



**European Photochemistry Association**

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# **NEWSLETTER**

**December 2006**

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## EDITORIAL

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### Chairman's Letter



**Professor David Phillips**

The EPA has been declining in membership and activity over the past decade or so, as the subject of Photochemistry has become more fragmented. Thus many scientists who would formerly have belonged to our Association have joined groups with more specifically defined interests, e.g. atmospheric chemistry, nanoscience, photobiology, PDT organisations etc. However, since there is a common basis to all such work, that is, the interaction of light with molecules, EPA is making an attempt to revive the interest in the Association, particularly among new members.

It is noticeable that the Japan Photochemistry Association has increased its numbers over the past few years, and their recent 30<sup>th</sup> Anniversary Meeting held in Sendai in September was attended by some 700 delegates, many of them students. EPA would like to bring all of our European colleagues back into a state of such vigour! To be fair, some National Associations are indeed very active.

The EPA has recruited new Executive Committee Members, Dimitra Markovitsi, and Eric Vauthey who have taken over the Newsletter and Web-site, respectively. However, the activity of the EPA depends critically upon the activity of its National associations, and these vary enormously. We are encouraging every National Association to hold a National Meeting each year, along the lines that several leading and active Associations have established.

The Executive Committee has taken the decision to offer a prize, beginning early in 2007, for the best Ph.D thesis published in the previous year [ie 2006 for the first competition], and full details will be announced on the web-site early in 2007. We hope this will encourage younger members to take an interest in EPA.

EPA Members currently receive the RCS Journal Photochemical and Photobiological Sciences, PPS (<http://www.rsc.org/Publishing/Journals/pp/index.asp>). This is our journal, and I would urge all EPA members to use it- submit manuscripts, and make sure you receive your subscription.

It is clear that the future of the Association depends upon a process of renewal of membership, executive committee and officers at both national and EPA level, and the recruitment of a new Chairman, since it is my intention to stand down at the next General Assembly, which will be held at the International Conference on Photochemistry in Germany, 2007. May I urge all EPA members to attend this Conference, and the General Assembly and take part in assuring the future of the Association.

**David Phillips**  
*Chairman, EPA*

## PERSONALIA

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### 2006 Porter Metal Awardee



**Professor Howard E. ZIMMERMAN**  
*Department of Chemistry*  
*University of Wisconsin-Madison*

A native of Connecticut, Howard Zimmerman graduated from Yale in 1950, majoring in chemistry (minors in math and German) and with the Chittenden Award, given to the top B.S. student at Yale. His undergraduate years and research with Harry Wasserman were preceded by a tour of duty in the European theater as a tank gunner, which gave him his lecture (aka the "Sarge") voice, somewhat impaired his hearing, but most importantly made him mature and taught him not to waste time, work hard and always try to run ahead of the pack which, six decades later, is still Howard's modus operandi. He completed his PhD studies with English at Yale in 1953 and joined R.B. Woodward's lab as a Lilly National Research Council postdoc. In 1954 he started his independent faculty career at Northwestern University where, among other things, he published seminal papers on the stereochemistry of ketonization of enols and kinetic protonation, and introduced what is now known as the *Zimmerman-Traxler* transition state for the aldol condensation (the concept is used widely in synthetic chemistry). It was at Northwestern where Howard's passion for theory and computations started to blossom. His early studies on carbanion rearrangements (the Grovenstein-Zimmerman Rearrangement) included a theoretical description with MO theory. He contributed a lot to the development of new ideas in theoretical organic chemistry including the first organic correlation diagram and the inhibition of a reaction when occupied MOs become antibonding.

In 1960 Zimmerman moved his laboratory to Wisconsin where he took the experimental and theoretical mechanistic chemistry to a new and literally exciting level - the theory of photochemical reactions; initiating the lifetime work that made him a founding father of modern mechanistic organic photochemistry. Arguably, most notable among his numerous contributions to the field are: the theoretical basis for meta electron transmission in excited states; the Möbius-Hückel concept for reaction allowedness and forbiddenness, with the Möbius counterpart of the Frost-Musulin's mnemonic; the free rotor-effect for energy dissipation of electronic excitation; polarizability predictions of organic reactions; evidence on the relative roles of conical intersections and energy barriers in photochemistry; development of quantitative theories of solid-state reactivity; the Delta-Density Matrix method of predicting both excited and ground state reactivity.

His experimental work uncovered numerous new photochemical transformations for which he provided a modern mechanistic rationale: the Type-A and Type-B rearrangements of unsaturated cyclic ketones, first synthesis of barrelene and the mechanism of di- $\pi$ -methane rearrangement, which now carries his name; the discovery of semibullvalene and its very

facile tautomerism; the  $\alpha,\beta$ -epoxyketone rearrangement to  $\beta$ -diketones and mechanism; the triplet rearrangement of vinylcyclopropenes to cyclopentadienes; the photochemical cyclohexenone to vinylcyclobutanone rearrangement; the tri- $\pi$ -methane rearrangement. From early sixties Zimmerman was preaching an integrated experimental and theoretical approach to treating the reactivity of excited states. He was among very few mechanistic organic chemists, who were capable of bridging the gap between rigorous quantum mechanical computations and the classical (simple and elegant) electron pushing schemes. His theoretical deductions were augmented with state of the art computations, be it the programming of PDP-11 to carry out CI matrix diagonalization in 70's, or running in-house modified Gaussian or Gamess packages to dissect spin-orbit coupling in NHO basis in the 90's.

Zimmerman has a prolific mentoring track record. More than 85 of his former students or postdocs went into academia and gained tenure. About the same number took industrial jobs.

His celebrated accomplishments are acknowledged with numerous awards, including the first Northeast ACS Award for Photochemistry (1971), the ACS James Flack Norris Award in Physical Organic Chemistry (1976), the Halpern Award of the New York Academy of Sciences (1980), election to the National Academy of Sciences in 1980; American Institute of Chemists Pioneering Award (1985), a Senior Alexander von Humboldt Award (1988), the Hilldale Award in the Physical Sciences from the University of Wisconsin (1990), and the Arthur C. Cope Scholar Award of the ACS (1991).

Now the Porter award crowns this list. Still going strong, Zimmerman turns 80 this summer.

Congratulations Howard!

**Professor Andrei Kutateladze**  
*Department of Chemistry and Biochemistry*  
*University of Denver*  
*Colorado*

**PERSONALIA**

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**2006 Porter Metal Awardee**

***Professor Hiroshi MASUHARA***  
*Department of Applied Physics*  
*Graduate School of Engineering*  
*Osaka University*

Hiroshi Masuhara was born in Tokyo in 1944 and started his career in Department of Chemistry at Tohoku University in Sendai under the supervision of Prof. Masao Koizumi, who is one of the pioneers in photochemistry in Japan. After taking the Master Course, Hiroshi moved to Professor Noboru Mataga's laboratory in Osaka University in 1968. A nanosecond ruby laser was available there which he used to measure, for the first time, the excited singlet-singlet absorption spectra of electron-donor-acceptor (EDA) complexes. His Ph.D. thesis completed in 1971 was entitled "The Electronic Structure and Dynamics of the Electron Donor Acceptor Complexes in the Excited Singlet State". This research heralded the start of the nanosecond era in Japan, which of course was followed quickly by picosecond photochemical studies. With Professor Mataga and several students, he conducted systematic studies on EDA complexes and exciplexes, and elucidated their electronic structure and dynamics. Much of this pioneering research on electron transfer, ionic dissociation, triplet formation, and non-radiative relaxation was summarized in *Accounts Chemical Research*, 1981, 14, 312. Around 1980 Hiroshi's interest gradually shifted to molecular aggregates and polymers in solution, and then to their films and powders. The detection technique also shifted from absorption to reflectance spectroscopy, and his efforts became focused on improving the time-resolution.

In 1984 he was appointed Professor in Faculty of Textile Science and Engineering of Kyoto Institute of Technology, and there the exceptional high standard of his work and his ingenuity were recognized and ERATO (Exploratory Research of Advanced Science and Technology) Masuhara Microphotoconversion Project was funded by Japan Science and Technology Agency for 1988-1994. Through his systematic research, Hiroshi understood that photochemistry was expanding and laser chemistry was becoming more important as a new tool which induces heating, high pressure, expansion, melting, fragmentation, and even mechanical force in addition to laser induced chemical reactions. Furthermore, this tool can be conducted freely in space at arbitrary times. Hiroshi recognized the importance of interdisciplinary areas of photochemistry and understood deeply the high potential of photochemistry in modern science and technology. He and his group started to explore new photochemical and photophysical phenomena by developing time-resolved grating, scattering, and various micro/nano spectroscopies, fs-ns imaging techniques, and micro/nano manipulation and patterning methods, and several new interdisciplinary areas of molecular

photoscience were initiated. Hiroshi moved to his present position as Professor in Department of Applied Physics at Osaka University in 1991 where he continues to do carry out innovative research of the highest standard. Hiroshi Masuhara's pioneering and seminal contributions cross borders of many research fields such as materials science, physics, optics, and lately even bioscience.

His seminal contributions are summarized as follows.

1. Time- and space-resolved photophysics and photochemistry of organic nanomaterials.
2. Time-resolved spectroscopy and time-resolved imaging of nonlinear photochemical processes: from laser ablation to protein crystallization.
3. Manipulation by the photon pressure of a focused laser beam: laser trapping dynamics and laser-induced chemistry of individual nanoparticles.

For this pioneering work on the integration of time and spatially resolved measurements in the emerging fields of nanosciences, he was awarded the 2006 Porter Medal under the title of "Pioneering Laser-induced Time- and Space-resolved Micro/Nano-size Photochemistry"

Hiroshi Masuhara has contributed to the photochemistry world not only in scientific research but also as a member of associations and editorial boards and in organizing international conferences. He has worked as a member of IUPAC Photochemistry Commission (1998-2001), was the President of Japanese Photochemistry Association (2000–2001), and was largely responsible for the formation of the Asian and Oceanian Photochemistry Association of which he became the first President in 2002. He has served on the editorial boards of 13 International journals dealing with physical chemistry and photochemistry, and in 2003 he was a joint chairperson of the 21st International Conference on Photochemistry held in Nara, Japan.

Hiroshi Masuhara's scientific achievement has been recognized widely and resulted in his receiving the Japanese Photochemical Association Award (1989), the Moët Hennessy Louis Vuitton International Prize "Science for Art" Da Vinci of Excellence (1993), the Divisional Award of Chemical Society of Japan, the Osaka Science Prize (1994), the Chemical Society of Japan Award (2006), and the Japan Spectroscopy Society Award (2006). He was also honored by being selected as a Foreign Member of the Royal Flemish Academy of Science, Literature, and Art of Belgium in 1998 and he is still serving as a Member. He has been a Guest Professor at several Universities in Europe as well as in Japan.

