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# *CONTENTS*

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INTERNATIONAL
YEAR OF LIGHT
2015

# EDITORIAL

## President's Letter

Dear Colleagues,

Last time I wrote my President's letter, I commented on the weather; we tend to talk a lot about the weather in the UK as we have so much of it! As I write summer is arriving, bringing with it the annual exodus of undergraduates so our campus will be going quiet fairly soon.

I went out for lunch with the family recently to a restaurant owned by a good friend of ours (stick with me, this is going somewhere!), and we were discussing his recent refurbishment. He had installed LED lighting to reduce energy consumption, but found the light too "cold"; he therefore had bought some translucent paint and had painstakingly painted each bulb to give a warmer hue. Light and the perception of food seemed an appropriate theme given this is the UNESCO Year of Light. I then got to thinking about the photostability of his paint, and started wondering when he would need to again get out his stepladder and paintbrush – photochemistry all around us.

At the recent Photochemical and Photobiological Sciences ownership board meeting we met the new Executive Editor, Andrew Shore. The journal seems to be doing well, with an impact factor which stands up well relative to other journals in the sector. Many thanks to all colleagues who are supporting the journal though their submission of high quality manuscripts.

The EPA website will be undergoing a redesign in the coming months, which should enhance the user experience. As always, feedback and input from the membership is encouraged and welcomed. The Year of Light webpage should also be posted shortly; if members have any news to be added please contact the Webmaster.

This coming year, the EPA will be administering or assisting in the selection of three awards in the area of photochemistry. These are the *EPA-PPS Prize* for the most highly cited paper published in PPS during the previous two calendar years, the *EPA Prize for Best PhD Thesis in*

*Photochemistry* published during the previous two calendar years, and the *Porter Medal*, in cooperation with our Inter-American and Asian/Oceanian photochemistry association counterparts, I-APS and APA. Calls for the nominations for the latter two prizes appear later in the newsletter; please think about this and give your nominations to the Committee.

Finally, a reminder about our Facebook page; please "like" us to keep up-to-date with conferences, job opportunities and general news.

*Dr. David Worrall*
*Loughborough University*

## PUBLICATIONS

### Broadband Visible Light-Harvesting Triplet Photosensitizers

*Jianzhang Zhao*

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Triplet photosensitizers are versatile compounds and have been widely used in photocatalysis,[1] photovoltaics, photodynamic therapy,[2] and more recently the triplet-triplet-annihilation upconversion.[3] However, the conventional triplet photosensitizers are based on the single chromophore profile, i.e. there is only one light-harvesting chromophore in the photosensitizer molecule.[4] As a result, usually there is only one major absorption band in the visible light spectral range. This feature is a clear disadvantage if a broadband light source was used, such as solar light. Therefore, it is highly desired to develop new triplet photosensitizers which show broadband visible light-harvesting ability.

In order to address the above challenge, we devised multi-chromophore triplet photosensitizers based on the Förest-resonance-energy-transfer (FRET) and spin converter.[4] FRET was widely used in singlet excited related research, such as light-harvesting molecular arrays and fluorescent molecular probes.[5] With FRET, broadband visible light and funnelling of the singlet excited state energy to the energy acceptor can be achieved. However, FRET was rarely used for preparation of broadband visible light-harvesting triplet photosensitizers.[4]

The designing rationales of FRET-based broadband visible light-absorbing triplet photosensitizers are like this.[4] Two different visible light-absorbing chromophores, which give different absorption wavelength, are connected together by covalent bond (or supramolecular interaction, such as hydrogen bonding), the chromophores should selected in such a way that FRET is ensured. Moreover, the singlet energy acceptor should be a spin converter, i.e., a chromophore with intersystem crossing (ISC) ability for triplet state formation. Thus, such as molecular assembly (or dyad) will show broadband visible light-absorption and the photoexcitation energy will be converted to the triplet excited state energy. It should be pointed out that with these multi-chromophore molecular assemblies, a few photophysical processes probably exist at the same time, such as FRET, photo-induced electron transfer (PET, or charge separation, CS), or charge recombination (CR), etc. Moreover, photophysical process which is not found in the singlet excite state-related FRET molecular assemblies may be encountered, such as the ping-pong energy transfer and triplet state equilibrium (see later section), etc.[4]

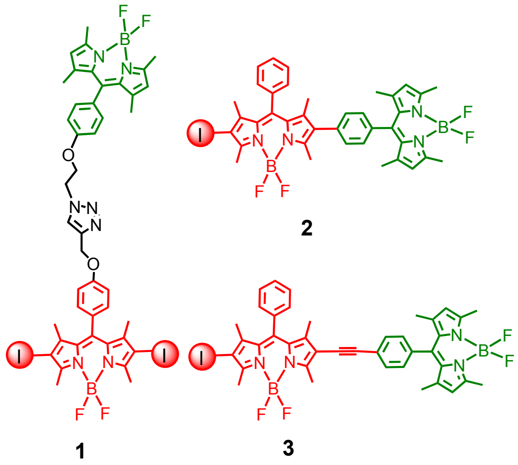
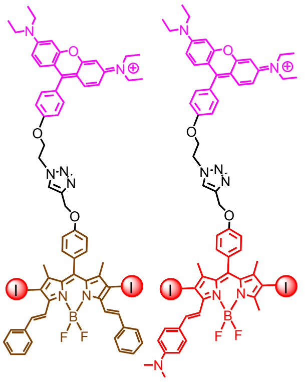


**Figure 1.** Bodipy-diiodoBodipy dyads showing broadband visible light-absorption. The iodine atoms are highlighted.[6]

Firstly we designed Bodipy-iodoBodipy dyads **1**-**3** (Figure 1).[6] Bodipy was selected as the visible light-harvesting chromophore due to its strong absorption of visible light and inhibited non-radiative decay channel. IodoBodipy gives slightly red-shifted absorption and fluorescence as compared with that of Bodipy, thus FRET process is envisioned for the dyads. Moreover, the iodoBodipy unit in the dyad **1**-**3** can be considered as the singlet energy acceptor, as well as the spin converter. Thus the singlet excitation energy was funnelled to the iodoBodipy unit and triplet excited state was formed due to the heavy atom effect of the iodine atoms in the spin converter unit.

The FRET was confirmed by the quenching of the fluorescence of the energy donor part. We also confirmed that the PET is not significant, by calculation of the Gibbs free energy changes of the electron transfer process. Using nanosecond transient absorption spectroscopy, we found that the triplet excited state of the dyads is not confined on one of the components, rather it is delocalized on the two units of the dyads.[6]

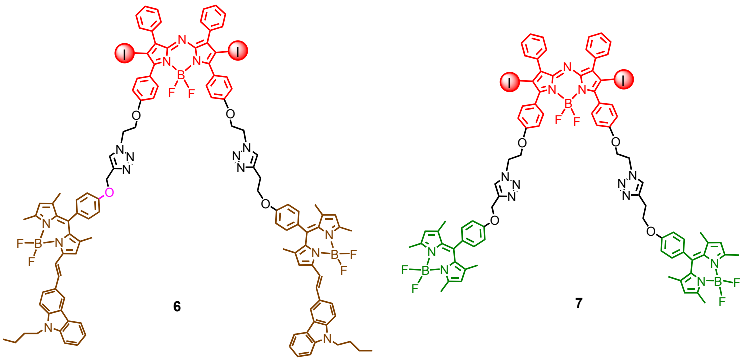


**4** **5**

**Figure 2.** Broadband visible light-absorbing Rhodamine-diiodoStyrylBodipy triplet photosensitizers **4** and **5**. The iodine atoms are highlighted.[7]

In order to further expand the absorption bands of the dyad triplet photosensitizers, we also used rhodamine and diiodoStyrylBodipy to construct triplet photosensitizers **4** and **5**, in which the rhodamine antenna absorbs at ca. 560 nm, whereas the diiodoStyrylBodipy part absorbs at 640 nm.[7] Thus broadband visible light-absorption was attained. We used the triplet photosensitizers **4** and **5** for photoredox catalytic organic reactions (oxidation/[3+2] cycloaddition/aromatization tandem reaction with tetrahydroisoquinoline derivatives to construct pyrrol[2,1-*a*]isoquinolines) and we found that these broadband visible light-absorbing triplet photosensitizers are more efficient that the mono-chromophore based triplet photosensitizers.

The rhodamine moieties in compounds **4** and **5** are slightly special as compared with the normal rhodamine in that no spirolactam opened amide from exist, which may complicate the photophysical studies of the dyads **4** and **5**. The reason is due to the judiciously selected building blocks so that no carboxyl moiety is introduced to the rhodamine part. The photophysical properties of the dyads were studied with steady state and time-resolved spectroscopy. FRET was confirmed with femtosecond transient absorption spectroscopy. Nanosecond transient absorption spectroscopy indicated that the triplet state is exclusively confined on the styrylBodipy part, there is no triplet state equilibrium, which is different from that of dyads **1** – **3**.[7]



**6**

**7**

**Figure 3.** Broadband visible light-absorbing Rhodamine-diiodoStyrylBodipy triplet photosensitizers **6** and **7**. The iodine atoms are highlighted.[8]

Following similar strategy, we prepared Bodipy-diiodoazaBodipy triads **6** and **7**, which show broadband visible light absorption in the range of 500 – 700 nm.[8] The triplet state of the triads is localized on the diiodoazaBodipy part.

For the dyads **1** - **7**, the spin converter is based on heavy atom-attached chromophore (singlet energy acceptor). We also show that $C_{60}$ can be used in heavy atom-free broadband visible light-absorbing triplet photosensitizers. Thus we prepared Bodipy-$C_{60}$ conjugations **8** – **11** (Figure 4).[9]

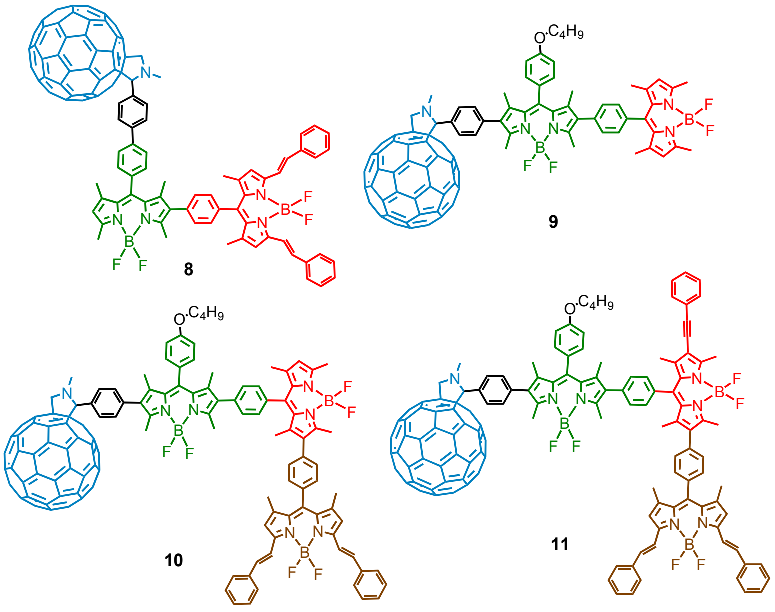


**Figure 4.** Broadband visible light-absorbing $C_{60}$-Bodipy conjugates as triplet photosensitizers **8** – **11**. The $C_{60}$ moiety is the singlet energy acceptor and the spin converter.[9]

In conjugations **8** – **11**, there are two or three different Bodipy chromophore in each compound, thus broadband visible light-absorption was resulted. $C_{60}$ is the singlet energy acceptor part, the photoexcitation energy was funneled to the $C_{60}$ part. The efficient ISC of $C_{60}$ part produce the triplet excited state of the conjugates. Interestingly, we found that the $T_1$ excited state of the conjugations is either localized on the $C_{60}$ part, or the Bodipy antenna. It is dependent on the triplet state energy levels of the antenna. For conjugate **9**, the $T_1$ state is localized on the $C_{60}$ part. For conjugates **8**-**11**, however, the triplet excited state is localized on the styrylBodipy part. This conclusion is dependent on the nanosecond transient absorption spectroscopy. We used these broadband visible light-absorbing $C_{60}$-Bodipy conjugates as triplet photosensitizer for photoredox catalytic organic reaction of aerobic oxidative hydroxylation of aryl boronic acid, and the photocatalytic efficiency is much higher than the conventional photocatalysts such as $Ru(bpy)_3Cl_2$ or the $Ir(ppy)_3$.

In summary, broadband visible light-absorbing triplet photosensitizers are promising to be used in various areas such as photodynamic therapy (PDT), photocatalysis (such as $H_2$ production or photoredox catalytic organic reactions), and triplet-triplet annihilation upconversion.

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# Azobenzene: Teaching an old dog some new tricks

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## Introduction

The past decades have witnessed an increasing research effort in the development of light-responsive molecular systems and materials based on photochromic compounds such as spiropyrans, diarylethenes, and azobenzenes (ABs). Although the later have been known to undergo *E*-*Z* isomerization upon UV and visible light irradiation for almost 80 years,[1] and several thousands of scientific papers have already been published on this topic, the azobenzene molecule is still good for a few surprises and can be taught some new "tricks", given proper molecular design and creative integration into larger functional systems. In this letter, we will present some of our latest efforts in both of these directions, in particular with the inherent optimization of the photoswitch by *ortho*-fluorination (first section), the synthesis of covalent multiazobenzene architectures undergoing drastic geometrical modification (second section), and the creation of switching self-assembled lattices at surfaces (third section).

## Optimization of azobenzenes by *ortho*-fluorination: All-visible light switches with very long-lived *Z* isomers and high photoconversions

In order to extend the scope of possible applications, it is critical that chemists optimize the intrinsic properties of their favorite photoactive compounds. The typical performance criteria of photochromic compounds are photoconversions, quantum yields of isomerization, thermal half-life of the thermodynamically less stable isomer, fatigue resistance, and last but not least, the possibility to isomerize in both directions without UV light,[2] which is often damaging and penetrates only partially through most media.

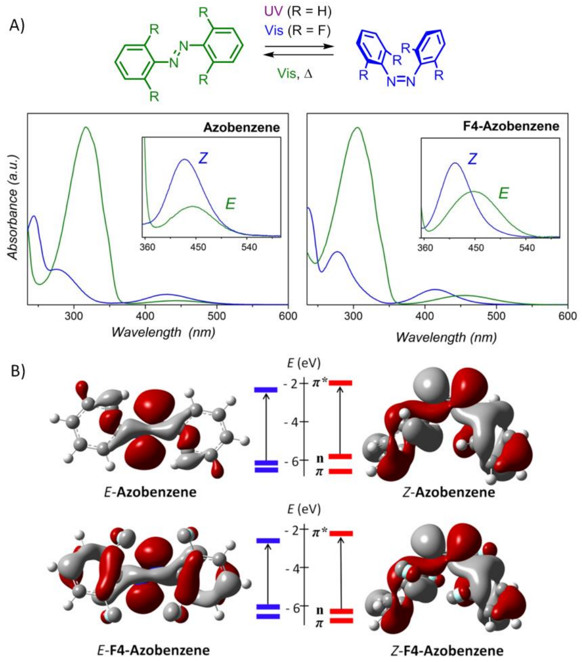

**Figure 1.** Comparison of electronic transitions in unsubstituted azobenzene (left) and *ortho*-tetrafluoroazobenzene (right). A) UV-vis absorption spectra in acetonitrile at 25 °C and B) energetic diagram of the π, n, and π* orbitals, and representation of the n orbitals (HOMOs) calculated at the B3LYP/6-31G level of theory (arrows highlight n→π*transitions).

Azobenzene is clearly a superior photoswitch in term of fatigue resistance, however, all the other criteria are typically not optimal. For example, although the *E*→*Z* photoconversion is typically high to very high (90-95%), the reverse *Z*→*E* photoconversion is often limited to 80-85%; the quantum yields are commonly not higher than 50%; the *Z* isomer persists only for a few hours to days in solution; and finally, UV light is typically essential to trigger the *E*→*Z* isomerization.

In order to tackle the visible light activation issue, and following pioneering work by Herges[3] and Woolley,[4] we decided to explore the possibility to separate the *E* and *Z* isomers' n→π* absorption bands, which typically overlap in ABs (see Figure 1A). We anticipated that introducing electron withdrawing groups (EWG) *ortho* to the N=N would decrease the electronic repulsion occurring between the N lone pairs in the *Z* form, therefore stabilizing its n-orbital and eventually increasing the n-π* gap of the *Z* isomer (compared to the n-π* gap of the *E* isomer). Encouraged by DFT calculations (see Figure 1B), we opted for F atoms, which, in addition to being σ-withdrawing and π-donating at the same time, are rather small and therefore do not significantly twist the typically planar *E* isomer.[5,6]

As expected, the *E* and *Z* isomers' n→π* absorption bands of *ortho*-tetrafluoroazobenzene significantly split with a 40 nm separation of the absorption maxima (see Figure 1A). This feature allows for triggering *E*-*Z* isomerizations with visible light only (green for *E*→*Z* and blue for *Z*→*E*). Further EWGs (such as ester groups) introduced *para* to the N=N work in concert with the *ortho*-F and lead to a superior photoswitchable compound, which exhibits a 50 nm separation of the n→π* bands. Such a high separation makes possible to address both isomers selectively and as a consequence very high photoconversions (up to 97%) can be reached in both directions. On the contrary, electron donating groups (EDGs) such as N-acyls introduced in *para*-positions counterbalance the effects of the *ortho*-fluorine atoms by pushing electron density into the N=N bond. The separation of the n→π* bands is reduced to 22 nm and eventually the two isomers cannot be selectively excited in the visible range, leading to only 69% *Z*→*E* photoconversion (when irradiated at 440 nm).

A very attractive, though totally unexpected additional feature of F-ABs is the very high thermal stability of the *Z* isomers: a half-life ($\tau_{1/2}$) of 2 years (!) measured at room temperature in DMSO *vs.* a few days for unsubstituted ABs. This effect can be partly attributed to the pronounced stabilization of the n-orbital of the Z isomer (while the n-orbital of the transition state is less stabilized), which eventually leads to a larger barrier for the thermal *Z*→*E* reaction and place ortho F-ABs among the most stable azobenzenes ever reported.

Noteworthy, in addition to offering visible-light addressability, isomerizing ABs *via* $n \rightarrow \pi^*$ transitions is also quite efficient (quantum yields of typically $\Phi = 0.3\text{-}0.5$ *via* $n \rightarrow \pi^*$ *vs.* $\Phi = 0.1\text{-}0.2$ *via* $\pi \rightarrow \pi^*$ transitions).

In summary, *ortho*-fluoroazobenzenes constitute a new class of photoswitches with outstanding properties. The high level of bistability combined with the possibility to isomerize without UV-light opens many possibilities in life-sciences, for example in the growing field of photopharmacology,[7] whose aim is to activate/deactivate drugs with (ideally NIR) light, but also in materials science, where many photo-responsive systems would benefit from sun-light harvesting or activation.

### Covalent multiazobenzene architectures: Maximizing the photodeformation of individual molecules

Integrating azobenzene photoswicthes into the backbone of oligomers and polymers with well-defined shapes offers some interesting possibilities, in particular for amplifying mechanical motion of single macromolecules and creating cooperative systems, where only a few switching event triggers dramatic changes in a particular self-assembly.

Our efforts in that direction focused on the integration of ABs into rigid-rod polymers and monodipserse foldamers (see Figure 2).

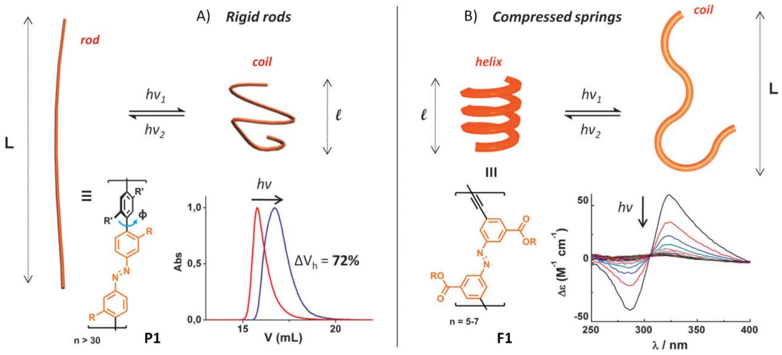

**Figure 2.** Large photodeformation of anisotropic macromolecules. A) Poly(*para*-phenylene)s rigid rods' light-induced shrinking, accompanied with a decrease in their hydrodynamic volume of $\Delta V_h = 72\%$. B) Oligo(*meta*-phenylene ethynylene) chiral foldamers' light-induced extension, accompanied with the vanishing of circular dichroism signals.

Rigid rods such as poly(paraphenylene) derivative *E*-**P1** are anisotropic objects displaying high aspect ratio. Therefore, upon *E*/*Z* isomerization the rods significantly shrink and stretch in response to UV and visible light, respectively.[8] The structural modification is accompanied with a marked decrease in their hydrodynamic volume ($\Delta V_h = 72\%$), as measured by light scattering, which list among the highest level of contraction reported for AB-based polymeric architecture. Large twist angles (Φ) were introduced into the rigid scaffold in order to electronically decouple the chromophores, an approach allowing for quantitative photoswitching in linear multi-azobenzene architectures.[9]

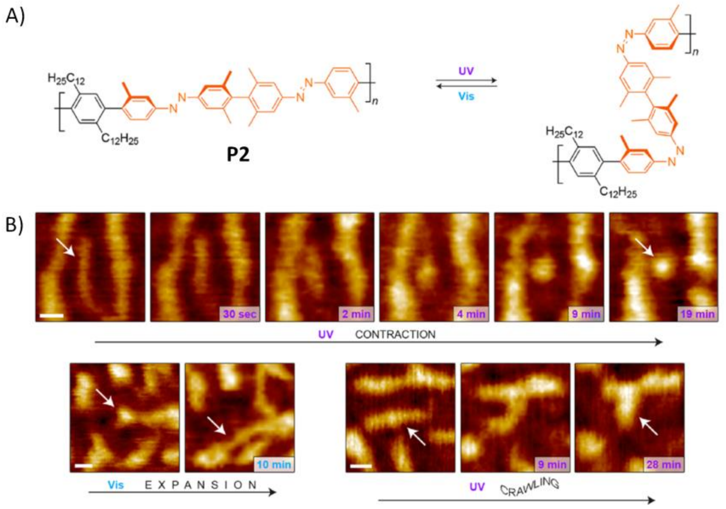

**Figure 3.** Photoinduced motion of single macromolecules at surfaces. A) Molecular structure of polymer **P2** and B) Surface force microscopy snapshots showing UV-induced contractions, blue light-induced expansions, and UV-induced contraction accompanied by crawling of single polymer chains (scale bars 20 nm).

