

# CHEMISTRY

conference

JANUARY-10-2007



Texas A&M University at Qatar



Texas A&M University  
at Qatar

جامعة تكساس إى أندام فى قطر

■ November 29, 2006

On behalf of Texas A&M University at Qatar, I would like to cordially invite you to our first annual Chemistry conference. The conference will celebrate the inauguration of our Chemistry facilities. With the recent arrival of our 400 MHz Bruker NMR (nuclear magnetic resonance), our labs are equipped with state-of-the-art instruments that are ready to serve both our research and teaching needs.

The meeting will focus on faculty research. Speakers from Texas A&M University, Qatar University, Weill Cornell Medical College in Qatar, and Texas A&M University at Qatar will present their most recent results in the various disciplines of Chemistry. You will have the opportunity to attend sessions on a variety of research topics from Polymer Chemistry, Physical, Organic, and Analytical Chemistry. This event reflects Texas A&M University's commitment to provide the best resources available to faculty and researchers in Education City and in the State of Qatar as they undertake the processes of innovation and the creation of knowledge.

I would like to thank our co-sponsor QAFCO (Qatar Fertiliser Company) for their generous support. I hope that you will be able to join us on January 10, 2007, for this most important event.

If you have questions, or to register, please email [chemistry@qatar.tamu.edu](mailto:chemistry@qatar.tamu.edu) (deadline for registration is December 21, 2006)

Sincerely,



**Dr. Mark Weichold**

Dean and CEO

Texas A&M University at Qatar

## ■ “Novel Biomimetic Polymers via ROMP”

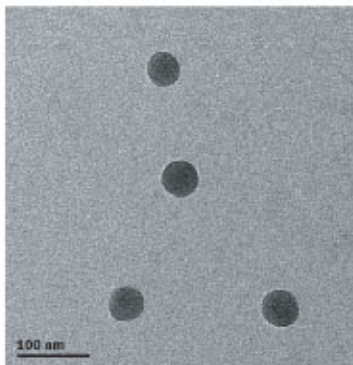
Hassan S. Bazzi<sup>1</sup> and Hanadi F. Sleiman<sup>2</sup>

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There has been recent interest in the synthesis of “smart” polymers that are able to mimic nature’s polymers (e.g. DNA, RNA, etc.). We have synthesized a novel thymine-containing monomer, and used ring-opening metathesis polymerization (ROMP) to generate di- and tri-block copolymers that contain the complementary diaminopyridine (DAP) and thymine (THY) units. These polymeric systems were shown to self-assemble into well-defined spherical morphologies held together by DAP-THY non-covalent interactions. The synthesis was performed in a mixed solvent system to prevent any interaction between the catalyst and the monomers, and to enhance solubility. Synthesis, self-assembly, and physical characterization will be described.



Transmission Electron Micrograph (TEM) showing the self-assembled triblock copolymer.

## ■ “Exploring Plant Defense as a Source of Novel Bioactive Compounds”

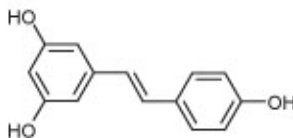
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Unlike animals, plants can not run from their attackers (e.g. other plants, animal and insect feeders or microorganisms). As a result, plants have developed complex biochemical and biophysical approaches to defend themselves. One of the most interesting “chemical interplays” occurs between microbial pathogens and their plant hosts. During infection, plants respond to the microbial attack by activating genes leading to the production of antimicrobial compounds known generally as “phytoalexins”. Phytoalexins have great structural diversity across plant families, genus and even species. As these compounds are only produced in response to microbial attack (i.e. not observed under normal conditions), they constitute a diverse but under explored resource for discovering novel biologically active compounds. Resveratrol (trans-3,5,4'-trihydroxystilbene, **1**), a phytoalexin produced in the vine and skin of the grape, has been the most widely studied. In 2006, some 300 articles and 19 reviews reported on the biological effects of this metabolite in various human diseases and processes.



