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EDITORIAL

President's Letter

Dear EPA Members,

The year 2020 is coming to an end and this coincides with our traditional December issue of the EPA Newsletter. For me this is a special occasion, because it is my first President's letter since I was elected last September. A difficult year is now nearly behind us, with implications for both our private and professional life. Most of us were (and are) forced to spend extended periods at home, trying to conciliate the increased demands of managing a family while keeping our professional routines and productivity. We have learnt to use video platforms, participated in online conferences, and managed academic duties and teaching from the distance. But we also had the chance to be more time with our families and to achieve a different kind of work-life balance. Not everything was bad, but we surely all yearn for this to be over or at least controlled so that most habits of our "old" lives become reality again.

EPA has been active during these times. The most significant task we had to manage was the transit of our journal "Photochemical and Photobiological Science" (PPS) from the Royal Society of Chemistry to our new publisher Springer-Nature. My special thanks go to our Task Force, whose tireless effort, in collaboration with the European Society of Photobiology and the Editors of PPS, made it possible that we are now starting a new chapter of our journal. The first issue of PPS, published with Springer Nature, will appear in January 2021. I would like to encourage you to show your ongoing support for the journal by sending your research work, acting as referee, etc. It is our society journal and its consolidation as leading photochemistry publication depends on all of us.

It can be foreseen that at least the first half of 2021 will still be ruled by the pandemic situation. Hence, it may take a while until we can meet in person again, but one day it will be the case. We, the Executive Committee of EPA, will go on working on the positioning of our association and do our best to provide support to its members in these

times. Should you have any requests or suggestions, please get in touch with us!

For now I wish you and your beloved ones good and safe a New Year 2021.

With my best regards,

Uwe Pischel

PHOTOCHEMICAL & PHOTOBIOLOGICAL SCIENCES

Quo Vadis, PPS?

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Dear EPA members, dear friends,

Our EPA general assembly is also the occasion for us to share some of the latest news regarding our journal, *Photochemical & Photobiological Sciences*. Usually, this is a simple task, as there is not much more to say other than the number of submissions is similar to those of the previous years; that it would be good to have more submissions from our members; that revenue is up and, consequently, so are the royalties payable to the societies.

Not this year.

This year, we have a lot of changes and things to discuss, but unfortunately the health crisis left us without our venue and opportunity to meet. Hopefully, that change soon and we will once again be able to meet in person. In the meantime, I would like to present the most important changes afoot at PPS.

Change of publisher: For the last 18 years, the production of PPS has been entrusted to the Royal Society of Chemistry through their journals division. Like the EPA and the European Society for Photobiology, the RSC is a non-profit chemistry-oriented organization and this greatly contributed to the synergy between the journal's owners and publishers. The RSC has been fully committed to promoting PPS, and you have seen that through its presence and support at photochemistry meetings everywhere. Likewise, the persons behind the screens that manage the day-to-day operations for the journal are incredibly dedicated and knowledgeable. They deserve credit for keeping PPS operational and seeing it grow over time to become one of the most prominent journals in our field.

Two years ago, the RSC communicated to the EPA and the ESP its intention to cease production of PPS to, in their own words, focus on their core journals. We are of course sorry to see our partnership with the RSC ending, but this also provided us with the opportunity to energize our journal and to forge a fresh relationship with a new publisher. Both the EPA and the ESP appointed a task force to identify a scientific publisher that would commit to the continued growth of PPS. I would like to express my sincerest thanks to the members of the EPA task force: Alberto Credi, Alexandre Fürstenberg, Werner Nau, and Julia Perez-Prieto for their time, effort and hard work in examining all possible ways forward. Many options were on the table and considered with care, including moving to a full open access publishing model or even a new name for the journal.

The joint EPA-ESP task force deserves great credit for striking a deal with Springer-Nature, one of the most renowned and respected scientific publishers today. It was decided that, for the time being, PPS will continue as a hybrid journal in which both journal subscriptions and open access are available. A transition to a full open access model will eventually be considered and Springer-Nature has already agreed to help us with this when we are ready. In the meantime, our new journal web page is up and we are open for business!

Yearly report: In 2019, the number of submissions was similar to those of the previous years. PPS received 252 photochemistry manuscripts, which represents a small drop with respect to 2018 and 2017. The overall rejection rate (60.3%) remains stable, with 107 manuscripts (42%) being rejected without peer-review. Asia and Australasia account for half of the manuscript published (60% of submissions), followed by Europe and North America accounting for 30% and 14%, respectively, of manuscript published in PPS (Table 1). Handling times remained steady at 46 days from submission to first decision. As always, it would be good to have more submissions from our members. It is, after all, our journal!

Table 1. Distribution of manuscripts by geographical area

Geographical area	Submitted*	Published	% Total
Asia and Australasia	150 (166)	50	50%
Europe	43 (53)	30	30%
Middle East	18 (24)	0	0%
North America	18 (22)	14	14%
Africa	11 (8)	1	1%
South and Central America	12 (17)	5	5%
Total	252 (290)	100	

*Values in parentheses refer to 2018.

In 2020, things were different and we received an alarmingly-low number of just 117 submissions for photochemistry. Many countries were hit hard with COVID-19 and saw large drops in their submissions: Asia and Australasia: -50%, Europe and the Americas: -60%, Africa: -40%. Our thoughts go to the scientists and their families, the lost productivity is just another sign of how many people's lives have been impacted by the ongoing health crisis.

The journal's impact factor for 2019 was back up to 2.8, near its record-high of 2017. The figures for the 2020 year will be released in June 2021 and, based on current citations, the RSC predicts that it will be similar to that of 2019. As always, perspective articles are amongst the most read and cited articles so please keep them coming! If you have an idea of where a particular area of your field is going, or of a significant advance – or bottleneck – they are a great way of letting others know.

Editorial board: We have had some recent movement in the editorial board that has been implemented in a timely fashion to coincide with the journal's move to Springer-Nature. After many years of incredible service and dedication, Joggi Wirz decided that it was time for him to let go of his activity with PPS. Joggi was kind enough to continue working with PPS even after his retirement and I am extremely grateful for this. His experience and knowledge are a great asset and, on behalf of the entire

editorial board, I would like to thank him for all these years of work and wish him all the best in his future activities and travels. Thank you Joggi! Starting from 2021, Julia Perez-Prieto will take on the duties of Deputy Editor-in-Chief for Photochemistry. Julia has served on the journal's Ownership Board for many years (including as EPA president!) and has experience in the journal's inner workings as well as in its editorial activities. I would also like to extend a warm welcome to four new members of our Editorial Board: Cornelia Bohne (U. Victoria, Canada); Petr Klán (Masaryk U., Czech Republic); Cláudia Gomes da Silva (U. of Porto, Portugal); Oliver Wenger (U. of Basel, Switzerland). Their experience will greatly help the journal in handling new submissions in diverse areas of photochemistry.

As you can see, there was a lot to talk about this year! The important news is that PPS is doing better than ever and, alongside with our colleagues from the ESP, will continue to serve our communities. I will end this report with the usual plea for more contributions from you: we really need them at this difficult time to ensure a good flow of photochemistry papers. It is a win-win situation for us: improving PPS's standing will also improve its impact in the field and help the EPA.

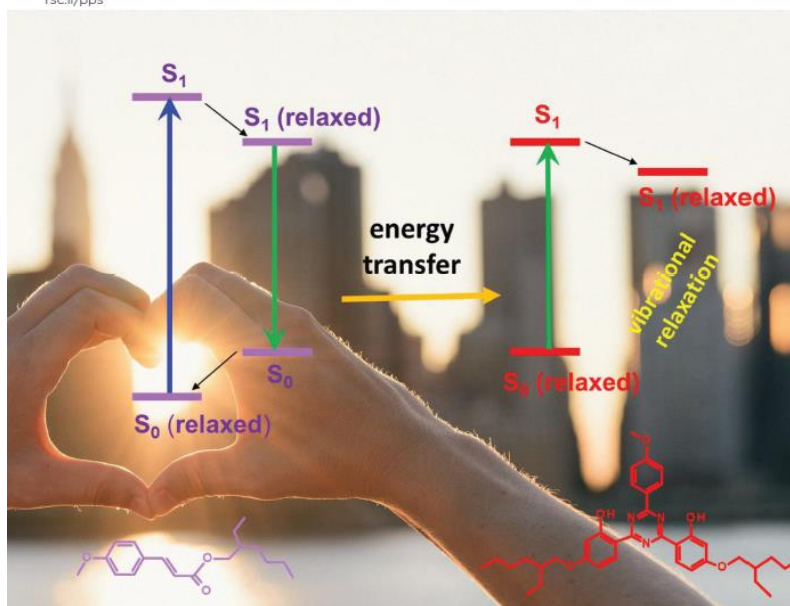
With best wishes,
Dario

Quo vadis, PPS? – Ante!

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PUBLICATIONS

Synthesis, characterization, and performance of gC₃N₄ based materials decorated with Au nanoparticles for (photo) catalytic applications

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To date, humankind is facing an energy and environmental crisis simultaneously due to mainly three factors: high atmospheric carbon dioxide concentration, growth population and the dependency on fossil fuels. In this context, the urgency of using renewables sources, *e.g.*, solar energy, is a potential solution. For example, non-carbon based H₂ production from solar light driven water splitting is a promising approach. Nevertheless, to target the mentioned objective, an ideal hybrid photocatalytic system (semiconductors, SCs) has to meet four main features: **(1)** excellent capacity of absorption of visible-light **(2)** suitable VB and CB positions of SCs to undergo the two half reactions of water splitting **(3)** efficient use of absorbed photons and high generation rate of charge carriers and **(4)** good stability over time. For this purpose, this project contributes to the design and optimization of three innovative materials: Au/gC₃N₄, Au/TiO₂(P25)-gC₃N₄, and Au/TiO₂(NTs)-gC₃N₄ composites. Their photo (catalytic) activities were correlated with their physicochemical properties. Moreover, Au/TiO₂(NTs)-gC₃N₄ composite family exhibited interesting CO conversion yields. To highlight the efficiency on the as-prepared composites, comparative studies were tested using commercial, pertinent references, and physical mixtures homologs.

Keywords: Solar energy, (photo) catalysis, H₂ production, CO conversion, Au/gC₃N₄, Au/TiO₂-gC₃N₄

Energy transition

The current economy model has led to a vast consumption of modern commodities. This trend started with industrial revolution when society

shifted to a fossil fuel-based economy. The shift led to decades of industrial prosperity fuelled by petroleum, which resulted in a direct dependency on this limited resource. The prosperity which society has enjoyed did not slow down despite M. King Hubbert prediction and warnings about the imminent depletion of Earth's oil reserves.¹ The prediction gained veracity with the first oil crisis from 1973 to 1979,^{2,3} and since then CO₂ emissions continue to rise unattained. The burn of fossils fuels and subsequent release and accumulation of CO₂ created the well-known greenhouse effect which has caused the rise of Earth's temperature with unforeseeable consequences.⁴ In recent decades this has stirred the debate on the necessity of changing society's primary energy supply, a debate which has culminated in the making and promotion of new laws, *e.g.* Kyoto protocol⁵ and Paris agreement.⁶ With this context, the current transportation system, electric urban grid, and industrial processes that continue using fossil fuels as a raw material have to be replaced by other renewable sources, to guarantee a liveable Earth.

Relevance and context of the research project

Fossil fuels main drawback relies on their reserves lifetime that depends on a variety of factors, mainly the management of the industrialized countries in how fast they want to transform them and in which volume of production. This scenario demonstrates the need of substituting the fossil fuels by any other means. Renewable energies are considered a potential avenue for substituting the fossil fuels.⁶⁻⁸ Among the developed and existent renewable energies such as ocean currents, wind, hydroelectric, biomass, geothermal and solar type, solar energy is the most promising alternative due to the use of the most powerful natural source of energy known: the sun.^{3,7,9} Within the solar energy technologies consisting of converting sunlight to storable chemical energy, one can highlight photocatalysis. Photocatalysis (PC) is considered as a promising technology for environmental and energy applications. PC is often referred as "artificial photosynthesis", which arises from mimicking the natural photosynthesis to generate energy-storage molecules the so-called solar fuels. Hydrogen (H₂) is an energy carrier for its extraordinary energy density of 142 KJ mol⁻¹, which is about three times that of fossil fuels, such as methane (55 KJ mol⁻¹).¹⁰ In this direction, artificial photocatalytic systems to obtain solar fuels processes may accomplish several criteria to enable technological transfer and scale-up. The desirable (photo) catalytic material features are sustainability, simple synthesis, moderate cost, feasible scalable process, high quantum yield, high conversion efficiency,

and excellent stability. However, as the best of our knowledge, there is no such existent material that fulfilled all the mentioned requirements.

