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EDITORIAL

President's Letter

Dear Colleagues,

The membership of EPA has been very stable these past years and several actions will be undertaken to recruit new members as well as keeping existing ones. The financial situation of EPA is good and our available financial resources can be used for larger projects, such as the redesign of our website, which is already an on-going project aimed to making it more lively and appealing. Such actions for promoting and maintaining a robust membership will soon be posted on the new webpage.

The visibility obtained via Facebook is quite good, with a recent trend in a faster growth of the number of people who like the EPA page. The posts published are seen by a fair amount of followers, including many non-members. We should continue our efforts on this front. It is expected that the new webpage with interesting and up-to-date content will increase the number and types of posts on Facebook. And it would be good to have external contributors, ideally some students who are willing to share interesting posts.

The EPA will stick with its policy of supporting attendance of EPA members to meetings by offering discounted registration fees whenever possible.

Calls for the nominations for the EPA Prize for the Best PhD Thesis in Photochemistry, during the previous two calendar years, and and the Porter Medal, in cooperation with our Inter-American and Asian/Oceanian photochemistry association counterparts, I-APS and APA, are advertised in this Newsletter and will soon be announced on the new website. The next EPA-PPS Prize for the most highly cited paper published in PPS, during the previous two calendar years, the EPA Prize for the Best PhD Thesis and the Porter Medal will be awarded at the 27th IUPAC International Symposium on Photochemistry in Dublin (8th-13th July 2018).

Finally, I want to comment that Silvia Braslavsky, chairwoman of the IUPAC Sub-Committee on Photochemistry, will pass the chair of the Sub-Committee to the team Axel Griesbeck and Trevor Smith at the General Assembly and Congress of the IUPAC to be held next July in Sao Paulo. She is asking for help from our community to define new projects that the Sub-Committee could undertake. Projects related to state-of-the-art areas, some of them involving photoactive materials, would be of great interest for the photochemistry/photobiology community as reflected in the recently held and up-coming symposia. We encourage EPA members to participate actively by posting their ideas on Facebook.

Our warm thanks to Silvia for her great work in the IUPAC sub-committee.

Julia Pérez-Prieto

PUBLICATIONS

Japanese Photochemistry Association: Past and future.

Hiroshi Miyasaka
President of JPA
Osaka University

The Japanese Photochemistry Association (JPA) celebrated its 40th anniversary in 2016. Although the foundation of the association was 40 years ago, the first domestic symposium on photochemistry with 19 lectures, which was organized by Professors Masao Koizumi, Ikuzo Tanaka and Daijiro Yamamoto, was held in Tokyo in 1960. So as to hold the symposium on photochemistry, research results are to be prepared and common concept on "photochemistry" should be shared among many researchers. In this context, researchers in Japan already realized the photochemistry as a field of science at least several years before the first domestic symposium. In these several decades, many researchers in Japan have been contributing to the developments in photochemistry together with researchers all over the world. In 2016, JPA has some 1100 members, although it was only 370 in 1976. The annual symposium on photochemistry in Japan 2016 was held with some 700 participants, 143 oral lectures (including award and invited lectures) and 317 poster presentations. More than 30 % of these presentations were given in English and many foreigners participating in the symposium contributed to the progress in the research field through the excellent lectures and active discussion. On behalf of JPA, I express my sincere gratitude to international coworkers and senior researchers in Japan who have been contributing to the development of photochemistry in Japan and JPA.

1. **Aim and Activities of JPA**

The aim of the academic societies and associations all over the world may not be so much different from one another. With the aim of the

advancement and development of fundamental and applied research of photochemistry and contribution to the industrial field, JPA has been engaging mainly in three activities; (1) progress in communication, cooperation and exchange of information between the members, (2) training of young researchers including graduate students, and (3) construction of international cooperation systems.

For the activity (1), we have been organizing the annual symposium on photochemistry (once / year) and participating in the organization and joint organization of other small symposia, seminars, and lectures (ca. 20-30 / year). Publication of Japanese journal, Koukagaku (Photochemistry) (3 issues /year) has been continued in these 40 years and since 2000 we have been publishing an international journal, Journal of Photochemistry and Photobiology C: Photochemistry Reviews (IF: 16.091, 2014) with Elsevier (4 issues / year). In the organization and joint organization of seminars, we have been holding a two-day tutorial seminar on photochemistry in these 20 years. This seminar is aimed to educate undergraduate and graduate students just starting the research on photochemistry and to cultivate industrial researchers engaging in R&D relating to photochemistry in their jobs. Every year, more than 60 persons are attending this seminar. In addition, we also organize one seminar on the recent topics relating to photochemistry, such as solar cells, photocatalysis, advanced spectroscopy and so forth. Main attendants of this seminar are researchers in industries.

In addition to the tutorial seminar for the education and cultivation of young researchers, JPA has been awarding excellent oral and poster presentations by graduate students in the domestic annual symposium on photochemistry (8 presentations for oral lectures and 8-10 presentations for the poster papers). Particularly excellent presenters (one or two) receive some special prizes including the one-year subscription right of journals with the cooperation of RSC and Elsevier. JPA also financially supports the three-day seminar of the young researchers and graduate students, which is held in resort areas. All the participants staying in lodges study the lectures of senior famous scientists and discuss their own research results together.

In the research field of photochemistry, active international cooperation and collaboration have been continuing for a long time. Each photochemical association in Europe and American areas (North and South America) has been cooperating with other societies

relating to photochemistry. Also in Asia and Oceania, Asian and Oceanian Photochemistry Association (APA) was founded in 2002 and JPA, as one of the members of APA, has been continuing its cooperation with many countries and regions in these areas as well as European and American countries.

2.   **Photochemistry in future.**

Not only the increase in the number of members in JPA, members of JPA have been contributing to the progress in photochemistry and its related fields, especially in the elucidation of fundamental photochemical processes, new laser photochemistry, developments of new photo-functional materials / molecules and so forth. Research works of Porter Medal winners, Professors Kenichi Honda, Noboru Mataga, Hiroshi Masuhara and Masahiro Irie, are prominent examples representing photochemistry in Japan. In many developed countries in these days, however, it is not so easy to prepare sufficient budget for basic research owing to the recent deterioration of the fiscal situation of the government. In Japan, we have the same situation and the reduction of the fundamental research expenses in many universities is a serious problem, while a large amount of budget concentrates on specific research subjects that are quite urgent issues to solve. Under the circumstances where public research funds are limited, it might be inevitable to select and focus research subjects. We know, however, that basic fundamental research sometimes yields unexpected result that will grow into large and important subjects. I think it is an imperative mission of JPA to keep the diversity of the research and to provide an important platform cultivating the central research subjects in the next generation.

Under such recent situations in developed countries, international collaboration is an effective method in research projects where a sufficient budget cannot be obtained in one country. The budget for constructing international collaborative research system has been recently launched in Japanese research funds (JSPS Programs). As written above, the research field of photochemistry has long been keeping an active international relationship. Photochemistry in Europe has longer history and much more achievements than those in Japan. Both European countries and Japan have shared similar problems as developed countries. Although there are problems that

must be solved individually, I hope that research exchange and collaboration between Japan and Europe will be further developed for the future development of the field of photochemistry.

Integrated continuous-flow photooxygenation processes with solid-supported sensitizers for the safe and sustainable production of fine chemicals and pharmaceuticals (PICPOSS)

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What is PICPOSS? – PICPOSS is a multidisciplinary and multi-institutional research project on "integrated continuous-flow photo-oxygenation processes with solid-supported sensitizers for the safe and sustainable production of fine chemicals and pharmaceuticals" (**P**rocédé **I**ntensifié **C**ontinu de **P**hoto-**O**xygénation avec **S**ensiblisateur **S**upporté pour une production durable et sure de

molécules d'intérêt pour la chimie fine et l'industrie pharmaceutique) funded by the French Research Agency ANR (ANR-15-CE07-0008-01) under its Collaborative Research Project (projet de recherche collaborative, PRC) program. The project has a total value of 503k€, started in March 2016 and will run for 42 months. It involves funded positions for one PhD student (36 months) and two post-doctoral researchers (18 and 24 months).

The PICPOSS consortium – PICPOSS consists of five partner organizations, four from France and one from Australia.

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This multidisciplinary team brings together different fields of expertise, in particular on photochemical reactor engineering &

process intensification, mechanistic & preparative photochemistry, solid-supported sensitizer development, organic chemistry and continuous-flow photochemistry & reactor development. The broad and complementary expertise of the PICPOSS team will help to identify photochemical reaction and process limitations as soon as they arise, and to develop strategies to overcome these.

Research context and background – To face the growing challenges of industrial sustainability, new production technologies must be urgently developed. As part of the more general concept of "green engineering", process intensification combines a set of tools and methods that implement Green Chemistry principles into manufacturing processes.[1]   Due to their resource- and energy-intensive natures, Fine Chemical and Pharmaceutical industries are especially concerned of these engineering and research needs.[2]

Organic photochemistry has the potential to emerge as a key synthesis pathway and technology for sustainable chemical production.[3]   Selective transformations with high chemical and quantum yields can be typically accomplished, in many cases without any chemical activation. The ability to achieve molecular complexity and diversity with a "flick of a switch" makes photochemistry essential for the synthesis of biologically active compounds in medicine or agriculture. It also plays a crucial role in many other chemical fields including material and environmental sciences.

Among the large portfolio of photochemical transformations, **sensitized photooxygenations** involving singlet oxygen ($^1O_2$) are particularly attractive and have been applied to the oxygenation of terpenes such as alpha-pinene, citronellol or furfural, and more recently to the industrial synthesis of the antimalarial drug artemisinin. These transformations enable the incorporation of molecular oxygen under mild conditions.[4] Despite this advantage, photooxygenations have not found widespread implementations in the chemical industry. This reluctance is mainly due to the currently available technologies and procedures, which (i) require outdated batch reactors (often operating in a circulating loop and with high dilutions, requiring intensive cooling) equipped with energy-demanding mercury lamps (having limited lifetimes and high

replacement costs), (ii) implement soluble sensitizers (that need to be removed by resource-intensive purifications) and (iii) commonly utilize non eco-friendly solvents (that are transparent and chemical inert but hazardous).

Continuous micro-structured technologies play a key part in the process intensification strategy. Their advantages for preparative photochemistry have been recently highlighted on lab-scales, however, flow photochemical studies in industry are still rare.[5] The combination of continuous microstructured technologies with energy- and cost-efficient **LEDs light sources** represents a promising alternative for industrial implementation of photooxygenations under greener, safer and atom- and energy-efficient conditions.

