

QAFCO - TAMUQ  
**CHEMISTRY**

CONFERENCE 2013  
GREEN CHEMISTRY AND  
GREEN ENGINEERING



Welcome on behalf of Texas A&M University at Qatar to the 2013 Qatar Fertiliser Company-Texas A&M University at Qatar Chemistry Conference.

This is the sixth annual chemistry conference hosted at Texas A&M at Qatar and sponsored by Qatar Fertiliser Company (QAFCO), and it is evidence of the strong partnerships the University shares with its stakeholders in industry. QAFCO's generous sponsorship is a wise investment in your opportunity to exchange ideas that benefit academia and industry alike.

Thanks to QAFCO for its unwavering support of Texas A&M at Qatar.

This year's chemistry conference comes as Texas A&M at Qatar celebrates its 10-year anniversary. In the past decade, our enrollment has grown steadily to more than 500 students, including a master's program in chemical engineering, and since 2007 we've graduated more than 300 Aggie engineers.

Our impressive research program has earned more than \$140 million in funding, and the University provides broad expertise to support Qatar's industrial and commercial sectors, and scholarly gatherings such as this are invaluable part of that effort. Through all that it does, Texas A&M at Qatar remains committed to supporting this country's development and its progress toward the Qatar National Vision 2030.

The conference's technical program is impressive, as is the list of participants, and I want to offer a warm welcome to your keynote speaker for today, Dr. Paul T. Anastas, professor of chemistry and director of the Center for Green Chemistry and Green Engineering at Yale University.

Thank you for participating in the 2013 QAFCO-Texas A&M at Qatar Chemistry Conference, and, again, welcome to Texas A&M at Qatar.

Best wishes for a great conference.

Sincerely,

**Mark H. Weichold, Ph.D.**  
Dean and CEO



On behalf of the Science Program at Texas A&M University at Qatar, I am pleased to welcome you to the sixth annual QAFCO-TAMUQ Chemistry Conference. We are very proud of our partnership with QAFCO, which has generously supported this event since 2007.

In the sixth edition of our conference, we have chosen green chemistry as the main theme because we are aware of the environmental challenges that our world is facing. I am very pleased with the great of caliber of speakers that have accepted our invitation to the meeting, and I would like to express our sincere gratitude to them. This year's meeting adds to the successful series that we started in 2007.

Since Texas A&M at Qatar is celebrating its decennial milestone this academic year I am especially excited to host this conference, which highlights our progress in research activities which have been ongoing since we started our operation in Qatar in 2003. The Science Program is one of the most successful programs at Texas A&M at Qatar thanks to the hard work of its faculty. Our program has received more than \$33 million in external funding since 2007.

Your presence at this conference affirms our pursuits of cutting-edge chemistry research in Qatar and the region.

On behalf of my colleagues I am glad to have you with us, and I hope this conference will be an outlet for the exchange of scientific knowledge and to discuss future collaborations.

Best regards,

**Hassan S. Bazzi, Ph.D.**  
Chair, Science Program

## SCHEDULE OF EVENTS

**07:30** Registration Open and Light Breakfast

**08:25** Welcome Session

**8:50** Session I

**10:20** Coffee break

**10:40** Session II

**12:10** Lunch

**13:20** Session III

**14:50** Coffee Break

**15:10** Session IV

## SCIENTIFIC PROGRAM

### Welcome Session

- 08:25** Dr. Hassan S. Bazzi, Chair, Science Program,  
Texas A&M University at Qatar
- 08:30** Dr. Mark H. Weichold, Dean & CEO,  
Texas A&M University at Qatar
- 08:40** Mr. Khalifa Al-Sowaidi, Vice Chairman & CEO,  
Qatar Fertiliser Company

### Session I (Chair: Dr. Hassan S. Bazzi)

- 08:50 – 09:50** **Keynote Speaker**  
**Dr. Paul T. Anastas**  
Director, Center for Green Chemistry and  
Green Engineering, Yale University, USA  
"Green Chemistry: Current Status and  
Future Challenges"

- 09:50 – 10:20** **Dr. Tobin J. Marks**  
Northwestern University, USA  
"Catalytic Activation of Challenging Bonds:  
New Approaches to C-O and C-H"

### Session II (Chair: Dr. Dave Seapy)

- 10:40 - 11:10** **Dr. Shú Kobayashi**  
Department of Chemistry, School of Science,  
The University of Tokyo, Japan  
"The New World of Organic Reactions in Water"

- 11:10 – 11:40** **Dr. Peter Licence**  
School of Chemistry, The University of Nottingham, UK  
"An Enigma – Can XPS be used to decipher  
inter-ion communication?"