**Resveratrol** (trans-3,5,4'-trihydroxystilbene, **1**)

Recent efforts and future strategies for exploring novel phytoalexins will be discussed including the investigation of plants native to Qatar.

## ■ “Surface Science of Electrocatalysis”

Manuel P. Soriaga

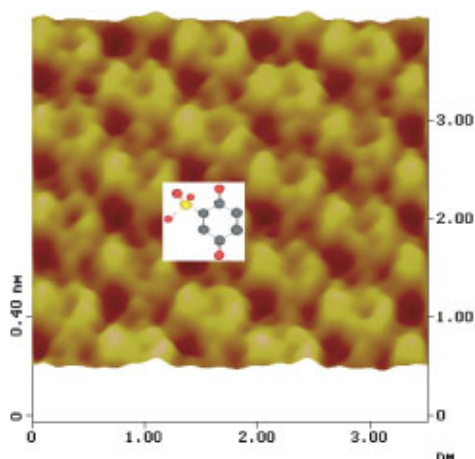
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The description of an electrocatalytic reaction must consider the physico-chemical interactions between the electrified surface and the components of the solution. The traditional approach to the study of the electrode-solution interface has been to monitor the thermodynamic responses to electrical perturbations; but the interpretation of results relies on phenomenological models that bear minimal atomic-level specificity. The past few decades have spawned major advances in experimental strategies for the atomic-level characterization of the electrode-electrolyte interface. *Ex situ* methods take advantage of surface-sensitive analytical techniques to interrogate the electrode before and after a given reaction; our arsenal includes low energy electron diffraction, Auger electron spectroscopy, X-ray photoelectron spectroscopy, high-resolution electron energy loss spectroscopy, and mass spectrometry. *In situ* techniques allow the examination of the electrode surface under reaction conditions; we employ electrochemistry, infrared spectroscopy, scanning tunneling microscopy, and extended X-ray absorption fine structure. The electrodes of interest are the platinum metals; heterogeneous hydrogenation and oxidation are reactions that have received our recent attention. Extensive investigations on the surface electrochemical properties of well-defined Pd single crystals have uncovered unique phenomena that serve to establish the remarkably rich interfacial chemistry of this metal.



Such chemistry may have its origins in the anomalously weak inter-metallic palladium-palladium bond, a circumstance that is expected not only to enhance lateral surface mobilities but also facilitate the disruption of substrate-substrate bonds and/or the formation of substrate-adsorbate bonds. The talk will showcase three interrelated phenomena: (i) electrode-surface coordination/organometallic chemistry, (ii) adsorbate-activated electron-transfer sites, and (iii) adsorbate-induced substrate reactions.



## ■ “Non-Destructive Radiocarbon Dating”

Marvin W. Rowe

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A 'non-destructive' method for radiocarbon dating of perishable archaeological remains requires new replacements for the two very destructive steps in current radiocarbon dating: (1) pretreatment to remove contaminating humic acids, presently done by acid-base-acid (a-b-a) washings; and (2) extraction of the necessary carbon for accelerator mass spectrometric (AMS) analysis, currently done by totally burning the sample, releasing carbon dioxide. We have successfully replaced the second step with using low-temperature argon and oxygen plasmas to extract  $\sim 100 \mu\text{g}$  carbon from the exposed surface of an artifact without any visible change to the artifact. This negates the need for removal of bulk material for destruction. We saw no visible alteration in numerous fragile archaeological materials treated with plasma procedures. Known-age materials, previously dated charcoal samples, and many other artifacts were dated successfully with our technique. Now it only remains to replace the destructive a-b-a pretreatment with a non-destructive one. Super-critical fluid cleaning is being attempted as an alternative to that harsh treatment. Preliminary measurements are at the Lawrence Livermore AMS laboratory. Photographs of an archaeological textile before (A) and after (B) carbon extraction demonstrating the gentle nature of the plasma-chemical method are shown below. The width of the sample shown in the photographs is approximately 1 cm.



