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EDITORIAL

President's Letter

The quality of a PhD thesis is very often judged according to the number of papers published. I do not agree with this: the number of papers a student published during his thesis is certainly a criterion, but should not be the only one. What is the best thesis? A thesis where the student has worked on an ongoing and not risky project, obtained many results without much effort, and could thus publish a lot? Or a thesis where the student had to explore a new direction, had to solve many problems, had to surmount periods of doubt and discouragement, but could eventually write a paper with his first results obtained at the end of the PhD? Probably the student of the first thesis might first receive more recognition, but he might still not be ready to solve difficult problems or to conceive innovative and risky projects. On the other hand, I am quite certain that the student of the second thesis will be more experienced, mature, and well prepared for difficult and demanding research. Of course, these two examples are extreme cases, but I think that, when we are asked to evaluate a thesis, we should not forget what a PhD thesis is really about: learn to be a scientist, learn to solve problems, learn to think independently, and not just be a skilful lab technician. If the number of published papers became the only criterion of a good thesis, even ambitious and talented students will be afraid of starting a risky PhD project. We should be careful that this does not happen. The 'unpublishable' efforts should also be recognised and appreciated.

I am writing about this because we would like to have more 'Technical Notes' in the EPA Newsletter. There are so many technical difficulties and problems that cannot really be addressed in scientific journals and that each of us has to solve on our own. Why should we all the time reinvent the wheel? The Newsletter it the ideal place for publishing short notes on these technical aspects. Moreover, these Technical Notes would allow those PhD students that are struggling with their difficult project to express themselves. We can learn a lot from them and this is why we want to encourage students to contribute to these Notes. The EPA executive committee is planning to setup a yearly prize for the best Technical Notes authored by a PhD student.

We have also decided to periodically devote a section of the Newsletter to a given research topic. This section contains brief accounts on the activity of research groups in a given area. The topic of this June issue concerns nanoparticles and their interactions with light. We hope that this section will give our research a better visibility and will stimulate collaboration.

I hope you will enjoy reading this Newsletter and I wish you a most pleasant summer.

Prof. Eric Vauthey
Department of Physical Chemistry
University of Geneva

GRAMMATICAKIS-NEUMANN PRIZE 2011

The Photochemistry Section of the Swiss Chemical Society (which acts as the Swiss section of the European Photochemistry Association, EPA) is pleased to invite nominations for the international Grammaticakis-Neumann Prize 2011.

The Prize consists of a diploma and a financial award of 5'000 Swiss Francs (for each awardee, if there is more than one), and it is presented once a year to a young research scientist (<40 at the time when he or she receives the prize) from academia or from industry for outstanding contributions to the science of photochemistry, molecular photobiology, or molecular photophysics.

The Prize, for which nominations are now being invited, will be presented during the 2011 Fall Meeting of the Swiss Chemical Society. The award ceremony will be followed by a lecture of the laureate which is also to be published in the offical EPA journal, *Photchemical and Photobiological Sciences.*

Each member of the EPA, or one of its sister organizations (such as the Inter-American Photochemical Society) can nominate an individual as candidate for the Grammaticakis-Neumann Prize. Such nominations, accompanied by supporting documentation (detailed justification, curriculum vitae, list of publications, and at least two supporting letters), should be submitted by e-mail (with attachments) to info@scg.ch. The closing date for nominations is October 10, 2011 (see also www.scg.ch/awards/grammaticakis.html).

Previous laureates of the Grammaticakis-Neumann Prize are Sivaguru Jayarman (2009), Alexander Heckel (2008), Alberto Credi (2007), Torsten Fiebig and Achim Wagenknecht (2006), Dario Bassani (2005), Johan Hofkens (2003), Nicola Armaroli (2001), Dirk Guldi (2000), Werner Nau and Eric Vauthey (1999), Axel Griesbeck (1997), Matthew Zimmt (1996). Luisa de Cola (1995), Pedro Aramendia (1994), Mark van der Auweraer (1992), V. Ramamurthy (1991), Wolfgang Rettig (1990), Martin Demuth (1987), Ian Gould and Anthony Harriman (1985). In other years (e.g. 2002 and 2004) no prize was awarded, because no suitable candidate was proposed.

PERSONAL NEWS

Obituary: Noboru Mataga

Prof. Mataga during a work meeting with his coworkers (1981).

Noboru Mataga, Professor Emeritus at Osaka University and Special Researcher at Institute for Laser Technology, Osaka, passed away on last January at 83 years old. Prof. Minjoong Yoon, President of the Asian-Ocean Photochemistry Association, has paid homage to his career and great scientific achievement in the APA News (See the website http://www.asianphotochem.com/mataga.htm). Due to Prof. Mataga's outstanding contribution to photochemistry and unique personality, his death has left a profound vacuum in the community of photochemists, not only in Asia but also all over the world. We thus would like to pay a tribute to him in this European Photochemistry Association News Letter.

Prof. Mataga has left his mark in photochemical sciences by introducing new concepts in molecular interactions, solvation, hydrogen bonding and photo-induced phenomena in various chemical and biological media. He has also pioneered time-resolved spectroscopy pushed to its temporal limit with outstanding achievements notably in photoinduced electron transfer processes.

Noboru Mataga was only 28 years old when he proposed the first quantitative theoretical formula for fluorescence solvatochromism. The so-called Mataga-Lippert equation (because proved by E. Lippert independently at the same time) has been a major and fundamental contribution for the understanding of molecular interactions, solvation phenomena and solvent induced reactions, change in dipole moments of polar solutes upon photoexcitation and photoinduced charge-transfer processes. This early theoretical work commonly used by experimentalists up to the present time, has had a tremendous impact in photochemistry. As a young researcher, he also pioneered studies on hydrogen-bonding induced photo-properties, which have been demonstrated later on by ultrafast spectroscopy. As a Full Professor of Chemistry at the Faculty of Engineering Science of Osaka University (1964-1991), he indeed developed various transient spectroscopy methods for probing reaction dynamics in real time up to the femtosecond time range. His, most often pioneer, work on the photodynamics of families of compounds and related engineered chemical systems including photosynthetic reaction center models, led to a detailed understanding of the role of energetics, solvation dynamics and solute structure on the dynamics of charge transfer processes. His investigations of the energy gap dependencies of charge transfer rates in solution, and in particular, on the apparent absence of the Marcus inverted regime in certain cases of electron transfer, deserve a particular mention.

After his retirement from Osaka University, Prof. Mataga has kept devoting himself to Science for almost 20 years as a Special Researcher at the Institute for Laser Technology of Osaka. There he could notably develop studies at the frontier with photobiology and use his expertise in molecular interaction to reveal the effects of the protein nanospace on the ultrafast photoreaction dynamics in some photoresponsive proteins.

Prof. Mataga published close to 600 papers, reviews and book contributions. His book on "Molecular Interactions and Electronic Spectra" published with T. Kubota in 1970 has been extremely useful for a number of students and researchers. He received several awards in Japan, in particular the Purple Ribbon Medal from the Japan Government (1995) and the Japan Academy Prize (2006). He also received the Porter Medal award in 1996 from the Photochemistry Community. A Festschrift of the Journal of Physical Chemistry A, entitled "Fifty Years of Research on Chemistry with Light "was dedicated to him in 2002.

Prof. Mataga was strict, firm and rigorous when leading his group but very kind and generous in discussions face to face. Always positive, he permanently encouraged his coworkers. Very creative in the quietness of his office, he had much intuition and his ideas, views and projects abounded. When he was giving a lecture, his enthusiasm always prevailed.

It has been a great honor for us to be included among Prof. Mataga's students or coworkers at different period of his career. On behalf of the numerous students he trained and numerous scientists around the world who collaborated with him, we wish to express our most respectful feelings to the distinguished scientist he was.

May 2011

Monique M. Martin (CNRS, ENS, Paris)
Tadashi Okada (Osaka University)
Hiroshi Masuhara (NCTU Taiwan, NAIST Nara, Osaka University)
Hiroshi Miyasaka (Osaka University)
Haik Chosrowjan (ILT, Osaka)
Fumio Tanaka (Mahidol University, Bangkok)

SPECIAL REPORT ON NANOPARTICLES AND THEIR INTERACTIONS WITH LIGHT

Introduction

During the past decade, the research on the application of metal and semiconductor nanoparticles, related to their capacity to absorb light, has seen a dramatic development. The number of research groups worldwide, focusing on projects on photoactive nanoparticles, has grown enormously and consequently, so have the number of published papers. This EPA Newsletter issue is dedicated to European researchers keen to show their expertise in this area of research to our community.

This issue presents a number of aspects on what has been achieved most recently by European scientists. Thus, with respect to gold systems, the ability of gold nanoparticles to eject electrons upon excitation with visible light has been emphasised (H. Garcia). In addition, the reliability of fluorescence anisotropy spectroscopy for measuring nanoparticle size and the use of gold nanoparticles as probes in biological imaging are also reported (D. J. S. Birch, *et al.*).The directed orientation of gold nanorods on ITO substrate has been achieved by using a Gemini surfactant (L. M. Liz-Marzán *et al.*) and nanodiscs with the right diameter-to-height ratio have proved to enhance the production of singlet oxygen (P. Ogilby *et al.*).

Other contributions discuss semiconductors; thus, TiO_2 has been studied as a photocatalyst for hydrogen production and environmental purification (T. A. Kandiel *et al.*). The photosensitisation of TiO_2 by coordination compounds is of interest in the area of photovoltaics and photocatalysis (W. Macyk). The potential of dye-doped silica nanoparticles in imaging is stressed in another contribution (Zaccheroni *et al.*). Yet another study reports the versatility of QDs to be simultaneously decorated with a considerable number of donors and acceptors, providing biosensors for multiplexed diagnostics (N. Hildebrandt).

Finally, the application of nanostructures, such as fullerene-porphyrin architectures for PDT (R. M. Ion), TiO_2 nanotube arrays on Ti for hydrogen generation (G. Centi *et al.),* and TiO_2–coated activated carbon materials (J. M. Tobin *et al.*), is also included.

We would like to thank all those who contributed to this special issue and hope that it serves to increase interest in photoactive nanomaterials.

Julia Perez-Prieto
Associate Editor EPA Newsletter

Photophysics of Semiconductor Quantum Dots

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Semiconductor nanocrystals known as quantum dots (QDs) are spherical particles comprising from some hundreds to a few thousands of atoms, with diameters ranging between 1 and 15 nm. They exhibit peculiar optoelectronic properties;[1] in particular, they are strongly luminescent. Since their discovery in the early 1980s[2a] and the development of solution-based preparation methods affording an accurate size control,[2b] it became clear that these particles represent valid substitutes for molecular luminophores.[3] The interest on QDs as alternatives to organic dyes has increased dramatically, as witnessed by the number of research papers, reviews and books dealing with such nanomaterials.

In a semiconductor, absorption of a photon with energy equal or greater than the band gap results in excitation of an electron from the valence to the conduction band, leaving a hole in the valence band (Figure 1a). Such an electron-hole pair is bound by the electrostatic attraction between the opposite charges and is called an exciton. The Bohr radius measures the extension of the exciton wavefunction over the crystal lattice; for example, the Bohr radius for excitons in CdSe is about 5 nm. When the size of the particle approaches that of the exciton (i.e., the Bohr radius), the optical and electrical properties of the material become dependent on its physical dimension, owing to the so-called quantum confinement effect.[1,3] In these conditions, the band structure of the semiconductor changes into discrete levels, and the energy difference between the highest occupied level and the lowest unoccupied level widens as the particle size decreases (Figure 1b), following in many cases the behaviour expected for an electron inside a three-dimensional box.

QDs are characterized by large molar absorption coefficients in the UV-visible, thus they can be effectively excited in a wide spectral region and with low intensity light. They exhibit an intense emission band with a very narrow spectral profile (the fwhm is typically on the order of 30 nm), in contrast with molecular fluorophores. The emission maximum can be accurately tuned in a spectral region ranging from blue to near IR by adjusting the chemical composition and the size of the particles. The photobleaching resistance of QDs is much higher than that of molecular species; hence quantum dots are particularly fit for single-particle detection or in applications that require irradiation with high intensities and/or long periods. The emission quantum yield and the photobleaching resistance can be further improved by coating the nanocrystal with a layer of another semiconductor material having wider bandgap (e.g., QDs with a CdSe core and a ZnS shell).[4]

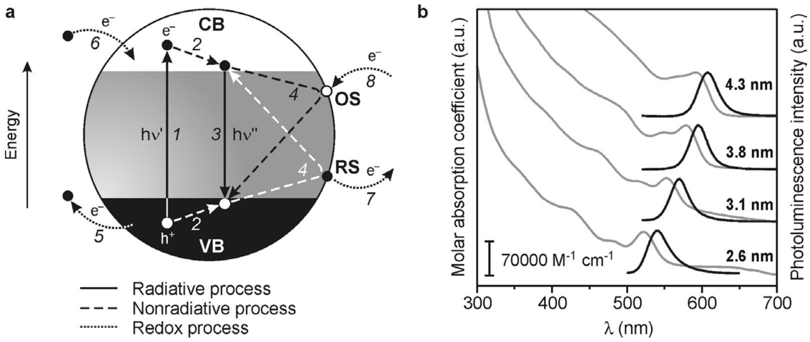

Figure 1. (a) Schematic representation of important optical and electronic processes in a semiconductor nanocrystal. Legend of symbols: VB, valence band; CB, conduction band; RS, reducing surface state; OS, oxidizing surface state. Legend of processes: 1, optical excitation; 2, thermal relaxation of the excited electron and hole; 3, luminescence; 4, nonradiative recombination mediated by surface states; 5, oxidation involving valence band electrons; 6, reduction into the conduction band; 7, oxidation involving a surface trap; 8, reduction involving a surface trap. (b) Absorption and photoluminescence spectra ($CHCl_3$ at room temperature) of CdSe QDs of different size capped with tris-*n*-octylphosphineoxide (TOPO) and *n*-hexadecylamine (HDA) ligands. Excitation was performed at λ = 480 nm. The spectra are vertically offset for clarity.

In most cases QDs are prepared in apolar organic solvents by reacting inorganic precursors in the presence of molecular ligands forming a coating that stabilizes the nanoparticle surface.[2b,4,5] A key aspect of most ligands is the dynamic nature of their binding to the nanoparticle surface, thereby allowing the exchange of the native ligands with other surfactants bearing different functionalities. Several examples of QDs functionalized with photo- or redox-active molecular units for luminescence sensing and switching have been reported.[6] Transduction mechanisms typically involve energy- and electron-transfer processes between the nanocrystal and the surface-bound molecules.[7]

Despite the rapid progress in the field, many aspects of the physico-chemical behaviour of QDs are not yet fully understood.[8] Indeed, the development of nanocrystal-molecule hybrids and investigations on nanocrystal-molecule interactions are crucial for extending the basic knowledge on these fascinating systems and foster the design of quantum dots tailored for specific applications.