Such articulated macromolecules could be isolated on templated surfaces and their photomovement observed at the single molecule level[10,11] (see Figure 3). The dramatic contraction/expansion indirectly measured in solution by light scattering could be directly visualized by scanning force microscopy. In addition, more complex motion such as crawling events accompanying light-induced isomerization at the surface could also be identified. Taking these structures to the next hierarchical level, *i.e.* supramolecular assemblies, is currently underway.

On the other hand, synthetic molecular helices or *foldamers* such as oligo(*meta*-phenylene ethynylene) **F1** experience an efficient helix to coil transition as a result of the *E*→*Z* isomerization of the embedded azobenzenes.[12-15] After optimizing the number[12] and location[14] of azobenzene photochromes per turn as well as the length of the oligomers,[12,14] quantitative unfolding could be achieved, as observed by vanishing circular dichroism signals. Remarkably, the light-induced denaturation of the helices overcomes both intramolecular stacking interactions and solvophobic effects. In analogy to the macroscopic world, these multiazobenzene foldamers can be viewed as compressed molecular springs releasing potential energy upon unloading.

Insight into the mechanism of the foldamers' denaturation was gained by incorporating only two azobenzene switching units within the foldamer backbone. By comparing the quantum yields of successive switching events a *cooperative* process could be uncovered in case when the azobenzene units are located near the core of the foldamer since the first switching event facilitates the subsequent one by intermediate unfolding resulting in a lowering of the isomerization barier.[13] In another foldamer series energy transfer from donor to acceptor azobenzene units was used to localize the excitation energy either at the core or at the periphery of the foldamer thereby initiating unfolding either from the inside-out or vice versa.[15] Such optimized photoswitchable foldamers could be used to design efficient photoswitchable dual catalysts,[16] where two units should be in close contact to be active, while light-induced denaturation would deactivate the catalyst.

## Switching self-assembled lattices at surfaces

Interfacing molecular switches with conducting and semiconducting surfaces while preserving their photoactivity is an important challenge for the construction of light-responsive hybrid systems. Our approach relies on *physisorbed* self-assembled monolayers, with azobenzenes either oriented up-right (see Figure 4) or in a flat fashion (see Figure 5). Due to the large geometrical difference between the structures of the *E* and Z isomers, a necessary prerequisite for photoisomerization to occur in azobenzene-containing molecular layers is to provide sufficient free volume to the system. Decoupling the photochromic unit electronically from the conducting surface by avoiding a direct contact is also crucial to preserve the photoisomerization ability.

In our up-right oriented approach[17] (see compound **3**) we used a terfluorene platform, equipped with COOH groups to direct the self-assembly via H-bonds and dodecyl chains to favor physisorption on highly oriented pyrolitic graphite (HOPG). This design provides free-space to the photoswitch and by scanning tunneling microscopy (STM) measurements at the solid-liquid interface we could confirm the self-assembly of **3** into linear polymers zipped together *via* alkyl chains' interdigitation. Upon UV-light irradiation, we observed a progressive change in the packing of the monolayer, indicating the transformation of the 2D crystal from *E*- to *Z*-azobenzenes.

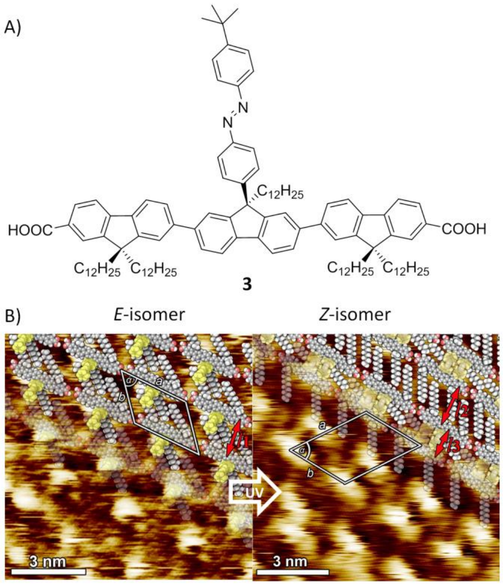

**Figure 4.** Photoswitching self-assembled physisorbed monolayers. A) Molecular structure of the terfluorene platform supported azobenzene derivative *E*-**3** and B) STM height image of **3** at the HOPG-phenyloctane interface in its *E*- (left) and *Z*-isomer (right), obtained upon UV irradiation for *ca.* 1 h.

The monolayer could be switched back *via* Z→E isomerization induced by blue light. However, in view of the dynamic nature of the system involving continuous desorption/adsorption and considering the large differences in the dimensions of the crystal lattices (unit cells) it is rather likely that the switching process occurs in solution and not when bound on the surface.

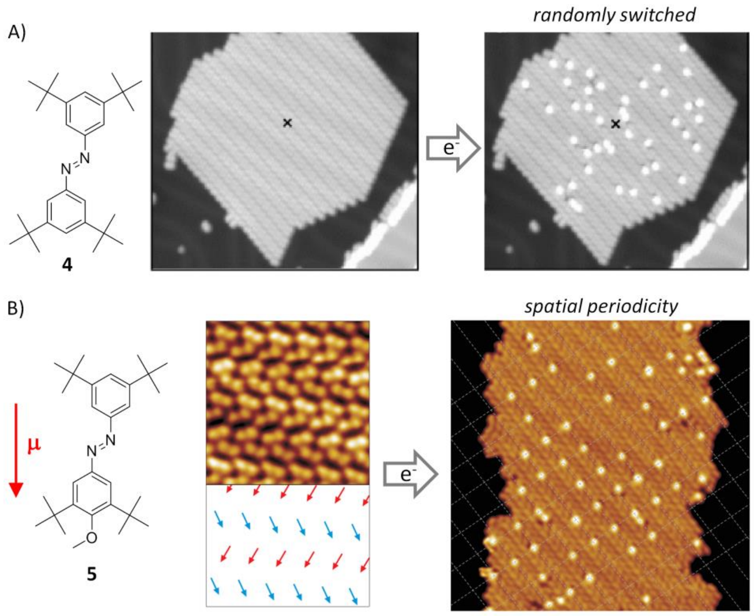

**Figure 5.** Electric field-induced isomerization of azobenzenes at surfaces. A) Electric pulses applied from the tip of a STM (localized at the cross) induce azobenzenes *E*→*Z* isomerization creating a random pattern of *Z*-isomers. B) When a dipole (μ) is introduced in the azobenzene derivative, a commensurability is established between the monolayer and the substrate, leading to the creation of a periodic array of

switched molecules upon scanning at elevated biased voltage (conditions: $10^{-10}$ mbar, 7 K, Au(111)).

In order to switch molecules in physisorbed monolayers directly at the surface without interfering desorption processes, interfaces in ultra-high vacuum environment are inevitably more suitable. Azobenzene was equipped with four *tert*-butyl "legs" in order to decouple the photochrome from the surface (compound **4**), and the resulting islands of densely packed building blocks on Au(111) analyzed by STM.[18] In that case the switching was electronically induced by the STM tip, and the *Z*-isomers appear as bright protrusions randomly located within the islands. In order to create arrays of ordered *Z*-isomers, an additional feature needed to be integrated into the switch: a permanent intrinsic *dipole*. This was achieved by attaching one methoxy group *para* to the N=N (see compound **5**).[19] Thanks to this new molecular property, a commensurability between the monolayer and the underlying substrate could be established, which defines the local switching ability of the molecules on the surface. Consequently, the same periodic lattices of *Z* isomers are created in repeated erasing and reswitching cycles. These results demonstrate a conceptually original approach to use self-assembled photoswitch arrays to simultaneously address single molecular entities on the length scale of few nanometers (nanopatterning).

Before concluding this letter, it should be emphasized that in order to create photoresponsive organic electronics, diarylethene photoswitches are arguably more promising candidates than ABs, as they require fewer free volume and therefore can be switched faster, in addition to offering a greater change in HOMO-LUMO gaps and relative levels, as recently demonstrated with the construction of light-addressable OFETs.[20,21]

## Conclusion

As illustrated in the previous sections, the azobenzene chromophore - despite being the oldest investigated photochromic family - remains attractive for creating advanced light-responsive functional systems. Thanks to molecular design and extensive structure-switch relationship studies, we were able to dramatically improve the intrinsic photoswitching properties of azobenzenes, in particular addressability with visible light, high photoconversion in both switching directions, as well as thermal half life. Furthermore, we could successfully amplify the significant geometrical changes occuring during the course of photochemical *E-Z* isomerization in an individual azobenzene unit by exploiting macromolecular architectures, such as rigid rod as well as helically folding azobenzene main chain polymers. Beyond the (macro)molecular level, we could create assemblies of azobenzene switches organized on surfaces and use them to generate periodic nanoscale patterns. Based on these examples and our experience over the past decade it is fair to conclude by comparing azobenzenes some good red wine – it get's better with age!

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# Solar light: the bridge between photocatalysis and biomass valorization

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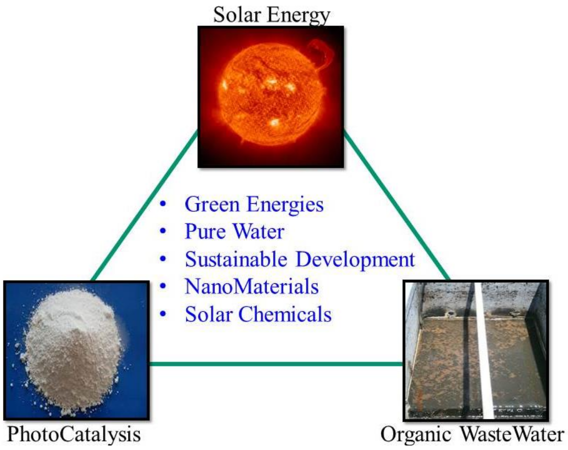
## 1. Introduction

The use of solar energy to drive organic syntheses is not a novel concept. The idea was originally proposed by Ciamician as early as 1912.[1] However, the common use of the generally accepted term *photocatalysis* and significant developments in this field properly started early in the 1970s after the discovery of water photo-induced electrochemical photolysis on a $TiO_2$ electrode by Fujishima and Honda.[2]

The utilization of heterogeneous photocatalysis to environment protection (both in the liquid and gas phase) has been extensively investigated as photoactivated semiconductors have proven activities to unselectively mineralize various types of toxic, refractory and non-biodegradable organic pollutants under mild conditions.[3,4] Closely related to selective synthesis, nanostructured photocatalytic systems have also been employed for the oxofunctionalization of hydrocarbons via selective oxidations.[5]

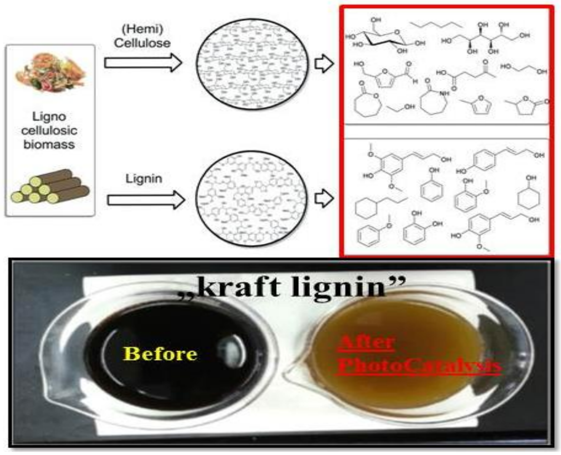
Photocatalysis, in which photons of the solar light are used to drive redox reactions to produce chemicals (e.g. fuels) is the central process to achieve the principles of green and sustainable chemistry.[6] Despite significant efforts to date, a practically viable photocatalyst with sufficient efficiency, stability and low cost is yet to be demonstrated. It is often difficult to simultaneously achieve these different performance metrics with a single material component. The ideal solid photocatalysts with multiple integrated functional components could combine individual advantages to overcome the drawbacks of single component photocatalysts. Research in this field has significantly evolved during the last four decades (especially titanium oxide, 2/3 publications up to 2015) with enhanced knowledge on mechanisms, development of new technologies for storage and conversion of solar energy, detoxification of liquid and gaseous environments, and the photocatalytic production of new materials. More recently, a new research avenue related to selective transformations of biomass and residues (which cover important issues such as renewable energies, sustainable materials and water decontamination) to high added value products has emerged as a potentially useful alternative to conventional heterogeneously catalyzed processes (Scheme 1).[7]



**Scheme 1.** Proof of concept of solar photocatalysis for chemicals production and water purification.

The effective utilization of clean, safe, renewable and abundant solar energy is envisaged to provide energy, chemicals as well as solving environmental issues in the future and an appropriate nanostructured semiconductor-photoinduced mediated biomass/waste conversion can be the key for such transformations.

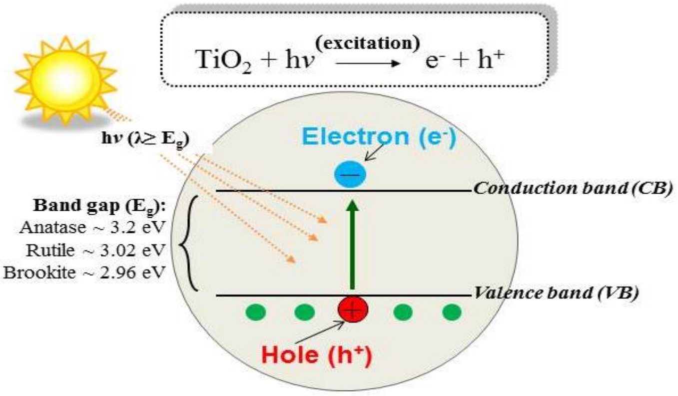
This article is intended to provide an overview of recent work conducted along the lines of selective photochemical transformations, particularly focused on heterogeneous oxidative photocatalysis for lignocellulose-based biomass valorization (Scheme 2). Future prospects and work to progress in this field will be also emphasized.



**Scheme 2.** A plethora of chemicals can be produced through lignocellulosic biomass photocatalytic upgrading

## 2. Fundamentals of heterogeneous oxidative photocatalysis

The basic principles of heterogeneous photocatalysis have been extensively reported in previous reports.[8] Briefly, a photocatalytic transformation is initiated when a photoexcited electron is promoted from the filled valence band (VB) of a semiconductor photocatalyst (e.g., $TiO_2$, ZnO, CdS) to the empty conduction band (CB) as the absorbed photon energy, $h\upsilon$, equals or exceeds the band gap of the semiconductor photocatalyst. As a consequence, an electron and hole pair ($e^-$–$h^+$) are formed (Eqs 1-4, Scheme 3). HOO• radicals (Eq. 4, Scheme 3) have also scavenging properties similar to oxygen, thus prolonging the photohole lifetime (Eqs 5-6, Scheme 3). Redox processes can take place at the surface of the photoexcited photocatalyst. Very fast recombination between electron and hole occurs unless oxygen (or any other electron acceptor) is available to trapp the electrons to form superoxides ($O_2^{\bullet -}$), hydroperoxyl radicals ($HO_2^{\bullet}$) and subsequently $H_2O_2$ (Scheme 3).



**Photon activation:** $TiO_2 + h\upsilon \rightarrow e^- + h^+$ (1)

**Oxygen Adsorption:** $(O_2)_{ads} + e^- \rightarrow O_2^{\bullet -}$ (2)

**Water Ionization:** $H_2O \rightarrow OH^- + H^+$ (3)

**Superoxide Protonation:** $O_2^{\bullet -} + H^+ \rightarrow HOO^{\bullet}$ (4)

$HOO^{\bullet} + e^- \rightarrow HO_2^-$ (5)

$HOO^- + H^+ \rightarrow H_2O_2$ (6)

$H_2O + h^+ \rightarrow OH^{\bullet} + H^+$ (7)

$R\text{–}H + OH^{\bullet} \rightarrow R^{\bullet} + H_2O$ (8)

$R^{\bullet} + h^+ \rightarrow R^{+\bullet} \rightarrow$ Mineralization (9)

Organic waste $\Rightarrow$ photocatalyst/$O_2$/ $h\upsilon \geq E_g \Rightarrow$ Intermediate(s) $\Rightarrow CO_2 + H_2O$ + Mineral Acid (10)

**Scheme 3.** $TiO_2$ photoactivation and formation of different reactive oxygen species (ROSs).

The input energy by a photo-induced step can help overcome the activation barrier in spontaneous reactions ($\Delta G < 0$) so as to facilitate photocatalysis at an increased rate or under milder conditions. Comparatively, part of the input energy is converted into chemical energy that is accumulated in the reaction products of non-spontaneous processes ($\Delta G > 0$).

Generated holes have high potential to directly oxidize organic species or indirectly via the combination with •OH abundant in water solution (Eqs 7-9, Scheme 3).[8ab]

The corresponding mineral acid of the non-metal substituent is formed as by-product (Eq. 10, Scheme 3).

### 2.1. Reactive oxygen species (ROS) in photocatalysis

A good number of reactive ROS species can oxidize a large variety of organic compounds in heterogeneous oxidative photocatalysis. These include:

*•OH (redox potential +2.81 V vs standard hydrogen electrode, SHE)*: •OH radicals act as a main component during photo-mineralization reactions, particularly for substances that have weak affinity to $TiO_2$ surface.[8ab] •OH can be produced by oxidation of surface hydroxyls or adsorbed water. For many organic compounds, the primary one-electron oxidation should be initiated by free or trapped holes.

*$O_2^{\bullet-}$ (redox potential +0.89 V vs SHE )/$HO_2^{\bullet}$*: Superoxide anions ($O_2^{\bullet-}$), easily protonated to yield $HO_2^{\bullet}$ in acidic solution (pKa = 4.8), are readily generated from molecular oxygen by capturing photoinduced electrons from semiconductor conduction band. $O_2^{\bullet-}$ species are generally less important in initiating oxidation reactions but mainly participate in total mineralization of organic compounds via reaction with organoperoxy radicals and production of $H_2O_2$ (redox potential +1.78 V vs SHE) through a $O_2^{\bullet-}$ disproportionation.

*$O_3^-$* species are obtained in reactions between the photoformed hole center on the lattice oxygen ($O_L^-$) and molecular oxygen.

*$^1O_2$ singlet molecular oxygen*: $^1O_2$ is usually formed via the energy transfer from the triplet state of a dye to molecular oxygen. It has been suggested that oxidation of $O_2^{\bullet-}$ by holes (redox potential +2.53 V vs SHE) at the $TiO_2$ surface should be a plausible mechanism to produce $^1O_2$.

Apart from the important role of ROS in photocatalytic total mineralization processes, the control and generation of ROS species is essential in heterogeneous photocatalysis to be potentially able to design and predict pathways in selective organic photocatalytic oxidations.

## 3. Chemicals from lignocellulose

Lignocellulosic feedstocks (i.e., forestry waste, agricultural residues, municipal paper waste and certain food waste residues) can be converted into a variety of useful products in multi-step processes.[9,10] However, due to the large complexity of such feedstocks, lignocellulosics have to be broken down by several processes and technologies into simpler fractions which can be converted into desired products. These include major routes such as gasification, pyrolysis and pre-treatment hydrolysis/fragmentation steps. Upon deconstruction, the obtained solid, liquid or gaseous fractions need to be upgraded via various processes which yield a plethora of chemicals.[9,10]

From a sustainability viewpoint, the development of low-temperature, highly-selective (photo)catalytic routes for the direct transformation of lignocellulosics into valuable chemicals or platform molecules (e.g. carboxylic acids, alcohols, furans, aldehydes) is of great significance.[9] These compounds can then be subsequently converted into useful products (Scheme 2). However, the selective conversion of lignocellulosics under mild conditions still remains a significant challenge owing to the high recalcitrant structure of cellulose and lignin fractions.

### 3.1. Lignocellulose valorization through photocatalysis

### 3.1.1. Photocatalytic production of hydrogen

Nanotechnology is offering a good number of possibilities for the synthesis of new and the modification of existing photocatalysts in the hydrogen economy. A large quantity of papers studied the effect of different nanostructured materials on the performance of photocatalysts, since their energy conversion efficiency is principally influenced by nanoscale properties.[11]

### *Water spliting by heterogenous photocatalysis*

In 1972 Fujishima and Honda[2] reported the splitting of water by the use of a semiconductor electrode of $TiO_2$ (rutile phase) connected through an electrical load to a platinum black counter-electrode. $TiO_2$ electrode irradiation with UV-A light caused electrons to flow from it to the platinum counter-electrode via the external circuit.

Hydrogen production by splitting of water using solar light offers a promising method for solar energy storage and photochemical conversion. The photocatalytic hydrogen production can occur when the semiconductor conduction band (CB) bottom-edge must be more negative than the reduction potential of $H^+$ to $H_2$ ($EH^+/H_2 = 0V$ vs SHE at pH = 0), while the semiconductor valence band (VB) top-edge should be more positive than the oxidation potential of $H_2O$ to $O_2$ ($EO_2/H_2O = 1.23$ eV vs SHE at pH = 0) for $O_2$ production from water to occur. This theoretical minimum band gap for water splitting of 1.23 eV corresponds to light of about 1100 nm.

Combinatorial methods have been developed and proved as a suitable way for rapid selection of nanophotocatalysts.[12] However, no semiconducting material has been prepared to be able of catalyzing the overall water splitting under visible light with quantum efficiency larger than the commercial application limit of 30% at 600 nm.[13]

With the aim of directly utilize solar light in the open atmosphere, a compound parabolic concentrator (CPC)-based photocatalytic hydrogen production reactor was recently designed by Jing et al.[14] Efficient photocatalytic hydrogen production under direct solar light was accomplished by coupling a tubular reactor with the CPC concentrator. This demonstration drew attention for further studies in this promising direction. Nevertheless, both for material and reactor design, reduction of cost will have to be given special priority, before the final utilization of semiconductor-based photocatalytic hydrogen generation.[15]

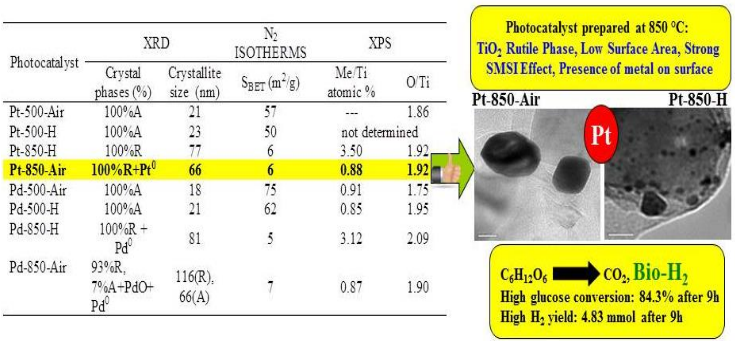
### *Photocatalytic reforming of lignocellulose-based organic wastes: bio-hydrogen production*

Biomass sources have been utilized for the sustainable production of hydrogen.[16,17] Several processes have been developed for this purpose (e.g., steam gasification,[18] fast pyrolysis,[19] and supercritical conversion[20]). However, these processes require drastic reaction conditions including high temperatures and/or pressures and consequently imply high costs. In comparison to these energy consuming thermochemical processes, photocatalytic reforming may be a good approach as this process can be performed at room temperature, atmospheric pressure and driven by sustainable sunlight. Producing hydrogen by photocatalytic reforming of renewable organic wastes (biomass) may also be more practical and viable than that of photocatalytic splitting of water due to its potentially higher efficiency.[21] Water splitting processes are relatively low efficient as limited by the recombination reaction between photogenerated electrons and holes.[22] The thermodynamics of photochemical water splitting were investigated in detail by Bolton et al.[23] who concluded that it is possible to store a maximum of approx. 12% of the incident solar energy in the form of hydrogen, allowing for reasonable losses in the electron transfer steps and the catalytic reactions of water oxidation and reduction.