Hiroshi Masuhara's pioneering work has attracted many young researchers and graduate students to join his group. At present more than 40 doctors from his research group are working in relevant areas of molecular photoscience as Professors and researchers. His seminal research work has been reported in over 430 original and innovative publications and in 13 books, which he and his friends have edited and written. Hiroshi Masuhara's contribution to modern photochemistry is unparalleled and what he has brought to this field is highly innovative and of great lasting significance. It is great pleasure for us to celebrate his 2006 Porter Medal and to wish his further successes and happiness in his coming years.

**Dr. Jai Pal Mittal**  
*President of Asian and  
Oceanian Photochemistry Association*

## PERSONALIA

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### In memory of Professor Jerzy PROCHOROW



*Jerzy Prochorow (1938 –2006) Scientist  
Specialist in molecular photophysics  
Member of the Scientific Councils  
of several Institutes of the Polish Academy of Sciences  
Member of the EPA  
Editor-in-chief of the Acta Physica Polonica A  
Translator of scientific literature*

We wished final farewell to Professor Jerzy Prochorow on October 26<sup>th</sup>, 2006. Professor Prochorow was the head of our molecular photophysics team for nearly 40 years and we owe him a lot. Not only for the scientific supervision he provided, but also for the best possible research conditions he created in the Institute of Physics of the Polish Academy of Sciences. This statement has a special meaning because for most of these years Poland belonged to part of the world dominated by ideology.

Professor Prochorow was a man of wide knowledge, great intelligence, exceptionally gifted with the ability to formulate his thoughts clearly and precisely. The brilliance, self-control, perseverance and obstinacy were behind his success. He was a cheerful, witty man with elegant manners. He led an extremely active scientific career. Apart from research work, he translated many scientific books and was the editor of the journal *Acta Physica Polonica A*. For 10 years (1982-1992), as the director of the Institute of Physics of the Polish Academy of Science, he carefully guided this institution through the stormy years of the martial law and critical times in postcommunist Poland.

He will be remembered as a fierce polemist at countless international scientific conferences and as a man full of humour during friendly chats.

Photophysics of intermolecular electron donor-acceptor (EDA) systems was the main subject of research carried out by the Prochorow group [1-7]. Prochorow started his scientific activity under the supervision of Professor A. Tramer, the head of the laboratory in the Institute of Physics at that time. The major achievement of Prochorow, in the early stages of his research, was the discovery of the ground-state charge-transfer (CT) interaction between molecules in the gas phase [1]. The figure below presents the spectra which made him known to the scientific community.

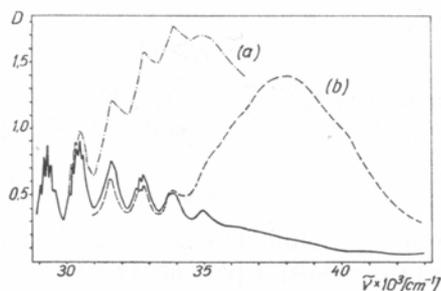


FIG. 4. Gas-phase absorption spectra of carbonyl cyanide ( $p=43$  mm Hg)—full line, and of gaseous mixtures—broken line: (a) carbonyl cyanide ( $p=43$  mm Hg) + benzene ( $p=64$  mm Hg), (b) carbonyl cyanide ( $p=43$  mm Hg) + ethyl ether ( $p=40$  mm Hg).

Consistency and versatility of the research he undertook, will amaze everyone who goes through several dozen of the articles from the Prochorow group. Many EDA systems (di-, tri- and tetra- cyanoethylenes and cyano-benzenes, pyromellitic and tetrachlorophthalic dianhydrides as acceptors and methyl substituted benzenes and polycyclic aromatic hydrocarbons as donors) were examined under different

conditions - in the gas phase, solution, crystals and low-temperature matrices, as well as in supersonic jet expansion. Many experimental spectroscopic methods, like absorption, fluorescence, phosphorescence, delayed fluorescence, time-resolved spectra and emission decays, electron paramagnetic resonance, etc. were applied in the course of the study. Within the framework of these investigations different photophysical parameters of EDA systems, like transition energies, quantum yields and polarisation of the transitions, spectrum bandwidths, etc. were determined.

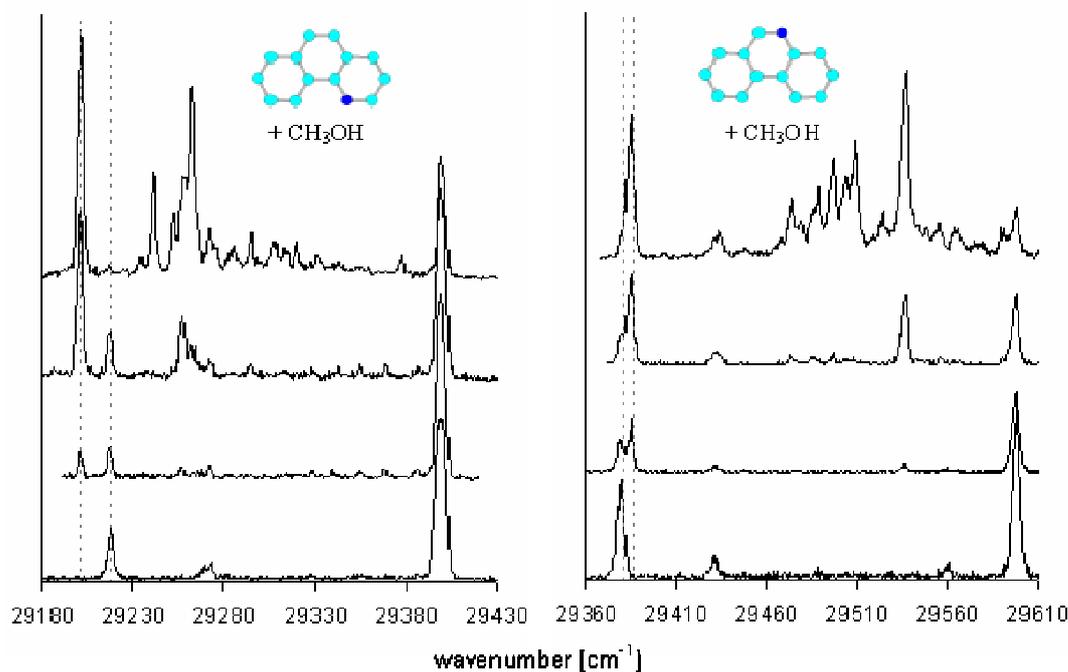
Results of these tedious measurements enabled formulation of the kinetic schemes for formation and decay of excited states of many EDA systems. Deuterium isotope and heavy-atom substituents were investigated as well as the effects of the polarity and rigidity of the solvents. Thermodynamic parameters for excited states of EDA systems were studied as a function of temperature.

The main purpose of these investigations was to learn the pathways and rate constants of formation and decays of excited CT states. These were studied in the context of specific physical parameters of the EDA systems, such as the energy gap between the CT and locally excited states, the ability of the system to form orientational isomers, etc. The importance of the obtained results and of the conclusions is confirmed by numerous citations in the most essential monographs concerning the photophysics of EDA complexes [8-10].

Prochorow was a genuine experimental physicist. He always considered experimental proof of a scientific hypothesis to be the most important. This, of course, does not mean that he didn't care for chemical calculations and modelling.

On the contrary - as experiments became more and more sophisticated, they were accompanied by the advanced methods of quantum chemistry calculations. These two pathways (inseparable and essential in the progress of scientific examinations) have their continuation in the works currently conducted by our team. The pursuit of the physical nature of basic molecular interactions, as in the case of electron donor-acceptor pairs, has been naturally extended by his former students to new areas. Let us mention the detection and spectroscopy of single molecules [11], as well as the advanced investigations of photostability of biologically important molecules [12].

In recent years, Professor Prochorow personally worked on the photophysical properties of N-heterocyclic aromatic hydrocarbons (acridine, monoazaphenanthrenes [13,14]) and their intermolecular interactions [15]). While his health was worsening he tried not to submit himself to the growing weakness and attended the Institute to the very last day of his life. An unfinished paper remained [15] concerning interactions of monoazaphenanthrenes with methanol.



**Figure:** Fluorescence excitation spectra of 7,8-benzoquinoline (on the left) and phenanthridine (on the right) and the complexes with methanol measured in supersonic jet expansion. The spectra of pure monoazaphenanthrenes are shown at the bottom. The concentration of methanol increases from the bottom to the top.

The figure above shows, still unpublished, fluorescence excitation spectra of phenanthridine and 7,8-benzoquinoline and their complexes with methanol measured in the supersonic jet [15]. As one can see, the spectroscopic properties of both investigated

complexes are different in line with Prochorow's earlier supposition [16]. The shift of the electronic transitions for complexes of both molecules is opposite: to the red ( $\sim 18 \text{ cm}^{-1}$ ) for 7,8-benzoquinoline-methanol and to the blue ( $\sim 5 \text{ cm}^{-1}$ ) for phenanthridine-methanol. Moreover, similar points apply also to the different behaviour of the low frequency vibration. However, at present, such small defects related to the electronically excited states can not be theoretically interpreted with sufficient credibility.

The work of Professor Prochorow is completed. This work, however, was not the only source of influence and inspiration for people around him. It was also his rich personality, his wisdom and his gentle ways of being. He will be remembered with fondness and respect.

**I. Deperasińska\*, J. Dresner\*, B. Kozankiewicz\*, A. L. Sobolewski\*  
and A. Tramer\*\***

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## PERSONALIA

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### In memory of Professor Dominique BURGET



#### **Dominique Burget**

*(1965-2006)*

*Professor at the Department of Photochemistry  
Ecole Nationale Supérieure de Chimie de Mulhouse  
France*

Dominique Burget, Professor at the Department of Photochemistry died in an accident on March 24, 2006. He was 41 years old.

Dominique was born on March 18, 1965, in Colmar, France. He started his chemistry studies in 1985 at the University of Strasbourg, and obtained two Master's Degree from the University of Haute-Alsace in Physical Chemistry and in the field of Safety in the chemical industry.

He obtained his PhD on 'Comparative study of the quenching of thioxanthone singlet and triplet excited states by electron transfer: influence of the donor structure and the solvent' in 1992, under the supervision of Professor Patrice Jacques at the Department of Photochemistry of the Ecole Nationale Supérieure de Chimie de Mulhouse. From the end 1992 to March 1993, he stayed at the University of Fribourg in Switzerland in the group of Professor Edwin Haselbach, where he studied the effect of chemical structure on electron back transfer rate constants.

In 1993 he returned to the University of Haute-Alsace where he was nominated assistant professor in the Department of Photochemistry in the group of Professor Jean-Pierre Fouassier. In 1994 he was awarded with Silver medal by the Fondation Alfred and Valentine Wallach for his promising research activity. He continued to work on electron transfer processes and solvatochromism and at the same time was more strongly involved in the study of photopolymerization processes. In this latter field of research, his main interests were the development of novel photoinitiating systems for visible light as well as the formulation of photopolymerizable media for industrial applications. He was promoted to full-professor in February 2005 and formed his own research group on 'Photomaterials, Nanocomposites and Photochemistry of Polymers' in September 2005. His research rapidly extended to nanocomposites included in photopolymerizable media, and particularly metallic nanoparticles. A lot of projects began to take root, and the Department of Photochemistry was willing to support the efforts of Dominique to develop his activity in this field.