Figure 1. Continuous-flow spiral-shaped microphotoreactor for gas-liquid photooxygenations (LGC, Toulouse).

Objectives and research goals – Ultimately, PICPOSS seeks to develop a continuous flow process for the sustainable production of fine chemicals and pharmaceuticals through sensitized photo-oxygenations. The specific research aims are:

- to **use LED-driven continuous-flow microreactors** as an energy-efficient and safe technology that increases yields and selectivity of industrially relevant sensitized photooxygenations due to the control of key operating parameters,[6]
- to **implement solid-supported photosensitizers** as a strategy to reduce or circumvent downstream separation processes, and also as an advanced photochemical synthesis concept,[7] and
- to establish a **methodology for smart scale-up** and to realize an **proof-of-concept on large demonstration-scales**.[8]

The breakthroughs developed will overcome safety and cost concerns of currently available technologies (batch reactors, energy-demanding mercury lamps, toxic solvents) and will thus open new opportunities for the industrial synthesis of valuable fine chemicals via sensitized photooxygenation. PICPOSS will focus on two benchmark reactions of industrial relevance: the photooxygenation of alpha-terpinene, a common essential oil component, and of furfural obtained from hemicelluloses contacting waste from agriculture. The anthelmintic drug ascaridole and the valuable synthesis intermediate 5-hydroxyfuran-2[5H]-one are obtained from these transformations. It is envisaged that the protocols developed by PICPOSS can be transferred to other photooxygenation reactions.

Scientific program – PICPOSS involves four scientific tasks, supported by an additional coordination and management stream.

Task 1 aims to study benchmark photooxygenations in batch reactors. Eco-friendly solvents will be studied and various sensitizers investigated (commercially available, advanced sensitizers synthesized in **Task 3**). Side reactions (including sensitizer decomposition) will be determined, and analytical conditions for an easy reaction monitoring in continuous-flow microreactors will be established.

Task 2 is devoted to the transfer of the benchmark photooxygenations to continuous-flow reactors using solubilized photosensitizers. It also includes the characterization of gas-liquid mass transfer in these microstructured reactors and the determination of the incident photon flux by actinometry.[9]

Task 3 concerns the preparation and characterization of various new sensitizing materials. Commercial and advanced lab-made sensitizers will be firstly immobilized on commercial silica/polymer beads. Subsequently, sensitizing colloids systems (polymer particles, microgels) will be synthetized as they offer higher surface areas

and/or enable core-functionalization. These materials will be fully characterized and their stability, photobleaching, turnover frequency and quantum yields for singlet oxygen production evaluated. The most efficient and stable sensitizing materials will be tested in batch reactors (**Task 1**) for their subsequent implementation in micro-reactors.

In **Task 4**, photooxygenations will be carried out in continuous-flow microreactors using solid sensitizing materials. For each reaction, a screening of operating conditions will be performed to define an operating domain and to maximize the reactions' outputs. Experiments will also be conducted in meso-scale flow-equipment to demonstrate the proof-of-concept for scale-up. Finally, the performances of the different batch and microreactors will be compared for each of the chosen sensitizing material. Likewise, the effectiveness of the advanced solid-supported sensitizers will be demonstrated by comparison with their solubilized counterparts. Combining experiments and modelling tools, guidelines will be established to assess the feasibility of flow photochemistry with sensitizing materials, and to address smart scale-up issues.

Conclusion – PICPOSS is a multidisciplinary research project that will develop novel processes, technologies and protocols for industrially relevant photooxygenation reactions under continuous-flow conditions using advanced, photosensitizing materials. The results obtained by PICPOSS will be of significant relevance to the fine-chemical (e.g. fragrance & flavour) and pharmaceutical industries.

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Carrier Recombination Losses in Organic Solar Cells

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Carrier losses in solar cells are due to either radiative recombination or non-radiative recombination processes. Our group has been studying the interfacial carrier recombination losses in different type of molecular solar cells including DSSC (Dye Sensitised Solar Cells)[1], OSC (Organic Solar Cells)[2] and PSC (Perovskite Solar Cells)[3]. Among the different techniques used to study carrier losses in solar cells we have specialised in photo-induced transient techniques (Figure 1).
For instance: Laser Transient Absorption Spectroscopy (L-TAS),
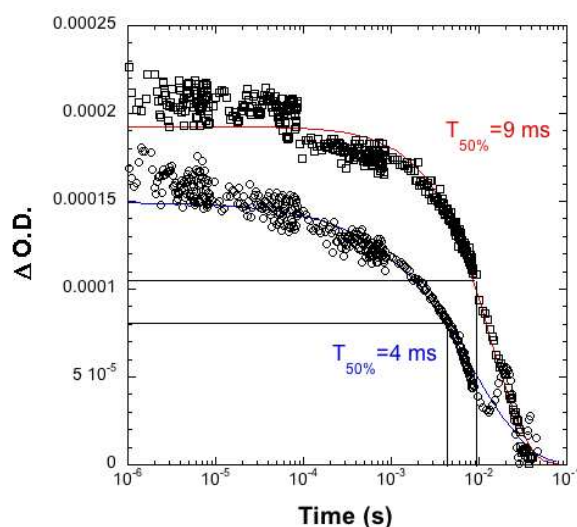
Figure 1. The L-TAS recombination decays of organic sensitizers anchored to 4μm thick mesoporous TiO_2 upon excitation at 535nm and monitoring at 800nm. The graph also shows the interfacial recombination half-lifetime for each sensitizer in milliseconds.

Transient Photo-Voltage (TPV) and Charge Extraction[4].

In all the cases, our intention is to study the carrier losses under illumination environments that reproduce the solar cells working conditions (namely 1sun illumination).

In order to compare different devices it is key to measure the charge density at the device at each light bias (device voltage due to the light irradiation intensity). Devices with similar carrier lifetime may well have different charge density at a given light intensity and, as carrier density is directly related to carrier lifetime we may be getting the wrong information. Figure 2 shows an example of different solar cells measured under light irradiation that apparently have similar carrier lifetime when compared versus voltage but the picture changes when plotted using their charge density at the same light bias.

Minimising the non-radiative interfacial carrier recombination losses is paramount to increase the solar cells efficiency. Thus, techniques such as TPV and CE are helpful and valuable tools to quickly record data and compare changes made to the components of the solar cells and get a direct relationship between changes in carrier recombination versus charges at the solar cells.
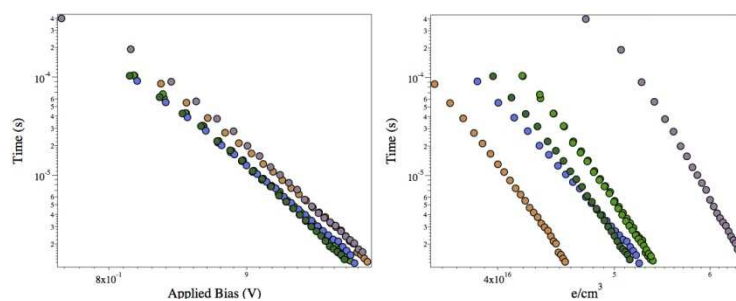

Figure 2. On the left, the carriers lifetime measured using TPV versus voltage (applied bias) and, on the right, versus charge density measured using CE. Notice the difference when comparing versus bias or versus charge density.

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PORTER MEDAL

The Porter Medal 2018 – Call for Nominations

The Porter Medal is awarded every two years to the scientist who, in the opinion of the European Photochemistry Association, the Inter-American Photochemistry Society, and the Asian and Oceanian Photochemistry Association, has contributed most to the subject of Photochemistry. The Porter Medal, named for the late George Porter FRS, Nobel Laureate, is awarded biannually to the scientist who in the opinion of the judges, has contributed most to the science of photochemistry with particular emphasis on more physical aspects, reflecting George Porter's own interests.

To nominate European candidates for The Porter Medal 2018, candidate's details should preferably be sent directly to the President of the European Photochemistry Association, Professor Julia Pérez-Prieto (julia.perez@uv.es). For nomination of candidates from other continents, see the Porter Medal webpage: http://www.portermedal.com. Nominations may also be sent to the Chair of the Porter Medal Committee, Professor David Klug. The nomination package should include:

• Curriculum Vitae of the candidate

• A list of publications

• A citation for the award, not exceeding five pages

• Two letters of reference

Provisional closing date for the receipt of nominations (based on the guidelines from previous years) will be 31 January 2018.

Previous winners:
1988   Lord Porter (George Porter), UK (Founding medal)
1990   Michael Kasha, USA
1992   Kinichi Honda, Japan

1994   Nicholas J.Turro, USA

1995   J.C."Tito" Scaiano, Canada (Special Medal for London ICP)

1996   Noboru Mataga, Japan

1998   Frans de Schryver, Belgium

2000   Vincenzo Balzani, Italy

2002   Josef Michl, USA

2004   Graham R.Fleming, USA

2006   Howard E. Zimmerman, USA

        Hiroshi Masuhara, Japan

2008   Michael R. Wasielewski, USA

2010   David Philips, UK

2012   Thomas J. Meyer, USA

2014   Masahiro Irie, Japan

2016   Jim Barber

EPA PRIZE

EPA Prize for Best PhD Thesis in Photochemistry
Call for Nominations

The EPA Prize for the best PhD thesis in photochemistry will be attributed during the 27th IUPAC International Symposium on Photochemistry in Dublin (8th-13th July 2018). The awardee will present his/her work at the Symposium. The Prize is 1000 Euros, plus travel costs to Dublin (within the limit of 300 €) and one free year of EPA membership. The candidate must have defended his/her PhD thesis in 2016/2017 and be nominated by an EPA member. Nominations should be sent (electronically only) to Julia Pérez-Prieto (julia.perez@uv.es). The nomination package should include:

• Curriculum Vitae of the candidate

• Copy of the thesis

• Abstract of thesis in English, no more than five pages

• List of publications arising from the thesis

• A letter of support.

Closing date for the receipt of nominations will be 31 December 2017.

Previous winners:
2008 Maria Abrahamsson (thesis supervisor: Leif Hammarström), Sweden, Alexandre Fürstenberg (thesis supervisior: Eric Vauthey), Switzerland
2010 Anne Kotiaho (thesis supervisior: Helge Lemmetyinen), Finland
2012 Karl Börjesson (thesis supervisior: Bo Albinsson), Sweden
2014 Giuseppina La Ganga (thesis supervisor: Sebastiano Campagna), Italy

2016 Tomáš Slanina (thesis supervisors: Petr Klán, Burkhard König), Czech Republic.

SPECIAL REPORTS ON LIGHT AND MOLECULAR INFORMATION PROCESSING

This Thematic Issue summarizes the efforts of various research groups that are dedicated to the use of light in order to stimulate and/or read the response of molecular and supramolecular entities. The broad common objective of the herein collected contributions is the use of these systems as platforms for information processing. In this detailed context light is a very attractive stimulus, allowing the devices to be addressed with spatiotemporal control. Further, fluorescence as output signal is highly versatile and intuitively implemented in the research programs of many laboratories.