- 11:40 – 12:10** **Dr. David E. Bergbreiter**  
Department of Chemistry, Texas A&M University, USA  
"Polyolefins as Nonvolatile Solid Cosolvents in  
Catalytic Reactions"

### Session III (Chair: Dr. Ashfaq Bengali)

- 13:20 – 13:50** **Dr. Philip G. Jessop**  
Department of Chemistry, Queen's University, Canada  
"CO<sub>2</sub>-Triggered Switchable Solvents and Surfactants"

- 13:50 – 14:20** **Dr. Terrance J. Collins**  
Director, Institute for Green Science,  
Carnegie Mellon University, USA  
"Two approaches for designing as green chemists  
against endocrine disruptors"

- 14:20 – 14:50** **Dr. Chao-Jun Li**  
Department of Chemistry and FQRNT Center for Green  
Chemistry and Catalysis, McGill University, Canada  
"Exploration of New Chemical Reactivities for  
Synthetic Efficiency"

### Session IV (Chair: Dr. Hassan S. Bazzi)

- 15:10 – 15:40** **Dr. Jürgen Klankermayer**  
Institut für Technische und Makromolekulare  
Chemie (ITMC), RWTH Aachen University, Germany  
"New Carbon Sources for the Energetic and Chemical  
Value Chain: Challenges and Opportunities"

- 15:40 – 16:10** **Dr. Abdel-Wahab, Ahmed**  
Chemical Engineering Program, Texas A&M University  
at Qatar, Qatar  
"Advanced Reduction Processes for Destroying  
Persistent Oxidized Contaminants"

## KEYNOTE SPEAKER

### Paul T. Anastas

Teresa and H. John Heinz III Professor in the Practice of Chemistry for the Environment

B.S. Chemistry, University of Massachusetts at Boston M.A. Chemistry, Brandeis University Ph.D. Chemistry, Brandeis University.

Paul T. Anastas is the Teresa and H. John Heinz III Professor in the Practice of Chemistry for the Environment. He has appointments in the School of Forestry and Environmental Studies, Department of Chemistry, and Department of Chemical Engineering. In addition, Prof. Anastas serves as the Director of the Center for Green Chemistry and Green Engineering at Yale. Anastas took public service leave from Yale to serve as the Assistant Administrator for the US Environmental Protection Agency and the Agency Science Advisor from 2009-2012. From 2004 -2006, Paul Anastas served as Director of the ACS Green Chemistry Institute in Washington, D.C. He was previously the Assistant Director for the Environment in the White House Office of Science and Technology Policy where he worked from 1999-2004. Trained as a synthetic organic chemist, Dr. Anastas received his Ph.D. from Brandeis University and worked as an industrial consultant. He is credited with establishing the field of green chemistry during his time working for the U.S. Environmental Protection Agency as the Chief of the Industrial Chemistry Branch and as the Director of the U.S. Green Chemistry Program. Dr. Anastas has published widely on topics of science through sustainability including eleven books, such as Benign by Design, Designing Safer Polymers, Green Engineering, and his seminal work with co-author John Warner, Green Chemistry: Theory and Practice.

## GREEN CHEMISTRY: CURRENT STATUS AND FUTURE CHALLENGES

*Teresa and H. John Heinz III Professor in the Practice of Chemistry for the Environment, Director, Center for Green Chemistry and Green Engineering Yale University E-mail: paul.anastas@yale.edu*

In its essence, green chemistry is a science-based, non-regulatory and economically driven approach to achieving the goals of environmental protection and sustainable development. The approach has been utilized in a number of industrialized and developing nations. The results in these countries have been that of extremely positive results in terms of both protection to human health and the environment as well as significant economic benefit to the industrial interests involved.