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Novel integrated photocatalytic adsorbents (IPCAs) for degradation of pharmaceuticals from water and wastewater

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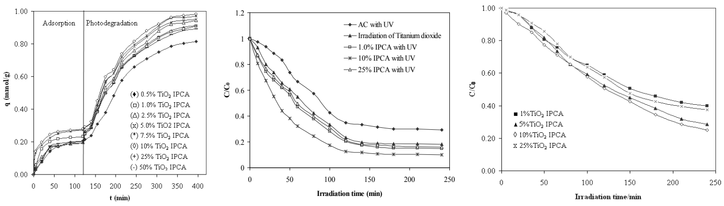
Introduction — The presence of pharmaceuticals and personal care products in the aquatic environment and their possible effects on living organisms has emerged as a serious environmental concern. There is an increasing need for a cost- and energy-effective clean technology for the removal and degradation of organic compounds before they find their way into ground water wells and surface waters. Photocatalysis using cheap and non-toxic TiO_2 has been recently used to degrade pharmaceuticals and pesticides in water, and was found to be superior to conventional methods. However, large scale application has been hindered by problems associated with its preferential use in slurry form and the high cost of radiation of large slurry volumes. Therefore, it is proposed to combine well-established adsorption on activated carbon with rather novel TiO_2 photocatalysis. This strategy will lead to the development of TiO_2-coated activated carbon materials, i.e. integrated photocatalytic adsorbents (IPCAs).

Within a wide research program focused on the removal of pharmaceuticals from waters by heterogeneous photocatalysis, a non-steroid anti-inflammatory drug, indomethacin (IND), a β-lactam antibiotic, amoxicillin (AMO) and acetaminophen (AMP), a common analgesic and antipyretic drug were selected as model compounds for the study. The occurrence of these pharmaceuticals have been reported in sewage, hospital effluents, surface water and drinking water samples, ranging from several hundred nanograms per liter up to 65μg L^{-1}, collected in Australia, UK, USA, and Ireland.[1-5]

Adsorption kinetics and isotherm — Various kinetic models have been suggested for the adsorption process, and three well-known models, pseudo-first-order and pseudo-second-order kinetic equations, are selected in this study. The regression coefficients (R^2) for the pseudo-first-order kinetic model were relatively low for adsorption of IND/AMO/AMP on AC or IPCAs. The pseudo-first order predicted values of the adsorption capacity, q_e (264.6 and 291.3-310.15 mg g^{-1}) were marginally higher than experimental values (257.1 and 283.7-302.19 mg g^{-1}) for AMO. The high R^2 and low SE and SSE values as well as the good agreement between the experimental and predicted equilibrium sorption capacities confirm better fit to the pseudo-second order model. Generally, the rate constant, k_2 increased with an increase in TiO_2 content (up to 10%) in IPCAs. Both the rate constant and the initial adsorption rate, h, as well as the equilibrium adsorption level, q_e, were higher for the 10 % IPCA than for any of the other IPCAs. Moreover, all IPCAs showed appreciably greater adsorption capacity than AC for AMO. This would suggest an activated adsorption between AMO and functional groups on IPCA surface involving valence forces through sharing or exchange of electrons between IPCA and AMO.[6]

The experimental adsorption equilibrium data for the various IPCAs, showed that 10 % TiO_2 IPCA had the highest capacity to adsorb IND/AMO/AMP, with no significant difference between them. Hence, the capacity of AMP adsorption on the IPCAs followed the order: 10% TiO_2 IPCA > 1% TiO_2 IPCA> 5% TiO_2 IPCA > 25% TiO_2 IPCA. With the TiO_2 content in the IPCA increasing from 1 to 10%, the adsorption capacity increased from 0.81 to 0.93 mmol g^{-1}, 409.3 to 449.03 mg g^{-1} and 18.2 to 28.4mg/g for IND, AMO and AMP, respectively, and further increase in TiO_2 content resulted in lower adsorption capacity due to greater aggregation of the TiO_2 particles on the surface of the AC.[7] The IND/AMO/AMP equilibrium sorption data exhibit better fit to the Sips/R-P/ Langmuir isotherms for all IPCAs as compared to the Freundlich model. Furthermore, both SE and SSE values were lower in case of the Langmuir model.

Photocatalytic degradation — The kinetics of photodegradation on various IPCAs (after attaining adsorption equilibrium) are illustrated in the Figure 1.



Indomethacin Amoxicillin Acetaminophen

Figure 1. Photocatalytic activity of AC, IPCAs and TiO_2

Irradiation in the absence of IPCA/ TiO_2 showed insignificant conversion of pharmaceuticals. As expected, the photocatalytic capability of IPCAs with UV increased with increasing TiO_2 content for all pharmaceuticals studied. However a maximum was attained at 10% TiO_2 loading and photodegradation rates decreased with further increases in TiO_2 content in IPCAs beyond 10%. The photocatalytic capacities of various IPCAs were of the following order for IND: 10% TiO_2 IPCA > 7.5% TiO_2 IPCA > 5.0% TiO_2 IPCA > 2.5% TiO_2 IPCA > 25% TiO_2 IPCA > 1.0% TiO_2 IPCA > 50% TiO_2 IPCA > 100% TiO_2 > 0.5% TiO_2 IPCA. Both AMO and AMP also showed similar sequence. This sequence is identical with the order exhibited with respect to adsorption capacity, which is strongly related to the TiO_2 content of IPCAs. In all cases optimal performance was achieved at a TiO_2 loading (10%) which is less than the maximum investigated. Generally, the greater the amount of TiO_2 present the higher the photocatalytic reaction rate due to increased generation of holes and hydroxyl radicals. However, more TiO_2 may also induce greater aggregation of the TiO_2 particles at the surface of the AC, leading to a reduction in reaction rates as seen here at 25 and 50% TiO_2 loadings.[8] Furthermore, the high degradation rate of 10% TiO_2 IPCA can be attributed to the synergistic effects of adsorptive properties of the AC and photocatalytic activity of the TiO_2 in the composite. The surface adsorption on the substrate enriches pharmaceuticals, causing a concentration effect in chemical reactions, followed by degradation intermediates on the site of the TiO_2, enhancing photocatalytic degradative activity.[9]

Conclusion — In conclusion, nanostructured titania supported over activated carbon, termed as integrated photocatalytic adsorbents (IPCAs), were prepared by ultrasonication and investigated for the photocatalytic degradation of various pharmaceuticals. The IPCAs in dark adsorption studies had high affinity for all pharmaceuticals with the amount adsorbed proportional to the TiO_2 content and the highest adsorption was at 10 wt% TiO_2. Generally, the photodegradation activity of IPCA was better than that of bare TiO_2. Kinetic studies on the photocatalytic degradation suggest that the degradation followed the Langmuir-Hinshelwood kinetics and the adsorption rate constant, was considerably higher than the photocatalytic rate constant, indicating that the photocatalysis is the rate-determining step during the adsorption/photocatalysis process. The IPCAs described here demonstrate potential for degradation of pharmaceutical compounds.

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Quantum Dots and FRET for the Lifesciences

Niko Hildebrandt
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Quantum dots (QDs) are semiconductor nanocrystals with special photophysical properties.[1] QDs exhibit very narrow and size-tunable emission bands ranging from the band-gap energy of the semiconductor material (for large QDs of ca. 10 nm diameter) down to the UV (QDs of ca. 1 nm diameter). The absorption spectra are extremely broad, starting just below the emission band with steadily increasing extinction coefficients with decreasing excitation wavelength. In addition QDs can have extremely large extinction coefficients and very high luminescence quantum yields. Thus, QDs are very well suited for multiplexed and highly sensitive diagnostic applications in lifesciences using optical spectroscopy and/or imaging.

FRET (Förster Resonance Energy Transfer) is a "long-range" (ca. 1 – 20 nm, without overlapping orbitals of the interacting molecules) radiationless energy transfer between an excited donor and a non-excited acceptor molecule due to coulomic interactions between the two transition dipoles of donor and acceptor. FRET continues to be an extremely useful tool for concentration and distance measurements within nanometer-scale biosystems *in vitro* and *in vivo* and the "original" theory of Theodor Förster[2] is still frequently "updated" by novel FRET systems and applictions, as can be found e. g. in a recent special issue about FRET in *ChemPhysChem*.[3]

QDs are very special candidates for FRET because their unique properties result in some important advantages for the energy transfer process. Due to their broad absorption range, QDs of various colors can be excited with the same wavelength or accept energy from many different donors. In combination with the narrow, size-tunable emission spectra this allows for an almost ideal design of FRET systems with minimal spectral crosstalk. Another major advantage is the QD size of several nanometers, which allows an interaction with several smaller molecules surrounding the nanoparticle. When being used as energy donors the FRET efficiency will increase with the number of acceptor molecules around one QD.[4] In connection with long-lived (long excited state lifetimes) energy donors such as lanthanide complexes one short-lived QD acceptor can be used successively for many donor molecules, thus leading to an increased brightness of the FRET system.[5] Another advantage of QD acceptors is their extremely large absorption cross-section opening the possibility of extremely long Förster distances (donor acceptor distance at which FRET is 50 % efficient) of more than 10 nm.[5]

Especially in the field of *in vitro* diagnostics (IVD) multiparametric measurements are of paramount importance in order to allow a simultaneous access to several diagnostic data from one single sample. High photostability (for long observation times), large surfaces (for labeling with many biomolecules - multiple molecule FRET) and equal surface chemistry for QDs of different color (one labeling procedure for all) are some of the advantages of QDs for diagnostics. Many different biomolecules can be attached to QD surfaces in order to establish a large variety of biological assays and to bring the FRET donor or acceptor in close proximity to the QD (Figure 1).

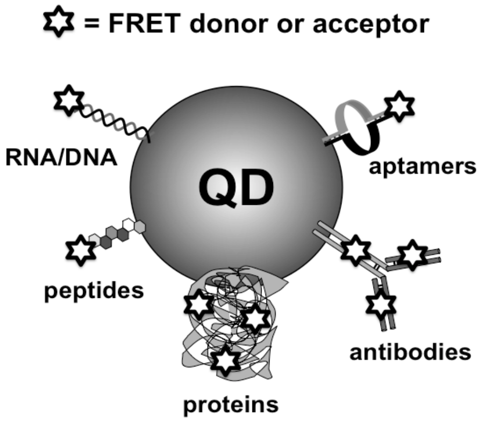

Figure 1. Schematic presentation of various biomolecules labeled to a quantum dot (QD). Figure not to scale.

Although FRET-multiplexing with four QD donors[6] and five QD acceptors[7]has been achieved within biological assay systems, there is still no clinical QD-based FRET bioassay available. The research project "NANOGNOSTICS - Quantum Dot-BasedHighly Sensitive Immunoassays for Multiplexed Diagnosticsof Alzheimer's Disease" (www.nanognostics.eu) funded by the European Commission (FP7 Collaborative Project NANOGNOSTICS-HEALTH-F5-2009-242264) aims at bringing the QD-FRET technology a significant step closer to the clinical application by using antibodies and aptamers as recognition reagents for multiplexed analysis of Alzheimer's disease. This is only one example of the possible use of QDs. Their application for the lifesciences is still in the development phase and the future is still wide open.

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ZeoFRET® Nanochannel-Materials for Solar Energy Conversion Devices

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Assemblies, polymers, crystals, and biological structures bearing nanochannels have been studied for many decades. Examples of nano-channel materials are zeolites, zeotypes, cyclodextrins, urea based assem-blies, mesoporous silica materials, collagens, metal organic frameworks, as well as organic, carbon and metal oxide channels. All have been investigated to some extent as hosts for molecules, complexes, ions, or clusters. An infinite number of combinations and objects with different properties are, however, still waiting to be explored. One dimensional (1D) nanochannels have special properties which have recently attracted considerable attention. We distinguish between several types of 1D channels: single file, ordered assemblies, amorphous, "semicrystalline", and crystalline. A common feature of 1D nanochannels is that they have only 2 entrances. Channels can therefore be open on both sides, plugged on one side, or plugged on both sides. This plugging can be isolating or it can be partial, allowing electrons, protons, or small molecules to pass, but blocking larger objects.[1]

The ZeoFRET® nanochannel-materials are highly organized dye-zeolite inclusion compounds with photonic antenna function. After absorption of the incident light by high local concentrations of dye molecules, the energy is transported by Förster resonance energy transfer (FRET) to an acceptor A. Large donor-to-acceptor (D:A) ratios and multi-donor systems are promising as active species in luminescent solar concentrators.[2] Large D:A ratios thereby open possibilities to reduce self-absorption while maintaining efficient light-harvesting.[3] An illustration of a zeolite L (ZL) channel with a D:A ratio of *n*:2 is shown in Fig. 1a while Fig. 2 shows the absorption and emission spectra of ZeoFRET® samples with D:A ratios of 33 and 52. In the latter case, one channel of ZL contains approximately 150 D and on average 1.5 A at each channel end.[3] These materials are

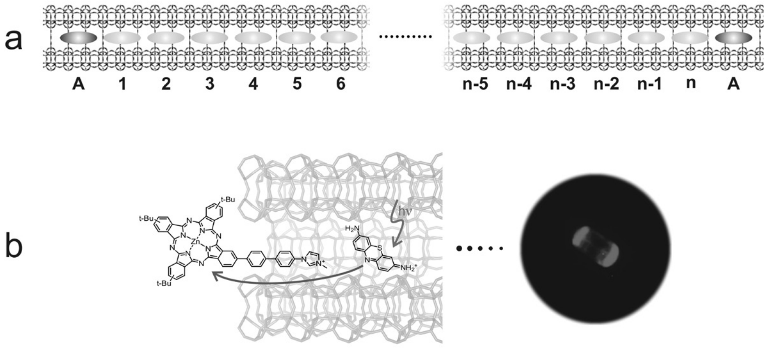

Figure 1. a) A channel of ZL containing *n* D and one A at each channel end. The D absorb the incoming light and transfer the energy to A, which subsequently emit light in a wavelength range where D do not absorb.[1] b) Energy transfer from a thionine to a ZnPc stopcock with a cationic tail and fluorescence microscopy image of a 5 μm long ZL crystal with ZnPc stopcocks located at the channel entrances.[5]

now tested for practical applications (see http://www.optical-additives.com).

Dye combinations with zinc phthalocyanine (ZnPc) molecules that are located at the entrances of the ZL channels are of interest for the sensitization of ZnPc-based solar cells.[4] However, selectively adsorbing ZnPc molecules at the channel entrances of ZL is challenging. We have therefore investigated van der Waals, electrostatic, and covalent binding, and developed methods that lead to a placement of the respective ZnPc at the ZL channel entrances in each of the three cases. Channel entrance adsorption of a ZnPc with

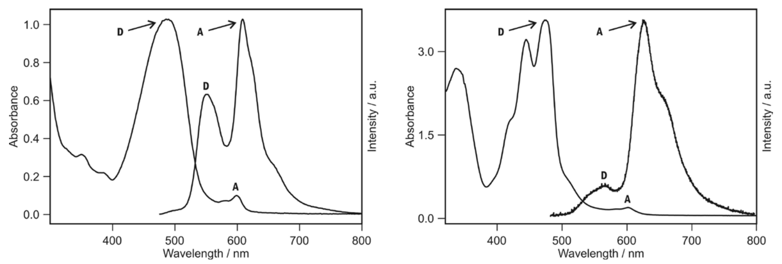

Figure 2. Left: Absorption and emission spectrum of a ZeoFRET® sample with a D:A ratio of 33. Right: The same for a sample with a D:A ratio of 52. The emission was measured upon excitation of D at 450 nm.

a cationic tail was found to be the most convenient route, making use of the exchange of charge-compensating cations in the ZL channels; Fig. 1b. Energy transfer from molecules in the ZL channels to the ZnPc molecules (acting as stopcocks) was observed.[5] The hexagonal ZL crystals can be assembled in several ways, subsequently inserting guests in the channels and adding stopcocks is possible if the free channel openings are not blocked or damaged during the preparation of the monolayer.[6]

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Photoactive nanosized materials based on TiO_2 for solar energy applications

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The nanoscience and nanotechnology developments have opened the door to tailoring materials and created a variety of nanostructures, bringing out new opportunities in a wide range of application areas concerning solar energy conversion.