The bandwidth of systems that are discussed in this Thematic Issue include semiconductor materials and the harnessing of photoelectrochemical effects (Prof. Szaciłowski, AGH University of Science and Technology, Cracow), fluorophore-receptor architectures with the characteristics of Pourbaix sensors (Prof. Magri, University of Malta) or for the implementation of molecular computational identification and edge detection (Prof. de Silva, Queen's University of Belfast), and the use of photoswitchable systems in the context of molecular machines and materials (Profs. Baroncini, Credi, and Silvi, CLAN, University of Bologna/CNR), Fuzzy logic (Prof. Gentili, University of Perugia), stimuli-responsive DNA architectures (Prof. Andréasson, Chalmers University of Technology, Gothenburg and Prof. Choi, Purdue University) or host-guest chemistry (Prof. Pischel, University of Huelva). The contributed examples from all over Europe are meant to illustrate the attractive role that photochemistry enjoys in the field of molecular information processing.

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Processing Light Signals by Molecular and Supramolecular Devices, Machines and Materials

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Research in the past two decades has shown that chemical substrates can operate as input/output devices and are capable of handling chemical, electrical and optical signals.[1,2] The conversion of the input(s) into the output(s) by the substrates, which include molecules, supramolecular systems, nanostructured and bulk materials, can give rise to functions spanning from chemosensing to smart drug delivery and mechanical actuation. Among the possible types of signals that can be processed by chemical substrates, light is certainly very attractive because it can be used both to write and read the system, it can be finely tuned in energy, time and space domains, and it is a potentially clean stimulus.[3]

Our group has been active in the area of photochemical (supra)molecular devices for several years, in particular for the investigation of light-activated logic gates and molecular machines.[1] For example, this research has led to the development of a molecule-based XOR gate,[4] plug/socket[5] and extension cable systems,[6] multiplexer/demultiplexer,[7] memories,[8] and molecular machines driven by photoinduced isomerization[9] or electron-[10] and proton-transfer[11] processes. Since May 2017 our activities are carried out at the recently founded Center for Light Activated Nanostructures (CLAN), a joint laboratory of the Università di Bologna and Consiglio Nazionale delle Ricerche whose mission is to perform frontier research on photochemical nanosciences.

In this context, we recently reported the realization of autonomous light-driven supramolecular pumps[12] and photoswitching of crystallinity and porosity in molecular crystals based on rigid star-shaped molecules.[13] Both systems exploit the appealing photochromic properties of azobenzene.
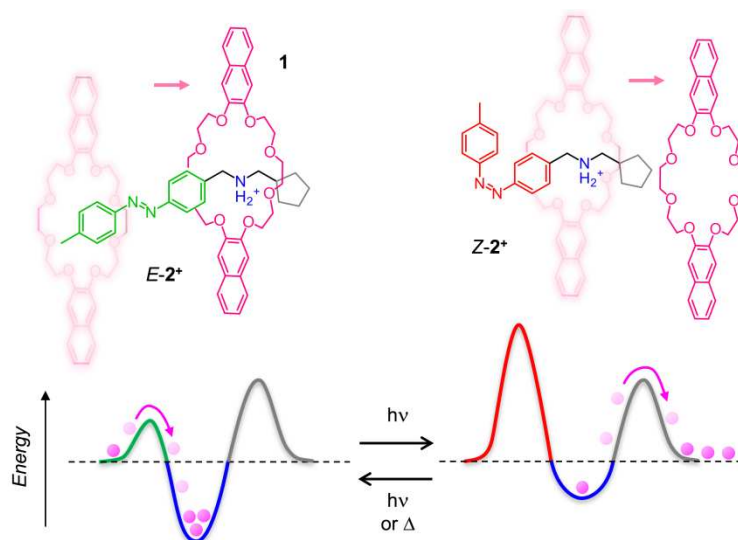
Figure 1. Structure formulae of the molecular components of the light-driven molecular pump with a schematic representation of the relative unidirectional translations of the ring and axle components (top), and simplified potential energy curves (free energy versus ring–axle distance), illustrating how periodic modulation of the energy barriers and wells can produce directional and repetitive threading–dethreading movements (bottom).

The first system (Fig. 1) is composed of the macrocyclic ring **1** and the molecular axle **2**$^+$, comprising a photoswitchable E-azobenzene unit and a methylcyclopentyl pesudo-stopper at the two extremities, and a central ammonium recognition site for the ring. The ring threads the axle exclusively from its E-azobenzene side for kinetic reasons, affording a pseudorotaxane; light irradiation converts the E-azobenzene into the bulkier Z form, simultaneously increasing the kinetic barrier and decreasing the stability of the complex. Considering that the dethreading is faster on the methylcyclopentyl unit than on the Z-azobenzene one, and that the $Z{\to}E$ transformation is also photoinduced, overall the axle transits *unidirectionally* and *autonomously* through the macrocycle according to a flashing energy ratchet mechanism, in which a single light stimulus controls both the relative stabilities of the assembled/disassembled

states (switching) and the relative kinetic barriers for threading/dethreading (gating). In 2016 the European Research Council has awarded an Advanced Grant to Alberto Credi for improving these light-activated supramolecular pumps and investigating their coupling with the environment to perform photoinduced transport and actuation functions.

In view of potential applications of azobenzenes for information storage, optoelectronic devices, memories and responsive materials, we have recently developed[13] molecular crystals based on star-shaped azobenzene tetramers **3** (Fig. 2). Owing to their rigid shape, the molecules afford extrisincally porous crystals in which the $E{\rightarrow}Z$ photoisomerization is allowed. The all-E crystals adsorb CO_2 from the gas phase selectively with respect to N_2, whereas the irradiated Z-form becomes amorphous and it is no longer porous. The porous all-E crystals can be fully restored by thermal annealing.
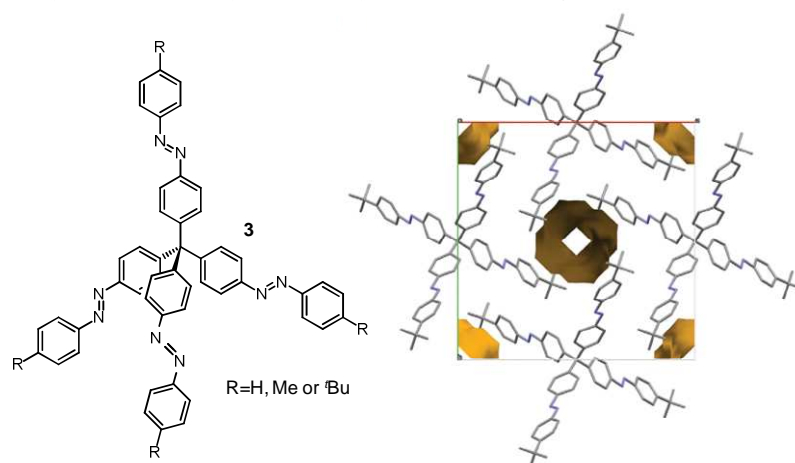
Figure 2. Molecular formula of the azobenzene tetramers **3** (left) and relative arrangement of molecular piles in the solid state with empty channels extending along the direction of the c-axis (right).

While pursuing the goal of creating modular light-driven nanodevices, we became interested in semiconductor quantum dots, as they are photophysically valuable nano-objects whose surface can be decorated with functional molecules.[14] We have exploited this approach to construct a ratiometric luminescent oxygen sensor[15] and,

very recently, to modulate the luminescence properties of the nanoparticle.[16]

The examples briefly discussed here provide a taste of the diverse properties and functions that can be obtained from the combination of light stimuli with (supra)molecular species and nanostructured materials. The development of nanoscale devices, machines and materials is indeed a playground where photochemists can exercise their skills and ingenuity.

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Learning Lessons in Logic with Light

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Light is a most direct way of communicating with 'ghostly' molecules. Exciting light can be chosen to be absorbed by molecules and their fluorescence will be absorbed by our retinas and be visualized in our brains. Our early work with fluorescent molecular sensors, involving a competition between fluorescence and photoinduced electron transfer (PET), demonstrated aspects of this idea.[1] Such gathering of chemical information from a molecule's neighbourhood with 'off-on' fluorescent sensors (important though it was) turned out to be a small part of a much larger idea, that of molecular information processing.[2-7]

The first experimental demonstration[8] of molecular information processing extended the 'off-on' fluorescent sensor design by equipping it to respond to two chemical species in a Boolean[9] AND logical fashion.[10] Rather than 'simply' gathering information, then it becomes possible to process the gathered information on-board the molecule according to various pre-set algorithms before releasing the result as an output to a waiting observer. Such operations can provide a simplified diagnosis of health status of a population in certain instances, so that medical professionals can attend to only those individuals who are flagged up.[11-13]

These 'lab-on-a-molecule' systems can relieve over-loaded health services.

Figure 1. Physical electronic representation of H^+-driven (YES + PASS 1) logic with fluorescence output, which represents one of the kinds of multi-valued logic tags useful for molecular computational identification.

Molecular logic-based computation can also allow the identification of individual microscopic objects in a large population. Current semiconductor devices[14] find this a challenge too far, because antennas limit the downsizing of wireless chips. Fluorescent molecular logic tags (available in several colours)[15,16] are nanometric in size. Besides Boolean logic tags, multi-valued logic[15,16] (Fig. 1) can also be co-opted to extend the applicability of such molecular computational identification (MCID). The size advantage held by molecular logic gates[17] is permitting progress at a new frontier with vital consequences – intracellular computation.[18-25]

Even human-level information processing – things we do everyday – are not immune to emulation by logically-empowered small molecules. We constantly evaluate the threat level of approaching objects as soon as we see them. This is done in our retinas by taking the outlines of the imaged objects. Then our brains take over to compare the outlines with those which are stored in order to determine which are safe and which are not.[17] Similar edge-detection algorithms are available in smartphones these days. Remarkably, a paper soaked in a weakly-buffered solution containing a photo-acid generator and an 'off-on' fluorescent sensor visualizes edges of objects with a resolution of 1-2 mm when it is dried carefully (Fig. 2).[26-28] The image is written with 254 nm light and read with 366 nm light, both of which are commonly available in laboratory ultraviolet lamps.

