

FRED L.M. PATTISON



Fred Pattison was born in Scotland, where he received his early education before going to the University of Cambridge in 1941 for undergraduate work in Natural Sciences, followed by a Ph.D. in Organic Chemistry. He then spent a

year at Dalhousie University as Lecturer before joining the faculty here at UWO as Assistant Professor in 1948.

He established a Ph.D. program in the department, and his research on biologically active organic fluorine compounds resulted in many publications, the award of an Sc.D. by the University of Cambridge, and a book: *Toxic Aliphatic Fluorine Compounds*. In 1959 he became Professor and Head of the Department, and he presided over the expansion of the department and its move to new facilities.

In 1965, Fred decided on a complete career change, and at the age of 42 he enrolled at UWO as a first-year.

On completing his M.D. four years later, he interned at St. Joseph's Hospital here in London and served for a year as resident in the Family Practice Program; he also took a diploma course in venereology at the University of Liverpool. In 1971-73, Fred followed up a long-standing interest in Canada's North people by working with the International Grenfell Association. He provided solo medical care for about 6,000 people scattered along 120 miles of the Atlantic coast of Newfoundland.

Fred returned to London in 1973, when he joined UWO's student health service, holding the position of Director at his formal retirement in 1988. During the same period he was clinical assistant professor in the Faculty of Medicine, giving instruction in venereology, and director of the Middlesex-London Sexually Transmitted Disease Clinic.

On his retirement, Fred was able to resume his connection with the Chemistry Department with the rank of Professor Emeritus. In view of Fred's long service and many contributions to chemistry and medicine at UWO, it is entirely fitting that the department should have a lecture series bearing his name.

Fred Pattison Senior Lectureships

- 1992 Sir Derek Barton, Texas A & M University
- 1993 Barry Trost, Stanford University
- 1995 Stephen J. Benkovic, Penn State University
- 1996 Steven V. Ley, Univ. of Cambridge
- 1997 Anthony J. Kirby, Univ. of Cambridge
- 1998 Larry E. Overman, Univ of California, Irvine
- 1999 J. Fraser Stoddart, Univ. of California, L.A.
- 2000 Dennis Curran, Univ. of Pittsburgh
- 2001 Joseph Lambert, Northwestern Univ.
- 2002 Anthony Barrett, Imperial College
- 2003 Richard Wolfenden, UNC Chapel Hill
- 2004 Victor Snieckus, Queen's University
- 2005 Lutz F. Tietze, Georg-August University Göttingen

Lecture 1: Monday, May 8th, 2006
in 270, 2nd Floor, Medical Science Bldg., 3:00 p.m.
“Fluorescence Sensor Application as Detectors for DNA Damage, Free Radical Formation and in Microlithography”

Lecture 2: Tuesday, May 9th, 2006
in 341, 3rd Floor, Medical Sciences Bldg., 3:00 p.m.
“Lactone Antioxidants: A Classic Case of Mistaken Identity”

Lecture 3: Wednesday, May 10th, 2006
in 341, 3rd Floor, Medical Sciences Bldg., 3:00 p.m.
“Exploring Metal and Semiconductor Nanoparticles from an Organic Chemist's Perspective”

Light Snacks/Refreshments will be served at 2:45 p.m. inside the lecture room

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Our website: <http://www.uwo.ca/chem/>



The UNIVERSITY of WESTERN ONTARIO

The Fred Pattison Senior Lecturer
in Chemistry for 2006

JUAN C. (TITO) SCAIANO

Distinguished University Professor
Department of Chemistry
University of Ottawa



London, May 8th - 10th, 2006
Medical Sciences Building
3:00 p.m.

JUAN C. (TITO) SCAIANO, PH.D., FRSC, O.C.

Dr. Scaiano was born in Buenos Aires, Argentina in 1945. He studied at the University of Buenos Aires (degree in chemistry in 1967) and at the University of Chile (Ph.D. in 1970). After post-doctoral work at University College London he returned to South America to join the University of Rio Cuarto in Argentina where he reached the level of Associate Professor before leaving in early 1975 to join the National Research Council of Canada (NRC) as a visiting scientist. In 1976 Dr. Scaiano joined the Radiation Laboratory at the University of Notre Dame as Assistant Professional Specialist until 1979 when he returned to Canada to join the staff of the National Research Council. Dr. Scaiano was Principal Research Officer and Head of the Reaction Intermediates Group before leaving the NRCC in 1991 to join the University of Ottawa as a Professor where he was named their first Distinguished University Professor and holds the prestigious CRC Chair in Applied Photochemistry.

He has authored about 600 scientific papers, book chapters and patents and is the only Canadian chemist on the list of the world's 100 most cited chemists, in the 2003 release by the Institute for Scientific Information. He has mentored numerous graduate and post-doctoral fellows. He is also an entrepreneur, and recently founded Luzchem Research Inc., an Ottawa-based company that manufactures photochemical equipment.

Professor Scaiano is an Officer of the Order of Canada, a Fellow of the Chemical Institute of Canada and of the Royal Society of Canada, and the 2002 winner of the Gerhard Herzberg Gold Medal for Science and Engineering, NSERC's highest honor and Canada's premier research prize. Other recent awards have included the 2003 Premier's Platinum Medal for Research Excellence, the Canadian Institute of Canada Medal in 1999, the Sir Christopher Ingold Lectureship and Medal (Royal Soc. of Chemistry, UK) in 1998, a Killam Prize in Science in 1998, Porter Medal in 1995, the Henry Marshall Tory Medal of the Royal Society of Canada (1995), a Killam Fellowship (1994-1996) and the 1994 University of Ottawa Award for Excellence in Research. He has been President of the Inter-American Photochemical Society (1990-92), is a member of the Editorial Boards of several journals, and was Editor in Chief of Photochemistry and Photobiology.