Material's community is searching for potential visible light-driven hybrid advanced heterostructure photocatalyst, to achieve the mentioned desirable features, where each component brings an asset to the formed multi-phasic photocatalyst. In this context, this research is focused on the design of nanomaterials based on graphitic carbon nitride (gC_3N_4). gC_3N_4 semiconductor (SC), an emerging material, with a band gap ($E_g > 2.7$ eV), with visible absorption capacity and cheap to prepare.¹¹ Thanks to its valence and conduction band positions (-1.3 and 1.4 eV vs. NHE), placed relative to those of TiO_2 , the coupling of these two SCs leads to the formation of a "Z-scheme" heterojunction. Such heterojunction is the best for its migration of charge carriers in opposite directions. Furthermore, the deposition of metallic (M) nanoparticles (NPs) onto the as-prepared support heterojunction aims to create M NPs/SC "Schottky junction". Indeed, the Au NPs deposited on the SCs introduce a plasmonic effect, in addition to their capacity to trap electrons and their co-catalytic functionalities.¹² Thus, Au/gC_3N_4 and $Au/TiO_2-gC_3N_4$ composites can promote synergies with the contribution of each component to improve hybrids' activity.

Objectives

The general objective of this research is to design, synthesize and engineer novel carbon nitride gC_3N_4 based 2D nanocomposites with higher activity than the state-of-the-art materials for photocatalytic and catalytic applications by applying three strategies:

- (1) Tuning gC_3N_4 synthesis atmosphere
 - a) Reductive (H_2 , NH_3), oxidative (Air), and inert (Ar, N_2)
- (2) TiO_2/gC_3N_4 heterojunction binary composites
 - a) Tuning TiO_2/gC_3N_4 relative proportion under two synthesis atmospheres (Air and NH_3)
 - b) Varying TiO_2 morphology, 0D (P25 NPs) and 1D (NTs)

The materials synthesized on the two strategies were (3) decorated with Au NPs with a constant loading (0.3 wt. %) to form an Au/SC metallic junction. The purpose of using Au NPs onto the SC is to photo activate and evaluate their activity performing H_2 evolution of the binary and ternary composites in assistance of a sacrificial agent, to take advantage of the Au NPs functionalities:

- a) Co-catalytic properties
- b) Electron trapping
- c) Surface plasmon induced effect (SPIE)

Globally, the heterojunction effect of the two SCs and the MNPs/SC Schottky junction provides several e^-/h^+ pathways. The advantages of using the heterojunction relies on the band edge potential of both SCs, which are staggered between TiO_2 and gC_3N_4 . One expected synergy result is on chemical potential aspects, upward or downward band bending between the both SCs, leading to the migration of charge carriers in the opposite direction. This allows a better e^-/h^+ spatial separation on several parts of the heterojunction to retard the charges recombination and to prolong the lifet

Results and discussion

I. gC_3N_4 materials. Structural XRD analyses showed that $\text{gC}_3\text{N}_4\text{-NH}_3$ exhibited the largest crystallite size and the thickest layering. Comparisons between ED (Electronic Diffraction), XRD and the theoretical values obtained by simulations show that the d_{TSTCN} (distance between two crystal planes of the TSTCN structure) is even lower than the theory, indicating a tilt angularity. Besides, the determination of the size values of TSTCN and STCN revealed the presence of tilt angularity as well, which could be explained by layer distortion. From BET (specific surface area) of both $\text{gC}_3\text{N}_4\text{-NH}_3$ and from $\text{gC}_3\text{N}_4\text{-commercial}$ (reference) showed the same value, the highest ($32 \text{ m}^2 \text{ g}^{-1}$). However, the two samples show a difference in photocatalytic activity by a factor of three, which suggests that the specific surface area is not the only influencing parameter. $\text{gC}_3\text{N}_4\text{-NH}_3$ exhibits the largest pore volume, mostly made up of mesopores, unlike other $\text{gC}_3\text{N}_4\text{-atm}$ samples. Yang *et al.*, have already observed in a post-synthesis treatment under NH_3 , NH_2^* and NH^* species are formed after the degradation of NH_3 at high temperatures; these active radicals could be responsible for the increase in porosity. The UV-vis establishes that the samples with the more pronounced redshift are not the most active. Contrarily, $\text{gC}_3\text{N}_4\text{-NH}_3$ exhibiting the lowest absorption is the one exhibiting the highest activity.

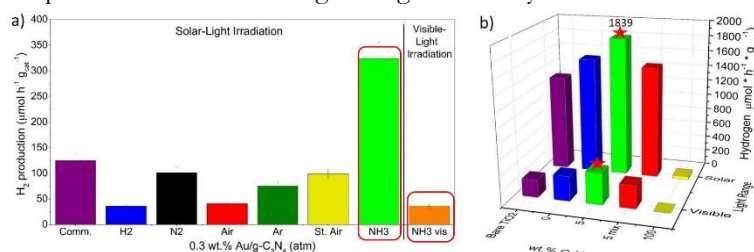


Figure 1. Photocatalytic H_2 production of a) $\text{Au/gC}_3\text{N}_4\text{-atm}$ b) $\text{Au/TiO}_2(\text{NP})\text{-gC}_3\text{N}_4(\text{X/Y})$.

Au/gC₃N₄ binary materials. The deposition of Au NPs use the precursor HAuCl₄ and it was by chemical reduction (NaBH₄). TEM observations confirm a very homogeneous size of Au NPs (*ca.* 3.2 nm) with very good dispersion. Studies have already indicated that these Au NPs were the optimal size for quantum effects, optimal charge transfer phenomena to and from the support as well as optimal positioning of corner Au⁰ atoms exposed and ready to interact effectively with reactive species. We confirmed that the predominant functionality of Au NPs was essentially co-catalytic (contributing at least 80% activity), which facilitated the reduction half-reaction of H⁺ in H₂. UV-vis spectra have highlighted the contribution of gC₃N₄ ($\lambda \approx 460$ nm) and that linked to the Au plasmon (550 nm). The results of the H₂ production tests under solar irradiation (Fig. 1 a). One can notice the superiority of Au/gC₃N₄-NH₃, with an activity between 3 and 9 times higher than that of the second most active composite (Au/gC₃N₄-Comm) and the less active (Au/g-C₃N₄-H₂). In visible irradiation, the composite Au/gC₃N₄-NH₃ was the only one with a measurable activity 26 $\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1} \text{H}_2$.

II. Au/TiO₂-gC₃N₄ ternary composites. The second approach consisted in designing ternary composites, two effects were evaluated: the variation of SCs proportion and the impact of the synthesis atmosphere of gC₃N₄ in presence of TiO₂. These two criteria determine the properties of the heterojunction and the impact of the morphology of TiO₂. The objective of gC₃N₄-TiO₂ is to get new benefits: (a) gC₃N₄-TiO₂ Z-scheme heterojunction of high quality allowing to increase the separation of photogenerated charges as well as sensitization of TiO₂ thanks to the visible absorption capacity of gC₃N₄ and (b) the homogeneous and well-distributed deposit of Au NPs for the formation of Schottky junction and benefit from its features.

A) TiO₂ – nanoparticles (NPs) associated with gC₃N₄

Contents of gC₃N₄ (<10% in weight) was selected because it has the most active production of H₂.

TiO₂(NPs)-gC₃N₄ binary materials.

The synthesis of TiO₂-gC₃N₄ consists of a wet impregnation. TiO₂(NPs)-gC₃N₄ (95-5)-Air composite was the most active. By measurements of TRMC (Time Resolved Microwave Conductivity) at 360, 450 and 500 nm confirmed the TiO₂ photosensitization towards the visible range. This result is in good agreement with experimental measurements of the optical band gap with 2.94 eV. Besides, it showed

that gC_3N_4 generates and injects e^- of its CB to that of TiO_2 thus improving the absorption capacity of photons.

Au/ TiO_2 (NPs)- gC_3N_4 ternary composites.

UV-vis spectra highlighted the three expected contributions, *i.e.* gC_3N_4 ($\lambda \approx 460$ nm), TiO_2 (360 nm), and Au plasmon (550 nm). From H_2 results under solar and visible irradiation (Fig. 1 b), shows that calcined TiO_2 exhibits greater activity compared to that of bare TiO_2 (P25), for its better crystallinity. Among the three composites Au/ TiO_2 (NPs)- gC_3N_4 (95)-Air exhibit higher activity compared to their counterparts and references with $1839 \mu\text{mol g}_{\text{cat}}^{-1} \text{h}^{-1}$, due to improved charge separation and TiO_2 visible sensitization.

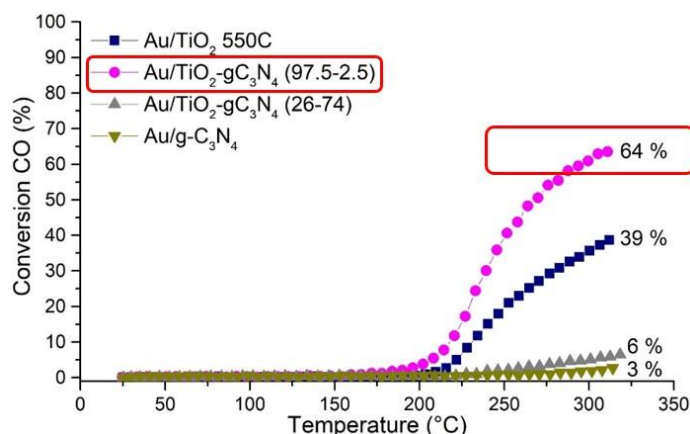


Figure 2. Catalytic results in PrOx of Au/ TiO_2 (NT)- gC_3N_4 (X/Y) composites.

B) TiO_2 – nanotubes (NTs) associated with gC_3N_4

Two composites Au/ TiO_2 (NTs)- gC_3N_4 -Air with gC_3N_4 content of 2.5 and 75 wt.% were selected, and their activity was evaluated by preferential oxidation reaction (PrOx).

TiO_2 (NTs)- gC_3N_4 binary materials.

Structural analyzes have shown that the characteristic XRD diagram of gC_3N_4 for the highest content (75 wt.%), but for the material with the lowest content (2 wt.%) is not observed. Yet the apparition of additional porosity was confirmed.

Au/TiO₂(NTs)-gC₃N₄ ternary materials.

From the results of PrOx (Fig. 2) a synergistic effect between gC₃N₄ and TiO₂(NTs) was observed for the composite Au/gC₃N₄-TiO₂(NTs) (2.5/97.5 wt.%)-Air, in terms of temperatures (T_{Light} et T_{OFF}), referring to the initial and final conversion temperature. We can say that a low content of gC₃N₄ in mono layers entangling the TiO₂ NTs allows both a good contact and a beneficial quality of the heterojunction.

Conclusions

I) Au/gC₃N₄-NH₃ pure has improved photocatalytic performance 3 to 9 times better (under sunlight and visible light) compared to that of gC₃N₄ prepared in other atmospheres. The innovation in structural characterization was the proposal for the first time in the literature, of a quantification to determine the contribution between the two predominant phases based on the tri-s-triazine and s-triazine units in the gC₃N₄ backbone.¹³

II) Au/TiO₂(NPs)-gC₃N₄ (95-5)-Air exhibits higher activity compared to their counterparts, references, and physical mixture with 1839 $\mu\text{mol H}_2 / \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$, probably to an improvement in charge separation due to photosensitization of TiO₂ in the visible. This superior activity and quantum yield is justified by: (a) improving its absorption in the visible (b) better separation of charge carriers thanks to the Z-scheme (c) the Au/SC Schottky interface junction with a major population of NPs of ≤ 5 nm, as a very good co-catalyst.¹⁴

III) Au/TiO₂(NTs)-gC₃N₄ (97.5-2.5)-Air exhibits the highest activity compared to their homologues and references in the PrOx reaction with a synergistic effect between g-C₃N₄ and TiO₂ (NTs) due to the fact that gC₃N₄ monolayers entangle the TiO₂ NTs allowing an intimate contact, resulting in a good quality heterojunction beneficial for this surface reaction.