The self-organizing titania proved to be particularly appealing for the synthesis of nanometer-sized structures with controlled properties for application as advanced electrodic materials. Nanostructured materials including nano-particles, -clusters, -layers, -tubes, and 2D and 3D structures are seen as tailored precursors for building up functional nanostructures. The properties of these building blocks may be controlled during synthesis and assembling procedures and may be significantly different from those of the corresponding bulk materials.

Anodic oxidation is a good method to prepare homogeneous TiO_2 materials in the form of thin and ordered films of vertically oriented nanotubes. As the properties of such materials are strictly dependent on the preparation conditions, the relationship between nanostructured characteristics and corresponding photoelectrochemical responses can give useful guidelines for obtaining photoactive materials with enhanced efficiency and/or reactivity.

Nanotubes have been found to be effective in improving the charge transport within the photoactive film. [1, 2] Comparison between a TiO_2 thin film sample obtained by anodic oxidation (AO) and a reference compact dense film prepared by sol-gel dip-coating (SGDC), showed that the photocurrent (per unit of illuminated area) was around twenty times higher for AO thin film and over hundred times higher per gram of TiO_2 present in the film.[1] It is thus well demonstrated that the nanostructured film possesses significantly higher performances in photocurrent generation. The large internal surface area and the precisely-oriented nature of nanotubular 1D structures promote light harvesting and direct the flow of photogenerated charge carriers through a vectorial-type transport minimizing charge recombination in comparison with films composed by random TiO_2 nanoparticles.

We have also observed that the nature of the nanostructure greatly affects the amount of photogenerated hydrogen as resulting from photoreforming measurements performed in 10% ethanol in water using different kinds of TiO_2 samples as photoelectrodic materials. *(see Table 1)*

Table 1. Hydrogen evolution rate for different kinds of TiO_2 samples during photoreforming of 10% ethanol in water.[d]

	TiO_2 sample	**H_2/mmol h^{-1} g^{-1}**
Slurry	Powder[a]	3.5
Film	Pressed powder[a] layered on Ti foil	7.0
	TiO_2 nanotube array on Ti[b]	47.8
	Sol-gel dip coating[c]	5.3

[a] Degussa P25 TiO_2 powder. [b] Ordered array of TiO_2 nanotubes prepared by anodization on Ti foil. [c] TiO_2 dense film prepared by sol-gel dip-coating. [d] In all samples 0.5 wt % Pt was added by wet impregnation.

The nanostructure of the titania thin film produced by anodic oxidation is strongly influenced from the specific conditions of anodization and, as a consequence, the photocurrent and photoactivity are also considerably dependent on the preparation method. In particolar, shape and length of the titania nanotubes strongly depend on the electrolyte used during the anodization whereas the applied potential determines the diameter of the tubes. It was found that the higher the applied potential the larger the diameter of the tubes. From the comparison of the behaviour in H_2 production by photoreforming and water splitting of two nanostructured TiO_2 films prepared at two different anodization voltages we observed an increase in photocurrent on increasing the anodization voltage. [1]

The periodic arrangements of these nanostructures may configure the materials as a photonic crystal. By forming photonic band gap, they exhibit a characteristic behaviour which may be applied in optics providing phenomena such as optical confinement or photonic localization useful in light manipulation and management. These unique properties enable nanomaterials to be attractive and they will be object of extensive investigation in the future for advanced energy applications.

A precise control of the surface physical structure, increasing surface area and favoring light absorption and charge separation on the nanotubular surface, may result in higher performances but, we have observed that there is not an unique and simple relationships between a critical parameter such as photocurrent generation and the characteristics of the nanostructure.[3] Oxidic films characterized by the presence of an ordered array of vertically-aligned nanotubes are quite interesting in catalysis for the possibility to create a definite nanoarchitecture, with specific structural parameters (nanotube length, diameter, wall thickness and voids), which can be finely tuned to enhance their efficiency and/or reactivity. These materials are suitable for the application in new technological fields concerning H_2 production in water photoelectrolysis and/or synthesis of liquid fuels from water and CO_2.[2] The charge transport, within the nanostructure of the film which characterizes these materials, plays an important role in determining photoconversion efficiency of the electrodes used in Photoelectrochemical (PEC) systems and in new generation solar cells.

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Fullerene-porphyrin architectures as potential new sensitizers in photodynamic therapy of cancer

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Photodynamic therapy (PDT) is an approved form of treatment for several types of cancers.[1] It involves a two step protocol which consists in the uptake and accumulation of a photosensitizing agent in target cells and the subsequent irradiation with light, usually in the visible range. It is generally accepted that the death of cancer cells is mainly mediated by the reactive oxygen species (ROS) subsequently produced by the irradiation of the photosensitizer. Despite their high cost, the most commonly used drugs are porphyrins, which exhibit high quantum yields of singlet oxygen and long activity on different tumor types. Several criteria must be accomplished by a porphyrin-nanoparticle adduct to be suitable for PDT:

- the nanoparticle emission band must fit the absorption wavelength of the photosensitizer for an efficient production of singlet oxygen upon photosensitizers activation;
- the chemical bond between nanoparticles and porphyrin must be easily achievable;
- the nanostructure must be preferable non-toxic or display low toxicity, water soluble and stable in biological media.[2]

The fullerenes became an attractive type of sensitizers; the most recent one reported by our group being tetraphenyl-porhyrin (TPP)–poly(vinylpyrrolidone)(PVP)–fullerene (C60) (TPP-PVP-C60), figure 1.[3]

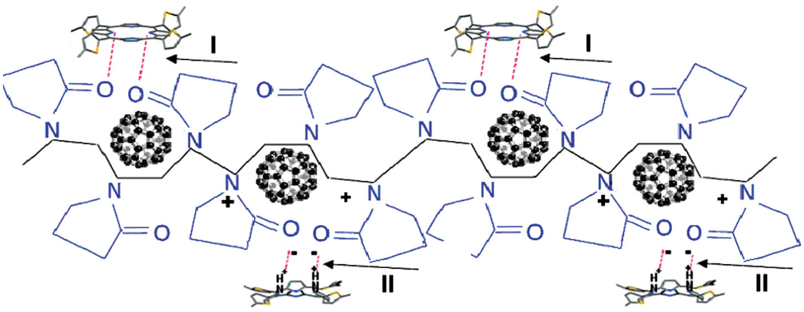

Figure.1. The structure of (TPP-PVP-C60) (from ref.4)

Non-adherent human cell lines K562 (myelogenous leukemia)] were used as cellular models for dark toxicity testing. We have evaluated the membrane integrity by LDH release test. The K562 cell line in the presence of the new compound after 24 h displayed a clear drop in cell viability at concentrations higher than 12 μM. Above 23 μM it will kill approximately 90% of the cells.[4]

Cell suspensions were pre-incubated for 24 h with the test compounds, and were subjected to irradiation after washing them 3x in culture medium and resuspending them at 3 × 10^5 cells/mL. Illumination of the cell suspensions (2.3 mL, on ice) in a 1 cm glass cuvette was performed using a 350 W short arc mercury lamp (HBO 350 W; Osram, Germany) positioned at a distance of 28 cm from the sample and equipped with a 495 nm long pass filter (Carl Zeiss Jena, Germany). The incident fluence rate was 200 W/m^2. Exposure of cells was done in 2 ml of phosphate buffered saline (PBS) containing 1.5 % fetal bovine serum (FTS) in 5 ml polystyrene plates at different temperature (35°C, 37.5°C, and 42°C) for 30 min., resulting in a dose of 18 J/cm^2. The cell suspension was mixed mechanically with a magnetic stirrer to assure adequate mixing and O_2 saturation during illumination. After PDT, the cell suspension was evaluated using a cell counting chamber (Roth) with 0.4% Trypan Blue stain.

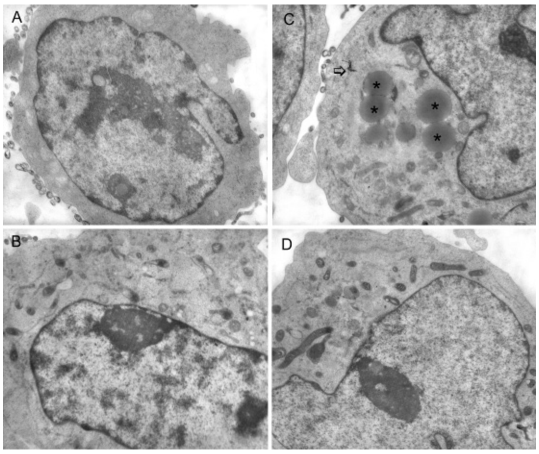

Figure 2. Transmission electron micrographs of control and treated K562. A- control K562; B - control for irradiated K562; C - K562 – 0.5microM TPP-PVP-C60; D - irradiated K562 - 0.5microM TPP-PVP-C60 with long and dark mitochondria. Magnification (9,100)(from ref.5).

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Silica and gold nanoparticles

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Our research on nanoparticles is largely focused on silica and gold nanoparticles. Silica nanoparticles were one of the earliest types of nanoaparticles to be manufactured and we label them with extrinsic fluorescence probes,[1] either electrostatically or covalently, in order to measure their size. This has proved particularly useful in studying the growth kinetics of the nanoparticles that are formed during the silica sol-gel process. Our early work[2] explained the bi-exponential fluorescence anisotropy decay of dye added to a silica sol in terms of free dye and dye bound to the nanoparticle. Using the Stokes-Einstein equation the former gave the microviscosity and the latter the particle size. This result reconciled fluorescence data with small angle x-ray scattering results and has provided a low cost and high resolution method of measuring nanoparticle size in-situ. It is particularly useful in the 1-10 nm range, which is beyond the resolution of many other techniques, such as light scattering. Table 1 uses the Dupont LUDOX colloid range to demonstrate the resolution available using fluorescence anisotropy decay as compared with SEM.[3] The lack of international metrology standards for nanoparticles is widely recognised as a barrier to progress in many areas of nanotechnology and the ease of use and reliability of fluorescence anisotropy provides a promising approach.

One interesting aspect we stumbled on was how to use a pH meter to measure nanoparticle size during the synthesis of silica gel. The synthesis involves mixing sodium silicate and sulphuric acid, whereupon highly reactive silicic acid ($Si(OH)_4$) is formed, which then undergoes condensation to produce silica. As the silicic acid is used up the pH rises and we have found a linear relationship between pH and nanoparticle size (Figure 1).[4]

Our interest in gold nanoparticles concerns studying their intrinsic luminescence and applying them as surface plasmon generators and probes in biological imaging. Gold nanorods are of great interest for optical imaging due to their remarkable absorption and scattering in the visible and near-infrared (NIR) regions enhanced by the surface Plasmon resonance NIR band absorption between 700 and 900 nm, a spectral window that permits photons to penetrate biological systems with relatively high transmission. Two-photon luminescence (TPL) from gold nanorods has been found to be particularly sensitive to the polarization of the incident excitation in accordance with the aspect ratio. Moreover, gold nanorods are photostable, offer low toxicity, and can be conjugated with biomolecules for specific cell targeting.

Table 1: particle radius in nm for various LUDOX

LUDOX	*r* (SEM)	*r* (FL)
SM30	3.5	4.0 ± 0.4
AM30	6.0	6.4 ± 0.5
AS40	11	11.0 ± 1.6

SEM - scanning electron microscopy
FL - fluorescence anisotropy

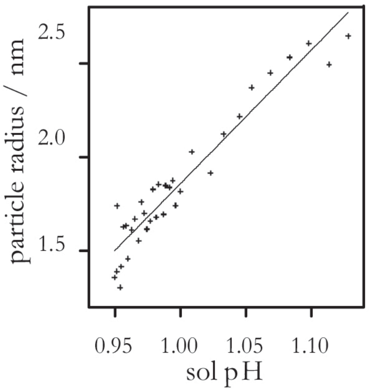

Fig. 1 Correlation between particle size and pH

We synthesise gold nanorods using the seeded growth method.[5] Recently we have used fluorescence lifetime imaging (FLIM) to separate out the fast luminescence (<100 ps) from the gold nanorods from the > 2 ns fluorescence lifetime of 4′-6-diamidino-2-phenylindole (DAPI) in Madin-Darby canine kidney (MDCK) cells.[6] Fig. 2(A) shows typical fluorescence decay curves of DAPI (black) and gold nanorods (red). The huge gap between the decay time from gold nanorods and DAPI results in superior contrast and easy distinguishing of gold nanorods in FLIM imaging, Fig. 2(B) shows a FLIM image taken from gold nanorods and MDCK cells with nuclei stained by DAPI. Further applications now seem possible on research into gold nanoparticle based drug delivery and therapy.

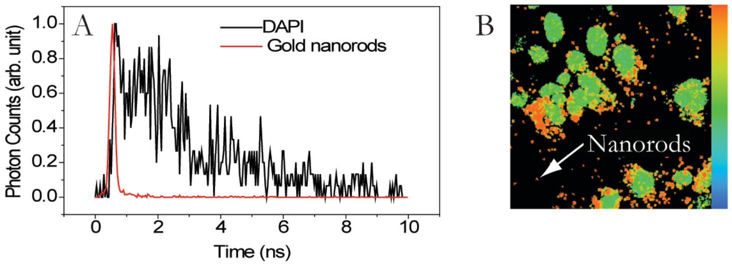

Figure 2 (A). Fluorescence decay curve recorded for DAPI and gold nanorods. (B). FLIM image of gold nanorods in MDCK cells.

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Light-induced Phenomena in TiO_2 Nanoparticles

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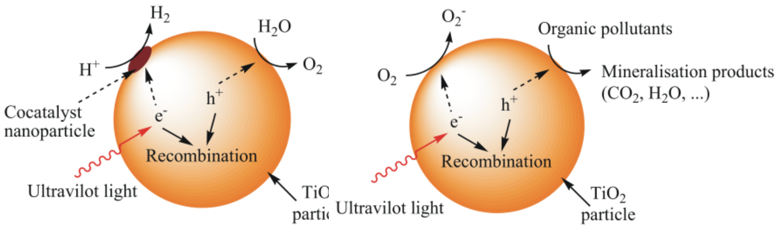
Titanium dioxide (TiO_2) is commercially produced since the early twentieth century. It has been widely used as a pigment and in sunscreens, paints, ointments, toothpaste, etc. In 1972, Fujishima and Honda, Japanese pioneers, discovered the phenomenon of photoelectrochemical water splitting on a TiO_2 rutile single crystal electrode under ultraviolet light illumination.[1] Since then, enormous efforts have been devoted to the research of the interaction of light with TiO_2, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo-/electrochromics and sensors. These applications can be roughly divided into "energy" and "environmental" categories. TiO_2 as a semiconductor can act as a sensitizer for light-induced redox processes due to its electronic structure, which is characterized by a filled valence band and an almost empty conduction band being an n-type semiconductor.[2, 3] Absorption of a photon with an energy exceeding the bandgap energy leads to the formation of an electron/hole pair. These electron/hole pairs are either dissipated within a few nanoseconds by recombination or undergo redox reactions.[2, 4]

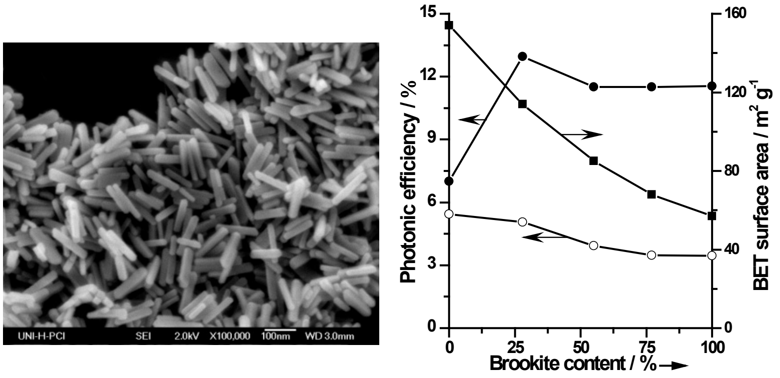


(a) (b)

Figure 1. (a) Photocatalytic overall water splitting and (b) photocatalytic mineralization of pollutants on a heterogeneous photocatalyst particle.

