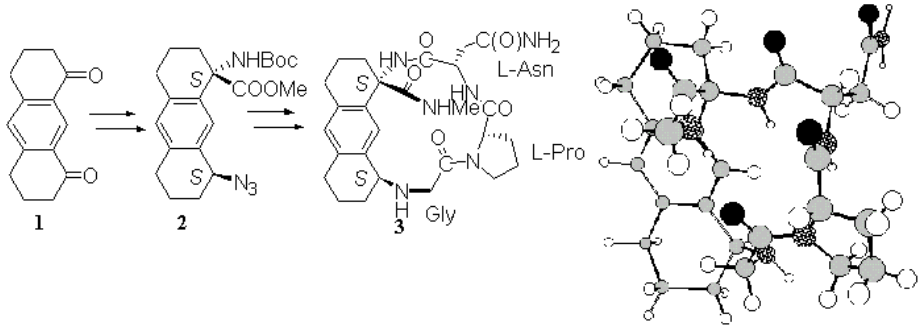
Efforts toward the utilization of various Capture-ROMP-release strategies will be presented. The use of norbornenyl-tagged molecules for standard solution phase chemistry is the main focus of this study. Tagged intermediates are then phase-switched post reaction via *in situ* ring-opening metathesis polymerization (ROMP) mediated by the Grubb´s catalyst. Further reactions can be carried out on the soluble ROM oligomer intermediate by standard solution phase chemistry. After each step, the product has been purified utilizing phase-switching techniques by simply precipitating the tagged oligomer in MeOH or ether. Studies focusing on differential solubility of the oligomers with respect to the by-products and excess reagents in organic solvents will be discussed.

234. RING-OPENING METATHESIS PHASE TRAFFICKING SYNTHESIS: APPLICATION TO RCM AND OTHER REACTIONS. Andrew M. Harned[1], Shubhasish Mukherjee[1], **Paul R. Hanson**[1], Daniel L. Flynn[2]; [1]University of Kansas, 5030 Malott Hall, Department of Chemistry, Lawrence, KS 66045-7582; [2]Neogenesis Pharmaceuticals, Inc., 840 Memorial Drive, Cambridge, MA 02139.

Ring-closing metathesis (RCM) reactions have been performed on soluble, oligomeric supports generated via the ring-opening metathesis polymerization (ROMP) reaction. This approach involves an initial reaction between a substrate and a norbornenyl-tagged capturing agent. Subjection of the crude reaction mixture to *in situ* ROM polymerization conditions utilizing the Grubbs second-generation catalyst generates a soluble oligomer that can be precipitated away from reaction impurities using methanol. Once isolated, the oligomer can be further functionalized before employing the RCM reaction. After each functionalization step, reaction products are isolated simply by precipitation with methanol, ether or water. Initial application of this technology for the construction of cyclic sulfamides and other recent results in this area will be presented.

235. ASYMMETRIC SYNTHESIS AND CONFORMATION OF MACROCYCLIC *ALPHA*-HELIX NUCLEATION SITES. Xiaoping Nie, James L. Bennett, **Ralf Warmuth**; Kansas State University, Department of Chemistry, 111 Willard Hall, Manhattan, KS 66506.

The asymmetric synthesis of macrocyclic α-helix nucleation sites, such as **3**, and their conformational analysis are described. These conformational constrained cyclic peptides are designed to mimic the first turn of an α-helix, and are expected to nucleate α-helix formation of short peptides that are covalently attached to the C-terminus or N-terminus of the nucleation sites. The key intermediate **2**, which can be viewed as a protected conformational constrained lysine derivative, was derived from diketone **1** via a serious of asymmetric reactions: 1) a highly stereoselective Strecker reaction of the first carbonyl; 2) a catalytic asymmetric reduction of the second carbonyl; 3) a Mitsunobu-type reaction of the resulting alcohol. After stepwise peptide-coupling reactions, macrolactamization finally gave α-helix template **3**. The general scope of the asymmetric methodology and macrolactamization will be discussed.



Energy-minimized structure **3**

236. DESIGN AND SYNTHESIS OF NEW DIVERSE HEMICARCERANDS. **Neil Brown**, Ralf Warmuth; Kansas State University, 111 Willard Hall, Manhattan, KS 66506

For almost 20 years, carcerands, hemicarcerands, carcerplexes, hemicarceplexes and their precursors have been extensively studied and several modifications upon the parent system synthesized. Their uses in chemistry are diverse, finding use in the study of inclusion phenomena, trapping of reactive intermediates, determination of unimolecular rearrangement pathways, triplet energy transfer and redox chemistry. However functionalization of broad scope beyond the parent system is not overly studied. Most functionalization is applied to the linking groups that tether the two polar 'caps' of a hemicarcerand, mainly

because this is the easiest part of a hemicarcerand to change. Not much work has been attempted in changing the appending groups (the feet) of hemicarcerands. Most hemicarcerands studied make use of simple alkyl feet (derived from the corresponding aldehyde), due to either cost or solubility reasons. Recently our group has developed hemicarcerands **1** and **2**. These hemicarcerands have an easily transformable carbon-carbon double bond at the terminus of the feet group. It is now conceivable that many modifications could be made to the new parent system. For example, polymers or resins could be made, oxidation to carboxylic acids leading to peptide coupling or epoxidation for entry into many different systems via `click´ chemistry. Also asymmetric hemicarcerands could also be constructed with two different caps; one cap being from an existing system, the other from our new system, which could lead to a hemicarcerand with possible ambiphilic properties for use in the study of surface interactions, micelles or even membrane transport. The synthesis of **1** and **2** and recent modifications will be presented and discussed.

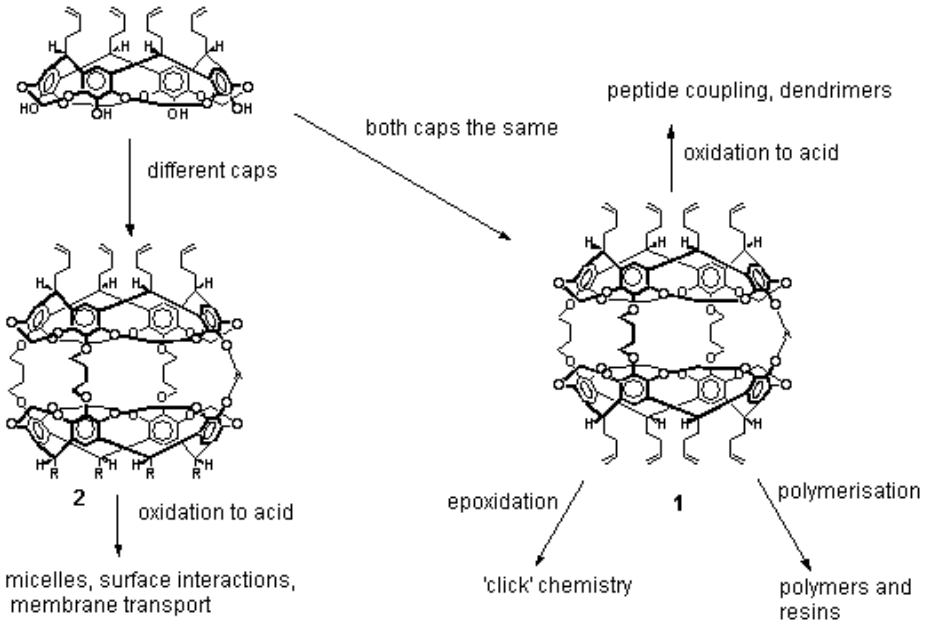


Figure 1

237. DESIGN, SOLUTION-PHASE CONSTRUCTION AND EVALUATION OF COMPOUNDS THAT EMPLOY A CYCLIC SULFAMIDE SCAFFOLD. Jiaying Zhong, Tzutshin Wong, Xiangdong Gan, Hongyi Yu, Christopher S. Groutas, **William C. Groutas**; Wichita State University, Department of Chemistry, Wichita, KS 67260.

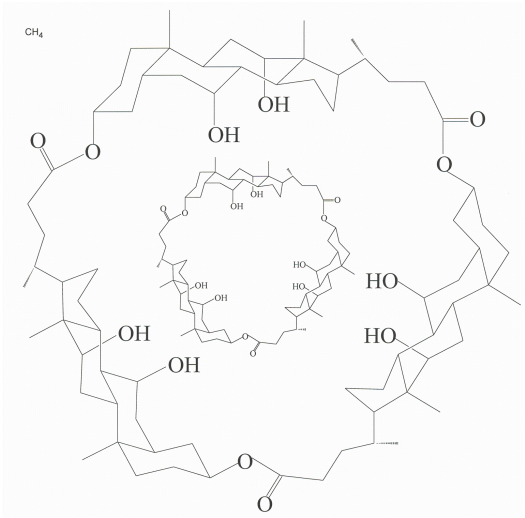
Combinatorial chemistry is currently a powerful and integral component of the drug discovery process. The effectiveness and general applicability of a combinatorial library in terms of lead identification and optimization are largely determined by the nature of the scaffold used to construct the library. The use of novel, non-peptidyl scaffolds that provide an effective means for linking recognition and diversity elements in a specific spatial relationship, and are well-suited to exploiting multiple binding sites for optimizing potency and selectivity, in the construction of libraries offer many advantages. The design and solution-phase construction of a highly-functionalized cyclic sulfamide scaffold was readily accomplished starting from (DL) serine methyl ester hydrochloride. A series of compounds was obtained using parallel synthesis and the inhibitory activity of the synthesized compounds toward human leukocyte elastase was then determined. This study has led to the identification of a micromolar competitive inhibitor of the enzyme having a novel structure. The design and construction of the template, as well as the results of biochemical studies, will be presented. Acknowledgement. This work was generously supported by a grant from the Heart and Blood Institute of the National Institutes of Health (HL 57788).

238. NIKKOMYCIN STRUCTURE-ACTIVITY RELATIONSHIP STUDIES: SYNTHESIS OF A NOVEL PYRANOSYL NUCLEOSIDE ANALOG. Christina S. Stauffer, **Apurba Datta**, Pushpal Bhaket; University of Kansas, 4062 Malott Hall, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

Nikkomycins are a naturally occurring family of complex peptidyl nucleoside antibiotics. As selective inhibitors of chitin synthase, these compounds show strong and selective antifungal activity, while being non-toxic to plants, fishes and mammals. This class of compounds show promise as useful models towards the development of novel, non-toxic antifungal agents. A major research objective in our lab is directed towards development of new synthetic strategies for the stereoselective synthesis of natural and non-natural compounds of biomedical significance. As part of this project, stereoselective synthesis of a novel pyranosyl nucleoside analog of nikkomycin has been undertaken. Details of the synthesis will be presented.

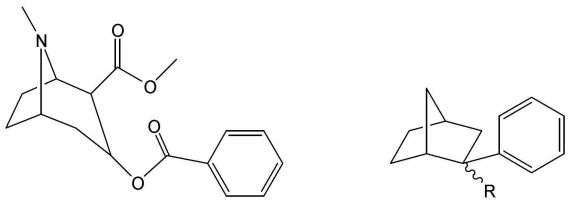
239. SYNTHESIS OF OLIGOMERS OF CHENODEOXYCHOLIC ACID. **Suad A. Rashdan**, Jerry R. Dias; University of Missouri-Kansas City, Department of Chemistry, Kansas City, MO 64110-2499.

Dimers and cyclocholates of chenodeoxycholic acid have been synthesized and characterized. Cyclocholates were synthesized by two methods, the Yamaguchi method using 2,6-dichlorobenzoyl chloride and a method using N,N'-dicyclohexylcarbodiimide. For cholic and deoxycholic acids, cyclocholates were obtained only when the 12-OH groups were protected as OAc groups. This 12-OAc protection was necessary to avoid the formation of the intramolecular ester between the 12-OH and C_{24}-COOH groups which does not occur in chenodeoxycholic acid because of the absence of the 12-OH substituent.



240. TOWARDS COCAINE TREATMENT: PHENYL-NORBORNANE ANALOGS. **Michael S. Day, Jr.**[1], Adeboye Adejare[2], William C. Putnam[1]; [1]Midwest Research Institute, 425 Volker Blvd., Kansas City, MO 64110; [2]970 S. 5th Avenue, Pocatello, ID 83209.

Cocaine abuse and addiction continues to be an omnipresent and growing problem in America with estimates of 5000 new users of cocaine each day. Currently, there is no FDA-approved pharmaceutical for treatment of cocaine abuse. It has been established that the dopamine transporter plays an essential role in cocaine addiction. Synaptic dopamine concentration is increased due to cocaine´s inhibition of dopamine reuptake at the dopamine transporter. A series of 3-phenyl-norbornane analogs have been synthesized to antagonize cocaine´s binding at the dopamine transporter while maintaining normal dopamine reuptake. The syntheses of these potential therapeutic agents will be presented. The series was evaluated by the cocaine treatment discovery program at the



National Institute of Drug Abuse. The determined pharmacological properties will be discussed.

241. MECHANISM-BASED INACTIVATION OF HUMAN LEUKOCYTE ELASTASE VIA AN ENZYME-INDUCED SULFONAMIDE FRAGMENTATION PROCESS. Liuqing Wei, Xiangdong Gan, Sumei Ruan, Juan Tu, Jeffrey B. Epp, Rongze Kuang, **William C. Groutas**; Wichita State University, Department of Chemistry, Wichita, KS 67260.

A mechanism-based inhibitor is an inherently unreactive compound that acts as a substrate and is processed by the catalytic machinery of an enzyme, generating a highly reactive electrophilic species which, upon further reaction with an active site nucleophilic residue, leads to irreversible inactivation of the enzyme. Mechanism-based inhibitors which, when processed by an enzyme, undergo a fragmentation reaction that results in the formation of a reactive electrophilic species, are not known. Using a saccharin scaffold, the first example of a mechanism-based inhibitor of the serine protease human leukocyte elastase which appears to inactivate the enzyme via an unprecedented enzyme-induced sulfonamide fragmentation process, has been synthesized. The inactivation of the enzyme was found to be time-dependent (k_{obs}/[I] 120 M^{-1} s^{-1}) and to involve the active site. The design, synthesis and mechanistic studies will be presented. Acknowledgement. Financial support of this work by the Heart, Lung and Blood Institute of the National Institutes of Health (HL 57788) is gratefully acknowledged.

242. COMBINATORIAL METHOD YIELDS POTENTIAL NOVEL DISEASE-RESISTANCE STRATEGY. **Sarah A. Mounter**[1], James G. Laskey[1], Sharon L. Bishop-Hurley[2], Francis J. Schmidt[3], James T. English[1]; [1]University of Missouri-Columbia, Plant Microbiology & Pathology, Columbia, MO 65211; [2]University of Missouri-Columbia, Molecular Microbiology & Immunology, Columbia, MO 65212; [3]University of Missouri-Columbia, Biochemistry, Columbia, MO 65212.

Plant pathogens have destroyed crops for centuries. The combinatorial method described here may lead to an effective method for preventing host infection by a particular plant pathogen, *Phytophthora spp*. *Phytophthora ssp.* detect and respond to environmental signals during development and pathogenesis. Affinity-selected phage-displayed peptides were bound to *Phytophthora capsici* zoospores. A subset of these bound phage-displayed peptides induce premature encystment of the zoospores thus interrupting the pathogenesis cycle. Premature encystment is detectable by time-averaged photo-imagining. Synthetic peptides recapitulate the encystment effect observed in the phage-displayed format. The synthetic and phage-displayed peptides induce premature encystment at concentrations of less than 100 micromolar. Subsequently, affinity-selected peptides can

be used to identify zoospore surface receptors. Finally, the isolation of peptides that act on plant pathogens may yield a novel disease-resistance strategy.

243. SYNTHESIS AND BINDING STUDIES WITH DI-SUBSTITUTED PHENYL UREA PORPHYRINS. **Kenichi E. Calderon-Kawasaki**; Organic Synthesis Laboratory, 1845 Fairmount, Wichita, KS 67260.

In the past we have studied the binding trends of porphyrin receptor with anions in protic solvent environment. From the studies it was established that the tetra appended porphyrin (figure 1) and the tri-appended porphyrin(figure 1) show a strong binding preference with the spherical halide anions compared to tetrahedral and trigonal planar anions. Our hypothesis is that the solvent plays an important role in this selectivity. From x-ray crystallography it is clear that the anions are bound to the DMSO molecules via electrostatic interaction. In the absence of anions the four urea functional groups are each occupied with a DMSO solvent molecule inside the porphyrin pocket. In the presence of the halide ions it is shown that two anions have replaced two DMSO molecules. Further more, it was thought that in the presence of dihydrogen phosphate, hydrogen sulfate and nitrate more than two DMSO molecules would be replaced. Therefore it was hypothesized that the halides are able to make that interaction in the pocket with lower energy expenditure whereas the tetrahedral and trigonal planar anions are accompanied with higher solvation energy to displace more solvent molecules from the pocket. From the x-ray crystallography and experimental data of tri and tetra compounds we know that at least three urea groups must be present to have the solvent-anion interaction. In theory, by reducing the number of urea arms on the porphyrin we reduced the number of sites for the solvent to aid in the selectivity of anion binding. We are synthesizing and characterizing the di-substituted porphyrin (figure 1). Upon binding with an anion, both of the urea arms on the di-appended system will be occupied with the anions and there will be no room left for the solvent to bind. The di-urea porphyrin is expected to show a significant change in the binding selectivity. In that event it will be clear that the solvent is the factor which increases the selectivity towards halide anions, especially that of chloride.