Before plasma

After plasma for 15 radiocarbon dates

## ■ “Carbon-Hydrogen Bond Activation”

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Selective, low-temperature, catalytic carbon-hydrogen bond activation, especially for methane, has been an important goal for organometallic chemistry. Density functional calculations have proven to be helpful in elucidating details of the mechanistic steps in this transition metal catalyzed reaction. Activation may occur by oxidative addition or by sigma-bond metathesis. Results on a variety of systems will be presented. For example, in the catalytic methane activation by  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{CH}_3)]^+$  the experimentalist favored a sigma-bond metathesis path as the oxidative addition path would produce an Ir(V) intermediate, a species that was thought to be too unstable. DFT calculation prove that the lowest energy path is through this Ir(V) species and explain why it is more stable than might be expected.

In a second example, the complete reaction mechanism including the identification of new intermediates and corresponding transition states has been possible through the use of density functional theory. The TRIR of the UV photolysis of  $\text{Tp}^*\text{Rh}(\text{CO})_2$  in the presence of alkane (RH) has been interpreted as involving the sequential formation of three species on the route to the final alkyl hydride product:

$\text{A} \rightarrow \text{B} \rightarrow (\text{C}) \rightarrow \text{D}$ . The DFT results show that the A species is the triplet state of a 5-coordinate, square-pyramidal  $\text{TpRh}(\text{CO})\text{—RH}$  species, in which the alkane is weakly bound. Subsequently, this A species decays to the singlet state of a nominally 5-coordinate, square-pyramidal  $\text{Tp}^*\text{Rh}(\text{CO})(\text{RH})$  with a strongly bound alkane and one pyrazolyl partially decoordinated, but occupying the axial position of the square pyramid; this species is unobserved as it has the same CO stretching frequency as the dicarbonyl reactant. The first barrier (A  $\rightarrow$  unobserved species) is calculated by determining the minimum-energy crossing point on the seam of intersection between the triplet and singlet surfaces and is in good agreement with the observed rate.





The unobserved species is predicted to be in rapid equilibrium with a 4-coordinate  $\text{Tp}^*\text{Rh}(\text{CO})(\text{RH})$ , in which one pyrazolyl ring is rotated to essentially decoordinate one N; this is the observed B species. The calculated CO frequency difference between this species and the solvated triplet is in good agreement with the observed difference between A and B. The 6-coordinate, oxidative-addition product,  $\text{Tp}^*\text{Rh}(\text{CO})(\text{R})(\text{H})$  (species D), is formed from the unobserved intermediate. This unobserved species, structurally quite different from the postulated species C, lies on the reaction path between A and B. Thus, species B must return to this species by partially re Coordinating the rotated pyrazolyl ring before the concerted oxidative-addition produces the fully coordinated product.



■ **“Screening for Novel Inhibitors for Human Alpha-Amylases: An Effective Approach to Control Diabetes Mellitus and Obesity”**

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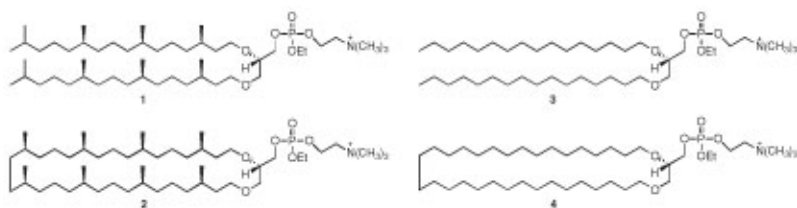
Non-insulin-dependent diabetes mellitus (NIDDM), which is one of the main adult diseases, is caused by the secretory decrease in insulin from pancreatic Langerhans cell or the lowering of insulin resistance due to excess glucose absorption. Serious side effects such as retinopathy, neuropathy, and cataracts are also brought about by its long-term manifestation. Alpha amylase and glucosidase catalyze the cleavage of glucose from starch and maltose respectively. Thus, the retardation of the action of these enzymes by inhibitors may be one of the most effective approaches to control NIDDM. Our study therefore, aimed to screening for human amylases inhibitors. This was achieved by the collection of natural products, randomly and based on the tradition use in diabetes mellitus control. Preparation, fractionation of total natural products extracts, and isolation of the active principles have been carried out using different solvents and column chromatography.