On March 24, 2006, an explosion in the research building of the Ecole Nationale Supérieure de Chimie de Mulhouse completely destroyed the Dominique's group's premises in the Department of Photochemistry. He was in his office at the time.

**Professor Xavier Allonas,**  
*Head of the Department of Photochemistry,*  
*E.N.S.C.Mu*

Dominique Burget died on Wednesday March the 24<sup>th</sup> 2006, hapless victim of an explosion, of "*fatum*".

It is hard to do adequate credit to the photochemist, to the colleague and to a friend. I will endeavour to share happy memories of him and his kaleidoscopic personality. But, in fact, what can be said about Dominique since his modesty made him so reserved?

His doggedness faced with experimental data contrary to standard wisdom? As during his thesis, when an addition of a thioxanthone fluorescence quencher in acetonitrile resulted in an increase of the emission, a fact totally at variance with the mechanisms accepted at that time. It required much effort before we were able to demonstrate that not all exciplexes are forced to dissociate in acetonitrile.

His encyclopaedic culture? We were stunned when Dominique could not field any question concerning science or everyday life.

His fanciful alertness of mind? His office was always full of colleagues and students. His involvement in high level teaching certainly sparked the enthusiasm of many students!

His profuse inventiveness which spawned a new idea each working day? His critical mind (so crucial in our field) which could pinpoint the weakness in your line of thought?

Oh yes! the eager discussions until late at night which render our activity so exciting.

Dominique was an endearing mystery and he took his secret with him. He left in the team, both a presence and an aching void, may I dare this oxymoron, a "dense vacuum". It brings a smile to his enigmatic face. The curtain falls.

**Professor Patrice Jacques**  
*Department of Photochemistry*  
*E.N.S.C.Mu*

## CONFERENCE REPORT

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### **Applied Photochemistry and Semiconductor Photocatalysis Symposium, Runcorn, April 2006**

The Royal Society of Chemistry Photochemistry Group is chaired by Dr. David Worrall (Loughborough), with the committee composed of Prof. Bob Brown (Glamorgan, Treasurer), Dr. Gareth Williams (Durham, secretary), Dr. James Bruce (Open), Dr. Peter Douglas (Swansea), Dr. Tony Byrne (Ulster) and Guy Grantham. The group organises typically one major meeting per year, with the latest being a symposium on Applied Photochemistry and Semiconductor Photocatalysis, held at The Heath Conference Centre, Runcorn, on 4<sup>th</sup> April 2006. This one-day symposium attracted over 40 participants from all around the UK to showcase research in this area. Dr. Mike Hawkins, then Chairman of the Photochemistry group, opened the meeting.

The first plenary speaker was Prof. David Birch, from the Centre for Molecular Nanometrology in the Department of Physics, Strathclyde University, part of the Scottish Universities' Physics Alliance. His talk was entitled "a skin full of photophysics", and he described his work in non-invasive metabolic sensing and diagnostics in skin. Such detection, via optical techniques, allows early diagnosis and treatment of a variety of conditions. In his talk Prof. Birch concentrated on the management of diabetes, which affects 3% of the western population and accounts for some 5% of the UK healthcare budget. He described fluorescence lifetime methods using multiphoton excitation of endogenous chromophores, using phase modulation detection. Such an approach has the advantage of absolute calibration, in contrast to intensity measurements. Glucose itself however is non-fluorescent, and hence using this approach to monitor glucose levels requires indirect approaches, e.g. glucose affinity/dextrose displacement FRET sensing. Here glucose binding to an enzyme changes the conformation of tryptophan residues and hence their fluorescence. Embedding the sensor in a silica sol-gel system allows for control of analyte access and reduction of interferences.

The next contribution was from Alexander Orlov (Cambridge) who described photocatalytic decomposition of gasoline additives (typically MTBE) and 4-chlorophenol on TiO<sub>2</sub> modified with gold nanoparticles. A peak in catalytic activity was noted at 0.42 atom % gold, an effect attributed to the gold particles facilitating electron transfer to oxygen. Field studies into using the catalyst for remediating MTBE in ground water in Canada are underway.

This was followed by Samantha Handa (Imperial College) who discussed nanocrystalline solar cells and the drive towards replacing the liquid electrolyte with a solid hole transporting material (HTM). She emphasised the need to minimise interfacial charge recombination in order to achieve high device efficiencies.

The final short presentation of the morning session was from David Rochester (Durham), who talked about the use of metal ions to enhance emission from triplet excited states to improve the efficiency of OLEDs. He described how modifying the coordination geometry at a platinum metal centre modulates electron density and hence emission yield. He also described how mixed molecule systems can act as oxygen sensors, where the wavelength of emission changes in response to oxygen concentration as a result of differential quenching of the two emitters.

The morning session was rounded off with the second plenary of the day, given by Prof. Peter Robertson (Robert Gordon University). He discussed the role of cyanobacteria in freshwater contamination. Such bacteria release two classes of toxin – neurotoxins and hepatotoxins, the latter being principally microcystins. Microcystin LR attacks hepatocytes and causes severe haemorrhaging; it also acts as an inhibitor of protein phosphatase, an

enzyme involved in cell division. These toxins are released when cell death of the bacteria occurs, and hence a remediation strategy needs to not only kill the bacteria, but also mineralise the toxins. Semiconductor photocatalysis is promising in this area, although currently long mineralisation times are required. In contrast the neurotoxin anatoxin-a, an acetylcholine esterase inhibitor, is broken down quite effectively by TiO<sub>2</sub> photocatalysis.

Over lunch there was a poster session, which in common with the previous group meeting was a lively affair with plenty of discussion going on.

The afternoon session kicked off with a plenary from Prof. Andrew Mills (Strathclyde) entitled "Is your photocatalyst any good?" where he discussed approaches to assessing and demonstrating photocatalytic activity. Since many technological applications involve films, he described the standard tests for demonstrating catalytic activity including contact angle measurements and stearic acid and methylene blue photodegradation measurements. Stearic acid is mineralised by TiO<sub>2</sub> and the process can be followed by e.g. IR measurements. He mentioned the problems associated with the complexity of the methylene blue system, where careful control of conditions is required to prevent side reactions from giving misleading results. Where air purification is being measured, removal of NO is a standard test. Finally, he described the development of "intelligent" inks for the purpose of testing photocatalytic activity (Chem Comm 2005, 2721).

Dr Patrick Dunlop (Nanotechnology and Advanced Materials Research Institute, University of Ulster) described the use of nanocrystalline TiO<sub>2</sub> for the disinfection of water through inactivation of microorganisms. His team have investigated Ti foil electrodes upon which anatase of different particle sizes has been immobilised electrophoretically. The photocatalytic disinfection of *E. coli* and *C. perfringens* spores in water was demonstrated, with pseudo zero order and first order kinetics respectively. In all cases, the disinfection is electrochemically assisted: the application of a positive potential to the electrode leads to an increase in the rate of inactivation.

Moving to a quite different area of research, Dr Jacqui Cole (University of Cambridge) described the techniques that are available, and new methods being developed, for single crystal X-ray diffraction studies of excited states of molecules. She highlighted the importance of such studies to phenomena including photoisomerism and spin-crossover magnetic transitions, and summarised some of the steady-state methods that have been used to date. She then went on to explain some of the exciting developments taking place in time-resolved excited state photocrystallography, for example at the new DIAMOND synchrotron facility being constructed in Oxfordshire.

Dr Jim Thomas (University of Sheffield) took us into the realms of coordination chemistry, describing some fascinating macrocyclic structures that assemble from trisbipyridyl ruthenium(II) complexes, appended with two mutually *cis* 4-pyridyl units, upon addition of square planar platinum(II) units. The resulting central cavity can act as a host for aromatic molecules. Dr Thomas also described how, in organic solvents, the structure can function as a luminescent sensor for anions, the binding of which leads to enhancements in the host emission intensities.

The meeting was wrapped up by a plenary lecture from Dr Jason Riley (then University of Bristol, now at Imperial College), who described new methods for preparing nanoparticles for use as wide band-gap photosensitisers in, for example, Grätzel-type solar cells. During the preparation of the nanoparticles, the precipitation of solids is inhibited by using organic moieties, and the particles can subsequently be capped with CdSe by using thiosilane linker molecules bound to the surfaces via the sulfur atom. In this way, structures such as metal-insulator-semiconductor junctions have been prepared. Photoelectrochemical studies have subsequently permitted investigation of the rate of charge transfer across the insulator. Multilayer deposition allows more complex structures to be formed. Using selective

excitation of the nanoparticles in the layer, the influence of particle ordering on the rate of charge transfer has been accomplished.

We all agreed it was a very successful meeting, with some exciting science presented and an excellent networking opportunity. A further broader-themed meeting is planned for 2007. Further information about the group and its forthcoming meetings are available on the group website:

<http://www.rsc.org/Membership/Networking/InterestGroups/Photochemistry/index.asp>

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## CONFERENCE REPORT

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### Autumn Meeting of the French Group of Photochemistry Arcachon, November 2006

The autumn meeting of the Groupe Français de Photochimie (GFP) was held in the shadow of the sand dune of Pyla, near Arcachon (16th-17th November 2006). In addition to the numerous participants from all corners of France, the plenary lecturer Frans De Schryver (Katholieke Universiteit Leuven, Belgium) was counted among the number. His opening lecture of the photophysics session dealt with diverse state-of-the-art spectroscopies with particular regard to studies of energy and electron transfer in multichromophoric single molecules and single enzyme studies, highlighting the differences between single molecule and ensemble measurements. The session continued with a study of a new series of fluorescent  $\pi$ -conjugated cyanine-type dyes by Valerie Guieu (Toulouse) and the fluorescent quenching of fluorophore-decorated gold nanoparticles by Martinus Werts (Rennes). Jean-François Lamere (Toulouse) highlighted the effect of applied electric fields on optical non-linear properties, while Celine Frochot (Nancy) described the behaviour of macromolecules in solution, as determined by fluorescence. The first session closed with Jerome Berthet's (Lille) presentation of a new series of photochromes.

The second session was oriented towards applications of photochemistry in biology and the environment. Dimitra Markovitsi (Saclay) opened this session on considering UV absorption by DNA bases and reconsidering the localisation of excitation energy. The session continued as Patricia Vicendo (Toulouse) described the application of protein-ruthenium polypyridine systems with a view to potential applications in the phototreatment of different medical conditions. The day's final oral presentations were assured by Martin Byrdin (Saclay) and Sabrina Halladja (Clermont-Ferrand) who described mechanistic aspects with regards to electron transfer in amino acids and phototransformation of phenols in the presence of organic matter, respectively.