Outlook

The coupling of gC₃N₄ and TiO₂ with other SCs like graphene, metal organic frameworks (MOFs), CeO₂, Cu₂O, BiVO₄, among others with different properties but ideal to design new Z-scheme heterojunctions that can bring advantages compared to the two individual SCs.

The bimetallic plasmonic catalysts by coupling Au with Pt, Pd, Cu and Ni, for example. Systematic studies should be performed to identify optimal morphology, proportions and loading.

The overall objective on the rational design of visible light activated catalysts to better use the solar spectrum is to combine efficient Schottky bimetallic systems deposited onto Z-scheme heterojunction supports. These multiphase heterostructures can be used for energy applications either the water splitting or CO₂ reduction reactions.

In that direction, within the framework of the recently granted European project H2020 SUN2CHEM (884444) that Dr. Jimenez Calvo have led the elaboration and writing on CNRS (French partner) behalf with well-known partners in the global and European renewable energy community. It is proposed to synthesize innovative systems comprehending optimized SC1/SC2 Z-scheme configuration and plasmonic bimetallic catalysts M1/M2 separately. Thus, merging both strategies Z-scheme and Schottky junctions, resulting in M1/M2-SC1/SC2 advanced hybrid multiphase heterostructures is the ultimate objective for photocatalytic reduction of CO₂ into C1/C2 products, which are of great economic interest in the global chemical market.

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Methylene Blue for photo-disinfecting masks.

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The production of singlet dioxygen after the absorption of the energy of the photons by a dye, is the working principle of the Photo-Dynamic Therapy of cancers¹, that is an active community of photochemistry.² It can be turned into a tool against epidemic.

The consensus was for disposable masks renewed every hour or two masks a day to be washed every day.

Textiles that kill the virus in 30 min, are as effective as masks changed every hour (Fig.1) and only need to be cleaned every three days, when they are dirty.

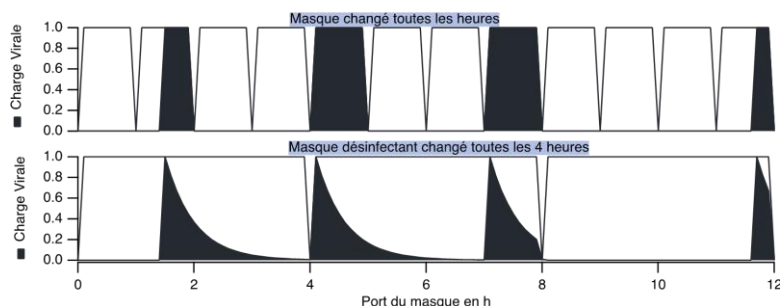


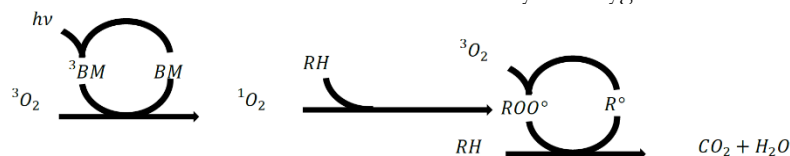
Figure 1. Simulation of viral load on masks changed regularly for infections at $H=1.5$ h; 4.1 h; 7.1 h; 11.7 h. The average viral load rate of a disinfecting mask with a virus survival lifetime of 30 min is equal to that of a single mask changed every hour.

These masks, impregnated with disinfectants are proposed based on the release of ammonium, silver or copper ions.³

But how can we accept to wear a chemical disinfectant on the mouth?⁴ A limited list of allowed disinfecting agents and their usage is maintained by EU. And the disinfectants allowed for fabrics are not recommended for human disinfection.⁵ Furthermore, how can we monitor the presence of the disinfectants after a usage?

Photochemistry offers two possible solutions: Methylene Blue and Titanium Oxide. We shall present results on Methylene Blue that has the advantage to work under indoor light.

The principle of action of light on the virus thanks to Methylene Blue is as follows. Methylene Blue absorbs visible light and stores 1.36eV of the photon's energy for 80 μ s in its triplet excited state. This time is sufficient for the energy to be efficiently transferred by collision to the oxygen, which will rise to its singlet excited state. The latter is extremely reactive and during the 20 μ s before its deactivation, it diffuses towards the virus where it initiates a chain reaction of oxidation by the oxygen in the air.



Methylene Blue is a dye patented 143 years ago by Heinrich Caro.⁶ It is available in pharmacies, as well as from aquarists and veterinarians. It can be used in intravenous injection for extreme indications such as cyanide poisoning⁷ or septic shock⁸, or anodyne such as lymphatic duct visualization⁹. Methylene Blue is used in the treatment of angina and as a substitute for mercurochrome or eosin. It is not a food colorant, nor is it a constituent of blue inks, probably because it fades. This presence of Methylene Blue in the culture allows an acceptance by the most pusillanimous of our fellow citizens.

This antiquity and this multiplicity of uses mean that, for Methylene Blue, the marketing costs are very low. No serious pharmaceutical company has an interest in investing in Methylene Blue, as it is sure to compete quickly with countries with low production costs. Nevertheless, this molecule should be systematically tested in a general drug screening.¹⁰

Beyond its redox and intercalation properties, Methylene Blue belongs to the small family of molecules (along with eosin, hypericin, curcumin, ...) capable of storing light energy in its triplet excited state.

The ability of Methylene Blue to photo-activate oxygen is used in France by the company Macopharma for the photo-disinfection of blood plasma bags.¹¹ This principle is implemented by the Canadian company Ondinebio¹² for the disinfection of patients' noses in the fight against nosocomial diseases. In Brazil, the University of Sao Paulo is promoting dynamic phototherapy and Methylene Blue to solve the problem of pathogen resistance to antibiotics.^{13,14}

Research on photo-disinfectant textiles is one of the objectives of the POLYTHEA Marie Curie European network.¹⁵ The network has produced a review.¹⁶ So the idea that photo-disinfection works on tissue is acquired. As an example, the publication we used to start the dyeing process is about the disinfecting properties (out of light) of jute dyed with Methylene Blue.¹⁷

As early as April 2020, we knew that Methylene Blue is a possibility for the photo-disinfection of masks. It remained to know the order of magnitude of the effectiveness of a mask. This was possible thanks to private funding which paid for the tests at the Microbiological Safety Unit of the Pasteur Institute in Lille.

We received the results of the covid HCoV-229E tests at the end of July:

86.66% of the viruses deposited on a tissue stained with Methylene Blue are killed in 30 min in indoor light (590±20 Lux).

It can be extrapolated that this same mask will be disinfected (disappearance of the virus) in 3 min of sun exposure. Methylene Blue is not the best and most practical (it fades) of the dyes we have tested, but it is the only one that is commercially available.

The intensity of the ambient light is varying over orders of magnitudes. 500 Lux is the intensity recommended for a class room. This is the intensity present in subway wagons. It is small compared to the 100 000 Lux recorded under a summer sun. It's a lot more than the 5 Lux recorded in a romantic Parisian restaurant. (But these places are closed nowadays).

The recipe:

There are at least two commercial forms of Methylene Blue.¹⁸

- A hydrate $C_{16}H_{18}ClN_3S \cdot xH_2O$ with $x = <3 \text{ MM}> = 320 \text{g/mol}$.

- A double salt $C_{16}H_{18}ClN_3S \cdot 0.5ZnCl_2 \cdot xH_2O$ $\text{MM}> = 388 \text{g/mol}$.

The first is a black powder with a green sheen. The second is black with a red sheen. Zinc-free hydrate is preferred.

For three masks (3x20g) made of cotton¹⁹ you need 2 litres of solution in a large aluminium pan (It's easier to clean after use).

Make the pharmacist weigh 68mg of methylene blue (2,1e-4mol). Mix 100mL of vinegar and 1,9 L of water. Empty the Methylene Blue into the solution and discard the container in the same solution.²⁰

For a first dyeing, bring the solution containing the textile to 90°C for 15 min. Allow to cool and wring out by twisting the fabric. Keep the dye liquor. Rinse with cold water in 1 L of water.²¹ Clean the kitchen. The best is the CIF Cream with Bleach which makes stains disappear, even encrusted ones, in a few minutes.

Methylene Blue whitens in the light. It is probably destroyed by singlet oxygen. Gloves and masks get dirty. They should be washed and re-dyed every three days of continuous use.

Textiles are washed by hand because they release the Blue. They are then immersed in the rest of the dyeing liquor. They are wrung out and rinsed in 1 L of water.

When you are tired of these biweekly dyeing, you can destroy the rest of the dye liquor by forgetting it on the fire. After evaporation and oxidation, there remains a thin layer of carbon and a very slight smell of sulphur.

Methylene Blue rubs off on the skin when one sweats. From time to time, I ended up with a shadow on my beard that went in the water. Soap is sovereign.

Other dyes can photo-sensitize dioxygen. Among the common ones, Rose Bengal has been promptly and successfully tested by an US team for covid viruses.²² But eosin, mercurochrome,²³ hypericin, curcumin, are also potential candidates. A panel of colour is thus available. Cationic dyes²⁴ have the double advantage of their good dyeing properties of cotton²⁵ and of the common toxicity of cations for microbes.

The fading of these dyes upon washing is a problem that has been already addressed by the dyeing industry that developed reactive dyes.²⁶ The fading of these dyes under light, due to their destruction by the singlet oxygen they produce, is still an open problem that we are currently addressing on other photo-sensitizers with very encouraging results: better efficiency and better color fastness to light compared to Methylene Blue.

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19. Cotton is the only textile that is easily dyed with Methylene Blue. Commercial cotton is usually mercerized because it improves its whiteness and feel, so it is easy to dye. The quality of its contact with the skin and its hydrophilicity mean that masks often contain cotton.
20. The grains of Methylene Blue have a formidable tinting power. The powder stuck in the thread of the cap can repaint a kitchen in blue. A microscopic grain can generate a stain of several tens of cm².
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Photoacid generators and photoacids, an overview of particular behaviors

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Being involved in numerous chemical reactions and biological functions, proton transfer is one of the most fundamental processes in nature. The control of the latter is therefore a major stake in chemistry. Photoacids are molecules releasing high concentrations of protons upon light irradiation.^{1,2} The growing interest in these molecules has made it possible to highlight numerous applications in various fields, such as material chemistry (mostly polymers), energy, and biomedical areas. Photoacids are divided into three categories, depending on their chemical properties, photoacid generators (PAGs), excited-state photoacids, and meta-stable photoacids.

Photoacids generators (PAGs)

Photoacid generators are molecules generating high concentration of strong acids upon irradiation. In contrary to the other types of photoacids, this reaction is irreversible. Early 70's, the discovery of high quantum yield PAGs,^{1,3} has greatly improved the development of high photosensitivity photoresists in the field of submicron photolithography⁴ and the research in free-radical polymerizations.⁵ PAGs can be divided into two groups, ionic and non-ionic compounds. Ionic PAGs generally involve so called "onium salts", such as aryldiazonium, diaryliodonium, triarylsulfonium and triarylphosphonium salts that contain metal halides like BF_4^- or SbF_6^- . (example of diaryliodonium salt is provided in Figure 1).

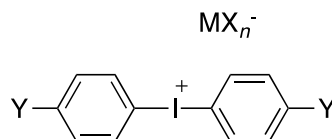


Figure 1. General structure of diaryliodonium salt (ionic PAG). MX_n^- refers to counteranion such as BF_4^- or SbF_6^- . Y is a given chemical group.