Utilizing these redox reactions induced by solar energy, TiO_2 can be used as a photocatalyst for hydrogen production and/or environmental purifications.[5, 6] Figure 1 shows simple cartoons illustrating the photocatalytic processes on TiO_2 for hydrogen production (a) and for mineralization of pollutants in the presence of oxygen (b).

In nature, TiO_2 exists mainly in three crystal phases: anatase, rutile, and brookite. Since most of the synthetic processes produce anatase, rutile, or a mixture of them, both phases are readily employed for photocatalytic applications. In contrast, the brookite phase is rarely being studied, mainly due to the difficulties encountered in obtaining its pure form. Recently, the synthesis of high quality TiO_2 brookite nanorods (see Figure 2a) with the advantage of tailoring the anatase/brookite ratio by a simple hydrothermal method have been performed in our labs.[6] Assessment of the photocatalytic activity of those TiO_2 nanoparticles by the hydrogen production from aqueous methanol solutions indicates that the photocatalytic hydrogen production activities of anatase/brookite mixtures and brookite nanorods, all loaded with 0.5 wt.% Pt nanoparticles, are higher than that of pure anatase loaded with the same amount of Pt despite the fact that the former exhibits a lower surface area (see Figure 2b).



(a) (b)

Figure 2. (a) SEM micrograph of brookite TiO_2 nanorods, (b) Relation between the photonic efficiencies, the surface area and the content of brookite: (●) photonic efficiency of hydrogen production, (○) photonic efficiency of DCA degradation, and (■) surface area.

This behavior is explained by measuring the flatband potential of the brookite nanorods. It was found that the flatband potential of brookite nanorods is cathodically shifted by 140 mV in comparison with that of anatase nanoparticles. Assessment of the photocatalytic degradation of dichloroacetic acid (DCA) in aqueous solution employing anatase nanoparticles, anatase/brookite mixtures and brookite nanorods indicates that anatase/brookite mixtures and brookite nanorods are photocatalytically less active than anatase nanoparticles alone (see Figure 2b). This agrees with the higher surface area of the latter.

Besides the photocatalytic applications of TiO_2 nanoparticles for hydrogen production and organic pollutant degradation, the interaction of TiO_2 and UV light leads to changes in the water wettability of the TiO_2 surface. These surface changes have been explained by the increase of the number of hydroxyl (OH) groups on the TiO_2 surface as detected by X-ray photoemission spectroscopy (XPS).[7] With the discovery of this phenomenon,[8] the application range of TiO_2 coatings has been largely widened. The photo-induced hydrophilicity of TiO_2 surfaces upon weak UV-A illumination has removed the limitation of the cleaning function of TiO_2 photocatalysis, that is, the function is limited by the number of available photons. Even though the number of photons is not sufficient to completely decompose adsorbed stains, the surface can be maintained clean when water is supplied because water soaks between the stain and the highly hydrophilic TiO_2 surface.

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Metal Nanoparticle-Perturbed Electronic Transitions: Enhancing Singlet Oxygen Phosphorescence

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There has been growing interest in how metal particles and surfaces can influence optical transitions in nearby molecules. Among these phenomena are surface enhanced Raman scattering (SERS) and metal enhanced fluorescence. Recent developments in the engineering of nanoparticles with well-defined structures and properties have made it easier to study and exploit the effects that a metal can have on enhancing a specific electronic transition in a given molecule. Metal-enhanced phenomena constitute a rather new addition to the toolbox of the photochemist, and introduce novel concepts that challenge our understanding of photophysical processes. There is no doubt that this field will grow rapidly due to the abundance of fundamental ramifications and practical applications.

Singlet oxygen, O_2 ($a^1\Delta_g$), is the lowest excited electronic state of molecular oxygen and is an important intermediate in many oxidation reactions, particularly in biological systems. Although singlet oxygen is ideally monitored by its characteristic 1275 nm phosphorescence, this is a highly forbidden transition. Thus, the prospect of enhancing this transition is of great practical interest.

A convenient method for producing singlet oxygen is photosensitization (Fig. 1a). In principle, any electronic transition in this photosensitization scheme can be enhanced using metal structures whose optical properties match those of the transition. We have opted to focus solely on the radiative transition from singlet oxygen to ground state oxygen. To accomplish this, one must tune the structure and, hence, the properties of the neighbouring metal nanostructure in a specific way.

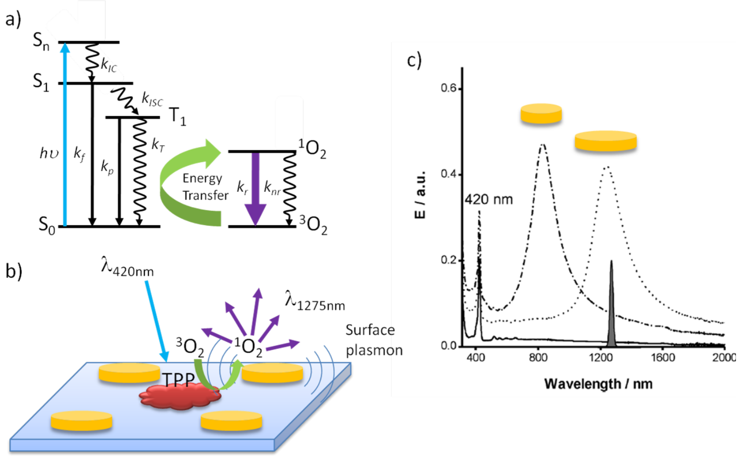

Figure 1. a) Jablonski diagram illustrating the photosensitized production of singlet oxygen. b) Illustration of sensitized singlet oxygen production followed by gold-nanodisc-enhanced phosphorescence. c) Extinction spectra of a sample with no discs (solid line), a sample with discs of the "incorrect" size (dashed dot) and of the "correct" size (dotted), respectively. The Soret band of the photosensitizer, tetraphenylporphyrin (TPP) is located at 420 nm. The spectral profile of singlet oxygen phosphorescence is indicated by the curve shaded in grey.

A characteristic feature of a metal nanoparticle is the localized surface plasmon (LSP), which reflects the confined motion of the surface electrons and depends on the material, size and shape of the nanoparticle. A surface plasmon can be excited when the incident light matches the energy of the plasmon, and this defines the localized surface plasmon resonance (LSPR). Gold nanodiscs on a glass substrate (Fig. 1b) allow for the proper control of spectral tunability and reproducibility while retaining a relatively narrow LSPR. In such gold nanodiscs, the LSPR is readily tuned simply by changing the disc diameter-to-height aspect ratio (AR), where increasing the AR results in a red-shift of the LSPR as illustrated in Fig. 1c.

In a proof-of-principle experiment, we established that singlet oxygen phosphorescence can indeed be enhanced through the use of gold nanodiscs with a discrete LSPR centred at ~1275 nm[1, 2] (Fig 1c).

At present, more experiments are needed to elucidate the underlying mechanism(s) of this phenomenon.

From a more global perspective, correlating experimental LSPR and enhancement data with theoretical predictions will certainly add further insight into the general understanding of the interaction between light and matter.

Use of other metal surfaces, such as silver island films, may also prove useful in this regard. With respect to the latter as applied to the photosensitized singlet oxygen system, this type of inhomogeneous metal surface, with its broad LSPR spectrum, allows several distinct transitions to be influenced.

Finally, we foresee that the development and implementation of specially engineered metal particles,[3] including those suitably functionalized with a singlet oxygen sensitizer, could prove extremely useful in a number of applications. Of particular benefit would be the detection of singlet oxygen in a single biological cell during studies of cell death.[4]

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For a more comprehensive list of references, the reader is referred to papers cited in the abovementioned articles.

The Unique Potential of Fluorescent Silica Nanoparticles in Nanotechnology

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Over the last decades the interest of photochemists has shifted from the study of purely molecular aspects to supramolecular architectures and nanostructures. Multi-component structures are, in fact, an ideal platform to realize nanosized functional photochemical systems combining elementary processes (light absorption and emission, energy- and electron-transfer) to obtain more complex ones (directional excitation energy migration, or multielectron photo-injection).[1] These architectures present many advantages, for example a remarkably increased signal-to-noise ratio in comparison with traditional dyes, that is a very appealing feature for analytical applications in diverse fields of great social and economical impact, such as medical diagnosis, imaging, and environmental monitoring.[2] Among the new contributions introduced by the advent of nanotechnology to solve important analytical problems, we look at dye doped silica nanoparticles (DDSNs) as one of the most appealing.[3-8] In particular, applications related to medical diagnostics and imaging can take great advantage from the implementation of dedicated DDSNs for many reasons such as:

1. silica, as a material, is not intrinsically toxic, although more in-depth investigations are under way to completely rule out possible hazards related to the tiny dimensions of nanoparticles;
2. silica is a hydrophilic material that is photophysically inert, i.e. it is transparent to visible light and it is not involved in quenching mechanisms such as energy- and electron-transfer processes;
3. the silica matrix protects the dyes segregated inside the nanoparticle from external species, thus increasing their (photo)stability and, in some cases, their luminescence quantum yield (Φ);
4. each DDSN may contain many fluorophores and reach a molar absorption coefficient (ε) that easily overcomes 10^6 M^{-1} cm^{-1};

5. DDSNs can be very stable in water solution, also under simulated physiological conditions;
6. their synthesis is based on modular approaches, is flexible and typically requires very mild conditions (also for core/shell DDSNs, as in figure 1);
7. DDSNs offer a confined environment in which collective processes, such as energy- and electron- transfer, can occur with very high efficiency.

Having all this in mind, it is not surprising the impressively high brightness (defined as the product ε x Φ) that characterizes some of them.

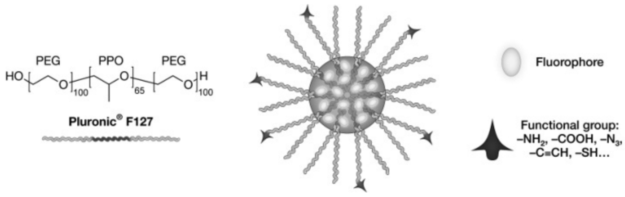

Figure 1: Scheme of Core Shell DDSNPs as described in ref. 3)

It has also been shown that DDSNs can enhance the potential shown by electrochemiluminescence (ECL), that already offers better performances than photoluminescence in many applications. In this context we have demonstrated that DDSNs, can produce luminescence intensities much higher then the ones produced by molecular systems since many dyes can participate to the generation of the ECL signal. In addition, many water insoluble dyes can be inserted in the silica structure and then taken into an aqueous solution, widely enlarging the library of ECL labels suitable for biological applications.[3]

DDSNs can be also engineered to present a large separation between the excitation and the emission wavelengths, which, via a substantial suppression of scattering and Raman effects, facilitates the development of suitable species for bar-coding and multiplexing analysis. This is possible taking advantage from the proximity of the doping molecules in these systems that allows to exploit efficient energy transfer processes between them. This strategy opens up many possibilities to obtain, for example, a set of nanoparticles presenting emissions at different wavelengths, but which can be efficiently excited with the same source, a feature that can otherwise be achievable only using QDs. It is important to underline that a proper design of efficient, intra-particle FRET processes can yield DDSNs able to perform also other highly valuable functions such as light harvesting, signal processing and energy conversion. All these features make silica nanoparticles unique platforms in the nanotechnology arena. In particular DDSNs are already competitive in many applications with the most commonly used commercial dyes, including fluorescent proteins and QDs. Nevertheless, we strongly believe that new powerful possibilities in the field of silica nanoparticles have still to be explored, and we are actively working in this very fascinating area.

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Plasmon Mode Selection Through Directed Orientation of Gold Nanorods

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Localized surface plasmon resonances (LSPRs) in metallic nanoparticles have been known for a long time.[1,2] However, the recent advances in fabrication methods, both lithographic and chemical, have boosted research in this area, which is currently known as *Nanoplasmonics*. Although many applications have been predicted and described for plasmonic metal nanoparticles, most of them require post-synthesis assembly into organized nanostructures. This is of particular interest in the case of elongated nanoparticles, such as nanorods,[3] since their morphological anisotropy leads to well-defined LSPR modes, parallel (longitudinal LSPR) or perpendicular (transverse LSPR) to the nanorod long axis. However, for these LSPR modes to be separated, all nanorods must be oriented in the same direction. An early demonstration of the possibility to separate

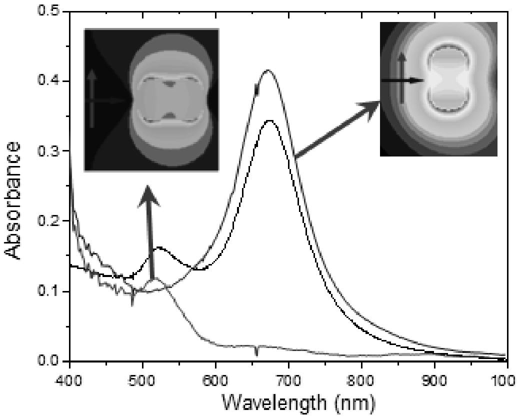

Figure 1. UV-visible spectra of Au nanorods showing decoupling of longitudinal (~670 nm) and transverse (~520 nm) LSPR modes. The insets show the respective near field enhancement maps, showing the respective mode symmetry.

both contributions was reported by simply embedding Au nanorods in a poly(vinyl alcohol) thin film.[4] Upon gentle heating and stretching, the nanorods were (irreversibly) oriented along the stretching direction and the LSPR modes could be separated under illumination with polarized light (Fig. 1). Although this obviously allows optical manipulation, no additional processing is possible, since the nanorods are trapped within the PVA film. Thus, reliable methods for nanorod self-assembly with orientational order are strongly preferred.