The first day's scientific programme concluded with an animated poster session, the interest was no doubt aided by the three minute flash presentation by the participants prior to the start of the session. Among the posters, molecule-based fluorescent sensors were well-represented in high performance solid-state devices for detection of nitroaromatics and formaldehyde by Isabelle Leray (Cachan) and Romain Dagnelie (Saclay), respectively, while Sandra Pinet's (Pessac) poster described a sensor for acetylcholine in solution. Posters describing the use of substituted anthracenes as organogelifiants and photosensitizers as well as certain structural and dynamic properties were given by Alexandre Olive (Talence), Sylvie Blanc (Pau) and Patrice Bordat (Pau), respectively. Equally, Nadia Chouini-Lalanne (Toulouse) described photosensitization of DNA, Aurelien Trivella (Marseille) described photochemistry in cryogenic matrices, while Jean-Pierre Galaup (Orsay) reported his latest results concerning spectral hole-burning.

The second morning's opening session focussed on solar energy conversion and photocontrolled materials. Chih-Hao Huang (Talence) described self-assembled organic devices derived from hydrogen-bonding fullerenes and electron donors and their application in plastic solar cells. Electron donor-appended fullerenes were then presented as candidates for molecular photovoltaic materials in Stephanie Leroy-Lhez's (Angers) talk, while Luc Brohan (Nantes) took a different approach, basing his work on solar-energy storage on titanium oxide sols and gels. The session concluded with in-depth looks at the role of oxygen in different photochemical processes :- as an inhibitor in photopolymerization reactions by

Carole Ecoffet (Mulhouse), singlet oxygen emission in sol-gels by Christophe Cantau (Pau) and oxidative damage in conjugated polymers by Sylvain Chambon (Clermont-Ferrand).

The final session of the eclectic scientific programme was consecrated to sensors and molecular probes for a plethora of analytes. Marie Laurence Dumartin (Pessac) reported three-dimensional fluorescent hosts for acetylcholine, Vincent Souchon (Cachan) focussed on calixarene and podand receptors for the detection of heavy metal ions in water. Patrice Baldeck (Grenoble) described biphotonique techniques and applications in biological media while Philippe Banet (Saclay) reported on optical detection of industrial contaminant boron trifluoride. The meeting concluded with complementary electrochemical and photophysical studies on ferrocene-based sensors by Beatrice Delavaux-Nicot (Toulouse) and Suzanne Fery-Forgues (Toulouse).

As well as the outstanding turnout by French researchers representing a diversity of subjects in photosciences, the success of the meeting was assured by the local organizing committee at the University of Pau, in particular chairman Ross Brown and Sylvie Lacombe. In his closing speech Edmond Amouyal (Palaiseau), the new president of the GFP, showed his appreciation along with all the gathered members, to his predecessor Thu-Hoa Tran-Thi (Saclay) for her three years of sterling service. Undoubtedly many participants are already thinking of how to get to Mulhouse for the next meeting, spring 2007.

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## TOPICAL ARTICLES

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### Solar Disinfection of Drinking Water: Saving Lives with Sunlight

Lemme Olangadi is eight years old and lives in the Maasailand Region of the Kenyan Rift Valley. Three times each week she helps her mother carry empty water containers from her bomah - a small collection of mud-huts surrounded by a protective fence of thorn bushes, where she and her extended Maasai family live - to the nearest water source which is a 6 km journey away, on foot. On arrival at the small surface-water pond upon which the local community relies, they wait until a herd of cattle has finished drinking. When their turn comes, Lemme collects turbid water that is heavily contaminated with microbiological pathogens while her mother washes clothes at the opposite end of the same pond. Afterwards it takes more than 3 hours to carry the full containers, some of which now weigh more than 30 kg, back to the bomah.



*Figure 1: A Maasai girl collects contaminated water from a surface pond. The water is then placed in bottles in direct sunlight for at least 6 hours to inactivate the microbiological pathogens it contains.*

In many ways, Lemme's situation is not unique. The World Health Organisation estimates that in 2003 more than 1.1 billion people around the world did not have reliable access to safe drinking water. In Sub-Saharan Africa 769,000 children of less than 5 years of age, died annually from diarrhoeal diseases between 2000 and 2003 (this is nearly twice the total death-toll of the 2004 Indian Ocean Tsunami). However, in one important respect, Lemme is special. If we take a close look at Lemme's bomah we see plastic bottles of water perched on the top of each mud-hut in full sunshine. For the past 10 years the Maasai Community in Southern Kenya has been using Solar Disinfection (SODIS) to improve the quality of their drinking water.

Solar disinfection is not a new technology. Descriptions exist of communities on the Indian Sub-Continent nearly 2000 years ago who placed their drinking water in open trays to be "blessed" by the sun. The bactericidal effect of sunlight was first rigorously investigated by Downes & Blunt in 1877 [1] but it was not until 1984 that Aftim Acra and co-workers in Beirut [2] published their seminal work on using sunlight to disinfect contaminated water for use in oral rehydration therapy. Since then several groups have investigated the full potential of SODIS to inactivate a wide range of waterborne pathogens.

The modern SODIS protocol for making microbiologically contaminated drinking water safe, requires that clear transparent containers are filled with contaminated water and placed in direct sunlight for at least 6 hours. The containers can be made from glass or plastic (usually polyethylene-terephthalate – P.E.T.) – even plastic bags have been used. Previous studies have showed that plastic bottles tend to be more robust than glass bottles. Few glass bottles can survive a fall from the top of a mud hut or a bumpy cross-country journey in the back of a 4-wheel drive vehicle.

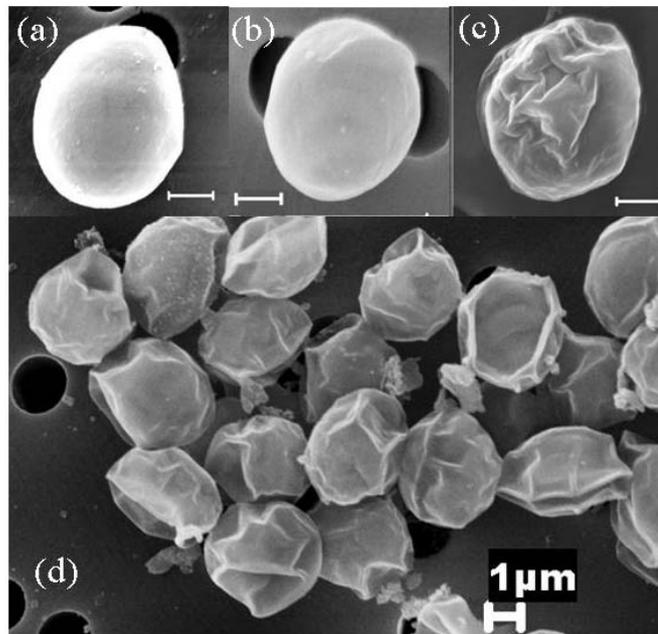


**Figure 2:** An information booklet describing the solar disinfection technique (reproduced by kind permission of EAWAG: see [www.SODIS.ch](http://www.SODIS.ch))

The biocidal effect of sunlight is due to both optical and thermal processes and a strong synergistic effect occurs at temperatures exceeding 45°C. In addition to direct UV killing, sunlight is absorbed by natural photosensitizers present in the water that then react with oxygen producing highly reactive oxygen species such as hydrogen peroxide and superoxide dismutase which exert a disinfecting effect. Solar UV (290-400nm) has been proven to have mutagenic and lethal effects on DNA. The purine and pyrimidine bases, which absorb at 250-270nm, are the main targets of UV damage often through the formation of pyrimidine dimers on bacterial the DNA which halts the cellular fission process and prevents further proliferation of the organisms. We have been able to reduce faecal contamination levels from 1 million *E. coli* bacteria per ml to zero in less than 1.5 hours using the comparatively feeble Irish summer sunlight. SODIS has been shown to be completely effective against many of the most important waterborne pathogens which are responsible for some of the most devastating waterborne diseases such as cholera, dysentery, typhoid, salmonella, gastroenteritis, cryptosporidiosis, giardiasis and polio. A retrospective analysis of an outbreak of cholera which took place in a region of Kenyan Maasailand where a Health Impact Assessment of SODIS was taking place showed that children under 5 years of age in households using SODIS were 7-times less likely to contract cholera than a child of a similar age in a house that did not use SODIS.

This simple intervention has been shown to produce irreparable damage to cellular membranes. Berney et al [3] showed how 6 hour sunlight exposures equivalent to less than half of what might be experienced at sea-level at the equator, is enough to reduce the proton motive force, efflux pump activity, glucose uptake activity, ATP synthesis, membrane

potential and culturability in *E. coli* K12. The results strongly suggest that these exposed cells were no longer able to repair the damage and recover. Cell membrane damage is clearly visible in the scanning electron micrograph image of *Cryptosporidium parvum* oocysts which were exposed to simulated sunlight for 10 hours [4].



**Figure 3:** A scanning electron micrograph of oocysts of the protozoa *Cryptosporidium parvum*. In each case the scale bar represents 1  $\mu\text{m}$ . (a) *C. parvum* at 40°C at time = 0 h. (b) *C. parvum* at 40°C at time = 10 h. (c) *C. parvum* at 40°C + 870  $\text{Wm}^{-2}$  at time = 10 h. (d) Wide field view of *C. parvum* at 40°C + 870  $\text{Wm}^{-2}$  at time = 10 h

Even when strong sunlight is not reliably available SODIS has been found to be surprisingly effective. This may be because roughly half of the incident solar UV is received at ground level as diffuse sunlight which is present even on cloudy days. In addition, infectivity studies using *Salmonella typhimurium* and oocysts of *C. parvum* that we have carried out have proven that even when the pathogen is not completely killed the surviving pathogens lose their capacity to induce the associated disease [4, 5].

In January 2005, in the immediate aftermath of the Indian Ocean Tsunami Disaster, the World Health Organisation approved solar disinfection as an appropriate emergency intervention against waterborne disease. Emergencies come in a variety of forms. We are familiar with earthquakes or Tsunamis and it is obvious how SODIS can assist under such circumstances. However the failure of the a water distribution pumping system or poisoning of the local well by an animal carcass might not seem to be obvious emergencies but for those people directly effected, the emergency and its possible ramifications are very real. We do not see SODIS as the solution to all household water safety problems. A variety of alternate household water treatment and storage technologies are available such as boiling, chlorination, ozonation or filtration and may be more appropriate. However, each of the previous technologies involves a significant financial or man-power investment.

As you read this, solar disinfection is currently in use by more than 2 million people who rely on it to provide safe drinking water in more than 20 developing countries. Most of the microbiological questions have been answered. We know that it is effective against the majority of waterborne biological pathogens. However, many questions remain unanswered, particularly in the area of Photochemistry, such as:

- **What roles do natural photocatalysts play in SODIS?**
- **Can safe photocatalysts be identified and used to speed up or enhance the disinfection process in a Pro-Poor, cost efficient way?**
- **How long can plastic bottles be used before photodegradation of the container material renders them inefficient or even hazardous?**
- **Which photoproducts are produced during the photodegradation of PET?**
- **If so, what are their toxicities?**

Over the years in the course of my research I have collected faeces from Maasai children, run from poisonous snakes, been attacked by Africanised (killer) bees, been bitten by bedbugs, been stalked by lions and have had my experiments stolen at spear-point. At the same time I have had the opportunity to share the hospitality of some of the kindest and welcoming people on the planet such as Lemme and her family. As someone who started his career in semiconductor physics I find it hugely satisfying to be involved in a project whose success is measured by a reduction in infant mortality rate. I would challenge photochemists everywhere, especially early stage researchers to consider a career in this fascinating and rewarding field of research.