We also carried out and tested a big collection of the synthetic compounds for our screening program. The results of our study have led to the isolation, purification of two new natural occurring compounds with the complete structural elucidation of the active compounds. The study also identified 5 new synthetic compounds as inhibitors for human salivary amylase. The two classes of these compounds may provide good therapeutics for diabetes mellitus as well as obesity.

## ”Cationic Archaeal-Derived Lipids as Gene Therapy Reagents”

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The discovery of archaeobacteria, organisms that thrive in extreme physical conditions, has generated much interest in the membrane characteristics and biotechnological applications of the unique class of lipids that originate from these microorganisms, named *Archaea*. In this study, four archaeal-like cationic phospholipids were characterized as nucleic acid delivery reagents. These four lipids are comprised of two sets; each set contains a cyclic and an acyclic counterpart. The first set is made up of naturally occurring archaeal-derived lipids with saturated isoprenic chains (lipids 1 and 2), and the second set is made up of saturated methylene chains (lipids 3 and 4). Particle size analysis revealed that the cyclic lipids, 2 and 4, assembled into smaller, more compact particles compared to their acyclic counterparts. A serum protection assay suggested that cyclic isoprenic lipid 2 offered better DNA protection against serum degradation than its acyclic counterpart, 1, while the same assay revealed no difference in DNA degradation comparing lipids 3 and 4, which lack the methyl side chains. *In vitro* transfection of CHO cells showed that the acyclic lipids typically outperformed their cyclic counterparts, and furthermore, acyclic lipid 3, the least challenging to synthesize of the four, generally showed the most promise as a transfection reagent.



## ■ "Chemistry Program at Texas A&M University at Qatar"

The Chemistry Program at TAMUQ, an extension of the Texas A&M College of Science, serves as an important part of the foundation for the Chemical Engineering program at TAMUQ. Although TAMUQ does not offer a degree in Chemistry, Chemical Engineering majors qualify for a minor in Chemistry after completing the required courses. The Chemistry program at TAMUQ was established in September 2004 to provide the necessary chemistry courses for Electrical, Mechanical and Petroleum Engineering majors. It supports the Chemical Engineering program with both theoretical and experimental Chemistry courses, including General, Organic, Analytical, Physical, and Polymer Chemistry.

Although it is an ongoing process, the Chemistry labs at TAMUQ are now equipped with a variety of state-of-the-art instruments to help support the teaching and research needs of the program. The Chemistry program now is up and running with excellent infrastructure and resources. We have a variety of instruments, a big library of chemicals and laboratory supplies (glassware, analytical balances, hot plates/stirrers, melting point testers, multi-purpose probes, computer interfaces, tools, glass-drying ovens, refrigerators, pH-meters, conductivity meters, rotary evaporators, vacuum pumps, water circulating baths, UV lamps, water distillation system, and others) needed for day-to-day operation in the teaching labs and for the research labs.

The Chemistry labs occupy around 10,000 square feet in the Liberal Arts and Science Building, the temporary location of TAMUQ. Following the completion of the Engineering Building in Education City, the Chemistry program will have space for teaching labs, research labs, instrumentation rooms, chemical storage rooms, NMR facility room and more. TAMUQ faculty are aggressively setting up their research projects and looking forward to collaborations with the other universities in Qatar, the industry, and universities abroad.



The most recent addition to the Chemistry Lab was a 400MHz Bruker Biospin Nuclear Magnetic Resonance (NMR). This is the first instrument with this level of resolution in the State of Qatar. The instrument is equipped with accessories that allow researchers to run experiments at temperatures varying from  $-80^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , and with the broadband probe, spectra for Hydrogen, Carbon, Phosphorus, Nitrogen, and Fluorine nuclei can be collected.

With the latest addition of the NMR, the Chemistry Instrument Lab has been significantly enhanced and will greatly serve TAMUQ and Education city researchers.