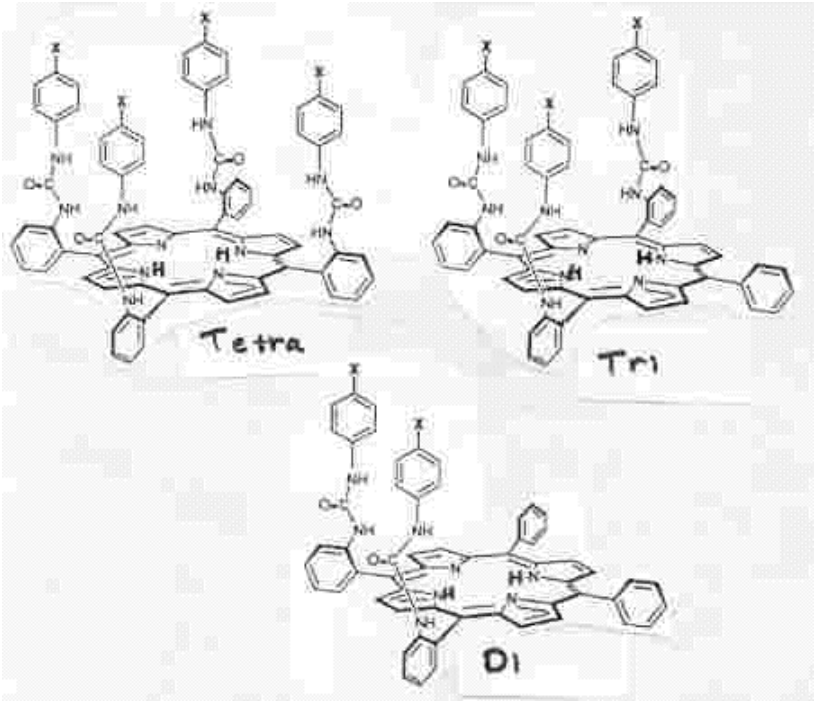
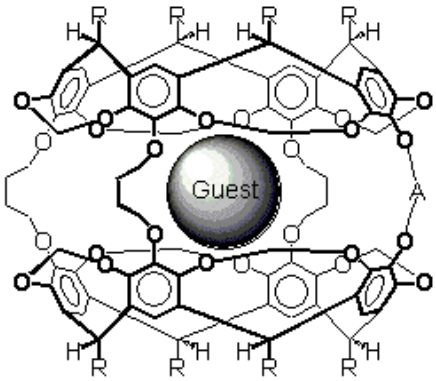


Figure 1

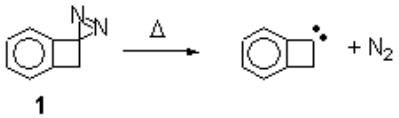
244. RATE ACCELERATION THROUGH DISPERSION INTERACTIONS: EFFECT OF A HEMICARCERAND ON THE TRANSITION STATE OF INNER PHASE DIAZIRINE DECOMPOSITIONS. Sigifredo Sanchez Carrera[1], Neil Brown[2], **Ralf Warmuth**[2]; [1]Instituto Tecnológico y de Estudios Superiores de Monterrey, Departamento de Química, Monterrey, N.L. 64849, Mexico; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506-3701.

Molecular container compounds are spherical, hollow molecules with an inner cavity (the inner phase) that allows for the accommodation of a single molecule with appropriate size and shape. The ability to fully encapsulate a guest molecule and to prevent the physical contact or a reaction with bulk phase components that are too large to enter the inner phase, allows one to address very fundamental questions important to physical and structural organic chemistry and biochemistry. We are particularly interested in the question of how the surrounding host modulates the reactivity of an encapsulated guest molecule as compared to other bulk phases. As an example, we have studied the thermolysis of various aryldiazirines, **1-3** in the inner phase of hemicarcerand **4**. As compared to the bulk phase, the rate of the thermolysis of these diazirines strongly changes upon

incarceration. These observations are discussed in terms of the unusual properties of the inner phase (polarizability-anisotropy) and the guest´s inner phase orientation and space occupancy.



4⊙Guest



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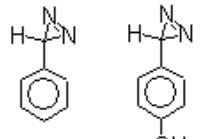
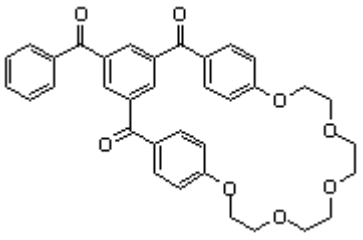


2 **3**

R = Phenethyl

245. MOLECULAR RECEPTORS FORMED FROM 1,3,5-TRIAROYLBENZENE DERIVATIVES. Angela V. Schmitt, Fatemah Nichols, **F. C. Pigge**; University of Missouri-St. Louis, Department of Chemistry and Biochemistry, St. Louis, MO 63121-4499.

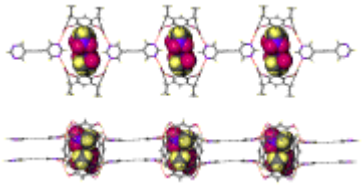
The design and synthesis of molecular receptors that can interact with biological substrates is a main objective for supramolecular chemistry. As part of research focusing on the synthesis of heteroditopic receptors suitable for binding inorganic salts and organic zwitterions, we have begun to explore the possibility of acces- sing innovative cyclophane building blocks via benzannulation-macrocyclization processes. Therefore, a number of crownophane derivatives (*e.g.*, **1**) have been prepared using an enaminone-directed cross-cyclotrimerization reaction. The ability of these crown ether-like cyclophanes to bind cationic substrates has also been examined.



1

246. THE QUEST FOR CHAIN-LINK HYDROGEN BONDED CAPSULES: SELF-ASSEMBLY OF C-METHYL CALIX[4]RESORCINARENE WITH 1,2-BIS(5´-PYRIMIDYL)ETHYNE. Ivan Georgiev, **Eric Bosch**; Southwest Missouri State University, 901 South National Avenue, Springfield, MO 65804.

The structures of three three-dimensional hydrogen bonded networks formed on self-assembly of the tetradentate ligand 1,2-bis(5'-pyrimidyl)ethyne with C-methyl calix[4]resorcinarene under a variety of conditions are presented. Two of the structures contain ligand-bridged resorcinarenes with a "chain-link" capsule motif.



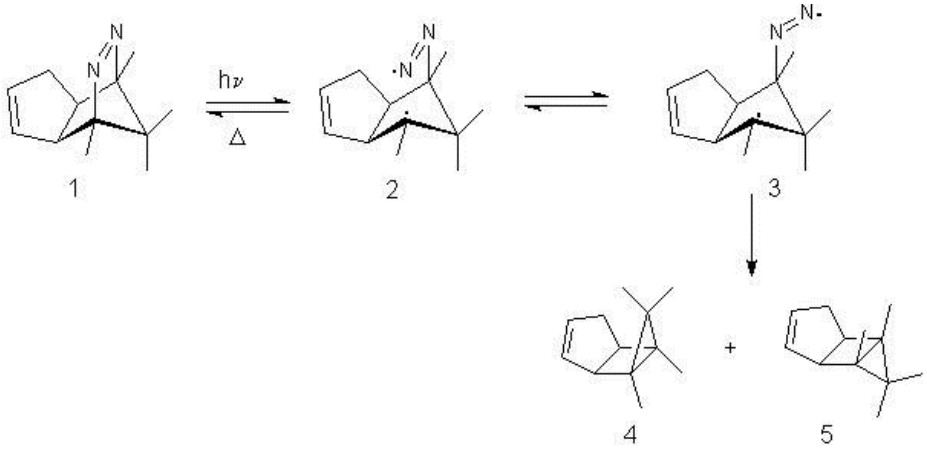
247. SYNTHESES OF SULFONATED PEEK MONOMERS. **Scott E. McKay**[1], Robert W. Kopitzke[2], Robert W. Lashlee III[1]; [1]Central Missouri State University, Department of Chemistry, Warrensburg, MO 64093; [2]Winona State University, Dept. of Chemistry, Winona, MN 55987.

Several sulfonated monomers are being prepared for the investigation of substituents on the sulfonic acid bearing ring effects the conductivity of solid proton-exchange membranes (PEM). 1,1'-(*p*-Phenylenedioxy)bis[4-(4-chlorobenzoyl)benzene[1] and 1,1'-(*p*-Phenylenedioxy)bis[4-(4-fluorobenzoyl)benzene were prepared in high yields using phosphorus pentoxide/methanesulfonic acid (PPMA).[2] Poly(ether)etherketone (PEEK) can be sulfonated with sulfuric acid and precipitated out in high yield. However, the fluoro and chloro monomers suffer from high solubility in sulfuric acid. Sulfuric acid with continuous extraction and sulfur trioxide were used to obtain adequate sulfonated products in this study.

[1]Ueda, M.; Ichikawa, F. *Macromolecules* 1990, **23**, 926.
[2]Eaton, P.E.; Carlson, G.R. *J. Org. Chem.* 1973, **38**, 4017.

248. PHOTOLYSIS OF A BICYCLIC AZO COMPOUND: FURTHER EVIDENCE FOR A DIAZENYL RADICAL. **Rick C. White**[1], David A. Corley[1], Alexei V. Trofimov[2], Waldemar Adam[2]; [1]Sam Houston State University, P.O. Box 2117, Huntsville, TX 77341; [2]Institut für Organische Chemie, Am Hubland, Würzburg, Germany D-97074, Germany.

Azo compound **1** undergoes photolysis to yield housanes **4** and **5**. The quantum yield for loss of azo compound decreases with increasing solvent viscosity which suggests the formation of an intermediate diazene radical and that the diazenyl radical may be reversibly formed.



249. PRODUCTION OF AZO DYE IMAGES ON POLYSTYRENE SURFACES. **Nancy J. Seybold**, Robert R. Pavlis; Pittsburg State Univ., Department of Chemistry, 1701 S. Broadway, Pittsburg, KS 66762.

Aromatic diazonium salts are light sensitive. Because these materials are cations, they can be attached to the surfaces of ion exchange resins. It is possible to sulphonate the surfaces of commercial polystyrene sheets, in effect creating sheets of ion exchange resin. When these sheets are placed in solutions of diazonium salts, the counter ion for the sulphonates on the surface becomes diazonium cations. Sheets with attached diazonium cations are light sensitive. Therefore, images can be produced on the surfaces by irradiation through suitable masks and the subsequent reaction with an aromatic amine or phenol produces azo dyes.

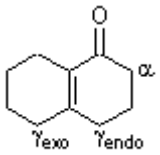
250. GAS PHASE STUDIES OF REACTIVE ORGANIC SPECIES. **Xinping Liu**[1], Paul G. Wenthold[2], Daryl Giblin[2], Michael L. Gross[3]; [1]Washington University, Chemistry Department, St. Louis, MO 63130; [2]West Lafayette, IN 47907.

The enthalpy of formation of methylhydroxycarbene, CH_3COH, has been determined from measurements of the threshold energy for collision-induced dissociation of protonated 2,3-butanedione in a flowing afterglow-triple quadruple mass spectrometer, and found to be 16.4 ± 3.8 kcal/mol, 57.2 ± 3.8 kcal/mol higher than that of acetaldehyde. From the measured enthalpy of formation, the difference between the first and second C-H BDEs in ethanol is found to be 16.6 kcal/mol, which implies a singlet - triplet splitting of 28.2 kcal/mol in the carbene. The activation energies for loss of ketene and carbon monoxide from protonated butanedione are found to be 2.59 ± 0.18 and 2.16 ± 0.18 eV, respectively. On the

basis of experimental and computational results, the loss of carbon monoxide is proposed to proceed through a tight transition state. Although calculations suggest a tight transition state for loss of ketene as well, the experimental data indicate that it occurs via a loose transition state, possibly forming by proton transfer along the direct dissociation pathway. The similar approach has also been applied to determine the enthalpy of formation of methylmethoxycarbene, CH_3COCH_3, and found to be 8.5 ± 3.2 kcal/mol. Comparing the enthalpies of formation of the carbene with that of acetone (-52.2 kcal/mol), the energy of the carbene is 60.7 kcal/mol higher than acetone. This result is in fair agreement with the calculated energy difference between the carbene and acetone at B3LYP/6-31+G* level of theory (64.2 kcal/mol).

251. ANALYSIS OF THE MASS SPECTRUM OF $\Delta^{9(10)}$-1-DECALENONE VIA STUDIES OF DEUTERIUM EXCHANGE. **David C. Hawkinson**, Ying Wang, Lei Yao; University of South Dakota, 414 E. Clark Street, Vermillion, SD 57069.

The mass spectrum (EI) of $\Delta^{9(10)}$-1-decalenone (**1**) shows major fragmentation peaks at m/z (% of base peak) 150 (57.3%), 135 (26.7%), 122 (75.5%), 94 (30.0%), and 79 (100%). In most cases, there is more than one plausible pathway that could lead to a particular fragment. Using ^{1}H-NMR spectrometry, we have determined that the three enolizable positions of $\Delta^{9(10)}$-1-decalenone exchange with solvent deuterium under basic conditions (50% CD_3OD:D_2O with 0.3 M NaOD) at greatly different rates. Analysis of the ^{1}H-NMR coupling pattern during the course of deuterium exchange shows that the α protons exchange first, followed by the γ_{exo} protons, with the γã$_{endo}$ protons exchanging last. $\Delta^{9(10)}$-1-decalenone was allowed to exchange with solvent deuterium under basic conditions (10% CH_3OD:D_2O with NaOD), with aliquots quenched and analyzed by GCMS at appropriate time intervals. Comparison of the changes in m/z of the daughter ion peaks relative to that of the molecular ion allow elucidation of the fragmentation pattern of $\Delta^{9(10)}$-1-decalenone.



1

252. ANTIFUNGAL SESAMOL DERIVATIVES. Gwen Schaunaman[1], Nancy Brooker[2], **Gerald Caple**[3]; [1]Univ. of South Dakota, Vermillion, SD 57069; [2]Pittsburg State Univ, Pittstburg, KS 66762; [3]Univ. of South Dakota, 387 Gunflint Narrows, Grand Marais, MN 55604.

Charcoal rot, (*Macrophomia phaseolina*), is a fungal disease that causes significant crop loss in soybean, (*Glycine max*.), agriculture. Soybean seeds coated with micrograms of sesamol,(3,4-methylenedioxyphenol),show resistance to charcoal rot infection. We began a study to see if derivatives of sesamol could

improve resistance to charcoal rot or give information as to the mechanism which leads to the resistance. Here sesamol was treated with methyl-4-bromobutanoate and 5-bromopentanoate in base to yield sesamol derivatives. The resulting esters were treated with methylmagnesiumbromide and ethynylmagnesiumbromide to yield tertiary alcohols with the hydroxy group situated four or five carbons from the sesamol part of the molecule. The effect of these compounds on charcoal rot will be compared with compounds prepared earlier where the hydroxy group was two carbons away from the sesamol part of the molecule.

253. SYNTHESIS OF (*R*) AND (*S*) 4-FLUORO-2,3,4,5-TETRAHYDRO-1H-2-BENZAZAPINES AS NEW INHIBITORS OF PHENYLETHANOLAMINE (*N*)-METHYLTRANSFERASE. **Joju Davis**, Kevin R. Criscione, Gary L. Grunewald; University of Kansas, joju davis.room no-4016, Department of Medicinal Chemistry, Lawrence, KS 66045.

The (*R*) and (*S*) enantiomers of 4-fluoro-2,3,4,5-tetrahydro-1H-2-benzazapines were synthesised with high enantiomeric purity for biological evaluation as inhibitors of phenylethanolamine *N*-methyltransferase(PNMT). The key step in our reaction sequence involves the enzymatic resolution of the 4-hydroxy(*N*)-protected benzazapine to its two different enantiomers. The synthesis of enantiomerically pure compounds can lead to better biological activity. The racemic 4-fluorobenzazapine and its analogues were synthesized by our group and biological evaluation was carried out. The 4-fluoro-8-nitro THBA was found to be one of the most selective inhibitors of PNMT known, with a selectivity ratio greater than 900.

254. IMPROVED PREPARATION AND CHARACTERIZATION OF 9-ARYL-9-XANTHYLIUM CARBOCATIONS AND COMPARISON WITH THE PARENT ALCOHOLS. **V. Prakash Reddy**, Meher Perambuduru, Ramesh Alleti, Ekkehard Sinn; University of Missouri-Rolla, Chemistry Department, Rolla, MO 65401.

We have developed a convenient and improved method for the preparation of the 9-aryl-9-xanthylium tetrafluoroborates. The corresponding alcohols were reacted with HBF_4-Et_2O in anhydrous dichloromethane solution at –80 ºC and the carbocation salts were obtained as yellow crystals by simple dilution with dry ether. Single crystals for X-ray diffraction result from slow evaporation of the solvent at –20 ºC. The results are complemented by NMR and theoretical calculations.

255. GEM-DIFLUORINATION OF DIARYLTHIOLANES BY SELECTFLUOR AND PYRIDINIUM POLYHYDROGEN FLUORIDE. Ramesh Alleti[1], **V. Prakash Reddy**[1], Meher K. Perumbuduru[1], G.K. Surya Prakash[2]; [1]University of Missouri-Rolla, 142 Schrenk Hall, #340, Rolla, MO 65401; [2]University of Southern California, University Park, Los Angeles, CA 90089-1661.

Diaryl dithiolanes were readily transformed into the corresponding gem-difluoro compounds using Selectfluor™ and pyridinium polyhydrogen fluoride (PPHF) under mild conditions. This reaction is applicable to substrates which can generate stable carbocation intermediates. The dithiolanes derived from the aromatic aldehydes or acetophenone derivatives consistently gave the corresponding carbonyl compounds almost exclusively. The reaction is very convenient and efficient for the preparation of the 1,1-diaryldifluoromethanes and complements other existing methods.

256. ROM POLYMERIZATION TO OLIGOMERIC SULFONYLCHLORIDES: VERSATILE REAGENTS FOR ORGANIC SYNTHESIS. Joel D. Moore[1], Russell H. Herpel[1], Joy Lichtsinn[1], **Paul R. Hanson**[2], Daniel L. Flynn[3]; [1]University of Kansas, 5024 Malott Hall, Lawrence, KS 66045-7582; [2]University of Kansas, 5030 Malott Hall, Department of Chemistry, Lawrence, KS 66045-7582; [3]Neogenesis Pharmaceuticals, Inc., 840 Memorial Drive, Cambridge, MA 02139.