Object   Image
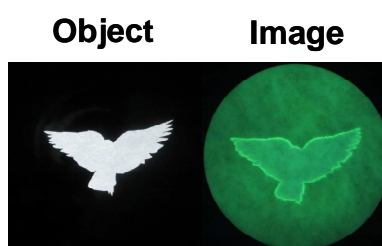
Figure 2. The edges of a binary object are visualized as bright green fluorescent lines on a paper treated with a molecular logic system.

The sketches above show that photochemical principles and techniques can be usefully applied to molecular systems designed with an awareness of Boolean principles, in order to tackle various

problem areas. Generally, many chemical/biochemical reactions, interactions and processes can be classified within a Boolean logical framework.[2] Multi-valued logical concepts carry such organization even further so that even more lessons in logic can be learned by molecular scientists. However when fluorescence switching is involved, seeing is believing.

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Fluorescent Molecular Logic Gates for pE and pH

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From the cross-fertilization of fluorescent pH indicators with fluorescent redox switches we have established a new class of molecular information processing molecules known as 'Pourbaix sensors'.[1] The origin of the name stems from the late electrochemist, Marcel Pourbaix, who provided an understanding of the relationship between the redox potential (pE) and proton concentration (pH) of metal ion species in aqueous solution.[2] The universally renown potential-pH diagrams specify the thermodynamic and boundary conditions when an element will dissolve, precipitate, corrode or be immune to corrosion by passivation of an oxide layer.

The molecular engineering of fluorescent pE-pH logic gates is based on the concept of modularity. Modularity allows for the interconnection of several elementary units to build more elaborate molecules with useful functions. Considering that the 2016 Nobel Prize for Chemistry was awarded to Stoddart, Sauvage and Feringa for the "design and synthesis of molecular machines", it is worth
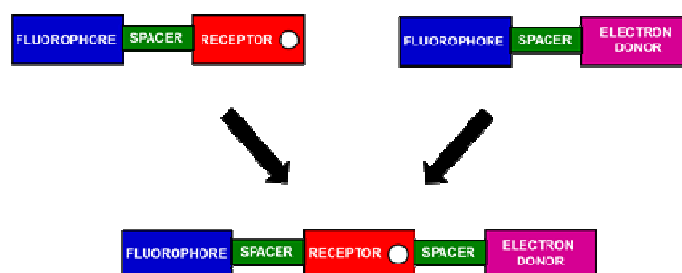
Figure 1. A schematic illustrating the inception of the first 'Pourbaix sensor' from the cross-fertilization of design concepts from pH fluorescent indicators 'fluorophore–spacer–receptor' and pE fluorescent indicators 'fluorophore–spacer–electron-donor'. Reproduced with permission from Francis & Taylor.[3]

noting that an early example of a molecular shuttle by Stoddart switched by two different stimuli, namely protons and electric potential inputs.[4] The dynamics of the rotaxane were studied by UV-visible absorption and NMR spectroscopy. Tian has developed this idea further by engineering pE-pH rotaxanes with a fluorescence output.[5]

Fig. 1 shows the design concept for fluorescent pH indicators and pE indicators, and the resulting amalgamation of the two formats to create the first 'Pourbaix sensor' prototypes.[1] Both of these classic single-input chemosensor formats consist of three modules. In the case of pH indicators, the modules are a fluorophore, a spacer and a receptor connected in a 'fluorophore–spacer–receptor' arrangement. The chemical literature is rich with numerous examples of chemosensors (i.e. pH, cation, anions, biomolecules etc.) and more advanced variations of multi-input molecular logic gates.[6] In the case of pE indicators, the modules are a fluorophore, a spacer and an electron donor (redox unit) connected in a 'fluorophore–spacer–electron-donor format. The development of fluorescent redox indicators, by comparison, provides ample opportunity for development.[7]

The working principles of fluorescent pH sensors and redox sensors are based on a competition between photoinduced electron transfer (PET) and fluorescence. In digital terms, either the fluorescence will be 'off' or 'on'. In the 'off' state, PET from the receptor (or electron donor) to the excited-state fluorophore quenches the fluorescence. In the 'on' state, fluorescence is observed. Binding of the analyte to the receptor, most often, results in coordination of an electron lone pair with the analyte, which prevents PET. However, when the target species is treated as an oxidant (or reductant) rather than an analyte, there is no binding. Instead in the simplest ideal case, the electron donor losses (or gains) an electron, and becomes a radical cation (or anion), which is lower in energy due to the absence of charge repulsion from only one electron in the HOMO level of the electron donor.

Our earliest prototypes incorporated anthracene as the fluorophore,[1,8] while our most recent examples incorporate naphthalimide.[9,10] The latter are advantageously hydrophilic and emit fluorescence in the visible region compared to the former, which are

naturally hydrophobic and emit blue fluorescence. The 4-aminonaphthalimide fluorophore has allowed us to further develop pE-pH logic gates incorporating PET and internal charge transfer (ICT) mechanisms. In collaboration with Nathan McClenaghan at the University of Bordeaux, we have elucidated that in the 'on' state the singlet fluorescence lifetime is 8.5 ns, and the 'off' state results from PET on a time constant of 20 ps (Fig. 2).[10]

With the concept of 'Pourbaix sensors' now established, we are at a stage where we can contemplate real-life applications.[3] We are excited about the prospect of using these smart molecules in various domains from living cell imaging, corrosion detection, water quality and environmental analysis and medical diagnostics. The future of molecules powered by light with molecular information processing capabilities continues to look bright and promising.
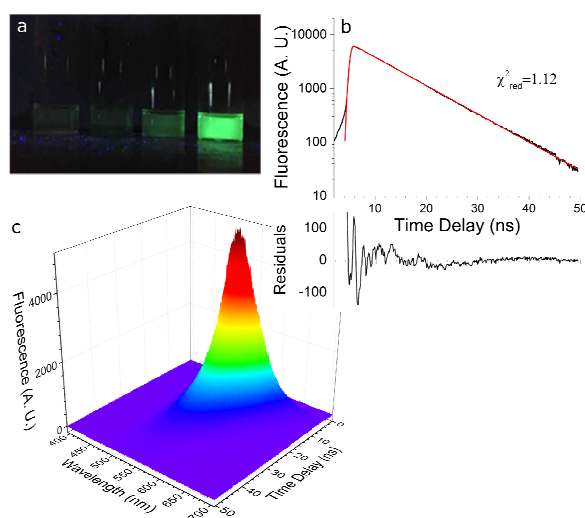
Figure 2. (a) Vials of a 'Pourbaix sensor' in 1:1 (v/v) MeOH/H_2O under the four conditions for AND logic irradiated with a 365 nm lamp (b) fluorescence decay curve and residual time delay (c) 3D plot at pH 4 and 60 μM Fe^{3+}. λ_{ex} = 438 nm. Reproduced with permission from the Royal Society of Chemistry (RSC) for the National de la Recherche Scientific (CNRS).[10]

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Shining Light on Molecules and DNA Origami

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The study of small DNA-binding molecules, and how their action can be triggered by light-exposure, has been motivated mainly by their relevance for chemical biology, e.g., chemotherapeutics. This is due to that the function of many cytotoxins relies on the drug's capacity to bind strongly to DNA, preventing the genetic code from being read and translated. Lately, it has become apparent that the DNA biopolymer can be used not only to store the genetic information, but also for various other applications within materials and nanoscience. Needless to say, DNA origami is a revolutionary method in the precise assembly of 2D and 3D nanostructures, and countless examples of intricate structures have been built by the well-predictable self-assembly approach.[1] In the majority of these examples the origami constructs are used as static templates, e.g., for organizational purposes (decorated with chemical functionalities) or as lithographic masks.

Until very recently, small molecule (non-covalent) DNA-binding to origami structures has found limited use. Non-covalent interactions implies, of course, a loss of the nm-precision labelling offered by the covalent approach. On the other hand, it is much more appealing from the organic chemist's viewpoint, as tedious functionalization of the strands is not required.

In two recent studies, Choi, Andréasson and co-workers demonstrated how UV light and DNA intercalation (a non-covalent interaction) by small molecules can be used to control the conformation of DNA origami in a dynamic and progressive fashion.[2,3] A molecule that intercalates DNA is inserted between the bases. As a result, the DNA double strand experiences not only elongation but also unwinding, implying that the helical twist is being

changed. The helical twist is an important parameter in the design of origami tiles, as the double helices should twist an integer number of turns between the crossover points (the position of the cross links formed by the staple strands) in order for a planar tile to be formed. If not, internal stress is being imposed, resulting in a curved, non-planar tile. The intrinsic helical pitch of natural B-DNA of ~10.5 base pairs (bp) per turn, is typically not optimal for an integer number of turns, resulting in the abovementioned curvature. This is where the DNA intercalating molecules are the key players: at an adequate intercalator density, the abovementioned unwinding results in "pitch compensation", and a planar tile is observed.

This phenomenon was demonstrated by the "stem and flags" origami constructs (Fig. 1).[2] Here, origami shafts consisting of a "stem" equipped with two "flags" were designed so that the conformational changes could be readily visualized using AFM. In the absence of the well-known DNA-intercalator ethidium bromide (EtB), the flags are oriented in the *trans* conformation due to the helical mismatch. It was shown that upon continuous addition of EtBr the conformation of the shafts gradually changed from *trans* to *cis* as a result of the intercalation-induced pitch change.
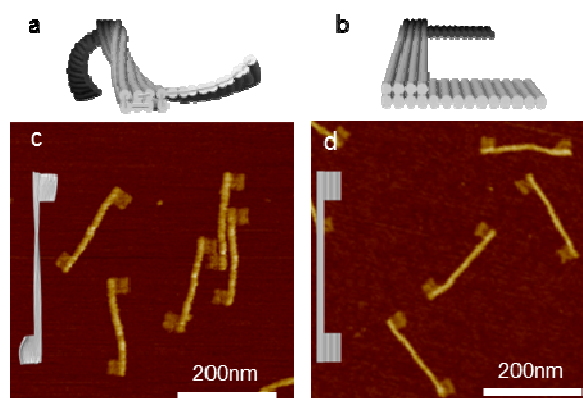
Figure 1. Simulations (a and b) and AFM images (c and d) of the intercalator-induced conformational change of the origami shafts. EtBr concentration = 0 M (a and c), 0.75 μM (b and d).