Professor Scaiano will give three lectures:

Lecture 1: Monday, May 8, @ 3:00 p.m., MSB 270, 2nd Floor

FLUORESCENCE SENSOR APPLICATIONS AS DETECTORS FOR DNA DAMAGE, FREE RADICAL FORMATION AND IN MICROLITHOGRAPHY

Time resolved fluorescence studies of dye-DNA complexes have been used for the detection of DNA damage. The use of time resolved data has advantages over methods based on amplitude, in that it has much more tolerance for sample

variability. The possibility of using this methodology in the health sciences and in issues related to food authenticity will be discussed.

Fluorescence techniques can also be used to detect latent images for lithographic applications. For example, in the 157 nm exposure of thin films, it was possible to detect both positive and negative acid-base latent images using the same chromophore, by careful choice of the excitation and emission detection parameters. In other cases it was possible to map the distribution of free radicals in a thin resist film applied to a silicon wafer.

In another aspect of the research, pre-fluorescent probes (combining a fluorescent moiety with a paramagnetic center) have been used to detect free radicals in polymer films, in enzymatic processes and in zeolites. Pre-fluorescent probes do not emit (or have very weak emissions) because the paramagnetic center is an excellent excited state quencher; when the probe traps a free radical the molecule becomes diamagnetic and the fluorescence is restored. The concept of pre-fluorescent probes has been extended to the use of semiconductor quantum dots as the emitter.

In the presence of very good hydrogen donors (such as some phenolic antioxidants), pre-fluorescent probes can abstract a hydrogen atom, yielding the fluorescent hydroxylamine. The reaction can be used to test for antioxidant activity.

Lecture 2: Tuesday, May 9, @ 3:00 p.m., MSB 341, 3rd Floor

LACTONE ANTIOXIDANTS: A CLASSIC CASE OF MISTAKEN IDENTITY

Several molecules, including lactone, fluorenyl and ester structures, were examined in order to test the reactivity of various carbon-centered radicals towards oxygen. Some of the radicals that proved unreactive towards oxygen are surprising; notably, the radical derived from coumaranone is unreactive, while coumaranone itself shows enhanced reactivity towards hydrogen abstraction by alkoxy radicals. Similarly, nitrile substitution greatly attenuates the reactivity toward oxygen of vicinal radical centers. We conclude that five parameters influence diminished reactivity towards oxygen, i.e., (a) benzylic resonance stabilization; (b) unpaired spin delocalization on heteroatoms; (c) favorable stereoelectronic effects, such as the forced planarity introduced by the presence of five-member rings; (d) electron withdrawing effects; and (e) steric effects. While all parameters do not need to operate simultaneously, combination of several contributions can lead to dramatic effects in attenuating reactivity towards oxygen.

While unreactive towards oxygen, many of these radicals react readily with an identical or different radical. The dimers formed by self-reaction of two radicals have interesting thermal properties, with typical C-C bond dissociation energies well below 30 kcal/mol.

A study of solvent and isotope effects on the reactivity of lactones with various radicals reveals that the antioxidant properties of lactones are due to the presence of small amounts of enols, while the lactones themselves are not antioxidants.

Lecture 3: Wednesday, May 10, @ 3:00 p.m., MSB 341, 3rd Floor

EXPLORING METAL AND SEMICONDUCTOR NANOPARTICLES FROM AN ORGANIC CHEMIST'S PERSPECTIVE

Metal nanoparticles (e.g., silver and gold) can be readily prepared in solution by reductive processes. Photochemistry can provide temporal and spatial control for the generation of nanoparticles following the photogeneration of reducing organic free radicals. When the radical-forming reactions are carried out in micellar solutions the rate and size of the nanoparticles can be further controlled by external magnetic fields. In these systems the lifetime of the initially-formed triplet radical pairs responds to external fields through Zeeman splitting of the triplet sublevels that in turn influences the lifetime and micellar exit probability of the radicals.

Semiconductor nanoparticles have received attention due to their exceptional luminescent properties. We have examined the quenching of fluorescent CdSe quantum dots by the free radical TEMPO in toluene solutions. Stern-Volmer plots for fluorescence quenching by TEMPO are characterized by major deviations from linearity; typical Stern-Volmer plots are linear, and deviations from linearity are frequently attributed to quenching of more than one electronic state, or to a combination of static and dynamic quenching; the case of quantum dots the changes in slope are too large to be accommodated within this model. The data show an exponential dependence with quencher concentration, of the type $I_0/I = \exp(\alpha[Q])$. Interestingly, the values of α show remarkable size dependence. E.g. the values are 13.7 and 1.6 M^{-1} for quantum dots of 2.4 and 6.7 nm in diameter, respectively. The nature of the molecular interactions leading to this unusual behavior will be discussed.

Association constants for the interaction of TEMPO with CdSe quantum dots are small; however, they are much larger in the case of 4-amino-TEMPO, with extensive binding at submicromolar concentrations. A comparison of fluorescence data with ESR parameters for the nitroxide leads to a better understanding of the interactions involved. The fluorescence of the quantum dot can be restored by free radical generation, thus converting the quenched quantum dots into an effective radical sensor.

We have also examined the interactions of quantum-dots with nitroxides in photonic crystal fibers (PCFs), where the non-linearity mentioned above leads to unusual time dependent fluorescence, as monitored by fluorescence microscopy. The potential of quantum-dot filled PCFs in the design of functional materials, will be discussed.