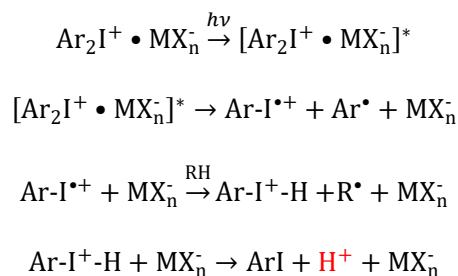


Figure 2. Photolysis mechanism of a given diaryliodonium salt. RH stands for a hydrogen-atom donor.

Upon light irradiation around 200-300 nm, Ionic PAGs undergo a photolysis reaction, leading to a protic acid.⁶ Each of the atoms composing the onium salt has a specific function. The cation of the onium salt is the light absorbing portion and the structure of the onium determines the wavelength sensitivity and the quantum yield of the PAG. James V. Crivello proposed in 2009 a mechanism for the electron-transfer photosensitization of diaryliodonium salts.¹

Onium salts have several advantages, among which a high thermal stability and a possible structural design in order to change the wavelength at which they absorb light. Photolysis can also be sensitized by organic dyes. Nevertheless, one should keep in mind that these salts are generally not soluble in solvents commonly employed in organic synthesis. An example of photosensitization was given, using curcumin (a classical organic dye whose structure is depicted in Figure 3). This latter possesses a deep yellow color and is soluble in a large variety of polymerizable monomers and oligomers.

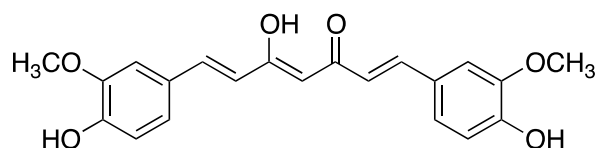


Figure 3. Chemical structure of curcumin.

Non-ionic PAGs generally lead to the formation of sulfonic acids upon light irradiation. These can involve molecules like 2-nitrobenzyl esters of

sulfonic acids, 1-oxo-2-diazonaphthoquinone-4-sulfonate derivatives, *N*-hydroxyimide sulfonate, and tri(methanesulfonyloxy)-benzene and its homologs. *O*-Nitrobenzyl esters of carboxylic acids and diazonaphthoquinone-5-arylsulfonate derivatives generate carboxylic acids upon irradiation (2-nitrobenzyl esters photorearrangement is presented in Figure 4). Non-ionic PAGs usually have a decent solubility in common solvents. Their main drawback being their thermal stability, although it can be easily improved by structural modifications.

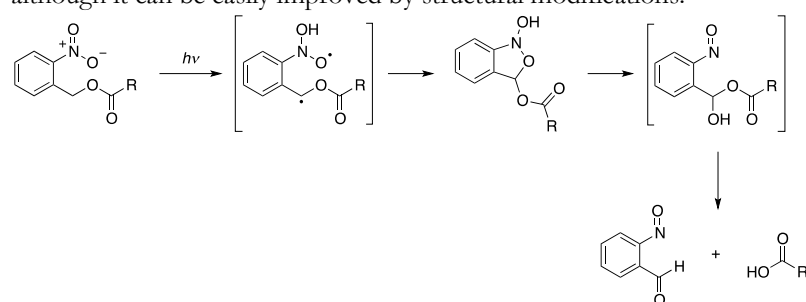


Figure 4. Photorearrangement of 2-nitrobenzyl esters.

However, it should be noted that photobases also exist and are mostly based on cobalt complexes, *O*-acyloximes and benzyloxycarbonyl derivatives. As an example, *O*-acyloximes are known to generate primary amines upon light irradiation (Figure 5).⁷

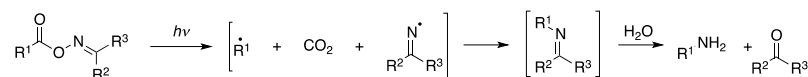


Figure 5. Photochemical reactions of *O*-acyloximes.

Excited-state photoacids

Excited-state photoacids are molecules that reversibly develop a very acidic character at the excited state. In many cases, the excited-state lifetime isn't long enough to provide a significant proton concentration increase. As a result, these latter don't have many applications in synthetic organic chemistry or in polymers industry. Derivatives of phenols and naphthols have been extensively described as excited-state photoacids (example given in Figure 6).

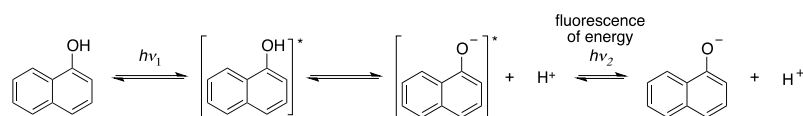


Figure 6. Excited-state of naphthol photoacid.

Thermodynamic models for the ground and excited state of proton-containing (AH) predict that its excited state (AH)* is a stronger acid than the corresponding molecule at the ground state if the absorption or emission spectrum of the conjugate base is characterized by a bathochromic shift relative to that of the conjugate acid. Such thermodynamic cycle is described by the following Förster equation:

$$pK_a^* = pK_a - \frac{\Delta G_a^*}{2.3RT} = pK_a - \frac{h\nu_1 - h\nu_2}{2.3RT}$$

$\frac{\Delta G_a^*}{2.3RT}$ is the ground (excited-state) acidity constant whereas $h\nu_{1(2)}$ is the energy of the 0—0 electronic transition. In the following Figure 7, we write k_{pt}^* the rate constant for forward excited-state proton transfer and k_{-pt}^* the rate of back excited proton transfer. $k_f(\prime)$, $k_{nr}(\prime)$, $k_q(\prime)$ stands for rates of acid (base) fluorescence, non-radiative decay and acid (base) quenching by protons respectively. One major approximation is to take ν_1 and ν_2 as the averages of the absorption and fluorescence transitions of each species (acids and bases).

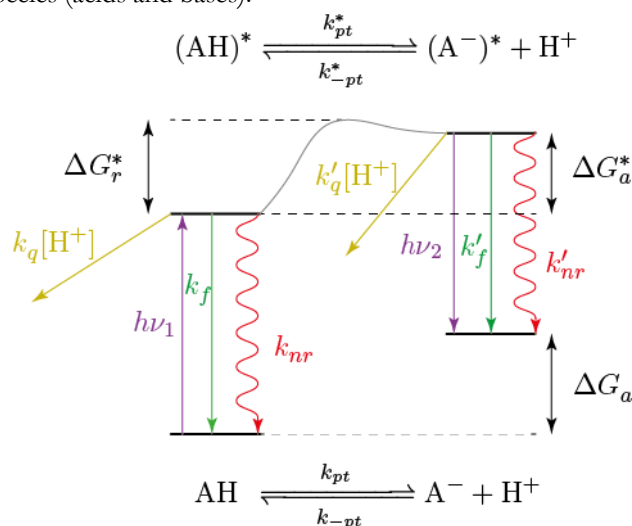


Figure 7. Photoacids: decay processes and proton transfer.

pK_a^* refers to Förster acidity since it is obtained from the Förster calculation. Nevertheless, this acidity is an approximation as it is calculated as well:

$$pK_a^* = -\log\left(\frac{k_{pt}^*}{k_{-pt}^*}\right).$$

Access to pK_a^* is also possible from fluorescence titration in which emissions from base and conjugate acid are related to pH.⁸ Tolbert et al explained and described the photoacidic behavior of many compounds, using time-resolved spectroscopy and Förster's calculations.⁹ They conclude that these photoacids' efficiency was very dependent on the solvent.¹⁰ Naphtols derivatives turned out to be "super-acids" at the excited state. The presence of electron-withdrawing groups at positions C-5 and C-8 produce even higher acidities by lowering the energy of the conjugate base.¹¹⁻¹⁴ Recently, Pithan et al introduced a novel quinolizinium-based photoacid whose acidity in the ground and excited state can be modulated by adding cucurbit[7]uril.¹⁵

Meta-stable photoacids (mPAH)

Meta-stable photoacids are molecules that are able to reversibly release a high proton concentration upon light irradiation. Interest in these molecules has continued to grow in recent years. These photoacids are designed to have a long excited-state lifetime, and a good reversibility after the irradiation stops, and are activated by visible light (LEDs or even sunlight). A pH drop around 2 units was originally reported.¹⁶ Meta-stable photoacids are composed of two distinct parts: an electron-accepting moiety (EA) and a weakly acidic nucleophilic moiety (NuH), being linked by a double bond.¹⁷ Most recent meta-stable photoacids are merocyanines or spiropyranes derivatives (example in Figure 8). This process is similar to but different from the photochromic reaction of SP which has been extensively studied.¹⁸

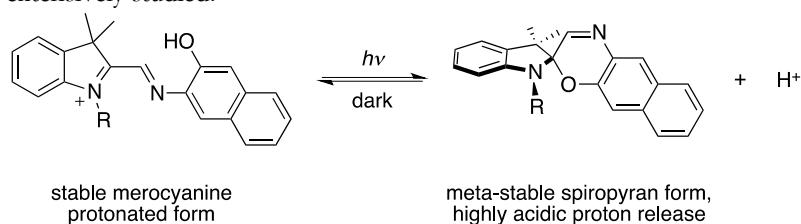


Figure 8. Intramolecular cyclisation of a merocyanine-based meta-stable photoacid upon visible-light irradiation.

Based on this merocyanine/spiropyrane equilibrium, bond-breaking reactions,¹⁹⁻²² molecular motors,²³⁻²⁵ responsive hydrogels²⁶ and inhibition of bacterial growth have been reported.²⁶ In an impressive article, Ganglong Cui et al discussed the mechanism towards this intramolecular cyclisation via quantum calculations,²⁷ and confirmed the spectroscopic investigations previously realized.²⁸

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Consequences of COVID

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For me personally, the first lock-down in Holland coincided with the start of the preparations for a new course in molecular photochemistry. At the same time, during home-schooling sessions, my 10-year-old son taught me how to start a YouTube channel. So, I decided to collect my on-line teaching materials there. And instead of collecting links to YouTube videos in a Word document (which I actually did!), I also started creating playlists.

In doing so I learned new things. It was enlightening to hear Nobel prize-winner Rudy Marcus tell how he found Libby's paper in the library and realised it violated the law of the conservation of energy, and in that way, started his work on the reorganisation energy (UoH lecture). It was

soothing to hear the voice of A. P. De Silva again. Music to my ears, such kindness. Next to talks of Rudy Marcus, also giants like Mike Wasielewski, Dan Nocera, Nathan Lewis, Harry Gray and Ahmed Zewail can be found (see playlist on photochemistry below). And this is something I really would like to share with you, the members of the EPA. There is a wealth of information there. And I tried to collect some interesting material together, for myself and anybody who wants to have a look. Some people cannot be found there. No recordings of, for instance, Jan W. Verhoeven, *mein Doctor-Vater*, are available.

Some made me remember, like the first time I heard Josef Michl present his work on singlet fission. It was probably at the Gordon EDA conference in Newport in 1999. I did not understand a thing. Now I try to explain the basics to my students.

It has taken some trial and error, but I have come to some kind of format and even learned how to translate the subtitles into Chinese! But when I find myself correcting the Google auto-generated subtitles of my close captioning I do think: what the am I doing now.

So, if you Google “Williams uva photochemistry” and click on video’s, you should find my YouTube channel, and perhaps you will find something of interest to you. If not in my lectures than certainly in the playlists. After giving lectures about the Marcus theory of electron transfer for ~15 times, now an extra 140 hours of “watch time” perhaps doubles the learning output (in just 9 months).

I know I am not David Attenborough and I do not expect four million followers in an hour, but anybody who can learn something extra from these materials is a positive outcome for me.