While very broadly applicable, Green chemistry has a very specific and well-defined scope. Green chemistry is chemistry for pollution prevention which strives to reduce or eliminate the use and generation of hazardous substances. This scope explicitly does not include approaches such as waste treatment, waste control or re-mediation even though these elements are recognized as important, but separate, elements of an environmental protection programs. While many countries have those elements capable of reacting to environmental problems once they are formed, there is a need for the introduction and focus on initiatives that design products and processes such that these environmental problems never occur. This is the focus of green chemistry.

The range of green chemistry includes products and processes. This means that not only the structures of a final product can be designed to be non-hazardous but also each of the transformations along the way to manufacture of a product are designed so that they don't use or generate hazardous substances. There is an implicit consideration life cycle impacts with the scope of sustainable chemistry. Although traditionally

pollution prevention was thought to focus on waste reduction and waste minimization sustainable chemistry includes and expands this focus to all stages of the life cycle. The importance of this expansion is seen through commonly reported achievements from industry where the greatest economic benefit as well as the greatest environmental benefits are being realized as much in the early stages of the process or product life cycle as they are in the latter stages.

The green chemistry programs implemented by government industry and academia on a voluntary basis have achieved success in reducing risk through the reduction of intrinsic hazard at the molecular level. The types of hazards that can and are being addressed by scientific and industrial concerns include physical hazards, toxicological hazards (both human & ecotox, and global hazards), all of which are effected by proper and innovative molecular design.

As we review the success of green chemistry thus far, it is as important to keep an eye on the challenges of the future and identify the scientific challenges confronting green chemistry and especially the role of catalysis in Green Chemistry. Questions such as "What is the role of nanoscience on green chemical catalysis?" "Can we use energy in the place of matter to effectively carry out transformations catalytically on a commercial scale?" "Are the reaction types we use currently in chemical manufacturing the one's we should be using in the next ten, twenty years?". If we are to meet the challenges of sustainability, it will require that we address the problem at the molecular level as one part of the solution.

## CATALYTIC ACTIVATION OF CHALLENGING BONDS: NEW APPROACHES TO C-O AND C-H

**Tobin J. Marks**

Northwestern University, Evanston IL 60208, USA

This lecture focuses on two thermodynamics/mechanism-based strategies for converting abundant feedstocks into useful chemicals. In the first area, new approaches to the cleavage of C-O bonds are discussed with the ultimate goal being the processing of biomass feedstocks. It is shown that selective hydrogenolysis of cyclic and linear etheric C-O bonds is effected by a tandem catalytic system consisting of recyclable lanthanide triflates and sinter-resistant supported palladium nanoparticles in "green" ionic liquids. The lanthanide triflates catalyze endothermic dehydroalkoxylation of the ether, while the palladium nanoparticles hydrogenate the resulting intermediate alkenols to afford saturated alkanols with high overall selectivity. This catalytic C—O hydrogenolysis is shown to have significant scope, with C—O bond cleavage being turnover-limiting. The second area focuses on developing efficient catalytic processes for converting methane into useful feedstocks via new coupling processes that employ abundant, thermodynamically "mild" oxidants together with appropriate catalysts. We report that elemental sulfur is a promising "soft" oxidant for selective methane conversion to ethylene over  $\text{MoS}_2$ ,  $\text{RuS}_2$ ,  $\text{TiS}_2$ ,  $\text{PdS}$ , and  $\text{Pd/ZrO}_2$  catalysts. Experimental data and density functional theory reveal that methane conversion is directly correlated with surface metal-S bond strengths. Surfaces with weakly bound S are more basic and more readily activate methane C-H bonds. In contrast, experimental and theoretical selectivities to ethylene scale inversely with surface metal-S bond strengths, and surfaces having the strongest metal-S bonds afford the highest ethylene selectivity. High  $\text{CH}_4 : \text{S}_2$  ratios, short contact times, and supported catalysts maximize the coupling of  $\text{CH}_x$  intermediates and selectivity to ethylene since these conditions yield surfaces with stronger metal-S bonding (e.g.,  $\text{Pd}_{16}\text{S}_7$ ) which suppress methane over-oxidation.