■ **"Chemistry Program at Texas A&M University at Qatar"**  
**Chemistry Lab Instruments:**

- Perkin Elmer Clarus 500 gas chromatography (GC).
- Perkin Elmer Clarus 500 gas chromatography (GC) coupled with Perkin Elmer mass spectrophotometer (MS).
- Perkin Elmer Spectrum One V B FTIR spectrophotometer.
- Perkin Elmer Double Beam Lambda 950 UV-Vis-NIR spectrophotometer System.
- Perkin Elmer series 200 LC based GPC system (Size Exclusion Chromatography).
- Varian Cary Eclipse fluorescence spectrophotometer.
- Beckman Coulter DU520 general purpose UV-Vis spectrophotometer.
- Chemat Technology KW-4A Spin coater.
- Precision Centrifuge Durafuge 100.
- MBraun Lab master glove box.
- Total organic Carbon analyzer.
- YSI 9100 Water Analysis System.
- ICP-MS (ordered).
- Ion Chromatograph (ordered).
- Bruker Biospin Nuclear magnetic resonance (NMR) 400 MHz.



■ TAMUQ Chemistry Conference 2007  
Texas A&M University at Qatar  
January 10, 2007  
Liberal Arts & Sciences Building  
Education City-Doha, Qatar

#### Schedule of Events

8:00	Registration Open and Light Breakfast
8:30	Welcome Session
9:00	Session I
10:35	Coffee break
10:50	Session II
12:25	Lunch
13:30	Session III
14:40	Coffee Break
15:10	Session IV
17:00	Chemistry Lab tour

■ TAMUQ Chemistry Conference 2007  
Texas A&M University at Qatar  
January 10, 2007  
Scientific Program

Welcome Session	
8:30	<b>Dr. Hassan S. Bazzi</b> , Science Program Coordinator, TAMUQ
8:40	<b>Dr. James C. Holste</b> , Associate Dean for Academic Affairs, TAMUQ
Session I (Chair: Dr. Hassan S. Bazzi)	
9:00-9:45	<b>Dr. Donald J. Darensbourg</b> "Polycarbonates Produced from the Copolymerization of Oxiranes or Oxetanes and CO <sub>2</sub> , or the Ring-Opening Polymerization of Trimethylene Carbonate"
9:45-10:10	<b>Dr. Ashfaq Bengali</b> "Reactivity of the Metal- $\eta^2$ -Arene Bond: A Laser Flash Photolysis Study"
10:10-10:35	<b>Dr. Mamoun M. Bader</b> "n- and p-Channel Transport Behavior in Thin Film Transistors Based on Tricyanovinyl-Capped Oligothiophenes"
Session II (Chair: Dr. Marvin W. Rowe)	
10:50-11:35	<b>Dr. David E. Bergbreiter</b> "Stimuli Responsive Polymer Solubility – a Probe of Macromolecule Solvation and a Tool for Synthesis"
11:35-12:00	<b>Dr. Hassan S. Bazzi</b> "Novel Biomimetic Polymers via ROMP"
12:00-12:25	<b>Dr. Kevin C. Smith</b> "Exploring Plant Defense as a Source of Novel Bioactive Compounds"

Session III (Chair: Dr. Ashfaq Bengali)	
13:30-14:15	<b>Dr. Manuel P. Soriaga</b> "Surface Science of Electrocatalysis"
14:15-14:40	<b>Dr. Marvin W. Rowe</b> "Non-Destructive Radiocarbon Dating"
Session IV (Chair: Dr. El-Metwally Nour)	
15:10-15:55	<b>Dr. Michael B. Hall</b> "Carbon-Hydrogen Bond Activation"
15:55-16:20	<b>Dr. Sayed K. Goda</b> "Screening for Novel Inhibitors for Human Alpha-Amylases: An Effective Approach to Control Diabetes Mellitus and Obesity"
16:20-16:45	<b>Dr. Michael D. Pungente</b> "Cationic Archaeal-Derived Lipids as Gene Therapy Reagents"



■ **Polycarbonates Produced from the Copolymerization of Oxiranes or Oxetanes and CO<sub>2</sub>, or the Ring-Opening Polymerization of Trimethylene Carbonate**