Lignocellulose-derived compounds can serve as sacrificial agents (electron donors) to reduce the photocatalyst recombination $e^- - h^+$ rate. A large variety of organic compounds (most of them model compound of lignocellulose structure, e.g.: alcohols, polyols, sugars, aromatic compounds as well as organic acids) have been used as electron donors for photocatalytic hydrogen production.[24] As previously mentioned, one of the major drawbacks of semiconductor photocatalysts, especially those involving photoinduced hydrogen production from water, is their relatively low efficiency, which is mostly limited by the fast recombination reaction rate between photopromoted electrons and holes. One way to suppress or retard this recombination rate is with the use of electron donors as sacrificial agents, the role of which is to react irreversibly with the photogenerated holes and/or oxygen thereby increasing the rate of hydrogen production.

Pioneer studies in biomass photocatalytic reforming were conducted in 1980.[25] Kawai and Sakata reported that hydrogen could be generated from carbohydrates in presence of $Pt/RuO_2/TiO_2$ hybrid material and under 500W Xe lamp irradiation. They also subsequently reported that hydrogen could be generated under identical conditions from other biomass sources including cellulose, dead insects, and waste materials.[26] These studies demonstrate the feasibility of the photocatalytic production of hydrogen from biomass.

Glucose partial photocatalytic oxidation in liquid phase gave strong fundaments for a new proof of concept of a low environmental impact technology related to biomass valorization (organic wastes) by a photocatalytic selective oxidation process. As one selected good example of an interesting basic and promising application science is the case of photocatalytic wet reforming of glucose solution to produce hydrogen which was possible (mostly) due to the strong metal support interaction effect (first report in the open literature for this kind of process) what it's found in a series of photocatalysts prepared by one of the methodologies (the combination of ultrasound-assisted sol-gel with a high-temperature redox post-treatment) (Scheme 4).[24b]



| Photocatalyst | XRD | | $N_2$ ISOTHERMS | XPS | |
|---|---|---|---|---|---|
| | Crystal phases (%) | Crystallite size (nm) | $S_{BET}$ ($m^2/g$) | Me/Ti atomic % | O/Ti |
| Pt-500-Air | 100%A | 21 | 57 | --- | 1.86 |
| Pt-500-H | 100%A | 23 | 50 | not determined | |
| Pt-850-H | 100%R | 77 | 6 | 3.50 | 1.92 |
| **Pt-850-Air** | **100%R+$Pt^0$** | **66** | **6** | **0.88** | **1.92** |
| Pd-500-Air | 100%A | 18 | 75 | 0.91 | 1.75 |
| Pd-500-H | 100%A | 21 | 62 | 0.85 | 1.95 |
| Pd-850-H | 100%R + $Pd^0$ | 81 | 5 | 3.12 | 2.09 |
| Pd-850-Air | 93%R, 7%A+PdO+ $Pd^0$ | 116(R), 66(A) | 7 | 0.87 | 1.90 |

**Scheme 4.** Nano-engineering of new nobel metal-based photocatalysts for glucose wet reforming hydrogen production. Two-step photocatalysts preparation: a. ultrasound-assisted sol-gel method, and b. high-temperature post-redox treatment.

Taking into account the lowering cost for solar-to-$H_2$ energy conversion, polluting byproduct from industries, the low-cost renewable biomass from animals or plants are preferential sacrificial electron donors in water-splitting systems. At little or no cost, they could be exploited to accomplish both the tasks of hydrogen production and waste treatment and biomass reforming simultaneously.

Photocatalytic wet reforming of biomass is relatively in the infancy level, and at present most investigations on it are still largely on the laboratory scale. There is not yet a single report about any pilot studies on photocatalytic reforming for commercial hydrogen production. Nevertheless, since the process is frequently carried out at room temperature and both the energy and feedstock are from renewable sources, photocatalytic reforming can be considered to be especially promising for sustainable large scale production of green bio-hydrogen.

### 3.1.2. Photocatalytic upgrading of cellulose-based molecules: production of high value chemicals

Catalytic oxidations have traditionally been carried out in environmentally harmful chlorinated organic solvents at high temperatures and pressures by employing stoichiometric amounts of various inorganic oxidants as oxygen donors (e.g. chromate and permanganate species). Such oxidants are expensive and toxic but they also produce large amounts of hazardous waste, therefore needing to be replaced by safer systems.

Comparably, a photocatalytic process can bring about significant benefits in terms of milder and more environmentally sound reaction conditions and better selectivities to the desired product. Unstable substances at high temperatures may be synthesized via selective light-assisted processes.

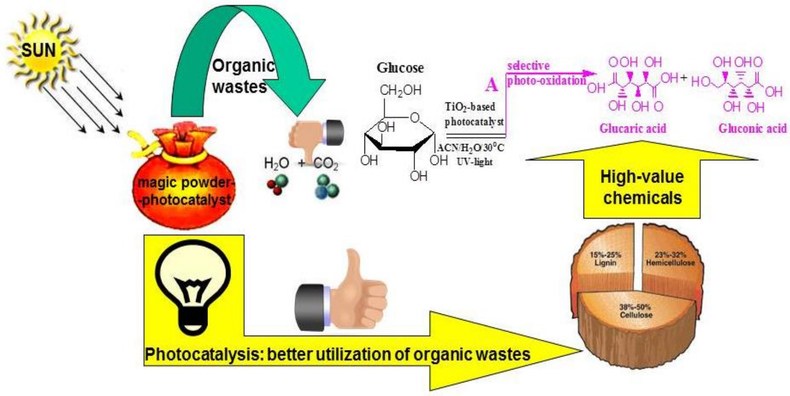
Alcohol oxidation to their corresponding ketones, aldehydes, and/or carboxylic acids is one of the most important transformations in organic synthesis.[27] Semiconductor photocatalysts have not been frequently employed in selective synthetic oxidation processes as the replacement of traditional oxidation methods has been mostly covered with heterogeneously catalyzed systems.

The working mechanism in metal oxidation catalysts involves an electron transfer-mediated step by the metal which thereby induces the formation of singlet oxygen species.[28] In this context, the search for an oxidation photocatalyst capable of directly activating dioxygen under solar light is an interesting as well as challenging task.

Catalytic selective photo-oxidation of cellulose-based molecules can provide a wide range of high added-value compounds as it was reviewed earlier.[7] In this section I will present some key studies on photocatalytic selective oxidation of cellulose-based model compounds to valuable chemicals.

A range of different nano-titania-based systems synthesized through sol–gel processes varying the precursor and/or the ageing conditions (sonication, microwave, magnetic stirring, or reflux) was recently reported for the liquid-phase selective photo-oxidation of crotyl alcohol to crotonaldehyde. The gas-phase selective photooxidation of 2-propanol to acetone was also chosen as model reaction.[29] Iron, palladium or zinc presence in the photocatalysts was found to be detrimental for the activity. Zirconium and particularly gold improved the results as compared to pure titania (95% conversion of crotyl alcohol with >80% selectivity to crotonaldehyde and for Pt-based system approx. 30% conversion of 2-propanol with approx. 80% selectivity of acetone).

Aliphatic carboxylic acids can be transformed to shorter chain acids (e.g. malic to formic acid)[30] or decarboxylated to the corresponding reduced hydrocarbons or hydrocarbon dimers in the absence of oxygen and in pure aqueous or mixed aqueous/organic solutions by means of photo-Kolbe-type processes.[31] As an example, the selective aqueous conversion of malic acid into formic acid has been conducted under visible light irradiation using a magnetically separable $TiO_2$-guanidine-(Ni,Co)-$Fe_2O_4$ nanocomposite (80% selectivity to formic acid after 2h). The photocatalyst featured a simple magnetic separation and offered the possibility to work under visible and sunlight irradiation due to titania modification with guanidine, which remarkably decreased the band gap of the metal oxide semiconductor.[30]



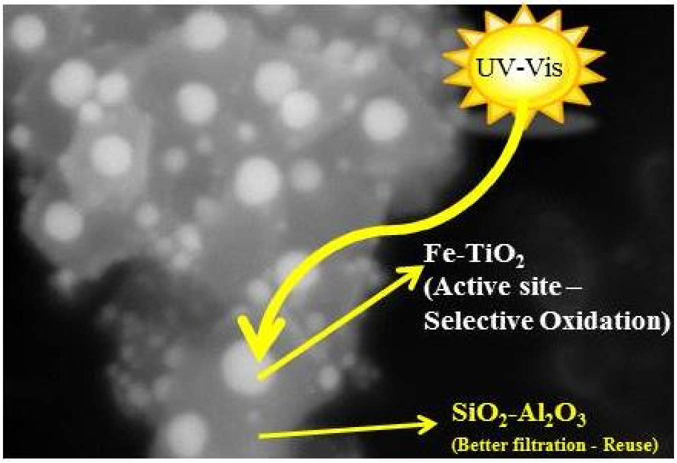
**Scheme 5.** Sustainable photocatalytic production of carboxylic acids from glucose.

The efficiency of heterogeneous nano-$TiO_2$ catalysts in the selective photocatalytic oxidation of glucose into high-valued organic compounds has been also recently reported (Scheme 5).[32] This reaction was found to be high selective (>70%) towards two important organic intermediates, namely: glucaric (GUA) and gluconic acids (GA). Among all photocatalytic systems tested, the best product selectivity was achieved with titania synthesized by an ultrasound-modified sol–gel methodology ($TiO_2$(US)).[32] Solvent composition and short illumination times were proved to have a considerable effect on photocatalysts activity/selectivity. Total organic compounds selectivity was found to be 39% and 71% for liquid phase reactions using $1H_2O : 9CH_3CN$ and $1H_2O : 1CH_3CN$, respectively. These values were obtained using the optimum nano-$TiO_2$(US) photocatalyst. In posterior studies, those results were systematically improved by homogeneously supporting nano-$TiO_2$(US) on a zeolite type Y (total selectivity of GUA and GA was ca. 68% after 10 min illumination time using a 1:1 = $H_2O:CH_3CN$ solvent composition).[33] Further photocatalyst optimization via development of transition-metal

(Fe or Cr) containing supported (crystalline alumina-silicate as support) nanotitania materials (Scheme 6),[34] provided advanced systems able to achieve improved selectivities to carboxylic acids. No metal leaching (Fe, Cr, Ti) was detected after photoreaction, with Fe-$TiO_2$ systems being the most selective (94 % after 20 min of illumination under similar conditions previously reported.[34] Such results suggested that synthesized nano-$TiO_2$ material could be in principle used in the decomposition of waste from the agricultural industry with the simultaneous production of high-value chemicals when residues (here glucose) act as electron donors (Scheme 5).

The oxidation mechanism, efficiency and selectivity of the photocatalytic oxidation of alcohols using $TiO_2$ Evonik P25 was reported to strongly depend on the nature of the dispersing medium. Shiraishi *et al.*[5] and Morishita *et al.*[35] demonstrated the positive influence of acetonitrile on epoxides formation in the selective photo-oxidation of alkenes. The addition of small amounts of water to $CH_3CN$ strongly inhibited alcohol adsorption and its subsequent oxidation as evidenced by ESR-spin trapping investigations.[36] The reactivity of alcohols on the surface of photoexcited $TiO_2$ was also found to be affected by the nature of their hydrophobic aliphatic chain.[36] Molecules including geraniol and citronellol were observed to be more susceptible to water content as compared to shorter chain analogues such as trans-2-penten-1-ol and 1-pentanol.

Similarly, glycerol is a relevant polyol currently produced in large quantities as by-product of the biodiesel industry. The mechanism of the selective photocatalytic oxidation of glycerol was also recently reported in presence of $TiO_2$ Evonik P25 and Merck $TiO_2$.[37] The product distribution observed at low glycerol concentration (glyceraldehyde and dihydroxyacetone) changes after a sharp maximum giving formaldehyde and glycolaldehyde as main products for P25 Evonik (mechanism derive from a direct electron transfer). Interestingly, mainly glyceraldehyde and dihydroxyacetone were observed on Merck $TiO_2$ (•OH-based mechanism), a material characterized by a lower density and more uniform population of hydroxyls groups at surface sites. These findings suggested that photocatalyst structures can significantly influence product distribution in photo-assisted processes. This example is particularly relevant to engineer valuable products from a biofuel-derived by-product.



**Scheme 6.** SEM images of the highly selective Fe-TiO$_2$/SiO$_2$-Al$_2$O$_3$ in liquid phase selective oxidation of glucose to glucaric and gluconic acids (image with 45k magnification).

The gas-phase selective photo-oxidation of methanol to methyl formate is another interesting process.[38,39] The reaction can be carried out in a flow-type reactor to avoid deep oxidation of methanol in the presence of TiO$_2$ particles and under UV light irradiation. A high selectivity to methyl formate was observed (91 %) with no catalyst deactivation.[38] By the development of a new approach which combines synergistically the energy of sonication and photon energy (based mostly on the principles of photocatalysis) as a green pathway for the synthesis of metal nanoparticles (MNPs)-containing semiconductors (supported or unsupported), Colmenares et al.[39,40] prepared a very active and selective bimetallic hybrid photocatalysts (Pd-Au/TiO$_2$) for the gas phase methanol oxidation to methyl formate (83% conversion and 70%

selectivity). These results demonstrated a positive effect of photon energy on improving the work of ultrasounds to further ensure the reduction of the metal precursor on the substrate and obtain very active and selective photocatalysts for the valorization of cellulose-based alcohols (e.g. methanol, ethanol).[39,40]

### 3.1.3. Photocatalytic selective oxidation of lignin-based aromatic alcohols

Photocatalytic pre-treatments of lignocellulosics have rarely been reported in the literature. Interestingly, Yasuda *et al.*[41] have recently devised a 2 step process for biological bioethanol production from lignocellulose via feedstock pre-treatment with titania photocatalyst under UV-illumination. Selected lignocellulosic feedstocks were napiergrass (*Pennisetum purpureum Schumach*) and silver grass (*Miscanthus sinensis Anderss*). The photocatalytic pre-treatment did not significantly affect final product distribution, demostrating that $TiO_2$ was not interfering on biological reactions promoted by cellulases and yeast. Most importantly, the photocatalytic pre-treatment was remarkably effective to reduce the time in enzymatic saccharification and fermentation reactions with respect to untreated and NaOH pre-treated feedstocks. The photocatalytic pretreatment was also proved to be an environmentally sound replacement for acid and alkal- based processes.

Another example of the combination of photocatalytic process with biomass valorization through oxidation comprised an integration of photochemical and electrochemical oxidation processes for the modification and degradation of kraft lignin.[42] $Ta_2O_5$–$IrO_2$ thin films were used as electrocatalysts with $TiO_2$ nanotube arrays as photocatalyst. Lignin deconstruction provided vanillin and vanillic acid, relevant compounds with important applications in the perfumes and food industries.

In spite of these recent reports that exemplify the potential of photocatalysis for lignocellulosics pre-treatment, selective photocatalytic transformations of lignocellulosic feedstocks are rather challenging due to the complex structure of lignocellulose, particularly related to the highly recalcitrant lignin fraction. Comparatively, relevant research has been conducted on model compounds which have been selected on the basis of representing structural motifs present in lignin.

Aromatic alcohols have been used as model lignin compounds to be converted into various compounds via photocatalytic processing. Among selective oxidation processes of alcohols, the conversion of benzyl alcohol to benzaldehyde is particularly attractive. Benzaldehyde is in fact the second most important aromatic molecule (after vanillin) used in many industries. Synthetic benzaldehyde is industrially produced via benzylchloride hydrolysis derived from toluene chlorination or through toluene oxidation. In this regard, alternative synthetic routes able to selectively produce benzaldehyde from benzyl alcohol are in demand. While most volume of research on selective production of benzaldehyde has been reported via heterogeneously catalyzed protocols, there are some relevant examples of such reaction under photo-assisted conditions.

The oxidation of benzyl alcohol was performed using differently prepared $TiO_2$ catalysts, reaching selectivities 3- to 7-fold superior to those of commercial $TiO_2$ catalysts.[43] In terms of benzyl alcohol derivatives, the aqueous phase photocatalytic oxidation of 4-methoxybenzyl alcohol was achieved by using uncalcined brookite $TiO_2$. A maximum selectivity of ca. 56% towards aldehydes (i.e. ca. 3 times higher than that obtained with commercial $TiO_2$) was reported.[43]

A similar selective photocatalytic oxidation of aromatic alcohols to aldehydes was systematically studied under visible-light irradiation utilizing anatase $TiO_2$ nanoparticles.[44] The unique features of the protocol rely on the possibility to use visible irradiation apart from UV due to the formation of surface complex species by the adsorbed aromatic alcohol. Studies using fluorinated $TiO_2$ pointed to a dramatic decrease of photocatalytic activity under visible irradiation which suggested a significant role played by the adsorption of the aromatic alcohol species on the surface of the solid involving the surface OH species.[44]

Metal oxides with large band gap energies (e.g. $Nb_2O_5$ with $Eg > 3.2$ eV) can be used in selective photo-oxidation of aromatic alcohols as was demonstrated recently.[45] A strong interaction between the aromatic alcohol and $Nb_2O_5$ surface generates a donor level within the forbidden band of $Nb_2O_5$, which provides a visible-light-harvesting ability and high activity/selectivity (>90% conversion and >95% selectivity after 16h of λ>420 nm).

In other studies, benzyl alcohol and some of its derivatives (*para*-structures) could be converted into their corresponding aldehydes at high conversions and selectivities (ca. 99%) both under UV and visible irradiation. The only exception to this behavior was 4-hydroxybenzyl alcohol which was oxidized to 4-hydroxy benzaldehyde (selectivity of ca. 23% at ca. 85% conversion) along with some unidentified products. Authors claimed that OH groups from $TiO_2$ surface reacted with the aromatic compound to form Ti–O–Ph species, exhibiting strong absorption in the visible region by ligand to metal charge transfer. These findings confirmed the results reported by Kim *et al.*[46] which proposed a direct electron transfer from the surface-complexes to the conduction band of the $TiO_2$ upon absorbing visible light. Importantly, results evidenced that visible light can induce reactions by substrate–surface complexation enabling the visible light absorption. Similar observations were recently reported by Li and co-workers[47] with nanorods of rutile titania phase synthesized by a hydrothermal reaction using rutile $TiO_2$ nanofibers obtained from calcination of composite electrospun nanofibers. The authors proposed a tentative mechanism where selective photocatalytic activities were proposed to be due to the visible-light absorption ability of benzyl alcohol–$TiO_2$ nanorod complex and the unique properties of rutile $TiO_2$ nanorods. Excelling properties of these materials including high surface-to-volume ratio, unidirectional 1D channels and superior survivability of electrons may contribute to more efficient electron transport, further required for benzaldehyde formation (>99% selectivity to benzaldehyde). The importance of such hierarchical spatially organized 1D nanostructures in photocatalytic solar energy conversion has been reviewed recently.[48]

An innovative class of carbon nanomaterials denoted as Carbon Quantum Dots (CQDs) with sizes < 10 nm can also work as an effective near infrared light (NIR) driven photocatalyst for the selective oxidation of benzyl alcohol to benzaldehyde.[49] Based on the NIR light driven photo-induced electron transfer property and its photocatalytic activity for $H_2O_2$ decomposition, this metal-free catalyst could efficiently provide high yields of benzaldehyde under NIR light irradiation (>85% conversions and 95% selectivity, 12h NIR irradiation ). Such metal-free photocatalytic system also selectively converts other alcohol substrates to their corresponding aldehydes with high conversion, demonstrating a potential application of accessing traditional alcohol oxidation chemistry.

Plasmonic photocatalysis have also been reported for selective formation of organic molecules.[50] Nanosized (<5 nm) gold nanoparticles supported on anatase-rutile interphase ($TiO_2$ Evonik P-25) by a deposition-precipitation technique could take advantage of plasmonic effects to achieve the photocatalytic selective production of several aromatic aldehydes from their corresponding aromatic alcohols (>80% conversions and >90% selectivity under 4h of visible light). This photocatalysis can be promoted via plasmon activation of the Au particles by visible light followed by consecutive electron transfer in the Au/rutile/anatase interphase contact. Activated Au particles transfer their conduction electrons to rutile and then to adjacent anatase which catalyzes the oxidation of substrates by the positively charged Au particles along with reduction of oxygen by the conduction band electrons on the surface of anatase titania.[50]

Recent progress on metal core-semiconductor shell nanohybrid has also demonstrated that these systems can be potentially utilized as photocatalysts for selective organic oxidations.[51] A (Pt)-$CeO_2$ nanocomposite has been prepared in an aqueous phase with tunable core-shell and yolk–shell structure via a facile and green template-free hydrothermal approach.[51] Authors found that the core–shell nanocomposite could serve as an efficient visible-light-driven photocatalyst for the selective oxidation of benzyl alcohol to benzaldehyde using molecular oxygen as a green oxidant.

Prof. Y-J Xu group has reported a very simple room temperature method to prepare a cubic phase, sheet nanostructured semiconductor CdS.[52] The as-prepared CdS is able to be used as a visible-light-driven photocatalyst for the selective oxidation of saturated primary C–H bonds in alkyl aromatics with high activity (>30% conversions) and selectivity (100%) under 10h of $\lambda>420$ nm and using molecular oxygen as a benign oxidant and benzotrifluoride as the solvent under ambient conditions. The ease of preparation of this CdS semiconductor and its highly active, selective visible light photoactivity for the selective oxidation of quite inert primary C–H bonds in alkyl aromatics points to its promising potential in photocatalytic selective activation of C–H bonds to high value chemicals.[52]

These photocatalytic protocols account for lab scale systems with relatively restricted applications. However, the possibility of scaling up photocatalytic processes to selective large scale processes has also been attempted in recent years.[53] With regards to photocatalytic selective oxidation processes, various aromatic alcohols could be converted in a liquid-phase solar pilot plant reactor using $TiO_2$/Cu(II) photocatalyst.[54] A maximum yield of 53.3% for benzaldehyde could be obtained with respect to initial benzyl alcohol concentration (approx. 63% selectivity, after six hours), at an average temperature of 38 ºC.