#### *Acknowledgements:*

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## TOPICAL ARTICLES

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### Photochemistry in the Development of Gene Therapy

It may not seem obvious but photochemistry has played important role in the research of gene medicines. In the future there are new challenges and opportunities for photochemical methods development in this important medical field.

In this short text we present some examples from our research program.

Gene medicine is a broader term for the pharmaceuticals that are derived from DNA, RNA or their modifications. These drugs include the nucleotide sequence and thereby also specific information related to the genetic code. Depending on the chemistry one can use gene medicine to *increase* expression of the gene (*gene therapy*: bring DNA into the nucleus which is followed by its expression into therapeutic protein) or decrease expression of the target gene (*gene knockdown* by oligonucleotides: gene expression is halted at the level of mRNA and the production of the harmful protein is decreased). The latter case includes also siRNA technology that received the Nobel Prize in medicine in 2006.

Use of DNA, siRNA and other gene medicines is an attractive possibility for the treatment of various diseases, because the entire sequence of the human genome is already known. Therefore, finding the relevant nucleotide sequence for the disease treatment is relatively easy, at least if compared to the synthesis of thousands of small molecular weight drugs against a protein target. However, the delivery of DNA and related compounds into their target tissues and cells is difficult. The gene medicines are in most cases rapidly degraded by the enzymes in the body and they do not get across the cell membranes to reach their target. Therefore, special delivery systems are needed to protect the cargo and deliver it to the target cells. These carriers are typically nanoparticulate systems comprising of lipids, surfactants, polymers, or peptides, and their combinations. These nanoparticulates are usually 50-200 nm in diameter and they should assemble and disassemble in controlled and predictable way.

*Assembly of nanoparticulates.* Upon addition of the cationic liposomes to the water solution with gene medicines complexation takes place. This is not surprising taken the multiple negative charges of gene medicines (i.e. phosphate bridge between the nucleotides). By using FRET measurement and NBD- and rhodamine labeled lipids in the liposomes, we could show that in fact the liposomes fuse with each other upon complexation forming new structures (*BBA-Biomembranes* 1195: 115, 1994). However, even now the exact assembly of the complexes at the molecular level is still unknown.

*Interaction of the complexes with polysaccharides and proteins.* After their administration the nanoparticulates may interact in the blood stream or in the tissues with polyanionic polysaccharides (e.g. heparan sulfate). These interactions may lead to relaxation of the DNA complex and even to the premature release of DNA from the nanoparticle before it enter the cells. These issues were studied by labelling DNA with ethidium bromide (EB). When DNA is packed and condensed in the particle the fluorescence emission of EB is low, and it increases when DNA complex with polycation is relaxed in the presence of heparan sulfate. Significant changes were seen between various lipids and polymers as DNA complexing agents. Some of them (like polyethylene imine) pack DNA efficiently but release DNA easily, while others (e.g. poly-L-lysine) do not seem to release DNA (*J Control Rel* 93: 213, 2003). Controlling DNA release is important because otherwise DNA can not be further transcribed in the nucleus. On the other hand, DNA should not release too early before it enters the cells. Photochemical methods are important in the future in the design of such controlled nanoparticulates.

*Interaction of the complexes with lipid bilayers.* Interaction of the nanoparticulates with cell membranes is important for the delivery. These interactions were modelled with cell membrane mimicking liposomes that were co-incubated with the oligonucleotide nanoparticulates. Fusion with the target membrane was investigated using FRET measurement (i.e. dilution of the FRET pair in the unlabeled lipid matrix during lipid fusion) (*Int J Pharm* 167: 191-203, 1998). Another useful fluorescence method in this context is the lipid bilayer leakage test. Calcein or sulforhodamine B are hydrophilic fluorophores that are encapsulated inside the liposomes at self-quenching high concentrations (*Eur J Pharm Sci* 15: 449-460, 2002, *BBA-Biomembranes* 1195: 115, 1994). Nanoparticulate induced disruption of the cell mimick lipid bilayer is seen as increased fluorescence when self-quenching is relieved upon dilution of the fluorophore.

*Cell uptake and distribution.* Nanoparticulates of gene medicines are taken up into the cells by an active process called endocytosis. After endocytic intake the DNA must be delivered into cell nucleus and siRNA into the cytoplasm of the cells. These are not easy tasks: only a small fraction of the DNA entering the cells reaches the nucleus. Therefore, understanding the intracellular kinetics is important. Total cellular uptake can be measured by incubating the fluorescently labelled particles (e.g. covalent labelling of DNA with ethidium monoazide, rhodamine labelled polyethylene imine) with the cells. The samples are washed and injected to fluorescence activated cell sorter (FACS) that counts the fluorescence intensity of each cell in the suspension and gives the distribution of fluorescence in the cell population (*J Gene Med* 6: 405, 2004). This does not tell about the intracellular localisation of the fluorescence. For that purpose confocal microscope (or two photon microscope) is the method of choice. This allows following the different nanoparticulates in the cells. Studies with rhodamine labelled DNA demonstrated the importance of intracellular distribution: efficient lipid carriers had more DNA localised into the nucleus as compared to the less efficient DNA carriers (*J Control Rel* 99: 177-190, 2004). Luminescence assay of secreted alkaline phosphatase (SEAP) allows non-invasive way to monitor the expression of SEAP transgene from difficult cell cultures without the need to lyse the cells (*Curr Eye Res* 30: 345, 2005).

*In vivo studies* Non-invasive methods are needed for animal experimentation. They allow multiple sampling and generation of the time course from each animal. Luminescence detection of secreted SEAP protein is useful for the pharmacokinetic analysis of the transgene expression. SEAP secretion was followed non-invasively from the surface of the eye into the tear fluid and to the aqueous humor in the inner eye using this method (submitted 2006). Current rapid development in the field of in vivo imaging allows visualisation of nanoparticulates in the animal organs and the levels of gene expression at the target sites (e.g. in tumours).

*Future challenges.* Controlled assembly and disassembly are prerequisites for effective gene medication. It is also necessary to include different protecting and activating signal molecules into the particulates to overcome the multiple barriers. In this respect these systems approach the concept of artificial virus. Good and precise photochemical methods are needed to solve these problems both in the physical, chemical and biological sense. Quantitative and mechanistic analysis of the nanoparticulates function and fate in biological milieu (in the cells, in the body) would be extremely useful in the development of the delivery systems for gene medicines. We are investigating these technologies at DDTC, University of Helsinki, and are open for collaborations in this exciting field.

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## TECHNICAL REPORT

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### Absolute photoluminescence quantum yield determination of solid-state samples

#### Introduction

In the photochemical characterization of materials, a useful figure which can be measured is the photoluminescence quantum yield (PLQY) of a solid sample. From a practical point of view, absolute quantum yields are important: (a) they allow one to assess the sensitivity of a proposed fluorimetric determination of materials and the extent of interference; (b) they are necessary for calculating thresholds for laser action and for judging the suitability of materials as wavelength shifters in optical pumping experiments or for use as energy donors; (c) yields, coupled with other luminescence data, also allow evaluation of the purity of materials. Theoretically, absolute yields are of central importance: (a) for studies of radiationless processes in molecules, (b) for correlation of predicted luminescence lifetimes with the observed lifetime, and (c) for making assignments of electronic transitions.

The luminescence quantum yield of a compound is defined as the fraction of molecules that emit a photon after direct electronic excitation.<sup>1</sup> This quantity does not coincide with the total number of emitted photons which escape a bulk sample divided by the total number of absorbed photons, although in many situations the two quantities are nearly equal. According to the above definition the absolute radiative quantum efficiency,  $\eta$ , can therefore be expressed by the equation:

$$\eta = \frac{N_{em}}{N_{abs}} \quad (1)$$

where  $N_{em}$  and  $N_{abs}$  are the number of emitted and absorbed photons per unit time, respectively.

The procedures used to determine the PLQY are based on two different experimental approaches: the comparative and the absolute methods. In the first approach, a known luminescence standard is used as reference and the PLQY is obtained by a comparison of the luminescence spectra of unknown and standard samples with the same absorption. This is a widely used method, and is suitable for the study of weakly absorbing, isotropic samples such as dilute solutions. However, it has some drawbacks: (a) the chosen reference sample should ideally have similar absorption and luminescence properties as the sample under investigation; (b) it is not uncommon to find different PLQY values reported in the literature for the same standard. In the second method the PLQY is determined relatively to the absorption of the excitation intensity, hence relieving the need of a reference sample.

The absolute method has been the normal approach for measurements on thin films over the last decade. In contrast to measurements of photoluminescence quantum efficiencies in solution, measurements on thin solid films are not straightforward, since the angular distribution of the emitted light is highly sensitive to: (a) the refractive index of the material, which may induce wave-guiding effects and modify the angular distribution of the emission, and (b) the orientation of emitting dipoles within the film, which may lead to an anisotropy in emission dipole moments. The orientational dependence of the emission can be overcome by using an integrating sphere that collects all the ( $2\pi$  steradians) emission from a sample, allowing the determination of the PLQY by an absolute measurement.

In the past decade, several methods for the measurement of the absolute photoluminescence efficiency of solid state samples using an integrating sphere to collect the emitted light have been proposed. In this article two of them, the widest employed ones, will

be reviewed and compared.

### The integrating sphere.<sup>2</sup>

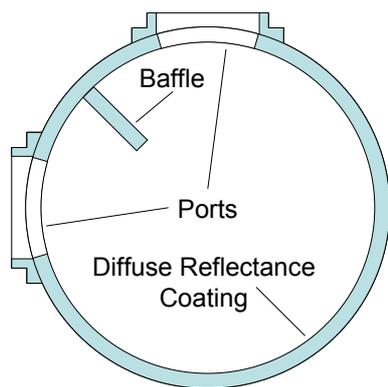
An integrating sphere is a simple device that spatially integrates the radiant flux. It typically consists of a large hollow globe which has its inner surface covered with a diffuse reflectance coating (for instance: barium sulfate, magnesium oxide, gold, Teflon or other thermoplastic resins). The exciting light passes in through the entrance port, and the emission reaches the detector via the exit port. The sample can be placed at the centre of the sphere or side mounted on the sphere wall. A reflecting baffle within the sphere shields the detector from direct source and sample emission (see Figure 1). The primary function of the integrating sphere is to average out, by multiple diffuse reflections, any spatial anisotropy of the emission; refractive index and polarization errors are eliminated too. In an ideal integrating sphere, the light is redistributed isotropically over a Lambertian reflectance surface.

