



**University  
of Victoria**

## **Program for the 2009 RISE Workshop**

**14<sup>th</sup> Annual Reactive Intermediates Student Exchange (RISE)  
Workshop**

**August 20-21, 2009**

**Department of Chemistry  
University of Victoria**

Organizers: Cornelia Bohne & Cathy Rzeplinski

RISE gratefully acknowledges the following for their generous support:

Department of Chemistry, University of Victoria  
Faculty of Sciences, University of Victoria  
Vice-President Research, University of Victoria  
Dean of Graduate Studies, University of Victoria

# **EVENTS**

## **DAY 1: Thursday August 20<sup>th</sup> Arrival Day**

- 1530 – 1745**      **SUPERVISOR'S MEETING**  
**ELLIOTT BUILDING ROOM 161**
- 1800 – 2000**      **NACHOS & DRINKS FOR ALL RISE PARTICIPANTS**  
**AND THEIR GUESTS**  
**UNIVERSITY CLUB**
- 1830**              *WELCOME TO RISE*  
**DR. CLAIRE CUPPLES**  
**ACTING DEAN, FACULTY OF SCIENCE**  
**UNIVERSITY OF VICTORIA**

## **DAY 2: Friday August 21<sup>st</sup> Work Shop**

- 0800 – 1330**      **WORKSHOP**  
**BOB WRIGHT SCIENCE CENTRE**
- 1330 – 1345**      **DR. AFZAL SULEMAN**  
**ASSOCIATE VICE-PRESIDENT RESEARCH**  
**UNIVERSITY OF VICTORIA**
- 1345 – 1800**      **WORKSHOP**  
**BOB WRIGHT SCIENCE CENTRE**
- 1900**              **RISE BANQUET AT THE *LURE* RESTAURANT**

## DAY 2: Friday August 21<sup>st</sup> Workshop Day

### BOB WRIGHT CENTRE (BWC) LECTURE HALL B 150

- 0800 – 0830                    **BREAKFAST (BWC) FOYER**
- 0830 – 0835                    **CORNELIA BOHNE: WELCOME REMARKS**
- CHAIR: William Leigh, McMaster University**
- 0835 – 0900                    **Kiana Lahring (U of Calgary), Jun Zhu, and Mark S. Workentin, Department of Chemistry, University of Western Ontario**
- “Preparation of Functionalized Monolayer-Protected Gold Nanoparticles (MPGNs) for Fluorescent Probe Delivery via Photo-Induced Radical Ligand Cleavage”
- 0900 – 0925                    **B. Alexander Fage (Acadia), Amy Tekrony, Dr. Ira Probodh and Dr. David Cramb, Department of Chemistry, University of Calgary**
- “Two-Photon Excitation Photodynamic Therapy: Investigations with Chicken Embryos, Multilamellar Vesicles, and Human Cancer Cell Lines”
- 0925 – 0950                    **Gage Sonntag (U of Saskatchewan), Hao Tang, Cornelia Bohne, Corinne L. D. Gibb, Bruce C. Gibb, Department of Chemistry, University of Victoria**
- “Dynamics of Pyrene Incorporation into Octa-Acid Nanocapsules”
- 0950 - 1020                    **REFRESHMENT BREAK (BWC)**
- CHAIR: Linda Johnston, NRC - SIMS**
- 1020 – 1045                    **Adam Friedman (Queen's University) and Glen R. Loppnow, Department of Chemistry, University of Alberta**
- “Initial Excited-State Structural Dynamics of 2'-deoxyadenosine”
- 1045 – 1110                    **Carolyn L. Ladd (U of Calgary) and Christian Reber, Department of Chemistry, Université de Montréal**
- “Absorption Studies of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and Pressure-Dependent Luminescence Studies of  $[\text{M}(\text{bpy})_2\text{Pt}(\text{SCN})_4]$  Complexes”
- 1110 – 1135                    **Jacqueline Schulman (Western), Cheng Lu, and R. J. Dwayne Miller, Department of Chemistry, University of Toronto**
- “Preparing for the Molecular Movie: Growing  $\text{VO}_2$  for Femtosecond Electron Diffraction”
- 1135 – 1200                    **Joey Sheff (U of Alberta), Thamayanthy Sriskandakumar and Pierre Kennepohl, Department of Chemistry, University of British Columbia**
- “S K-edge XAS of S-N bonding in compounds with varying sulfur and nitrogen oxidation states”
- 1200 – 1210                    **PHOTOGRAPHS**
- 1210 – 1330                    **LUNCH (BWC)**

1330 – 1345 **Dr. Afzal Suleman,**  
**Associate Vice – President Research, University of Victoria**

**CHAIR: Glen Loppnow, University of Alberta**

1345 – 1410 **Hollis Roth (U of Victoria), Pierre Karam, Matthias Götte and Gonzalo Cosa, Department of Chemistry, McGill University**  
“Single Molecule and Ensemble Fluorescence Studies on Polymerase Activity”

1410 – 1435 **Jack Guan (McGill), L. Johnston, and D. Carter, NRC-SIMS, University of Ottawa**  
“Dye partitioning and fluorescence resonance energy transfer in lipid bilayers”

1435 – 1500 **Amani Farhat (U of Ottawa), and R. Scott Murphy, Department of Chemistry, University of Regina**  
“Photochromic Reactivity of Dithienylethenes as Potential Membrane Disruptors”