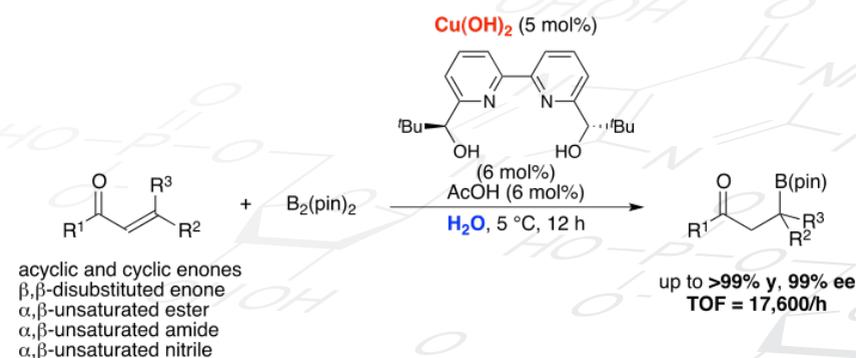
## THE NEW WORLD OF ORGANIC REACTIONS IN WATER

### Shú Kobayashi

Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan email: shu\_kobayashi@chem.s.u-tokyo.ac.jp

Different reactivities and selectivities are observed in water compared with those in organic solvents. In this lecture, such examples are discussed.

Enantioselective 1,4-addition of diboron to  $\alpha,\beta$ -unsaturated carbonyl compounds and nitrile has proceeded smoothly in the presence of catalytic amounts of  $\text{Cu}(\text{OH})_2$  and a chiral bipyridine ligand in water. Similar reactions were previously carried out using chiral  $\text{Cu}(\text{I})$  in organic solvents. A wide substrate scope of  $\alpha,\beta$ -unsaturated carbonyl compounds including acyclic, cyclic, and  $\beta,\beta$ -disubstituted enones,  $\alpha,\beta$ -unsaturated esters,  $\alpha,\beta$ -unsaturated amides, and an  $\alpha,\beta$ -unsaturated nitrile has been shown. This is the first case that a single catalyst covers all these substrates with high yields and high enantioselectivities.<sup>1</sup> It is noted that no or sluggish reactions occurred in organic solvents under the conditions.



1. S. Kobayashi, P. Xu, T. Endo, M. Ueno, T. Kitanosono, *Angew. Chem. Int. Ed.*, in press.

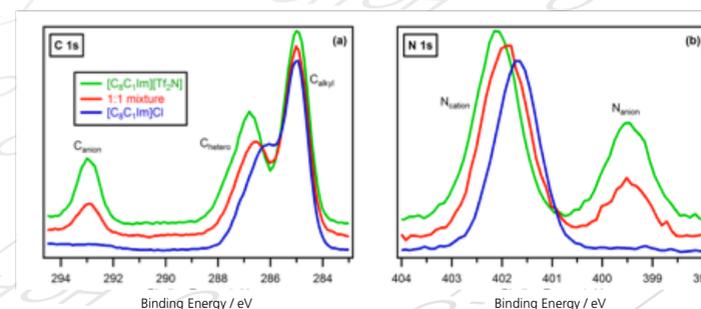
## AN ENIGMA - CAN XPS BE USED TO DECIPHER INTER-ION COMMUNICATION?

Ignacio J. Villar-Garcia, Shuang Men, Kevin R. J. Lovelock, Peter Licence

### Peter Licence

School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK, e-mail: Pete.licence@nottingham.ac.uk

It was not until 2005 that the rather obvious compatibility of ionic liquids with ultra high vacuum (UHV)-based spectroscopies was fully realised. Since that time, an ever-increasing portfolio of UHV based techniques including XPS, UPS, SIMS, TPD, SEM, TEM, and related synchrotron based experiments have been applied to the study of both pure ionic liquids and solutions thereof.<sup>1-5</sup> UHV techniques give tremendous insight into many aspects of ionic liquid properties and the role that they play in chemical reactions and processes.<sup>6</sup>