The radiance  $L$  of an integrating sphere is a function of its diameter, coating reflectance, and port fraction:

$$L = \frac{\Phi_i}{\pi \cdot A_s} * \left[ \frac{\rho}{1 - \rho \cdot (1 - f)} \right] \quad (2)$$

where  $\Phi_i$  is the input flux,  $A_s = 4\pi r^2$  is the area of the inner surface ( $r$  being the sphere radius),  $\rho$  is the coating reflectance, and  $f$  is the port fraction, i.e. the ratio between the ports area and the total inner surface. The term in square brackets of the above equation is also called the sphere multiplier,  $M$ . The first rule of thumb for integrating spheres is that no more than 5% of the sphere surface area must be consumed by port openings. The smallest sphere produces the highest radiance in general. However, since the integrating sphere is usually employed for its ability to spatially integrate an input flux, a large sphere diameter and a small port fraction will improve the spatial performance. The coatings of the integrating sphere, although highly reflecting, show a slight wavelength dependence of the reflectance which causes large changes in the reflectivity of the sphere. The sphere thus acts like a filter placed in front of the detector, whose transmission coefficient is wavelength dependent. Therefore,

the selection of sphere coating or material can make a large difference in the radiance produced for a given sphere design. In using integrating spheres, it is important that the radiance flux generated by the sphere inner wall and viewed by the detector does not include a portion of the sphere surface directly irradiated by incident flux. This would introduce a false response. Baffles coated with the same material as the integrating sphere wall block the view of incident flux which has not undergone at least two reflections from the sphere surface. Baffles can be considered extensions of the sphere surface, and their contribution to the sphere area is usually quite small.



**Figure 1.**  
*Schematics of an integrating sphere.*

### The Greenham's method

This method has been originally proposed in 1995 by Greenham et al.<sup>3</sup> for the

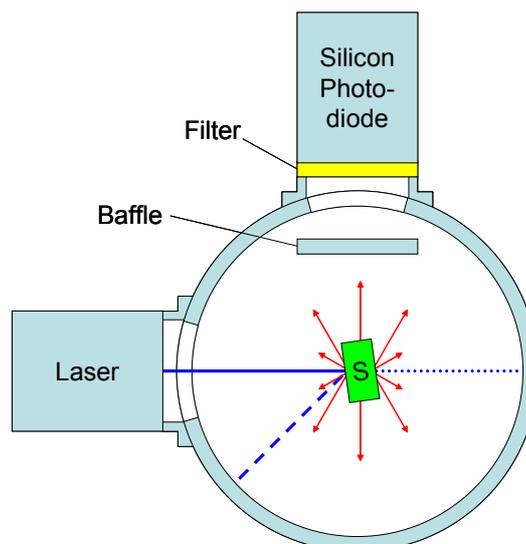
measurement of absolute PLQY in conjugated polymers. The experimental setup consists of a custom built 10 cm diameter integrating sphere with samples mounted at the centre of the sphere. The excitation source is an Ar<sup>+</sup> laser (power 0.1 – 0.5 mW, beam diameter ca. 1 mm), and the detector is a calibrated silicon photodiode. Near normal incidence of the laser beam on the sample surface is used, so that the excitation light cannot be directly reflected back and escape through the input port. A suitable high-pass filter is placed in front of the detector to absorb the excitation light whilst transmitting the emitted light. When the laser beam hits a luminescent sample positioned at the centre of the integrating sphere, the light is absorbed, transmitted, or reflected (see Figure 2). The excitation light which is not absorbed at first strike, is reabsorbed by the sample after reflection from the integrating sphere refractive wall, thus contributing to an enhancement of the emission. To calculate the absolute PLQY,  $\eta$ , it is important to know how much incident light is absorbed by the sample,  $N_{abs}$ , and how much emission is produced by direct excitation,  $N_{em}$ . Three distinct experiments are necessary:

1. in the first experiment, the incident laser light,  $X_{laser}$ , is measured from the empty sphere with the filter removed (Figure 3a);
2. in the second experiment, the sample is placed inside the integrating sphere but off the laser excitation beam, which incides directly on the sphere inner wall. Then, the amount of luminescence due to subsequent reabsorption,  $X_{sphere}$ , is determined from the measurement of light output (Figure 3b);
3. the third experiment is similar to the second one, but now the laser beam directly incides on the sample surface (Figure 3c), and the total amount of emitted light,  $X_{sample}$ , is measured.

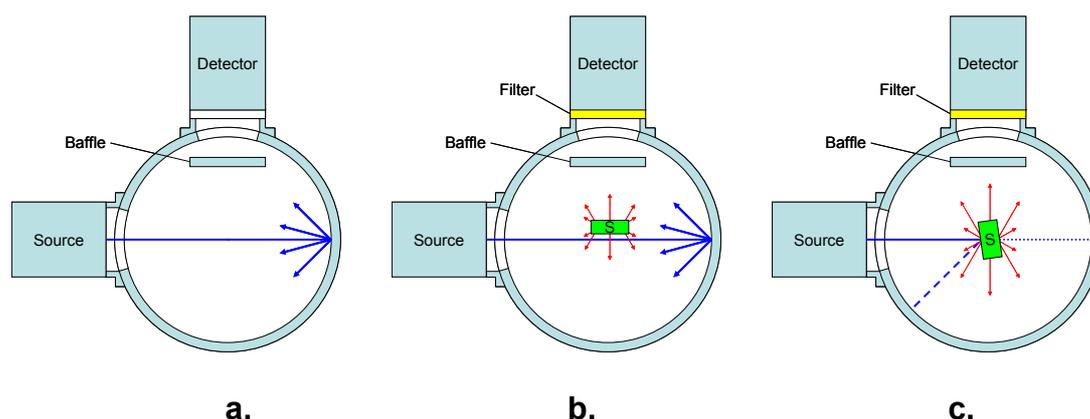
Then, the quantum efficiency,  $\eta$ , neglecting the spectral variation of the system response, is given by:

$$\eta = \frac{X_{sample} - (R + T)X_{sphere}}{(1 - R - T)X_{laser}} \quad (3)$$

where  $R$  and  $T$  are the sample reflectance and transmittance at the excitation wavelength, respectively,  $X_{laser}$  is the signal measured with the laser incident on the sphere with no sample or filter,  $X_{sphere}$  and  $X_{sample}$  are the signal measured with the sample and filter in place, with the laser incident on the sphere wall and on the sample, respectively. In this equation, the laser light diffusely scattered by the sample surface is neglected, but the authors state this shouldn't introduce a significant error.



**Figure 2.** Experimental setup for the Greenham method, *S* indicating a centre mounted sample, red arrows the anisotropic emitted light, blue lines the direct (continuous line), transmitted (dotted line), and reflected (broken line) excitation light, respectively.



**Figure 3.** Experimental setup for the measurement of  $X_{laser}$  (a),  $X_{sphere}$  (b), and  $X_{sample}$  (c), respectively. For the definition of the three quantities, see text.

The spectral response of the sphere is determined using a tungsten lamp and a CCD spectrometer, with optical fiber input. The spectrum of the lamp,  $S_{lamp}(\lambda)$ , is first measured outside the sphere. The lamp is then used to illuminate the sphere through the laser entrance hole, and the spectrum,  $S_{sphere}(\lambda)$ , is measured at the exit port. The correction factor for the spectral response is given by:

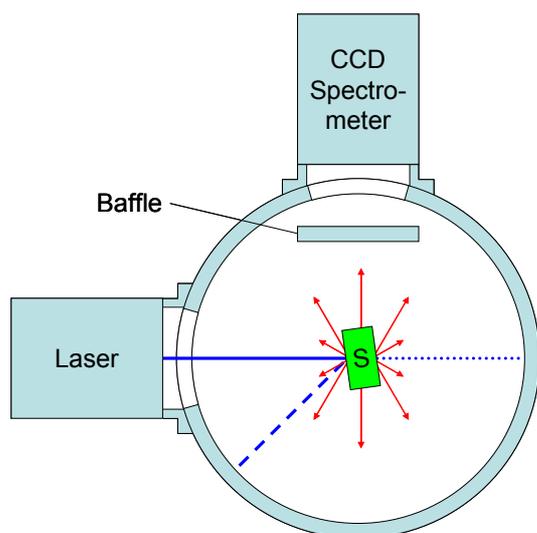
$$cf = \left( \int \frac{S_{sphere}(\lambda)L(\lambda)G(\lambda)F(\lambda)}{S_{lamp}(\lambda)} d\lambda \right) \times \left( \frac{S_{sphere}(\lambda_{ex})G(\lambda_{ex})}{S_{lamp}(\lambda_{ex})} \int L(\lambda)d\lambda \right)^{-1} \quad (4)$$

where  $L(\lambda)$  is the emission spectrum of the sample,  $G(\lambda)$  is the quantum efficiency of the photodiode,  $\lambda_{ex}$  is the excitation wavelength, and  $F(\lambda)$  is the transmission of the cut-off filter. The PLQY is then simply given by  $\eta / cf$ .

This method has proven to be very reliable for the determination of absolute photoluminescence quantum yield of many solid state samples. Nevertheless, it suffers of some drawbacks that limit its application to highly emitting, non-scattering samples with large Stokes shifts:

- i. the absorption coefficient at the excitation wavelength has to be determined by separate measurements of reflection,  $R$ , and transmission,  $T$ , coefficients, which can only be reliably made for non-scattering samples;
- ii. the use of a filter to distinguish between absorption and emission places a lower limit on the measurable quantum yields, which depends on the performance of the filter itself. In fact it is not possible to measure quantum yields of samples whose luminescence is comparable to the filter fluorescence;
- iii. it is not possible to make a reliable estimate of PLQY for samples exhibiting small Stokes shift, because the finite filter roll-off makes difficult to distinguish between the excitation laser light and the luminescence;
- iv. reabsorption of emitted light, redirected onto the sample after reflection from the sphere inner coating can not be avoided. This effect is obviously severe when there is a strong overlap between absorption and emission spectra.

### The de Mello's method



**Figure 4.** Experimental setup for the de Mello's method. The detection system consists of a CCD spectrometer without any filter. The meaning of symbols is the same as in Figure 2.

The method proposed in 1997 by de Mello et al.<sup>4</sup> represents an improvement over the above commented Greenham's method. The experimental setup (sketched in Figure 4) is similar to the previous one, using a laser excitation source and an integrating sphere with the sample mounted at the centre, but this time the detection system consists of a grating spectrometer with a CCD detector, rather than a silicon photodiode, coupled to the integrating sphere through an optical fiber.