So, how about the light? Controlling the abovementioned process by an external, waste-free stimulus such as photons would doubtlessly add to the appeal. In a follow-up study by the same authors, it was shown that the same effect could indeed be induced by photonic means. Both as a "direct" and an "indirect" ingredient.[3] It is well-known that (UV) photons absorbed by the DNA bases can induce photochemical changes, e.g., the formation of cyclobutane pyrimidine dimers. Lesions like these were shown to relieve the internal stress in the origami constructs imposed by the pitch mismatch, and result in a planar, or flat, conformation. Depending on the wavelength of the UV light, the respective "flattening doses" were determined, i.e., the UV dose required for the formation of flat origami tiles.

However, there is also a possibility to achieve this without imposing permanent lesions to the DNA. In 2008, Andréasson, Lincoln, and co-workers reported the first example of photocontrolled DNA-binding.[4] The authors demonstrated that a photochromic spiropyran derivative could be converted from a non-binding form (the closed spiro-isomer) to a form that does bind to DNA (the open merocyanine form) using UV-light.[4] Since then, several examples of similar schemes have been reported. One of these is the 1N-pyridyl-2,4,6-triphenyl-pyridinium photoswitch (**1** in Fig. 2).[5] This species does not intercalate into DNA, but it was shown to do so after UV-induced isomerization to the cyclized form **2**. As 366 nm UV photons can be used for this photoinduced reaction, no photons are absorbed by the DNA itself.
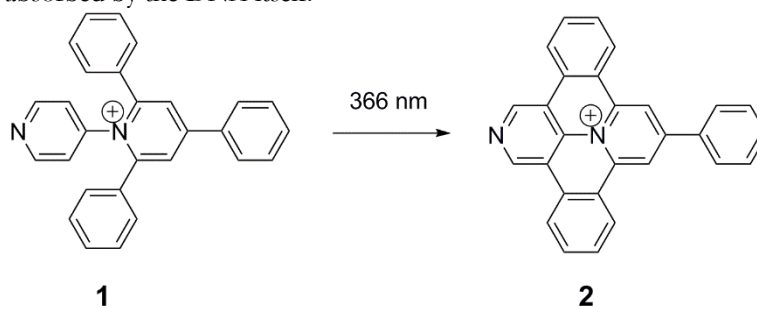
Figure 2. Structure and isomerization scheme of the 1N-pyridyl-2,4,6-triphenyl-pyridinium photoswitch.

Instead, the flattening effect of the origami tiles could be achieved by in situ irradiation of the origami constructs at 366 nm in the presence of **1** that displays intercalation after UV-induced isomerization to **2**.

It is acknowledged that the herein demonstrated "flag twisting" is of limited practical use, but should instead be considered as a proof of principle study. The ability to change the conformation of DNA origami constructs by photonic means could, however, be of high value for actuation and the exposure of molecular payloads (e.g., controlled drug release). Furthermore, the progressive nature of the conformational changes allows for fine-tuning of excited state interactions, such as energy transfer reactions, between any appended chromophores. Thus, the spectral fluorescence pattern from these chromophores would be very sensitive to the origami conformation, implying that fluorescence readout could be used for data storage and information processing much in line with the study of Dwyer and co-workers.[6] This is why we anticipate that our proposed scheme could be very useful for other practitioners in the design and functional characterization of dynamic DNA origami structures of increased complexity and functionality.

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Photocurrent Switching and Information Processing in Nanoparticulate Systems

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Semiconducting nanoparticles offer a versatile platform for various applications. Main applications encompass photovoltaics and photocatalysis. They can be easily prepared in high quantities (and using environmentally - friendly protocols)[1] and their electronic[2,3] and optical properties[4,5] can be tuned via alloying, bulk doping or surface modification. Furthermore, due to very large specific surface area (in the case of small nanoparticles most of the atoms are on the surface) and coordinative unsaturation of surface atoms, semiconductor nanoparticles strongly adsorb molecules on their surfaces.[6] Thus obtained objects combine collective transport properties of solids with structural versatility of molecules.[7,8] Furthermore, mutual interplay between these two components leads to emergent optical and electrical properties.[9] These specific interactions generate novel properties, which can dominate the immanent properties of components, *i.e.* nanoparticles and molecules.

Photoelectrochemical properties are a complex function of the band gap energy, the kinetics of interfacial electron transfer processes, the presence of charge trapping states and interactions of their surfaces with molecular species. Due to small dimension nanoparticles may find application in novel IT platforms which require massively parallel architectures. The best example are the HTM (Hierarchical Temporal Memory) networks, [10, 11] where advanced information processing occurs within large hierarchical network of simple computing nodes. This approach mimics the structure of cerebral cortex, where information is processed in layered circuits (usually six main layers) which undergo characteristic bottom-up, top-down, and horizontal interactions. Such computational approach does not require high numerical efficiency of a single node, but rather large number of simple, interconnected nodes. The other possible niche of

their applicability will be low power disposable devices which do not require high performance, but extremely low fabrication costs (e.g. in next generation RFID tags, remote sensing, etc.).

As classical, silicon-based hardware platforms are limited by technological constrains, one should look for a feasible alternative. One of intensively studied alternatives are molecular logic devices. They can perform complex logic operations at single molecule levels, but on the other hand they present very serious problems associated with addressing and concatenability.[12] While the idea, first presented by Arieh Aviram and Mark Ratner was revolutionary,[13,14] its practical implementation is rather difficult. Single molecules can be addressed using scanning probe microscopes or nanogap electrodes,[15] but construction of more complex single molecule devices is at present virtually impossible, although there are several appealing designs.[16] While the molecule-based information processing systems may not find immediate application in construction of novel computing systems, the offer deep insight into various fundamental processes, including those associated with the essence of life.[17-20] While the single molecule computing is a tempting idea, application of chemically modified semiconducting surfaces is much more feasible and also offers great flexibility as compared with pure semiconductor technologies.

Similar constrains are valid for single nanoparticle devices, however modern lithographic techniques give a possibility of contacting individual nanoparticles or their assemblies at solid substrates. Modification of nanoparticles with non-innocent molecules relaxes the technological constrains of molecular logic devices, both those operating as single molecule level and also those operating in solutions. These hybrid materials serve as an interface between the world of molecules and the world of bulk materials. Nanoparticulate/nonporous semiconductors generate photocurrents capable of controlling classical electronic devices, whereas information processing takes place at the interface between semiconductor and molecule.

Information processing is based on changes. Thus, if everything stays the same, we do not receive a message. The crucial factors that cause some changes in semiconductors and molecules are light, potentials, and/or the binding of atomic/molecular species. One of the most

important characteristics of semiconductors and molecules is their ability to alter after appropriate stimulation. Furthermore, many of these changes are reversible. Light is the most powerful carrier of information, so it is natural that photochemical and photophysical processes are recognised as the most suitable for information processing at the molecular scale. Semiconductors separate electron-hole pairs when illuminated within an appropriate wavelength range. This property is applied widely in photovoltaics, photocatalysis, and general photochemistry. It also allows the use of materials in semiconductor laser technology and optoelectronics, as well as in molecular photochemical industry. In terms of information processing, charge separation within molecularly-modified or unmodified semiconductors is embodied in the photoelectrochemical effect of photocurrent switching (PEPS), which can be applied in the construction of switches, logic gates, and other basic elements used in computing systems.[21]
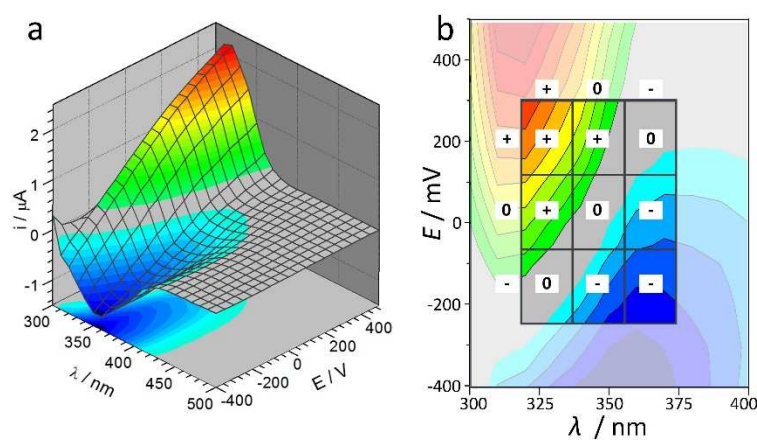
Figure 1. An example of a photocurrent action spectra map (a) and assignment of logic values (ternary in this case) (b). Adapted from Ref. 22.

The PEPS effect has only been observed in several groups of semiconducting materials, where we can distinguish unmodified and surface-modified semiconductors. In the first group, the

photocurrent switching effect has been observed mainly in unmodified oxide semiconductors, such as $Bi_xLa_{1-x}VO_4$ solid solutions (x between 0.23 and 0.93),[23] lead molybdate,[24] and V-VI-VII semiconductors: bismuth oxyiodide,[25,26] bismuth oxynitrate,[27] and antimony sulfoiodide,[28] as well as cadmium sulphide[29,30] and lead sulphide.[31] In unmodified semiconductors, the observation of the switching effect is possible only with sufficiently low potential barrier at the solid-liquid junction, which may be achieved by reducing the grain size of the semiconductor and decreasing the doping level,[32] or when appropriate surface states are present. Much more flexibility is offered by molecular modification of semiconducting surfaces. In this case both incident light wavelength and photoelectrode potential are responsible for photocurrent polarity. This in turn leads to more complex switching patterns which can be utilized for more complex information processing schemes, including binary, ternary and fuzzy logic.
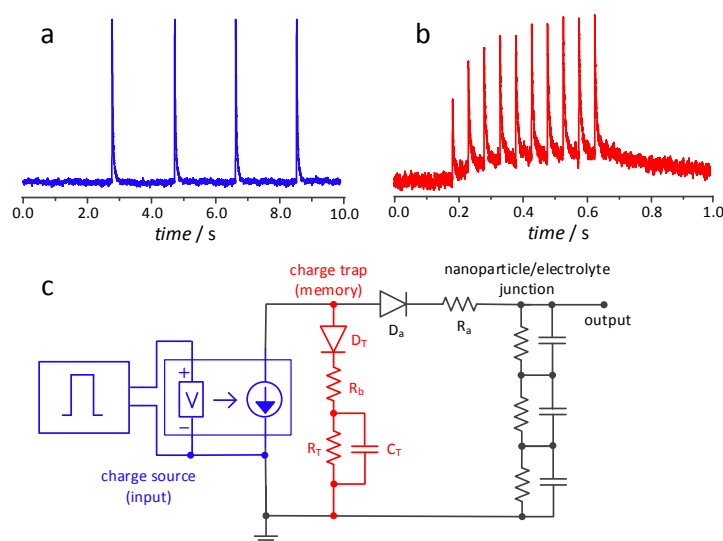
Figure 2. Synaptic behaviour of photoelectrochemical synapse: change in the stimulation frequency modulated the photocurrent intensity (a, b). The device can be described as a circuit consisting of two Schottky diodes and a set of resistor-capacitor loops. Adapted from Ref. 33.