Since 2005 we have developed a series of robust spectroscopic protocols that allow the direct comparison of spectroscopic data, and more critically allows the investigation of subtle changes in binding energy that result from chemistry within the sample itself.<sup>7</sup> The application of rigorous charge referencing protocols reveals subtle variations in the observed binding energies of photoemissions corresponding to elements located in charge carrier moieties. This data suggests partial charge transfer between the charged components of a given liquid, i.e. anion-cation interactions,

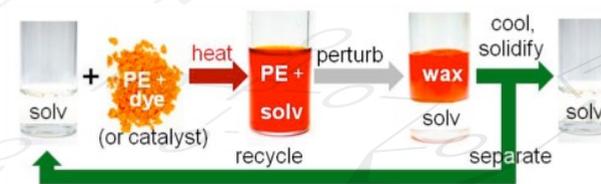
particularly when the anion component is highly coordinating or strongly basic. XPS data will be used to illustrate the extremes of both coordinating ( $\text{Cl}^-$ ) and passive  $[\text{Tf}_2\text{N}]^-$  behavior in commonly used ionic liquids.

The chemistry of ionic liquid mixtures is an emerging area of research that offers tremendous potential in applied fields, particularly those that are based upon the electrolytic properties of the liquid itself. The direct combination of different ions could provide a fine tuned balance between electrochemical stability, viscosity, conductivity and melting points. We explore the nature and local electronic environments within simple ionic liquid mixtures by direct XPS measurement. Common cation mixtures based upon both dialkyl imidazolium and dialkyl pyrrolidinium<sup>8</sup> based liquids are investigated and XPS data will be used to illustrate speciation and bulk structure in mixed anion-based systems as a function of molar fraction. The experiments illustrate opportunities to tune the electronic environment within ionic liquid mixtures and highlight a strategy that may be used to develop a palette of ionic liquids that may be blended to produce mixtures with tuneable chemical properties that could potentially impact upon catalytic performance.

## POLYOLEFINS AS NONVOLATILE SOLID COSOLVENTS IN CATALYTIC REACTIONS

**David E. Bergbreiter**

Texas A&M University, Department of Chemistry, P.O. Box 30012, College Station, TX 77842-3012, USA, bergbreiter@tamu.edu



This talk will describe studies where polymers are used to partially or fully substitute for conventional solvents. These studies will emphasize examples with hydrocarbon polymers and polyolefins in particular are used as nontoxic, nonvolatile, recyclable and sustainable replacements for conventional hydrocarbon and arene solvents. For example, we will describe the use of relatively low molecular weight, narrow polydispersity polyethylene (Polywax) as a solvent. This commercially available form of polyethylene serves as a non-polar solvent phase alternative in catalytic organic reactions carried under latent biphasic conditions. In this application, this nonvolatile and low toxicity polymer substitutes for a conventional hexane or heptane solvents. In addition to advantages of being nonvolatile and nontoxic, this polymer solvent has the advantage that it can sequester nonpolar soluble polymer-bound catalysts after a reaction and separate them from products. The extent of this separation and its generality were studied using poly-isobutylene (PIB)- and poly(4-dodecylstyrene)-bound dyes and PE-bound Pd allylic substitution catalysts, PIB-bound Pd cross-coupling catalysts, and PE- and PIB-bound metathesis catalysts.

<sup>1</sup> C.S. Santos, S. Baldelli, *Chem Soc Rev* **2010**, 39, 2136.

<sup>2</sup> H.-P. Steinrück, *Surf Sci* **2010**, 604, 481.

<sup>3</sup> T. Torimoto, T. Tsuda, K. Okazaki, S. Kuwabata, *Adv Mar* **2010**, 22, 1196.

<sup>4</sup> K.R.J. Lovelock, I.J. Villar-Garcia, F. Maier, H.-P. Steinrück, P. Licence, *Chem Rev* **2010**, 110, 5158.

<sup>5</sup> K.R.J. Lovelock, *Phys Chem Chem Phys* **2012**, 14, 5071.