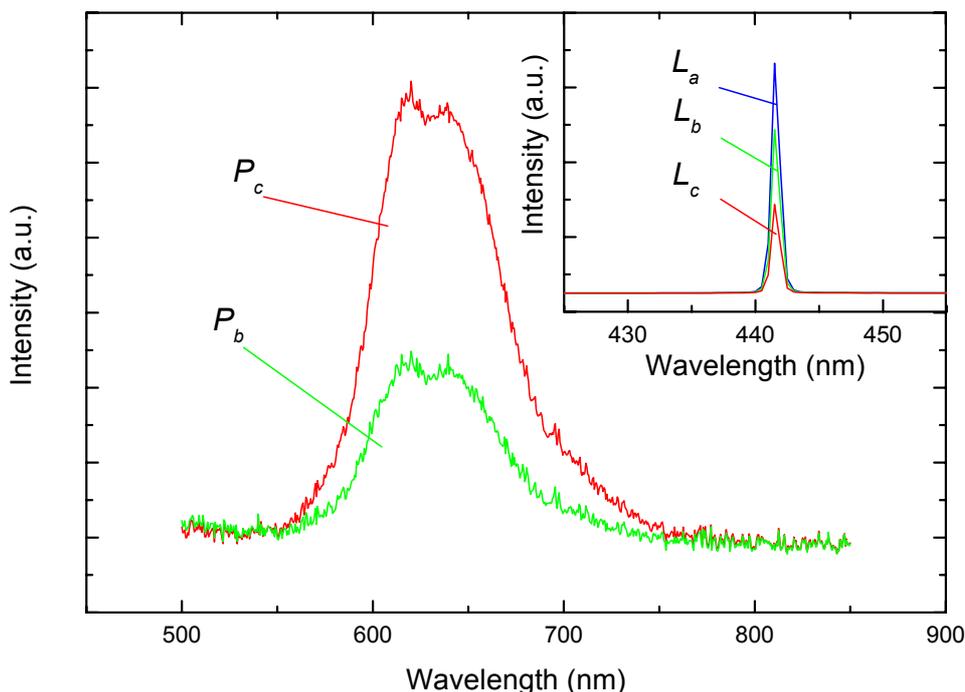
As in the Greenham's method, three experiments are needed in order to determine the absolute luminescence quantum yield of the sample, but this time a full spectrum is recorded in each experiment (see Figure 5). In the spectra the sharp high energy peak corresponds to the detection of the laser excitation, and the broader profile extending to lower energies is due to the emission from the sample. The area under the laser profile,  $L$ , is proportional to the amount of unabsorbed light, while the area under the emission profiles,  $P$ , is proportional to the amount of emitted light.

1. From the first experiment, where the laser beam directly strikes the inner wall of the empty sphere, the total amount of excitation light,  $L_a$ , is obtained (see Figure 5).
2. In the second experiment, where the sample is positioned inside the sphere but off the laser beam pathway, the detected signal is composed by the scattered laser light,  $L_b$ , and the light emitted by the sample,  $P_b$ , after absorption of scattered excitation light. A fraction  $\mu$  of the laser light scattered from the sphere wall is absorbed by the sample, then:

$$L_b = L_a(1 - \mu) \quad (5)$$

3. In the third experiment the laser beam directly hits the sample surface and a fraction  $A$  of excitation light is absorbed. The unabsorbed fraction  $(1 - A)$  is either transmitted or reflected, and a fraction  $\mu$  of this scattered light is then reabsorbed by the sample. The area of the detected excitation light spectrum ( $L_c$ , Figure 5) can therefore be expressed by the equation:

$$L_c = L_a(1 - A)(1 - \mu) \quad (6)$$



**Figure 5.** Laser beam ( $L$ , inset) and emission spectral profile ( $P$ ) detected for the three experiments described in the text (de Mello's method).

Combining equations 5 and 6, an expression for the absorption coefficient  $A$  is obtained:

$$A = \left( 1 - \frac{L_c}{L_b} \right) \quad (7)$$

The emission profile measured in this experiment has two contributions: (a) the first,  $\eta AL_a$ , where  $\eta$  is the photoluminescence efficiency, is due to the absorption of the excitation laser light; and (b) the second is due to the light emitted after absorption of the scattered excitation light, given by  $(1 - A)P_b$ . Thus:

$$P_c = \eta AL_a + (1 - A)P_b \quad (8)$$

Rearranging this equation, an expression for the absolute PLQY is obtained:

$$\eta = \frac{P_c - (1 - A)P_b}{AL_a} \quad (9)$$

It is to be noted that the recorded spectra have to be corrected for the spectral response of the whole detection system, i.e. the integrating sphere / spectrometer assembly, before the integration procedure.

The use of a spectrometer in these efficiency measurements provides several advantages over the previous Greenham's method:

- i.* absorption and photoluminescence are measured simultaneously, so the effects of sample degradation are minimized;
- ii.* the method can be applied even to highly scattering samples, because no separate measurements of reflectance and transmittance are needed;
- iii.* no cut-off filter is used, which could put a limit to the lowest measurable absolute

quantum yield;

- iv. reliable determination of PLQY can be performed irrespective of the nature of the sample, i.e.: solid / liquid, transparent / opaque, with reflecting / scattering surface.

In Table 1, the relevant quantities obtained in each of the three experiments, needed by the Greenham's and de Mello's procedure, and the equations for the determination of PLQY are summarized.

**Table 1.** Relevant quantities obtained in each of the three experiments following the Greenham's and de Mello's method (see text).

	Greenham's method	de Mello's method	
		Laser profile	Emission profile
Exp. 1	$X_{laser}$	$L_a$	–
Exp. 2	$X_{sphere}$	$L_b = (1 - \mu)L_a$	$P_b$
Exp. 3	$X_{sample}$	$L_c = (1 - A)(1 - \mu)L_a$	$P_c = (\eta A)L_a + (1 - A)P_b$

$$\eta = \frac{X_{sample} - (R + T)X_{sphere}}{(1 - R - T)X_{laser}} \quad A = \left(1 - \frac{L_c}{L_b}\right) \quad \eta = \frac{P_c - (1 - A)P_b}{AL_a}$$

### Practical hints

These two methods have been applied to a wide variety of materials and with different experimental setups. Up to now the original papers by Greenham and coworkers and de Mello and coworkers have been cited in more than 360, and 150 scientific journal articles, respectively.<sup>5</sup> The two original procedures for the determination of PLQY of solid state samples based on the use of an integrating sphere have been implemented by different groups with many different experimental setups: among others the use of CW laser (HeNe, HeCd, and Ar<sup>+</sup>) or collimated arc lamp (Xe, Hg, Hg/Xe) sources has been suggested; a variety in size of integrating spheres, with central or wall mounted samples, have been used; the detection systems proposed range from simple photodiode to CCD spectrometer or to the more sensitive monochromator / photomultiplier combination. Recently, the de Mello's method has also been implemented by the use of an integrating sphere hosted within a commercial fluorimeter.<sup>6</sup>

The Greenham's and de Mello's procedures have been compared<sup>7</sup> measuring the absolute photoluminescence quantum yield of a series of solid state samples, consisting of metal complexes, inorganics, or organics, emitting in different spectral regions, and with quantum yields ranging from 0.05 to unity. The PLQY values obtained from the two methods were comparable within the experimental errors, except for those materials that exhibited a significant spectral overlap between absorption and emission. In the last cases the quantum yields obtained by the Greenham's method, as expected, were significantly underestimated (see discussion above). In Table 2 the pros and cons of each of the two methods described in this note are compared.

Recently, the Molecular Photoscience Group at ISOF-CNR has been interested in the

**Table 2.** Comparison of advantages (PROs) and drawbacks (CONs) of Greenham's and de Mello's absolute PLQY determination procedures.

	Greenham's method	de Mello's method
PROs	<ul style="list-style-type: none"> <li>• <i>Simple setup for the measurements of the absolute PLQY in solid films</i></li> </ul>	<ul style="list-style-type: none"> <li>• <i>Simoultaneous measurements of absorbance and emission efficiency</i></li> <li>• <i>Reliable measurements of quantum efficiency of highly scattering samples</i></li> </ul>
CONs	<ul style="list-style-type: none"> <li>• <i>Absorbance at the excitation wavelength cannot be measured for highly scattering samples</i></li> <li>• <i>The use of a cut-off filter place a lower limit on the measurements of the quantum efficiency</i></li> </ul>	<ul style="list-style-type: none"> <li>• <i>Re-absorption (if a strong overlap in the absorption and emission spectra exists).</i></li> </ul>

study of the photophysical properties of organic films doped with emitting metal complexes. From that circumstances, we drew interest in the determination of absolute PLQY of solid state samples. After a thorough literature search, we were able to select an appropriate methodology, and decided to implement and setup in our lab an appropriate adaptation of the de Mello's method. This was accomplished by using:

- i. a Kimmon He-Cd continous wave laser source ( $\lambda_{em} = 325.0$  and  $441.6$  nm, P = 5 and 35 mW, respectively);
- ii. a Spectrafect (a specially formulated barium sulfate) coated LabSphere general purpose integrating sphere (d = 6 in);
- iii. a custom built Teflon central mounted sample holder;
- iv. a solarization resistant fiber optic for deep UV applications (d = 600  $\mu$ m, L = 2 m);
- v. a computer controlled Avantes AvaSpec-2048 Fiber Optic Spectrometer, with 0.8 nm FWHM resolution.

In our experimental setup, the laser is directly coupled to the integrating sphere input port. Inside the sphere, a baffle is placed in front of the sphere output port in order to protect the detector from direct illumination by non-diffuse light. The CCD spectrometer is connected to the sphere output port either directly or by means of an optical fiber. With this assembly, great care is taken in order to avoid perturbation by external light. The total response of the integrating sphere + detection system assembly has been corrected by using a calibrated 45 W quartz-halogen tungsten coiled filament lamp standard of spectral irradiance by Optronics Labs (calibration range from 250 to 2500 nm).

In order to test the reliability of the system, we have measured the absolute quantum yield of some liquid and solid reference materials. The absolute yields obtained, and collected

in Table 3, match the corresponding values reported in the literature within the experimental errors.

**Table 3.** Photoluminescence quantum yields of some liquid and solid reference materials.

	PLQY	
	found	reported
[Ru(bpy) <sub>3</sub> ]Cl <sub>2</sub> in H <sub>2</sub> O	0.024±0.005	0.028 <sup>8</sup>
Quinine Sulfate in 1 N H <sub>2</sub> SO <sub>4</sub>	0.51±0.05	0.546 <sup>9</sup>
LUMOGEN® F Orange 240 in PMMA (BASF)	1.08±0.09	< 0.99 <sup>10</sup>

### Conclusions

The great importance of the determination of emission quantum yield in solid state samples is a topic of increasing importance, as testified by the great number of relevant citations in a relatively short time frame (*ca.* 10 years), after decades of substantial overlooking. Now, with reliable and simple instruments at hand, it is possible to measure the absolute photoluminescent quantum yields of virtually any kind of materials, from powders to films and solutions. Presently, the use of absolute methods looks a convenient way towards the determination of PLQYs, and results in a better approach than the exclusive reliance on a luminescence standard for its calculation.