Donald J. Darensbourg

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The design of efficient metal catalysts for the selective coupling of epoxides and carbon dioxide to afford completely alternating copolymers has made significant gains over the past decade. Hence, it is becoming increasingly clear that this "greener" route to polycarbonates has the potential to supplement or supplant current processes for the production of these important thermoplastics, which involve the condensation polymerization of diols and phosgene or organic carbonates. This presentation summarizes our efforts at optimizing (salen)Cr<sup>III</sup>X catalysts for the selective formation of polycarbonates from alicyclic and aliphatic epoxides with CO<sub>2</sub>. An iterative catalyst design process is employed in which the salen ligand, initiator, cocatalyst, and reaction conditions are systematically varied, with the reaction rates and product selectivity being monitored by *in situ* infrared spectroscopy. Our initial findings of the coupling of oxetanes and CO<sub>2</sub> to provide aliphatic polycarbonates will also be described. An alternative, very controllable, route to aliphatic polycarbonates involves the ring-opening polymerization of the six-membered cyclic carbonate, trimethylene carbonate. Because these polymers have numerous medical applications, the design of effective biocompatible metal catalysts is highly desirable. Research accomplishments in this area of polymer synthesis will also be presented.



■ **“Reactivity of the Metal- $\eta^2$ -Arene Bond:  
A Laser Flash Photolysis Study”**

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The  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2\text{-}(\eta^2\text{-C}_6\text{H}_5\text{R})$  complexes [R = H, CH<sub>3</sub>, CF<sub>3</sub>] are generated upon photolysis of  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_3$  in the appropriate arene. The energetics and mechanism of the displacement of the  $\eta^2$ -coordinated arene from the metal center by piperidine are studied using the technique of laser flash photolysis. The substitution reaction is tentatively assigned as proceeding through an I<sub>d</sub> mechanism, and the activation enthalpy of  $11.5 \pm 0.9$  kcal/mol provides a lower limit for the strength of the  $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2\text{-}(\eta^2\text{-C}_6\text{H}_5)$  bond. The substitution rate decreases as the metal center becomes more electron poor or the arene electron rich, suggesting that L to M  $\sigma$  donation is the primary bonding interaction between the  $(\eta^6\text{-C}_6\text{H}_5)\text{Cr}(\text{CO})_2$  fragment and the arene ligand. This reactivity is different from that of the Cr- $(\eta^2\text{-alkene})$  bond, where it was found that increasing the electron density on the metal center decreased the rate of substitution of cyclooctene from the  $(\eta^6\text{-C}_6\text{H}_5\text{R})\text{Cr}(\text{CO})_2\text{-}(\eta^2\text{-cyclooctene})$  complex by pyridine.



■ **“n- and p-Channel Transport Behavior in Thin Film Transistors. Based on Tricyanovinyl-Capped Oligothiophenes”**

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Recent results on structural and electrical characterization of thin films of organic semiconductor molecules consisting of an oligothiophene core capped with electron-withdrawing tricyanovinyl (TCV) groups. X-ray diffraction and atomic force microscopy of evaporated films of three different TCV-capped oligothiophenes showed that the films were highly crystalline. Electrical transport was measured in thin film transistors employing silver source and drain contacts and channel probes to correct for contact resistance. Three compounds exhibited n-channel (electron) conduction consistent with cyclic voltametry data that indicated they undergo facile reduction. Maximum electron mobilities were  $0.02 \text{ cm}^2/\text{V}\cdot\text{s}$  with an on/off current ratio of  $10^6$ . A fourth end-capped molecule, TCV-6T-TCV, which had six thiophene rings, exhibited both p- and n-channel transport. Overall, these results confirm that substitution of oligothiophene cores with electron-withdrawing groups is a useful strategy to achieve electron-transporting materials. In addition, the effect of strong electron acceptors on solid state structures of a series of related molecules as shown by single crystal structural analysis will be presented. Initial findings on the electronic and geometric structures from density functional theory (DFT) calculations on the same materials will also be discussed.