Desired logic functions are assigned according to photocurrent profiles: input and output signal are assigned to appropriate values of incident light wavelength, photoelectrode potential (inputs) and photocurrent intensity (output), as shown in Fig. 1.[22,34] In the case of fuzzy logic system appropriate membership functions are defined and a set of rules is formulated in the second step. Finally, the membership functions and the set of rules are used to recover the original data. In following steps the membership function can be optimized in order to achieve good correlation between the original data and the reconstructed one.[21,35]

Finally, the kinetic features of these processes are crucial as well. The electron donor/acceptor system present in the electrolyte should ensure that the charge is transferred through the semiconductor-liquid junction at a sufficiently rapid speed to avoid recombination events. This is very important for rapid and reliable responses in the case of both crisp and fuzzy logic. Modulation of electron transfer rated and deliberate introduction of trapping states may be utilized in neuromorphic computation and mimicking of synaptic activity in photoelectrochemical systems (Fig. 2).[33]

Photoelectrochemical properties of nanostructured materials has proved to be suitable for various information-related applications. More advanced computing approached, including hardware neural networks, reservoir computing and *in materio* computing are also available.

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A Contribution to the Development of Chemical Artificial Intelligence: The Implementation of Biologically Inspired Photochromic Fuzzy Logic (BIPFUL) Systems that Extend Human Vision to UV

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Science is engaged to face both Natural and Computational Complexity Challenges.[1] To try to win the Complexity Challenges, it is necessary to store and manipulate a huge amount of data. Therefore, there are two main strategies to succeed: one consists in improving current electronic computers; the other is the interdisciplinary research line of Natural Computing. Researchers, contributing to Natural Computing, draw inspiration from nature to propose new algorithms, new materials to compute and new models to interpret Complexity, based on the rationale that every natural transformation is a kind of computation. In our research, we are contributing to Natural Computing by focusing on the human nervous system (HNS) that has human intelligence as its own emergent property. HNS is a complex network of billions of nerve cells. It allows us to handle both accurate and vague information, by computing not only with numbers but also with words. By computing with words, we make decisions in complex situations when there are many intertwined variables involved. Moreover, we recognize quite easily variable patterns. Therefore, to tackle the Complexity Challenges, it is worthwhile trying to deeply understand and mimic the working principles of human intelligence. To emulate the performances of human intelligence, we are using not electronic circuits and software, but chemicals and chemical reactions. In other words, we are developing Chemical Artificial Intelligence.[1] Our methodology grounds on an analysis of HNS at three levels. First, an analysis at the computational level that consists in determining the inputs, the outputs and the computations the system performs. Then, an analysis at the algorithmic level follows. It consists in formulating algorithms that might carry out those computations. Finally, an

analysis at the implementation level starts. It consists in looking for chemical systems that would make the algorithms work.

For example, by analyzing the way humans distinguish colors at the computational and algorithmic levels, we have observed that a good model is Fuzzy logic.[2] Fuzzy logic has been defined as a rigorous logic of vague reasoning. It is based on the theory of Fuzzy sets. A Fuzzy set is different from a classical set because it breaks the law of excluded-middle. In fact, an item may belong to a Fuzzy set and its complement at the same time, and with the same or different degrees of membership. The degree of membership (μ) of an item to a Fuzzy set can be any number included between 0 and 1. The visual sensory system grounds on a "hierarchical Fuzzy architecture". At the bottom level, it has four types of photoreceptor proteins; each one has its own absorption spectrum in the visible. At an upper level, we have four types of photoreceptor cells. Each one contains millions of replicas of one particular photoreceptor protein. At the highest level, we have millions of replicas of the four types of photoreceptor cells spread on a tissue that is the retina located inside our eyes. One type of photoreceptor cell, the so-called rod, is distributed on the periphery of the retina and it works when there is just scattered light. The other three types of cells, the so-called cones, are concentrated in the center of the retina, the fovea, and they allow us to distinguish the colors. The absorption spectra of the three types of photoreceptor proteins within the cones play as three molecular Fuzzy sets and the information regarding the spectral composition of the light stimulus is encoded as degree of membership of the light to the molecular Fuzzy sets ($\bar{\mu}_{ML}$). The three types of photoreceptor cells play as cellular Fuzzy sets and the information regarding the intensity of the light stimulus is encoded as degree of membership of the light stimulus to the cellular Fuzzy sets ($\bar{\mu}_{CL}$). Finally, we have an array of cellular Fuzzy sets on the retina, and the information regarding the spatial distribution of the light stimulus is encoded, at the tissue level ($\bar{\mu}_{TL}$), as degree of membership to the array of the cellular Fuzzy sets. Overall, a matrix of data, reproducing the spatial distribution of the photoreceptor cells on the fovea, represents the codification of the total information of the light stimulus. Each term of the matrix is given by

$$(\bar{\mu}_{ML} \times \bar{\mu}_{CL}) = (\Phi_{PC} I_{0,\lambda}(1 - 10^{-\varepsilon Cl})) \qquad (1)$$

where Φ_{PC} is the photochemical quantum yield for the photo-isomerization of retinal, ε is its absorption coefficient, C its concentration, l is the optical path within the cell, and $I_{0,\lambda}$ is the intensity of the light stimulus at wavelength λ. To corroborate the idea that color vision grounds on a "hierarchical Fuzzy architecture", we have mimicked human color vision by using a collection of direct, thermally reversible, photochromic compounds.[3] Each direct photochromic compound has a spectral profile in the UV, which depends on its molecular structure. Moreover, each photochrome produces a specific color upon UV irradiation, i.e., a specific band in the visible region. By mixing at least two photochromic compounds having appreciably different absorption spectra, it is possible to obtain systems suitable to distinguish the three UV regions (UVA, UVB and UVC) depending on the features of the colors they produce. To prepare such systems five criteria have been followed. First, the absorption bands of the uncolored forms have been conceived as input Fuzzy sets. Second, the absorption bands of the colored forms have been conceived as output Fuzzy sets (see Fig. 1).
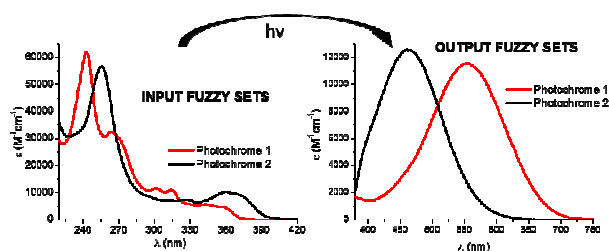
Figure 1. Examples of input and output Fuzzy sets for two photochromes.

Third, equation (2) below, represents the degree of membership of UV radiation with intensity $I_{0,\lambda}$ to the input Fuzzy set for the *i*-th photochrome ($\varepsilon_{UV,i}$ is its absorption coefficient at wavelength λ, and $C_{0,i}$ is its analytical concentration in solution):

$$\left(\mu_{UV,i}\right) = \Phi_{PC,i} I_{0,\lambda}(1 - 10^{-\varepsilon_{Un,i} C_{0,i} l}) \tag{2}$$

Fourth, equation (3) describes the activation of the output Fuzzy set for the i-th photochrome ($\varepsilon_{Co,i}(\lambda_{an})$ is the absorption coefficient of the colored form at the wavelength of analysis λ_{an}, and ($1/k_{\Delta,i}$) is the lifetime of colored species):

$$A_{Co,i} = \frac{\varepsilon_{Co,i}(\lambda_{an})}{k_{\Delta,i}} \mu_{UV,i} \tag{3}$$

Fifth, the equation suitable to predict the color of the solution when we have N photochromic species is:

$$A_{exp} = \sum_{i=1}^{N} A_{Co,i} \tag{4}$$

Equation (4) expresses the sum of the contribution of activated output Fuzzy sets for all the photochromic compounds present into the system. Based on these five criteria, we have found that systems with three or more photochromic compounds are effective in distinguishing the UV regions and their intensities.[4] They have been called Biologically Inspired Photochromic Fuzzy Logic (BIPFUL) systems. One of the best BIPFUL systems is a quaternary solution[3] that becomes green upon UVA, grey upon UVB, and orange upon UVC. All these colors can be predicted by using equations (2) – (4). The same equations are useful to predict the color when the BIPFUL system is irradiated by many UV frequencies.

The analysis of color vision and the implementation of BIPFUL systems prove that the development of Chemical Artificial Intelligence can be useful to tackle the Complexity Challenges. In fact, the study of human intelligence promises to unveil secrets of Natural Complexity and the attempts of mimicking it, by using chemical systems, will boost the development of a new generation of computing machines. These new computing machines will ground on wetware and they will look more like a brain rather than like an electronic computer. These new computational machines promise to be useful for facing the problem of recognizing variable patterns, that is one compelling challenge in the field of Computational Complexity.

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Supramolecular Logic with Cucurbituril Hosts and Fluorescent Guests

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Molecular logic is a rapidly developing field that is nourished by the universality of the concept of logic, the definitions of Boolean algebra, and the creativity of chemists.[1] Indeed, since the very beginning of this field, fluorescence and its control via the manipulation of excited-state mechanisms has attracted photochemists. The first example of a fluorescent molecular logic gate was reported by the de Silva group in 1993.[2] An anthracene fluorophore, equipped with two electron-transfer-active receptors, was used by them. Each receptor quenches the anthracene fluorescence by photoinduced electron transfer (PET) and only when both of them are occupied by the corresponding chemical inputs, these pathways are switched off, leading to a high fluorescence output. If high and low signal intensities (input concentrations, fluorescence) are defined as 1 and 0, respectively, the described situation corresponds to a logic AND gate.