## 4. Future Perspectives and Challenges

The idea of taking use of the solar light at room temperature and atmospheric pressure via one-pot photocatalytic process to selectively convert lignocellulosic biomass to valuable chemicals is a highly innovative approach that can bring several benefits from the energetic and environmental viewpoints. Several important conclusions come out from this article. They are as follows:

- Photocatalytic reactions require milder conditions to those generally present in thermal processes which may allow the conception of short and efficient reaction sequences, minimizing side processes making use of sunlight as a completely renewable source of energy (waste-free energy).
- Hybrid systems of simultaneous photocatalyst-mediated chemicals evolution and water purification may be possible.
- Nanotechnology and nanomaterials design are currently bringing innovative concepts, ideas and protocols to the design and preparation of well-defined heterogeneous multifunctional photocatalysts with highly controllable and desirable properties.
- Low-temperature conversion of biomass to high-value chemicals: thanks to the novel synthesized materials with special photocatalytic

properties, it is promising, challenging and feasible to transform huge amounts of organic wastes (e.g. lignocellulose-based biomass) produced in Europe into chemicals by the rational and effective use of solar energy. Chemicals produced from the selective transformation of biomass would be a good solar energy carrier. All this will be possible by preparing a novel family of solid hybrid nanophotocatalysts.

- The development of the concept of looking at organic wastes not as a problem but as a solution (at least for part of our problems: depleting sources of chemicals).

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# The presence of photochemistry in the literature. A personal selection between the articles published in 2015

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In the year of light I think it is important to verify the impact of this discipline in the scientific literature. The success of photochemistry can be visually observed examining the diffusion of articles related to photochemistry in the most diffused chemical journals.

In the following pages you can find a personal selection of the photochemistry articles appeared on the Journal of the American Chemical Society, on Chemical Communications, and on Chemistry European Journal in the period January-May 2015. You will be able to see the diffusion of the our discipline in several fields of the chemical research.

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# The Eradicate Insect-borne Diseases with Sunlight Initiative at James Cook University in Australia

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Introduction – Insect bites from mosquitos or sand-flies are widespread in tropical North-Queensland and have a significant impact on Life, Health and Economies. They affect the well-known 'tropical Australian outdoor lifestyle' and can cause allergic reactions or diseases such as dengue, Ross-river fever or even malaria. These symptoms also inflict significant social and economic costs on the local communities of tropical Northern Australia. Likewise, city councils are forced to spend substantial financial and staff resources on preventive programs. The *Eradicate Insect-borne Diseases with Sunlight Initiative (EIDSI)* at JCU is utilizing tropical Queensland's two major natural resources, sunlight and biomass. Its research activities thus help to safeguard public health in the region and covers prophylaxis, treatment as well as cure. The team is led by Associate-Professor Michael Oelgemöller and supported by various undergraduate and postgraduate students.[1] The group has raised significant public interest in its solar chemistry work and has, for example, manufactured fragrances and important pharmaceutical building blocks on kilogram-scales with sunlight.[2]

Prevention – The heating capacity of the sun is utilized for the production of natural insect repellents that can help to protect from insect-borne tropical diseases. At present, N,N-diethyl-meta-toluamide (DEET) is used as the most common, 'artificial' insect repellent, but it is an irritant, unpleasant in smell, expensive to manufacture and known to damage surfaces and fabrics. 'Natural' citronella-based insect repellents are thus often preferred, but these products suffer from low efficacy due to the high volatility of its active ingredients. Consequently, these natural repellents require frequent reapplication.[3] Using the essential oil from a local Australian tree, water, heat and catalytic amounts of a household acid, the EIDSI team has produced a significantly more potent repellent that maintains a pleasant 'natural' odour. It is active against a range of blood-sucking insects over a long period of time and is safe to users. The team will soon launch large-scale thermal conversions using its advanced solar reactor (**Figure 1**). In an extension of this process, the team members were able to convert a minor component of the oil simultaneously into a valuable rose fragrance using solar light, air and catalytic amounts of a red dye.[4] The procedures can be conducted in series, in a one-pot fashion, thus significantly reducing the material and energy load of the process. The residual, unreactive constituents of the essential oil are known anti-inflammatory agents. The final treated oil product thus comprises of a natural repellent with a floral odour and anti-inflammatory properties. The individual components can be produced on demand in separate processes. This important health protection project has recently received seed-funding from the North Queensland Hospital Foundation.

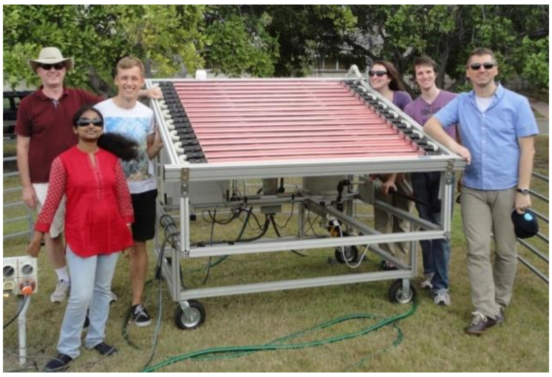

**Figure 1.** A/Prof Michael Oelgemöller (far right) and members of the EIDSI team with their solar reactor for large-scale solar manufacturing.

Treatment – For the treatment of insect bites, the EIDSI team has produced an anesthetic with a reported activity level of that of lidocaine, a widely used local anesthetic. The three-step process was realized in the laboratory for the first time in a continuous flow operation without any isolation or purification of intermediates. Flow photochemistry has recently emerged as a new chemical manufacturing concept that allows for on-site and on-demand synthesis.[5] In contrast to traditional batch processes, the continuous operation mode avoids the accumulation of hazardous or potentially explosive chemicals. The protocol developed gave an almost two-fold increase in material produced and a six-fold reduction in reaction time. This has led to a significant reduction in chemical waste. The crucial photochemical step was subsequently realized in aqueous medium using concentrated sunlight and easily accessible reagents. The reactor used concentrates sunlight onto a thin Teflon capillary that is wrapped around a glass tube through which cooling water is passed (**Figure 2**). Product yields and qualities far exceeded those obtained with artificial light. After further optimizations, the EIDSI team will realize the entire three-step process outdoors using combinations of solar light and heat.

**Figure 2.** Concentrating solar trough continuous flow photoreactor.

Cure – The synthesis of antimalarials from natural compounds has likewise been achieved under mild conditions using artificial and natural sunlight. The team has first constructed an effective air-bubble/liquid-flow ‘indoor’ reactor that utilizes common, energy-efficient office lighting, i.e. a white fluorescent tube (**Figure 3a**). In parallel, solar floats (initially developed by Prof. Liu at the University of Hawaii, USA[6]) were investigated that operate independent from ‘artificial’ electricity or cooling-water needs (**Figure 3b**). Solar concentrators and air-bubble/liquid-flow technologies have recently been merged in the solar trough continuous flow photoreactor and have been successfully applied to the synthesis of the current frontline antimalarial, artemisinin.[7] This important project has attracted seed-funding from both, the Clinton Health Access Initiative and the Australian Institute of Tropical Health and Medicine (AITHM).

**Figures 3.** (a) Tyler next to his air-bubble/liquid-flow ‘indoor’ reactor; (b) Amy and her solar float reactor.

**Figure 4.** TropEco research award 2014 presentation to the EIDSI team at JCU.

Conclusion – In conclusion, the EIDSI team is utilizing the abundant natural resources of Northern Australia for the prevention, treatment and cure of insect-borne diseases. The products and processes developed can be easily transferred to other tropical regions. The initiative furthermore offers interesting investment opportunities for local essential oil, solar technology, cosmetic and pharmaceutical industries. James Cook University has thus recognized these activities with the TropEco Research Award 2014 (**Figure 4**).

Acknowledgment – This initiative is financially supported by the North Queensland Hospital Foundation, the Clinton Health Access Initiative, the Australian Institute of Tropical Health and Medicine (AITHM) and the Australian Research Council (ARC, DP130100794). The EIDSI team thanks JCU for the TropEco research award 2014.

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# Light as a Reagent for Asymmetric Synthesis, Catalysis and Degradation of Polymers

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## 1. INTRODUCTION

As we celebrate the international year of light, it is fascinating to know how light plays a vital role in our day-to-day activities. It has been a source of many life-sustaining processes like photosynthesis by plants, the ability to see objects (vision), circadian rhythms etc. Light is not only a solution to several of the challenges that confronts our society today *viz.*, energy crisis, but also a key component to further our advancement in the technology ranging from medicine, to materials to electronics. Chemists have realized the importance of light and have incorporated its utility in science several centuries ago. The most notable of these is to employ sunlight for chemical reactions such as burning mirror of Archimedes,[1] and light induced reduction of metal ions.[2] Yet, synthesis of organic molecule(s) using light was at nascent stage. [1-2] In 1834, Hermann Trommsdorff observed the first photo transformation of Santonin, a sesquiterpene lactone, when he exposed the crystals to light and noticed the color change to yellow and rupture.[3] Since then, synthetic organic photochemistry has been progressing steadily towards achieving complex molecular structures with an emphasis towards obtaining them in stereoenriched form. However, designing a successful methodology for asymmetric phototransformations in solution did not have a smooth transition and has met with several challenges. Implementing the strategies from the well-developed thermal reactions that employ chiral perturbers such as chiral auxiliaries or chiral catalysts, for phototransformations yielded only modest success at best.[4] The challenges in achieving high stereoselectivity lies in controlling the short lived excited state(s) in the desired reaction pathway in a stereocontrolled fashion. Many research groups have shown that photoreactions performed in a confined media such as supramolecular templates or in the solid state resulted in moderate to high selectivity.[5] However, achieving selectivity in photoreactions that occurs in solution that lack the confinement or preorganization of the reactant(s) is still a challenge. In this vein, as a potential solution, research in our group introduced the concept of "axial to point chiral transfer during light induced transformations" that employs non-biaryl atropisomeric chromophores to perform atropselective phototransformations in solution. We have successfully demonstrated the versatility of this methodology for various phototransformations. Apart from this, we have also employed light to address several other challenges that synthetic organic and material chemists face today and have highlighted them below.

In the Sivagroup, we have been investigating four diverse sets of projects that involve light as the primary tool to initiate the transformation of interest or as a product of excited state deactivation. To provide a flavor of these projects we have highlighted the critical aspects from our investigations below.

**Atropselective reactions:** The pioneering work of Curran, Clayden and others[5d,6] have utilized atropisomers in asymmetric thermal transformations. They have shown that this method efficiently transfers chirality from the reactant to the product. The strategy of atropisomers in photoreaction was attempted by Bach and coworkers[7] wherein they illustrated intermolecular photoreactions of benzaldehyde and atropisomeric enamides that resulted in 63% diastereomeric excess. Here the atropisomeric compound was utilized as a ground state partner with the aldehyde reacting from the excited state. We were interested in evaluating the excited state reactivity of the atropisomeric compounds. To achieve this, we utilized atropisomeric chromophores where they reacted from the excited state leading to atropselective phototransformations. We successfully showcased the efficacy of our strategy of 'axial to point chiral transfer' displaying the feasibility and practicality of various atropselective photochemical transformations.[8] These include 6π-photocyclization of acrylanilides,[8a,8b,9] 4π-photocyclization of pyridones,[8c,8d] [2+2]-photocycloadditions,[8e,8i,8j] Norrish Yang cyclization[8f,8g] and Paternó Büchi reactions of oxoamides.[8h]

**Supramolecular photocatalysis:** As eluded before, controlling the excited states during photoreactions within confined media like cyclodextrins, zeolites etc., have been a successful strategy that was demonstrated by various research groups. We extend the use of one such supramolecular assembly as a catalyst to perform photochemical transformations. For this we have explored Cucurbit[8]uril (CB[8]) as a supramolecular vessel in catalytic amounts showcasing it as a superior supramolecular catalyst for controlling photoreactions. Detailed investigations were performed with CB[8] as a host and coumarins as guest molecules. With 6-methylcoumarin as a model system, the [2+2]-photodimerization reaction was found to be under allosteric control with the formation of 1:2 host:guest complex being the rate-limiting step. Detailed photophysical studies revealed that the excited state was protected inside the CB[8] cavity (from oxygen quenching). Additionally, thermodynamic binding measurements showed that the 1:1 host: guest complex had an association constant of $\sim 10^4$ $M^{-1}$ and the 1:2 host:guest complex had an association constant $\sim 10^6$ $M^{-1}$. Stopped flow kinetics revealed the formation of 1:1 host:guest complex occurred in the seconds time scale and the 1:2 host:guest complex occurred in the minutes time scale. The turnover was found to be 3.4 $min^{-1}$. The allosteric response was rationalized based on the guest induced shape change of the CB[8] cavity (1:1 host:guest complex) that accommodated the 2nd guest molecule leading to the formation of the reactive 1:2 host:guest complex. Thus this system was reminiscent of catalysis by enzymes making the supramolecular catalytic photoprocess biomimetic. [10]

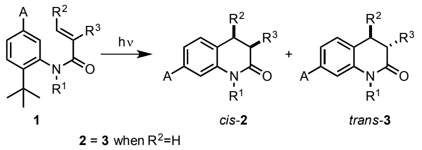
**Enantioselective organophotocatalysis:** Using atropisomeric thiourea catalysts, [2+2] photocycloaddition of 4-alkenyl substituted coumarins were evaluated leading to photoproducts with high enantioselectivity (77- 96% *ee*).[11] This research added new dimension for developing enantioselective organo photocatalysis, as the traditional methods involved energy transfer or electron transfer whereas our work exhibited enantioselective photocatalysis by energy sharing via exciplex formation (both static and dynamic) between the catalyst and the substrate promoted by hydrogen bonding. The thiourea catalysts were synthesized in collaboration with Prof. Sibi group at NDSU.

**Renewable and degradable polymer from biomass:** With an increase in usage of plastics and its slow degradation has left us with environmental challenges of unwanted stockpiles and plastic landfills. To address the challenges, a proof of concept was developed in collaboration with NDSU colleagues Prof. Sibi (monomer synthesis) and with Prof. Webster (for polymer characterization) where we synthesized polymers from biomass that had built-in phototriggers. Exposure of these polymers to UV light resulted in complete photodegradation of the polymer.[12] We have also showcased that the monomer can be recovered after photodegradation and can be used to remake polymers. By employing this strategy, we have not only addressed the challenge of degradation of polymers, but also we reduced our dependence on fossil fuels by making the process recyclable and sustainable.

Due to space constraint, we will highlight one of our ongoing research efforts *viz.*, UV/Visible light initiated atropselective photoreactions.

## 2.1 6π-PHOTOCYCLIZATION OF ACRYLANILIDES (DIRECT IRRADIATION)

Axially chiral acrylanilides (Scheme 1) were investigated for 6π-photocyclization because of the well-established literature precedence of their photochemical pathways, presence of molecular chirality (axially chiral) due to restricted rotation of N-C (aryl) bond and ease of synthesis. We observed different mode of cyclization in both achiral and atropisomeric acrylanilides. The N-substitution (N-H *vs.* N-Me) dictated the regiochemistry of cyclization on the phenyl ring. In case of atropisomeric acrylanilide **1a**, the cyclization occurred at the *ortho*-carbon bearing the *tert*-butyl group leading to *cis*-**2** and *trans*-**3** products (scheme 1). On the other hand, for the achiral acrylanilide **1m**, the cyclization occurred at the unsubstituted *ortho* carbon leaving the *tert*-butyl group intact in the photoproduct. In order to understand and propose a mechanistic rationale for the difference in reactivity between achiral N-H acrylanilide and atropisomeric *N*-alkyl and *N*-cycloalkyl acrylanilides, we obtained and analyzed their corresponding single crystal X-ray structures.[13]

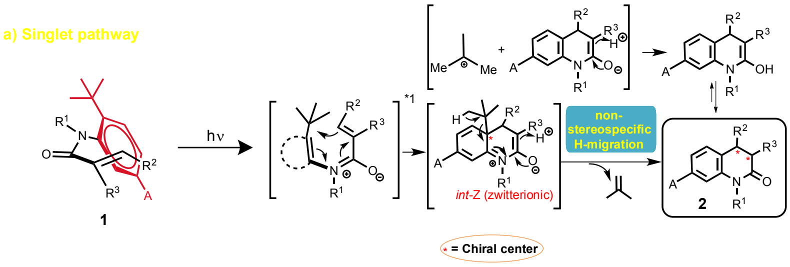


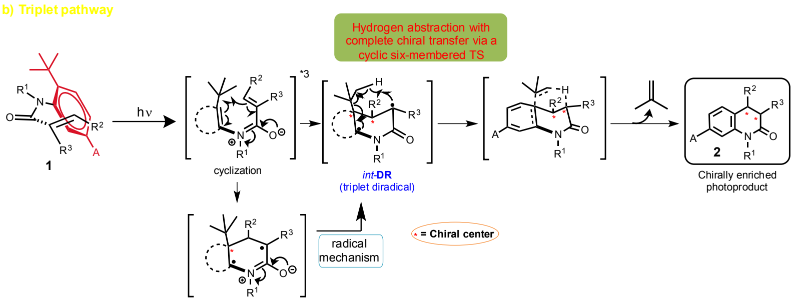
|  | $R^1$ | $R^2$ | $R^3$ | A |
|---|---|---|---|---|
| **a:** | Me | Me | Me | H |
| **b:** | Me | Me | Me | $^t$Bu |
| **c:** | Me | $H_2C$ | $CH_2$ | H |
| **d:** | Me | $H_2C$ | $CH_2$ | $^t$Bu |
| **e:** | Me | H | Me | H |
| **f:** | Me | H | Me | $^t$Bu |
| **g:** | Me | H | Et | $^t$Bu |

|  | $R^1$ | $R^2$ | $R^3$ | A |
|---|---|---|---|---|
| **h:** | Cp | H | Me | H |
| **i:** | H | H | Me | $^t$Bu |
| **j:** | Me | H | Ph | $^t$Bu |
| **k:** | ipr | H | Me | H |
| **l:** | Cy | H | Me | H |
| **m:** | H | Me | Me | H |

**Scheme 1:** 6π-Photocyclization of acrylanilides **1a**-**m.**

For 6π-photocyclization of the acrylanilides to occur the distance between the β-alkene carbon and the *ortho*-carbon on the N-phenyl ring is crucial.[14] Based on the literature precedence, the favorable distance for photoreactivity must be less than ~ 4 Å for reactions to occur in crystalline media.[15] From X-ray crystal structure, the distance between the β-alkene carbon and the *ortho*-carbon bearing the $^t$Bu substituent is 5.24 Å for **1e** (*Z*-isomer) and 3.64 Å for **1f** (*E*-isomer). Similarly, the distance between the β-alkene carbon and the unsubstituted *ortho*-carbon is 5.37 Å for **1e** (*Z*-rotomer) and 3.34 Å for **1f** (*E*-rotomer) respectively. Based on the distances between β-alkene carbon and the *ortho*-carbon, photocyclization can occur only from the amide N-CO *E*-isomer. $^1$H-NMR studies indicated that both *Z*- and *E*-isomer were present in the solution. Irradiation of optically pure (*P*- or *M*-isomers) atropisomeric acrylanilides led to the formation of 3,4-dihydro-2-quinolin-2-one photoproduct **2** and **3** with loss of *ortho*-*tert*-butyl group as isobutene. Direct irradiation of atropisomeric acrylanilides resulted in high enantiomeric excess in the photoproducts (Table 1). Upon inspection of Table 1, direct irradiation of α, β-substituted acrylanilides (e.g. **1a**) resulted to give *cis*-3,4-dihydro-2-quinolin-2-one photoproduct **2** and *trans*-3,4-dihydro-2-quinolin-2-one photoproduct **3** with similar enantiomeric excess. However, α-substituted acrylanilides (e.g. **1e**) gave racemic 3,4-dihydro-2-quinolin-2-one photoproduct. These results clearly indicated that β-substituent in the alkene was crucial for achieving high enantiomeric excess under direct irradiation conditions that presumably occurred via singlet excited state.


a) Singlet pathway


b) Triplet pathway

Hydrogen abstraction with complete chiral transfer via a cyclic six-membered TS

**Scheme 2:** Mechanistic rationale for 6π-photocyclization of atropisomeric acrylanilides: a) direct irradiation (singlet pathway) and sensitized irradiation (triplet pathway).

**Table 1:** Enantiospecific $6\pi$-photocyclization of acrylanilide derivatives[a]

| Ent. | Compd | % *ee* in $CHCl_3$ | | | % *ee* in MeOH | | | % *ee* in acetone | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | *cis* | *trans* | *cis:trans* | *cis* | *trans* | *cis:trans* | *cis* | *trans* | *cis:trans* |
| 1 | (-)-**1a** | - | 91 (B) | 61:39 | - | 87 (B) | 38:62 | - | 90 (B) | 55:45 |
| 2 | (+)-**1a** | - | 88 (A) | | - | 84 (A) | | - | 94 (A) | |
| 3 | (-)-**1b** | - | 85 (B) | 61:39 | - | 92 (B) | 35:65 | - | 94 (B) | 46:54 |
| 4 | (+)-**1b** | - | 99 (A) | | - | 94 (A) | | - | 91 (A) | |
| 5 | (-)-**1c** | 92 (*R*,*S*) | - | 29:71 | 85 (*R*,*S*) | - | - | 92 (*R*,*S*) | - | 67:33 |
| 6 | (+)-**1c** | 92 (*S*,*R*) | 95 (*S*,*S*) | | 99 (*S*,*R*) | 99 (*S*,*S*) | | 92 (*S*,*R*) | 88 (*S*,*S*) | |
| 7 | (-)-**1d** | 98 (A) | 99 (A) | 41:59 | 99 (A) | 99 (A) | 70:30 | 90 (A) | 91 (A) | 63:37 |
| 8 | (+)-**1d** | 91 (B) | 95 (B) | | 99 (B) | 99 (B) | | 87 (B) | 90 (B) | |
| 9 | (-)-**1e** | 0 | | -[b] | 0 | | -[b] | - | | -[b] |
| 10 | (+)-**1e** | 0 | | | 0 | | | - | | |

[a]For irradiation conditions see referenced work. *cis:trans* ratio and conversion are based on relative integration of corresponding peaks in NMR and HPLC/GC. [b]*cis* and *trans* isomers not feasible in photoproducts from **3e** and **3f**. Reproduced with permission from Ref [8a]; Copyright American Chemical Society, 2009

Based on experimental observation, we postulated a likely mechanistic pathway where the photocyclization occurred at the *ortho*-carbon via zwitterionic intermediate "*int-Z*" (Scheme 2a), with removal of the *ortho-tert*-butyl group. The mechanistic rationale was based on the identical enantioselectivity observed in *cis*-**2** and *trans*-**3** photoproducts, as the resulting zwitterionic intermediate "*int-Z*" has a defined chiral center at the benzylic position. The second step involved proton transfer (from solvent or intramolecularly) that occurred in a non-stereospecific manner that led to the formation of *cis*-**2** and *trans*-**3** photoproducts with identical enantiomeric excess values. Based on the assessment of Table 1, acrylanilides lacking β-substituent led to an achiral benzylic carbon ($-CH_2-$) in the zwitterionic intermediate "*int-Z*" followed by non-stereospecific H-migration resulting in the racemic photoproduct. Thus the intermediate "*int-Z*" with β-substituent acted as a 'mechanistic bridge' for the axial to point chiral transfer from the reactant to the photoproduct.