Several reports have shown short range oriented nanorod assemblies, both lying and standing on solid substrates. The advantage of standing arrays is that the directionality can be basically perfect, with negligible substrate effects. We have recently reported[5] that when the standard cationic surfactant employed for Au nanorod synthesis (cetyl-trimethylammonium bromide, CTAB) is replaced by a Gemini surfactant ((oligooxa)dodecanediyl-α,ω-bis(dimethyldodecylammonium bromide), GEM-1), spontaneous self-assembly occurs during solvent (water) evaporation on a variety of substrates. Interestingly, the assemblies invariably comprise parallel nanorod arrays, which under suitable conditions become long range (tens of microns) supercrystals. An example of the quality of such assemblies is shown in Fig. 2, where we chose on purpose an area where partial tilt of the standing nanorods was observed. Such perfect and long-range order is also reflected in the optical response

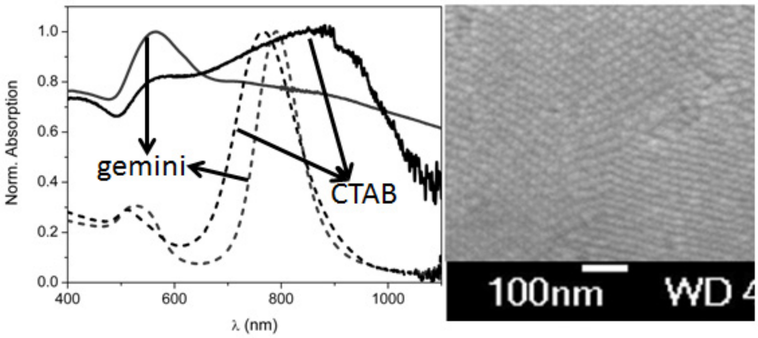

Figure 2. Left: UV-vis spectra of dilute dispersions (dashed lines) and dried assemblies on ITO substrate (solid lines) of Au nanorods capped with CTAB and Gemini surfactant, as labeled. Right: SEM image of an Au nanorod supercrystal made of Gemini-nanorods, where some tilting is shown on purpose.

of assemblies on ITO-coated glass substrates, as also shown in Fig. 2, and compared to deposited CTAB-capped nanorods. While the spectra of dilute nanorod dispersions (dashed spectra) are quite similar for both systems, dried CTAB-nanorods display two broad bands as a result of plasmon coupling in disordered assemblies. On the other hand, the highly ordered Gemini-nanorods display a single band because exclusively the transverse mode can be excited in these oriented arrays.

Since these supercrystals with directional order spontaneously grow from solution, they can be deposited on surfaces with arbitrary shapes and allow further manipulation. This opens new avenues toward implementation of optical devices with exceptional properties and novel functionalities.

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Photoinduced electron ejection upon excitation of gold nanoparticles at their surface plasmon band

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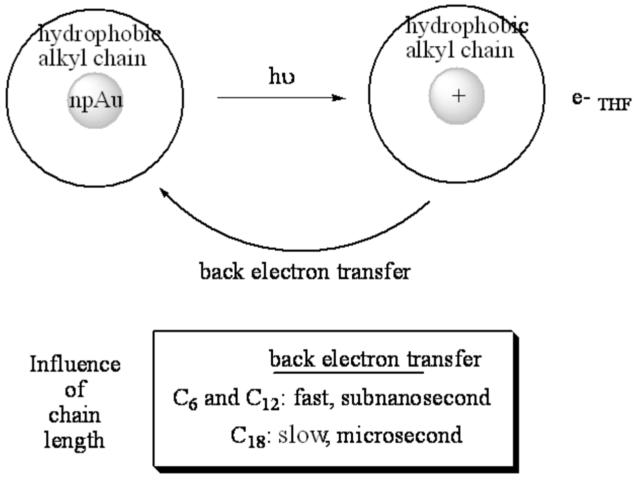
In the last decades there has been an intense effort determining specific properties that arise in the nanoscale domain and that have not been previously observed for larger particles. Due to the ease and reliability in which these nanoparticles are consistently prepared with narrow size distribution, noble metal nanoparticles and gold in particular have attracted considerable attention.[1]

One of the properties of gold nanoparticles is to exhibit a surface plasmon band as consequence of the collective vibration of the electrons in the conduction band caused by photon absorption.[2, 3] Kamat and coworkers have made extensive contributions in this field showing that photochemical excitation of gold nanoparticles in the surface plasmon band leads to a prompt relaxation of the photon energy into heat.[4, 5] A recent study using the decomposition reaction rate of dicumyl peroxide has estimated that the local temperature can be above 500 °C during tens of microsecond time scale.[6]

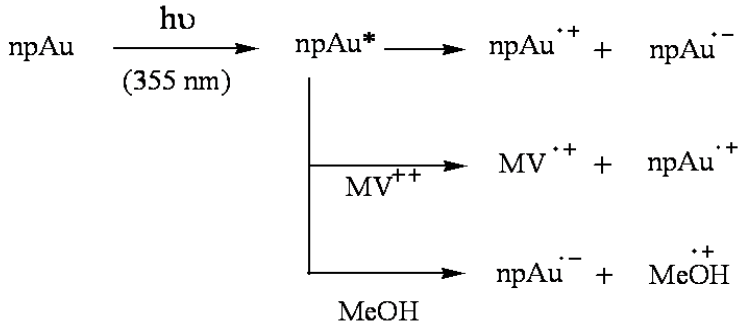
Besides the local temperature increase, we have observed that other event that can take place as consequence of the photochemical excitation of gold nanoparticles at their surface plasmon band is the ejection of electrons to the media.[7] For colloidal solutions of gold nanoparticles having an average size of 5 ± 1 nm and *n*-alkanethiol ligands in THF it has been observed that an increase in the length of the alkyl chain from 6 to 18 carbons favors the observation of microsecond transients that have been attributed to solvated electrons. It has been proposed that the apolar alkyl chain surrounding the gold core is long enough, once the electron has been ejected outside the gold nanoparticles recombination becomes impeded. Scheme 1 summarizes the proposal.



Scheme 1. Proposal to rationalize the influence of the ligand chain length on the lifetime of charge separation (taken from ref. [7]).

Alternatively, if instead of THF and long alkyl chains in the ligands, gold nanoparticles (even those being stabilized by hexanethiol) are excited in more polar solvents like ionic liquids, then, a transient signal characterized by a broad absorption spanning the whole wavelength range is also detected in the microsecond time scale.[7] The temporal profiles of the signal at different wavelengths were similar except some variations in the initial microseconds and its decay was not complete 100 μs after the laser pulse.

Assignment of this transient, at least in part, to electrons was supported by quenching with electron acceptors such as CH_2Cl_2 and methyl viologen. Scheme 2 provides an overall rationalization of the photoinduced electron ejection upon excitation of the gold surface plasmon band and the corresponding quenchings.



Scheme 2. Proposed rationalization of the photochemistry of npAu in imidazolium ionic liquid (taken from ref. [7]).

In addition, if a metal complex is bound to the gold nanoparticles by partial replacement of the ligands employed in the synthesis of the gold nanoparticles by a suitable thiol functionalized ligand, then, the charge separation induced upon surface plasmon band excitation can lead to change in the oxidation state of the bound complex[8]. One example from our own work is an Fe(II) terpyridyl complex bound through a thiol linker to gold nanoparticles.[9] Photoexcitation of gold nanoparticles at 532 nm leads to the generation of the Fe(III) terpyridyl complex as a transient that can be detected by optical spectroscopy.

Besides the use of ligands, we have shown that gold nanoparticles can be also stabilized by inclusion inside cucurbit[7]uril (CB7,0.8 nm internal diameter).[10] Cucurbiturils are cyclic oligomers of glycoluril units conneceted by methylene bridges defining a pumking-like molecular geometry.[11, 12] It is inside this organic capsule where gold clusters of about 1 nm average size can be included.[10] Apparently other cucurbiturils with smaller CB6 or lager CB8 size fail to stabilize gold nanoparticles in its interior. 532 nm laser flash photolysis of these Au@CB7 clusters reveals also the formation of millisecond transients.[13]

Beyond colloidal solutions of gold nanoparticles, the ability of these gold nanoparticles to eject electrons upon excitation in their surface plamons band has been also recently observed in gold nanoparticles supported on metal oxides and diamond nanoparticles.[14] Irradiation of these gold nanoparticles can serve to enhance the dark catalytic activity of these materials in Fenton oxidation.[14]

In summary, the present letter intend to draw the attention to the ability of gold nanoparticles to eject electrons upon excitation with visible light. This findings can be of interest in areas such as the solar light water splitting, solar fuels and general photocatalysis.[15]

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Coordination compounds as TiO_2 photosensitizers

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Photoactivity of micro- and nanocrystalline titanium dioxide limited to UV-light is the main factor constraining its use. Both photocatalytic and photovoltaic applications of TiO_2 profit by photosensitization of this wide bandgap semiconductor. Coordination compounds appear particularly efficient in achieving this effect. Dye-sensitized solar cell (DSSC) built on the platform of TiO_2 grafted with ruthenium(II) complexes is a good example of system characterized by high visible light-induced activity. In the process of titania photosensitization photoinduced electron transfer from the modifier (photosensitizer) to conduction band should appear. Alternatively, the hole transfer to valence band may play the main role, however in the case of TiO_2 such mechanism is very rare due to a high redox potential of valence band.

Mechanisms of photosensitization by coordination compounds usually involve excitation of surface complexes within their charge-transfer bands. A variety of possible CT transitions differentiates them. Figure 1 presents simplified pictures of selected modes of photoinduced electron injection to the conduction band of TiO_2. The first mechanism, observed upon coordination of catecholate-, salicylate-, or phthalate-derivative ligands to surface Ti^{IV} centres, is a one-step process involving a direct electron injection upon LMCT excitation (Fig. 1a).[1] Similarly, the optical charge transfer caused by MMCT excitation takes place in some binuclear complexes formed upon coordination of another complex to Ti^{IV} through a bridging ligand (Fig. 1b). $[Fe(CN)_6]^{4-}$ chemisorbed at TiO_2 surface is a good example of such system.[2] Both mechanisms lead to optical electron injection into the conduction band, i.e. the semiconducting support is reduced in one step.

Two-step processes involve CT excitation within the surface-bound photosensitizer followed by the dark electron transfer to conduction band of TiO_2. Either MLCT or LMCT excitation may operate here (Fig. 1c, d). The metal-to-ligand charge transfer process, followed by TiO_2 reduction, is responsible for photosensitization by anchored $[Ru(bipy)_3]^{2+}$-derivatives.[3] The opposite direction of charge transfer, LMCT, governs the photoinduced electron injection in the case of photocatalysis based on TiO_2 impregnated with platinum(IV) chloride complexes.[4]

In every presented example further steps should implicate reduction of the oxidized complex or ligand and processes involving electrons from the conduction band, mainly photocurrent generation (photovoltaics) or oxygen reduction (photocatalysis).

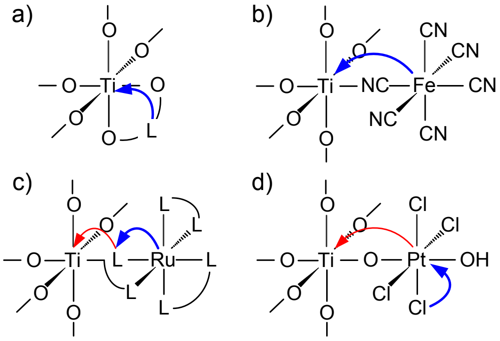

Figure 1. Possible mechanisms of TiO_2 photosensitization by coordination compounds: (a) LMCT transition within the Ti^{IV}-L moiety; (b) one-step electron injection resulting from MMCT transition; (c) two-step electron injection initiated by MLCT, followed by dark ET; (d) LMCT transition followed by dark ET. Thick lines denote optical ET processes, while thin lines stand for dark reactions.

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PUBLICATIONS
Abstracts of Theses in Photochemistry

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Ultrafast Excited-State Dynamics of Radical Ions in Liquid Solution
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The spectral and dynamic features of photoexcited radical ions have been studied by ultrafast spectroscopy, mainly transient absorption spectroscopy. The aim was to measure their excited state absorption spectrum, to establish the excited states lifetimes (very short lifetimes are anticipated from fact that only a small number of radical ions is fluorescent)[1,2] and to determine the influence of parameters like excess excitation energy, solvent or temperature on the photophysical behavior. To this purpose, chemically distinct systems (nitrogen centered radical cations, polycyclic aromatic and heterocyclic radical ions) have been chosen to span a certain range of chemical diversity, excited state energies (1 to 2 eV) and oxidation state (cationic or anionic). The radical ions have been generated either chemically or

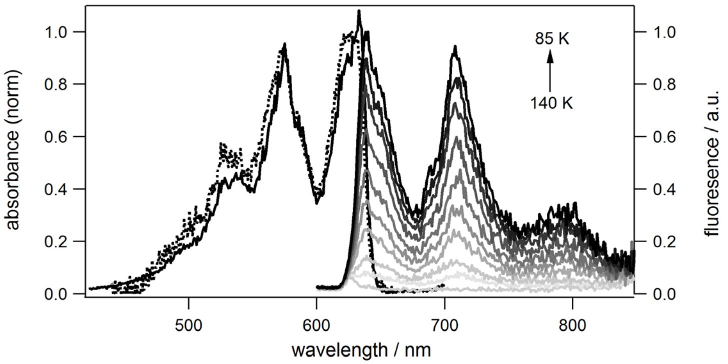

Figure 1: Absorption (•••) and fluorescence excitation spectra (—) at 85 K, and fluorescence spectra at various temperatures for Wurster's Blue in 1:1 methanol/ethanol.[3]

electrochemically in a home-built flow cell.

The results reveal that the electronic excited state, D_1, of the open shell species investigated is on the order of picoseconds only. The widely known Wurster's salts (*p*-phenylenediamine radical cations), for example, have a D_1 lifetime of 0.2 ps at room temperature irrespective of the solvent, the nitrogen substituent, or phenyl ring deuteration. The D_1 lifetime is, however, a function of temperature, reaching 650 ps at liquid nitrogen temperature and therefore fluorescence can be detected below a threshold of ca. 120 K (see Figure 1) but not in room temperature solid matrix.[3]

The contrary is the case for the polycyclic aromatic hydrocarbons studied — while temperature does not play a role for the D_1 lifetime of perylene radical cation,[2] the solvent has an substantial impact and a 4 fold increase is observed when changing acetonitrile for sulfuric acid.

In general, the data clearly shows that the energy gap law, which relates the rate of non-radiative relaxation of a state to the energy difference between this and the next lower lying state and which is often invoked to explain the lack of fluorescence from radical ions, is not obeyed. Instead conical intersections are involved whose accessibility is governed by subtle effects like the nature of substituents, structural flexibility, or the environment.

For all the examples studied, the excited state absorption showed very weak extinction coefficients and the transient absorption spectra were dominated by the contributions of the (vibrationally hot) ground state (Figure 2 and 3). This might explain why excited state radicals have not been observed in highly exergonic photoinduced charge separation corresponding to reactions in the so-called Marcus inverted region,[4] the absence of which remains one of the issues under debate in photoinduced electron transfer theory.[5]

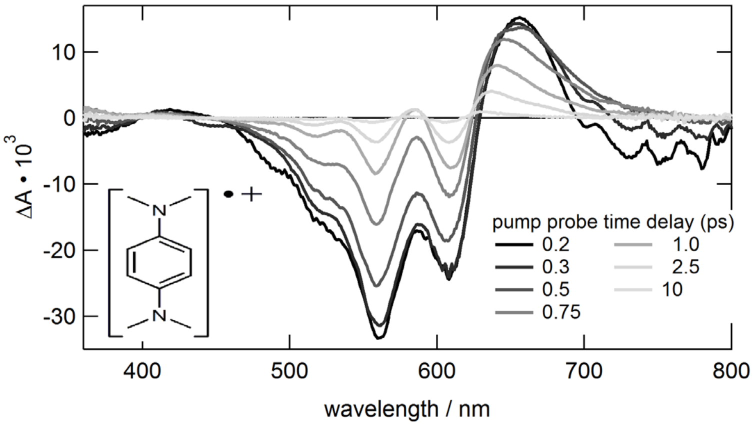

Figure 2: Transient absorption spectra of Wurster's Blue at different time delays after 610 nm excitation. Only the small positive signal around 420 and the negative signal above 700 nm are ascribed to the electronic excited state.[3]

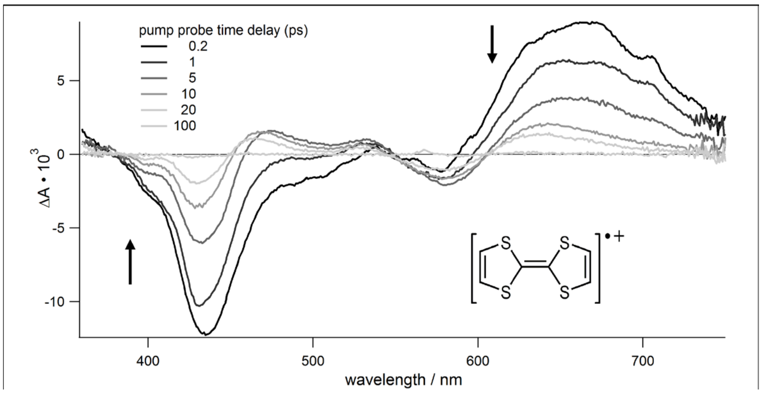

Figure 3: Transient absorption spectra of tetrathiafulvalene radical cation at different time delays after 580 nm excitation.[6]

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PUBLICATIONS

Bakunin, Paternó and Coworkers in the Development of Organic Photochemistry in Italy

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Most of the recent works on the history of photochemistry assign a crucial role in the development of this research field to the Italian scientist Giacomo Ciamician.[1,2] Only recently, some authors noted that the cultural environment in Italy in that period could produce some important contributions, not only by Ciamician, but also by Paternò.[3] In this case, the definition of "belle époque" of photochemistry has been used, also considering that the cultural production in photochemistry by Italian researchers finished with the First World War.