In a recent work our group has been drawing on the use of supramolecular host-guest complexes for the realization of a series of logic operations, including the AND gate.[3] As host macrocycle the water-soluble cucurbit[7]uril (CB7) was employed. The supramolecular binding of guests by cucurbiturils depends markedly on the pH. Through the complexation of a PET-active fluorophore-anchor construct and the concomitant protonation of the anchor it was possible to implement various logic gates. As the involved processes are of supramolecular nature or acid-base reactions, the system can be relatively straightforward reset to its original initial state or reconfigured to any other state. However, there is a risk that with prolonged operation time chemical waste products are accumulated.
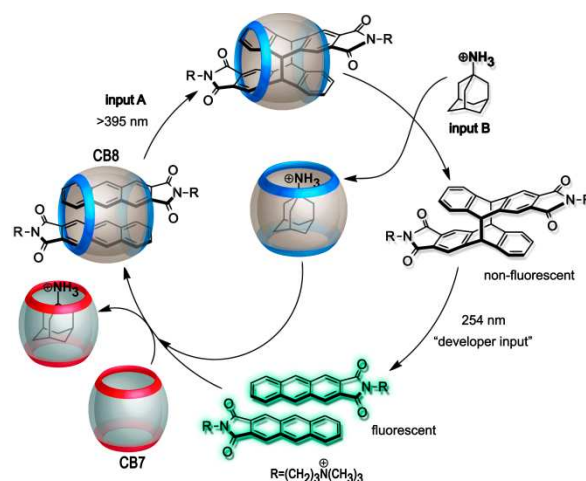
Figure 1. Photodimerization of an anthracene guest within CB8 and use for the realization of a supramolecular keypad lock. Reproduced from Ref. 5 with permission from the Royal Society of Chemistry.

The mentioned drawbacks of employing chemical signals for the implementation of logic operations can be often avoided by harnessing reversible and fatigue resistant photoswitching, relying on optical signals as external stimuli (inputs) and for reading the state of the system (outputs). This has been shown for the all-photonic operation of (multi)photochromic architectures.[4] In the context of applying supramolecular host-guest assemblies for molecular logic we were interested in the possibility of using homoternary cucurbit[8]uril (CB8) complexes in order to achieve the templated bimolecular photodimerization of anthracene guests by means of irradiation with visible light.[5] The underlying [4+4] photocycloaddition is known to be reversible when submitting the dimer to UV light or heat. Combining the guest photoreactivity with competitive displacement by other guests a supramolecular keypad lock can be devised (Fig. 1). In brief, the photodimerization produces only in the CB8 cavity and not in dilute solution. Hence, the chromophoric guest has to be irradiated first (input A) and then the photoproduct can be displaced by an adamantane derivative (input B). Changing the order of input application yields no photoproduct. The formation of free photoproduct is visualized by the generation of the fluorescent

monomers upon cycloreversion with 254-nm light. The whole process can be recycled by using the quality of cucurbiturils in self-sorting processes. In the specific case CB7 was added, which binds input B stronger than CB8 does.

Finally, another aspect of molecular logic that is related with the chemical communication between molecular entities should be mentioned. This is an essential point for the concatenation of logic devices, where the output of one device should trigger the operation of a second device. Supramolecular complexes could constitute an interesting platform that integrate input (complexation) and output (release) processes.[6] Drawing on the known pH-dependence of the binding of protonable guests by cucurbiturils we developed approaches for the release of guests by means of a light-induced pH jump.[7] Alternatively, photochromic processes may be used to generate strong competitors that are able to displace guests from CB7.[8] Effectively, a photoactivatable process is coupled to a host-guest equilibrium, resulting in chemical communication between systems.

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PILLS OF HISTORY

The contribution of Ciamician to the development of organic photochemistry

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The first contribution of Ciamician in the photochemistry is dated 1886. In that period Ciamician worked at Rome under the direction of Cannizzaro. He reported that quinone, irradiated in alcoholic solution, was transformed into hydroquinone.[1] During 1886 Ciamician reported in another communication, the first with P. Silber, that the irradiation of nitrobenzene in ethyl alcohol gave, although in incomplete manner, aniline and acetaldehyde.[2] After these preliminary communications, Ciamician abandoned the photochemistry and he presented a note only in 1901, where the ancient experiments were resumed and expanded. Ciamician renews his previous work on the basis of an erroneous opinion that photochemical transformations can occur in the plants. The reaction of quinone with ethanol is reexamined and extended by using isopropanol, *t*-butanol, glicerin. In the latter case glicerin was oxidized to glycerose.
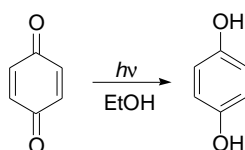
The same reaction occurred by using erythritol, mannitol, dulcitol, and glucose.[3] The reaction worked well by using other quinones, such as thymoquinone, while it did not work with phenanthrenequinone. Quinone reacted also with formic acid, giving hydroquinone and carbon dioxide.[3] In the same article Ciamician studied the

photochemical behaviour of benzophenone that is transformed into benzopinacol.[3] The same reaction was found by using acetophenone, and benzaldehyde.[3] Quinone, benzophenone, acetophenone, and benzaldehyde gave the same type of products observed after the irradiation in an alcohol when the irradiation was performed in ethyl ether.[3] During the same year, 1901, Ciamician published a second note where he reported that the irradiation of *o*-nitrobenzaldehyde, in benzene, or in ether, gave *o*-nitrosobenzoic acid, while the irradiation of the same substrate in methanol or in ethanol, gave the corresponding esters. The benzoic acid derivative was obtained when isopropanol was used as solvent.[4]
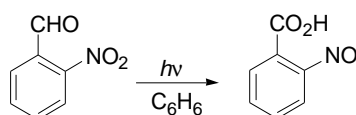
In the following note Ciamician reexamined the photochemical reaction performed in 1886 at Rome between nitrobenzene and ethanol. He showed that, using absolute ethanol, a different main product was obtained. He found that quinaldine was the main product of the reaction.[5]
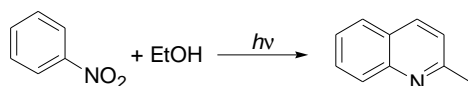
Furthermore, he found that also *o*-nitropiperonal gave the corresponding nitroso derivative, and, finally, he showed that in the reaction of *o*-nitrobenzaldehyde in ethanol, besides the ethyl ester of *o*-nitrobenzoic acid, some other products were obtained.[5]
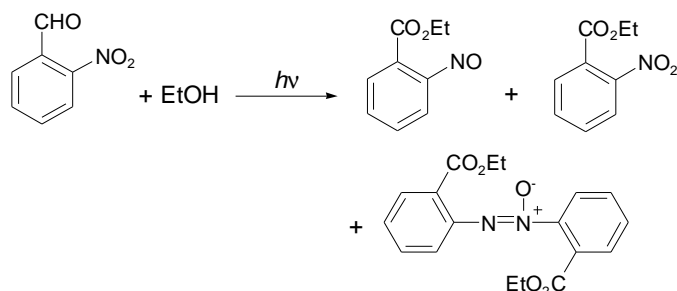
Obviously, both the reduction of quinone and the reaction of *o*-nitrobenzaldehyde occurred by irradiation with violet light, while a red light was completely unable to perform the reaction.[6]

The irradiation of benzaldehyde in the presence on ethanol gave as the only product a polymerization product.[7] On the contrary, benzaldehyde reacted with benzyl alcohol to give the corresponding coupling product. The same reaction was found by using benzophenone.
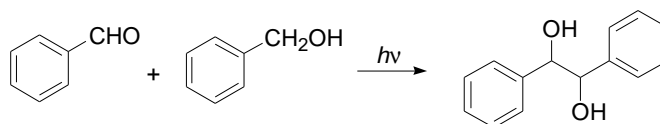
Benzophenone reacted in the presenceof *p*-cymol to give only penzopinacol. Also benzyl reacted in ethanol giving benzoin as the only product. Benzoin was the main product also in the reaction between benzyl and paraldehyde.

Opianic acid reacted in ethanol to give the opianic pseudo ester.[7]
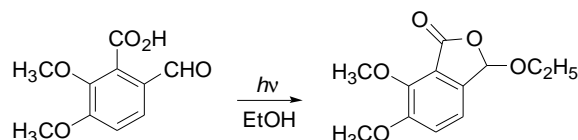
Alloxan, irradiated in ethanol gave a dimeric compound (alloxantin).[7]
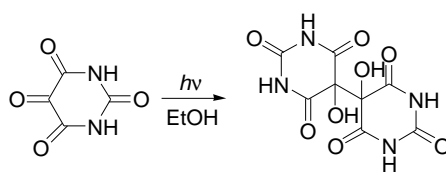
Finally, he found that the irradiation of acetone in water gave as the main product acetic acid, one of the first example of Norrish Type I reaction.[7]

The irradiation of solid cinnamic gave the corresponding dimer while the same reaction cannot be obtained in ethanol.[8] On the contrary,

both stilbene and cumarin gave the corresponding dimers. Prolonged irradiation of stilbene gave benzaldehyde as decomposition products. Furthermore, Ciamician studied the photochemical behaviour of the oxims of nitrobenzaldehydes. He found that the only observable reaction was a *cis-trans* isomerization of the oxims.[8]

In the seven note on the chemical effects of light Ciamician reported the reaction between benzaldehyde and nitrobenzene, in the hope to obtain the intermolecular version of the reaction of *o*-nitrobenzaldehyde.[9] He obtained a mixture of several compounds.
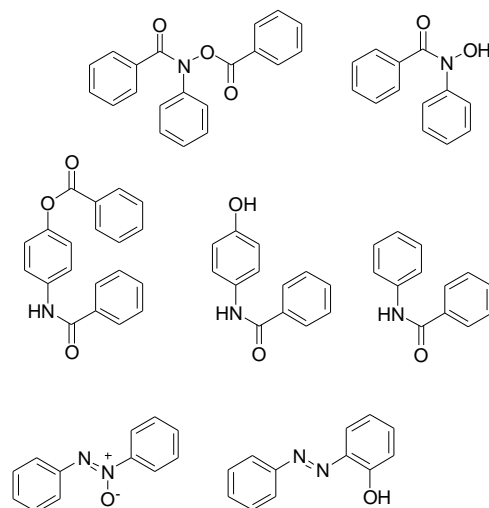
Studying the reaction of nitrobenzene with alcohols, Ciamician found that methanol did not give any reaction. In the reaction with ethanol, besides quinaldine and aniline he found also *p*-amidophenol. When the reaction was performed in propanol, besides aniline and *p*-amidophenol, ☐-ethyl-☐-methylquinoline was obtained. The reaction of nitrobenzene in 3-methylbutanol gave aniline, *p*-amidophenol and ☐-isobutyl-☐-isopropylquiniline.[10]