## 2.2 6π-Photocyclization of Acrylanilides (triplet sensitization)

Direct irradiation of atropisomeric acrylanilides showed that β-substitution was essential for efficient transfer of axial chirality from the reactant to point chirality in the photoproduct. Next, the questions we wanted to address were a) can there be chirality transfer in substrates that lack β-substitution? and b) what will be the role of the triplet excited state? In order to answer these questions, triplet sensitized irradiations of optically pure atropisomeric α-substituted acrylanilides **1f** and **1g** were carried out in acetone (acting as both solvent and triplet sensitizer) (Tables 1 and 2) leading to 3,4 dihydroquinolinone photoproduct with 92-94% *ee* at ambient temperature. Atropisomeric α-substituted acrylanilides (Scheme 1) upon triplet-sensitized irradiation also underwent photocyclization with very high enantioselectivity in the corresponding photoproduct. Conversely, direct irradiation in methanol and trifluoroethanol as solvents gave racemic photoproducts.

In order to ascertain the role of reactive spin states, detailed photophysical investigations were performed with α-substituted acrylanilides. Phosphorescence profile for **1f** and **1g** were observed at 77 K in MCH glass with triplet energy ($E_T$) of ~77 kcal·mol$^{-1}$ and lifetime of ~1.58 sec (Figure 1).

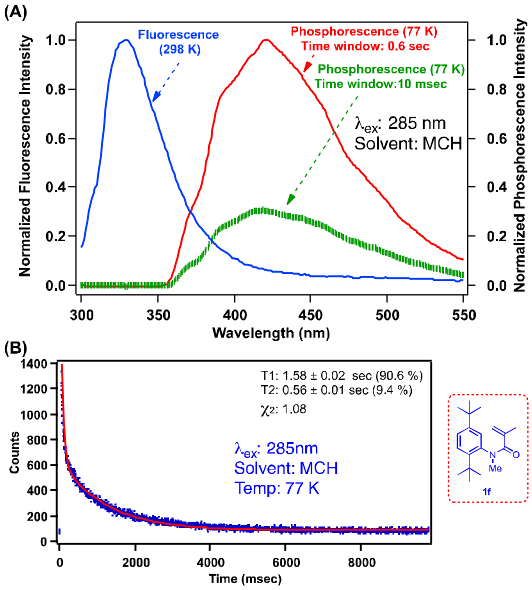


**Figure 1:** (A) Fluorescence and Phosphorescence of **1f** in methylcyclohexane (MCH). (B) Phosphorescence decay kinetics of **1f** at 77 K in MCH glass.

These results clearly indicated that the triplet excited state for **1f** and **1g** has a π-π* configuration. Based on the reactivity in acetone, it is clear that an efficient triplet energy transfer from acetone ($E_T \approx$ 79 kcal·mol$^{-1}$).

**Table 2:** Atropselective 6π-photocyclization of α-substituted acrylanilides in presence of alkali metal ions.[a]

| Entry | Compd | Abs config. | % *ee* values in the presence of additives in TFE[b] | | | | | | Acetone[c] |
|---|---|---|---|---|---|---|---|---|---|
| | | | CsF | KF | KF/3Å MS | NaF | NaF/3Å MS | 3 Å MS | |
| 1 | **(-)- 1f** | - | 90 (B) | 90 (B) | 88 (B) | - | 90 (B) | 88 (B) | 94 (B) |
| 2 | **(+)-1f** | - | 87 (A) | 90 (A) | 85 (A) | - | 90 (A) | 85 (A) | 92 (A) |
| 3 | **(-)-1g** | - | 90 (B) | 85 (B) | 85 (B) | - | 95 (B) | 90 (B) | 92 (B) |
| 4 | **(+)-1g** | - | 90 (A) | 80 (A) | 80 (A) | - | 89 (A) | 90 (A) | 94 (A) |
| 5 | **(+)-1h** | *P* | (+)-90 (*R*) | (+)-77 (*R*) (*R*) (*R*) (*R*) | - | (-)-16 (*S*) | (+)-80 (*R*) | (+)-70 (*R*) | - |
| 6 | **(-)-1h** | *M* | (-)-85 (*S*) | (-)-77 (*S*) | - | (+)-16 (*R*) | (-)-80 (*S*) | (-)-70 (*S*) | |

[a]For specific reaction conditions refer to previous work. Without additives only racemic mixtures were observed. [b](+) and (-) represent of the Cotton effect at 285nm. Reported values are an average of a minimum of 3 runs with ±8% error. A and B refers to the first and second peak that elute out of the HPLC chiral stationary phase separation for a given pair of enantiomers. The conversion in all samples were kept between 10-30% to ascertain the true *ee* values in the presence of cations as the photoproduct can also bind competitively to alkali metal [c]Acetone was used as both solvent and sensitizer and *ee* values correspond to reactions done at 27 °C. Reproduced with permission from Ref [8b]; Copyright Royal Society of Chemistry, 2014

Hence based on the irradiation conditions, 6π-photocyclization of **1f** and **1g** can occur from either singlet ($S_1$) or triplet ($T_1$) excited states or a combination of both. Based on established paradigm for photochemical reactions, a zwitterionic intermediate is likely expected from a π-π* singlet excited state ($S_1$ π-π*), whereas a diradicaloid intermediate is likely formed from the corresponding π-π* triplet excited state ($T_1$ π-π*). Based on this paradigm, we postulated that the photocyclization of atropisomeric α-substituted acrylanilides **1f** and **1g** from the triplet π-π* excited state occurred via a radical mechanism leading to triplet diradical intermediate "*int*-DR" (Scheme 2b). This diradical intermediate "*int*-DR" abstracted H-atom from *ortho-tert*-butyl group that led to the formation of chirally enriched photoproduct **2**. High enantioselectivity in the photoproduct **2** under sensitized irradiation can be rationalized based on the stereospecific H-abstraction via a cyclic six-membered transition state via "*int*-DR". It is important to highlight that the photocyclization from both $S_1$ and $T_1$ not only led to the same photoproduct via two different reactive intermediates and/or transition states, but also determined *ee* values in the photoproduct.

## 2.3 Heavy Atom Effect: 6π-Photocyclization of Acrylanilides Mediated by Alkali Metal Cation

In our continued effort to achieve high stereoselectivity in the photoproduct, 6π-photocyclization of α-substituted acrylanilides was evaluated in the presence of alkali metal ions. Literature precedence[16] has shown that metal ions have been exploited to alter the excited state photoreactivity of organic molecules. α-Substituted acrylanilides under direct irradiation in solution gave racemic photoproducts (Table 1; Scheme 2a). While their reactivity from the triplet state led to high enantiomeric excess in the photoproduct (Table 2; Scheme 2b). With this in mind, we chose to investigate the role of alkali metal ions (e.g. $Cs^+$, $K^+$ and $Na^+$) for the photocyclization of α-substituted acrylanilides.[8b] Irradiation of optically pure α-substituted acrylanilides in the presence of alkali metal ions afforded cyclized photoproduct **2** in high enantiomeric excess (Table 2). Addition of CsF and KF afforded *ee* values of *ca.* 80% whereas in the case of NaF there was a dramatic decrease (*ca.* 16%) in the selectivity leading to formation of optical antipode of the photoproduct.

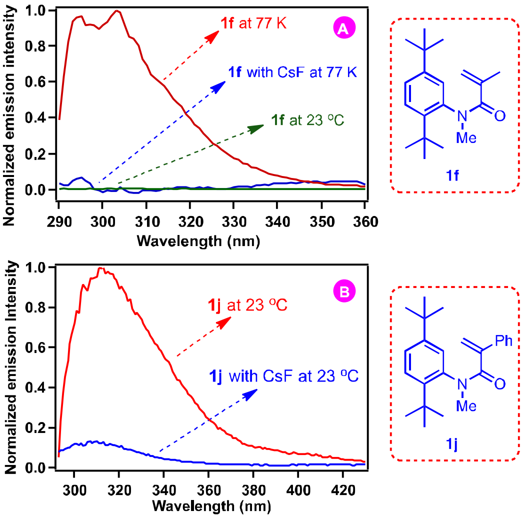


**Figure 2:** (A) Fluorescence of **1f** in presence and absence of CsF both at room temperature and 77K in ethanol glass. (B) Fluorescence of **1j** in the presence and absence of CsF at room temperature.

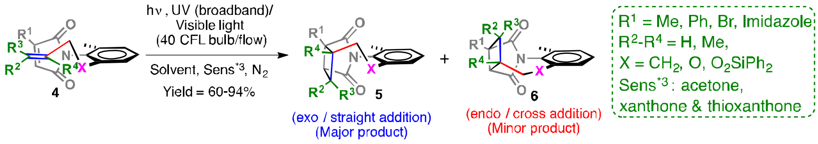
This was attributed to the presence of moisture due to the charge density of small alkali metal ions (e.g. $Na^+$). In order to address this issue, the photoirradiation was performed in the presence of molecular sieves (3 Å) that afforded photoproduct with ca. 80% *ee* with the enhancement of the same enantiomer as obtained in case of $Cs^+$. It is important to note that moisture played a critical role in altering the selectivity in the photoproduct **2**. In order to study the effect of alkali metal ions, steady state emission and fluorescence lifetime measurements were performed with atropisomeric α-substituted acrylanilides **1f** and **1j** at room temperature and at 77 K both in presence and absence of alkali metal ions. Weak fluorescence was observed at room temperature, however enhanced fluorescence intensity was seen at 77 K in ethanol glass. In presence of $Cs^+$, weak fluorescence was observed at both room temperature and at 77 K. This is likely due to the enhanced intersystem crossing (*ISC*) from the singlet excited state to the triplet excited state due to spin-orbit coupling. Irradiation of atropisomeric α-substituted acrylanilides **1** in presence of heavy metal cations led to *ISC* leading to triplet excited state. This triplet-excited state underwent cyclization via a diradical intermediate ("*int*-DR") (Scheme 2-triplet pathway) leading to enantioenriched photoproduct.

## 3.1 [2+2]- PHOTOCYCLOADDITION OF ATROPISOMERIC MALEIMIDES

Among the photochemical transformations, [2+2]-photocycloaddition is one of the widely utilized reactions in the field of synthetic organic chemistry. Maleimides are one of the versatile compounds that display a rich chemistry both in thermal and photochemical reactions. [2+2], [4+2] and [5+2] Photocycloaddition are few of the well-studied photochemical reactions that are reported in the literature.[17] Booker-Milburn and others[17c,18] have extensively investigated [2+2], and [5+2] photocycloaddition of maleimides as an avenue for the synthesis of complex organic scaffolds. Switching one product to another ([2+2] vs [5+2]) was also demonstrated by altering the type of irradiation (sensitized vs. direct irradiation).[17c,19] Milburn and co-workers have also demonstrated the large-scale synthesis by using a flow set up and extended it to the synthesis of natural products.[20] But, to our knowledge atropselective photoreactions of maleimides were not known in the literature. This gave us an opportunity to incorporate our methodology of axial-to-point chiral transfer in maleimides and investigate them for atropselective photocycloaddition.

Atropisomeric maleimides **4** (scheme 3) with different substitutions were synthesized with good yield in two-steps.[8i] Based on computational studies, N-aryl maleimides prefers to be twisted at N-C aryl axis due to steric hindrance between imide carbonyl and ortho hydrogens. However simple hydrogen will not provide enough sterics to be atropisomeric.[21] In this regard, the newly synthesized atropisomeric maleimide with methyl group at 6-position played a crucial role in providing stable atropisomers by increasing the energy barrier for N-C aryl bond rotation. Analysis of racemization kinetics in the newly synthesized maleimides revealed that they have fairly high racemization barrier. For example in the case of **4a,** the half life for racemization was 3.5 days at 100 $^{o}$C in toluene with racemization rate constant of $2.27 \times 10^{6}$ $s^{-1}$ and activation energy barrier of ~31.6

kcal·mol$^{-1}$. Such a high racemization barrier allowed us to carry out atropselective photoreaction without the loss of absolute configuration.



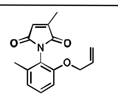
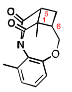
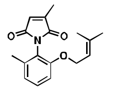
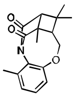
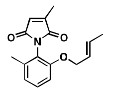
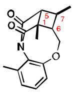
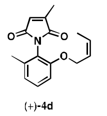
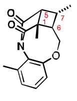
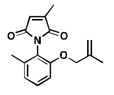
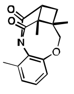
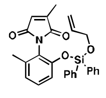
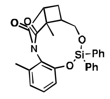
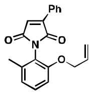
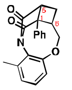
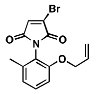
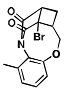
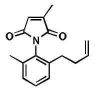
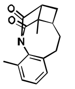
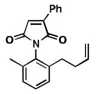
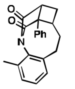
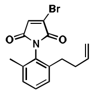
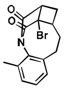
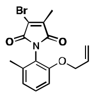
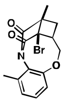
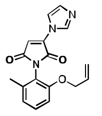
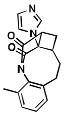
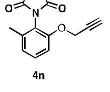
**Scheme 3:** Intramolecular [2+2]-Photocycloaddition of atropisomeric maleimides.

The photoreactions of maleimides were performed under different irradiation conditions and in various solvents. The reaction proceeded smoothly to yield [2+2]-photoadduct with complete regiocontrol over competing [5+2]-photocycloaddition. Three different sets of irradiation conditions were evaluated a) direct irradiation (450 W a medium pressure Hg lamp); b) sensitized irradiation under UV light (e.g. xanthone as a sensitizer in a Rayonet reactor at ~350 nm) c) Sensitization under metal-free visible light irradiation (e.g. thioxanthone as a sensitizer in a Rayonet reactor at 420 nm). After the photoreaction, NMR spectroscopy analysis revealed the presence of two diastereomeric products (scheme 3). The major product was the *exo* photoadduct **5**, where the carbon of the alkene tether is away from the carbon bearing R$^1$ substituent in the maleimide ring. The minor photoadduct was the *endo* product **6**, where the carbon of the alkene tether is towards the carbon bearing R$^1$ substituent in the maleimide ring. After several screening of the reactions, optimized conditions were obtained using **4a** as a model system. These reactions provided insights about the solvent choice, sensitizer and type of irradiation. The reaction proceeded smoothly under sensitized irradiation both with xanthone as a sensitizer for ~350 nm irradiation and thioxanthone as sensitizer for ~420 nm irradiation and the reaction completed within 1 h. Neither temperature nor the solvent had any significant influence on the diastereomeric ratio of the photoproducts (*exo*:*endo*). The conversion was moderate to very high in solvents screened (MeOH, MeCN, ethyl acetate, chloroform, $CH_2Cl_2$ etc.,) whereas in THF, the product decomposed and in benzene, MCH the conversion was low. The photoreactions of atropisomeric maleimides were carried out with the optimized conditions i.e., with xanthone or thioxanthone as sensitizers in MeCN which resulted in high isolated yields. Investigation of the table 3 clearly disclosed that the enatioselectivity of photoproducts were >98%.

The *dr* (*exo*:*endo*) values was dictated by substituents at the maleimide double bond ($R^1$), alkenyl tether ($R^2$-$R^4$) and X on the N-aryl ring (Table 3). However, the X group had very little influence over the *exo:endo* ratio. Among $R^1$ substituents, phenyl and imidazole (**4g**, **4j** and 4**m**) had the highest control over *dr* values resulting in *exo:endo* ratio of >99:1. These result showed that the $R^1$ substituent in the maleimide ring has influence on the *dr* values, which is also evident from the table 3. To our surprise di-substituted maleimide **4l** gave an *exo*:*endo* ratio of 42:58, i.e. slightly favoring the *endo* photoadduct. The substituents at the alkenyl tether ($R^2$-$R^4$) were varied systematically to understand its influence on the *dr* values. The gem dimethyl **4b** at the terminal alkene did not influence the *dr* values (table 3; entry 2) whereas monomethyl substitution **4c, 4d** showed slight increase in the *dr* values. The internal substitution as in case of **4e**, resulted in reduced *exo:endo* ratio (62:38). Interestingly, when alkene reaction partner was replaced by alkyne **4n,** the photoreaction did not result in the cyclobutene product.

Detailed photophysical investigations were performed to gain insights into the excited state reactivity of the maleimides. To avoid the photochemical reaction that competes with our photophysical studies, maleimide **7** with saturated alkene tether was synthesized with retention of the maleimide chromophore.

**Table 3:** Intramolecular [2+2] photoreactions of atropisomeric maleimides

| Entry | Substrate | Major photoproduct | Yield [%],[c]<br>*dr* (**5**:**6**),[d] % *ee* |
|---|---|---|---|
| 1 | <br>(+)-**4a**<br>(-)-**4a** | <br>(-)-(1*R*,5*S*,6*R*)-**5a**<br>(+)-(1*S*,5*R*,6*S*)-**5a** | 84<br>(79:21)<br>> 98% *ee*<br>> 98% *ee* |
| 2 | <br>(+)-**4b**<br>(-)-**4b** | <br>(-)-**5b**<br>(+)-**5b** | 60<br>(79:21)<br>> 98% *ee*<br>> 98% *ee* |
| 3 | <br>(+)-**4c**<br>(-)-**4c** | <br>(-)-(1*R*,5*S*,6*R*,7*R*)-**5c**<br>(+)-(1*S*,5*R*,6*S*,7*S*)-**5c** | 84<br>(87:13)<br>> 98% *ee*<br>> 98% *ee* |
| 4 | <br>(+)-**4d**<br>(-)-**4d** | <br>(A)-(1*R*,5*S*,6*R*,7*S*)-**5d** [e]<br>(B)-(1*S*,5*R*,6*S*,7*R*)-**5d** [e] | 90[f]<br>(84:16)<br>> 98% *ee*<br>> 98% *ee* |
| 5 | <br>**4e** | <br>**5e** | 77<br>(62:38) |
| 6 | <br>**4f** | <br>**5f** | 76<br>(77:23) |
| 7 | <br>(+)-**4g**<br>(-)-**4g** | <br>(-)-(1*R*,5*S*,6*R*)-**5g**<br>(+)-(1*S*,5*R*,6*S*)-**5g** | 90<br>(> 99:1)<br>> 98% *ee*<br>> 98% *ee* |
| 8 | <br>**4h** | <br>**5h** | 82<br>(69:31) |
| 9 | <br>**4i** | <br>**5i** | 88<br>(74:26) |
| 10 | <br>**4j** | <br>**5j** | 82<br>(> 99:1) |
| 11 | <br>**4k** | <br>**5k** | 80<br>(61:39) |
| 12 | <br>**4l** | <br>**6l** | 94<br>(42:58) |
| 13 | <br>**4m** | <br>**5m** | 74<br>(>99:1) |
| 14 | <br>**4n** | Dimers / Decomposition | |

[a] Irradiation of **4b** was performed with 30 mol % xanthone as the triplet sensitizer in acetonitrile solvent at room temperature using a Rayonet reactor equipped with 300 nm lamps. Irradiations of **4g**, **4j**, and **4m** were performed with 30 mol % thioxanthone as the triplet sensitizer in acetonitrile solvent at room temperature using a Rayonet reactor equipped with 420 nm lamps. For all other substrates, the photoreactions were performed in acetone at room temperature using a 450 W medium-pressure Hg lamp with a Pyrex cutoff filter. [b] The *ee* values were obtained from HPLC analysis on a chiral stationary phase, and the results are averages of three runs with an error of ±3%. The absolute configuration was determined by XRD with Flack parameters. [c] The ratios were determined by $^1$H NMR spectroscopy of the crude samples. [d] A and B refer to the order of HPLC elution for a given pair of enantiomers. [e] Yield based on $^1$H NMR spectroscopy using triphenylmethane as an internal standard. Reproduced with permission from Ref [8i]; Copyright American Chemical Society, 2014

Laser flash photolysis studies of **4g** and **7** were studied in acetonitrile solution. The transient absorption of **7** was centered at 400 nm with lifetime of 50 μs, which was quenched by molecular oxygen ($K_q = 2 \times 10^9$ $M^{-1}s^{-1}$) and was assigned to triplet-triplet absorption of maleimide chromophore. Similar studies with **4g** revealed a lifetime as 450 ns. The lifetime between **4g** and **7** evidently proved that the excited state of **4g** was deactivated by the photocycloaddition reaction. To understand the interaction between the thioxanthone and maleimide, triplet-triplet absorption studies were carried out with thioxanthone in presence of maleimide. The initial triplet absorption was quenched by maleimide **7** (decay of the absorbance at 620 nm) to generate $^3$(**7**)* (rise in absorbance at 420 nm) that was monitored at 420 nm (Figure 3). This suggested that the excited state thioxanthone acted as a donor, while the maleimide acted as an acceptor. The triplet quantum yield of **7** was evaluated by generating the singlet oxygen. The relative triplet quantum yield of the maleimide **7** ($\Phi^1O_2 \approx 0.04$) was calculated by comparing the efficiency with phenalenone as the reference standard ($\Phi^1O_2 = 0.98$).[22] This result revealed that the maleimides had very poor intersystem crossing (*ISC*) quantum yield and produce very low amounts of triplet upon direct irradiation.