<https://www.youtube.com/channel/UCnxnZhN6aJrbych8WRIqAMw/featured>

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<https://www.uva.nl/en/profile/w/i/r.m.williams/r.m.williams.html>

ABSTRACTS OF THESIS ON PHOTOCHEMISTRY

Recipient of the 2020 “Ugo Mazzucato” Prize for the best Italian PhD thesis in Photochemistry, awarded by the Gruppo Italiano di Fotochimica. www.fotochimica.org

Tunable Photochromic Building Blocks for Molecular Machines and Supramolecular Systems

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Light is universally considered as a most efficient and clean fuel to operate molecular and supramolecular machines¹ that are properly endowed with a photoresponsive component.^{2,3} Photochromic molecules⁴ represent the best candidates for this purpose, as they can be reversibly switched under different luminous or thermal inputs. In order to design photoactive nanomachines, it is of cardinal importance to thoroughly investigate how the photochromic properties can be affected by chemical or supramolecular modifications.

We recently developed supramolecular pumps based on the prototype reported in 2015 (figure 1).⁵ A pseudorotaxane, *i.e.*, a supermolecule composed of a linear molecule (*axle*) inserted in a macrocycle, exhibits relative unidirectional motion of the two components, namely a crown ether and an ammonium salt. A photochromic azobenzene unit, placed at one extremity of the axle, can be converted by light between its *E* and *Z* isomers, which possess interesting differences. First, the axle threads fast in the macrocycle with the *E*-azobenzene end, but it does not thread with the bulkier *Z*-end (thus called *stopper*). Second, the *Z*-complex is less stable than the *E*-complex. As a result, if, after threading with the *E*-azobenzene end, photoisomerization is triggered, the axle is forced to dethread with the opposite extremity, also defined *pseudostopper* (PS) because its steric hindrance is intermediate between those of the two azobenzene isomers.

In order to improve the efficiency of this pump and allow further integration in more complex architectures, we have either modified the azobenzene substituents or its linker with the ammonium recognition site, or changed the pseudostopper moiety.

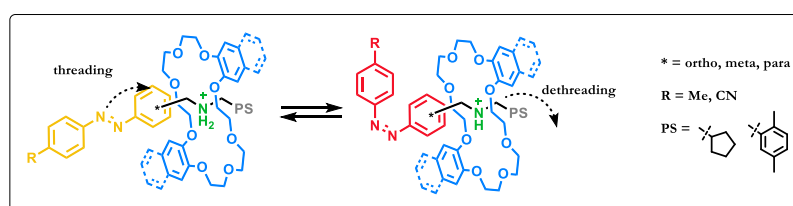


Figure 1. Structure and operation of the supramolecular pumps.

We found out that benzyl units, easier to synthesize and functionalize, can replace the methylcyclopentyl moiety as pseudostoppers. Among these axle-macrocycle combinations, the best prototype resulted to be the one bearing the ammonium linker in *meta* position of the azobenzene. We demonstrated via UV-vis and NMR techniques that this system is able to pump under continuous irradiation, in a non-equilibrium regime. Interestingly, when the azobenzene is functionalized with a cyano group, the axle shows an erratic photochemical behaviour in its free form, most likely due to a photoejection of the ammonium protons.⁶ Instead, this behaviour is supramolecularly rectified in the pseudorotaxane, where the protons are involved in the complexation of the crown ether.

To have a deeper insight on this concept, we focused on photochromic terarylenes, whose bridging unit is an imidazolium, able to give pseudorotaxanes with crown ethers (figure 2a).^{7,8} The closed form of the free axles, obtained upon UV-irradiation, reverts to the open isomer within tens of seconds, following, in some cases, an unusual zero-order kinetic profile. Nevertheless, the pseudorotaxanes showed an improved photochromic behaviour in terms of reaction order and/or lifetime elongation. In summary, both this example and the previous one can be considered as cases of supramolecular enhancement of photochromism.

To elucidate if and how photochromism can be tuned also through covalent chemistry, a parallel study was devoted to the reaction of fullerene with bis-malonate derivatives of azobenzene.⁹ We found out that *E*- and *Z*-*meta*-derivatives yielded the same *E*-bisadduct, where the photochromism is suppressed. Conversely, *E*- and *Z*-*para*-derivatives yielded different regioisomers and, in the *Z*-bisadduct, the *Z* configuration

becomes the thermodynamically stable form. Therefore, this behaviour can be considered both as a molecular tuning/locking of photochromism and light-tunable regioselectivity in fullerene functionalizations.

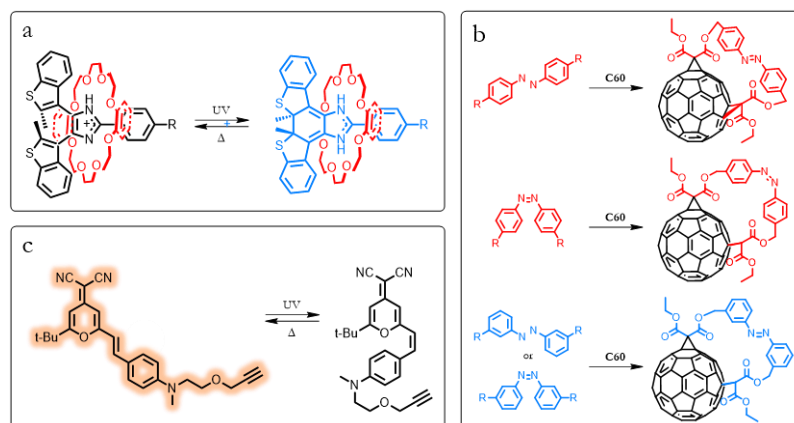


Figure 2. a) Structures and reactions of the terarylene-based pseudorotaxanes; b) structures of the azobenzene precursors and of the fullerene bisadducts; c) fluorescence and photoisomerization of a DCM derivative.

Finally, we investigated the possibility to reciprocally tune the fluorescence and photochromism of a DCM (dicyanomethylene-*p*-dimethylaminostyryl-pyran) derivative.¹⁰ This molecule can be photoswitched between the fluorescent *E*- and the non-fluorescent *Z*-form, with solvent-dependent emission and photoisomerization quantum yields. Thus, we can consider this as a case of solvent- and photochromism-gated fluorescence.

In conclusion, the research here presented dealt with (supra)molecular systems based on photochromes, with a particular focus on the mutual influence exerted by the building blocks on the assembly and *vice versa*. Indeed, if on one hand, a proper tuning of the photoresponsive unit can affect the energetics of the supermolecule, on the other hand the supramolecular interaction can modulate or block the photochromism. These results highlight the importance of balancing these two reciprocal effects to achieve a proper design of photoresponsive (supra)molecular machines and devices.

Acknowledgements

I am deeply grateful to the GIF – Gruppo Italiano di Fotochimica, for awarding me the prize “Ugo Mazzucato” for the best Italian PhD thesis in photochemistry. I would like to warmly thank Serena Silvi and Alberto Credi, my PhD supervisors. This work was supported by the Horizon 2020 research and innovation program ERC Advanced Grant “Leaps” no. 692981.

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Recipient of the 2020 “Ugo Mazzucato” Prize for the best Italian PhD thesis in Photochemistry, awarded by the Gruppo Italiano di Fotochimica. www.fotochimica.org

Photoactive Tools for Biomedical Applications. From Supramolecules to Micro-Objects.

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The importance of the research in nanomedicine is to work within development of new multifunctional materials for future theranostic applications. Therefore, starting with the study of various components able to play different functions that could be then implemented in more complex multifunctional platform, it is possible to obtain different systems able to perform separately, advantageous functions for biomedical applications (imaging, sensing and drug delivery). Following a sort of ‘increasing in dimension’ logic, firstly, is presented a new luminescent chemosensor for Mg^{2+} detection in mitochondria based on a diaza-18-crown-6 appended with two 8-hydroxyquinoline(8-HQ) derivative. It has been synthesized a new species, precisely designed to detect and quantify Mg ions selectively inside mitochondria, thanks to the insertion of two phosphonium moieties on the periphery of the chemosensor.



Figure 2. Left: Pictures of the system with Na^+ Ca^{2+} K^+ Mg^{2+} ; Right: different concentration of Mg^{2+} amount.

The photophysical characterization confirmed the efficiency and sensitivity of the new supramolecule vs the Mg^{2+} also respect to the others physiological cations competitors, up to 300 times increasing in emission when linked (Fig 1). The preliminary in vitro test (on a human leukemia (HL60) and osteosarcoma tumor (U2Os) cell lines) have allowed to II

evaluate the suitable non-toxic concentration to be use for further investigation on the mitochondria target ability of the chemosensor.

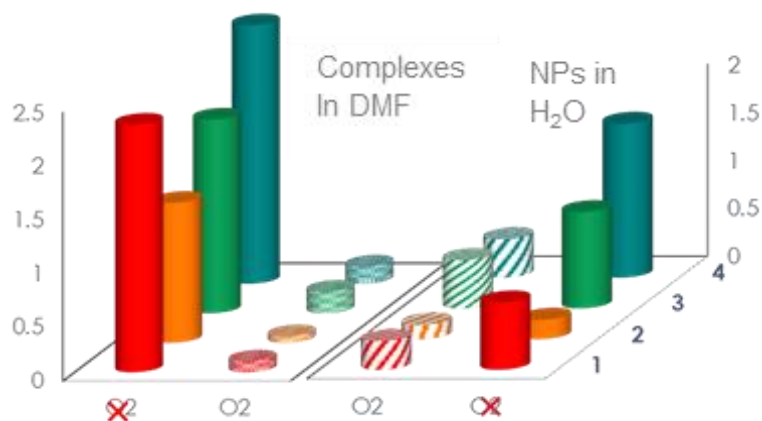


Figure 3. Φ_{EM} of 4 different complexes (metallo porphyrins) in oxygenated and de-oxygenated conditions (filled tubes vs line tubes). Left complexes free in DMF, right complexes inside SiNPs.

Increasing in dimension, is reported a new synthetic strategy based on the micellar assisted method, to prepare silica core/PEG shell nanoparticles doped with phosphorescent non soluble emitters such as organic molecules called “asterisks” and metal-porphyrins. It has been obtained very promising nanostructured phosphorescent chemosensors for molecular oxygen¹ (Fig 2), suitable also for two-photon excitation². They present appropriate features for oxygen sensing in the physiological pO₂ range, they are water soluble, stable and biocompatible. In a pilot *in vivo* test, in collaboration with Professor B. Weber from the University of Zurich, the phosphorescence intensity decays measurement in mouse brain at increasing depths and the signal was detectable up to 400 μm below the tissue surface, results never obtain before for a nano chemosensor. Going towards the dimensions, it has been showed the study carried out at the New York University, centred on the synthesis of microstructures suitable to mimic invading microbial pathogens. Their study can allow a full physicalmechanical understanding of the phagocytosis process. Based on previous achievements, a novel and reproducible method to obtain irregularly shaped colloids is described,

that allows to obtain stable colloids with dimensions in the range of 10-12 μm (Fig. 3).

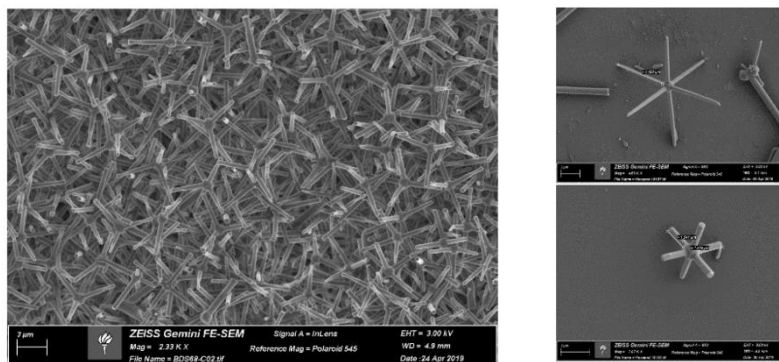


Figure 4. SEM pictures of hexapods. Left: large field picture of the optimum monodispersion; right: tuned dimension of the hexapods. dimension

The efficient biotinylation method that it has been also optimized results in synthetic-mimetic materials that are better recognized by primary dendritic cells as shown by a preliminary *in vitro* test. In parallel, there were also prepared other active magnetic colloids able to be propelled by the oxygen bubbles formed by a chemical reaction that is UV-light activated in the presence of hydrogen peroxide. Going forward, it was designed with bioresorbable electrospun nanofiber mat that, if doped with theranostic agents can be used to release the active species, during their degradation after post-surgical implantation. The fine tuning of the electrospinning parameters was pivotal in order to prepare fibers doped with luminescent targeted nanoparticles that present uniform dimensions and dispersion of the included agents (Fig. 4). Photophysical characterization is reported together with a study of the PLGA fibers degradation that proves that the nanoparticle release correlates very well with the degradation profile in physiological conditions. This can allow to tune the release over time simply modulating the polymer composition.