A new method for homogeneous nucleophilic scavenging employing oligomeric sulfonylchlorides (OSC) is described. The method utilizes OSC to scavenge a variety of amines that are present in excess. The OSC reagent is generated from the ROM polymerization of 2-chlorosulfonyl-5-norbornene utilizing the second generation Grubbs catalyst to produce oligomers of varying size. Following the scavenging event, these oligomers can be precipitated with ethyl acetate leaving products in excellent yield and purity. In addition, the use of OSC to generate versatile oligomeric derivatizing agents is reported.

257. PROGRESS TOWARD A CHIRAL-POOL SYNTHESIS OF OXIMIDINE II. **Torsten Haack**[1], Gunda I. Georg[2]; [1]University of Kansas, 4065 Malott Hall, 1251 Wescoe Hall Drive, Lawrence, KS 66045; [2]University of Kansas, Lawrence, KS 66045.

The oximidines I and II, isolated in 1999 from *Pseudomonas sp*. belong to a new group of cytotoxic natural products. Their structural features include a salicylic acid moiety, a 12-membered macrocycle with an unusual (E,Z,Z)-triene system and a labile enamide side-chain. We will report on our efforts toward the total synthesis of oximidine II based on a chiral-pool approach.

258. PROGRESS TOWARDS THE TOTAL SYNTHESIS OF TYLOINDICINE I. **Brandon J. Turunen**[1], Gunda I. Georg[2]; [1]School of Pharmacy, 5009 Mallot Hall, Westcoe Hall Drive, Lawrence, KS 66046; [2]University of Kansas, Lawrence, KS 66045.

Tyloindicine I is a structurally novel indolizidine alkaloid, which displays promising tumor selective cytotoxicity. Unfortunately, this compound has only been isolated in very small quantities. Therefore, a synthetic strategy has been developed to obtain sufficient quantities for further biological testing. Our chiral pool approach, which will allow for an enantiopure synthesis, is amendable to analog generation for further SAR study. The progress towards the development of this synthetic route will be discussed herein.

259. A NOVEL METHOD FOR THE EFFICIENT REMOVAL OF RCM BY-PRODUCTS USING POLYMER-BOUND TRIPHENYL-PHOSPHINE OXIDE (TPPO) AND DIMETHYLSULFOXIDE (DMSO). **KyoungLang Yang**, Yu Mi Ahn, Gunda I. Georg; University of Kansas, 1603 W. 15th St. #605A, Lawrence, KS 66044.

The powerful method to install a double bond in a ring system, RCM (ring-closing metathesis), using ruthenium catalysts, generates unidentified ruthenium by-products that are difficult to remove from the reaction product. We developed previously a practical method to remove these by-products with the aid of TPPO or DMSO (Ahn, Y. M.; Yang, K.; Georg, G. I. *Org. Lett*. 2001, **3**, 1411-1413). Herein, we report the use of polymer-bound TPPO and DMSO as an extension of this work.

260. SELECTIVE REDUCTION OF γ,δ-UNSATURATED β-KETO ESTERS TO THE CORRESPONDING γ,δ-UNSATURATED β-HYDROXY ESTERS. **Gunda I. Georg**, Reddy S. Bollu, Emily A. Reiff, Jun Inagaki; University of Kansas, 1251 Wescoe Hall Drive, Malott Hall, Lawrence, KS 66045.

Asymmetric hydrogenation by chiral transition-metal complexes has been one of the most powerful methods for the synthesis of optically active compounds. Noyori's (*S*)-Binap$RuBr_2$ catalyst is able to convert a range of functionalized β-ketoesters to the corresponding secondary alcohols in high yield and with excellent enantiomeric purity. In order to explore this methodology for the reduction of γ,δ-unsaturated β-hydroxy esters using Noyori's ruthenium binap catalyst, as well as expanding our options for the formation of epothilone analogues, several β-ketoesters were prepared and subjected to the Noyori reduction. The results of the studies will be presented.

261. CONFORMATIONAL ANALYSIS OF A SYNTHETIC PEPTIDE INHIBITOR. Megan Condon[1], Christy Sasiela[2], David Vander Velde[3], Gerry Lushington[3], **Sandy Vigil-Cruz**[3]; [1]University of Connecticut, Storrs, CT 06269; [2]University of Maryland, Baltimore, MD 21201; [3]University of Kansas, Lawrence, KS 66045.

Our research has resulted in the design of small synthetic peptides derived from the stromal-cell derived factor-1 (SDF-1) protein which is the endogenous ligand for the CXCR4 chemokine receptor. These peptides inhibit the proliferation of the T-47D breast cancer cells in a dose-dependent manner. There is a strong expression of the CXCR4 chemokine receptor on the surface of primary breast cancer cells and in breast cancer cell lines. Neither the receptor nor the endogenous ligand is expressed in normal breast tissue. It has been hypothesized that this ligand-receptor interaction contributes to the abnormal proliferation of breast cancer cells. In order to enhance our design strategy for the next generation of these breast cancer cell-inhibiting peptides, the conformation of our lead peptide was evaluated by two-dimensional nuclear magnetic resonance spectroscopy (2D-NMR). The lead peptide exhibits two definite structural regions in β-type turns that are robust at both 4° and 25°C.

262. NMR COMPARISONS OF NANOCRYSTALLINE AND COARSE-GRAIN PALLADIUM-HYDRIDE AND DEUTERIDE. **Steven K. Brady**[1], Ivan C. Salazar[1], David B. Baker[2], Jeffrey A. Eastman[3], Mark S. Conradi[1]; [1]Washington University in St. Louis, One Brookings Drive, C.B. 1105, St. Louis, MO 63130-4899; [2]William Jewell College, 500 College Hill, Liberty, MO 64068; [3]Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439.

Two distinct proton NMR lines were previously reported in nanocrystalline PdH_x ($r \cong 5$ nm, $x \cong 0.70$) and were tentatively assigned to H in the crystalline cores and in grain boundaries. Here we show this assignment to be incorrect, with all of the H in the Pd forming a single line and the second line arising from surface-bound H_2O formed by reaction with an initial oxide layer on the Pd. Distinct spectroscopic signatures of deuterium in grain boundaries and in crystalline cores are sought in the rigid lattice ^2D spectrum of nano-PdD_x and in the onset of motional narrowing. In neither case is two-part behavior found; the results are essentially identical to those in coarse-grain PdD_x. The spin-lattice relaxation rate R_1 of ^2D in nano-PdD_x is compared to that in coarse-grain material. The electronic (Korringa) contribution, dominant below 125 K, is 1.58 times as large in nano-PdD_x, indicating a difference in the electronic structure in the grain boundary / free surface regions of nano-PdD_x. Above 200 K, a contribution to R_1 from exchange with D_2 gas is observed for nano-PdD_x, a result of the large surface area.

263. DEVELOPMENT AND APPLICATION OF IMPROVED METHOD OF DETECTION FOR CAPILLARY ISOTACHOPHORESIS USING ON-LINE CONDUCTIVITY AND MICROCOIL NMR. **Valentino K. Almeida**[1], Amy Carr[2], Kenneth L. Ratzlaff[1], Cynthia K. Larive[1]; [1]University of Kansas, Department of Chemistry, Lawrence, KS 66044-7582; [2]Fort Lewis College, 1000 Rim Drive, Durango, CO 81301.

The goal of this study is to develop a new on-line method of analysis using capillary isotachophoresis (c-ITP) and dual detection involving microcoil NMR and contactless conductivity. A solenoidal NMR microcoil of high mass sensitivity serves as a detector providing optimal NMR observation. c-ITP is carried out in a modified fused silica capillary to reduce electroosmotic flow. It not only separates the components of the sample based on their electrophoretic mobilities, but also concentrates the analytes by two to three orders of magnitude, greatly improving the concentration limits of detection. In contactless conductivity detection the change in solution conductance affects the IR drop across the electrodes of the detector indicating the presence of the c-ITP focused bands. Contactless conductivity detection would allow trapping of stacked analyte bands in the c-ITP experiment prior to NMR detection. This would facilitate signal averaging and enable 2D experimentation. Parameters such as electrode diameter, gap between the two electrodes, optimum frequency for conductivity detection, optimum distance between the conductivity detector and the NMR microcoil are being examined.

264. DETERMINATION OF MOLAR EXTINCTION COEFFICIENTS FROM LC-UV-NMR DATA. **Albert Korir**, Christine Hellriegel, Cynthia K. Larive; University of Kansas, Chemistry Dept., 2010 Malott Hall, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

LC-NMR can be used for structure elucidation of analytes in complex mixtures. UV-absorbance has been adopted as the standard method of detecting peaks as they elute from the chromatographic column, allowing stopped-flow NMR detection. NMR has the advantage that a pure standard of the compound of interest is not required for quantitative analysis. Quantitative data can be obtained with LC-NMR using an internal standard such as maleic acid added to the mobile phase. The analyte concentration determined by LC-NMR can be used with the on-line UV-absorbance data to determine the molar extinction coefficient of the analyte without isolation. LC-UV-NMR has the capability of on-line separation and immediate analysis, a characteristic that is especially useful for volatile, unstable and air-sensitive solutes. The test compounds chosen for this study are the pharmaceuticals caffeine, ibuprofen and ciprofloxacin. Molar extinction coefficients obtained by LC-UV-NMR will be compared with those obtained from conventional UV-absorption measurements. In the case where the NMR internal

standard absorbs at the wavelength of interest, the true analyte absorbance can be calculated by subtraction. Low sensitivity problems associated with LC-NMR may be encountered especially in instances where substances being analyzed are dilute and the molar extinction coefficients are large. We are extending this strategy to incorporate column-trapping techniques in order to concentrate the analyte prior to NMR analysis. Studies are underway to use this technique for the characterization of breakdown products of ciprofloxacin in aquatic ecosystems.

265. STRUCTURE ELUCIDATION OF HUMIC SUBSTANCES WITH NMR, UV/VISIBLE AND FLUORESENCE SPECTROSCOPY. **Christine Hellriegel**[1], Ceyda S. Uyguner[2], William Otto[3], Cynthia K. Larive[1]; [1]University of Kansas, Chemistry Department, 2010 Malott Hall, Lawrence, KS 66045; [2]Bogazici University, Bebeck, Istanbul, Turkey; [3]University of Maine-Machias, Machias, ME 04654.

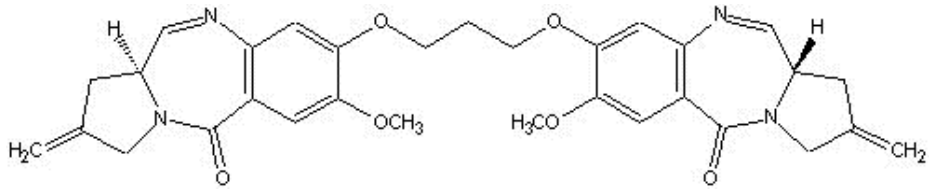
Humic substances are heterogeneous mixtures of decay products of plant and animal biomass in aquatic as well as terrestrial environments. They are well known as the source of color in surface waters. Humic substances are implicated as precursors of carcinogenic trihalomethanes (THM) formed during disinfection in water treatment processes. For that reason, the understanding of the structural elements comprising humic substances is very important. Here we present an investigation of six humic substances (fulvic as well as humic acids), which are extracted from different sources. To identify and understand the relationship between THM formation potential (THMFP) and reactive sites of humic materials, such as isolated protons located at activated aromatic structures or aliphatic β-dicarbonyls, structural elements of the humic substances were investigated using NMR, UV/visible spectroscopy and fluorimetry. NMR spectroscopy is well recognized as the premiere analytical method for structure elucidation. The recently developed gradient modified spin-echo (GOSE) NMR pulse sequence is a unique technique to reject resonances of coupled spins and selectively detect singlet resonances, enabling examination of isolated protons. The GOSE pulse sequence has been used to measure relative concentrations of singlet resonances in different humic substances. The humic substances were also characterized by UV/visible spectroscopy at several wavelengths and by fluorescence spectroscopy, which provide additional information about typical structural properties of humic and fulvic acids.

266. CONFORMATIONAL ANALYSIS OF CYCLIC ANALOGS OF THE OPIOID PEPTIDE DYNORPHIN A. **Matthew W. Leighty**, David G. Vander Velde, Jane V. Aldrich; University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Our research focuses on the development of potent and selective, peptide-based antagonists for kappa opioid receptors and examination of the structure-activity relationships for antagonist activity at these receptors. We recently synthesized novel peptide analogs of dynorphin A, an endogenous ligand for kappa opioid receptors, cyclized through the N-terminus, encapsulating the "message" sequence of the peptide. In order to further direct our studies, the conformation of two analogs were evaluated by NMR. DQF-COSY, HOHAHA and ROESY spectra of the novel analogs were acquired on a Varian Inova 600 MHz spectrometer. Inverting the stereochemistry of a single amino acid was found to alter dramatically the conformation of the cyclic portion of the molecule. The NMR results and structural models of the peptides will be presented.

267. ANALYSIS OF SJG-136 DRUG SUBSTANCE: ADDUCT FORMATION AND SOLUTION STUDIES BY FT-NMR ANALYSIS. **Gregory A. Turner**[1], Jeremiah Morris[1], Paul S. Liu[2]; [1]Midwest Research Institute, 425 Volker Boulevard, Kansas City, MO 64110; [2]National Cancer Institute, Executive Plaza North, Room 8048, Bethesda, MD 20892.

SJG-136 (bis-pyrrolobenzodiazepinone) is a member of the pyrrolo[2,1-c][1,4]-benzodiazepine (PBD) family of antitumor antibiotics derived from various *Streptomyces* species. SJG-136, a dimer of C_2-methylene DC-81, has shown significant cytotoxicity and antitumor activity in the Hollow Fiber assay and cisplatin-resistant ovarian cell lines. The cytotoxicity of SJG-136 is in the picomolar region, with the biological activity exerted through covalent binding with guanine residues in DNA, by cross-linking via its N_{10}-C_{11} imine moiety. This imine moiety also spontaneously forms adducts with protic solvents such as water and methanol, complicating the characterization and purity determinations of SJG-136 by reverse-phase chromatography. ^{1}H NMR analysis was utilized to study the formation, solution stability and equilibrium of water, methanol, ethanol and *tert*-butanol adducts. Additional characterization of SJG-136 adducts was performed



by FT-IR, LC-MS and normal phase chromatography. **SJG-136**

268. QUANTITATION OF CRYSTALLINE AND AMORPHOUS FORMS OF NEOTAME USING ^{13}C CPMAS NMR SPECTROSCOPY. **Thomas Offerdahl**[1], Eric Munson[1], Jonathon Salsbury[1], David J. Grant[2], Zedong Dong[2]; [1]University of Kansas, Department of Pharmaceutical Chemistry, 2095 Constant Ave., Lawrence, KS 66047; [2]University of Minnesota, Minneapolis, MN 55455.

The ability to effectively deliver solid pharmaceuticals is directly related to the form of the drug in the solid state. Although most drugs are formulated in the crystalline state, amorphous forms are often generated during the formulation process. Moreover, many of these drugs exhibit polymorphism, or the ability to exist in two or more crystalline phases that differ in the arrangement or conformation of the molecules in the crystal lattice. The ability of solid-state ^{13}C NMR spectroscopy with cross polarization (CP) and magic-angle spinning (MAS) to quantify the amounts of multiple crystalline and amorphous forms present in formulations of the artificial sweetener neotame will be described. In a mixture of two polymorphic forms of anhydrous neotame, we have identified the presence of one polymorph at levels below 0.25%. We have also been able to quantify the amount of each polymorph to within 2%. More accurate quantitation could be possible if pure crystalline forms were used. In mixtures of amorphous and crystalline forms of neotame, the amorphous content could be determined to at least 10%. The effects of differences in relaxation parameters and cross polarization efficiencies on characterizing mixtures of different polymorphs will be addressed.

269. PALLADIUM-CATALYZED OXIDATION WITH MOLECULAR OXYGEN. **Shannon S. Stahl**; University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706.

Selective chemical oxidation is central to the synthesis of organic molecules. We have focused our attention on a growing class of palladium-catalyzed oxidation reactions that employ molecular oxygen as the stoichiometric oxidant and don't require the use of redox active co-catalysts to achieve efficient catalytic turnover. Mechanistic features of these reactions and applications to synthetic organic chemistry will be described.

270. CATALYTIC REACTIONS FOR ORGANIC SYNTHESIS. **F. Dean Toste**; University of California, Berkeley, Department of Chemistry, Berkeley, CA 94720.

The development of catalysts for selective addition to multiple bonds will be discussed.

271. THE EVOLUTION OF NEW OXIDATION REACTIONS FOR FINE CHEMICALS SYNTHESIS. **Justin Du Bois**; Stanford University, 333 Campus Dr., S.G. Mudd, Stanford, CA 94305.

The invention of new reaction chemistry for the selective functionalization of saturated hydrocarbons is a central objective of our research program. We have focused our early efforts on the development of a catalytic process that makes possible the oxidative amination of C–H bonds. This work is stimulated by the formidable challenges associated with the generation and control of reactive oxidizing agents using metal coordination complexes and by the large and varied number of potential applications for reactions that promote N–atom insertion into C–H centers. The evolution of these new chemical methods together with investigations in catalyst design, mechanism and target-directed synthesis will be discussed.

272. NEW RHODIUM-CATALYZED CROSS-COUPLING AND CYCLOADDITION REACTIONS. **P. A. Evans**; Indiana University, 800 E. Kirkwood Avenue, Bloomington, IN 47405.

The transition metal-catalyzed allylic substitution reaction represents a powerful and fundamentally important transformation for the construction of vicinal ternary and quaternary stereogenic centers. Despite the enormous synthetic potential, this reaction has been restricted to symmetrical or stereoelectronically-biased substrates in order to circumvent problems associated with regioselectivity. The seminar will describe many of the recent developments on the regio- and enantiospecific rhodium-catalyzed allylic substitutions, with particular emphasis on the development of hard nucleophiles which will undoubtedly expand the scope of this important transformation. Finally, the development of a new metal- mediated [4+2+2] cycloaddition reaction will also be described.

273. PERIODIC TABLES FOR BENZENOID HYDROCARBONS. **Jerry R. Dias**; University of Missouri-Kansas City, Department of Chemistry, Kansas City, MO 64110-2499.