1500 – 1530 **REFRESHMENT BREAK (BWC)**

**CHAIR: Michelle Chrétien, Xerox Research Centre of Canada**

1530 – 1555 **Ben Fregeau (McMaster), Reinaldo Moya-Barrios, and Frances L. Cozens, Department of Chemistry, Dalhousie University**  
“Halo(Pyridinium)Carbenes: Electrophilic Reactive Intermediates”

1555 – 1620 **Dominica Wong, (McMaster), and M. Lukeman, Department of Chemistry, Acadia University**  
“Investigation of substituent effects on the photodecarboxylation of phenylacetic acid in aqueous solution”

1620 – 1645 **Oliver MacLean (UBC), and Michelle Chrétien, Developer Physics Group at the Xerox Research Centre of Canada**  
“Fundamental Studies of Carrier Aging”

1645 – 1710 **Robyn Porterfield (Concordia), and Matthew Paige, Department of Chemistry, University of Saskatchewan**  
“Fluorescence Spectroscopy and the Characterization of Phase-separated Films Doped with Nile Red”

1710 – 1735 **Mihaela Ceausu (University of Toronto), Maria Gonzalez Bejar, Marta Liras, Kathy McGilvray, Laetitia Rene-Boisneuf, and J.C. Scaiano, Department of Chemistry, University of Ottawa**  
“Fluorescent Studies Towards the Application of Functionalized BODIPY Dyes as Metal Sensors”

1735 -1745 **MARK WORKENTIN: CLOSING REMARKS**

1815 **TRANSPORTATION TO LURE RESTAURANT**

1900 - ??? **RISE 2009 BANQUET AT LURE RESTAURANT  
DELTA VICTORIA HOTEL 45 SONGHEES ROAD, # 250- 360-5802**

# Preparation of Functionalized Monolayer-Protected Gold Nanoparticles (MPGNs) for Fluorescent Probe Delivery via Photo-Induced Radical Ligand Cleavage

Kiana Lahring<sup>#</sup>, Jun Zhu, and Mark S. Workentin\*

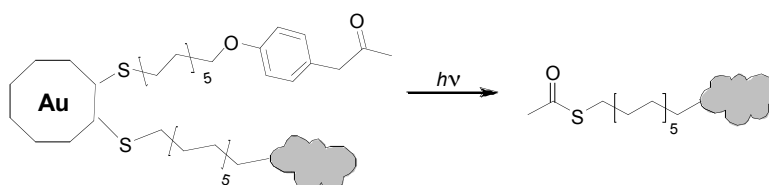
*Department of Chemistry, The University of Western Ontario, London, ON*

<sup>#</sup>*Home Institution: University of Calgary*

---

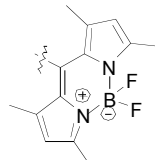
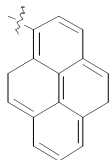
## ABSTRACT

---



could be an electrophore, fluorophore, biomolecule etc.

Such as



There has been recent interest in the application of monolayer-protected gold nanoparticles (MPGNs) in biotechnology due to their non-toxicity.<sup>1,2</sup> Previous research demonstrates that substrates on MPGN surfaces can be liberated efficiently through a photochemically-induced radical abstraction process.<sup>3</sup> In this study, which is an extension of a previous RISE project, a fluorophore delivery system using MPGNs was developed. Alkylthiolate-protected MPGNs ( $2.2 \pm 0.2$  nm) were synthesized via the Brust-Schiffrin method<sup>4</sup> and mixed ligands were incorporated onto the MPGNs by simple place-exchange reactions. Fluorescent probes were applied to test the efficiency of this system as their fluorescence will be quenched when attached to the MPGN and re-generated after cleavage from the gold core surface. Although BODIPY has a very high quantum yield ( $>0.95$ ), it suffers from low stability under UV light; thus, pyrene-terminated ligands were synthesized instead. The results showed that pyrene-substituted ligands could be cleaved from MPGNs and this system therefore has potential for use as a controllable probe/drug releasing system.

---

<sup>1</sup> Daniel, M.-C.; Astruc, D. *Chem. Rev.*, **2004**, 104, 293-346.

<sup>2</sup> Murphy, C. J.; Gole, A. M.; Stone, J. W.; Sisco, P. N.; Alkilany, A. M.; Goldsmith, E. C.; Baxter, S. C. *Acc. Chem. Res.*, **2008**, 41(12), 1721-1730.

<sup>3</sup> Kell, A. J.; Alizadeh, A.; Yang, L.; Workentin, M. S. *Langmuir*, **2005**, 21(21), 9741-9746.

<sup>4</sup> Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. *J. Chem. Soc.*, **1994**, 801-803.

## **Two-Photon Excitation Photodynamic Therapy: Investigations with Chicken Embryos, Multilamellar Vesicles, and Human Cancer Cell Lines**

*B. Alexander Fage, Amy Tekrony, Dr. Ira Probohdh, Dr. David Cramb*

Department of Chemistry, University of Calgary

Two-Photon Excitation Photodynamic Therapy (TPE-PDT) is a novel amendment to traditional photodynamic therapy techniques. Traditional One-Photon Excitation Photodynamic Therapy (OPE-PDT) utilizes a combination of light, oxygen, and photosensitizing drugs to induce cellular death. Ideal photosensitizing drugs accumulate preferentially in problem tissues and under a photochemical reaction upon the application of light, ultimately leading to apoptosis. Photodynamic therapy has been used successfully in treatment of age-related macular degeneration (AMD) and soft tissue cancers.