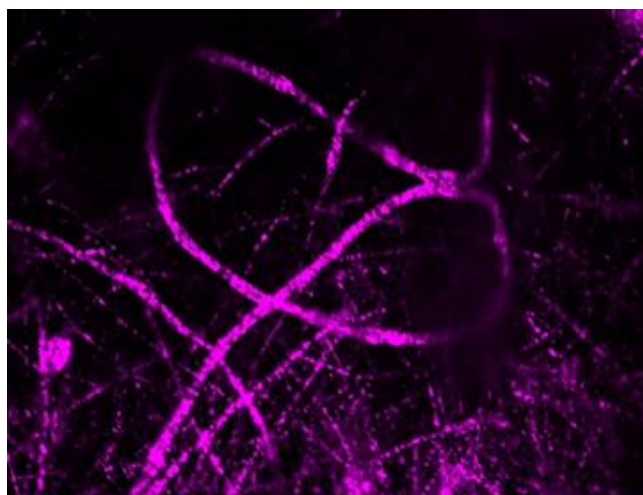


Figure 5. Electrospun luminescent NPs completely inside PLGA fibers.

The last section merged some research works on different species that could have, or could take to, interesting properties for the design of multifunctional platforms. The attention has been focused on NIR emitters that are luminescent component of election for medical application *in vivo* due to the maximum depth of penetration in tissues of light falling in the range 650-1350 nm. It has been discussed the results obtained with rhenium(I) and lanthanide metal complex³ from a photophysical point of view both in solution and in the solid state. Moreover, in this section is also presented a basic study that aims to assess the possible pro-oxidant or antioxidant effects induced by gold nanoparticles⁴, key features determining their safety and suitability for specific applications.

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And at the end, many thanks to the GIF committee for the Ugo Mazzucato Prize, ending in this way my PhD in this very trouble year it was an expected and rewarding moment. Thanks.

Photochemical fiber-optic luminescent sensors for *in situ* monitoring of quality parameters in biomethane

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Supervisors: Prof. Guillermo Orellana and Dr. Maximino Bedoya

Biomethane is a sustainable **biofuel** composed mainly of methane, which can be used as a vehicle fuel or injected into the natural gas distribution lines. Among the future energy sources, this gas is becoming increasingly interesting due to its environmental, economic and social benefits. However, so far, this energy source has some limitations. It requires

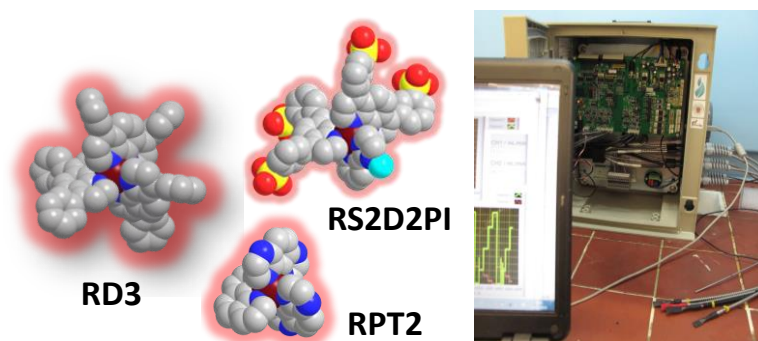


Figure 1. Chemical structures of the synthesized luminescent indicator dyes for O₂ (**RD3**), H₂S/RSH (**RPT2**) and NH₃ (**RS2D2PI**) sensing, and dedicated field-deployable fiberoptic photochemical multisensor, developed in our research group.

technological advancements in the production process to obtain a high quality biomethane from urban or agro-industrial waste, ensuring the quality of the generated energy, the consumers' safety and the infrastructures protection.

The most common biomethane production process (biological pathway) consists of two major steps: anaerobic fermentation of organic feedstock to produce the so-called '**biogas**' and a subsequent *upgrading* process through which biogas is cleaned of particles, water, CO₂, and other minor components (H₂S/RSH, O₂, NH₃). Although biomethane is composed mainly of methane (> 96%), it can also contain small amounts of other gas impurities such as those mentioned above. The presence of those impurities may provoke infra-structural, safety or environmental problems, e.g. corrosion of equipment and fittings, gas explosions and emission of contaminants into the atmosphere as a result of the biomethane combustion.

In order to prevent those problems, the European Organization for Standardization has recently released the European norms EN 16723-1 and EN 16723-2 that establish the biomethane *specifications* for its injection into the natural gas **distribution grid** and its use as a **vehicle fuel**, respectively. Since then, on-line analysis of biomethane has become mandatory and, consequently, reliable monitoring must be installed in biomethane production plants, ensuring that the gas meets the legal limits. Although several commercial sensing technologies (electrochemical, chemoresistive, gas chromatography coupled to a detector, optical) are currently available for O₂, NH₃ and H₂S/RSH quantification, the need of developing new sensors is unquestionable as each of the current sensors shows its own set of negative issues when deployed in an actual biomethane production plant. Some of them are poorly selective or sensitive for the sought application, demand frequent and/or time-consuming maintenance, require a gas sample pre-conditioning system, are costly and need qualified personnel, or simply cannot operate in the environment of a biomethane production plant.

The **aim** of this thesis was the **development** and **application** of three sensitive, sufficiently selective and reliable **luminescent sensors** for *in situ*, real-time, **O₂, H₂S/RSH and NH₃ gas monitoring** in biomethane. Taking into account our 30+ years' experience in the development of *fiber-optic luminescent sensors* for environmental, industrial and aeronautical applications, due to their *superior features* (sensitivity, selectivity, long distance monitoring capability, immunity to electrical interference and risks, lack of analyte consumption, robust calibration and scarce maintenance), and our *mastering of the photochemical principles*, we set out to fulfill the requirements of the end-user (Naturgy Energy Group), the

leading gas utility in Spain (more than 5 million customers) and Latin America, and the third world's largest one based on market value.

These luminescent sensors consist each one of a **tailored photoactive indicator dye** (Figure 1), exclusively or mostly sensitive to the target analyte, immobilized onto a siliceous support behind a thin metal or PTFE mesh to keep the dyed particles tightly packed. **Luminescent ruthenium(II) complexes** with polyazaheteroaromatic ligands were used as indicator dyes due to their versatility and rich photochemistry. Taking into account the nature of the analytes, we prepared Ru(II) complexes **with specific photochemical properties** in a sort of '*photochemical Meccano*' through a judicious selection of the chelating ligands, so that the emission of each indicator molecule would be quenched by the target analyte (O₂, H₂S/RSH or NH₃). The dyes were immobilized onto silica beads to yield the resulting sensing layers, which were all interrogated by a **single dedicated field-deployable fiberoptic phase-sensitive luminometer**, developed in our research group.

In the presence of the analyte, the luminescence intensity and lifetime of the immobilized photoexcited indicator dye are (*reversibly*) quenched by the target analyte as a result of the photochemical reaction (**energy transfer** for O₂, **electron transfer** for H₂S or **proton transfer** for NH₃ process) with the engineered Ru(II) complex. The concentration of the analyte is directly related to the change in the emission intensity and lifetime, by the most famous equation in Photochemistry (Stern-Volmer equation):

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q] = 1 + K_{SV} [Q]$$

where I_0 (τ_0) and I (τ) is the luminescence intensity (lifetime) in the absence and in the presence of the analyte, k_q is the bimolecular quenching constant, and $[Q]$ the analyte concentration. Due to the superior stability and lack of deleterious effect of the indicator photodegradation on the **luminescence lifetime**, our chemical sensors are based on this parameter quenching. There are several ways to determine the emission lifetime of a luminophore; we have chosen the **phase-sensitive detection** due to the higher simplicity and affordability.

The synthesized indicator dyes were *immobilized* onto a siliceous support (typically, silica microbeads) in order to increase the sensor sensitivity thanks to the well-known gas physisorption properties of this material. Each sensitive layer was placed behind a nylon mesh at the distal end of a multimode bifurcated industrial optical fiber to carry the excitation light (from a 470-nm LED) to the supported indicator dye and its luminescence

back to the detector (Hamamatsu compact PMT). Under these conditions, the unquenched and quenched luminescence lifetimes of the luminophore span from ca. 0.1 to 7 μ s. These lifetimes are conveniently interrogated with modulation frequencies of the LED source of 39, 78 or 156 KHz.

The first chapter describes the development of the **luminescent O₂ sensor** and its application to real-time monitoring in an actual biomethane production plant.¹ The O₂ sensing layer consisted of a long-lived luminescent Ru(II) complex (Figure 1) bearing extended π -conjugation in its polyazaheteroaromatic chelating ligands, immobilized on silica gel particles. The sensing photochemistry relies on the highly efficient luminescence quenching of the (triplet) excited Ru(II) complex by O₂ through an **energy transfer mechanism**. The sensor exhibited an impressive 3–10000 ppmv (0.0003–1 mol%) O₂ range, excellent sensitivity and selectivity with a limit of detection (LOD) of 1.0 ppmv, short response and recovery times (< 30 s), good repeatability and reproducibility values, and excellent stability under the laboratory conditions. The *effect of temperature* on the sensor response was automatically corrected by measuring the sensor response in the 5–35 °C range. The O₂ sensor was installed at a biomethane production plant and its performance was verified for *more than six months*. It represents a solid alternative to current field gas chromatographs used for O₂ monitoring.

The following chapter reports the development and application of the **luminescent H₂S sensor**.² This is the first *reversible* luminescent H₂S/RSH sensor described so far in the literature. The sensing layer is based on a highly photooxidizing phosphorescent Ru(II) complex (Figure 1) immobilized on alkali pre-treated silica microspheres. The novel optode was interrogated by the very same portable instrument employed for the O₂ sensing, specifically designed for *in situ* biomethane monitoring. In the presence of H₂S, the luminescence of the Ru(II) complex is quenched due to a **reversible electron transfer** from the analyte to the photoexcited dye. The sensor also responds to volatile *mercaptans* present in the biomethane. The luminescent H₂S sensor displays a 0.34–50 ppmv (0.44–65 mg S m⁻³) measuring range and good selectivity (no response to O₂ within the concentrations typically found in biomethane, see above), with a LOD of 0.025 ppmv, relatively short response and recovery times (< 240 s), and repeatability and reproducibility better than 3.2%. The effect of temperature on the sensor response was automatically corrected by measuring the sensor response in the 10–35 °C range. The luminescent H₂S sensor demonstrated an excellent performance in the biomethane production plant, showing excellent stability and an operational *lifetime of*

over six months, thanks to the automatic cleaning system installed. Our results make the novel H₂S luminescent sensor a superior alternative to existing monitoring technologies such as the lead acetate tape monitor.