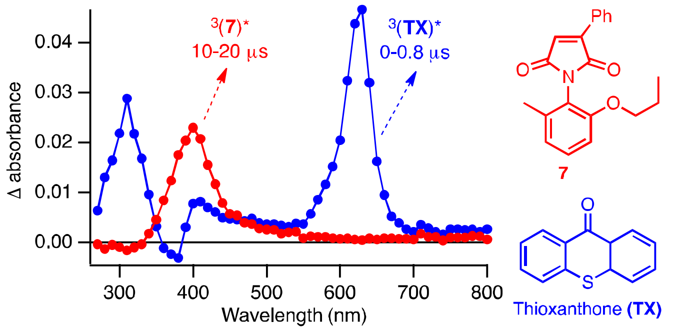
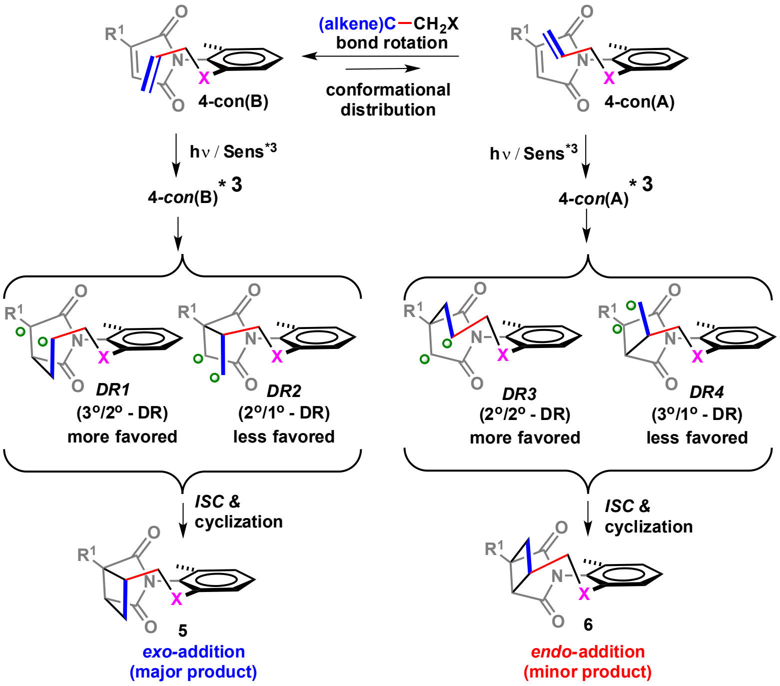


**Figure 3:** Transient absorption spectra monitored at 0-0.8 μs (blue) and 10-20 μs (red) after pulsed laser excitation (355 nm, 7 ns pulse width) of argon-saturated MeCN solutions of **TX** and **7** (0.05 mm).

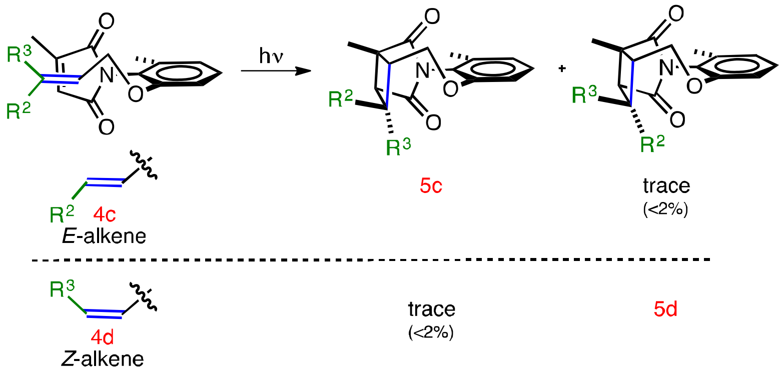
### 3.2 Mechanistic studies to decipher the reactivity of atropisomeric maleimides

Based on our photochemical and photophysical investigation, we proposed that the photoreaction occurred from triplet-excited state. The electron rich alkene likely interacted with the half-filled π orbital of the ππ* excited state of the maleimide.



**Scheme 4:** Mechanistic rationale for [2+2] photocycloaddition of atropisomeric maleimides **4**.

This triplet reaction proceeded via two step process where the first step is the formation of triplet 1,4 diradical and the second step is the cyclization (after intersystem crossing to its singlet state) to form the desired photoproduct(s). The formation of *exo* and *endo* products can be explained as below (scheme 4): The *exo*- photoproduct was likely formed from the conformer "**4**-*conf*(A)" in which the CH$_2$ group of the alkenyl tether is pointed away from the R$^1$ substituent of the maleimide double bond. The initial step of the photoreaction could likely lead to the formation of either DR1 or DR2. Similarly, the formation of *endo*-photoproduct was likely formed from the conformer "**4**-*conf*(B)" in which the $CH_2$ group of the alkenyl tether is positioned towards the R$^1$ substituent of the maleimide. In this case diradical, DR3, DR4 is feasible. These 1,4 diradicals intersystem cross to form singlet 1,4 diradical and cyclize to the photoadducts (Scheme 4).



**Scheme 5:** Scrambling studies with maleimides **4c** and **4d**.

To gain more insights on initial bond formation, scrambling studies were performed with **4c** and **4d** (Scheme 5). Analysis of photoreaction mixture showed no scrambled photoproducts. The absence of scrambled photoproducts reflected two scenarios. In the first scenario, the 1,4 diradical DR1 was likely preferred over the diradical DR2 leading to the major *exo* product and DR3 was likely preferred over DR4 leading to the minor *endo* product. In the second scenario, the diradical formed (DR1 or DR2 for exo photoproduct and DR3 and DR4 for endo photoproduct), in the first step cyclized at much faster rate than the bond rotation resulting in the absence of any observable scrambled photoproduct(s). The second scenario was unlikely as the reactions took place from triplet excited state that had to intersystem cross to singlet excited state. This presents enough time for scrambling to occur. Hence the lack of scrambling likely indicates the first scenario as the likely mechanistic pathway.

### 3.3 Flow Photolysis Setup For Large Scale Photoreactions Involving Of Atropisomeric Maleimides

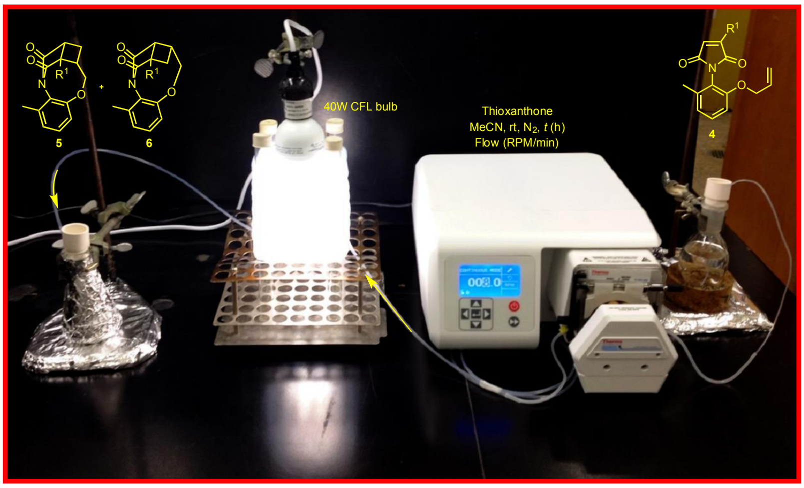
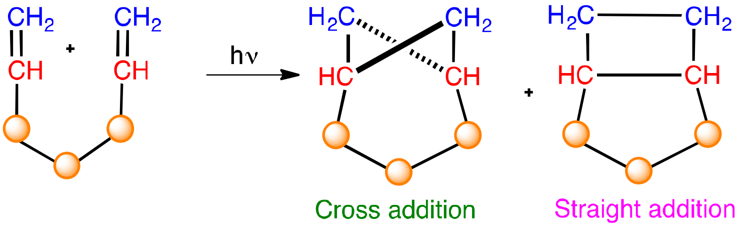


**Figure 4:** Flow setup for visible light photocatalysis of maleimides **4**.

The efficiency of the thioxanthone as the sensitizer in the phototransformation of maleimide provided us an opportunity to employ low intensity irradiation such as compact fluorescent light (common household lamp) to carry out the phototransformation. This idea was appealing, as the reaction conditions was redox-neutral and metal- free. Apart from using visible-light, we also attempted to carry out the reaction under flow conditions in an attempt to showcase the scalability of our methodology (figure 4). We designed a simple flow set up and optimized the irradiation conditions. The results demonstrated the feasibility of our strategy to utilize abundant sunlight (visible light) and easy scale up to access enantioenriched photoproducts (flow set up) in multi-gram scale.

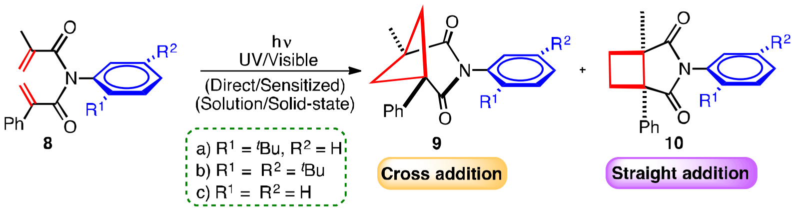
## 4. Photoreactivity through Restricted Bond Rotations: Cross [2+2]-Photocycloaddition of Acrylimides:[8j]

The cross [2+2] photocycloaddition-involving alkenes is a rare and one of the less investigated reactions in the literature. This is because of the general preference of straight addition over cross addition in the solution (Scheme 6). Extensive research for the formation of straight photoproduct has been reported.[23]



**Scheme 6:** [2+2] Photocycloaddition involving alkenes tethered by three atom spacer.

We were interested in accessing cross photocycloaddition products as they are structurally unique and exhibit interesting excited state chemistry. We initially started our investigations with atropisomeric acrylimides in solution and later we extended our strategy to the solid state with control over reactivity due to the confinement within the crystal lattice. Literature precedence showed contrasting reports on formation of straight and cross photocycloaddition products during photoreactions involving acrylimides.[24] Intrigued by these reports we incorporated the axial to point chiral strategy for controlling the photoreactions leading to higher selectivity in the photoproducts.



**Scheme 7:** Cross photocycloaddition of atropisomeric acrylimides **8**.

Atropisomeric acrylimides **8** were synthesized by sequential acylation reactions starting from the corresponding aniline derivative. The energy barrier for the atropisomeric acrylimides was determined by racemization kinetics at 45 °C in acetonitrile and methanol. Analysis of the racemization kinetics revealed that the acrylimides have energy barrier of ~26 kcal·mol$^{-1}$ with half-life of 1-2 days. Having ascertained the high energy barrier, we carried out photoreactions in isotropic media with either methanol or acetonitrile as a solvent. The photoreaction of acrylimides **8a-c** proceeded smoothly with good mass balance and conversion. Three different sets of irradiation conditions were studied. a) direct irradiation (450W a medium pressure Hg lamp or Rayonet reactor equipped at 254 nm), b) sensitized irradiation under UV (xanthone as sensitizer in Rayonet reactor at 350 nm) and c) sensitized irradiation under visible light (thioxanthone as sensitizer in Rayonet reactor at 420 nm). Acrylimide **8a** was employed to optimize the irradiation conditions. Analysis of the photoproducts by NMR spectroscopy revealed that the acrylimides yielded exclusively cross [2+2] photoproducts in both the solvents (MeOH and MeCN). The reactivity remained unaffected under oxygen and nitrogen conditions (Table 4). To investigate the reaction under sensitized reaction condition, we explored sensitizer with varying triplet energies ($E_T$) between 78 and 63 kcal·mol$^{-1}$.

**Table 4:** Reaction conditions optimization for intramolecular [2+2] photoreactions of acrylimides[a]

| Entry | Cmpd | Irradiation conditions[b] | solvent | % convn.[d] | **9:10** |
|---|---|---|---|---|---|
| | | Direct irradiation | | | |
| 1 | **8a** | BB - Pyrex cut off / 3 h / $N_2$ | MeCN | 97 | >99:1 |
| | | RR, ~254 nm / 5 min / $N_2$ | | 71(70)[e] | |
| | | RR, ~254 nm / 5 min / $O_2$ | | 68 | |
| | | BB - Pyrex cut off / 3 h / $N_2$ | Acetone[c] | 100 | >99:1 |
| | | Sensitized irradiation | | | |
| 2 | **8a** | benzophenone (10 mol %) / RR, ~350 nm / 3 h / $N_2$ | MeCN | 100 | >99:1 |
| | | xanthone (10 mol %) / RR, ~350 nm /1.5 h / $N_2$ | MeCN | 100(71)[e] | |
| | | xanthone (10 mol %) / RR, ~350 nm /30 min / $N_2$ | MeOH | 100 | |
| | | thioxanthone (10 mol %) / RR, ~420 nm /15 min / $N_2$ | MeCN | 100 | |
| | | Sensitized irradiation | | | |
| 3 | **8b** | xanthone (10 mol %) / RR, ~350 nm /1.5 h / $N_2$ | MeCN | 100(86)[e] | >99:1 |
| | | xanthone (10 mol %) / RR, ~350 nm /30 min / $N_2$ | MeOH | 100 | |
| | | thioxanthone (10 mol %) / RR, ~420 nm /15 min / $N_2$ | MeCN | 58 | |
| | | Sensitized irradiation | | | |
| 4 | **8c**[f] | xanthone (10 mol %) / RR, ~350 nm / 3 h / $N_2$ | MeCN | 100 | 82:18 |
| | | xanthone (10 mol %) / RR, ~350 nm /1.5 h / $N_2$ | MeCN | 100 | 80:20 |
| | | xanthone (10 mol %) / RR, ~350 nm /30 min / $N_2$ | MeOH | 100(78)[e] | 82:18 |
| | | thioxanthone (10 mol %) / RR, ~420 nm /15 min / $N_2$ | MeCN | 60 | 82:18 |

[a] Irradiation at room temperature. Values based on $^1H$ NMR spectroscopy (±5% error). [**8a**] = 2.88 mM, [**8b**] = 2.48 mM, and [**8c**] = 3.43 mM. [b] BB = broadband irradiation performed using 450 W mercury lamp with a Pyrex cutoff filter (<295 nm cutoff); RR = Rayonet reactor equipped with either 254 nm or ,~350 or~ 420 nm light (16 tubes X 14 W). [c] Acetone as solvent and sensitizer. [d] % conversion and mass balance calculated by $^1H$ NMR spectroscopy using triphenylmethane as internal standard. [e] Isolated yield. [f] The values were similar to the one reported in literature for other achiral acrylimides with N-aryl substitution . The major and minor photoproducts were assigned based on similarities in $^1H$ and $^{13}C$ NMR resonances in the reaction mixture as reported . The major photoproduct was characterized by single-crystal XRD. Reproduced from Ref[8j]. Copyright American Chemical Society,2014.

The reaction was efficient in acetone (which acted both as solvent and sensitizer), benzophenone, xanthone at ~350 nm irradiation and thioxanthone at ~420 nm irradiation in MeCN as solvent. The reactivity was not only efficient but also exclusively resulted in cross [2+2] photoproduct. For the achiral acrylimide **8c**, both cross and straight [2+2] products were observed. We believe that the N-C(aryl) restricted bond rotation in **8a-b** was responsible for the regioselectivity (straight vs cross photocycloaddition). Optically pure atropisomeric acrylimides **8a-b** resulted in >98% *ee* under triplet sensitized (xanthone and thioxanthone) irradiation.

The crystal structure of **8a**, gave interesting insights on bond distance between the reactive alkene units resulting in exploring solid-state irradiation. Analysis of the crystal structure (Figure 5) revealed that the distance between alkene carbons for straight addition i.e. $C_1$-$C_4$ is 3.189 Å, $C_2$-$C_3$ is 3.856 Å, similarly for cross addition $C_1$-$C_3$ is 3.158 Å, $C_2$-$C_4$ is 3.189 Å which are within the Schmidt distance of 4.2 Å for a solid state photoreaction to occur.[25] Additionally the torsional angle between the double bonds was 21.7°. Solid-state irradiation of optically pure crystals of **8a** was performed at room temperature on a petri dish using Rayonet reactor equipped with 254 nm bulbs. The reaction was clean and resulted exclusively in cross [2+2] photoproduct with >98% *ee*.

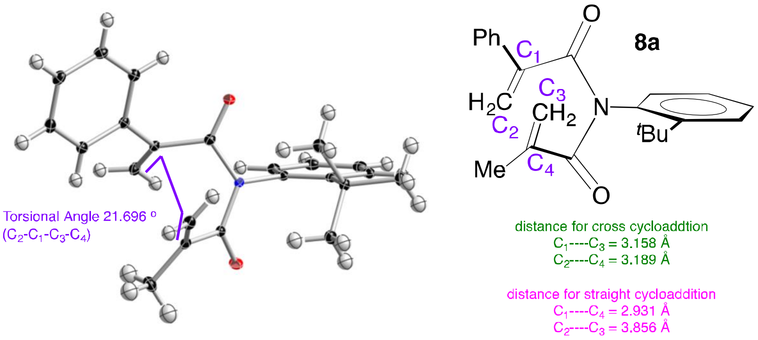


**Figure 5:** Single-crystal X-ray structure of **8a**.

Though the analysis of the bond distance between the atoms in the crystals favored both the straight and cross photocycloaddition, we only obtained cross product exclusively. We attributed the preference of cross product to the minimum atomic movement required for the formed cross photoproduct compared to the straight photoproduct.

Detailed photophysical investigations were carried out to gain insights on the photochemical reactivity leading to cross photoproduct. Fluorescence and phosphorescence measurements showed negligible luminescence both at room temperate and at 77 K. Transient absorbance spectra of **8a** was centered at 320 nm with lifetime of 40 ns (Figure 6). This transient was quenched by molecular oxygen ($K_q$ = 6 x$10^9$ $M^{-1}s^{-1}$) and was assigned to the triplet-triplet absorbance of styrene unit in **8a**. Similar studies with **8b-c** also showed the transient absorbance is around 320 nm with the lifetime of 41 ns for **8b** and ~20 ns for **8c**. The shorter lifetime of **8c** is attributed to the free rotation of the N-C(aryl bond). Since these reactions were efficient with triplet sensitizer, we investigated the energy transfer using laser flash photolysis. The bimolecular quenching rate constants of sensitizer (xanthone and thioxanthone) triplet state by **8a** were determined. Based on these studies the triplet energy of **8a** was estimated to be close to 63 kcal·mol$^{-1}$. The triplet quantum yield of **8a** was evaluated by generating the singlet oxygen upon direct irradiation. The relative triplet quantum yield of the **8a**

($\Phi_T \approx 0.02$) was calculated by comparing the efficiency with phenalenone as the standard ($\Phi_T \approx 0.98$).[22]

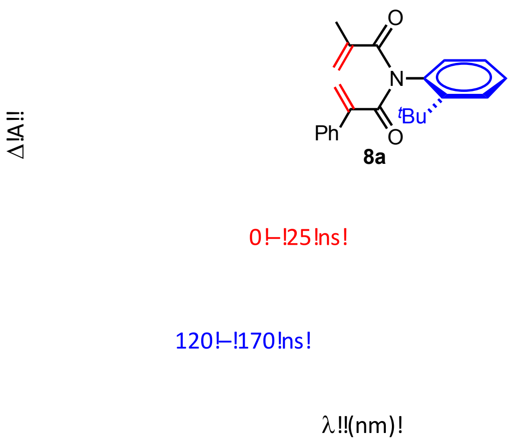


**Figure 6:** Transient absorption spectra monitored at 0-25 ns (red) and 120-170 ns (blue) after pulsed laser excitation (266 nm, 5 ns pulse width) of argon-saturated MeCN solution of **8a**.

Based on low triplet quantum yield and low impact on oxygen quenching studies on photoproduct yields, we believe that the [2+2] photocycloaddition proceeded via singlet excited states upon direct irradiation and via triplet excited state for sensitized irradiation (with xanthone or thioxanthone as sensitizer).

## 5. Conclusion

Research from our group showcases that light can be effectively employed in various fields from asymmetric synthesis to supramolecular catalysis to materials chemistry with excellent control of reactivity to product selectivity. Our methodology of transferring axial to point chiral makes it possible to afford complex molecular scaffolds with high stereocontrol in the resulting products. We have also showcased our methodology for metal free-redox free visible light catalysis for photoreactions. Diversity in the light initiated research is a clear testament to the power of photons in empowering different fields and facets of chemistry.

## Acknowledgments

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# PORTER MEDAL

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To nominate European candidates for The Porter Medal 2016, candidate's details should preferably be sent directly to the President of the European Photochemistry Association, Professor David Worrall (d.r.worrall@lboro.ac.uk). For nomination of candidates from other continents, see the Porter Medal webpage: http://www.portermedal.com. Nominations may also be sent to the Chair of the Porter Medal Committee, Professor David Klug. The nomination package should include:

- Curriculum Vitae of the candidate
- A list of publications
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Provisional closing date for the receipt of nominations (based on the guidelines from previous years) will be 31 January 2016.

Previous winners:

| | |
|---|---|
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| 1990 | Michael Kasha, USA |
| 1992 | Kinichi Honda, Japan |

| | |
|---|---|
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| 1995 | J.C."Tito" Scaiano, Canada (Special Medal for London ICP) |
| 1996 | Noboru Mataga, Japan |
| 1998 | Frans de Schryver, Belgium |
| 2000 | Vincenzo Balzani, Italy |
| 2002 | Josef Michl, USA |
| 2004 | Graham R.Fleming, USA |
| 2006 | Howard E. Zimmerman, USA |
| | Hiroshi Masuhara, Japan |
| 2008 | Michael R. Wasielewski, USA |
| 2010 | David Philips, UK |
| 2012 | Thomas J. Meyer, USA |
| 2014 | Masahiro Irie, Japan |

## EPA PRIZE

# EPA Prize for Best PhD Thesis in Photochemistry
# Call for Nominations

The EPA Prize for the best PhD thesis in photochemistry will be attributed during the CECP 2016 Meeting which will be held in Bad Hofgastein, Austria, in 2016. The awardee will present his/her work at the Symposium. The Prize is 1000 Euros, plus travel costs to Bad Hofgastein (within the limit of 300 €) and one free year of EPA membership. The candidate must have defended his/her PhD thesis in 2014/2015 and be nominated by an EPA member. Nominations should be sent (electronically only) to David Worrall (d.r.worrall@lboro.ac.uk). The nomination package should include:

- Curriculum Vitae of the candidate
- Copy of the thesis
- Abstract of thesis in English, no more than five pages
- List of publications arising from the thesis
- A letter of support.

Closing date for the receipt of nominations will be 31 December 2015.

**Previous winners:**

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

# SPECIAL REPORTS ON PROMOTING PHOTOCHEMISTRY

## Introduction

Dear EPA members,
This issue of the EPA Newsletter, June 2015, is dedicated to the understanding of Photophysics/Photochemistry concepts via simple, eye-catching experiments performed by researchers, addressing students, teachers, and the general public.

*David Philips* is well known not only as a prestigious researcher but also as an excellent communicator of the importance of science to the general public. He mentions relevant points to captivate the audience while learning science. The amount of science introduced would depend on the age and experience of the audience while the demonstrations themselves would be simple and relevant to the concept being introduced.

*Peter Douglas* has given quite a few demonstration lectures addressing students, families, and teachers, in a variety of countries. He firmly believes that this is a valuable tool for presenting the wonder and delight of science at different audiences as well as for inspiring next generation of researchers to deal with issues facing mankind.

*John Sodeau* reflects on two totally different research subjects that have caught his attention. One of them is related to gaining information into the Antarctic ozone hole problem by using the matrix isolation technique. The other is related to real-time monitoring of airborne primary biological aerosol particles and their content by using fluorescence.