In this article we want to note that, in the Italian cultural environment at the beginning of the XX secolo, there are several actors participating to the efforts in the development of the use of light in chemistry, and that the research in photochemistry does not finish at the beginning of the war, but continua considering the scientific work of some pupils of Paternò.

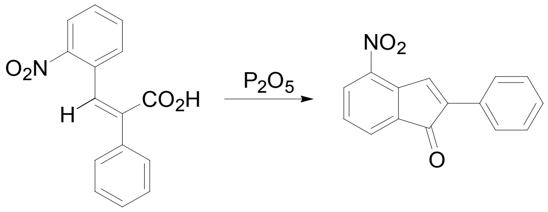
If the figure of Ciamician, is so important in the development of photochemistry, we have to consider that all the scientific environment in Italy was conscious that light could be a potent instrument in the hands of the chemists. At this purpose we can consider the work of Marussia Bakunin.

Maria Bakunin was born in 1873, 2nd February, at Krasnojarsk, Siberia, by Michail Bakunin, the important russian revolutionary men, father of the anarchism, at that period in Siberia owing to a punishment, and Antossia Kwiatowoska. The family was able to escape from Siberia and took refuge at Locarno, in Switzerland, guest in a villa of Cafiero, an Italian socialist. Bakunin died in 1876 at Berna, when Marussia was only three years old. Antossia accepts to move to Napoli, in the villa of the socialist Carlo Gambuzzi. After two years Carlo Gambuzzi and Antossia married and, then, Marussia will grow up and will live at Napoli. She attended the lessons at the Italian secondary school (Liceo) and, then, at the University, where she was noted by Agostino Oglialoro-Todaro, an organic chemist, pupil of Cannizzaro. She became "preparatore" (preparer) of the Chemical Institute. She obtained the degree in 1895, when she was twenty-two years old, and in the years she married with Oglialoro. In 1906 she was professor of Applied Chemistry at the Polytechnic school of Napoli. In 1912 she obtained the chair of Organic Technological Chemistry; in 1936 she had the chair of Industrial Chemistry. In the period 1943-1947 she was president of the Accademia Pontaniana. In 1948 she was nominated emeritus professor. She died in 1960.[4] Who knew her remember a woman with an extremely strong character, able to oppose the German soldiers attempting to destroy her institute, but also able to be a tender woman.

The scientific activity of Bakunin cannot be described in a few words. We can pass from the study of the natural products (picrotoxin, morphine, strychnine) to the study of bituminous schist, from the study of mechanism of the Perkin reaction to the photochemistry.

The first mention on the photochemical reactivity of cinnamic derivatives is dated 1898.[5] Bakunin writes: "Only exposing to the direct sun light of July a solution of the para isomer with m.p. 143 °C a partial transformation was observed just after one day and after some days it is complete. The acid melted at 214 °C" (p. 37). The conversion of the Z isomer 2-phenyl-p-nitrocinnamic acid into the corresponding E isomer is described. The same reaction was achieved by using an ultraviolet lamp, but it is slower.[6] Furthermore, Bakunin observed that both phenylcinnamic acid and 2-phenyl-o-nitrocinnamic acid did not gave this reaction.

However, the most important activity in photochemistry of Bakunin was the study of the photochemical behavior of the cinnamic acid derivatives described before (Scheme 1).

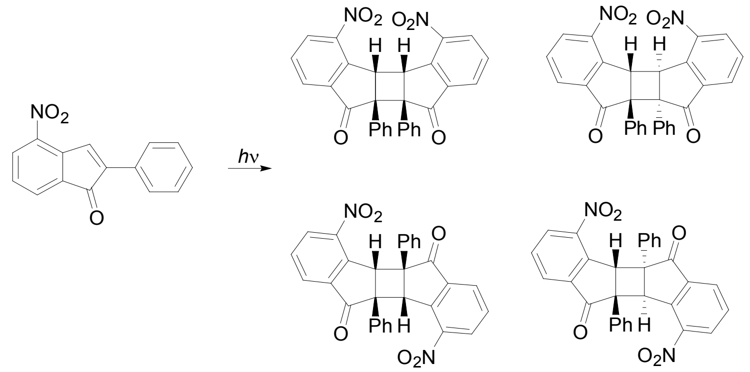


Scheme 1

In an article of 1902 the author observed that 2-phenyl-4-nitroindone under the effect of light converted in a different product similar to that obtained during the dehydration as a by-product after the evaporation of the solvent.[7] 2-Phenyl-4-nitroindone, exposed to ultraviolet light, did not give a reaction, but the exposition to the sun of the pure substrate (not in solution) allowed the formation of a single product with a high melting point.[8] These preliminary results were developed in three articles published in different periods.[9-11] What have Bakunin found? She found the dimerization reaction of cinnamic derivatives. This argument will be the object of a research of Ciamician[12] but Bakunin was a pioneer in Italy in this field.

The first described experiments regard the irradiation in the presence of sunlight of 2-phenyl-4-nitroindone in the solid state. Advancing the work performed by Stobbe on cinnamic acid, she found that this compound gave only one product.

The photochemical dimerization of the substrate could gave four different isomers of the dimer (Scheme 2). Bakunin found that the reaction showed a good stereoselectivity. However, she was not able to determine the structure of the product: she thinks it is a dimer, but she has not any prove able to confirm this hypothesis. She does not have instruments able to determine the relative stereochemistry of the substituents. This reaction has not be performed recently. Then, we are not able to assign the correct structure of the reaction product.



Scheme 2

When the same compound was irradiated in solution a mixture of three products was obtained. Probably, the head-to-head syn dimer cannot be obtained for steric reasons, but, nevertheless, in these conditions the reaction lost its stereoselectivity. Bakunin was not able to determine whether all the products were dimers. Subsequently, cryoscopic determinations induced her to consider the formation of trimers and tetramers; however, we think she in this case made a mistake. The irradiation of 2-phenyl-6-nitroindone in solid state did not give a product. On the contrary, in benzene, chloroform, and acetone the corresponding dimers were obtained.

Finally, 2-phenylindone, irradiated in the solid state, also in this case gave a single product, and it was a dimer.

Emanuele Paternò was born in Palermo on 12 December 1847 to Giuseppe and Caterina Kirchner. The Paternò family could boast of noble and ancient origins, dating back to the Infante Don Pedro de Aragon, who lived in Spain in the 13th century and was the son of James I the Conqueror. One of Don Pedro sons, Miguel, rebelling against his cousin, Don Alfonso, King of Aragon, was stripped of his father's possessions and forced to seek his fortune elsewhere. In 1287 he purchased Paternoy Castle, as the foot of the Spanish Pyrenees, from which the name of the household was taken. A descendant of Don Miguel, Giovanni, then moved to Sicily in the 14th century. In one of the several collateral lines issuing from him Giuseppe Paternò was born who, in 1756, purchased the title of Marquis of Sessa of which the family of Emanuele Paternò was a direct descendant. However, over the centuries and after the abolition of feudal privilege in the early 19th century, the financial situation of the family ceased to be flourishing. Further and more serious problems were caused by the participation of Emanuele's father, also called Giuseppe, in the anti-Bourbon revolution of 1848. When the Bourbons returned to power, Giuseppe was banished and much of his remaining property was confiscated. What little remained was then lost through the mismanagement of others during the period of his exile.

His wife and children, five in all, followed Giuseppe in a pilgrimage that took him first to Liguria, then to Piedmont, to Malta and finally to Alexandria, in Egypt. Giuseppe Paternò died there in 1858 and Emanuele's mother at that stage was taken in by her brother in Genoa, who was also dedicated to the cause of Italian independence. These family figures and the intensely Italian atmosphere that Emanuele breathed from his early childhood represented a guide and an example that accompanied him throughout his life. Also his uncle then died, but finally, several months later, following the enterprise of Garibaldi's Thousand, the Paternò family succeeded in returning to Palermo.

The young Emanuele was thirteen at the time and, as a result of his previous vicissitudes, had been unable to follow any regular course of studies. Consequently, on returning to Palermo, he was admitted to the second class of elementary school. However, he quickly made up for lost time, also because of his lively intelligence and his natural inclination above all for mathematics and political history and soon enrolled at the Palermo Technical Institute where his brother Franco, through the recommendation of Stanislao Cannizzaro, had been appointed to the post of assistant to the professor of Physics and Chemistry, the Frenchman Alfredo Naquet. One should not be surprised by the help given by Cannizzaro to Franco and later to Emanuele Paternò. The distinguished Italian chemist, who also had returned to his native Palermo soon after Garibaldi's expedition, had participated actively in the 1848 uprisings and had thus been a friend and companion of the father of the two young men in his political commitment. Among other things, during the years of his exile he was actually Franco's godfather and it was at his baptism that Emanuele Paternò first met the man who was to be his mentor and guide, and not only in scientific matters. A similar concern for the children of an old friend and companion of adventure was shown in those years by Garibaldi himself who, in a decree of 21 October 1860, nominated the young Emanuele 2nd class midshipman.

It was thus these circumstances and perhaps the personality of Naquet and Cannizzaro that directed Emanuele's interest towards chemistry. Moreover, it was mainly the merit of Cannizzaro that Naquet was appointed to the Palermo Technical Institute. Naquet was born in Paris and was pupil of the famous chemist Wurtz, one of the main champions in France of the atomic molecular theory which precisely Cannizzaro contributed through his research to develop and strengthen. According to Cannizzaro's plans, Naquet's posting to Palermo could serve to reinforce the new theory, of which he was one of the main founders, also in this country. Incidentally, the presence of Naquet and his family in Palermo, which lasted until 1865, although important for the early chemical training of Emanuele, who was thus able almost daily to participate in meetings packed with discussions and scientific communications, was also the indirect cause of a family tragedy, the suicide of his brother Franco in 1867, because of the unhappy relationship between him and Naquet's young wife. This event nevertheless did not weaken the contacts between Emanuele and the French chemist, who continued to write long letters to each other, even though as the years passed, Naquet increasingly preferred to speak not so much of chemistry as above all of political events in Italy or France. Indeed the radical republican ideas professed by Naquet plunged him deeper into French political life, which also brought him considerable personal difficulties and problems.

Naquet, was also, albeit for only a brief period, one of the young Paternò's teachers. Two other foreign chemists also had the same role in those years, Adolf Lieben and Wilhelm Körner. Both came to Palermo thanks to the work of Cannizzaro who, from the time he was summoned to the university in the Sicilian capital, was determined to defend the polycentric nature of Italian science and strove in particular to ensure Palermo set up structures, above all in the field of chemistry, that could compete at Italian and European level. It was Cannizzaro, as we saw, who found a place for Naquet at the Technical Institute. It was again Cannizzaro who had Lieben appointed to the newly established University Chemistry Laboratory (1863) and later (1865) enabled him to obtain the Inorganic Chemistry chair when his own chair, which previously included both inorganic and organic chemistry was split.

Cannizzaro had met Lieben for the first time in 1860 at the famous Karlsruhe Congress, in which the Palermo chemist is known to have illustrated to the scientific community his ideas on atomic molecular theory. He later met him again in Paris, like Naquet, at the laboratory of Wurtz, who had come from the University of Heidelberg, where he had studied under Robert Bunsen. Lieben's background in chemistry was as solid as ever both in the inorganic and organic sector and above all he was able to bring to Palermo his direct knowledge of the organization of one of the most advanced chemical laboratories in Europe and of the latest apparatus and experimental techniques used and developed in it.

During his training years, Paternò made the most of Lieben's presence, as he later explained in the following words: "…my true teacher of chemical techniques was Adolf Lieben; he guided me through quantitative analysis, organic analysis, and introduced me to scientific research with a patience and affection that I have never forgotten".

Lieben left Palermo in 1866, just before the outbreak of the Third War of Independence. Correspondence between Lieben and Paternò went on for a long time. Their letters, always marked with the maximum respect and reciprocal affection, nevertheless here and there reveal traces of a difference of opinions linked to the different policies of their respective nations, Italy and the Austro-Hungarian Empire, above all as far as the irredentist aspirations of Italy were concerned or the upheaval in international peace caused by the 1911-12 war in Libya.

As we have seen, another eminent foreign chemist worked at Palermo during Paternò's formative years, the German Wilhelm Körner. The latter had worked at Giessen with Heinrich Will and Hermann Kopp, later in London with Lyon Playfair, but above all for a number of years had been Kekulé's assistant in Ghent. He arrived in Palermo in 1867, when Kekulé moved from Ghent to Bonn. Körner thus brought to the Sicilian capital the ideas of the eminent German chemist on the equivalence of the four bonds of the carbon atom and on that of the carbon atoms in the benzene ring. The following is another direct quote from Paternò's testimony referring to those years: "*Cannizzaro, who was always thirsting for knowledge, often held evening gatherings in his own home on scientific subjects in which Koerner illustrated the entire scientific work carried out in Ghent by Ladenburg, Wurtz, Baeyer, as well as Kekulé's ideas; I was present at this highly effective kind of* *lecture, which was made all the more instructive by Cannizzaro's interjections. You can imagine how much I profited from this two-man school, which I do not hesitate to call wonderful…*".

However, it must also be said that relations between Körner and Paternò deteriorated quite rapidly in those years: "*A quarrel arose between Koerner and myself over the fact that in the lectures I have spoken of I had learned more than Koerner would have liked, and that it took only a few months for me to able to discuss with him the most difficult problems regarding the construction of aromatic substances and synthesis in organic chemistry. The fact that a young student, as I had not yet graduated and was barely 20, should dare compete with him in topics of which he was an expert, irritated him…*".

Whether or not these were the causes of the dispute between the two, it continued for a considerable time, even after Körner left Palermo and moved to Milan. The reconciliation between the two, which took place many years later, was sealed on the occasion of the social dinner at the I Congress of Pure and Applied Chemistry of Turin in 1899. It must however be said that the influence of the ideas Körner brought to Palermo was instrumental in directing research on the equivalence of the four carbon valences, which Paternò addressed in the first few years of his scientific activity.