### Acknowledgements

The authors thank the colleagues Dr. Sandra Monti and Dr. Francesco Barigelletti (ISOF-CNR) for the help in the preparation of the manuscript, Dr. Marco Montalti (Dept. of Chemistry, Univ. of Bologna) for the technical assistance in the setting up of the system, and the EC for the financial support through the FP6 – Integrated Project “OLLA – Organic LEDs for Lighting Applications” (*contract n° IST-2002-004607*).

Please visit the website of the OLLA Project, [www.olla-project.org/](http://www.olla-project.org/), and that of the Molecular Photoscience Group at ISOF-CNR, <http://www.isof.cnr.it/photoscience/>.

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## PUBLICATIONS

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### Abstracts of theses in Photochemistry

**Namrata SINGH TOMER**

*Assessment and improvement of elastomer long term behaviour for electrical insulator application*

Ph.D Thesis, Université Blaise Pascal, October 2006

Working place : Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, Université Blaise Pascal, F-63177 Aubière-Cedex, France

Supervisors: Jacques Lacoste et Florence Delor-Jestin

This research deals with the study of long term behavior of elastomer housings used for the protection of the central epoxy and fiber glass composite rod of the electric insulators. Four types of industrial formulations having bases of polydimethylsiloxane (PDMS) or ethylene propylene diene (EPDM) are studied.

The formulations were subjected to various types of ageings in order to simulate an exposure similar to natural degradation which the insulator experiences during its service life time. We have compared the evolution of properties of the different components of the formulations, to help us in identifying the influence of the polymer matrix and the different components on its aging. The Al(OH)<sub>3</sub> filler was identified as the weakest component of the formulations in presence of nitric acid vapour.

The formulations having a base of PDMS are not very sensitive to usual ageings (thermal and photochemical). No oxidation is detected after 10,000 hours of exposure. The formulation based on EPDM present at the same time a traditional oxidation of the dienic elastomer during photochemical and thermal ageings and the reactions of cross-linking. We have used the thermoporosimetry technique to calculate the pore size distribution of the polymer network giving us a new view about the cross-linking of the elastomers. Using this study we can rapidly characterize the period of induction before degradation and modification of the properties, an important post cross-linking is detected upon ageing for the EPDM and Siloxane formulations.

We have carried out a fundamental study on uncross-linked polysiloxanes without fillers. It helps us to better understand the ageing behaviour of silicones compared to the cross-linking and to study the structure property relationships. Polydimethylsiloxane do not oxidize but are degraded by cross-linking and chain scissions reactions upon thermal and photo-ageing. They are stable in presence of nitric acid vapours. However, polysiloxanes having a carbon chain in the backbone undergo oxidation, cross-linking and chain scission reactions upon thermal and photo-ageing. They are also degraded by nitric acid vapours.

Lastly, we have tested new stabilized formulations in presence of nitric acid vapours and photochemical ageing.

**Clelia CANUEL**

***Photophysics of isolated nucleobases and their hydrates: femtosecond dynamics study by photoelectrons, photoions and fragments detection***

PhD thesis, University of Paris XI, October, 2006

Working place: Laboratoire Francis Perrin

CEA/DSM/DRECAM/SMAP-CNRS URA 2553

91191 Gif-sur-Yvette Cedex, France

Supervisor: Iliana Dimicoli

The photophysical properties of the nucleobases are believed to play an essential role in the response of DNA molecules to UV radiation exposition. The aim of the present study is a detailed characterization of the various intrinsic relaxation pathways of these molecules.

Femtosecond dynamics of the excited states of nucleobases (adenine, guanine, cytosine, thymine, uracil) and model derivatives (9-methyladenine, N,N-dimethyladenine, 6-methyluracil, 1,3-dimethyluracil, 1-methylcytosine) were studied in supersonic jet by pump-probe photo-ionization followed by velocity imaging of the photoelectrons or time-of-flight mass spectrometry of the ions. A pertinent choice of the derivatives studied allows us to limit the number of tautomers possibly observed and to model the biologically relevant structures of the bases. The changes observed in the derivatives studied are used to investigate the vibration modes involved in the relaxation process.

Our excellent time-resolution (80 fs) combined with an accurate internal calibration demonstrated the existence of an ultra-fast relaxation pathway in the purinic bases consisting of two successive steps of  $\sim 100$  fs and  $\sim 1$  ps, respectively. In the case of pyrimidinic bases, a third long-lived component was evidenced, partly thanks to the detailed study of the ionic fragments dynamics. Typical lifetimes measured are in the range of 50-100 fs/ 2-6 ps/ ns. The fragmentation phenomenon, widely considered so far as a perturbation of the parent ions signal, is demonstrated to provide a complementary diagnostic tool for the characterization of the excited states probed especially in terms of vibrational energy content. Comparison of these results to the most recent ab initio theoretical calculations allows establishing a link between these experimental data and the excited states potential surfaces topologies, to propose different relaxation mechanisms for purinic and pyrimidinic bases and to explain the different effects of hydration on the excited states of these molecules. The study of small nucleobase-water clusters already shows trends that can be compared to those obtained in solution.

**Hélène PAOLACCI*****Chemical Sensors of Atmospheric pollutants based on Nanoporous Materials and Optical Transduction. Application to Formaldehyde and other Carbonylated Compounds***

PhD thesis, University of Paris XI, December, 2006

Working place: Laboratoire Francis Perrin

CEA/DSM/DRECAM/SMAP-CNRS URA 2553

91191 Gif-sur-Yvette Cedex, France

Supervisor: Thu-Hoa Tran-Thi

Formaldehyde (CH<sub>2</sub>O) is one of the well-identified volatile chemical contaminants responsible for indoor pollution and “building sick” syndrome disease and was recently classified as carcinogenic. New regulations for the air quality, imposing level as low as a few ppb, are expected and therefore, there is a need for low-cost sensors, sensitive and selective with a fast response time for the detection and quantification of the formaldehyde content outdoor and indoor. In the present work, we had developed strategies aimed at developing a chemical sensor which allows the detection of ppb concentrations of gaseous formaldehyde. These strategies are based on the use of nanoporous transparent matrices doped with Fluoral-P and optical methods of transduction, absorption and fluorescence.

The nanoporous matrices, elaborated via the sol-gel process, display nanopores whose cavity is tailored for the trapping of the targeted pollutant. They provide a first selectivity with the discrimination of the pollutants by their size. A second selectivity is then obtained with a molecular probe, Fluoral-P, which reacts specifically with formaldehyde leading to the 1,6-diacetyl-2,5-dihydrolutidine (DDL). The optical properties of DDL and reactants being very different, the formaldehyde can be quantified via the measurements of either the absorbance of DDL at 410 nm or its fluorescence at 510 nm. The efficiency of the reaction of Fluoral-P with CH<sub>2</sub>O was studied as functions of many parameters such as the concentration of Fluoral-P in the matrix, the pollutant content in gas mixture, the flow rate, the relative humidity of the gas mixtures and interference with other carbonylated compounds.

The present chemical sensor can detect, via absorbance measurements, 2 ppb of formaldehyde within 30 minutes over a 0 to 60% relative humidity range. Moreover, to detect the total carbonylated compounds, we also explored the potentiality of a chemical sensor using, as a probe molecule, the 2,4-dinitrophenylhydrazine which forms with these compounds the corresponding hydrazone derivatives. A patent was deposited for these two sensors. We have also developed a semi-miniaturized prototype for demonstration, using a flow cell, a miniaturized spectrophotometer, a light source and a laptop.

## UPCOMING MEETINGS

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□ **14th International Conference on Photoacoustic and Photothermal Phenomena (ICPPP)**

January 6-9, 2007

Cairo, Egypt

Website : <http://www.icppp.org/>

□ **International Symposium on Radiation and Photochemistry (PhotoRadChem-2007)**

February 08-11, 2007

Kottayam, India

Website : <http://photoradchem.org/prc2007/>

□ **Journées Francophones de Photochimie, Photocatalyse et Catalyse Environnementale**

May 3-4, 2007

Saint-Avold, France

Website : <http://pages.unibas.ch/epa/newsite%20frames/images/JFP2CE.pdf>

□ **9<sup>th</sup> European Conference on Atoms Molecules and Photons (ECAMP IX)**

May 6–11, 2007

Crete, Greece

Website : <http://www.iesl.forth.gr/conferences/ecamp9/committees.aspx>

□ **4th International Conference on Advanced Vibrational Spectroscopy (ICAVS 4)**

June 10–15, 2007

Corfu, Greece

Website : <http://icavs.info/corfu2007/>

□ **World of Photonics Congress**

June 17-22, 2007

Munich, Germany

Website : <http://www.global-electronics.net/id/46732/cubesig/b883bbdcbca8ef02979ebbf6e0576d0e>

□ **62nd Ohio State University International Symposium on Molecular Spectroscopy**

June 18–22, 2007

Columbus, Ohio, USA

Website : <http://molspect.chemistry.ohio-state.edu/symposium/>

□ **Radiation Damage in Biomolecular Systems**

June 19-22, 2007

Dublin, Ireland

Website : <http://www.isa.au.dk/networks/cost/radam07/index.html>

□ **17<sup>th</sup> International Symposium on Photochemistry and Photophysics of Coordination Compounds**

June 24-28, 2007

Dublin, Ireland

Website : <http://www.dcu.ie/conferences/isppcc/>

□ **Faraday Discussion 137: The Spectroscopy and Dynamics of Microparticles**

July 2–4 2007

Bristol, United Kingdom

Website : <http://www.rsc.org/ConferencesAndEvents/RSCConferences/FD137/>

□ **Gordon Research Conference on Photochemistry**

July 8-13, 2007

Smithfield, Rhode Island, USA

Website : <http://www.grc.org/programs.aspx?year=2007&program=photochm>

□ **6th International Conference on Tunable Diode Laser Spectroscopy**

July 9–13 2007

Reims, France

Website : <http://tdls.conncoll.edu/>

□ **Second International Conference on Semiconductor Photochemistry**

July 23-25, 2007

Aberdeen, United Kingdom

Website : [www.rgu.ac.uk/cree/sp-2](http://www.rgu.ac.uk/cree/sp-2)

□ **XIVth International Congress on Photosynthesis**

July 23-27, 2007

Glasgow, Scotland

Website : <http://www.sebiology.org/Meetings/pageview.asp?S=2&mid=84>

□ **XXV International Conference on Photonic, Electronic and Atomic Collisions**

July 25-31 2006,

Freiburg, Germany

Website : <http://www.mpi-hd.mpg.de/ICPEAC2007/index.php>

□ **XXIII International Conference on Photochemistry**

July 29 - August 3, 2007

Cologne, Germany

Website : <http://www.icp2007.net/>

□ **12<sup>th</sup> Congress of the European Society for Photobiology**

September 1–6, 2007

Bath, United Kingdom

Website : <http://www.esp-photobiology.it/congresses/conference2007.html>

□ **European Conference on the Spectroscopy of Biological Molecules**

September 1–6, 2007

Bobigny, France

Website : <http://www.ecsbm.eu/>

□ **Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy (EMSLIBS 2007)**

September 10–13, 2007

Paris, France

Website : <http://www.emslibs.com/>