In AMD, small blood vessels grow out of the choroid and into the retinal space, causing structural damage to the macula and vision loss. Photodynamic therapy can be used to stop the growth of these blood vessels and minimize vision loss caused by angiogenesis.

Problems arise when photosensitive drugs are activated in areas adjacent to the treatment area. The use of TPE-PDT alleviates this problem by making use of two lower energy photons to cause similar excitation. Two-photon excitation is dependent on the square of the laser beam intensity, and is most efficient at the focus of a highly focused laser beam. Thus, there will be less collateral damage to the surrounding tissue.

Using the Chicken embryo chorioallantoic membrane (CAM) as an angiogenic model, TPE-PDT was applied in an attempt to close larger blood vessels whose closure had previously not been attempted. The photosensitizing agent used was verteporfin, a benzoporphyrin derivative known commercially as Visudyne. The treatment parameters varied included laser power, treatment time, and treatment procedure. A verteporfin solution was injected into the egg intravenously and allowed to circulate for approximately seven minutes before treatment with laser.

Lemuteporfin, a photosensitizing agent similar in structure and function to verteporfin, is currently being investigated as a potential alternative for use in TPE-PDT. In an attempt to characterize differences in the photosensitizers, photobleaching and quenching experiments were performed in multilamellar vesicles and U343 glioblastoma cells.

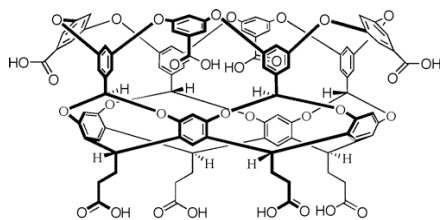
## Dynamics of Pyrene Incorporation into Octa-Acid Nanocapsules

*Gage Sonntag<sup>1</sup>, Hao Tang<sup>1</sup>, Cornelia Bohne<sup>1</sup>, Corinne L. D. Gibb<sup>2</sup>, Bruce C. Gibb<sup>2</sup>*

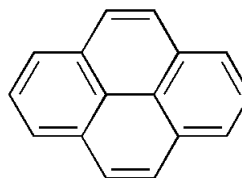
1. Department of Chemistry, Univ. of Victoria, PO Box 3065, Victoria, BC, V8W 3V6 Canada

2. Department of Chemistry, University of New Orleans, New Orleans, LA 70418 (USA)

Octa-acid (OA) is a deep-cavity cavitand with eight carboxylic acid groups. Each OA is 1nm deep and 1nm across and the cavity of the nanocapsule is non-polar relative to the aqueous environment. Two OA molecules can form a dimeric molecular capsule, which can bind with a variety of hydrophobic guest molecules. The understanding of the dynamic process of the guest binding within OA is desirable to understand how the binding of guest with OA affects the guest reactivity.



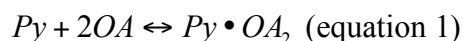
Scheme 1: Molecular structure of octa-acid cavitand



Scheme 2: Molecular structure of pyrene

The polyaromatic hydrocarbon pyrene is ideal for studying the dynamics of incorporation into the OA complex due to its long lived singlet excited state and emission sensitivity to the polarity of its environment. Incorporation into the octa-acid increases the lifetime of the singlet excited state pyrene and dramatically changes the fluorescent intensity of the pyrene molecule.

Steady state fluorescence experiments were used to determine an equilibrium constant of  $(6.1 \pm 1.3) \times 10^{11} \text{ M}^{-2}$  for the incorporation of pyrene within the OA capsule (equation 1). The kinetics of incorporation of pyrene into a supramolecular nanocapsule was studied by employing the stopped flow technique. A  $1.0 \mu\text{M}$  pyrene solution in pH 9.3 buffer was mixed against various concentrations of OA in buffer. A two step kinetic process was observed for the formation of a 2:1 OA/pyrene complex occurring on a ten second time scale. Upon mixing the fluorescent intensity increases over 0.2 seconds. The  $k_{\text{obs}}$  of this step was found to increase when increasing concentrations of OA were mixed with pyrene. After 0.2 seconds the intensity begins to decrease, reaching equilibrium after five seconds while a trend was found for the  $k_{\text{obs}}$  of the second step to decrease with increasing concentration of OA.

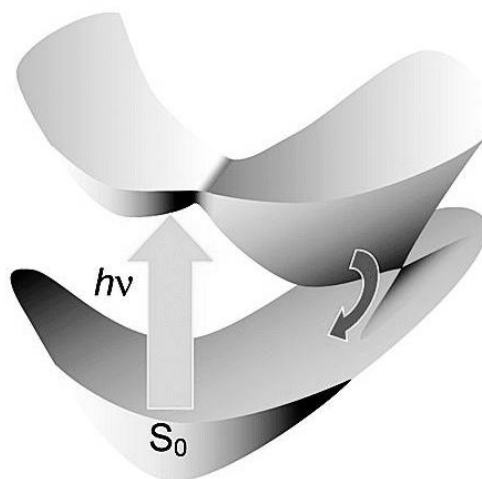
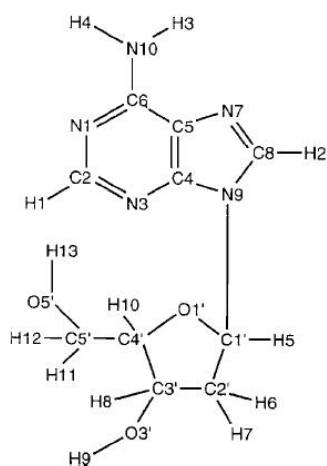


The fast dynamic process could be related to the incorporation of pyrene into one OA molecule while the following slow dynamic process could be related to the incorporation of pyrene into the OA dimer.