In the preceding paragraphs we dwelled on the role that Naquet, Lieben and Körner had in Emanuele Paternò's scientific education. There is no doubt however that for many years Stanislao Cannizzaro was not only his teacher but also his paternal guide, as it were, particularly in the years after his return to Palermo. He had the role of looking after Giuseppe Paternò's orphans, both of whom he directed towards a university career in chemistry. After Franco's death in the circumstances described above, Cannizzaro's attention was focused more strongly on Emanuele, whom he supported and sustained, both scientifically and in other ways, both during the Palermo years and, as we shall see, also later, in the years following 1871, the year in which Cannizzaro is known to have moved to the University of Rome. The relationship between Cannizzaro and Paternò was however always one between two strong personalities who had a lot of esteem for each other but in which the pupil often did not fail to display and pride and a critical and independent spirit of his own. Paternò himself recounts an enlightening episode in this connection probably dating back to 1868 (Paternò was barely 21 at the time). One evening, his mentor asked "*which, in my opinion, of the chemists currently in vogue would go down in history. Without any malice I* *answered: 'Certainly not you or Hofmann, nor Kekulé, nor Wurtz, nor Wöhler, but Liebig and Bunsen, and not for their great discoveries but the former for his meat extract and the second for the carbon battery and the gas lamp'. My fierce judgment did not impress Cannizzaro who wanted to discuss case by case, man by man, the reasons that had led me to such a discouraging opinion and did not find them completely unfounded*".

In 1871 Paternò graduated in physics and chemistry. A few months after taking his degree, the completion of the publication of his first organic chemistry research was sufficient to earn him first place in the competitive examination for the chair of General Chemistry at Turin University. Furthermore, since, as we have seen, Cannizzaro was moving to Rome, the Faculty of Physical, Mathematical and Natural Sciences of Palermo University asked the Ministry for permission instead to appoint him full professor in the same subject in the University of the Sicilian Capital. The Education Minister gave the necessary permission and in October 1872 Paternò became professor of General Chemistry in Palermo, a chair he then held for about twenty years. The appointment as professor at such a young age perhaps raised a few eyebrows at the time. Paternò himself later recounted the following anecdote in this connection, which once again confirms that he had a strong, proud and certainly not easy character: "*When, in the summer of 1872 I had the honour of being introduced to the great Brioschi [an important 19th century mathematician, who was Chancellor of the Milan Polytechnic and Senator of the Realm] he, astonished to see how young I was, uttered words that might have sounded critical of the Commission that had selected me for such an important post, my respect for the high authority of the eminent mathematician did not prevent me from replying: 'You should know that study time is calculated not in years but in hours'*".

Within the period (1872-1892) in which he was held the chair at Palermo, Paternò, from 1885 to 1890, was also Chancellor of the University. They were years in which he participated actively in the city's political life and from 1890 to 1892 he was also mayor of Palermo. In those years he also attempted twice to be elected to the Chamber of Deputies, and was defeated on both occasions. I shall dwell at greater length on Paternò's involvement in local politics, and later at the national level, in a subsequent chapter. Here I shall merely mention the efforts he made on behalf of the citizens during the 1885 and 1887 cholera epidemics, which among other things earned him the award of a gold medal for public health merits.

From the personal point of view, one important event during this Palermo period was his marriage in 1878 to Giuseppina Paleologo Vassallo, who bore him three children, Giuseppe, Caterina and Eleonora Michela. In the meantime also his scientific prestige was increasing and this allowed him in those years to become a member of several important scientific societies. Included among the Italian societies was the Lincean Academy, of which he became a corresponding member in 1879 and an ordinary member as from 1883. It was precisely his membership of this Academy that led him on 4 December 1890 to be nominated senator. It is a known fact that, at the time, one became a senator not by election but by direct nomination by the king, on the basis of merit as indicated in Art. 33 of the Albertine Statute. Among others, this article included among the possible categories having entitlement to the seat of senator members of the Royal Academy of Science of seven years standing. The Academy of Science originally referred to in the Statute was the Royal Academy of Science of Turin, although the benefit was later extended to other Academies, including the Lincean Academy, after the proclamation of the Kingdom of Italy.

Substantial efforts were made by Cannizzaro himself to facilitate Paternò's Senate nomination, he himself already a senator and holding the office of Vice-President. Probably the nomination was backed by Crispi himself, the then President of the Council and from Sicily like the two scientists. He too in 1848 had been involved with Cannizzaro and Paternò's father in the insurrections aimed at obtaining the reunification of Sicily with Italy. As we shall see in the following chapter, a part of Paternò's political life developed precisely under the umbrella of the famous Sicilian statesman.

Coming back to the relations in that period between Cannizzaro, busy organizing the Chemical Institute of Rome in via Panisperna and endeavoring to give the whole of Italian Chemistry a unitary structure under his guidance, and Paternò, it must be said that the mentor did everything in his power to convince Paternò to move to Rome. In this sense, the nomination as senator was meant to act as a further encouragement to the move. The correspondence of this period often reveals Cannizzaro's irritation at Paternò's involvement in local politics which made it even more difficult for his pupil to come to Rome. The move was also hindered by the Ministry of Education which was not in favour, also for budget reasons, of setting up two chemistry chairs in the Rome location.

Lastly Cannizzaro's persuasive powers and efforts achieved the desired effect and, on 4 December 1892, Emanuele Paternò became professor of Applications of Chemistry at Rome University. It must however be said that this did not immediately mean Paternò's complete detachment from Palermo political life, and he even served as President of the Provincial Council from 1898 to 1914. Nevertheless, from 1892 until 1930 he resided for most of the time in Rome and it was here that, from that time on, he carried on his teaching and research activities. These activities and the role he played in the national and international scientific community will be described at greater length in the following chapter. Here I shall mention only a few important institutions to which his growing prestige took him either as member or president: Superior Education Council; Superior Health Council; College of Customs Experts; Explosives Chemical Laboratory; Public Health Chemical Laboratory (the original nucleus out of which the Higher Health Institute grew); Agrarian Chemical Station.

He did honor also to his seat in the Senate of the Realm, taking a constant and active part in its activities without interruption from 1892 to 1930. In all these years he proposed numerous bills and frequently took part in debates of importance to the life of the country. These were years in which Italy was engaged in the serious and painful struggle of World War I.

In the period from 1892 and 1910 both Cannizzaro, who was still professor of General Chemistry, as well as Director, and Paternò, were simultaneously present in the Chemical Institute in via Panisperna. The cohabitation of two such strong personalities was probably not always easy. Nevertheless, their great mutual esteem never flagged. As Cannizzaro wrote in a letter to his pupil dated 7 September 1903: "our brains must have similar structures and configurations". Paternò was for instance one of the few with whom Cannizzaro could exchange opinions on the exaggerations with which the champions of thermodynamics in those years were trying practically to exclude the molecular theory from chemistry.

After Cannizzaro's death Paternò was appointed (9 June 1910) full professor of General Chemistry and Director of the Institute. It was then he who prepared his succession well in advance, recalling from Florence to Rome his own pupil Nicola Parravano, reserving for himself the organic chemistry chair, for the few years remaining before his retirement.

In 1923, at the age of 75, he gave up teaching and resigned from the post of Director of the Chemical Institute. The event was celebrated with a big ceremony held at the Via Panisperna Institute. The honour committee included the most important Italian chemists of the time, such as Ginori Conti, Nasini, Parodi Delfino and Marotta but also the physicist Corbino and the mathematician Fano. This was the year in which the Paternò medal was established, which is still today periodically assigned on the occasion of the national congresses of the Italian Chemical Society. The first to receive the award was F. W. Aston.

Also after his retirement, for several years Paternò continued to act above all as President of the XL Society (the name at the time of the present National Academy of Science, socalled of the XLs), of which he had been a member since 1889, becoming its President in the period 1921-1932. He defended the independence and prestige of the Academy, founded by Antonio Lorgna in 1782, imagining it could play a role as an active centre of Science History studies, a role that the Academy indeed pursued over the years, becoming one of the main centres in which the records of the most important Italian scientists, including Paternò, were conserved.

Advancing age and the onset of serious eye disorders weighed heavily on his remaining years, in which he preferred to return to Palermo, his native city. Also during these last few days he endeavoured to follow, albeit by reading the publications of others, chemistry research and discussed the problems related to it, often repeating: "one must work as though one might die tomorrow, and think as though one will never die". He died at the age of 87 on 18 January 1935.

Paternò published eleven articles on the Gazzetta Chimica Italiana, and they represent almost all the contribution of Paternò in the photochemistry.

What are the contents of these articles? The first one is a review of the state of art in organic photochemistry.[13] The author attempts a classification of the organic photochemical transformations giving this type of indications: "*In my opinion, I incline to distinguish:*

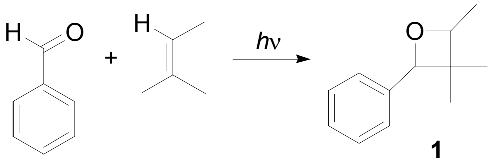
1° Transformations of a single substance, completely or partially, into a single substance; in this section we consider the isomerizations, the stereoisomerizations, the polymerizations, the phototropic phenomena, and the intramolecular oxidations.

In this class various reversible and irreversible reactions can be distinguished.

2° Decompositions and hydrolyses.
3° Reactions occurring between two or more substances (additions, substitutions, reductions, oxidations, etherifications, etc.).
4° Synthetic processes."[13]

The article describes the results obtained by another important Italian personality in organic photochemistry, Giacomo Ciamician. In this contest he describes the Ciamician's work with the due emphasis.

The second article published here reported the most important contribution of Paternò to the organic photochemistry.[14] The results obtained in the reaction of aromatic carbonyl compounds with olefins were reported. The reaction described here is the well-known Paternò-Büchi reaction (Scheme 3).



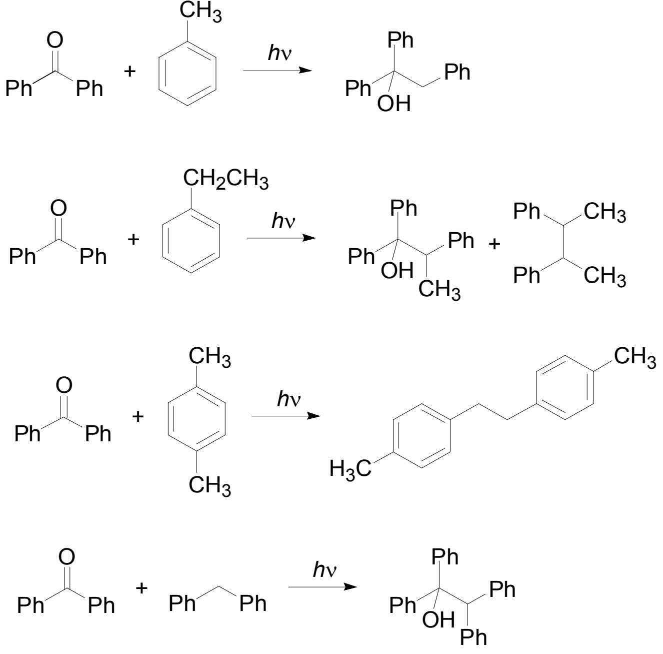
Scheme 3

The regiochemistry of this reaction appeared to be a difficult problem to solve from the first (Scheme 3). Paternò performed a reaction between 2-methyl-2-butene and benzaldehyde, and he could not assign the exact structure of the product. Büchi solved the problem after several years showing that **1** was the actual product.[15]

Paternò reported his results in the reaction between benzaldehyde, p-methoxybenzaldehyde, acetophenone, benzophenone, 4-phenyl-2-butenone, benzoylacetone and 2-methyl-2-butene and some other olefins.

The third article of the series is connected with the previous one.[16] In this article, considering the reaction between benzaldehyde and 2-methyl-2-butene, he wants to confirm the oxetane structure showing that the product is not isoamylphenylketone. At this purpose, this compound was prepared and the chemical and physical properties of the two products were compared, showing that isoamylphenylketone is not obtained in the photochemical reaction.

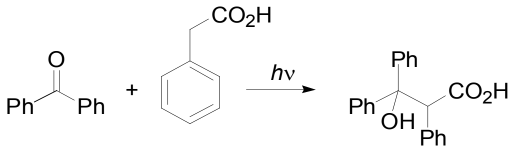
The fourth article of the series contains some interesting results.[17] Paternò examined the reactivity of benzophenone in the presence of some aliphatic hydrocarbons and found the some benzopinacol was obtained. Another fraction of the reaction mixture, after purification, gave benzophenone. The author supposed that benzophenone oxidizes the hydrocarbons to give the olefins; the obtained olefins give the coupling products with benzophenone that, in the distillation conditions, are destroyed giving benzophenone.



Scheme 4

Furthermore, examining the reactivity of benzophenone in the presence of aromatic hydrocarbons, he found that toluene, ethylbenzene, p-xylene, and diphenylmethane give the corresponding dimmers or a coupling product with benzophenone (Scheme 4). Benzaldehyde gave, in the same conditions, polymeric materials.

The same type of reactivity was observed when phenyl substituted carboxylic acids were used.[18] Also in this case the coupling products between benzophenone and the acid were obtained (Scheme 5). In the same article also the reactivity in the presence of diethyl ether was examined. Paternò proposed the formation of an addition product.

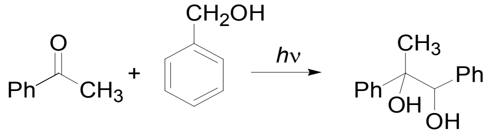


Scheme 5

In the sixth article of the series Paternò reported another similar reaction: in this case the reaction between benzophenone and benzyl acetate was described. Also in this case the coupling product was obtained.[19]

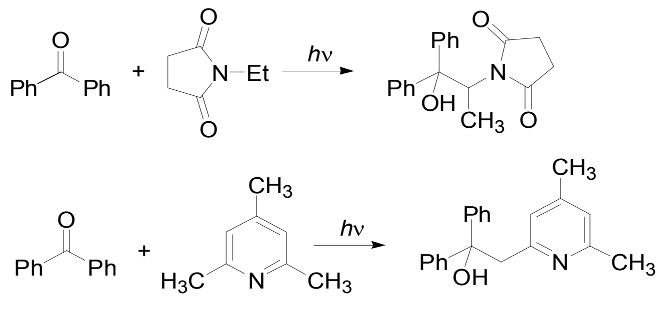
The seventh article describes the reaction between acetophenone and ammonia in ethanol.[20] The authors obtained a product with formula $C_{18}H_{18}N_2$, but they was not able to identify the product.

In the eighth manuscript the most relevant results are the reaction between benzophenone and benzaldehyde, giving, in the opinion of Paternò, to a benzaldehyde polymer (this result will be one the object of a violent controversy with Ciamician), the reaction between p-tolualdehyde with 2-methyl-2-butene to give the corresponding oxetane, the reaction of acetophenone with benzyl alcohol to give the corresponding adduct (Scheme 6), and the reaction of 2,6-dimethyl-□-pyrone with 2-methyl-2-butene to give a pyrone dimer.[21]



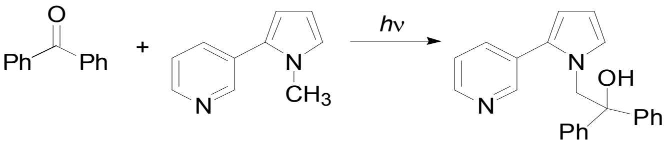
Scheme 6

In the ninth article we found some other application of the same reactivity described above (Schemes 4-6). Benzophenone reacts with benzylamine to give the corresponding adduct. N-Ethylsuccinimide reacts with benzophenone to give, also in this case, an adduct (Scheme 7), an adduct is obtained also in the reactions benzophenone with 2,4,6-trimethylpyridine (Scheme 7), with p-tolunitrile and phenylacetonitrile.[22]



Scheme 7

Finally, the tenth article of the series is related to the reactivity of acetophenone and benzophenone with some alkaloids.[23] Paternò used six alkaloids and in all the cases he found the a reaction occurred. However, only in the case of nicotine, he was able to identify the product (Scheme 8).