The irradiation of acetone in the presence of HCN gave a mixture of product where an urea derivative was the main product.[11]
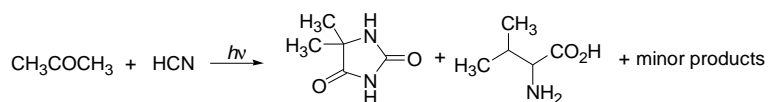
In a subsequent note Ciamician reconsidered the reaction of acetone in water. 2-Butanone gave mainly acetic acid. Levulinic acid gave a mixture of products where methanol, formic acid, and propionic acid were found. When menthone was used as substrate a mixture of two product were obtained.[12]
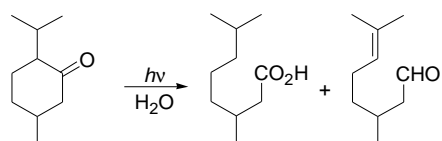
The same behaviour as observed by using ciclohexanone, 2-, 3- and 4-methylcyclohexanone.[13] Dihydrocarvone also showed the same behaviour.[14] On the contrary, carvone gave an interesting chiral 2+2 cycloaddition.[14]
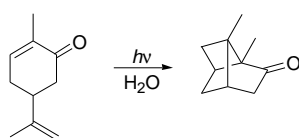
The irradiation of safrole in the presence of iodine, no reaction occurred. On the contrary, isosafrole, where a conjugated double bond is present, gave the corresponding dimer.[15] The same behaviour was observed in the irradiation of methyl eugenol, that did not react, and isomethyleugenol that gave the dimer. The reaction of safrole and isosafrole in the presence of benzaoldehyde gave the corresponding adducts. Probably they correspond to the oxetanes found in the year before by Paternò, but Ciamician did not give the structure of the products.[15]

In another note Ciamician reexamined the aldehyde obtained in the photolysis of menthone assigning a new structure to the product.[16]
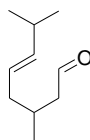
When the irradiation was performed in the presence of oxygen an acid was obtained.[16]
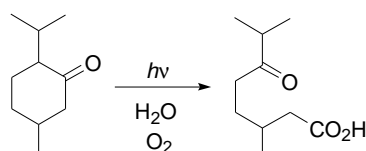
The irradiation of acetone in methanol and ethanol gave the corresponding coupling products. In the case of methanol the main product was 2-methyl-1,2-propandiol, while, when the irradiation was performed in ethanol, 3-methyl-2,3-butandiol was obtained. On the contrary, when acetone reacted also with benzyl alcohol only hydrobenzoin was obtained.[17]
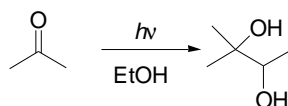
The irradiation of camphor gave a mixture of two product where Ciamician was able to determine the structure of only one of the products.[18] The irradiation of fenchone gave a product where addition of water occurred. It probably was a diol.[18]
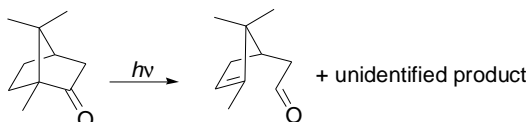
Furthermore, the irradiation of 3,3-dimethylbutanone gave acetaldehyde and 1-methylpropene.[18]

In the reaction between benzophenone and cymol, benzophenone was converted into benzopinacol while cymol was converted in a dymeric compound. They confirmed the results obtained by Paternò in the reaction between benzophenone and toluene, ethylbenzene, and *p*-xylene.[19] Furthermore, in the reaction between acetone and methanol the authors now found, besides isopropanol, 2-methyl-2,3-propanol; in the same way they found 2-methyl-2,3-butanol in the

reaction between acetone and ethanol, and 2,3-dimethyl-2,3-butanol in the reaction between acetone and isopropanol.[20] In the reaction between acetone and diethyl ether, they found an addition product, but they did not assign the structure of the product.[21] Quinaldine reacted with acetone giving a product whose formula corresponded to two molecules of quinaldine plu one molecule of acetone minus water.[22]

In the following communications Ciamician an Silber studied the effect of the irradiation in the presence of oxygen. This way, toluene was converted into benzoic acid. *p*-Xylene gave *p*-toluic acid and terephthalic acid. *m*-Xylene gave *m*-toluic acid and isophthalic acid. *o*-Xylene gave *o*-toluic acid. Cymol gave a mixture of *p*-cuminic acid and *p*-idrossipropylbenzoic acid.[23]

The irradiation of 2-butanone in methanol gave a dimeric compound that was converted into a pyrrole derivative through treatment with ammonium acetate.[24]
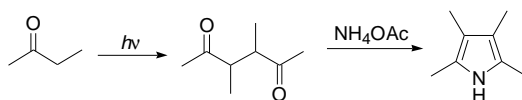
The irradiation of pyrrole in the presence of oxygen gave succinimide, while the irradiation of a dihydrocollidin derivative gave the corresponding colliding.[25]
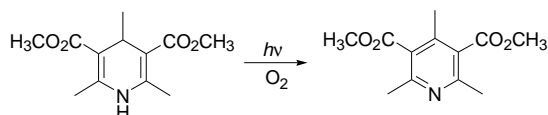
Ethylbenzene gave in the presence of oxygen benzoic acid. Mesitylene gave corresponding acid, such as the isomer 1,2,4-trimethylbenzene gave a mixture of 1,2-dimethyl and 1,3-dimethyl-4-benzoic acid. Indene gave phthalic acid and the same compound was found in the reaction of tetrahydronaphthalin.[26]

The irradiation in the same conditions of tartaric acid gave pyruvic acid and glyoxal. Citric acid gave acetone while lactic acid gave acetaldehyde and acetic acid. Mandelic acid gave a mixture of benzaldehyde and salicylaldehyde. Minor quantities of benzoic acid and salicyclic acid were recovered. Malic acid furnished acetic acid

and formaldehyde. Chinic acid gave minor amount of hydroquinone while the main product was the corresponding phenolic acid. Finally, 2-furylcarboxylic acid gave $OHC-CH=CHCO_2H$.[27]
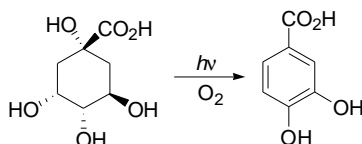
The irradiation of acetone in the presence of oxygen gave acetic acid, while that of cyclohexanone led to the formation of hexanedioic and hexanoic acids. 2-Methylcyclohexanone gave heptanoic and 6-oxoheptanoic acids. 3-Methylcyclohexanone gave 3-methylhexanoic and 3-methylhexanedioic acids. Furthermore, 3-hydroxy-3-methylhexanedioic acid was determined. 4-Methylcyclohexanone gave 4-methylhexanoic acid and 4-hydroxy-4-methyl-hexanedioic acid. 6-Methyl-5-hepten-2-one gave a complex mixture of 6-methyl-5,6-dihydroxy-2-heptanone, 6-hydroxy-6-methylheptan-2,5-dione and levulinc acid.[28]

In another article Ciamician studied the photochemical behavior of compounds that cannot be oxidized in the irradiation in the presence of oxygen when they were irradiated in the presence of compounds that were oxidized in the same conditions. *p*-Xylene, irradiated in ethanol (a compound that cannot be oxidized) gave *p*-toluic acid while ethanol was not modified. When the same compound was irradiated in the presence of pentanol, pentanoic acid was obtained. When the irradiation was performed in the presence of glycerin, no oxidation product was obtained. The same result was obtained in the irradiation of *p*-xylene in the presence of mannitol. When glucose was irradiated in the presence of *m*-xylene, some oxidation products of glucose were observed (i.e. 2-ketoglucose). Finally, the irradiation of naphthalene in the presence of toluene gave benzoic acid but also phthalic acid.[29]

The Irradiation of acetic acid in the presence of oxygen gave formic acid, 2-hydroxyethanoic acid gave formaldehyde, oxalic acid gave only carbon dioxide. Malonic acid gave acetic acid, while succinic acid gave acetaldehyde and glyoxal. Glyceric acid furnished formaldehyde and glyoxal. The irradiation of coumarin gave mainly the dimer of the starting material, together with salicylic acid. The photochemical

oxidation of oleic acid gave nonanoic and nonandioic acids. Furthermore, dihydroxystearic acid was recovered.[30]

The irradiation of acetophenone in ethanol gave only the corresponding pinacol, such as the irradiation of benzophenone in isopropanol. Ethylphenylketone in ethanol gave also the corresponding pinacol derivatives. The reaction between acetophenone and benzyl alcohol gave the pinacol derivative of acetophenone, dibenzoylhydrobenzoin and the benzoate of 1,2-diphenyl-1,2-ethandiol.[31]

The following article is related to a discussion between Ciamician and Paternò, and we discussed this problem elsewhere.[32,33]

The irradiation in the presence of oxygen of nicotin gave the corresponding *N*-oxide.[34] Finally, the irradiation Cu(II)benzoate and benzaldehyde gave cuprum and benzoic acid, while the reaction of Cu(II)benzoate with acetaldehyde, gave cuprum, benzoic acid, and acetic acid.[35]

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CONFERENCE REPORTS

The Giants of Photochemistry

Bologna, February 2nd 2107, there is not a good weather today, but there is an interesting meeting of Italian Photochemistry Group today at the Accademia delle Scienze dell'Istituto di Bologna, in Via Zamboni. GIF wants to recognize the persons that gave an important contribution to the recent history of Italian photochemistry. The meeting has title "the Giants of Photochemistry".

Margherita Venturi is the chairman of the first chairman and the first speaker is **Claudio Chiorboli**, that introduces the meeting retracing the history of GIF. After this introducing talk, **Carlo Alberto Bignozzi** describes the synthesis of metal complexes used for the preparation of antenna systems able to induce electron

transfer processes versus   titanium dioxide in the preparation of photovoltaic cells.

Gianna Favaro addresses the issue of applications of fluorescence in the study of cultural heritage. She discusses also the vibrionic effect in photochromic systems. **Angelo Albini** is the last speaker of the morning and describes the photochemical activation of chemical bonds. He reported the preparation of aryl cations and their use in the organic synthesis. Furthermore, he discusses the formation and the possible uses of biradicals in organic synthesis.

After the lunch, the afternoon session of the meeting has **Alberto Credi** as chairman. **Ugo Mazzucato** and **Vincenzo Balzani** are the speakers of this session. **Mazzucato** describes how he decided to

devote himself to the photochemistry and then describes the most important research fields he studied during his activity: the *cis-trans* photochemical isomerization and the photocyclization of stilbenes.

Balzani starts his talk remembering the role of Ciamician in the development of photochemistry in Italy, and then retraces its scientific path by describing its enormous (the adjective is mine) contribution to the development of molecular machines.

The meeting is finished. I am going to the station, I have to return at my University, but I feel I spent a good day together with people who have marked the history of photochemical development in Italy in recent decades. I think the GIF initiative was truly meritorious: because a society, whatever it is, that does not have the memory of its past and does not cultivate it, deserves to exist. The GIF merits to exist.
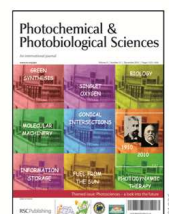
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