## Initial Excited-State Structural Dynamics of 2'-deoxyadenosine

Adam Friedman (Queen's University), Glen R. Loppnow  
Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2

Nucleic acids are essential constituents of the cell, providing the molecular basis of life. There has been much interest in nucleobase photochemistry, as  $[2\pi+2\pi]$  photoaddition reactions are the main source of UV-induced DNA damage and such lesions are responsible for skin cancers induced by sunlight. While pyrimidines are more prone to damage, purines, particularly adenine, have been shown to participate in photochemistry. In order to explore the relationship between photochemistry and molecular structure, 2'-deoxyadenosine was studied using ultraviolet resonance Raman (UVRR) spectroscopy, a sensitive probe of the initial excited-state structural dynamics. UVRR spectra were obtained for 5 wavelengths about the 260 nm absorption band of 2'-deoxyadenosine, and Raman scattering cross sections were calculated for each vibrational mode from the resulting intensities. The UVRR excitation profiles for each mode and the absorption spectrum were fit self-consistently using a time-dependent model in order to determine the initial excited-state structural dynamics of 2'-deoxyadenosine. It was found that the greatest distortion in the initial excited-state was along the N7=C8-H bond. This correlates with the known initial formation of an A $\leftrightarrow$ A photodimer, whose cyclobutane ring links the 5'A N7=C8 and the 3'A C5-C6. The results suggest that some of the initial excited-state structural dynamics of 2'-deoxyadenosine tend towards photochemical outcomes, with the expected observation of a structure-photochemistry relationship, while some lie along primarily dissipative coordinates. All results will be discussed in the context of adenine photochemistry and other important excited-state processes.



*Absorption Studies of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  and Pressure-Dependent Luminescence Studies of  $[\text{M}(\text{bpy})_2\text{Pt}(\text{SCN})_4]$  Complexes*

Carolyn L.Ladd<sup>1</sup>, Christian Reber<sup>2</sup>

University of Calgary<sup>1</sup>, Université de Montréal<sup>2</sup>

Spectroscopic studies of transition metal complexes provide important information regarding their applications and potential uses. Absorption spectroscopy identifies a complex's electronic transitions; luminescence provides information regarding the HOMO-LUMO gap, whereas Raman spectroscopy provides information regarding the complex's vibrational states.

Previous work demonstrated that the double maxima observed in the absorption spectrum of  $\text{Ni}(\text{H}_2\text{O})_6^{2+}$  resulted from the crossing of electronic states close in energy. To further explore this phenomenon, the absorption spectrum of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  was studied. Literature precedence indicates discrepancies in the assignment of the electronic transitions. Solution and single-crystal absorption spectra indicated that the second band of low intensity correlated to the two electron excitation  ${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}$  instead of  ${}^4\text{T}_{1g}(\text{P}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ . B value calculations supported this assertion.

In contrast to octahedral  $\text{Co}(\text{H}_2\text{O})_6^{2+}$ ,  $[\text{M}(\text{bpy})_2\text{Pt}(\text{SCN})_4]$  complexes are square planar. Pressure-dependent luminescence was conducted on these compounds and their solvated analogs to determine the effects. These complexes were unique as they contained both red and blue shifts within the same complex. The effects of solvent and metal type on luminescence will also be discussed.

A discussion of the utility of spectroscopic methods in understanding the properties of metal complexes will be presented.

## Preparing for the Molecular Movie: Growing VO<sub>2</sub> for Femtosecond Electron Diffraction

Jacqueline Schulman, Cheng Lu, R. J. Dwayne Miller.

Department of Chemistry at the University of Toronto.

Femtosecond electron diffraction (FED) allows us to directly observe molecules in their transition states by capturing chemical events on the femtosecond timescale. These molecular movies help us understand the basic processes of molecular reaction dynamics. One of the greatest challenges with respect to FED is the sample limitation. In order for FED to function, the sample thickness must be of the order of 100 nm or less, thin enough to let electrons through. Vanadium dioxide is a material of growing interest in modern optics. At 68 °C VO<sub>2</sub> undergoes a reversible semiconductor-to-metal transition, along with a change in the symmetry of the unit cell. The metal oxide is very suitable for FED studies, as its phase transition mechanism may be investigated. Two methods were used to prepare thin samples of VO<sub>2</sub> for FED. In the first one the aqueous sol-gel technique was used to spincoat a metal organic precursor, vanadyl acetylacetonate, on silicon nitride plates. These were then heated under vacuum conditions to obtain polycrystalline VO<sub>2</sub> thin films. The second method involved the growth of VO<sub>2</sub> single crystals from V<sub>2</sub>O<sub>5</sub>, using the isothermal flux-evaporation principle described by S. Aramaki and R. Roy. The single crystals were then to be microtomed to obtain 100 nm thick slices. VO<sub>2</sub> is one of the most promising thermochromic materials, and thus has many potential applications. Smart windows, temperature sensing devices, and optical switching devices are examples of the uses of thermochromic materials such as VO<sub>2</sub>.