<sup>6</sup> C. Kolbeck, N. Niedermaier, N. Taccardi, P.S. Schultz, F. Maier, P. Wasserscheid, H.-P. Steinrück, *Angew Chem In Ed* **2012**, 51, 2610.

<sup>7</sup> I.J. Villar-Garcia, E.F. Smith, A.W. Taylor, F. Qiu, K.R.J. Lovelock, R.G. Jones, and P. Licence, *Phys Chem Chem Phys* **2011**, 13, 2797.

<sup>8</sup> S. Men, K.R.J. Lovelock, and P. Licence, *Phys Chem Chem Phys* **2011**, 13, 15244.

Catalytic reactions were typically effected using single phase reaction mixtures containing Polywax, THF, and DMF at 75 °C, mixtures that phase separate into two liquid phase on addition of a perturbing agent. The hydrocarbon-bound dyes or catalysts separate into the hot liquid Polywax phase at this point and subsequently form a solid nonvolatile Polywax solid phase on cooling that contains the dye or the recyclable catalyst. In addition to their separability and recyclability, these Polywax entrapped catalysts also are stabilized toward adventitious reactions with polar reagents that would decompose an unprotected catalyst. Extensions of these studies to include polypropylene solvents and polyarene solvents will be described.

## CO<sub>2</sub>-TRIGGERED SWITCHABLE SOLVENTS AND SURFACTANTS

**Philip G. Jessop**

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, ON, Canada K7L 3N6, Canada

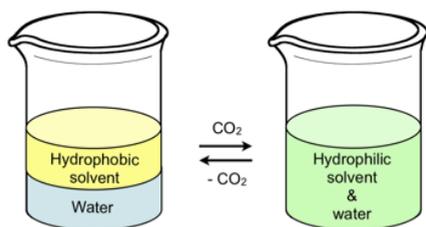
For many practical applications of solvents and surfactants, the ability to "switch" the material's properties during a process would be exceedingly useful. Imagine, for example, a solvent that is capable of dissolving a desired product during an extraction, and then afterwards can be "switched off" so that it is no longer capable of dissolving the product. The product would then precipitate and be easily collected, without any need for distillation. The author invented the first switchable solvents in 2004 and has been working with his students to develop many more switchable liquid and solid materials since then. This presentation will summarize the series of switchable solvents and surfactants developed in the author's labs:<sup>1</sup>

- a) "Switchable-polarity solvents". These solvents have low polarity until they are exposed to an atmosphere of CO<sub>2</sub>, which changes them into high-polarity solvents. The process is reversed by removal of the CO<sub>2</sub> from solution.
- b) "Switchable-hydrophilicity solvents" normally form a biphasic mixture when mixed with water but, when exposed to CO<sub>2</sub>, these solvents become very hydrophilic and completely miscible with water (Figure 1).
- c) "Switchable water". An aqueous solution of a polyamine has a very low ionic strength. However, after CO<sub>2</sub> is introduced, the polyamine changes to a salt, raising the ionic strength. That change in ionic strength dramatically changes the properties of the water and its performance in many applications.

- d) "Switchable surfactants". These molecules are surfactants capable of stabilizing emulsions and suspensions only when CO<sub>2</sub> is present. When CO<sub>2</sub> is removed, the surfactants "switch off" and the emulsion or suspension is destabilized.

The presentation will give an overview of these four technologies and recent work on some of their many potential applications.

1. Jessop, Mercer and Heldebrant, *Energy & Env. Sci.*, (2012) 5, 7240



**Figure 1.** "Switchable-hydrophilicity solvents" are normally so hydrophobic that they form a biphasic mixture when mixed with water. However, when exposed to CO<sub>2</sub>, these solvents become very hydrophilic and completely miscible with water.

## TWO APPROACHES FOR DESIGNING AS GREEN CHEMISTS AGAINST ENDOCRINE DISRUPTORS

### Terrence J. Collins

Teresa Heinz Professor of Green Chemistry and Director, Institute for Green Science, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA, 15213, United States

In recent decades, environmental health scientists have discovered, named and characterized endocrine disruptors (EDs), chemicals that can disrupt the hormonal control of cellular development to impair living things at low doses, often at environmentally relevant concentrations. The feminization of fish by parts-per-trillion concentrations of ethinylestradiol (EE2) in rivers is an example. The synthetic estrogen, EE2, is found in birth control pills.