Scheme 8

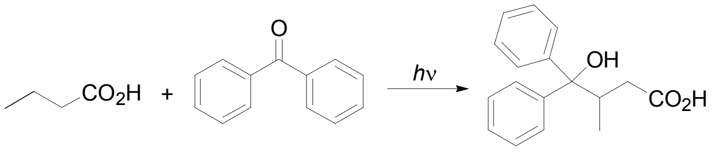
The eleventh contribution is an article containing some comments to the results described in the previous ones.[24] It is relevant only because it contains some elements of a controversy between Paternò and Ciamician. Paternò claims the originality of his results, while Ciamician asserts that the results of Paternò are only particular cases of a reactivity studied from a long time by his group. Paternò affirms that Ciamician did not cite his results and that he performed some experiments after he knew the Paternò's results. The position of Paternò can be summarized considering the following paragraphs at p. 474 of his article:[24] "*We have to remember once more that the synthetic reactions by means of light we obtained in a series of published memoirs during a period of almost six years, have to be considered as acquired from the first Memoir we entitled as Introduction, neither we want with these assertions to reproach Ciamician and Silber if, worried only of both the reducing properties of the alcohols and the formations from them of aldehydes, at the beginning they let slip* *some more important observations, and then, known our results, without waiting for the publication of the single experiments, they searched to take advantage of them. However, it is also evident that, if we want to discuss on the priority, we need to come back to dates preceeding February 1909. We tried to give to each one his own, with bibliographic researches performed with the greatest attention we are able, and we enjoin to correct the omissions which will be showed us and the errors which we incurred but we don't allow, at least this time, that others attempt with artifices to present our work in a wrong light.*"

We have to note that Ciamician replied to these statements.[25] However, we don't want to enter in the details of the controversy here.

In this notes I tried to give you a summary of the photochemical contribution of Paternò to the development of the photochemistry. Most of the reactions described in those articles are used in the modern organic photochemistry and this is the most important index of the success of a researcher.

Paternò in 1915 published a work not considered by his biography.[26] He reports part of the results obtained in the photochemical reaction of butyric acid with benzophenone.[27] In Note V of the series "Synthesis in organic chemistry by means of light" he described that acetic acid, irradiated in the presence of benzophenone, did not react, while phenylacetic acid gave triphenyllactic acid Scheme 5).[18] In this field Paternò describes part of the results obtained irradiating butyric acid in the presence of benzophenone. He notes both that at the opening of the tube a significant evolution of carbon dioxide was observed and one of the reaction products was propyl butyrate. Furthermore, he asserted that the accurate study of all the reaction products would be performed by his coworker dr. Remo de Fazi. Remo de Fazi has been a coauthor of the Note X of the series "Synthesis in organic chemistry by means of light".[23]

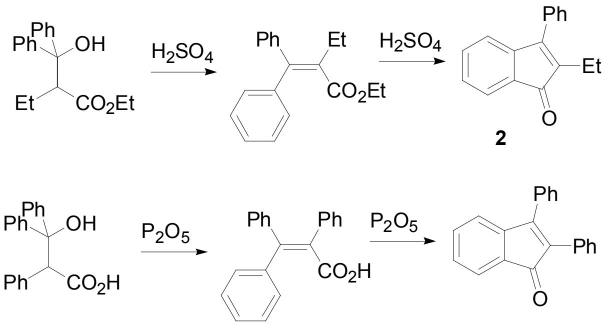
Remo de Fazi was born in Montefiascone at 1891 and obtained the degree in chemistry at 1914. At 1928 he was full professor in pharmaceutical chemistry at the University of Messina. The, three years later, he obtained the chair at the University of Pisa, where he remained until 1961. He died in 1979. De Fazi performed the task assigned him by Paternò and describes all the products isolated in the reaction between butyric acid and benzophenone.[28] In this article de Fazi isolated and identified, beyond propyl butyrate, the main product of the reaction (Scheme 9). The product resulted from the same type of the observed reactivity in phenylacetic acid: in this case, the stabilized benzylic radical could not be formed and the reaction occurred at the adjacent carbon.



Scheme 9

Some years later de Fazi ri-examined the reaction of phenylacetic acid with benzophenone showing that, also in this case, little amounts of benzyl phenylacetate can be obtained.[29]

De Fazi had centered his studied von the esters of phenyllactic acids, of the same type of those obtained by Paternò. In some articles of 1915 he observed that ethyl, α-ethyl-β,β-diphenyllactate could be obtained through a reaction between ethyl 2-bromobutyrate and benzophenone in the presence of zinc.[30,31] This product in the presence of sulfuric acid gave the corresponding 2-ethyl-3-phenylindone (Scheme 10).

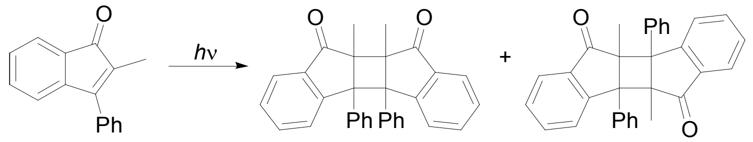


Scheme 10

The same reaction, in this case performed with phosphoric anhydride, was obtained by de Fazi on the product obtained by Paternò in the photochemical reaction between phenylacetic acid and benzophenone (Scheme 10).[31,32]

In a work published on 1921, de Fazi showed that Z-α-methylcinnamic acid gave the corresponding indone if treated with sulfuric acid, while the E-isomer, obtained through UV irradiation, did not be converted into the indone.[33]

After these preliminary studies, starting from a photochemical reaction found by Paternò, de Fazi started to study the photochemical behavior of these indone. He found, in some preliminary notes, that α-methyl-β-phenylindone, irradiated with an UV lamp, gave two dimers; however, he did not was able to discriminate between these two structures (Scheme 11).[34,35]

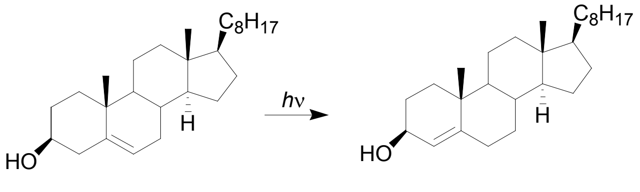


3 **4**

Scheme 11

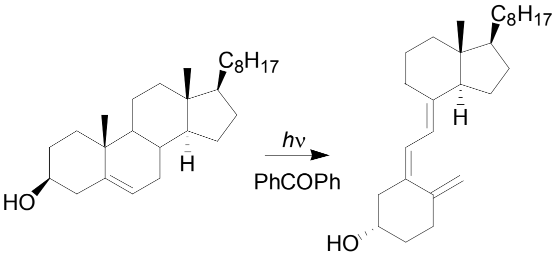
The complete work in this field appeared in the same year. The reaction gave two dimmers in different yields (56 and 8%). The main product was **3** while **4** was the by-product.[36] When the reaction was performed under solar irradiation the main product **2** was obtained in higher yields in the presence of traces of another dimer. On the contrary, the compound **2** did not give dimers.[37] Furthermore, he found that the dimers are not photochemically stable. He found that the dimers obtained by sulfuric acid treatment of the indones (two compounds), after irradiation, can be converted in other two dimer derivatives. On the contrary, irradiation of the dimers obtained through photochemical irradiation of□ -methyl-□phenylindone, gave a retrocycloaddition reaction reforming the indone.[37,38]

Connected with the work on the indones de Fazi started to study the structure of cholesterol, showing that the irradiation of cholesterol under solar light induced the formation of an isomeric product (Scheme 12).[39] de Fazi could not give the structure of the product, but the reaction has been studied several years later.[40]



Scheme 12

In an another communication, coauthor Augusto Banchetti, reported the formation of a dimer in the reaction of cholesterol in the presence of benzophenone, together with dihydrocholesterol.[41] Banchetti continued the study on the photochemistry of ketones. First, he studied the oxidation of some alcohols (related to cholesterol, such trans-β-decalol) in the presence of benzophenone,[42] then the formation of tetraphenylethene oxide in the reaction between benzophenone in isopropyl alcohol in the presence of hydrogen chloride.[43] Finally, he confirmed the formation of 1,1,2,2-tetraphenylethanol in the reaction between diphenylmethane and benzophenone.[44] The most important contribution of Banchetti to the photochemistry was the identificatione of Vitamin D_3 in the reaction of cholesterol and acetylcholesterol in the presence of benzophenone (Scheme 13).[45]



Scheme 13

de Fazi studied also the reaction between acenaphthene and benzaldehyde under solar irradiation. He found that the main products were the polymers of benzaldehyde but he found also the presence of a coupling product, a ketone, deriving from a Paternò-Büchi reaction between acenaphthylene (obtained through reaction between acenaphthene and benzaldehyde) and benzaldehyde, followed by oxetane cleavage.[46]

Furthermore, he found the sterilizing properties of UV irradiation showing that alcoholic fermentation by Saccaromyces Cerevisiae of previously irradiated aqueous solutions of glucose worked better that on control non irradiated solutions.[47]

In the last photochemical note de Fazi defended the results of Paternò in the synthesis of triphenyllactic acid against the work of D. Ivanoff and T. Ivanoff on Comptes Rendus where the authors questioned the idenfication the product.[48]

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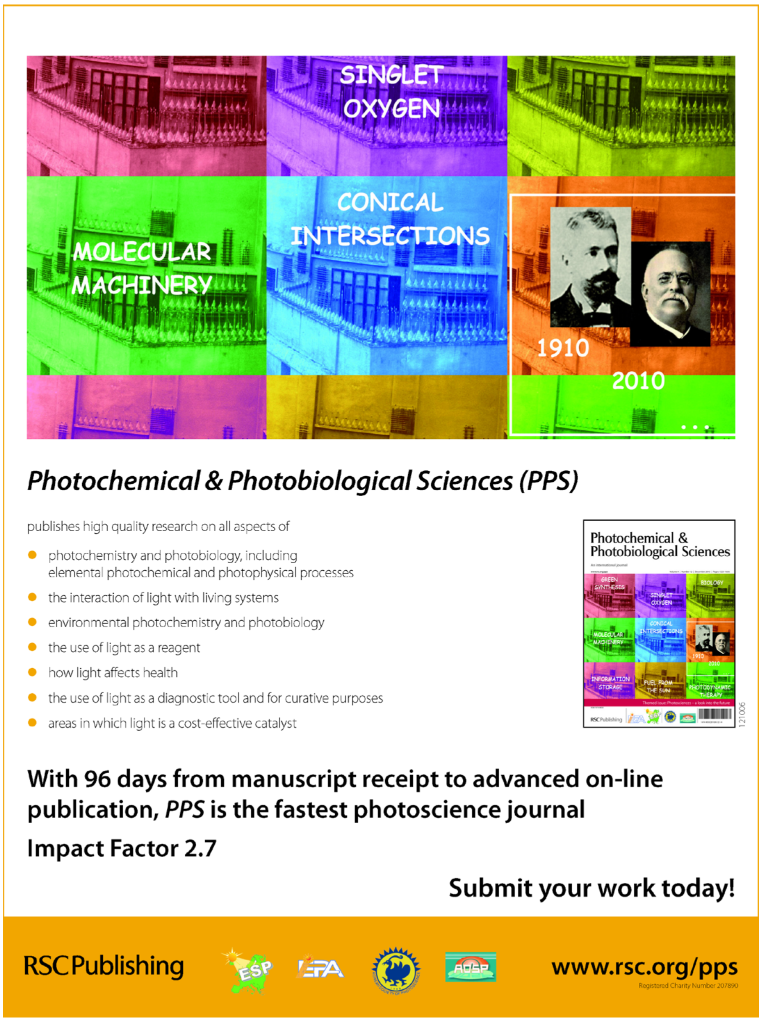

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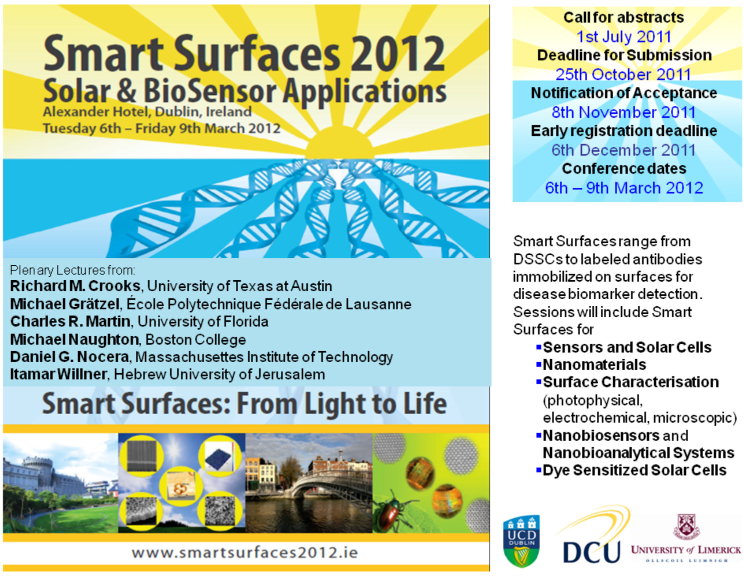

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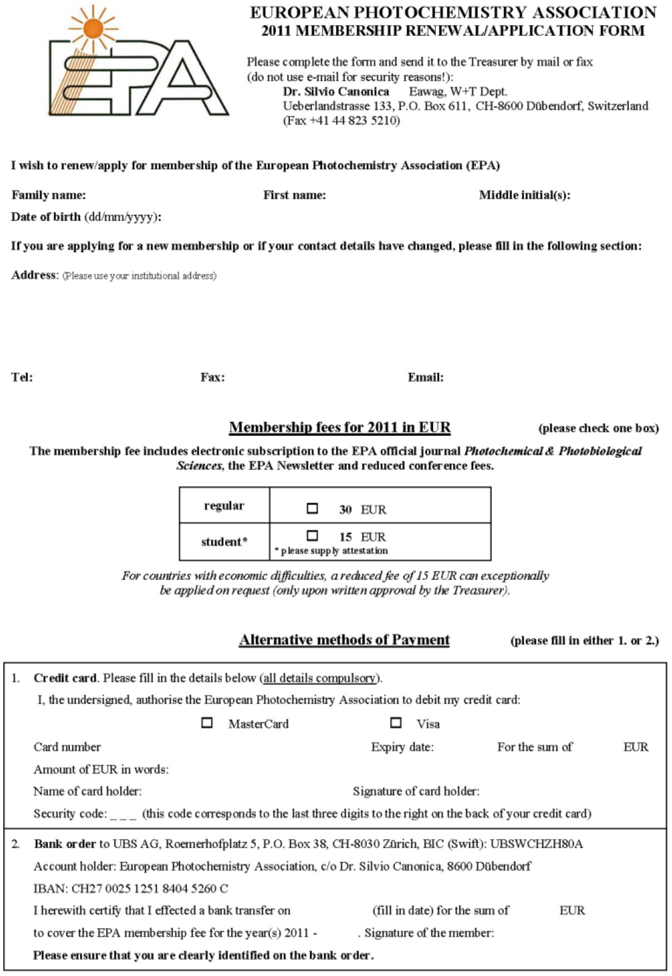

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