## **S K-edge XAS of S-N bonding in compounds with varying sulfur and nitrogen oxidation states**

*Joey Sheff, Thamayanthy Sriskandakumar, Pierre Kennepohl.*  
Department of Chemistry, University of British Columbia

The bonding properties of three compounds were investigated using sulfur k-edge X-ray absorption spectroscopy (XAS).<sup>1</sup> Two biological compounds, Piloty's acid (*N*-hydroxybenzenesulfonamide) and Pelouze's salt (*N*-nitrosohydroxylamine-*N*-sulfonate), which are involved in the release of the vasodilator nitric oxide, and *t*-butylsulfonamide, a useful compound for the preparation of enantiopure amines and aziridines were investigated.<sup>2</sup> Assignment of features in the XAS spectra was achieved by using time dependent density functional theory (TD-DFT). The effect of the oxidation of sulfur and nitrogen on the S-N bond was the main focus of the project. The results indicate that the oxidation state of the molecule does have a significant consequence on the energy and bonding of the sulfur centre. Since the S-N bond plays an integral role in the use of these compounds, a better understanding of its properties could lead to their more effective use in both the delivery of vasodilators and the organic synthesis of nitrogen containing molecules.

---

<sup>1</sup> Solomon, E.I. et al., *Coord. Chem. Rev.*, **2005**, 249, 97-129.

<sup>2</sup> Reglinski et al., *Inorg. Chem.*, **1999**, 38, 733-737.

# Single Molecule and Ensemble Fluorescence Studies on Polymerase Activity

**Hollis Roth**<sup>1</sup>, Pierre Karam<sup>1</sup>, Matthias Götze<sup>2</sup> and Gonzalo Cosa<sup>1</sup>

<sup>1</sup>*Department of Chemistry, McGill University, 801 Sherbrooke St. West, Montreal, QC, H3A 2K6*  
and <sup>2</sup>*Department of Microbiology and Immunology, McGill University, Lyman Duff Medical Building, 3775 University St., Room D6, Montreal, QC H3A 2B4*

Single molecule techniques have provided new paradigms in chemical biology, biochemistry, and biophysics by revealing unique information otherwise hidden in ensemble measurements. Among these techniques Single Molecule Förster Resonance Energy Transfer (SM-FRET) has enabled the study of bio/macromolecules tagged with donor and acceptor fluorophores, where FRET reports on the position, conformation, and mobility of large bio/macromolecules. SM-FRET, and in more general terms single molecule spectroscopy (SMS) have made it possible to probe the trajectory of a macromolecule from intermediate states to products, and to correlate its position or conformation with reactivity.

Herein we report on our single molecule and ensemble spectroscopy studies designed to obtain a molecular level understanding of *de novo* initiation of RNA synthesis (replication) catalyzed by the hepatitis C virus (HCV) RNA polymerase protein. Our work aims at detecting various intermediates in the replication process, from protein binding to initiation and elongation. Overall, we aim at providing a better understanding of the specific steps involved in HCV RNA genome replication, which in turn will improve the basis for the development of novel antiviral drugs with improved potency and specificity.

Our studies were conducted with a 5' acceptor-tagged DNA oligomer bound to an RNA oligomer with a 3' -26 nucleotide long- overhang and containing a donor dye at its 3' end. Significant FRET enhancements and increase in polarization anisotropy were observed upon HCV binding to the DNA-RNA construct. These changes are consistent with structural rearrangements along the RNA overhang template upon protein binding and sliding. In preliminary work towards monitoring real-time polymerase activity at the single molecule level, we have characterized the changes to be expected as protein replication converts a single stranded flexible RNA overhang into a double stranded rigid oligomer. Herein a dramatic drop in FRET was observed upon annealing complementary DNA sequences to the RNA overhang. We have further initiated studies on the effect of the bound protein on the donor dye (Cy3) photophysics. Consistent with recent reports, our studies show that Cy3 undergoes an emission enhancement following protein binding. We discuss the potential of these protein-mediated photophysical changes towards studying mechanistic aspects of HCV RNA replication.

## Dye partitioning and fluorescence resonance energy transfer in lipid bilayers

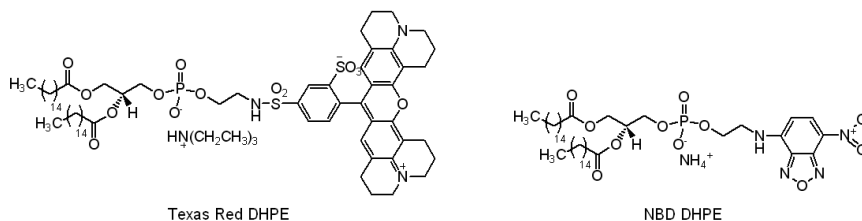
Jack Guan<sup>1</sup>, L. Johnston<sup>2</sup>, D. Carter<sup>2,3</sup>

<sup>1</sup>McGill University, <sup>2</sup>National Research Council, Ottawa, <sup>3</sup>University of Ottawa

The plasma membrane is a complex heterogeneous system that contains various microdomains, one of which is the sphingolipid and cholesterol-rich membrane raft. These rafts, which are involved in processes such as cell signalling and cell adhesion, have a distinct lipid composition from the surrounding liquid disordered membrane. In order to study this phase separated bilayer, we used a model membrane system called DEC 221, which is a lipid mixture of DOPC (dioleoylphosphatidylcholine), egg sphingomyelin and cholesterol in a 2:2:1 molar ratio. The investigation of these membrane rafts relies on the use of fluorescent dye-labelled lipids that partition preferentially into a specific membrane phase.