*Michael Tausch*'s research is focused on the didactics of chemistry and his contribution deals with the need for teaching photophysics/photochemistry at all levels and how valuable attractive experiments are for this purpose.

*Claudia Bohrmann-Linde* describes a set of interesting experiments aimed at children aged between 8 and 12 years old. An exploration of liquid crystals was made beyond the mere phenomenological approach by working with different types of models which progressively introduced the underlying concepts.

*Axel Griesbeck and co-workers*' contribution describes how photochemical processes are more easily understood by visualising them using analytical techniques, i.e., tracing photochemistry with simple experiments that can be followed by different methods, such as absorption and emission spectroscopy.

The EPA committee wants to highlight the importance of the input of excellent communicators and we think that this special year (the international year of light) is a good occasion for that.

Finally, companies related to this field of research can also act as diffusion agents through their webpages. All of them are encouraged to increase their role in dissemination of science related to LIGHT as an innocuous reagent and as an activating agent of physical processes.

*Julia Pérez-Prieto*
*Associate Editor EPA Newsletter*
*Universidad de Valencia*
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*C/ Catedrático José Beltrán 2*
*46980 Paterna, Valencia*

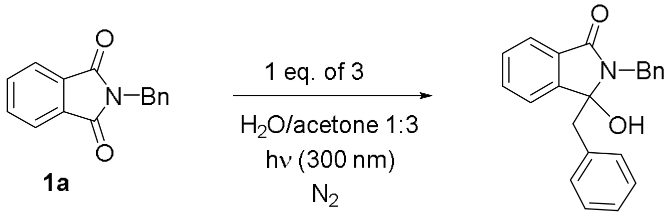
# Tracing Photochemistry with simple experiments and not-so-simple Spectroscopy

***Axel Griesbeck, Sebastian Hanft, and Sabrina Molitor***
***Department of Chemistry, Cologne University, Organic Chemistry Institute, 50939 Köln, Germany***

Many photochemical reactions are not easy to understand for most undergraduate students at universities, not to talk about college students or pupils in high schools. One obvious problem is that we add to the already complex world of electronic ground-state reactions, intermediates, and transition states the strange world of electronic excitation. Even worse, spin isomers, singlet and triplet excited states appear, intersystem crossing, internal conversions and, unavoidable, quantum chemistry dictates many events. Additionally, ultrafast processes from the microsecond down to the femtosecond time regimes add to the scene.

One way to make the understanding of these processes easier and, at the same time, not to oversimplify the chemistry, is to collect data that visualize reaction progress. Direct visualization might for example take advantage of the colour changing properties of photochromic molecules that can be deposited in polymeric matrices and switched by light sources such as laser pointers or overhead projectors. This approach uses however a direct visual impression that might hinder the deeper understanding of the relevant photophysical and photochemical processes. Thus, what we are currently developing is a combination of classical photochemistry with analytical methods that are well known to undergraduate students. One example (ref. 1) is the photodecarboxylation of alkyl carboxylates and aryl acetates by triplet phthalimides (N-benzyl phthalimide **1a** in Figure 1). The latter are well characterized excited states (family: aromatic imides like pyromellitic or perylene carboxylic acid imides, currently intensively investigated acceptor compounds) and are good electron acceptors in their triplet states (= reductive quenching processes). Simple carboxylates such as phenylacetate (**3** in Figure 1) are oxidized to the carboxy radical, and after rapid decarboxylation generate benzylic radicals that add to the phthalimide radical anions. By such a process, acetates are converted to alkoxides and this transitions leads in aqueous solution to a rise in pH.

Simultaneously, carbon dioxide is eliminated and can be measured in the gas phase. Thus, cheap and reliable sensor systems can be used to visualize light-induced chemical processes.



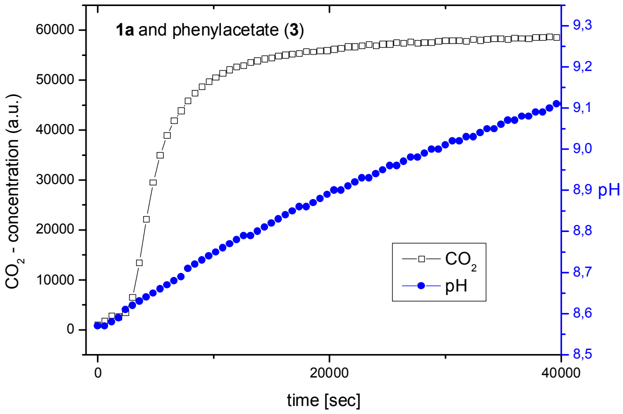


Figure 1. pH and $CO_2$ evolution traces with photolysis time for a mixture of a phthalimide **1a** and phenyl acetate starting at pH 8.5 in aqueous unbuffered solution.

Figure 2. Pyrex irradiation chamber with two outlets for the simultaneous determination of pH, electric conductivity and temperature (in solution, central outlet) and carbon dioxide measurements in the gas phase (right outlet) and registration by means of a PASCO Xplorer GLX Graphing Data Logger.

On the other hand, sensors that we need to for the development of the analysis of environmental conditions but also for kinetic evaluation of photochemical (and other) reactions, need improvement and constant development of new systems. The same kind of chromophore that we used for (stoechiometric) photodecarboxylation experiments is also useful as a synthetic building block for sensor molecules that are able to detect neutral analytes such as hydrogen peroxide or anions like fluoride, cyanide or sulfate. An application that gains more and more importance is the detection of the enantiomer composition of chiral analytes, i.e. enantiodifferentiating reporter molecules. These sensors can be obtained by a modular approach (ref. 2) combining the emitting fluorophore with a recognition unit and a chiral group that leads to enantiodifferentiation. A typical result is show in Figure 2 where the sensor recognizes R-lactate two times stronger than the S-enantiomer. These effects are depicted by absorption spectroscopy (new absorption bands), by fluorescence and by time-resolved fluorescence spectroscopy in the sub nanosecond time regime. This approach takes use the meaningful combination of all basic photophysical techniques.

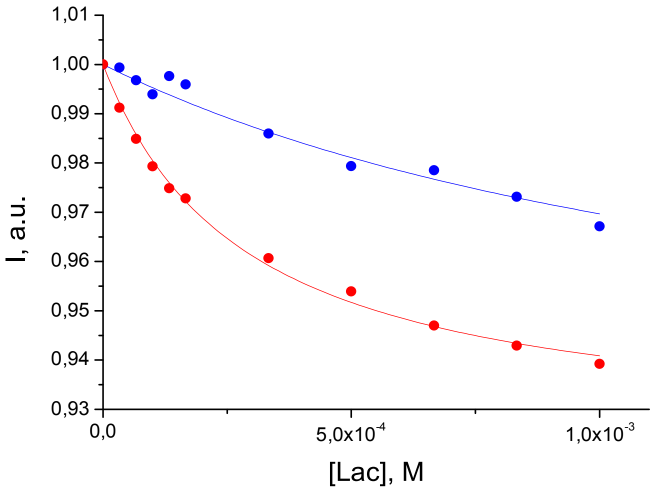


Figure 3. Fluorescence quenching of a chiral phthalimide-urea-amino alcohol sensor triade with additional amounts of (R)- versus (S)-lactate: proof of moderate enantiodifferentiation.

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## Catching the Light

***Peter Douglas***
***Chemistry Group, College of Engineering, Swansea University, SA2 8PP, UK***

Demonstration lectures and chemistry workshops have been an important, and highly enjoyable, part of my life in chemistry ever since I joined Swansea University almost thirty years ago. George Porter's Christmas Lectures from the Royal Institution were an inspiration while I was a teenager, I still remember how much fun Bob Cundall's 'explosions' lecture was when I saw it while an undergraduate at Newcastle University, and then studying at the Royal Institution gave me the chance to see some other superb demonstration lectures.

The first demonstration lecture I was involved in, 'Photochemistry in Action',[1] was put together with Andrew Mills for a University open day soon after I arrived in Swansea in 1986. Since then, and subject to many changes, (the most important of which was bringing Mike Garley into the two man lecture team when Andrew Mills left Swansea for Strathclyde), we've given the demonstration lecture, now called 'Chemistry and Light', perhaps 100 times at more than 30 venues around the world, to a total audience of something like 20,000-25,000 students, families, and teachers, across the UK and Ireland, and in Belgium, France, Switzerland, Malta, Singapore, and South Africa.

The lecture is a series of demonstrations around three themes: how light is made; how light is used in technology and everyday life; and how light might be used in the future in the production of clean water and clean energy. 'On how to get noticed in the club or disco' is probably the most notable part, since it is involves me dressing up in UV active 'club gear' and generally playing the fool (Fig. 1), but humour is an important part of how I like to present science. But the serious aim is to present the wonder and delight of science to students and the public, and to inspire the next generation of scientists to deal with the key technological, medical, environmental, and energy issues facing mankind, notably the need for clean water and clean energy – both very active areas of photochemical research. It takes us a transit van of equipment and quite a few hours setting up and taking down, so it is quite a bit of organising.

**Figure 1.** How to get noticed in the club or disco. Learned Society of Wales Inaugural Christmas Lecture, Cardiff 2013, (photo by Simon Gough).

Chemistry is an experimental science, and I've always been keen to give workshops where participants get the chance to do some experiments of their own. Phil Jones, at the International School of Paris in Versailles, invited us to give chemistry workshops for his IB students in 1992, and from this we developed a regular series of workshops, 'Catching the Light', between 1992 and 2004, held in Versailles with students from schools in UK, Belgium, France, Germany, Greece, Holland, Luxembourg, Spain, Turkey, Finland, and Switzerland. One of my favourite experiments in these workshops was a luminol chemiluminescent 'clock reaction' based on an experiment described by Peter Jones and Jane Frew from Newcastle University. The experiment gives a 'clock' pulse of bright blue chemiluminescence when two solutions are mixed. The delay time of the pulse is controlled by the concentration of vitamin C. So we'd get the participants gathered around a large table with the two solutions ready to mix, placing each team with a different, increasing, vitamin C concentration in order around the table; knock the lights off; give our eyes thirty seconds or so to adjust to the light; then on the count of three all rapidly mix the two solutions required to give the clock reaction and place the mixed solution on the table. These then would 'clock' in order round the table which is always great fun to watch. We also did some 'photogenic drawing' with Fox-Talbot salted paper prints, some experiments making carbon dioxide sensors, oscillating chemical reactions, and micro-column chromatography of plant extracts.

We met up with Phil Jones again in 2010, when we gave a 'Science Week' at St George's School, Neuchatel, where he was the Director. This was a series of workshops for junior, middle, and senior school pupils. We used some of the experiments described above, but added: blueprints; colour and chemiluminescence; paper chromatography; and acids and bases with red cabbage indicator colours, for the younger groups. This gave one of my favourite comments about any of the workshops, written on the St George's School Blog: "On Tuesday, we, the junior class, first did a lesson about acids and bases with the only woman of the week, Ingrid. I really enjoyed that lesson because I learned quite a lot and I discovered things I would never think of otherwise."

The most recent workshops were part of a project "*Catching the Light with the Rainbow Nation*", South Africa, 2013, organised with Matthew Davies from the SPECIFIC group in the College of Engineering, Swansea. Over a two-week period we ran workshops in Durban and Mafikeng for 1300 school children. For the senior school groups we concentrated on an experiment to make and test a dye sensitised solar cell. We introduced a bit of competitive fun by splitting each workshop into groups which used either fruit dyes or dyes from South African rooibos to see which gave the best cells, (Fig. 2).

**Figure 2.** Students at Mafikeng High School filter raspberry juice to extract the red dye to make a dye sensitised solar cell, (photo by Bruce Philip).

I like to include both historically important science such as Fox-Talbot photogenic drawing, and something linked to current research, such as dye sensitised cells, in the lecture and workshops. And in a twist in the research–demonstration lecture relationship, the work described in a recent paper[2] on the iconic dye mauveine was started because I wanted to find an original sample which could be shown during lectures.

I'd like to thank all of funding bodies and organisers who have made it possible for us to present the lecture and workshop over the years. And it all takes teamwork, and so, to all of the lecture and workshop teams over the past thirty or so years, thanks - it has been great fun!

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## Here comes the Sun

***Professor John Sodeau, Director of Centre for Research into Atmospheric Chemistry (CRACLab)***
***University College Cork, Ireland***

An article with a title like the above will go one of two ways: the "solar energy materials" route or the "our atmosphere" route. (It could, of course, go by both if it is about "understanding photosynthesis"). Photochemistry obviously is the foundation for all three pathways but where the road goes very much depends on where the student starts walking. My lifelong interest in "Photochemistry and Photophysics" began while still an undergraduate at the University of Southampton (I won't embarrass the person who sparked it all for me!) But my real journey started when, as a Postdoctoral Fellow at the University of California in Irvine (UCI), I met and worked with Ed Lee, had daily coffee with Sherry Rowland and Mario Molina and shared an office with Jack Calvert. I didn't stand much chance did I? Yes I chose the atmospheric chemistry, and now aerobiology, road to stroll along.

The Sun drives life on planet Earth by creating and breaking molecules in the atmospheric region above the water and land surface on which we live and rises up to about 120 km in altitude. It is not one static homogeneous layer of gas as was once thought to be the case….even before my time. No, it is a dynamic layered-by-temperature fluid containing gases, water vapour, droplets and solid particles that can be chemical or biological in origin, as well as various highly reactive radical species. And it was those radicals controlling the observed reaction pathways in the atmosphere that once again caused my interest to become sparked. My research project at UCI was directed toward identifying the intermediates formed in the photochemistry of formaldehyde, a very important pollutant in the lowest region of our atmosphere called the troposphere. The late Professor Ed Lee, who was my boss, had performed many studies on the photophysics of H2CO but not much about its break-up in light. The end products were known: hydrogen and carbon monoxide formed by two photolysis pathways, one direct and one by forming two radicals, HCO and a hydrogen atom. I had been hired to confirm this using IR spectroscopy. Fast scan-methods were not available then but a technique called matrix isolation was. (I had done a PhD in the subject showing that CO was not the only molecule that could be released from photolysed organometallic carbonyl compounds in low temperature solids; bulky old pyridine could be too).1 The subsequent results I got at UCI were strange to say the least. The observed photo-products in a solid Ar matrix held at 10 K could only be explained, I felt, by the formation of an unusual carbene called hydroxymethylene (HCOH) that only had an existence in the world of computer modelling until that point.2 That was in 1978. You can imagine my sigh of relief some 30 years after this prediction when HCOH was finally captured spectroscopically.3

I applied similar techniques with a whole team at the University of East Anglia between 1980 and 1998, although then we concentrated on trying to understand some stratospheric chemistry and a problem you have all heard of: the Antarctic ozone “hole”. This phenomenon leading to irreversible ozone destruction occurs when active chlorine atoms and the ClO radical are somehow released from the photochemically inactive compound, HCl. This molecule is a so-called atmospheric “sink” for chlorine in the stratosphere. Modelling calculations indicated that the molecular form would prevail even when it was cryo-pumped and adsorbed to the small, airborne ice particles there called Polar Stratospheric Clouds (PSCs). Our experiments showed at temperatures present in the Antarctic stratosphere during Winter that HCl became solvated by the water-ice, which allowed it to become ionized and make free chloride ions. These ions could rapidly react on the ice surface with other chlorine-containing compounds present there like HOCl and chlorine nitrate (ClONO2) to release photo-active molecular chlorine. This was a novel and key finding to help understand how ozone was destroyed over Antarctica because HCl, HOCl and ClONO2 react only very slowly in the gas-phase.4

One other parallel road I followed in my career at UEA was to modify microbes to become photo-protectors, photocatalysts and light-emitters by treating them so that they would form metal sulfide 'Q-particles' on their surfaces.5 After that time though, as I explained above, my research moved toward the study of atmospheric chemistry related mechanisms in the laboratory. We quickly realised that to validate any of those experiments air monitoring studies on real roads have to be undertaken and that is what I and the CRACLab research team at University College Cork have done over the last 10 years or so. At first the measurements were directed exclusively toward airborne chemical pollutants. But now, once again, after all those years away I have returned to luminescence to not only count and identify airborne Primary Biological Aerosol Particles (PBAP) like fungal spores and pollen in real-time but also to probe their biochemical contents using fluorescence lifetime measurements.6 In the field campaigns we have used a new type of instrument called WIBS (Wideband Integrated Bioaerosol Sensor) based on fluorescence detection to monitor biological particle emissions from trees7 and agricultural material like hay8 and most recently from composting/green waste sites.9 Those studies really came out of nowhere into my research orbit but it has shown me that although the road you are on is important, it's the people who are with you, those who have been with you and the view you get from looking around that should be valued the most.

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# Light up their Lives

***David Phillips***
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Many photochemical reactions are not easy to understand for most undergraduate students at universities, not to talk about college students or pupils in high schools. One obvious problem is that we add to the already complex world of electronic ground-state reactions, intermediates, and transition states the strange world of electronic excitation. Even worse, spin isomers, singlet and triplet excited states appear, intersystem crossing, internal conversions and, unavoidable, quantum chemistry dictates As a chemist interested in enthusing young people and the lay public in chemistry in general, photochemistry in particular, I have found it relatively easy to illustrate in an amusing but informative way the basic principles and applications of our subject, because demonstrations can easily be prepared and used to dramatise the science. The basic rules of demonstrations are that they should be simple, immediate, and relevant to the science one is trying to put across to the audience. I began using demonstrations when lecturing to undergraduates in the University of Southampton, in 1967, and turned these into my first demonstration lecture, 'Chemistry of Light' , inspired by a similar lecture given by J.C.Robb in the University of Birmingham, where I was an undergraduate and post-graduate student. Over the years, I have developed many others under the titles 'Lasers, the Light Fantastic', Chemistry of the Atmosphere' 1, and perhaps the most widely given 'A Little Light Relief'2,3.

All concern applications of photochemistry and lasers, the last concentrating on the uses of light in medicine, seen from a chemist's point of view. For this lecture, my closing demonstration, and my trademark, has always been the use of blue light to cure neonatal jaundice, a therapy in use since the mid 1950's. I had a glass baby 'Bobbitt' specially made in the University of Southampton in which a chloroform solution of bilirubin was shown not to dissolve in water, but after irradiation with blue light, then dissolved [ through a photochemical cis –trans isomerisation reaction which exposes carboxylic acid groups enabling the dissolution in water. The baby then urinates into a child's potty, causing great delight in young children ! The name 'Bobbitt was coined because the baby is essentially a separating funnel, with a very strategically located stopcock[clearly a male baby] Over the years, the stopcock proved to be the most vulnerable part of the baby's anatomy, and had frequently to be re-joined to the body, echoing the unfortunate fate of one Wayne Bobbitt jr. The original 'Bobbitt' was destroyed in transit to Berlin in 2013 where I was giving the Queen's Anniversary lecture at Technical University Berlin in , but the University of Southampton have generously constructed a replacement, shown in Figure 1 and named 'Mike' after the glassblower who made the original.

Luminescences, particularly fluorescence, are usually very well appreciated by audiences ranging in age from the very young , [ages five to 11],through older school students, undergraduates, post-graduates, to the elderly, typically U3A. The amount of science introduced into the lecture does of course vary with the age and experience of the audience, but the demonstrations remain the same.

One can use dyestuffs of every colour to illustrate fluorescence, but my favourite demonstration is to drink tonic [quinine ]water illuminated by uv light, where the intense blue colour of the quinine fluorescence causes delight in the audience. I invariably add a little gin to the mixture; the gin does not of course fluoresce, but makes the drink more palatable !

Explosions are also arresting for the audience, but should only be used where relevant to the science. Perhaps the simplest is the hydrogen/chlorine explosion, initiated with visible light, though care must be taken to exclude oxygen which inhibits the reaction. The demonstration can be carried out in a glass test tube, which gives an audible 'pop', but can also be done on a larger scale. I have on occasion used large plastic bags filled with the mixture, initiated either by a powerful visible lamp, or even in sunlight. Ventilation is essential, given the product is HCl !

There are many others- photo-polymerisation, photo-chromism, photo-degradation, the production of 'photochemical smog' in a fish-tank, and above all, the demonstration of powerful lasers, [made much easier by the advent of semiconductor battery-driven lasers of all colours] causes wonder and delight in audiences of all ages, but particularly the young4.

My only tip would be to write the lecture highlighting the science you wish to communicate, then fit demonstrations into this narrative to illustrate and dramatise the science. Done in reverse, ie starting with the demonstrations, there is a danger the science will take second place to the theatre, and you can end up with a 'magic show' which though enjoyed by the audience can be an ephemeral experience.

Figure 1 'Mike' the replacement glass baby used to demonstrate light treatment of neonatal jaundice, University of Southampton 2013

Over the years, I have reached live audiences in excess of 250 000 people, and appeared on TV [BBC Christmas Lectures], the Discovery Channel, Japanese TV,etc where the audiences are counted in millions. I hope I have lit the lamp of interest in our subject in many of these audiences; certainly my own life has been made hugely enjoyable by communicating photochemistry.

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# Exploring Liquid Crystals with Kids

***Claudia Bohrmann-Linde***
***Chemistry and Chemistry Education, University of Wuppertal, Germany***

They have been known for more than 125 years [1], everyone looks at them every day, yet many people know only little about them: liquid crystals. This is a class of matter which has turned from being a mere laboratory curiosity into an important component in digital displays, flatscreen TVs or displays for mobile phones in our homes. How can we imagine the particles inside a sample of a liquid-crystalline substance to look like and how must these particles be arranged in order to make a pixel visible? And – very important for people involved in teaching- how can we explain this complex topic to pupils?

Here simple experiments on liquid crystals and a didactical concept for exploring the function of a basic liquid crystal display (LCD) are presented. The latter was developed in the department of chemical education in Wuppertal, Germany, within a cooperation project with the company Merck. It was successfully tested in October 2014 within workshops during the „door opener´s day“, which is annually called for by a famous educational television format for children, “Die Sendung mit der Maus” [2]. The didactical exploration aimed at children aged 8 to 12. With simple experiments the future scientists could learn step by step how a basic LCD works (Fig.1).

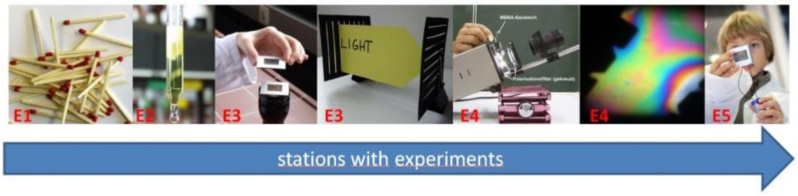

**Figure 1.** Experiments for exploring liquid crystals and LCDs

The first aspect to deal with is states of matter and to introduce the liquid-crystalline state as fourth state of matter. It is described as something inbetween the solid and the liquid state of matter. Further information that is given are the facts that liquid crystals are turbid and capable of flowing, they scatter light, their particles exist in some kind of order and they interact with an external electrical field.