Endocrine disruption challenges green chemists on two fronts. First, there is the vital need to learn how to keep future commercial compounds free of ED activity. This is no small task given the complexity of the endocrine system, the fact that it exerts developmental control at exquisitely low hormone concentrations, the findings that EDs can disrupt this control at miniscule concentrations, the knowledge that there are numerous disruption mechanisms, and the fact that we are just beginning to understand the system chemically. To this end, I will describe the so-called TIPED, a new living tiered assay protocol for identifying EDs. The TIPED has been produced from a four-year collaboration of environmental health scientists and green chemists. It will allow green chemists to identify whether or not a candidate commercial compound is an ED by the highest standards of the science of any particular time.

Second, for certain commercial EDs, valuable technical performance is tied directly to the biological activity that threatens health and the environment—EE2 is a classic case. While general comprehension of such

hazards may be decades away, it is unlikely that society would ever want to ban such compounds. Therefore, we need more effective technologies for reducing/eliminating such compounds after they have been used. We especially need to protect aquatic organisms by avoiding the most common ED fate of water contamination. This calls for the development of new nontoxic approaches to water purification. EE2, for example, often contaminates municipal effluents. Because of the enormous volumes typically involved, spectacular technical and cost performances are essential for allowing commercial development. To this end, I will describe the development of water ED purification processes based on the small-molecule peroxidase mimics called TAML activators. TAML activators exhibit such outstanding technical performance in removing trace drugs from water that they promise adequate cost performance also.

## EXPLORATION OF NEW CHEMICAL REACTIVITIES FOR SYNTHETIC EFFICIENCY<sup>4</sup>

**Chao-Jun Li**

Department of Chemistry and FQRNT Center for Green Chemistry and Catalysis, McGill University, 801 Sherbrooke Street West, Montreal, QC H3A 2K6 Canada

The efficient making of new molecules is central to any new product in the pharmaceutical, materials science, microelectronics, and biotech industries. The main challenges of developing synthetic chemistry for a sustainable future are two folds[1]: (1) developing highly efficient chemistry to utilize the current chemical feedstock more efficiently and (2) developing new chemistry that can utilize renewable resources readily.

Exploration of new chemical reactivities towards a sustainable future has been a long-term objective of our laboratory. We have explored various unconventional chemical reactivities that can potentially simplify synthesis, decrease overall waste and maximize resource utilization. We planned our research in three progressive stages: (1) developing Grignard-type reactions in aqueous media to simplify protection-deprotections[2]; (2) developing nucleophilic addition reactions by using C-H bonds as surrogates for organometallic reagents, to simplify halogenation-dehalogenation and avoid the utilization of a stoichiometric amount of metal for such reactions (possible in water)[3]; and (3) developing direct C-H and C-H coupling to explore the possibility of chemical transformations beyond functionalization and defunctionalization in syntheses[4]. Within the last decade, we have studied the development of various unconventional methodologies directed at increasing efficiency for multi-step chemical synthesis. Many of these new reactions can also be used to functionalize biomass directly.

[1] Li, C.-J.; Trost, B. M. *Green Chemistry for Chemical Synthesis*. Proc. Natl. Acad. Sci (USA), 2008, 105, 13197.

[2] Li, C.-J. "Quasi-Nature Catalysis: Developing C-C Bond Formations Catalyzed by Late-Transition Metals in Air and Water" *Acc. Chem. Res.* 2002, 35, 533. Li, C.-J. *Organic Reactions in Aqueous Media with a Focus on C-C Bond Formations: a Decade Update*. *Chem. Rev.* 2005, 105, 3095.

[3] Li, C.-J. "The Development of Catalytic Nucleophilic Additions of Terminal Alkynes in Water" *Acc. Chem. Res.* 2010, 43, 581.

[4] Li, C.-J. "Cross-Dehydrogenative-Coupling (CDC): Explore C-C Bond Formations beyond Functional Group Transformations" *Acc. Chem. Res.* 2009, 42, 335.