In the first part of the investigation, we looked at the fluorophore Texas Red DHPE, which partitions into both phases of the model membrane system but preferentially partitions into the liquid disordered phase. Our aims were to find whether Texas Red has equal fluorescence efficiency in the two phases and whether dye concentration affects the relative fluorescence intensities of the chromophore molecules in the rafts and the liquid disordered phase. In order to accomplish these objectives, TIRF microscopy was performed on DEC 221 bilayers to measure fluorescence intensities, and a combination of the spectrophotometer and the fluorometer was used to measure dye absorbance and emission in vesicles of lipid mixtures that represented the two phases. These absorbance and emission values were subsequently used to calculate Texas Red quantum yields through the method described by *Williams et al.*<sup>1</sup>

Although Texas Red is useful for visualizing the liquid disordered phase, an effective way to label the membrane rafts does not exist. Recently, however, we found that a mixture of Texas Red and another fluorophore Nitro-benzoxadiazole DHPE (NBD DHPE) does achieve this. In the liquid disordered phase, it is hypothesized that Texas Red quenches NBD through fluorescence resonance energy transfer. Thus, our goal was to confirm and quantify this phenomenon through measuring and comparing the fluorescent lifetimes of NBD on its own versus NBD in a mixture with Texas Red.



<sup>1</sup> A. T. R. Williams, S. A. Winfield and J.N. Miller, Relative fluorescence quantum yields using a computer controlled luminescence spectrometer, *Analyst*, 1983, 108, 1067.

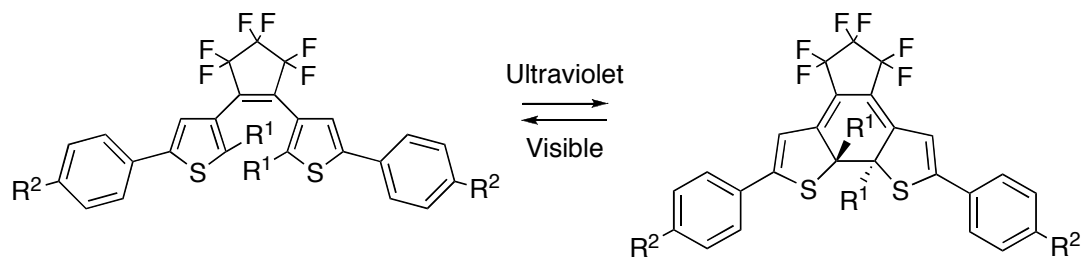
## Photochromic Reactivity of Dithienylethenes as Potential Membrane Disruptors

Amani Farhat, R. Scott Murphy

Department of Chemistry and Biochemistry, University of Regina

We are developing photoresponsive liposomes, through the integration of photochromic membrane disruptors, for their potential application in photoregulated drug delivery. We have synthesized photochromic compounds that contain elements of lipid complementarity. These compounds have thermally stable photoisomers, which is essential in achieving complete photocontrol over membrane permeability.

The dithienylethenes (DTEs) shown below possess the desired properties. They isomerize upon irradiation with UV light, forming a stable, closed-ring isomer. These photochromes also undergo large changes in molecular geometry upon photoisomerization. The primary objectives of this project were to examine the absorption properties and photochromic reactivity of three DTE derivatives.



1: R<sup>1</sup> = CPh, R<sup>2</sup> = H

2: R<sup>1</sup> = CPh, R<sup>2</sup> = Ph

3: R<sup>1</sup> = CPh, R<sup>2</sup> = *n*-C<sub>12</sub>H<sub>25</sub>

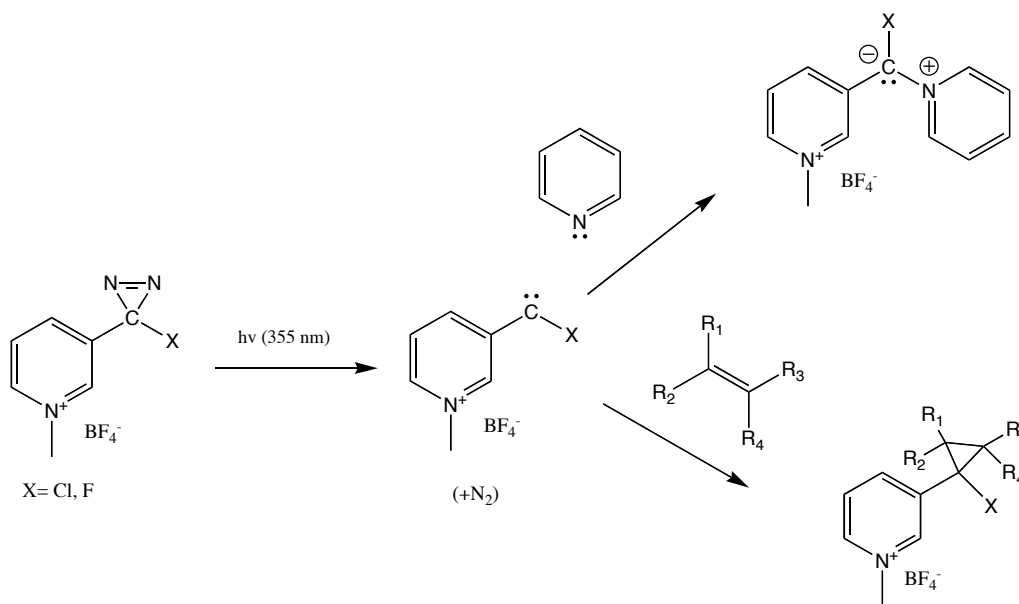
The absorption properties for both the open-ring and closed-ring isomers of **1-3** were examined in *n*-hexane. In order to obtain the molar absorptivities of the closed-ring isomers, the extent of the photoconversions were first determined through HPLC studies. The quantum yields of the cyclization and cycloreversion reactions were then determined for **1-3** using UV-Vis spectroscopy and Aberchrome 540 as a chemical actinometer. These values describe the efficiency with which the absorbed light produces the closed-ring or open-ring isomers. Although the cycloreversion quantum yields were higher than the cyclization, all three compounds exhibit efficient reactivity. Interestingly, the cyclization of **3**, which is most complementary to a lipid membrane, was at least 2-fold lower than **1** and **2**, thus lowering the quantum yield; we suspect the entanglement of the long alkyl chains may hinder the proper conformation for efficient ring closure.