In the third chapter, the fabrication and application of the **NH₃ luminescent sensor** is detailed.³ The novel *reversible* NH₃ optode capitalizes on a Ru(II) complex containing an acidic heterocyclic ligand (pyridylimidazole, see Figure 1), immobilized on acid pre-treated silica microspheres. The sensing mechanism is a **reversible proton transfer** from the Ru(II) complex to the basic analyte, leading to the observed indicator dye luminescence intensity and lifetime quenching. The emission phase-shift measurements with the developed optoelectronic unit led to a 0.5–20 ppmv (0.013–11 mg m⁻³) NH₃ measuring range. Moreover, a LOD of 0.15 ppmv, repeatability and reproducibility better than 4.8%, and response and recovery times less 4 and 13 min, respectively, characterize the sensor performance. The O₂ interference was solved by *in situ* real time correction of the NH₃ sensor measurements for the instant readings provided by the luminescent O₂ sensor. The ammonia optosensor was *tested for more than four months* in the biomethane production plant, showing excellent performance over a 10-day span. For longer operation periods the NH₃-sensitive film showed a progressive loss of sensitivity that required change of the sensing layer. The developed NH₃ optosensor may be a competitive sensing technology according to its analytical characteristics and good performance in the biomethane production plant. To conclude, the **novel lifetime-based luminescent sensors can be a competitive option** for *in situ* continuous real-time O₂/ H₂S/RSH and NH₃ monitoring. The sensors high sensitivity and relatively short response and recovery times, along with its ruggedness and low maintenance, make them a promising technology compared to existing devices. They have demonstrated great performance when installed at a real biomethane production line for more than 6 months. When it comes to the sensor *selectivity*, O₂ interference above 10 ppmv is readily solved by correction with the instant readings of the luminescent O₂ sensor itself. Other industrial applications of the photochemical sensors are being pursued.⁴

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SHORT ABSTRACTS OF THESES ON PHOTOCHEMISTRY

Azobenzene and chalcone photoswitches with fluorescence detection and Lewis-acid catalyzed thermal reversion

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The design and optimization of photoswitches is an essential challenge of the modern developments in photopharmacology.¹ Biological effects can be controlled by visible light excitation of molecules that selectively change their constitution or configuration and modulate molecule-receptor interactions or release bioactive molecules (*payload*) on demand. An essential desired feature of these photoswitches is the visualization of the photochemically induced biological effect, e.g. by photon emission as chemi- or photoluminescence. We have developed these compounds from structurally simple azobenzenes with adjacent phthalimide fluorophores (Figure 1).^{2,3} The red tagged Z-forms are fluorescent, the green tagged E-

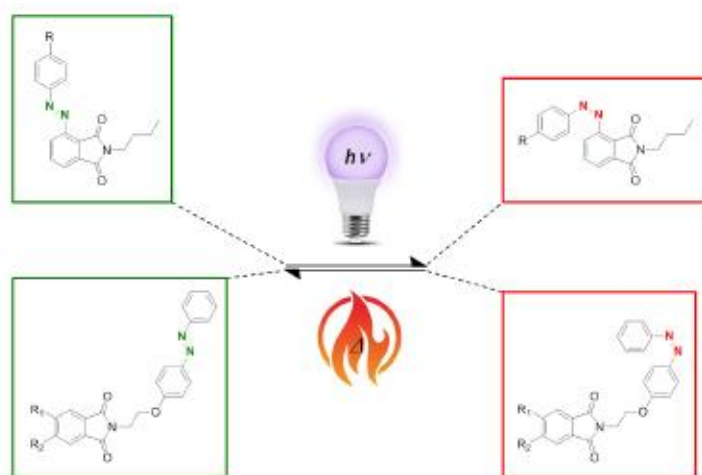


Figure 1. Two azobenzene-containing T-photochromic compounds with fluorescent probes based on donor-substituted phthalimides.

forms not. Another group of photochromic molecules are α -methyl chalcones that can be photoswitched to photostationary Z/E states (PSS~8:2) and completely re-switched to the E-isomer by the addition of Brønsted or Lewis acids like BF_3 (Figure 2). An additional benefit of these compounds is their high oxidative stability under photolysis conditions, i.e. E/Z-isomerization-inducing singlet oxygen physical quenching.

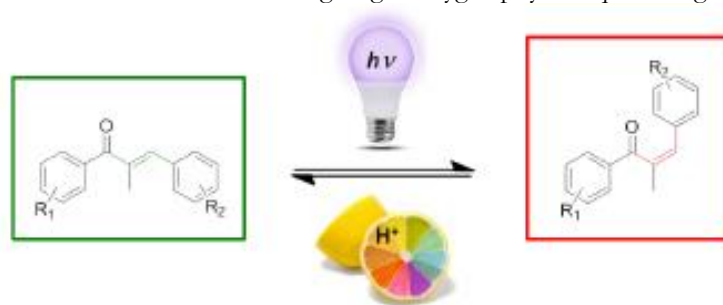


Figure 2. P-type α -methyl chalcone photochromic compounds that can be quantitatively back-switched by Brønsted- or Lewis-acids.

This approach allows the design of fluorescent/non-fluorescent photo-switchable E/Z-isomers which is useful for applications with concomitant read-out possibility.

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New singlet oxygen routes to allylic hydroperoxides and 1,2,4-trioxanes by photooxygenation of enones and allylic acetals

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Bioactive peroxides that resemble the structures of the natural role model *artemisinin* and semi-synthetic peroxides are in the research focus since two decades. One synthetic approach to these molecules involves singlet oxygen ($^1\text{O}_2$) as the reactive oxygen transfer reagent. Singlet oxygen is on one hand a very primitive oxidation reagent and on the other hand a fascinating small electronically excited molecule that nature can easily produce, e.g. during photosynthesis. The reactivity of $^1\text{O}_2$ is dictated by the ratio of physical and chemical quenching and this ratio is often hard to determine and even harder to explain. Cyclic enones such as butenolides (unsaturated γ -lactones) constitute precursors to 1,2,4-trioxanes (the pharmacophore of artemisinin) but surprisingly do not react with $^1\text{O}_2$ in contrast to the corresponding conjugated cyclopentenones (Figure 1).¹

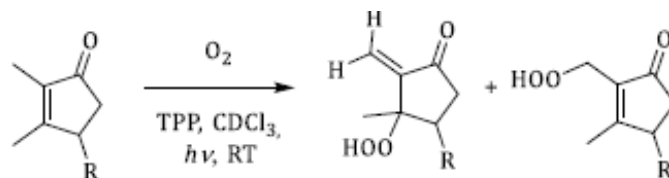


Figure 1. Singlet oxygen photooxygenation of cyclic enones with peroxide rearrangement.

Allylic alcohols, on the other hand are excellent precursors to β -hydroxy hydroperoxides that can be converted into 1,2,4-trioxanes by intermolecular peroxyacetalization, often with low yields because of this bimolecular step.^{2,3} An alternative route uses already allylic acetals as $^1\text{O}_2$ precursors which are transferred into allylic hydroperoxides and subsequently into 1,2,4-trioxanes by Lewis-Acid catalysis (Figure 2). The optimal catalysts are rare-earth triflates such as $\text{Sc}(\text{OTf})_3$ beside the classical catalysts TSOH and boron trifluoride

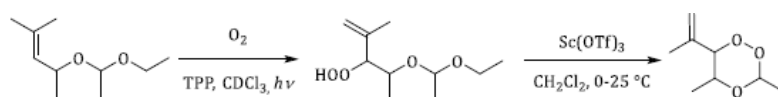


Figure 2. A new approach to 1,2,4-trioxanes by singlet oxygen ene reaction with allylic acetals and subsequent trans-peroxyacetalization..

This novel approach enables an unimolecular approach to 1,2,4-trioxanes, the artemisinin pharmacophore, with a broad substituent pattern.

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Think and print – new ideas and educational concepts for 4D printing of photochemical reactors

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Photochemistry constitutes the colorful part of chemistry: colors appear and disappear, visible light absorption makes molecules colored, fluorescence adds another and phosphorescence a third color. Solvents change the colors of absorption and emission largely, also temperature and many other environmental factors. Teaching chemistry thus often relies on color changes and relies on the use of sensors, probes and indicators that transport informations on the progress of a chemical reaction or the parameters that control reactivity. In this Thesis,¹ a technical approach was developed to realize (photo)chemical experiments by means of 3D- and 4D-printing techniques. The basic idea behind this project was to use the rapid and cheap 3D printing techniques to convert an idea into an

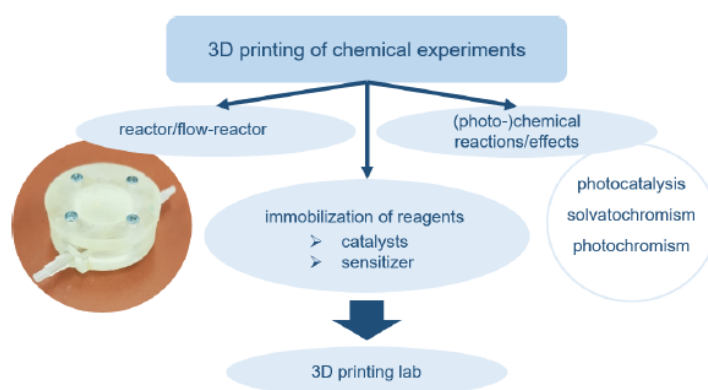


Figure 1. A schematic approach to develop experiments as 3D printed objects.

experiment directly at the computer using freeware available for printing objects that can be used as chemical reactors or as for chemical demonstration experiments. The reactors that were printed were flow reactors with quadrangular or cylindrical (flowmeter-type) geometries.² Post-functionalization (which constitutes the 4D part of the printing process) with organic photosensitizers and photocatalysts, respectively allows the conversion of these reactors into solvent and light-stable chambers transparent for UV-A and visible light that were applied for photooxygenation and photoinduced hydrogen transfer reactions.³



Figure 2. A two-bench 3D-lab for teaching and applications: DLP-printer, open FDM and three closed FDM printer, 3D scanner with camera and flow-reactors as printed from these printers (from left to right).

This novel approach for interdisciplinary teaching in chemistry for science and education students, opens a window for developing new tools for quickly producing experimental setups for diverse experiments that can be used in undergraduate and graduate chemistry teaching. The digitalization of objects by scanning techniques and the printing processes themselves by fused deposition modelling (FDM) or by digital light processing (DLP) are highly informative steps that visualize the converse concepts of digitalization and “analogization”.

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Fluorescence quenching with donor-substituted phthalimides for ROS sensor development

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Reactive oxygen species such as the superoxide radical anion, the hydroxy radical, hydrogen peroxide or singlet oxygen constitute the ROS family that is relevant in innumerable processes with positive and negative biological effects. Evaluation of these processes in cellular matrices require a sensitive and selective analytical tool that detects low amounts of ROS and differentiates between the different ROS species. Our sensor design combines a highly fluorescent chromophore with a fluorescence quencher part that can be oxidized by ROS and thus oxidation modulates the emission response.¹ The 4,5-dimethoxyphthalimides **1-5** showed no absorption effects on the long-wavelength $n\pi^*$ -transition but a strong chain-dependent fluorescence quenching effect (Figure 1).²

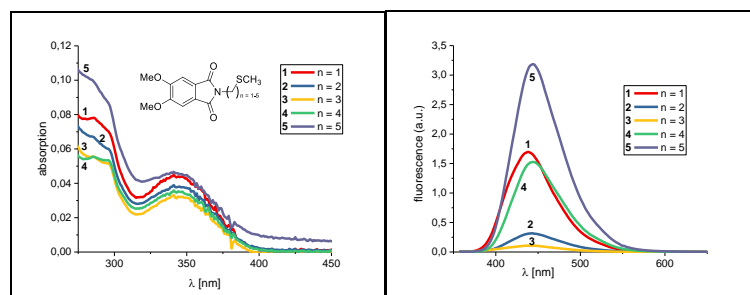


Figure 1. Donor-acceptor compounds **1-5** based on the phthalimide-thioether couple: no ground-state and very strong excited singlet-state effects by absorption and fluorescence spectroscopy.

With these compounds in hand, intermolecular ROS sensing was established for hypochlorite, hydrogen peroxide and singlet oxygen. $^1\text{O}_2$ gives efficiently the sulfoxide of **3** with strong fluorescence reconstitution (Figure 2). Hydrogen peroxide cannot be detected with **3** but addition of catalysts (transition metals) leads to rapid oxidation and likewise strong fluorescence.³

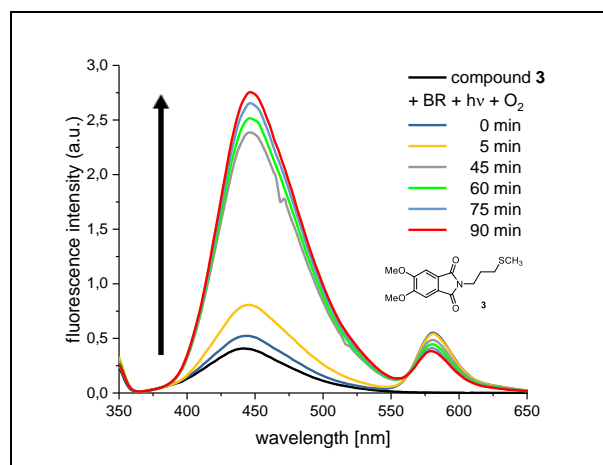


Figure 2. Singlet oxygen probe **3** with fluorescence ON effect by thioether oxidation: highly efficient for $^1\text{O}_2$, less efficient for hypochlorite and low efficiency for H_2O_2 .