## NEW CARBON SOURCES FOR THE ENERGETIC AND CHEMICAL VALUE CHAIN: CHALLENGES AND OPPORTUNITIES

### Walter Leitner - Jürgen Klankermayer

Institut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany; E-mail: leitner@itmc.rwth-aachen.de, JKlankermayer@itmc.rwth-aachen.de

The finite resources of fossil feedstock together with the increase in anthropogenic emission of carbon dioxide (CO<sub>2</sub>) are a major concern of global importance. The use of CO<sub>2</sub> as carbon source [1] and the valorization of biomass [2] offer the possibility to contribute to sustainable carbon cycles for energy and chemical supply chains.

This presentation highlights some of the key scientific challenges associated with these concepts and demonstrates how catalysis research provides key contributions to innovation and technological progress in this area. The general aspects will be illustrated with current research from our own laboratories concerning the hydrogenation of CO<sub>2</sub> to formic acid [3] and methanol [4], and the selective conversion of carbohydrate based-feedstocks to tailor-made products [5,6].

[1] *Chemical Technologies for Exploiting and Recycling CO<sub>2</sub> into the Value Chain*  
M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz, T.E. Müller, *ChemSusChem*. **2011**, 4, 1216 – 1240.

[2] *Selective and Flexible Transformation of Biomass-Derived Platform Chemicals by a Multifunctional Catalytic System*  
F.M.A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2010**, 49, 5510-5514.

[3] *Continuous-Flow Hydrogenation of Carbon Dioxide to Pure Formic Acid using an Integrated scCO<sub>2</sub> Process with Immobilised Catalyst and Base*  
S. Wesselbaum U. Hintermair, W. Leitner, *Angew. Chem.* **2012**, in press.

[4] *Hydrogenation of Carbon Dioxide to Methanol using a Homogeneous Ruthenium-Phosphine Catalyst*  
S. Wesselbaum, T. vom Stein, J. Klankermayer, W. Leitner, *Angew. Chem.* **2012**, published online 15 June 2012, DOI: 10.1002/ange.201202320.

[5] *From biomass to feedstock: One-step fractionation of lignocellulose components by selective organic acid-catalyzed depolymerization of hemicellulose in a biphasic system*  
T. vom Stein, P. Grande, H. Kayser, F. Sibilla, W. Leitner, P. Dominguez de Maria, *Green Chemistry* **2011**, 13, 1772-1777.

[6] *Novel synthetic pathway from biomass-derived platform chemicals to 1-octanol and 1,1-dioctylether*  
J. Julis, W. Leitner, *Angew. Chem.* **2012**, in press.

## ADVANCED REDUCTION PROCESSES FOR DESTROYING PERSISTENT OXIDIZED CONTAMINANTS

### Ahmed Abdel-Wahab

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Oxidation-reduction reactions are the primary way in which water treatment processes destroy environmental contaminants. Although every oxidation-reduction reaction must be feasible thermodynamically if it is to occur, many oxidants or reductants can be found that meet this requirement for a specific target compound. However, the requirement to achieve desired levels of destruction within a reasonable time is often not met. Therefore, the main limitation in developing redox treatment processes is normally related to the process kinetics. Although a multitude of reactions are possible, only a few occur at sufficiently rapid rates to be used efficiently for treatment. A new group of treatment methods called Advanced Reduction Processes (ARPs) has been developed by our research group for destroying oxidized contaminants such as nitrate, bromate, chlorate, halogenated organics, and a number of radionuclides. ARPs are based on combining a reducing reagent with activating methods to produce highly reactive reducing radicals. Effectiveness of a number of combinations of reagents (dithionite, sulfite, sulfide, ferrous iron) and activating methods (ultraviolet light from low-pressure Hg lamps (UV-L), ultraviolet light from narrow band lamps (UV-N), electron beam, ultrasound, microwave) on removal of several target contaminants (nitrate, perchlorate, chlorate, bromate, 1,2-dichloroethane, and vinyl chloride) was evaluated. This presentation will provide an overview of the ARPs and their effectiveness in destroying persistent hazardous contaminants.



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