Preliminary results on the incorporation of these compounds in the lipid membrane of hybrid liposomes and their photochromism will also be presented.

# Halo(Pyridinium)Carbenes: Electrophilic Reactive Intermediates

Ben Fregeau, Reinaldo Moya-Barrios, and Frances L. Cozens.  
Dalhousie University Department of Chemistry, Halifax, Nova Scotia

The reactivity of chloro(3-pyridinium)- and fluoro(3-pyridinium)carbenes was examined by laser flash photolysis. The carbenes were generated from the corresponding diazine precursors. Although the halo(pyridinium)carbenes were highly reactive and decayed within the timeframe of the ns laser pulse, their generation was verified by the observation of carbene ylides formed with acetone, acetonitrile, and pyridine, which are readily visible in the UV-vis range. The short lifetime of the transient carbenes precluded direct observation, however the relative order of reactivity of these species with a set of electron-rich and electron-poor alkenes was determined using the pyridine-ylide method. The results show that for all alkenes investigated the halo(pyridinium)carbenes are strongly electrophilic species, reacting faster with the more electron-rich alkenes. This contrasts the previously reported ambiphilic nature of the closely related halo(pyridyl)-carbenes.<sup>1</sup> The small spread of reactivities observed in the halo(pyridinium)carbene-alkene reactions (up to 100 times lower than those of their halo(pyridyl)-counterparts) reveals their very reactive nature. Computational studies demonstrated that the alkene(HOMO)-carbene(LUMO) interaction is predominant for the carbene-alkene reactions, providing support for the strongly electrophilic nature of these reactive intermediates.



1. Moya-Barrios, R., Schepp, N.P., and Cozens, F.L. *J. Org. Chem.* 2009, **74**, 1148-1155.

## Investigation of substituent effects on the photodecarboxylation of phenylacetic acid in aqueous solution

Dominica Wong, M. Lukeman  
Department of Chemistry at Acadia University

Unsubstituted phenylacetic acid has been reported to undergo an inefficient photodecarboxylation ( $\Phi < 0.01$ ) in the excited state to produce carbon dioxide and a benzyl radical through a homolytic cleavage. When phenylacetic acid is substituted with electron withdrawing groups ( $\text{NO}_2$ , COR), the photodecarboxylation occurs more efficiently and via a heterolytic mechanism to give  $\text{CO}_2$  and a benzylic carbanion. The benzylic carbanions produced are of interest because of their potential use as carbon-centered nucleophiles in synthesis. Additionally, a new class of photoremovable protecting groups (PPGs) has been developed that involve initial photodecarboxylation of a substituted phenylacetic acid to generate a carbanion intermediate that subsequently releases the leaving group. These PPGs boast several advantages including clean and efficient photochemistry, rapid release kinetics, and good aqueous solubility.

We have been interested in the chemistry of the intermediate carbanions since it is this chemistry that dictates both the release rates and 'cleanliness' of the PPGs. Depending on the intermediate carbanion involved, rates can range from the sub-nanosecond to several seconds range. In addition, we have been interested in finding new carbanion progenitors from which new PPGs can be designed. To this end, we have begun an exploration of phenylacetic acids bearing electron withdrawing activating groups beyond those already known. So far we have found very efficient ( $\Phi > 0.5$ ) carbanion formation from phenylacetic acids containing  $\text{CF}_3$ , CN, and coumarinyl groups.

The present study focuses primarily on the investigation of the photochemistry of a number of additional phenylacetic acids: 4-sulfonylphenylacetic acid and 3-formylphenylacetic acid in neutral aqueous solution. 4-sulfonylphenylacetic acid was prepared by sulfonation of phenylacetic acid, and 3-formylphenylacetic acid was made by reduction of 3-cyanophenylacetic acid using Raney Nickel. The photochemistry of these compounds was explored using UV-Vis, NMR and GC-MS techniques and both undergo efficient photodecarboxylation. Our results indicate that the ionic pathways to produce the toluene derivatives were generally preferred. Characterization of reactive intermediates using LFP was attempted and compared with available data for related systems.