A periodic table set is a partially ordered, large to infinite 2-dimensional array of elements having at least one metric property which obeys the triad principle. The periodic table set has a least element. When these characteristics are fulfilled, then this array will have hierarchical ordering and edge effects. All benzenoids can be generated from benzene using only three elementary aufbau units (C_2, C_3H, C_4H_2 attachments). Constant-isomer series are benzenoid sets of increasing formulas with the same number of isomers and generated by successive circumscribing appropriate excised internal structures. Formulas corresponding to constant-isomer benzenoids have the smallest range of structure types. The existence of constant-isomer series led to the discovery of a new topological

paradigm. In brief this topological paradigm consists of the following elements: (1) A corresponding formula periodic table with (x,y) = (ds,NIc) coordinates contains formulas on the left-hand staircase-like edge of a 2-dimensional array that belong to constant-isomer series generated by successive circumscribing (or augmented circumscribing for TRS benzenoids). (2) As the formula of the first generation members to each successive constant-isomer series increases so does the corresponding number of isomers. (3) The number of isomers increases according to a regular pattern where some of the isomer numbers repeat. (4) In those constant-isomer series having the same isomer numbers, there is a one-to-one matching of the topology between the structures of the two sets. (5) The topological invariants in this one-to-one matching of structures include symmetry, characteristics of 1- and 2- factorability, number of bay regions and selective lineations (±1 eigenvalues) and adjacency/nonadjacency of pentagonal rings (for indacenoid constant-isomer series). (6) The formula periodic tables and constant-isomer series for strictly pericondensed and strain-free total resonant sextet (TRS) benzenoids are isomorphic where the leapfrog algorithm associates any given benzenoid with its symmetry equivalent TRS isomorph. (7) The formula periodic tables and constant-isomer series for strictly pericondensed monoradical, diradical, triradical, tetraradical, etc. benzenoids are isomorphic. The aufbau, circumscribing, leapfrog and the hexagonal-to-pentagonal ring contraction algorithms are important tools used in the development of this unified formula/ structure organization.

274. A SIMPLE ALGEBRAIC METHOD OF BALANCING CHEMICAL EQUATIONS: A NEW LOOK. **Paul Karr**[1], John Karr[2]; [1]Wayne State College, 1111 Main, Wayne, NE 68787; [2]University of Nebraska, Lincoln, 1013 Hillcrest Road, Wayne, NE 68787.

Teaching students to balance chemical equations by the trial and error method has long been the accepted method used in general chemistry courses. The use of such a method requires practice, experience and in time critical test situations a little luck at quickly guessing the initial reactant and product coeficients. A much more concrete and logically satisfying method exists. The use of a series of equations or a simple matrix may be used to balance equations using a purely systematic approach that is both gratifying to learn and easy to teach.

275. USING QUANTUM MECHANICAL PROGRAMS TO UNDERSTAND THERMODYNAMICS. **Paul Karr**; Wayne State College, 1111 Main, Wayne, NE 68787.

Applying temperature corrections to the thermodynamic functions using traditional integral calculus can be confusing and frightening to students that are poorly prepared to manipulate the requisite differential equations. Often times the mathematical difficulties overshadow the underlying theoretical concepts. The use of a quantum mechanical program, like Spartan, may shed a great deal of light on the impact of temeprature on the thermodynamic functions and may serve as an introduction to the energy partition fucntions used in statistical thermodynamics. Spartan will be used to demonstrate the calculation of free energy, entropy, heat capacities and energy partition functions of gases at nonstandard temperatures.

276. SPECTACULAR ISOMORPHISM BETWEEN ORDINARY AND TOTAL RESONANT SEXTET BENZENOID STRUCTURES. **Jerry R. Dias**; University of Missouri-Kansas City, Department of Chemistry, Kansas City, MO 64110-2499

No abstract available.

277. GENERAL CHEMISTRY WITH TI-CBL SYSTEMS. **James Gordon**; Central Methodist College, 411 CMC Square, Fayette, MO 65248.

The ease of use, relative low cost and variety of sensors available for the Texas Instruments Calculator-Based Laboratory (TI-CBL) systems have made possible their wide application in the chemistry laboratories at Central Methodist College. The focus of this presentation is on the particular use of the spectrometer and pressure sensors for kinetic experiments and spectrophotometric titrations. Additional comments will be made on other sensors. The excellent compatibility between the CBLs and "dated" computer systems and the use of Microsoft Excel in data manipulation and presentation will also be discussed.

278. CHEMICAL SOFTWARE AND COMPUTATION IN 2002. **Robert R. Pavlis**; Pittsburg State University, Department of Chemistry, Pittsburg, KS 66762.

Today, over twenty-five years after microcomputers were first produced, the quality and quantity of scientific software is amazing. The vast majority of these computer programs are provided by their authors free of charge and they can simply be downloaded from the internet. Most of the free programs are produced at universities and government laboratories and are of at least as high quality as commercial programs. The present generation of microcomputers are more

powerful than the most powerful computer ever built prior to 1990. It seems almost criminal to use them only for typing and playing games! This talk will survey the most useful and the best free physical and chemical software.

279. ADVANCED SPREADSHEET FEATURES FOR CHEMISTS (STUDENTS AND FACULTY). **Charles Greenlief**; Emporia State University, Dept. of Chemistry, CB 4030, 1200 Commercial Street, Emporia, KS 66801-5087.

The ready availability of spreadsheets provides today's chemists with an impressive set of tools. Further, spreadsheets require only a short learning curve. We should make maximum use of these tools as a means of solving problems. Further, faculty must rethink some of the traditional ways that they use to analyze problems. Examples that require linear and nonlinear regression will be examined. The Solver function within Excel is used to investigate several different models. The model with the minimum sum of squared errors is generally selected as the most appropriate model. Statistical tests are used to choose between polynomial models of various degrees of complexity.

280. AN ORGANIC LAB COURSE THAT USES PRINCIPLES OF GREEN CHEMISTRY. **Peter Hamlet**; Pittsburg State University, 1701 S. Broadway, Pittsburg, KS 66762.

An organic chemistry laboratory course has been developed that applies the principles of green chemistry in matters of waste and safety. The procedures and concepts needed to run organic reactions can be taught using organic chemicals on the FDA GRAS list and water solvent. Research on soybean oil at the Kansas Polymer Reseach Center here prompted a green polymer experiment and a Raoult's Law experiment.

281. USING CRYSTAL STRUCTURES TO TEACH VSEPR AND VALENCE BOND STRUCTURAL MODELS. **Russell G. Baughman**; Truman State University, Division of Science, Kirksville, MO 63501.

Since chemistry is an experimentally-based endeavor, lecture and textbook topics would best be introduced by using lab results as the stimulus. Specifically, VSEPR and valence bond models can be more effectively introduced using the results of single crystal X-ray experiments (a.k.a. "crystal structures"). As these results are precise (4 significant figures for distances and angles) and are readily available, utilization gives a more realistic justification for the introduction of the models based on real results. Students see why and when one would predict central atom angles of 109°, 120°, etc. The values are from experimental results, not because a

model kit happens to be drilled at those angles. Initial anecdotal outcomes are positive.

282. GREEN CHEMISTRY FOR THE GREEN TEAM: TEACHING GREEN CHEMISTRY TO FOOTBALL PLAYERS. **Stanley E. Manahan**; University of Missouri-Columbia, 125 Chemistry Building, Columbia, MO 65211.

Green chemistry, defined most simply as sustainable chemistry, is the subject of much activity in the area of chemical education. Most of the green chemistry course materials developed so far have concentrated on organic synthesis. This paper describes a course and course materials for a terminal low-level chemistry laboratory course that emphasizes green chemistry principles. The clientele consists of a large variety of majors including agriculture, hotel/restaurant management, journalism, psychology and many others. Backgrounds range from no high school chemistry all the way through a second year honors chemistry course. Teaching green chemistry along with basic chemical principles seems to be successful in accommodating this diverse group.

283. *AB INITIO* COMPUTATION OF CARBOCATIONS. **Robert Pavlis**; Pittsburg State University, Department of Chemistry, Pittsburg, KS 66762.

Carbocations are extremely important intermediates in organic chemistry. Iso-energetic carbocation rearrangements occur on a nanosecond time scale. *Ab initio* computations on carbocations and on the structures that occur during rearrangement provide new insight into the rearrangement process. Three cations that can undergo isoenergetic hydride shifts--ethyl, 2-butyl, and 2-(2,3-dimethylbutyl)--were studied using a sixteen processor Beowulf system and the program mpqc. Cations were also studied that undergo "downhill" hydride shifts. The computational results from these studies make it apparent why these shifts occur so rapidly.

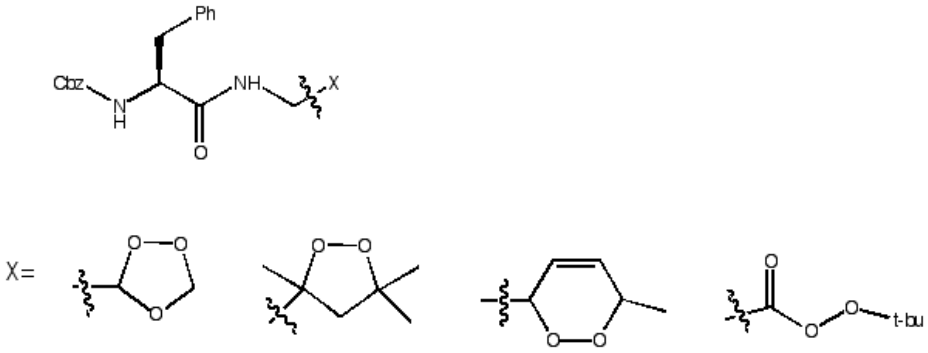
284. INHIBITORS OF EPINEPHRINE BIOSYNTHESIS THAT ARE POTENT, SELECTIVE, AND PREDICTED TO CROSS THE BLOOD-BRAIN BARRIER. F. A. Romero, Kevin R. Criscione, **Gary L. Grunewald**; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

An inhibitor of phenylethanolamine *N*-methyltransferase (PNMT) would be a useful pharmacological tool to aid in defining the role of epinephrine (Epi) in the CNS. We have prepared some new inhibitors of PNMT that should be able to cross the blood-brain barrier and that show very little affinity for other binding sites (*e.g.*, the α_2-adrenoceptor) by optimizing an earlier literature inhibitor (SK&F 29661). A

series of 3-fluoromethyl-7-*N*-(aryl- or alkyl-aminosulfonyl)-1,2,3,4-tetra-hydroisoquinolines will be described, some of which are the most potent and selective compounds yet reported. Variations of the sulfonamide side chain revealed that bulky substituents are disfavored, whereas straight chain alkyl substituents that posses an electronegative atom are favored. The 7-position binding pocket of THIQ is moderately shallow, but allows for a wide range of side chains. An interpretation of SAR results using the recently obtained crystal structure of hPNMT co-crystalized with SK&F 29661 and *S*-adenosyl-L-homo-cysteine will also be described.

285. INVESTIGATION INTO THE INHIBITION OF CYSTEINE PROTEASES BY PEROXIDES. Chunping Xu[1], **Patrick H. Dussault**[2], Tony K. Trullinger[3]; [1]University of Nebraska-Lincoln, 832 Hamilton, Lincoln, NE; [2]University of Nebraska-Lincoln, 835 Hamilton, Lincoln, NE 68588-0304; [3]University of Nebraska-Lincoln, 834 Hamilton Hall, Lincoln, NE 68588-0304.

A protected amino acid ozonide was found to accomplish rapid and stoichiometric inhibition of papain at less than 100 µM concentration. However, the instability of this particular ozonide led us to search for other classes of peroxides which could be incorporated into an amino acid framework. This presentation will discuss the preparation of two cyclic peroxides and a perester and their ability to inhibit papain.



structures of peroxides

286. DESIGN AND SYNTHESIS OF INHIBITORS OF PHENYLETHANOLAMINE *N*-METHYLTRANSFERASE (PNMT). **Jian Lu**, Kevin R. Criscione, Gary L. Grunewald; The University of Kansas, Medicinal Chemistry Dept., 1251 Wescoe Hall Dr.; Rm. 4016, Lawrence, KS 66045.

The design and synthesis of an agent that selectively regulates central epinephrine (Epi) levels has become of interest in drug design and the inhibition of the enzyme phenylethanolamine *N*-methyltransferase (PNMT) has been the most promising approach to this end. Unfortunately, most of the potent inhibitors of PNMT interact at other biologically relevant sites (*e.g.*, α_2-adrenoceptor) or are too polar to penetrate the blood-brain barrier (BBB) (*e.g.*, SK&F29661). Previous studies indicated that a 3-trifluoromethyl moiety on the 1,2,3,4-tetrahydroisoquinoline (THIQ) nucleus may not only increase the ability of these molecules to cross the BBB but also increase their selectivity for PNMT *versus* α_2-adrenoceptor due to a decrease in α_2-adrenoceptor affinity. The synthesis of a series of 3-trifluoromethyl-THIQs will be described. Some of them show high potency and selectivity toward PNMT. The effect of the 3-trifluoromethyl group on the biological activity will be discussed. Because PNMT is a bisubstrate enzyme, it is theoretically possible to make highly specific PNMT inhibitors through the multisubstrate analog approach. A series of multisubstrate inhibitors of PNMT have been designed and synthesized.

287. TENSILE STRENGTH OF PHOTOCHEMICALLY BONDED BOVINE LIGAMENT TISSUE. **Abraham L. Yousef**[1], Ricardo J. Aponte[2], George Timberlake[3], Richard S. Givens[1]; [1]University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045; [2]University of Kansas, Carr. #2 Calle Post 259N, Mayaguez, PR 00680; [3]University of Kansas Medical Center, 3901 Rainbow Blvd., Kansas City, KS 66160.

In the study of photoactivated welds as an alternative method for surgical wound repair, it is desirable to determine the strength of the weld in order to assess its performance as compared with existing wound repair technologies. The compound *N,N´*-bis-(3-diazopyruvoyl)-2,2´-(ethylenedioxy)bis-(ethylamine) (DPD) is a photoactivated diazopyruvate which acts as the welding substance for collagenous tissue. The experimental weld is realized by overlapping two rectangular slices of bovine Nuchal ligament that contain a determined amount of DPD in solution between the tissue contact surfaces; this area is then exposed to a source of light with a wavelength range of approximately 300 to 400nm for a specified amount of time. After the irradiation, the tissue samples are subjected to tensile strength measurements by pulling both ends apart with a tensiometer. Data are collected as raw voltages that are transformed into measurable units of force and used to generate stress - strain curves. After gathering a considerable group of data and comparing tensile strength values to the values obtained by control tests, no

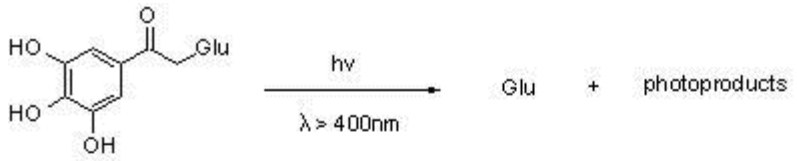
statistically significant difference could be observed for the bovine Nuchal ligament studies. To investigate the reasons for the failure of DPD to bond to primary amine groups of bovine Nuchal ligament, we performed an experiment to detect the presence of primary amine groups (RNH_2) in the tissue using the fluorescent probes dansyl chloride and *o*-phthalaldehyde. Ligament samples exposed to these fluorophores did not fluoresce more than control samples indicating that few primary amines were available for bonding. Nuchal ligaments are exceptional in their high percentage of elastin rather than collagen. In additional experiments, we examined apparently "welded" samples after tensile testing using Scanning Electron Microscopy (SEM). Examined samples showed areas of apparent bonding, but also may be exceptionally high in elastin rather than collagen. In summary, we investigated a new tissue model for photochemical tissue bonding using the bovine Nuchal ligament. Although this ligament is excellent for producing samples of uniform thickness, it is most likely inappropriate for photochemical bonding due to its high elastin content and low collagen content.

288. THE PHOTOACTIVATION OF AMINO ACID AND PEPTIDE SIDE CHAINS: NEW APPLICATIONS OF THE PHP PHOTOTRIGGER. **Jong-Ill Lee**, Christina L. Vizcarra, David R. Benson, Richard S. Givens; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Dr., Malott Hall, Lawrence, KS 66045.

The 4-hydroxyphenacyl (pHP) photoremovable protecting group has been employed to study fast biological processes through the release of the carbonylate group of a series of amino acids and oligopeptides. Now, the photorelease of pHP caged at sulfhydryl group of glutathione (γ-glutamyl-cysteinyl-glycine) and imidazole group of N-benzoylhistidine methyl ester have been studied as models for the photoactivation of pHP caged active sites for cysteine or histidine containing enzymes, respectively. The irradiation of pHP caged glutathione results in the release of glutathione accompanied by *p*-hydroxy phenylacetic acid, the rearrangement product of the protecting group, and *p*- hydroxy acetophenone, the reduced form of the protecting group. The release rate of the peptide is greater than 10^8 s^{-1} in accord with the results reported earlier for other pHP protected peptides. Rapid release of glutathione occurred from the triplet excited state of the phototrigger as shown by Stern-Volmer kinetics. The releasing efficiency was measured at various pHs and demonstrated a significant pH dependency. Upon irradiation of pHP caged histidine, released histidine and *p*-hydroxyphenyl acetic acid were generated. Side chain protection of histidine residue that extends the application of photoremovable protecting groups to metaloenzyme is in progress.

289. NEW LIGHT ACTIVATED CAGED COMPOUNDS: EXTENDING THE UTILITY OF THE *P*-HYDROXYPHENACYL PHOTOPROTECTING GROUP. **Abraham L. Yousef**, Richard S. Givens; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

The photochemical release of biologically active substrates from inactive precursors called photoprotecting groups represents a valuable tool for the investigation of biological mechanisms. Photoprotecting groups offer some advantages over other more traditional methods for releasing substrates, *e.g*. release occurs without the use of any reagents and can be spatially and temporally controlled. In the past we have found that changing the substituents on the *p*-hydroxyphenacyl chromophore affects the photochemical behavior. We wish to extend our studies of this phototrigger by synthesizing 3,4,5-trihydroxy-phenacyl glutamate, **1**, which should exhibit enhanced solubility in aqueous media and extended absorption into the visible region. This would allow for the photochemical release of substrates such as glutamate using light sources of much lower energy.