This approach for probing ROS by non-fluorescent donor-acceptor dyads is an efficient tool for selective analysis that can be modulated by the donor part of these probes.

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OBITUARY

In memoriam Hans Jochen Kuhn

16.01.1933 – 04.06.2020

Pioneer in the gathering and dissemination of information on Photochemistry

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With deep sadness we learned about the death of our colleague Hans Jochen Kuhn.

Jochen studied chemistry at the university in Göttingen and moved in 1959 to Mülheim an der Ruhr, to the so-called Radiation Chemistry Section (Abteilung für Strahlenchemie) in the Max Planck Institute for Coal Research (Kohlenforschung), together with his thesis supervisor and founder of the new section, Günther Otto Schenck. Already in those days Jochen worked on Photochemistry. He finished his Doctoral Thesis (“Photochemical and thermal transformations of some colchicine alkaloids and their lumi-compounds”) in Mülheim and defended it in Göttingen in June 1964.

With the incorporation of Dietrich Schulte-Frohlinde in 1970, and later on (1976) Kurt Schaffner as directors in the section, Hans Jochen Kuhn entered into fruitful scientific collaborations with both groups.

In the mean-time, and after preliminary meetings, the European Photochemical Association (EPA) held its official inaugural meeting in Strasbourg on September 10th 1970 with the participation of representatives of ten countries. On the occasion of the Sixth International Conference on Photochemistry at the University of Bordeaux (6-8 September 1971), the EPA founding members decided to

issue an Annual World List announcing scientific meetings on photochemistry and related topics as well as workshops and other educational opportunities in the field, to be sent to all EPA members and to other interested parties. This was the germ of what would become the EPA Newsletter. The General Council of the EPA, including all the members of the Association, was convened on July 25th 1972 in Reading on the occasion of the joint Royal Chemical Society–EPA meeting. The new Scientific Council elected the Executive Committee with Kurt Schaffner (Geneva, later Mülheim) as chairman. Ernst A. Koerner von Gustorf (Radiation Chemistry Section of the MPI in Mülheim) was designated Special Secretary for gathering and disseminating information.¹ Hans Jochen Kuhn started already in those days helping to issue the initial newsletters (proper letters sent in envelopes per post) of the recently created EPA.

Besides, and in order to outline how a career can be determined by proper timing and an understanding and supportive colleague, the following story: in 1973, Tito Scaiano and one of us (SEB) were both Associate Professors at the new University of Rio Cuarto in the middle of the Argentinian Pampas. Tito had become a member of EPA during his postdoctoral fellowship in the UK and received the “preliminary” EPA Newsletters in Rio Cuarto. SEB also joined EPA. Very valuable information on the developments in the field could be obtained reading the Newsletters. At the end of 1974, when the political situation in Argentina, in particular at the Universities, turned extremely difficult and personally dangerous, Tito left for Ottawa to Keith Ingold’s lab and SEB rejoined Julian Hecklen’s lab at Penn State University. During a research fellowship on July 1976 in Otto Strausz’s group in Edmonton (Canada), SEB started looking for a more stable position and, as a member of EPA, she wrote to Hans Jochen Kuhn, the editor of the Newsletters in Mülheim, who in turn handed the letter and CV over to Kurt Schaffner, just appointed director at the institute. He invited SEB to join the new section on photochemistry. The story lasted more than 30 years.

Jochen and his wife Dietlind received the small Braslavsky family in October 1976 with open arms and made the initial difficult adaptation times much easier. Her daughters went to the same elementary school as Kuhn’s children, Arvid and Astrid. Many years followed of a very friendly joint participation in Schaffner’s section with several collaborations, among them the writing of the widely used technical reports on actinometers for IUPAC.²

In his own work, Hans Jochen Kuhn became an expert on the photochemistry of organic compounds in aqueous solution. Moreover, inspired by a topic of Dietrich Schulte-Frohlinde's photochemical work, he published a review on stilbenes with one of us (HG).³



Photo taken during a brainstorming week of Schaffner's group in October 1980 at Schloss Ringberg, owned by the Max Planck Society, near Tegernsee in Bavaria; backrow: from left: Horst Kisch, Hans Jochen Kuhn, Martin Demuth, Kurt Schaffner; front row: Horst Hermann, Friedrich-Wilhelm Grevels, Alfred Ritter, Manapurathu V. George, Alfred R. Holzwarth, Werner Klotzbücher (foto taken by SEB, who was also part of the group).

The first printed issue of the EPA Newsletters saw the light in January 1978. Jochen Kuhn was the first Managing Editor and remained in that position until 1999, when he was already retired. His organizational and technical abilities, his networking, his knowledge, and his very soft and understanding manners were essential for the success of the EPA Newsletters. Through the Newsletters the association itself became a melting point for scientists from east and west, north and south, with colleagues from countries with different political regimes and/or at different stages of scientific development, not only receiving but also prominently writing articles for the EPA Newsletters. They were vital in times of the cold war with not many communication channels between the scientists from East and West European Countries. The promotion of

photochemical meetings and schools, the publication of Thesis abstracts, the description of the photochemical labs and equipment available, the listing of opening positions, etc., were all fundamental tools for the enhancement of communication, for the creation of national photochemical societies and, essentially, for the understanding between colleagues in all countries where some photo-science was carried out.

Without the engagement and dedication of Hans Jochen Kuhn to the production and publication of the Newsletters, the EPA itself would not be the success story it turned to be.⁴

We keep very warm memories of Jochen's personality and friendship.

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CONFERENCE REPORT

Conference report: 27th Lecture Conference on Photochemistry, Kiel – online

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The *27th Lecture Conference on Photochemistry* of the GDCh Division of Photochemistry was held on September 14 and 15, 2020. The event was planned to take place at the University of Kiel; however, because of the Corona pandemic and the anticipated regulations and travel restrictions the organizers decided to conduct the conference in an online format. Even under these circumstances, more than 120 participants from universities, research institutes and industry joined this meeting to discuss recent results and developments of photochemical and photophysical research. Likewise, the scientific program clearly showed that the photochemistry community readily accepted the new format. In fact, an overall collection of 10 invited lectures, 24 short oral contributions and more than 90 posters testified to the vibrant and interdisciplinary flavor of photochemistry, covering a number of aspects from topical research fields.

After the welcome address and opening remarks from the host, Rainer Herges, the scientific part of the conference began with a special opener presented by Uwe Meierhenrich, University of Nice. He was a member of the ESA Rosetta-Philae team that directed a robotic lander to touch down on the comet 67P/Churyumov-Gerasimenko in November 2014. Prof. Meierhenrich reported about the thrilling task to detect and analyze the products arising from the steady UV irradiation of ice, NH₃, CO, CO₂ and small dust particles of the comet. Specifically, mass spectrometric analysis revealed amino acids, aldehydes and ribose in cometary matter, thus confirming the photochemical experiments under artificial laboratory conditions.

The conference featured a broad section on synthetic photochemistry, opened by Thorsten Bach (TU Munich), who reported about impressive enantioselectivities of [2+2] photocycloadditions, as well as in photoinduced rearrangements and deracemization reactions. Ullrich Jahn

(Prag) showed that direct C-H amination reactions, that are usually very difficult to perform, may be accomplished efficiently and selectively with photoredox-catalyzed reactions that even enable the direct amination of aliphatic and aromatic hydrocarbons. Beyond basic academic research, photocatalysis has found its way into applied sciences with applications in synthesis, even in pharmaceutical industry. However, the conversion of strong bonds or ionic reactions still pose demanding challenges, that have been successfully addressed by Burkhard König (Regensburg), who presented elegant and synthetically useful solutions for selected problems in this field. Overall, the lectures from this vibrant field convincingly showed that photochemistry has become an important discipline in organic synthesis.

Light has been employed as a useful tool for the treatment of diseases already for a long time. As a new development in this field, photopharmacology uses photoswitchable drugs that enable the controlled activation of biological functions directly at the target, e.g. in tumor cells, without affecting the healthy tissue. In this context, Andrew Woolley (Toronto) demonstrated with selected examples that along with the azobenzenes, photochromic acylhydrazone derivatives may be employed as photoswitchable drugs. Another spectacular application of photoswitches was presented by Francisco Raymo (Miami) who showed that the motion of intracellular objects can be detected and monitored by a combination of photoswitchable fluorescent probes and ultrahigh-resolution fluorescence microscopy.

The session Photochemistry of Materials was highlighted by prominent representatives from the field. Namely, Krzysztof Matyjaszewski (Carnegie Mellon) and Yusuf Yagci (Istanbul) reported about recent trends and remarkable developments of the photochemically induced atom transfer radical polymerization (ATRP). To add to that, Tom Vosch (Copenhagen) presented his results on DNA stabilized silver nanoclusters with very useful photophysical properties, such as optically activated delayed fluorescence, upconversion fluorescence or NIR emission.

Contributions from chemical industry constitute a traditional element of this conference. Bernd Schäfer (BASF) reported about chemical and technical aspects that are crucial for industrial production with photoinduced *flow* bromination reactions. In addition, Martin Schwentenwein (Lithoz GmbH) presented concepts for photopolymerization-based shaping techniques that can be employed for 3D printing of ceramic and metal components.

Separate virtual meeting rooms were installed to organize the online poster session. Although such a format can certainly not substitute the real experience of a poster presentation, it provided a good opportunity for a scientific discussion between presenter and visitor at the virtual poster in a face-to-face interaction.

The final highlight of the conference was the awards ceremony. Firstly, Michael P. Kathan (Berlin) und Yusen Luo (Jena) received the Albert-Weller Award from the *Gesellschaft Deutscher Chemiker* and the *Deutsche Bunsen- Gesellschaft für Physikalische Chemie* in recognition of their outstanding doctoral theses within the field of photochemistry/spectroscopy. Finally, the Kiel Nano, Surface and Interface Science (KiNSIS), University of Kiel, awarded the Diels-Planck-Lecture to Michael Grätzel (Lausanne) in appreciation of his outstanding scientific contributions. After the award ceremony, Prof. Grätzel presented the Diels-Planck-Lecture with the title "*The stunning rise of perovskite solar cells*".

The *28th Conference on Photochemistry* will be held in September 2022 at the Heinrich Heine University of Düsseldorf.

CONFERENCE ANNOUNCEMENTS



**ICP
2021
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International Conference on Photochemistry

18-23 July 2021 Virtual Conference

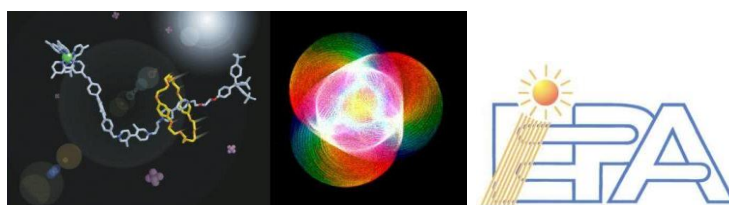
Plenary Speakers

- Chi-ming Che, **University of Hong Kong**
- Roberta Croce, **Vrije Universiteit Amsterdam**
- Thomas Ebbesen, **University of Strasbourg**
- Leticia Gonzalez, **University of Vienna**
- Katia Heinze, **University of Mainz**
- Kris Mc Neill, **ETH Zürich**
- W. E. Moerner, **Stanford University**
- Garry Rumbles, **NREL**
- Hiroko Yamada, **Nara Institute of Science and Technology**



Due to the current pandemic, the conference will take place fully online
EPA members will benefit from a discounted registration fee
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