## **Fundamental Studies of Carrier Aging**

Oliver MacLean: Developer Physics Group at the Xerox Research Centre of Canada

### Abstract:

Photocopiers and laser printers have become familiar objects in our daily life. The process used in these machines, xerography, uses a fine powder called toner to form the image. Toner is mixed with another component, carrier, to form developer. A toner particle is a polymer resin containing color pigment, as well as other functional ingredients, which is then coated with additives to control surface properties. A carrier particle is much larger, consisting of a magnetic core coated with a polymer.

To form the image, the toner must be charged triboelectrically by mixing the developer. Once the maximum charge is reached, further mixing will age the developer, causing the charge to drop and the charge distribution to broaden. Although the processes responsible for the aging of toner are known and accounted for in designing new toners, this is not true for carriers.

Possible mechanisms for the aging of carrier are degradation of the carrier coating integrity to expose bare carrier core, impaction of toner particles on to the carrier surface, and transfer of various additives from the toner surface to the carrier surface. For each mechanism, surrogate accelerated aging tests were performed for two different carriers. The materials from these accelerated tests were then compared to carriers aged in a machine under normal conditions. The materials were analyzed through chromatography, spectrometry, SEM imaging, and measurement of physical properties.

# Fluorescence Spectroscopy and the Characterization of Phase-separated Films Doped with Nile Red

Robyn Porterfield

Supervisor: Dr. Matthew Paige

Department of Chemistry at the University of Saskatchewan

In this project fluorescence spectroscopy was used to characterize monolayer films of mixtures doped with Nile Red. The films, a mixture of arachidic acid (AA) and perfluorotetradecanoic acid (PA), were prepared using a Langmuir-Blodgett trough. In the resulting film, there was a phase separation of the two components forming discontinuous domains of predominantly AA surrounded by a continuous domain composed mainly of PA. Nile Red is a dye whose photophysical properties are strongly dependent on the polarity of the surrounding environment.

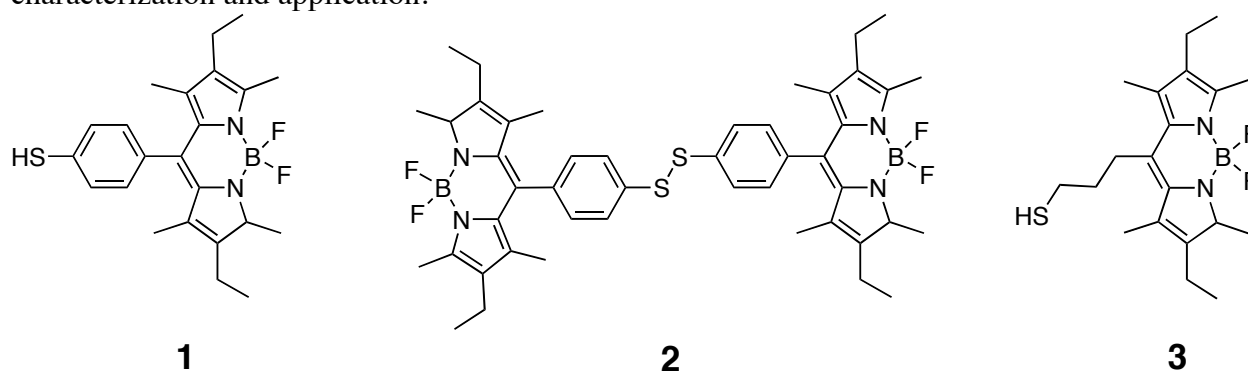
Ensemble fluorescence spectroscopy and microscopy was used to measure the photophysical properties of Nile Red in the different domains. These same properties were then measured by single molecule fluorescence spectroscopy in order to eliminate the effect of ensemble averaging. Results will be discussed in context of existing literature on phase-separated films and spectroscopic properties of Nile Red.

# Fluorescent Studies Towards the Application of Functionalized BODIPY Dyes as Metal Sensors

Mihaela Ceausu, Maria Gonzalez Bejar, Marta Liras, Kathy McGilvray, Laetitia Rene-Boisneuf, and J.C. Scaiano, Department of Chemistry, University of Ottawa

Fluorophores have been widely studied and utilized in a variety of applications in chemistry, and biology such as chemical sensing and molecular imaging. BODIPY dyes possess rich photophysical properties including convenient excitation in the visible region, high photostability, high molar extinction coefficients as well as a high fluorescence quantum yield in organics systems. We have coupled the fluorescent properties of the BODIPY dyes with thiol or disulfide functionalities to investigate the utility as a sensor for metal interactions.

BODIPY dyes **1**, **2** and **3** were synthesized in the laboratory prior to photochemical characterization and application.



Because the highly fluorescent BODIPY dyes include a disulfide or thiol functional group, they were used to study the strong interaction between sulfur and nanoparticles such as gold nanoparticles (AuNP's), and core-shell CdSe/ZnS quantum dots. Nanoparticles are of rising interest for potential applications such as drug delivery, and for molecular imaging. However, before nanoparticles can be used in any system, especially biological systems, their interaction with thiols and disulfides needs to be characterized. These interactions were studied on the surface of CdSe/ZnS quantum dots, and gold nanoparticles by monitoring the changes in fluorescence of the fluorophore. Further studies have investigated the potential use of these functionalized dyes as ion sensors for twelve different metal chloride salts including metals from group II, IV, transition metals, and lanthanides.