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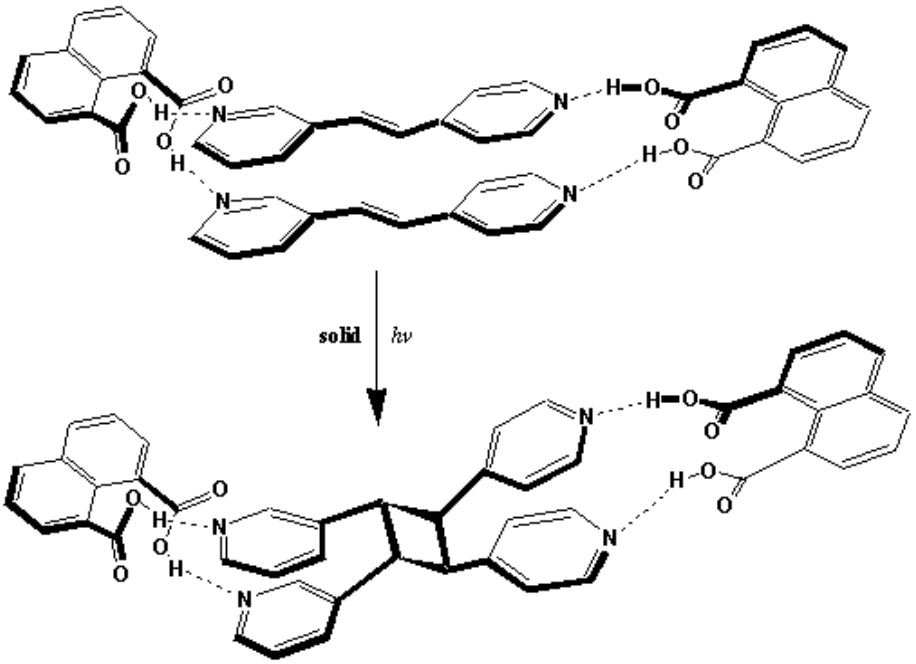
290. REGIOCONTROL OF REACTIVITY IN MOLECULAR SOLIDS USING LINEAR TEMPLATES. Dushyant B. Varshney, **Leonard R. MacGillivray**; University of Iowa, 423D Chemistry Building, Iowa city, IA 52242.

Our group is currently using rigid molecules as linear hydrogen bond donor templates (based on resorcinol or 1,8-naphthalenedicarboxylic acid) to organize olefins within discrete molecular complexes favorable for [2+2] photoreaction. This approach has been utilized to make rctt-tetrakis(4-pyridyl)cyclobutane stereospecifically by controlling reactivity in *trans*-1,2-bis(4-pyridyl)ethylene (hydrogen bond acceptor reactant) with symmetrically substituted pyridyl units. In this talk, we focus upon extending this approach to control reactivity regio-specifically if unsymmetrical pyridyl units (hydrogen bond acceptor site) are attached to the olefinic reaction center (Scheme 1). Such an approach to control reactivity in various unsymmetrical dipyridyl ethylene reactants will provide a general way to achieve regiocontrolled synthesis in solid-state.

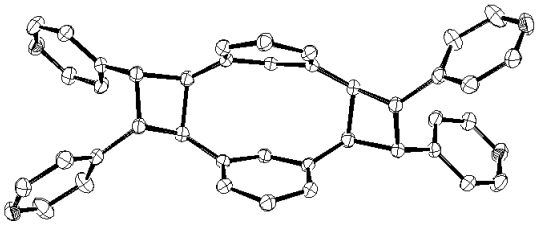


Scheme 1

291. TOWARDS SHAPE CONTROL: TEMPLATE-DIRECTED SOLID-STATE SYNTHESIS OF CYCLOPHANES. Tomislav Friscic, **Leonard R. MacGillivray**; University of Iowa, 305 Chemistry Building, Iowa City, IA 52242-1294.

Template-directed solid-state synthesis is a developing synthetic method of high stereoselectivity. That stereoselectivity comes from preorganizing reactants via linear template molecules, a concept regularly employed in nature. We have used substituted resorcinols as linear templates in orienting unsymmetrical olefins for a solid-state [2+2] photodimerization, thus enabling a regiospecific synthesis of cyclobutanes. Resorcinols have also been used to orient linear diolefins, providing a high yield route to *p*-cyclophanes. Further development of template-directed solid-state synthesis as a synthetic tool requires resorcinols to accommodate reactants of different shapes. This is now demonstrated by the preparation of photoreactive assemblies of a V-shaped substrate 1,3-bis[2-(4-pyridyl)-ethenyl]benzene (**1**) with substituted resorcinol templates. Formation of assemblies between **1** and various resorcinols has been accomplished by

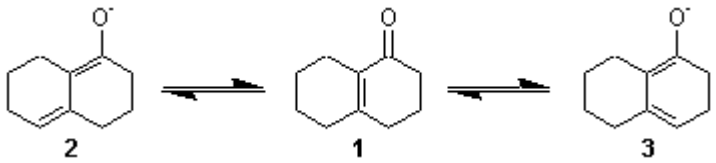
crystallizing **1** from a solution containing the resorcinol derivative and confirmed by X-ray crystallography and ^{1}H NMR spectroscopy. UV-irradiation of the cocrystals resulted in a highly stereoselective synthesis of *syn-m*-cyclophane products in 100 % yield.



An ORTEP picture of one of the cyclophane products

292. ENOLIZATION OF $\Delta^{9(10)}$-1-DECALENONE: RELATIVE STABILITIES OF ENDOCYCLIC AND EXOCYCLIC DIENOLATES. **David C. Hawkinson**, Ying Wang; University of South Dakota, 414 E. Clark Street, Vermillion, SD 57069.

In order to evaluate the relative stabilities of endocyclic and exocyclic dienolates, we have examined the enolization of $\Delta^{9(10)}$-1-decalenone (**1**). This α,β-unsatutated ketone has two distinct γ positions, γ_{exo} and γ_{endo}, deprotonation at which leads to, respectively, the exocyclic/s-*trans* (**2**) and endocyclic/s-*cis* (**3**) dienolates. GCMS and NMR studies of deuterium exchange with solvent (D_2O/CD_3OD/NaOD) demonstrate three pairs of protons in **1** (α, γ_{exo}, and γ_{endo}) exchange at different rates. Pseudo-first-order rate constants for exchange of the γ-protons with solvent deuterium were determined by monitoring the decrease in ^{1}H-NMR peak areas with time. These studies show that the γ_{exo} protons exchange ca. 11-fold faster than γ_{endo} protons (k_{exo} = 9.68 (± 0.63) x 10^{-3} $M^{-1}s^{-1}$, k_{endo} = 8.39 (± 0.49) x 10^{-4} $M^{-1}s^{-1}$). Using a Bronsted β value of 0.5 for deprotonation at the γ_{exo} and γ_{endo} positions, the exocyclic/s-*trans* dienolate (**2**) is calculated to be 2.9 kcal/mol more stable than the endocyclic/s-*cis* dienolate (**3**). The assumption that the contribution to the relative stabilities of **2** and **3** due to dienolate geometry (s-*cis* vs. s-*trans*) is 1.7 kcal/mol (Eldin, *et al*. *J. Org. Chem.* 1993, 7100.) leads to the conclusion that the differential effect of exocyclic and endocylic double bonds on dienolate stability is 1.2 kcal/mol.

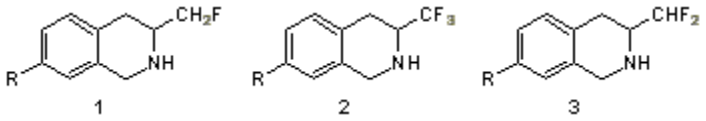


293. DOES CONTRACTION OF THE X-Y BOND SHOW SET CHARACTER IN *ALPHA*-NUCLEOPHILES? **Kenneth R. Fountain, Jr.**, Nathan Billington; Truman St. University, 221 Science Hall, Kirksville, MO 63501.

The *alpha*-effect is a nucleophilicity greater than predicted by pKAH of the nucleophile. We have previously shown that at least part of the expression of the effect is electronic. This paper is a study of computational chemistry of simple *alpha*-nucleophiles. The contraction of the :X-Y: bond length in the S_N^2 transition state may be related to the Hoz model for the *alpha*-effect. Discussion of two models of the *alpha*-effect will be included in this report.

294. SYNTHESIS AND EVALUATION OF 3-DIFLUOROMETHYL-1,2,3,4-TETRAHYDROISOQUINOLINE (THIQ) INHIBITORS OF PHENYL-ETHANOLAMINE-*N*-METHYLTRANSFERASE (PNMT). **Mitchell R. Seim**, Gary L. Grunewald, Kevin R. Criscione; University of Kansas, 4070 Malott Hall, Lawrence, KS 66045.

In order to elucidate the role of epinephrine in central nervous system functions, potent and highly selective inhibitors of PNMT are required. Most previously studied PNMT inhibitors also show activity at the α_2-adrenoceptor, which complicates the interpretation of their biological activity. Earlier work in our group has shown that modifying substituents on the 3- and 7-positions of the 1,2,3,4-tetrahydroisoquinoline (THIQ) nucleus affects potency and selectivity for PNMT over the α_2-adrenoceptor. We have synthesized a series of 3-fluoromethyl- (**1**) and 3-trifluoromethyl-7-substituted-THIQs (**2**), which are some of the most potent and selective inhibitors of PNMT yet reported. 3-Difluoromethyl-THIQs bearing various substituents in the 7-position (**3**) have now been synthesized. A comparison of the biological activity and the physical chemical properties of these new inhibitors with **1** and **2** will be presented. The data for these compounds will be explained using the newly acquired X-ray crystal structure of PNMT.



295. DYNAMICS, STRUCTURE AND INTERACTIONS OF CALMODULIN IN SOLUTION. **Krzysztof Kuczera**, Cheng Yang; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045.

Molecular dynamics simulations of 4 ns length have been performed for the protein calmodulin in its three functional forms: calcium-free, calcium-loaded and in complex with both calcium and a target peptide. The simulations employed

explicit water under realistic conditions of constant temperature and pressure, included the presence of a physiological concentration of counterions and the use of Ewald summation to avoid truncation of long-range electrostatic forces. The most interesting information provided by the simulations is that the dynamics of calcium-loaded and calcium-free calmodulin in solution is dominated by slow rigid motions of the globular N-terminal and C-terminal domains. In these motions the interdomain distance varies by up to 10 Å, and the relative orientations of the domains change by up to 110 deg. In the simulations calmodulin exhibited larger solvent accessible surface areas than seen in experimental structures determined by x-ray crystallography and solution NMR. A surprising outcome of this effect was that quite similar solvent accessibilities were seen for the hydrophobic patches of calcium-free and calcium-loaded calmodulin. Thus, our simulations suggest a re-examination of the standard model of the structural change of calmodulin upon calcium binding, involving exposure of the hydrophobic patches to solvent. In contrast to the calcium-free and calcium-loaded systems, the calmodulin-peptide complex was quite rigid and did not exhibit any significant domain motions. Analysis of the interactions showed that the largest favorable contribution to peptide binding comes from burial of nonpolar surface upon complex formation, consistent with a classic hydrophobic effect. In the nonpolar interactions a crucial role is played by the nine methionines of calmodulin. Our simulation results were consistent with a wide range of experimental studies, including NMR, fluorescence, x-ray, cross-linking, calorimetry and mutagenesis. Additionally, a range of mechanistic microscopic information emerged which is useful in explaining the activity of the protein but is difficult to measure experi- mentally.

296. UREA/WATER MIXTURES AND THEIR ROLE IN PROTEIN DENATURATION. **Paul E. Smith**; Kansas State University, Department of Biochemistry, Manhattan, KS 66506.

A new force field for the simulation of mixtures of urea and water will be presented. The force field reproduces the thermodynamics of urea solutions as described by Kirkwood-Buff theory. Simulations of native and denatured lysozyme in 8M urea using the new model give estimates for urea association with both forms of the protein which are in good agreement with experiment. Further analysis of the simulations suggests urea preferentially associates with the peptide backbone on denaturation.

297. HETEROGENOUS PHASE STRUCTURE IN COLLOIDAL SUSPENSIONS. **Kenneth S. Schmitz**; University of Missouri-Kansas City, 5100 Rockhill Road, Department of Chemistry, Kansas City, MO 64110.

Under certain conditions colloidal suspensions exhibit a heterogeneous structure sometimes referred to as a "two state" structure, "spinodal instability" or a "phase separation". The "conventional wisdom" is to approach this problem via "effective pair interactions". Shortcomings of analytical theories based on a screened Coulomb pair interaction are discussed. As an alternative view of colloidal suspensions an "orbital model" is proposed in which the distribution of the micro-ions are being dictated by the specific configuration of all the macro-ions in the system, much in the same way that electron distributions in molecules are determined by the array of atoms. Brownian dynamics simulations were performed for two similar clusters (a 7-particle diamond shape array or an 8-particle simple cubic array) at the volume fraction of *phi* = 0.01. It was found that as the two clusters approached each other the diamond cluster system became less stable whereas the simple cubic cluster system became more stable. This difference in behavior is attributed to the relative abilities of these structures to "share" counterions and the exclusion of the co-ions.

298. SIMULATION OF THE VIBRATIONAL RELAXATION OF IODINE IN XENON. **Shenmin Li**, Ward H. Thompson; University of Kansas, Chemistry Department, 2010 Malott Hall, Lawrence, KS 66045-7582.

A mixed quantum classical surface hopping approach is used to simulate the vibrational relaxation dynamics of iodine in liquid xenon for a long time scale up to 0.5ns. During the process, the vibrational degree of freedom of the I2 solute is treated quantum mechanically using a potential optimized discrete variable representation (PODVR) while all the other degrees of freedom are treated classically. A computationally efficient Lanczos algorithm is used to solve for the lowest several vibrational eigenvalues and eigenvectors. The vibrational relaxation of I2 is observed as vibrational nonadiabatic transitions among the three lowest vibrational states, included by the solvent bath which consists of up to 256 Xe atoms. The effects of quantum decoherence in the surface hopping simulations are considered. The results are also compared with the most prevalent approach for calculating relaxation lifetime based on perturbation theory.

299. PARTIAL CHEMICAL POTENTIALS IN THE VAPOR-LIQUID EQUILIBRIA OF HYDROCARBON-LIKE MIXTURES BASED ON THE MOLECULAR INTEGRAL EQUATION THEORY. D. S. Wilson, **Lloyd Lee**; University of Oklahoma, Dept. of Chemical Engineering, Norman, OK 73019.

In vapor-liquid equilibria of liquid mixtures where a supercritical component is present, many conventional correlations fail due to the ambiguities in deciding the reference fugacity for this substance at the temperature and pressure and the state of matter (liquid state) involved. This is particularly serious when the activity coefficient models are used (NRTL, UNIQUAC, Wilson, etc.) Since at the given temperature the supercritical component is gaseous, not a liquid, it does not have a "vapor pressure". Therefore the pure state cannot be used as reference and the activity coefficient is ill-defined. In this paper, we used the integral equations for the molecular distribution functions, as given by the Oznstein-Zernike equations in statistical mechanics, to calculate for mixtures of hydrocarbons (say, A+B species) the contributions from individual components, including the supercritical components, and determine the partial chemical potentials (μA= xAμAA + xBμBA)and partial pressures (PA= xAPAA + xBPBA). These statistical mechanical quantities are then characterized with respect to the state conditions and used as standards to test different Ansatzes (assumptions) used in literature. We find that these partial chemical potentials, not being analyzed thus far, are powerful tools for elucidating the phase behavior of vapor-liquid equilibria.

300. FREEZING OF WATER CONFINED TO HYDROPHOBIC NANOPORES. **Xiao Cheng Zeng**[1], K. Koga[2], H. Tanaka[3], Guang-tu Gao[4]; [1]University of Nebraska-Lincoln, 536 Hamilton Hall, Lincoln, NE 68588; [2]Fukuoka University of Education, Japan; [3]University of Okayama, Japan; [4]U.S. Naval Academy, MD.

Phase behavior of water confined to nanometer-sized hydrophobic pores was studied by means of molecular dynamics simulation method. In quasi-one-dimensional cylindric pores, it is found that the "polymorphous phase transition" is very sensitive to the diameter of the pore. The simulation suggests that upon cooling, a first-order freezing-like transition to hexagonal and heptagonal ice nanotubes, or a continuous phase transformation into solid-like square or pentagonal ice nanotubes can happen, depending upon the diameter (1.1 - 1.4 nm) of the hydrophobic pore. That the isotherms for a given diameter are found to be similar to those near the liquid-gas critical point of bulk fluids suggests possible existence of a phase boundary terminated by a critical point. In quasi-two-dimensional slit pores, both polymorphic and polyamorphic phase transitions were found. The latter transition arises in the supercooled water confined to the pore with a fixed width, in which crystallization to the bilayer ice is prohibited.

301. COMPUTATIONAL STUDY OF IONIC DEFECTS IN ICE IH. **Patricia L. Plummer**; University of Missouri-Columbia, 201 Physics, Columbia, MO 65211.

Continuing our investigations of the energetics associated with defect formation and migration, both *ab initio* energy structure calculations and molecular dynamics simulations are carried out on model ice clusters containing one or more ionic defects. Previous studies in this series have identified structures containing defects that are stable at 0 K or that are transition states between such structures. However, results from this lab and elsewhere have shown that the energy required for the production or migration of a defect is more complex than merely the energy difference between the static structures. Cooperative motion of neighbors to the defect site can either increase or decrease the energy involved to produce or annihilate the defect. Thus experimental measurements associated with the energy of defects in ice can differ substantially from those found using static models. By increasing the complexity of the model, the results described in this report attempt to more realistically simulate a defect-containing ice system. The initial structures are energetically stable—minima on the electronic energy surface—and contain one or more ion defects. Since the method and amount of energy injection can alter the migration path, the energy is introduced into the system in a variety of ways. The structural evolution of the ice system is then monitored as a function of time.

302. THE EFFECT OF ATTRACTIVE FORCES ON PARTICLE DIFFUSION. **Yao A. Houndonougbo**, Brian B. Laird; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

Understanding the role of attractive forces in fluid diffusion has been an important goal in liquid state physics and chemistry. Hard-sphere fluids with attractive potential tails have been used with success in understanding the structure and thermodynamics of simple liquids, but it has been difficult to extend this work to dynamics due to the lack of a viable molecular-dynamics method. Using an algorithm for isothermal (NVT) molecular-dynamics recently developed by us for mixed hard-core/continuous potentials, we present simulation results of the effect of the inverse-six attractive tail in hard-sphere particles diffusion. The change of the diffusion for a given density under the influence of the attractive tail strength as well as the relative effect of the attractive forces on the diffusion when the density is increased are discussed. Also, we compare our results with that of dynamical perturbation theory.

303. FREQUENCY-DEPENDENT FIRST HYPERPOLARIZABILITIES FROM LINEAR ABSORPTION SPECTRA. **Anne M. Kelley**; Kansas State University, 111 Willard Hall, Department of Chemistry, Manhattan, KS 66506-3701.

Some of the most promising new materials for electro-optic applications (*e.g*. fast modulators and switches in telecommunications) are polymers that contain donor-acceptor substituted "push-pull" organic chromophores. The first hyper-polarizabilities (β) of such molecules are generally described using a model in which the lowest excited electronic state dominates the optical response. It is shown that within the usual assumptions accompanying this two-state model, $\beta(-2\omega;\omega,\omega)$ can be expressed in terms of a Kramers-Kronig transform of the linear optical absorption spectrum. The method is applied to several push-pull chromo-phores and is compared with experimental data where available. Comparison of calculated and measured frequency dispersions is suggested as a purely experimental method, requiring no additional parameters, to test the assumptions of the two-state model.

304. STRUCTURAL DESIGN CRITERIA FOR OXYANION RECEPTORS. **Ben P. Hay**[1], David A. Dixon[1], Maciej S. Gutowski[1], Bruce A. Moyer[2], Jeffrey C. Bryan[2], [1]Pacific Northwest National Laboratory, P.O. Box 999, MSIN K1-83, Richland, WA 99352; [2]Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831.

Organic hosts for oxyanion complexation can be constructed by combining two or more hydrogen bonding sites. The deliberate design of architectures for such hosts requires knowledge of the optimal geometry for the hydrogen bonds formed between the host and the guest. Important structural parameters include the O--H distance, the O--H-D angle, the X-O--H angle and the X-O--H-D dihedral angle (H-D=hydrogen bond donor, X=any atom). This information can be obtained through the analysis of hydrogen bonding observed in crystal structures and electronic structure calculations on simple gas-phase complexes. In this talk, we present optimal geometric parameters for hydrogen bonds with trigonal planar and tetrahedral oxyanions based on a survey of the Cambridge Structural Database and density functional theory calculations on complexes of water, alcohol and amide hydrogen donors with the oxygen atom acceptors in nitrate and sulfate.

305. AMIDO-PYRROLE CLEFTS. Salvatore Camiolo, Christopher P. Chapman, Korakot Navakhun, Graham J. Tizzard, **Philip A. Gale**, Michael B. Hursthouse, Mark E. Light, Andy J. Shi, Colin N. Warriner; University of Southampton, SO17, Southampton, United Kingdom.

Recent developments in the area of anion recognition and sensing have produced a variety of new selective receptors for anions. However, the great variety of anionic species and their importance in the environment (pollutant anions from overuse of agricultural fertilizers cause eutrophication of lakes and inland waterways), biological systems (misregulation of anion transport is responsible for a number of medical conditions including cystic fibrosis) and in the clinic (the maintenance of sulfate anion concentration in dialysis patients continues to be problematic) presents a continuing challenge to design selective receptors. The anion coordination ability of receptors containing pyrrole groups has been an area of increasing interest in the last decade. A smaller sub-set of receptors containing both a pyrrole and an amide moiety have been described. Many of these systems are quite complex, for example Sessler and Vogtle's elegant catenane for oxo-anion complexation. More recently, Schmuck has shown that guanidinium groups that contain an appended pyrrole-amide moiety are useful in the selective complexation of amino acids. We decided to 'extract' the pyrrole amide unit and synthesize a variety of simple pyrrole-amide ligands in order to assess the anion complexation ability of this moiety alone. In addition to forming interesting hydrogen bonding arrays in the solid state, these compounds do function as anion receptors in solution. For example receptor **1** has been shown to be an oxo-anion selective (benzoate and dihydrogenphosphate) receptor in DMSO/water 0.5%. Receptor **2** shows a high affinity for hydrogen sulfate (presumably due to proton transfer from the anion to the receptor enhancing binding the interaction) whilst receptor **3** is a much weaker hydrogen sulfate receptor. Compound **4** acts as an electrochemical anion sensor through perturbations in the ferrocene/ferrocenium redox couple, whilst the anionic ligand **5** forms an unusual narcissistic dimer in solution and in the solid state.

306. ANION COORDINATION CHEMISTRY. **Kristin Bowman-James**; University of Kansas, 1017 Malott Hall, Lawrence, KS 66045.

As part of our investigation into the structural and binding aspects of anions with both polyammonium and polyamide receptors, we have identified certain structural motifs that correlate well with those found in transition metal coordination complexes. The polyaza cryptands derived from Schiff base condensations of tren with *m*- and *p*-xylyl dialdehydes are particularly illustrative of this trend. In their polyammonium form, they are capable of internal binding of anions, including ditopic inclusion of nitrate, as well as cascade types of complexes with bridging water molecules. In their neutral form these systems have long been noted for

their ditopic binding of metal ions and for forming cascade complexes in which two metal ions are bridged by an anion. In studies of mixed polyamine/polyamide systems, we have isolated a complex that mimics another type of transition metal corollary, a sandwich complex, where, instead of a metal ion, sulfate is bound between two tetraamide macrocycles. In extensions of these polyamine/ polyamide systems, we have quaternized the polyamine sites to add electrostatic complementarity to the host with the idea of forming even stronger complexes with a variety of anions. Structural and chemical aspects of these anion coordination complexes will be described.

307. CATALYTIC PARTIAL OXIDATION OF ALCOHOLS AT SHORT CONTACT TIMES. Brent E. Traxel, **Keith L. Hohn**; Kansas State University, 105 Durland Hall, Manhattan, KS 66506-5102.

Current efforts to use hydrogen fuel cells to power automobiles require novel catalytic solutions to selectively convert liquid fuels to hydrogen on-board. Such a catalytic process must be capable of producing CO-free hydogen in a small reactor and must be capable of rapidly responding to power demands. Catalytic partial oxidation at short contact times offers significant potential for this application. In these reactors, pre-mixed fuel and oxygen flow over a noble metal-coated ceramic monolith. Reaction is ignited by preheating the catalyst, after which time the reactor runs autothermally and adiabatically. These reactors are capable of producing large amounts of hydrogen in a small reactor without the addition of any process heat. Much is known about the use of these reactors for partial oxidation of hydrocarbons. However, our research group is the first to use them for conversion of alcohols. Because alcohols represent a possible liquid fuel for use in hydogen fuel cell-powered vehicles, our laboratory has started a research program to study catalytic partial oxidation of alcohols. Catalytic partial oxidation of methanol over rhodium or platinum occurs readily over a wide range of methanol to oxygen ratios. Ratios as high as five to one have been achieved without extinguishing reaction. This in contrast to hydrocarbons which have a much narrower operating region. While hydrogen and CO are always the primary products, the methanol to oxygen ratio dramatically affects reactor temperature, methanol conversion and product selectvities. As the methanol to oxygen ratio is increased, temperature and methanol conversion decrease while hydrogen selectivity increases. CO selectivity, however, initially increases until a ratio of around three, but then decreases. Results on platinum and rhodium are quite similar. A general reaction mechanism is proposed for these results. In this mechanism, methanol is partially combusted to generate heat for reaction but also is decomposed to CO and hydrogen. After oxygen is consumed, the water-gas shift reaction modifies the product composition. Equilibrium calculations support this argument. This paper will present the results for methanol partial oxidation as

well as ongoing work on ethanol oxidation. Reaction mechanisms will be discussed to explain the observed trends.

308. INVESTIGATION OF THE STABILITY OF $LaCoO_3$ AND $SrFeCO_{0.5}O_x$ SUPPORTS FOR THE CARBON DIOXIDE REFORMING OF METHANE IN THE PRESENCE OF OXYGEN. Bakul Pant, **Susan M. Stagg-Williams**; University of Kansas, 4006 Learned Hall, 1530 West 15th Street, Lawrence, KS 66045.

$LaCoO_3$ and $SrFeCo_{0.5}O_x$ (SFC) have been evaluated as potential catalytic supports for the dry reforming and combined dry reforming-partial oxidation reactions of methane. These supports were selected based upon their oxygen storage and release capacity, which has been shown to enhance performance for the dry reforming reaction. The catalysts investigated have been characterized by temperature-programmed reduction (TPR), BET surface area analysis, chemisorption and X-ray diffraction studies (XRD). Two $SrFeCo_{0.5}O_x$ supports were investigated. The first was prepared in our laboratory using citric acid as a solvent (SFC-citric). The second was obtained from Superconductive Components (SFC-comm). XRD prior to reaction showed that the structure of the two SFC materials was similar to the structure previously reported in the literature. Both materials showed no significant activity for the dry reforming reaction. Characterization after reaction by XRD showed that the structure of SFC-comm was significantly altered, while the SFC-citric was thermally stable. After exposure to 800°C, the BET surface area of the materials was very low resulting in low Pt dispersions. A small increase in the methane conversion was observed in the presence of oxygen. Surprising, no CO production was observed and CO_2 was produced during the reaction. The $Pt/LaCoO_3$ catalyst exhibited low activity for the dry reforming reaction. An induction period during the first two hours of reaction was observed in which the conversion of methane increased before decreasing again. In the presence of oxygen the induction period was not observed and the initial methane conversion increased to 20%. However, catalyst deactivation still occurred with minimal methane conversion after 5 hours. XRD analysis showed that the perovskite structure of the support was not present after exposure to reaction. Significant reduction of the supports below the reaction temperature was verified by TPR. This reduction of the support and, in some cases, complete structural change results in low levels of Pt being exposed for the reaction and subsequent low activity. Our studies have shown that these materials are not suitable for the dry reforming reaction at elevated temperatures, but may be promising materials for reactions requiring oxygen release at lower temperatures, such as CO oxidation.

309. RAPID ALGORITHMIC DETERMINATION OF STOICHIOMETRICALLY EXACT MECHANISMS OF THE CATALYTIC REACTIONS: ILLUSTRATION. Shahram Shafie[1], **L.T. Fan**[1], Botond Bertok[2], Ferenc S. Friedler[2], Hodong Seo[3], Sun Won Park[3]; [1]Kansas State University, 105 Durland, Manhattan, KS 66506-5102; [2]Egyetem U. 10, H-8200, Veszprem, Hungary; [3]373-1, Kusong-dong, Yusong-ku, Taejon, 305-701, Korea.

A rapid algorithmic method has recently become available to determine the stoichiometrically exact candidate mechanisms from a set of plausible elementary reactions for deriving the rate law of a catalytic reaction. The method is based on the unique graph-representation, a set of axioms and a group of combinatorial algorithms. In the method, the inclusion or exclusion of a step of each elementary reaction in the mechanism of concern hinges on the general combinatorial properties of feasible reaction networks. The method's efficacy is demonstrated with some examples.

310. DESTRUCTIVE ADSORPTION OF CF_2Cl_2 OVER NANOCRYSTALLINE MgO PROMOTED WITH VANADIA. Galina I. Aleshina[1], Ilya V. Mishakov[1], Maxim S. Mel'gunov[1], Sergei V. Tsybulya[1], Alexander F. Bedilo[2], **Alexander M. Volodin**[1], Kenneth J. Klabunde[2]; [1]Boreskov Institute of Catalysis, Prospekt Lavrentieva, 5, Novosibirsk, Russia 630090, Russia; [2]Kansas State University, Department of Chemistry, Manhattan, KS 66506.

Nanocrystalline MgO is an efficient sorbent for many halogenated organic compounds. Its modification with transition metal ions is known to be an effective means for decreasing the temperature of such reactions. In the present communication we suggest a new technique for vanadia deposition on the surface of nanocrystalline MgO from melted V_2O_5 and NH_4VO_3. VO_x/MgO samples with surface areas as high as 400 m^2/g have been prepared by this method. The phase composition and morphology of the compounds formed on the surface have been studied in a wide range of vanadium concentrations and catalyst activation conditions. The formation of VO_x/MgO catalysts has been found to result in a considerable decrease of the induction period during CF_2Cl_2 destructive adsorption and allow for much milder conditions of the process. The mechanism of the vanadium promoting action, the structure and properties of active sites on the surface of VO_x/MgO catalysts will be discussed.

311. DETOXIFICATION OF MICROCYSTINS BY HALOGEN-LOADED MAGNESIUM OXIDE NANOPARTICLES. **Peter K. Stoimenov**[1], George L. Marchin[2], Kenneth J. Klabunde[1]; [1]Kansas State University, 111 Willard Hall, Manhattan, KS 66506; [2]Kansas State University, Manhattan, KS 66506.

Microcystins are a group of hepatotoxins that are produced by blooming of the cyanobacteria *Microcystis Aeroginosa*. Blooming of these cyanobacteria has been found worldwide, including Canada, USA, Germany, France, Hungary, China, etc. Besides the high toxicity, the microcystins are found to be strong carcinogens as well as to have mutagenic properties. All well established water treatments, such as domestic water filters, chlorination and filtration only marginally affect the microcystins concentration and cannot decrease it to the levels recommended by EPA. There are methods developed to completely oxidize the toxin, which are expensive and difficult to implement or release non-acceptable residues in the treated water. Here we report quick (in less than 30 min) and complete detoxification of a microcystin loaded water by treatment with halogen-loaded magnesium oxide nanoparticles. The high surface area of the nanoparticulate material combined with the enhanced reactivity of the adsorbed halogen create very favorable conditions for halogen addition to a key part of the structure in all microcystin molecules. MALDI mass-spectra confirm the addition of halogen to the microcystin molecules, thus rendering them non-toxic.

312. SURFACE MODIFICATION OF NANOCRYSTALLINE MAGNESIUM OXIDE WITH SURFACTANT MOLECULES. **Jeevanandam Pethaiyan**, Kenneth J. Klabunde; Kansas State University, Willard Hall, Department of Chemistry, Manhattan, KS 66506.

Surface modification of nanoparticles can often resolve issues such as poor wettability, stability and dispersability. Proper control of the particle surface is necessary to avoid agglomeration. To modify the surface of nanocrystalline magnesium oxide prepared by aerogel route (AP-MgO), cationic as well as anionic surfactants have been adsorbed from various non-aqueous solvents. The adsorption properties of the surfactants have been studied by measuring the adsorption isotherms. Aerosil OT (AOT) and didodecyl dimethyl ammonium bromide (DDAB) have been chosen as examples of anionic surfactant and cationic surfactant, respectively. It was found that (1) anionic surfactant is adsorbed in higher amounts than cationic surfactant, (2) more surfactant is adsorbed from the least polar solvents, (3) surface hydroxyl groups on AP-MgO do not seem to play a role and (4) nanocrystals adsorb the most anionic surfactant/nm^2 compared to conventionally prepared magnesium oxide (CP-MgO) and commercial magnesium oxide (CM-MgO). These results have been interpreted on the basis of the fact that nanocrystals possess increased surface reactivity compared to microcrystals. The prepared surfactant coated AP-MgO

nanoparticles could be dispersed better in several organic solvents than the bare AP-MgO nanoparticles. The surface modification of AP-MgO by the surfactant molecules also leads to a reduction in the aggregate size as determined by dynamic light scattering (DLS) and visible spectroscopy.

313. SYNTHESIS OF MODIFIED Al_2O_3 AEROGELS AND THEIR ACTIVITY IN DEHYDROCHLORINATION OF 1-CHLOROBUTANE AND (2-CHLORO-ETHYL)ETHYL SULFIDE. **Alexander F. Bedilo**, Shawn Fultz, Kenneth J. Klabunde; Kansas State University, Department of Chemistry, Manhattan, KS 66506.

The effects of solvent and gel modification with several organic and inorganic acids, and β-diketones on the textural properties of nanocrystalline alumina synthesized by modified aerogel procedure have been studied. The highest specific surface areas exceeding 1000 m^2/g were obtained for samples prepared with an ethanol-toluene mixture used as the solvent. Addition of different agents limiting the growth of alumina nanoparticles in small concentrations had a positive effect on the surface areas of the aerogels. The activity of high surface area nanocrystalline alumina materials in dehydrochlorination of (2-chloroethyl)ethyl sulfide and 1-chlorobutane compares favorably with that of other nanocrystalline metal oxides. The initial reaction rates over alumina-based aerogels could be significantly increased by surface modification with sulfate groups achieved by addition of sulfuric acid before gelation.

314. STRUCTURAL CHARACTERIZATION OF SUPERLATTICES COMPOSED OF GOLD NANOPARTICLES. **Savka I. Stoeva**[1], B. L. V. Prasad[1], Christopher M. Sorensen[2], Peter K. Stoimenov[1], Sitharaman Uma[1], Vladimir Zaikovski[3], Kenneth J. Klabunde[1]; [1]Kansas State University, 111 Willard Hall, Manhattan, KS 66506; [2]Kansas State University, Manhattan, Kansas 66505; [3]Boreskov Institute of Catalysis, Novosibirsk, Russia.

Monodisperse gold nanoparticles have been prepared by solution and vapor phase methods. The synthesis in solution utilizes the reduction of gold salts in inverse micelle media. The vapor phase method is based on the Solvated Metal Atom Dispersion technique (SMAD). SMAD employs a co-deposition of metal and organic solvent vapors on the walls of a reactor cooled to liquid nitrogen temperature. Both preparative methods result in highly monodisperse Au nano-particles stabilized by alkanethiols with different chain length. The high degree of monodispersity is a prerequisite for the organization of the gold particles in long-range 2D and 3D nanocrystal superlattices. High-resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) and X-ray powder

diffraction (XRD) have been used for the thorough elucidation of the superlattice structure formed by the gold particles prepared by the two methods.

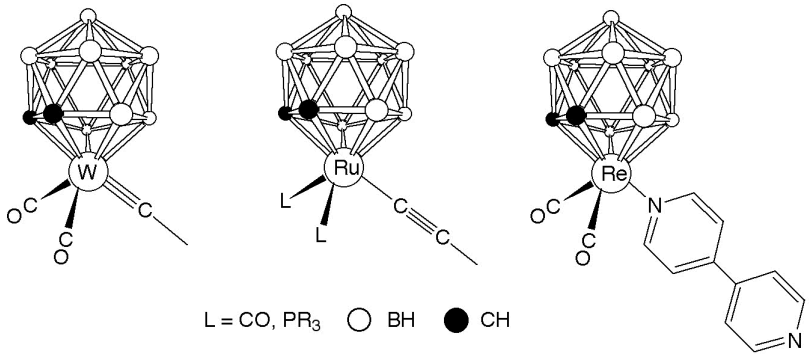
315. PRODUCTION OF ^{105}Rh FROM ^{104}Ru. Hendrik P. Engelbrecht[1], Cathy S. Cutler[2], Alan R. Ketring[2], Gary J. Ehrhardt[2], Moustapha E. Moustapha[1], Bary J. Higgins[2], **Silvia S. Jurisson**[1]; [1]University of Missouri-Columbia, Dept. of Chemistry, Columbia, MO 65211; [2]University of Missouri-Columbia, Research Reactor Center, Research Drive, Columbia, 65211.

^{105}Rh conjugated to bombesin is currently being investigated for its potential use in the treatment of prostate cancer. Radiotherapy is possible with ^{105}Rh due to its favorable half-life ($t_{½}$ = 35.4 hr) and β^- energy emission (0.567 and 0.250 MeV). Furthermore, the γ emission (306 and 319 KeV) makes imaging and dosimetry calculations possible. In the past MURR has produced milliCurie quantities of ^{105}Rh, and recently a problem was encountered with the ^{105}Rh not labeling. Extraneous metal contamination was suspected. Therefore, the aim of the study was to determine the source of contamination and try to find an oxidizing agent to replace the chlorine gas currently being utilized. The ^{105}Rh is produced by irradiating isotopically enriched ^{104}Ru (n, γ reaction) to yield ^{105}Ru, which *beta* decays to form ^{105}Rh. The current separation process involves passing chlorine gas through a solution of NaOH to generate NaOCl, which acts as the oxidizing agent. The Ru metal is oxidized to RuO_4, distilled off and trapped in an HCl trap for recycling, leaving the ^{105}Rh behind in the impinger. Natural and enriched Ru targets were prepared, processed and analyzed by ICP-MS to determine the source of contamination. Other oxidizing agents such as $NaClO_2$, $NaClO_3$ and $Na_2S_2O_8$ were investigated as replacements in the current process. The source of contamination was found to be trace metals in the enriched target material and new target material has been ordered. The best result for the oxidation of the Ru was obtained with $Na_2S_2O_8$ and $NaOH/H_2SO_4/HNO_3$, but the subsequent labeling procedures seem to indicate that the SO_4^{2-} introduced by the $S_2O_8^{2-}$ yields a Rh complex that is not chemically accessible for labeling. Other means of generating NaOCl are currently being investigated, such as the electrochemical production of NaOCl from NaCl. Other “innocent” oxidizing agents that would not introduce any metal contamination such as XeO_3 are also being considered.

316. METALLACARBORANE COMPLEXES FOR OPTOELECTRONICS. **Paul A. Jelliss**; Saint Louis University, Dept. of Chemistry, Monsanto Hall 201, St. Louis, MO 63103.

We are currently devising a number of synthetic strategies for the construction of hyperconjugated 'push-pull' molecular architectures incorporating *closo*-3,1,2-metallacarborane termini. Three types of fundamental organometallic π systems

are being investigated: tungstacarborane alkylidynes, ruthenacarborane acetylides, and rhenacarborane 4,4´-bipyridyls. The metallacarborane is likely to behave as an electron-donor in such molecules, but a variety of opposing termini, both electron-donating and -withdrawing are being sought after in order to establish the precise electronic nature of these metallacarborane moieties. Synthetic procedures and preliminary analytical data will be reported.



317. FORMATION OF BIMETALLABORANES USING RHODATHIABORANE OR RHODADICARBABORANE TEMPLATES. **Lawrence Barton**, Oleg Volkov, Nigam P. Rath; University of Missouri-St. Louis, 8001 Natural Bridge Road, St. Louis, MO 63121.

The phosphine ligands on [8,8-*bis*-(triphenylphosphine)-*nido*-8,7-rhodathiaundecaborane] (1) and [9,9-*bis*-(triphenylphosphine)-*nido*-9,7,8-rhodadicarbaborane] (2) may be replaced by the bidentate phosphine, dppm, to form the species [8,8-(dppm)-8-(dppm) -*nido*-8,7-rhodathiaundecaborane] (3), and [9,9-(dppm)-9-(dppm)-*nido*-9,7,8-rhodadicarbaundecaborane] (4). This paper will describe the formation of a series of bimetallaboranes based on 3 and 4 and their derivatives. For example 3 and 4 react with the *p*-(cymene)rutheniumdichloride dimer to afford dimetallaboranes which contain the moiety [*p*-(cymene)ruthenium-dichloride(dppm)] that coordinates in a multidentate mode to Rh. Analogous products are obtained when the pentamethylcyclopentadienyl-iridium (or rhodium) dichloride dimers are used. Extension of this chemistry will describe dimetallaheteroboranes containing metallated pendent diphenylphosphine groups and also dimetallaheteroboranes formed from the insertion of a metal moiety into the open face of an *isonido*-rhodathiaundecaborane cluster. The formation of novel species resulting from removal of ligand from 3, when more electrophilic organotransition metal reagents are used, will also be described.

318. DEVELOPMENTS ON THE SYNTHESIS OF A DOUBLY WOUND 2-CATENANE. **Eric Patterson**, John G. O'Brien; Truman State University, Division of Science, 100 E. Normal St., Kirksville, Missouri 63501.

In the field of microelectronics there is a growing need for smaller and smaller circuitry. Macrocylcic polar compounds, such as a doubly wound 2-catenane, possess these qualities. They have potential to be used as a trinary, or three way switch. Two different terpyridyl ligands were synthesized to be utilized as a central octahedral turn of a doubly wound 2-catenane. The first turn was synthesized using pyridinedicarboxaldehyde in a Schiff-base reaction with *m*- anisidine, and the second using pyridinedicarboxaldehyde in a Schiff base reaction with 3-aminophenol. The structures were confirmed using NMR spectroscopy. The *m*-anisidine ligand was complexed with Ni^{2+} and the 3-aminophenol was complexed with Fe^{3+}. These cations are both potential centers for the final doubly wound 2-catenane, which may have practical application in the field of microelectronics or as a base for an oxygen carrier.

319. FORMATION AND EPIMERIZATION REACTIONS OF HALOGEN TERMINATED OLIGOMERS, $X(ARSIME)_NX$ (X = F, CL). Kevin Trankler, **Joyce Y. Corey**; University of Missouri-St. Louis, 8001 Natural Bridge Rd., St. Louis, MO 63121.

Fluorination of the oligomers $H(PhSiMe)_nH$ (n = 2, 3, 4) has been achieved with $CuCl_2$/CuI/KF in THF to give $F(PhSiMe)_nF$ as oils. In all cases a nearly statistical mixture of $F(PhSiMe)_nF$ diastereomers (2 for n = 2; 3 for n = 3; 6 for n = 4) was obtained. However, when the diastereomers of the disilane were dissolved in hexanes a single diastereomer, the *meso* form, was isolated in >50% of the original weight while the mother liquor remained as a 1:1 mixture of the two diastereomers. Epimerization of the *meso* diastereomer was observed upon treatment with catalytic amounts of anionic fluoride and chloride sources resulting in a return to the statistical diastereomeric distribution. The chloride promoted epimerization was sufficiently slow to monitor by ^1H NMR enabling acquisition of kinetic data for the series $F(ArSiMe)_2F$ (Ar = C_6H_5, *p*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *p*-$CF_3C_6H_4$, *p*-FC_6H_4).

320. REDOR NMR STUDIES OF ESTRADIOL NEUROPROTECTANTS IN DPPC BILAYERS. **Charles V. Rice**[1], Lynette Cegelski[2], Amy L. Caruano[3], Gregory P. Tochtrop[3], Zu Yun Cai[3], Douglas F. Covey[3], Jacob Schaefer[2]; [1]University of Oklahoma, Department of Chemistry and Biochemistry, Norman, OK 73019; [2]Washington University - St. Louis, One Brookings Drive, Campus Box 1134, St. Louis, MO 63130; [3]Washington University in St. Louis, Mailstop 8103, St. Louis, MO 63110.

Estradiol and related sterols are effective neuroprotectants in animal stroke models and may be useful for the treatment of Alzheimers disease. Estradiol is a free-radical scavenger that prevents oxidation of unsaturated fatty acids incorporated into the lipids of cellular membranes. $^{13}C\{^{19}F\}$ REDOR NMR was used to characterize the location and orientation of the sterol in DPPC vesicles by incorporating ^{13}C labels into the sterol and ^{19}F labels into the DPPC. Additionally, the effect of the sterol on the lipid packing density was explored by modeling the dephasing of the CH_3 lipid tails by the ^{19}F label.

321. SOLID-STATE NMR STUDY OF PHARMACEUTICAL FORMULATIONS. **Eric J. Munson**, Thomas J. Offerdahl, Christie N. Jones, Sung Jung Hong, Loren J. Scheiber; University of Kansas, 2095 Constant Ave., Department of Pharmaceutical Chemistry, Lawrence, KS 66047.

The ability to effectively deliver solid pharmaceuticals is directly related to the form of the drug in the solid state. This is important because more than 90% of all pharmaceuticals are formulated as solids. Drugs may be formulated in several different states, including amorphous, crystalline or diluted with excipients. In addition, many drugs exhibit polymorphism, or the ability to exist in two or more crystalline phases that differ in the arrangement or conformation of the molecules in the crystal lattice. We are developing solid-state NMR spectroscopy as a technique for the analysis of pharmaceuticals. We are particularly interested in characterizing the effects of formulation on the properties of pharmaceutical solids. We will describe the ability of solid-state ^{13}C NMR spectroscopy with cross polarization (CP) and magic-angle spinning (MAS) to quantify the amounts of multiple crystalline and amorphous forms present in formulations of the artificial sweetener neotame. The effects of differences in relaxation parameters and cross polarization efficiencies on characterizing mixtures of forms will be addressed. We will also show the power of ^{13}C CP/MAS NMR with selective ^{13}C labeling to follow the transformations of small amounts of amorphous forms (< 5%) present in a crystalline matrix.

322. APPLICATIONS OF SOLID-STATE NMR SPECTROSCOPY IN THE PHARMACEUTICAL INDUSTRY: THE CHARACTERIZATION OF CRYSTALLINE HYDRATES. **Susan M. Reutzel-Edens**; Eli Lilly and Company, Lilly Corporate Center, Indianapolis, IN 46285.

Hygroscopicity is an important physical property of drug materials, which can significantly impact physicochemical stability and bulk processing and handling characteristics. The propensity of molecular crystals to rapidly equilibrate with the humidity in the environment, coupled with the resultant structure-property dependence, underscores the need for characterizing these materials in the solid state as a function of relative humidity. Solid-state NMR spectroscopy, which has emerged as an extremely effective tool for the characterization of pharmaceutical materials, particularly when used in conjunction with moisture sorption analysis and X-ray crystallography, can provide unique structural information pertaining to both the structure and dynamics of water-solid interactions in crystalline hydrates. In this presentation, the moisture sorption characteristics of several active pharmaceutical ingredients are examined. By observing water indirectly through its influence on both the ^{13}C environments of the drug using the basic ^{13}C CP/MAS NMR technique and the proton spin lattice relaxation times (T1H), the structures and dynamics of crystalline hydrates have been explored. It is demonstrated that water migration in and out of crystal structures can dramatically impact proton spin lattice relaxation times (T1H), providing another basis from which polymorphs and pseudopolymorphs can be differentiated.

323. TAXOL BOUND AND UNBOUND. **David G. VanderVelde**[1], Gunda I. Georg[2], James P. Snyder[3], Minmin Wang[3]; [1]University of Kansas, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582; [2]University of Kansas, Lawrence, KS 66045; [3]Emory University, 1515 Pierce Drive, Atlanta, GA 30322.

Paclitaxel (Taxol(r)) is a natural product now in wide clinical use as an anticancer agent. This work is aimed at understanding the solution conformation and dynamic properties of paclitaxel and its semisynthetic analogs. Like many medium-sized molecules, it does not have a single folded conformation, but rapidly equilibrates between multiple low-energy conformations. On the basis of spectroscopic data alone, it is not possible to determine the number or the population of these conformers. Fitting the experimental data to a single conformation is likely to generate a high energy virtual conformation. It is also not possible to determine the distribution of conformers by computational methods alone, as different force fields give widely differing values for the energies of paclitaxel conformers. However, calculated low energy structures and experimental constraints can be combined in a variety of ways; the strategy used by Snyder and co-workers is called NAMFIS ("NMR Analysis of Molecular Flexibility in Solution"). Typically, many plausible structures with low calculated energies turn out not to be populated

significantly in solution. Conversely, conformers that contribute little to the observed NOEs can turn out to be significantly populated. Using solution state NMR, we have looked at the following questions:

- How chemical modifications to paclitaxel affect its solution conformational properties and bioactivity
- How solvent polarity affects paclitaxel conformation and dynamics
- How to interpret observed J and NOE values in light of ^{13}C T1s
- How the conformations suggested to be low energy in solution compare to those observed in x-ray crystal structures

These investigations have led to the following conclusions:

- The widely accepted view is that paclitaxel has only one or two meaningfully populated conformations, depending on the solvent; we think the actual number is 10-15.
- Most paclitaxel conformational analysis has focused on two folded conformers that lead to observable NOE's.

Each of these conformers has been suggested as the bioactive one. But extended conformers, with no characteristic NOEs, constitute up to a third of the solution conformational ensemble. In a separate project, fitting of electron diffraction data of paclitaxel bound to zinc-stabilized sheets of tubulin (the intracellular target of paclitaxel) shows that the bound state is the extended conformation.

324. MIXTURE ANALYSIS WITH NMR. **David S. Wishart**; University of Alberta, 3118 Dentistry/Pharmacy Centre, Edmonton, AB T6G 2N8, Canada.

NMR spectroscopy offers a rapid and powerful way for collecting spectral data about complex chemical mixtures. Indeed because of its remarkably good resolving power, potentially dozens of compounds can be resolved in a single ^{1}D NMR spectrum -- without the need for chromatographic separation. However, because of the complexity of these spectra (sometimes containing thousands of peaks) they often defy quantitative interpretation with respect to compound composition or concentration. Recently, we have developed automated spectral processing and spectral fitting routines which can permit the identification and quantification of small molecules in biological fluids such as blood, urine, CSF, cell extracts, milk and saliva. This novel approach offers the possibility of being able to inexpensively and non-invasively monitor food or drug metabolism and catabolism with exquisite molecular detail. In this presentation I will highlight some of the applications that this technique can and does have in studying drug metabolism, distribution, elimination and toxicology. I will also illustrate some potential applications of the technology in drug screening, in combinatorial chemistry and in clinical diagnostics.

325. LC-NMR AND LC-MS/MS FOR THE STRUCTURAL ELUCIDATION OF CIPROFLOXACIN AND ITS AQUATIC TRANSFORMATION PRODUCTS. **Laurie Cardoza**, Cynthia K. Larive; University of Kansas, Department of Chemistry, Lawrence, KS 66045.

Pharmaceuticals, such as antibiotics, have become an increasing environmental concern due to the potential impact that these drugs may have on environmental ecosystems. While these compounds may be present in the environment at low concentrations, they have the potential of impacting the existing microbial communities. Antibiotics, such as fluoroquinolones, are often prescribed in relatively high doses of which only a percentage of the active drug is effectively metabolized by the body. Although the transformation of these drugs is known with regard to their medicinal applications, little is known about the transformation of these compounds when they are introduced into a natural aquatic environment through human or animal waste streams. Understanding the fate and transformation of fluoroquinolones in the natural environment can provide insight about the potential risk these drugs may pose to an aquatic community. The degradation of the fluoroquinolone, ciprofloxacin, is being studied in aquatic systems utilizing different environmental conditions. The fate of ciprofloxacin can be monitored using LC-MS, however, the analytical challenges of this work lie in the development of methods for the detection, quantitation and structural elucidation of predominant transformation products for which standard compounds are not available. LC-NMR methods have been established for separation and structural analysis. In addition to the information obtained from NMR, complementary structural information was obtained utilizing LC-MS/MS. The information gained from both techniques was used for overall structural analysis of several ciprofloxacin transformation products. General strategies for structural elucidation of environmental transformation products using both LC-NMR and LC-MS/MS will be discussed.

326. EXPLORING THE INFLUENCE OF EXPERIMENTAL PARAMETERS ON LIGAND-PROTEIN EQUILIBRIUM CONSTANTS MEASURED BY DIFFUSION NMR SPECTROSCOPY. **Laura H. Lucas**, Cynthia K. Larive; University of Kansas, Department of Chemistry, 1251 Wescoe Hall Drive, Lawrence, KS 66045-7582.

Determining binding constants is important in the drug discovery process, since protein binding may reduce drug bioavailability or improve its potency as an enzyme inhibitor. Calculating binding constants requires distinguishing physical or chemical parameters for free and bound ligand states. Resolving such parameters for chemically similar species without disrupting the equilibrium can be challenging but is possible with noninvasive spectroscopic methods such as NMR. Binding over a broad range of affinity constants can be quantitatively analyzed by

measuring diffusion coefficients with pulsed-field gradient NMR experiments, where the ligand diffusion coefficient changes significantly when it interacts with a macromolecular target. Signal decay as a function of gradient amplitude is related to translational diffusion. Since diffusion is a molecular property, the decay rate (diffusion coefficient) should be constant regardless of the specific NMR signal monitored. However, we have discovered that for relatively strong binding equilibria (~ µM K_d), the results obtained for different signals depend on the experimental parameters selected. The effect of experimental parameters on measured diffusion coefficients and binding constants will be presented for multiple ligand-receptor systems of differing binding affinities and the implications of such results on the affinity constants measured for unknown systems will be discussed.

327. POLYANILINE EPOXY COPOLYMERS. **Gerald Caple**[1], Keisha Williams[2], Trent Custis[2]; [1]Retired, 387 Gunflint Narrows, Grand Marais, MN 55604; [2]University of South Dakota, Chem. Dept., Vermillion, SD 57069.

By treating *p*-phenylenediamine, or 4,4'-diaminodiphenyl amine, with various ratios of aniline and a limited amount of ammonium peroxy disulfate, short segments of polyaniline could be prepared. These segments should be functionalized on both ends with amino groups. GPC analysis indicated the molecular weight of the segments were a function of the diamine to aniline ratio. The segments also had a fairly narrow MW distribution. Unlike the free base form of polyaniline the free base form of these segments were quite soluble in THF. Thin layer chromatography indicated the products did not include phenazine salts related to the safarins as products. These segments were treated with Dow's DER330, a diepoxide with a MW of 340 amu. Curing at 80 ºC for one hour produced a brittle polymer. DSC indicated a second reaction would take place at 150 ºC and the resulting polymer had a glass transition temperature of about 106 ºC. Thin films of these copolymers changed color upon protonation, typical of polyaniline, in turn this should affect the electrical properties. Copolymers were also prepared from Safarin-O, a N-phenyl phenazine chloride salt. The properties of these polymers will be discussed.

328. DETERMINATION OF THE VARIATION OF THE CALORIC CONTENT OF SOYBEANS BY OXYGEN BOMB CALORIMETRY. **Paul Karr**, Brandon McLaughlin; Wayne State College, 1111 Main, Wayne, NE 68787.

Oxygen bomb calorimetry has been the accepted method for the determination of the caloric content of foods, fuels and other combustible materials for several years. A Parr 1341 Oxygen Bomb Calorimeter was used to determine the caloric content of sample soybeans grown under various conditions. The growing variations examined were fertilization, irrigation, seed type and geographic growing region. Standard oxygen bomb procedures were followed in the analysis and the acid content was determined by mass balance titration of the bomb washings with a standardized sodium hydroxide solution.

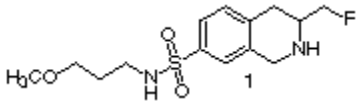
329. INORGANIC SUSPENDED SOLIDS INTERFERE WITH SPECTROPHOTOMETRIC DETERMINATIONS OF TOTAL PHOSPHORUS. **Val H. Smith**, Rebecca Evanhoe; University of Kansas, 6007 Haworth Hall, Lawrence, KS 66045.

Total phosphorus (TP) is measured worldwide by environmental chemists concerned with eutrophication. Following wet digestion of total P to orthophosphate with potassium persulfate, the digestate is reacted with a molybdate-mixed reagent to form a heteropoly acid; this phosphomolybdic acid is then reduced to an intense molybdenum blue with ascorbic acid and read at 885 nm. This spectrophotometric technique is highly sensitive and gives results which are highly precise and reproduceable in most freshwater systems. However, the turbid waters of midwestern reservoirs typically contain high concentrations of suspended soils and we hypothesized that these suspended inorganic solids could interfere with normal spectrophotometry. We tested this hypothesis by making TP measurements using standard protocols and making simultaneous TP measurements on digestates which were filtered through Whatman GF/F glass fiber filters to remove suspended inorganic solids. A comparison of these measurements confirmed an apparent upward bias of 10-20%.

330. INHIBITORS OF PNMT: INVESTIGATION INTO THE SULFONAMIDE SIDE CHAIN OF 3-FLUOROMETHYL-7-*N*-(SUBSTITUTED-AMINOSULFONYL)-1,2,3,4-TETRAHYDROISOQUINOLINES. Steven M. Vodonick, F. A. Romero, Kevin R. Criscione, **Gary L. Grunewald**; University of Kansas, 1251 Wescoe Hall Dr., Lawrence, KS 66045.

The physiological functions of epinephrine (Epi) within the CNS are unknown presently. In order to investigate the role of CNS Epi we have synthesized inhibitors of phenylethanolamine *N*-methyltransferase (PNMT) to act as pharma-

cological tools. 3-Fluoromethyl-7-*N*-(3-methoxypropyl-aminosulfonyl)-1,2,3,4-tetrahydroisoquinoline (**1**) is a potent PNMT inhibitor that is predicted to cross the blood-brain barrier and shows very little affinity for other pharmacologically relevant binding sites (*e.g.*, the α_2-adrenoceptor). To further optimize the sulfonamide side chain, a small series of 3-fluoromethyl-7-*N*-(methoxyalkyl or ethoxyalkyl-aminosulfonyl)-1,2,3,4-tetrahydroisoquinolines has been synthesized and evaluated. The results of these biological evaluations will be presented, along with an interpretation of SAR results using the the recently obtained crystal structure of hPNMT co-crystallized with SK&F 29661 and *S*-adenosyl-L-homocysteine.



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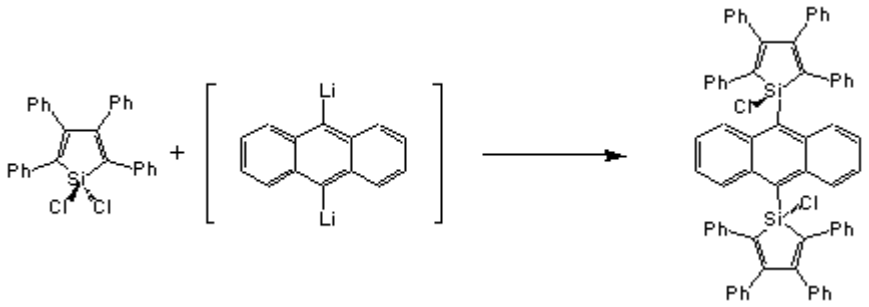
331. THE DEHYDRATION OF *CIS*- AND *TRANS*-2-PHENYLCYCLOHEXANOLS. **Rebecca L. Hrdy**, James K. Wood; University of Nebraska-Omaha, 60th and Dodge St., Omaha, NE 68182-0109.

The conventionally accepted mechanism for the dehydration of alcohols is explained as the protonation of the oxygen by a strong Lewis acid to yield an oxonium ion. This oxonium ion loses a water molecule to form a carbocation, which can then undergo possible rearrangements before losing a β-hydrogen to form alkene products. The planar carbocation intermediate is responsible for rearrangements and nonstereospecific products. However, Schaeffer and Collins reported in 1956 that stereospecificity with unexpected rearrangements does occur in the dehydration of the *cis*- and *trans*-2-phenylcyclohexanols. When these reactions were repeated and monitored using GC-MS, alkenes that were not previously reported were detected. The observed stereochemistry and rearrangements suggest a concerted loss of water to form the product without a carbocation intermediate. Using Spartan software, transition states for both the stepwise loss of water (E1cA) and the concerted loss of water (E2cA) were modeled.

332. SYNTHESIS OF A DISILYLANTHRACENE. **Barrett E. Eichler**, Brian J. Oxley; Northwest Missouri State University, 800 University Drive, Maryville, MO 64468.

Both siloles and silylanthracenes have been the focus of recent research because of their light-emitting properties. The dilithiated anthracene and the 1,1-dichloro-2,3,4,5-tetraphenylsilole couple together in a 1:2 ratio to form LiCl and the desired disilylanthracene. The molecule will be characterized by use of GC-MS, NMR (^{1}H, ^{13}C, ^{29}Si), X-ray crystallography and elemental analysis. The molecule may also be a precursor to polymeric compounds with interesting properties.



Disilylanthracene

333. COMPARATIVE STUDY BETWEEN THE BEHAVIOR OF IRON AND CHROMIUM WITH CITRATE. **Yahia Hamada**, Jeremy Shank; Wayne State College, 1111 Main Street, Wayne, NE 68787.

Citric acid is ubiquitous in nature. It is involved in the active sites of bacterial metalloenzymes including aconitase, a key enzyme in the citric acid cycle. Citrate is found in human blood plasma at a concentration of about 0.1mM. Many reports have dealt with the interaction of citric acid with a variety of metal ions, but there are still arguments on the identity of the major species present in solutions. We are reporting the interaction of Fe^{3+} and Cr^{3+} with citric acid using UV-Vis spectroscopy. For the Fe^{3+} system, it appeared that the simple 1:1 complex and the bis complex predominate. We observed the presence of two isosbestic points, one at 320 nm above the physiological pH and another at 350 nm in the acidic pH range of 2.10 to 3.73. These isosbestic points indicate the presence of a major species within a certain pH range. With the Cr^{3+} system, we gathered the UV-Vis absorption spectroscopy for the Cr^{3+}/citric acid system and the Cr^{3+}/tri-sodium citrate system. It appeared that the Cr^{3+}/citric acid system and the Cr^{3+}/tri-sodium citrate system had different UV-Vis patterns. The perturbation in the 4A2g to 4T1g electronic transition is dramatically different when comparing the two systems. These differences will be discussed as well as the differences between the Cr^{3+} system and the Fe^{3+} system.

334. ELECTRONIC AND PHYSICAL PROPERTIES OF COMPRESSED AND EXPANDED C_{60} AND ENDOHEDRAL C_{60} COMPOUNDS. **David Peitz**[1], Todd Young[1], Beau Denker[2]; [1]Wayne State College, 1111 Main Street, Math and Science Division, Wayne, NE 68787; [2]HC 65 Box 43D, O'Neill, NE 68763.

The compression and expansion of C_{60} and endohedral C_{60}, was simulated by locking the distances across the cage framework and then gradually decreasing or increasing these values and re-optimizing the structures. The amount of stain that can be applied to the different fullerenes before their destruction was calculated and compared. The strain energies were used to compare force constants (using Hooke's Law) for C_{60} and the various endohedral C_{60} compounds. All calculations were done using Gaussian 98W or Spartan '02 with optimizations performed using the AM1 or PM3 semiempirical method followed by single point *ab initio* energy calculations.

335. PREPARATION AND SOLVATION STUDIES ON CADMIUM(II) DIIMINE CATECHOLATE AND DITHIOLATE COMPLEXES. **Brian Leonard**, Christopher L. Exstrom; University of Nebraska at Kearney, Department of Chemistry, Kearney, NE 68849-1150.

Cadmium(II) complexes of the form Cd(diimine)(thiolate)$_2$ are known to exhibit solvatochromic interligand charge transfer (ICT) transitions, but the effects of structural changes on solute-solvent interactions are not well understood. In this work, a novel series of analogous Cd(diimine)(catecholate) and Cd(diimine)-(dithiolate) complexes have been prepared. UV-vis and ^{113}Cd NMR spectroscopy studies reveal that ICT solvatochromism is inhibited due to the formation of dimers in which the diimine and dithiolate/catecholate ligands deviate from co-planarity. Results from preferential solvation studies pertaining to this issue will also be discussed.

336. IDENTIFICATION OF THE [12.3] $^2\Sigma$ - *X* $^2\Pi_{½}$ TRANSITION OF NICKEL CHLORIDE, NICL. Barthemeaus Owen[1], **Leah C. O'Brien**[1], James J. O'Brien[2], [1]Southern Illinois University, Department of Chemistry, Edwardsville, IL 62026-1652; [2]University of Missouri-St. Louis, Depart- ment of Chemistry and Biochemistry, 8001 Natural Bridge Rd., St. Louis, MO 63121-4499.

The [12.3] $^2\Sigma$ - *X* $^2\Pi_{½}$ transition of NiCl has been observed by Fourier transform and Intracavity Laser Absorption Spectroscopies at rotational resolution. Results of the analysis and corresponding molecular parameters for each state will be presented.

337. ELECTROCHEMICAL EFFECTS OF SURFACE MODIFIED GLASS MICROSPHERES ON POLYSTYRENE SULFONATE MODIFIED ELECTRODES. **Christine M. Moore**, Nicholas J. Torrence, Shelley D. Minteer; Saint Louis University, Department of Chemistry, 3501 Laclede Ave., St. Louis, MO 63103.

Tailoring the interfacial region of composite modified electrodes has been a topic of discussion for over a decade. This research examines the electrochemical effects of the formation of unique interfacial regions in surface modified glass microspheres/polystyrene sulfonate composite modified electrodes. The surface of the glass microspheres are modified with different organic functional groups by binding organosilanes to the surface of the glass microspheres through a siloxane linkage. This research showed that surface modified glass microspheres can alter the electrochemical flux of hydroquinone and $Ru(bpy)_3^{+2}$ through surface modified glass microsphere/polystyrene sulfonate composites, but the surface modified glass microspheres had no affect on the electrochemical flux of Fe^{+3}. It was also shown that the polymer itself plays a crucial role in the formation and the properties of the interfacial region. The interfacial region was imaged using fluorescence microscopy and the microscopy showed that a highly concentrating interfacial region is formed for all of the surface modified glass microsphere/ polymer composites studied regardless of whether there is a statistically significant electrochemical effect. Further studies with smaller particles are necessary to obtain a large enough interfacial region to be useful for sensor development.

338. UNDERGRADUATE RESEARCH IN COMPUTATIONAL CHEMISTRY. **Khamis S. Siam**, Jake Clements; Pittsburg State University, Department of Chemistry, Pittsburg, KS 66762.

We will outline our recent efforts at introducing computational chemistry in undergraduate research and describe a research project involving the building of a BEOWULF cluster completely performed by an undergraduate student. We will show results of recent computations and describe the methodology.

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NOTES

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NOTES

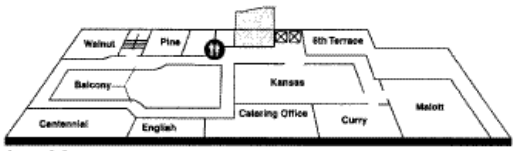
NOTES

Kansas Union.

- Entrance
- Elevator
- Restrooms
- Shaded Area
- Closed due to Construction
- Copy machine

LEVEL

4 Administrative Office
3 Alcoves (B-D)
4 Alderson Auditorium
4 ATM
3 Atrium
4 Banking
5 Big 12 Room
3 Business Office
4 Card Center, KU
4 Commerce Bank
6 Centennial Room
6 Curry Room
6 English Room
3 Food Services
4 Governor's Room (closed)
4 Herb Harris Computer Lab
4 Hawk Shop Convenience Store
3 Human Resources
1 Jaybowl (closed)
5 Jayhawk Room
4 Jayhawk Walk
6 Kansas Room
2 KU Bookstore
4 Lobby
6 Malott Room
5 Marketing Services
2 Oread Books
5 Oread Room
4 Organizations and Leadership
4 Public Phones
6 Pine Room
3 Prairie Room Dining
5 Regionalist Room
4 Room Reservations
6 6th Floor Terrace (outdoors)
4 Student Offices/Workstations
4 Student Union Activities
4 Student Senate
2 Textbooks
3 the Market
4 Traditions Area
3 TV (Near Atrium)
1 Tunnel Entrance (closed)
3 Union Computing Services
6 Walnut Room
5 Woodruff Auditorium



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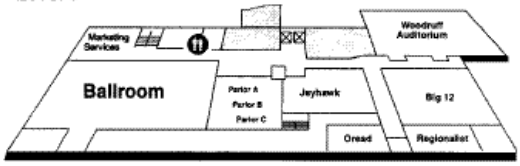

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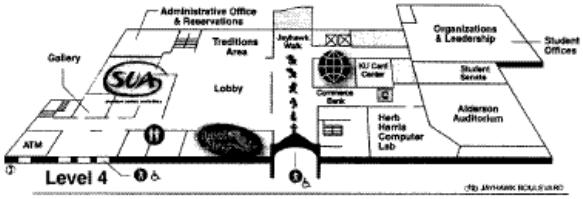

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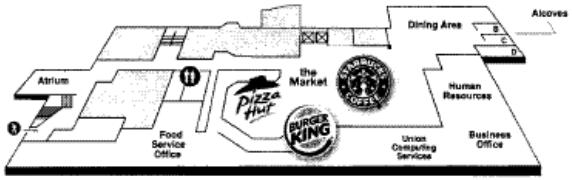

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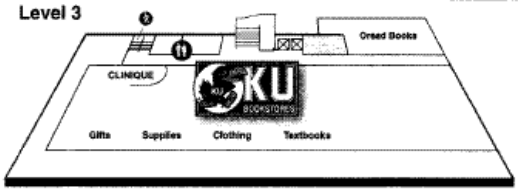

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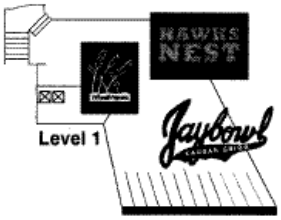

Level 1

38TH MIDWEST REGIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

NOVEMBER 5-7, 2003

HOSTED BY THE UNIVERSITY OF MISSOURI LOCAL SECTION

FEATURED SYMPOSIA:

Chemistry and Technology for the 21st Century
Biological Mass Spectrometry and Proteomics
Towards the Ideal Synthesis
Advances in Supermolecular Chemistry
Chemical Education
Surface Chemistry
Workshop: Chemistry and Home Brewing

GENERAL SESSIONS:

Analytical, Biochemistry, History of Chemistry, Chemical Education, Inorganic, Organic and Medicinal, Physical

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