- Order and disorder in a model experiment (E1)

Equipped with this information the pupils carried out the first experiment E1. Here a first encounter with models takes place and the aspect "order of particles" is focused on, which is relevant throughout the whole didactical sequence. The pupils were asked to bring order into a heap of matches which was placed on a sheet of paper and to explain the order they had chosen. The matches were introduced as models for the particles inside a liquid-crystalline sample and compared to a molecule model of the liquid-crystalline substance MBBA, which also has a relatively straight shape (Fig.2).

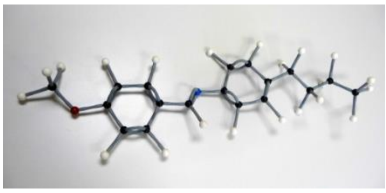

**Figure 2.** Model of an MBBA-Molecule

In a second step the pupils were asked to slightly shake the sheet of paper, so the order of the matches was destroyed. This simulates the heating of a liquid-crystalline sample, which causes the molecules to lose their ordered arrangement and spread irregularly through the sample.

- Clearing point of a liquid-crystalline sample (E2)

In the second experiment E2 the pupils got a sample of the liquid-crystalline substance *N*-(4-methoxybenzylidene)-4-butylaniline, MBBA, inside a glass ampulla.

The synthesis of MBBA by *Hans Kelker* in 1969 [3] is considered a milestone in the research of liquid crystals, because for the first time a substance had been found that is in the liquid-crystalline state at room temperature – a vital requirement for its use in liquid crystal displays. MBBA belongs to the group of calamitic liquid crystals. Their molecular shape can be considered rod-like, which is represented by the match models very well. From a didactical point of view MBBA is a very interesting substance, because it can even be synthesized by school means in the advanced chemistry classroom via a condensation reaction of 4-methoxybenzaldehyde (*p*-anisaldehyde) and 4-butylaniline and it can be used in further experiments [4].

In E2 the pupils´ task was to examine the light yellow, turbid substance in the ampulla at room temperature first and then to heat one ampulla with a blow-dryer, while cooling a second ampulla in a salt-ice-mixture. So the phase transitions from liquid-crystalline to liquid (at 47°C) and from liquid-crystalline to solid (at 22°C) could be observed. The new term "clearing point", which defines the transition temperature from liquid-crystalline to liquid or vice versa, was introduced. When the liquid-crystalline MBBA is heated, the turbid fluid clears up and becomes transparent. When the heat source is removed, the substance becomes turbid again (Fig.3).

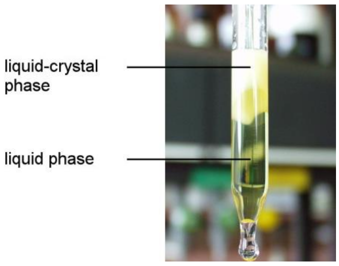

**Figure 3.** Glass ampulla with MBBA after heating the tip with a blow-dryer

- Experiments with light and polarization filters (E3)

In the third experiment E3 one deals with the topics light, polarization and polarizing filters. The pupils were asked to look into the light beam of a torch (with a weak light bulb, not an LED!) and to place one polarizing filter on top of the torch. In the next step a second polarizing filter was to be held at some distance on top of the first polarizing filter and to be rotated in plane. During this rotation one can see the light fading down to extinction and brightening up again, depending on the position of the polarizing filters towards each other. The terms parallel and crossed filters are introduced. The polarization of light and the passing and the extinction of light is explained by cardboard models (Fig.4).

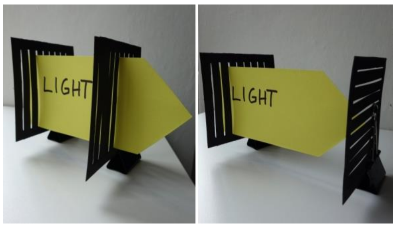

**Figure 4.** Models for the passing of light at parallel polarizing filters and for the extinction of light at crossed polarizing filters

- Colours and shapes by light passing liquid crystals (E4)

After having found out that crossed polarizing filters lead to the extinction of light one can make an astonishing observation in experiment E4. If you place a "sandwich" made of two microscope slides with a drop of MBBA within between crossed polarizing filters in the light beam of a slide projector, the light can pass in those areas covered by the liquid-crystalline sample even though the filters are crossed. Due to light scattering and interference phenomena one can also see beautiful colours in the areas where the liquid-crystalline layer is not uniform in thickness (Fig.5).

**Figure 5.** MBBA sandwich (left) and passing light at crossed polarizing filters (middle and right)

The observation that light can pass inspite of crossed polarizing filters focuses on a property of liquid crystals which is crucial for LCDs: the property of turning linearly polarized light. Now the topic "order" becomes relevant again. One can imagine the molecules of the liquid-crystalline substance to be ordered like the steps of spiral stair or like a helix. Along this twist the linearly polarized light is turned, so it can pass the second polarizing filter and is seen on a screen. From the MBBA-sandwich it is only a small step towards a liquid crystal display.

- Working with a simple 1-pixel-display (E5)

In the fifth experiment E5 the pupils got a 1-pixel test cell and a battery. By connecting the poles of the battery to the cell they could make a square pixel appear in black. Disconnecting the cell from the battery made the pixel vanish again. In this experiment the focus is on the interaction of liquid crystals with an electric field. It was explained that the molecules of the liquid crystal arrange in a twisted way, which is supported by orientation layers on the inner sides of the conductive glass plates of the LCD cell. The LCD is covered by two crossed polarizing filters. When applying a voltage the molecules arrange parallel towards the electric field. Now the light cannot move through the second polarizing filter and the pixel appears black.
Besides the finished 1-pixel-cell another test-cell was handed out which had not been equipped with polarizing filters. The pupils´ task was to make the cell work. By thinking back about the experiments E3 and E4 they could take two of the polarizing filters from E3, cross them and place the test-cell inbetween them. By connecting the cell with the battery they could make the black pixel appear (Fig. 6).

**Figure 6.** Making a pixel appear in a simple display

The possibility to make a pixel appear by applying an electric voltage and removing it is a link to talk about the addressing of pixels in commercial displays. This was only dealt with marginally in this experimental sequence. To take a step towards commercially available LCDs it was talked about how many single pixels need to be addressed in a typical TV screen, so the pupils could get a glance at the dimensions and the precision needed in manufacturing displays for TVs and monitors.

The experience with the realization of the concept with three groups of 30 pupils each has shown that it is well possible to make complex scientific topics accessible for children on a suitable level and to support them in their own experimental activities. The level of understanding of the underlying processes even reached beyond the mere phenomenological approach and the pupils were well able to work with different kinds of models.
As a follow-up regarding coloured displays the „LCD-Explorer" by the company Merck [5] can be recommended.

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# Chemistry and Light - An Imperative for Teaching at all Levels

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In the year 1865 A. F. KEKULÉ, the doyen of aromaticity, described chemistry as the "theory of the metamorphosis of matter". Analogously the didactics of chemistry can be described as the "theory of the curricular metamorphosis of the communication of chemistry". The major aim of *curriculum innovation* research is an increase in the quality of the teaching of chemistry by renewal and adaption of the contents and the methodology of the teaching to the state of the art of scientific knowledge, future-relevant issues and social life forms within the technological civilization.

In this sense *photoprocesses*, in which light participates as input or

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**Figure 1.** Experiments with light http://www.chemiedidaktik.uni-wuppertal.de/english/index.html

output, are of fundamental importance for all science subjects, however, this is particularly true for chemistry. They hold key functions in central research topics and innovative technologies of the 21st century. Among catchphrases such as energy transition, energy efficiency, photovoltaics, conservation of resources, climate change, sustainability and "green" chemistry, photo processes increasingly gain significance in economy, politics and the public debate. Under these conditions the stronger integration of photo processes into the teaching of chemistry at schools and universities becomes an up-to-date requirement. In order to realize that the following three prerequisites are needed:

1. "A pretty experiment is in itself often more valuable than twenty formulae extracted from our minds" – this often quoted aphorism by A. EINSTEIN should always be a leitmotif for the teaching a natural science, even when photo processes are concerned. Chemistry education is especially dependent on "pretty experiments", which deliver in sensual perceptible phenomena exactly those observations, which directly rise to interpretations and explanations on the intellectual level of models and concepts. Didactically concise experiments of this kind are the focus of the curricular innovative research at the didactics of chemistry at Wuppertal. In figure 1 there ten categories of phenomena are given, for which experiments dealing with photo processes have been developed and which are readily available. In different versions they are suitable for chemistry education at lower and higher secondary level as well as for education of future chemistry teachers. A comprehensive list of all these experiments together with literature citations and the necessary equipment can be found online at http://www.chemiedidaktik.uni-wuppertal.de/english/index.html.
2. Researchers in science and science education alike consider the communication of chemical key concepts as being an efficient method for the teaching and learning of chemistry, because these concepts are able to subsume large classes of phenomena, reaction types and mechanisms. An easy key concept is the paradigm of the ground state and electronic excited state of molecules and other atomic systems, which is described by N. J. TURRO as "the heart of all photoprocesses". This key concept is sufficient to explain photoprocesses with and without "metamorphosis of matter" on a first, scientifically consistent level of abstraction. Within innovative

chemistry courses at schools and universities this concept has to be assigned the same significance as other basic concepts such as matter and particles, structure and properties, donor and acceptor or energy and catalysis. Accordingly the concept of ground and electronic excited states has been integrated into the didactic material for teaching at schools and universities. It has been adapted to the respective photoprocesses. In most cases, in addition to print media (textbooks, worksheets), interactive Flash animations have been developed, which are illustrative and helpful for learners understanding the elementary processes at particle level. See http://www.chemiedidaktik.uni-wuppertal.de/flash/index.html.

3. Phenomena including the participation of light should be integrated into the chemistry syllabus as early as possible. In the sense of a cumulative learning process within a spiral curriculum photoprocesses should be applied and deepened for higher stages of the syllabus. It is an error to believe that photoprocesses only belong into the higher secondary or university level. Even at the beginners' stage at lower secondary schools e. g. fluorescence of luminous paints can become a topic within the teaching topic "properties of matter" or "light as a type of energy in chemical reactions". However, they should be taught at a phenomenological level. These phenomena are part of students' everyday experiences and can be integrated into the current curricula. Therefore, *innovative curricula* have to be re-adjusted, so that the communication of phenomenological, conceptual and technological basics of the interaction between light(quanta) and matter(particles) towards the young generation can be achieved. The contents which are linked to the teaching aims are both motivating and efficient for understanding of chemistry and other scientific disciplines.

The *International Year of Light 2015* is a great opportunity to bring photochemistry in the centre of attention of researchers and teachers at schools and universities alike. To achieve this, the divisions of the German Chemical Society GDCh "Photochemistry" and "Chemistry Education" have initiated different activities, which are coordinated via their own website http://www.iyl2015.uni-wuppertal.de/. After clicking on "Videos" a list of contributions by leading researchers in the field of photochemistry can be found. Likewise by clicking "Events" a list containing information about planned lectures and workshops as well as national and international conferences and symposia can be viewed.

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## PILLS OF HISTORY

# At the origin of photochemistry. The dimerization of cinnamic acid derivatives

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Several natural or biological active compounds are dimers of cinnamic acid derivatives. α- and β-Truxillines **1** and **2** are alkaloids found in *Erythroxylum coca* and *Erythroxylum novogranatense*,[1] and they are strong heart toxins (Figure 1).[2]

The compound **3** is active antidepolarizing curare-like agent able to induce tachycardia by blockade of muscarinic receptors of the heart (Figure 1).[3] Dimers of *p*-coumaric and ferulic acid are in graminaceous cell walls and are involved in the resistance of this structure.[4,5] Compound **4** has been isolated in *Verbesina caracasana* and showed hypotensive activity (Figure 1).[6] Finally, compound **5** was identified in Caribbean sponges *Agelas sceptrum* and *Agelas conifera*, and showed antimicrobial and antibacterial acrivity.[7-9]

The study of the photochemical behavior of cinnamic acid started at the end of XIX century when Liberrmann found that a cinnamic acid derivative, the cinnamylidenemalonic acid **6** (Figure 2), was not stable under light. The colored solid became uncolored under irradiation.[10] He wrote: "Die gelbe Farbe der Cinnamylidenmalonsäure wie auch der Cinnamenylcyanacrylsäure hält sich im Dunkeln (jetzt über ein Jahr) unverändert, dagegen sind beide Verbindungen, namentlich die am tiefsten gefärbte erstere, im festen Zustand gegen Sonnenlicht sehr empfindlich. Ihre Oberfläche entfärbt sich sehr bald; als grössere Mengen Cinnamylidenmalonsäure unter einer Glasglocke bei öfterem Umschaufeln dem directen starken Sonnenlicht ausgesetzt wurden, konnte die Säure im Sommer nach 14 Tagen bis 3 Wochen fast weiss erhalten werden."

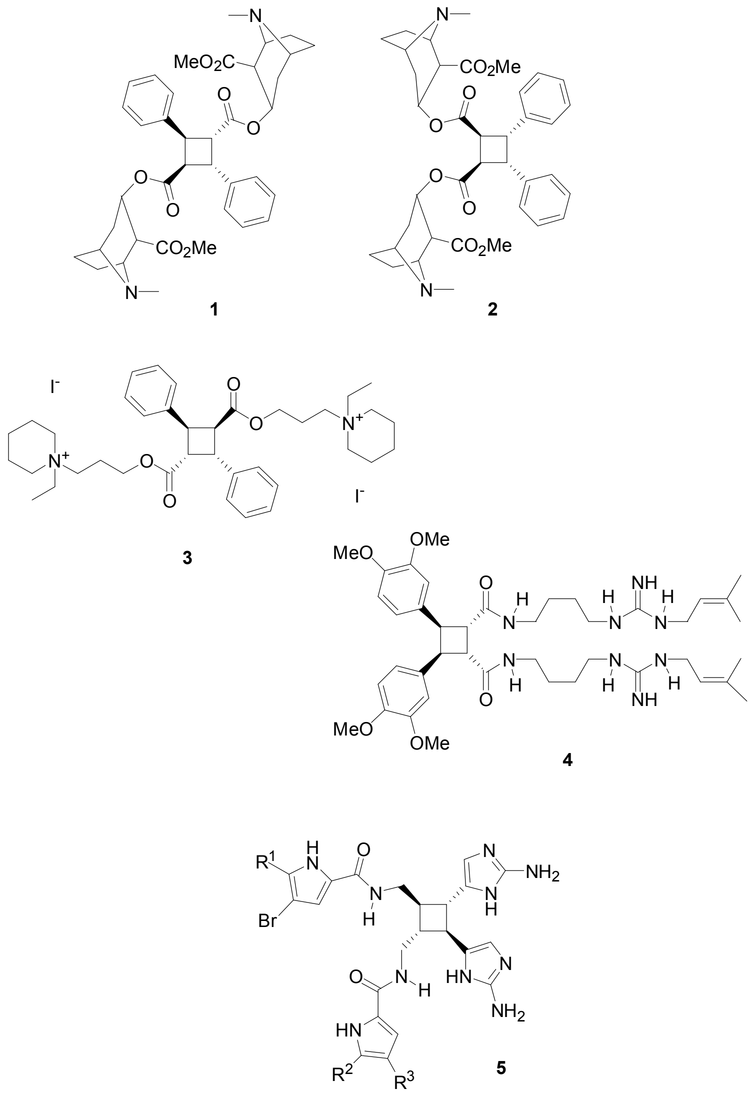
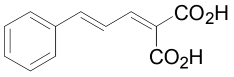


**Figure 1.** Naturally occurring compounds dimers of cinnamic acid derivatives and of the corresponding heterocyclic derivatives.

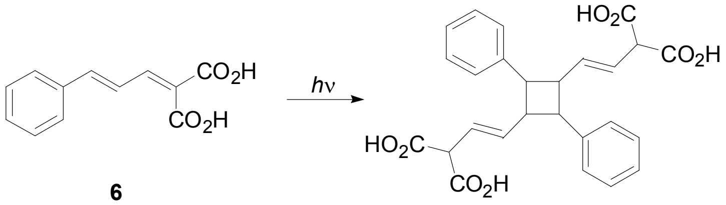


**6**

**Figure 2.** The cinnamyl derivative used by Lieberrmann.

He found also that a benzenic solution of furylacrylic acid under irradiation did not give a similar behavior showing only an isomerization reaction.[11] He found: "Es hat sich jetzt ergeben, dass die Umlagerung der in Benzol gelösten Allofurfurakrylsäure (Schmp. 103 °) zu gewöhnlicher Furfurakrylsäure (Schmp. 141°) im directen Sonnenlicht thatsächlich erfolgt, aber doch so langsam, dass sie selbst nach 14 tägiger bis 4 wöchentlicher directer Belichtung im Frühjahr noch recht unvollständig ist."

In 1902, Riiber found the irradiation of **6** gave the corresponding dimer **7** (Scheme 3).[12] The product was identified converting it into the corresponding truxillic acid.



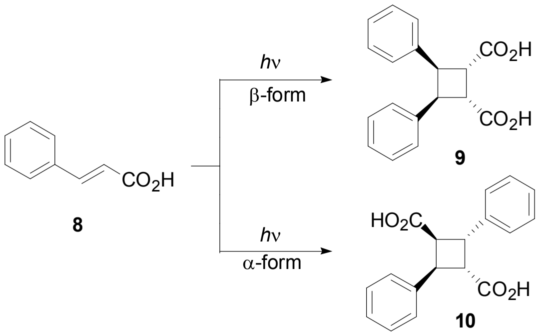
**Scheme 3.** The reaction of Riiber.

In the same year Kohler reported some results: "A solution of 20 grams of the acid, in the required amount of dilute sodium carbonate solution, is poured into an excess of dilute hydrochloric acid contained in a 3-liter balloon-flask and the liquid diluted to 2 liters.

The acid is thus obtained as an impalpable yellow powder which remains suspended in the liquid for a long time. The powder changes rapidly when the flask is exposed to the direct rays of the sun, and if the flask is shaken about once an hour the change is complete after exposure of twenty to thirty hours to bright summer sunlight. (...) The oxidation of the substance with potassium permanganate in alkaline solution gave essentially the same products as those obtained by Riiber. (...) The substance was identified as α-truxillic acid".[13]

In the same year Riiber reported that solid cinnamic acid, exposed to light, gave α-truxillic acid. He wrote: "Auf der Glasscheibe eines solchen Rahmens wurde die trockne, fein gepulverte Säure mittels eines feinen Siebes ganz gleichmässig vertheilt, und zwar in solcher Menge, dass ca. 1.5 g Säure auf jeden Quadratdecimeter kamen. Das Pulver wurde vorsichtig mit einem Bogen Glanzpapier bedeckt, die Glasscheibe in den Holzrahmen eingespannt und die Säure in die Sonne gestellt. Nach 3 ½ Wochen Stehen, in welcher Zeit der Rahmen wegen wechselndem Wetter kaum mehr als 50 Stunden von der Sonne direct belichtet war, wurde die Säure untersucht."[14] In the same year, Ciamician found that an alcoholic solution of cinnamic acid did not give any reaction.[15] The same behavior was observed in ether and acetone.[16] However, he found that cinnamic acid, suspended in paraldehyde gave the corresponding truxillic acid.[15] He wrote:"4 g Zimmtsäure, in Paraldehyd suspendirt und theilweise auch darin gelöst, blieben vom 30. Mai 1901 bis October 1902 dem Sonnenlichte ausgesetzt. Nach der Belichtung enthielt das Rohr ein feines, weisses Pulver und darüber eine hellgelbe Lösung. Das von der Flüssigkeit getrennte weisse Pulver war reine α-Truxillsäure."

Some years later Ciamician proposed to perform the reaction on a suspension of cinnamic acid in water.[17,18] He wrote: "Es wurden 40 g dieser Säure in 4 »5 Liter« haltenden Flaschen, deren jede 50 ccm Wasser enthielt und mit Saurestoff gefüllt war von Ende April bis Anfang November belichtet. Der Inhalt bestand nach dieser Zeit aus einer licht-gelb gefärbten Lösung, darin suspendiert Krystalle, hin und wieder bräunlich gefärbt. Durch Filtration getrennt, bestanden sie zum Teil aus der unverändert gebliebenen Säure, zum Teil aus α-Truxillsäure vom Schmp. 277-278°, deren Bildung sowohl wir als auch Riiber bei Belichtung von Zimtsäure schon beobachtet hatten."
Cinnamic acid (**8**), irradiated in the solid state, gave the corresponding dimers depending on the crystal form of the starting material: the metastable β-form was reported to yield β-truxinic acid (**9**), while the stable α-form gave α-truxillic acid (**10**) (Scheme 4).[19-25] Recently, solid-state NMR analysis of this reaction has been performed.[26]



**Scheme 4.** Photodimerization of cinnamic acid.

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## BOOKS

### Photochemistry and Photophysics - Concepts, Research, Applications

**by V. Balzani, P. Ceroni, A. Juris**

During the past two decades photochemistry has moved more and more from a fundamental discipline towards an applied science. Nowadays light is used as a tool in the most diverse fields, ranging from materials science to biologically motivated applications. These trends are often resumed in the term "photoscience". The authors of the herein reviewed book have shaped the field of photoscience in an influential manner. Therefore, and not only for their geographical situation (being based at the University of Bologna), they are rightful academic descendants of the famous Giacomo Luigi Ciamician, one of the founding fathers of organic photochemistry. This setting lifted my level of expectation when this book arrived on my desk, and I can already advance that I was not disappointed. But one after the other.

The book starts out with some informative chapters about elementary considerations of molecular orbital theory, how matter interacts with photons, thereby creating excited states and how these excited states can return to the ground state (photophysics) or perform chemically productive processes (photochemistry). Mathematical and quantum-chemical formalisms are kept to a necessary minimum, making these parts attractive for a wide and general readership. I teach in the Organic Chemistry curriculum at my University some brief introduction into photochemistry and found in the first chapters the required tools and language to address students that have a first contact with the field. In Chapter 3 "selected molecules" are presented and I was glad to encounter my all-time classics of photophysics and photochemistry among them, i.e., benzophenone, $[Ru(bpy)_3]^{2+}$, semiconductors. Personally I would also add $C_{60}$ fullerene to the list.

The book is very pleasant to read and the style is attractive to both the expert and the interested non-expert who plans on using light as a tool. Each chapter comes with its own bibliographic section offering a balanced mix of reviews and original research articles. Very helpful is the citation style which includes the article title and thereby allows the reader to see very fast if the reference is of general interest or likely to offer detailed primary data. The book is illustrated with informative figures which complete the text in a useful way.

During the last months I have inspected the book with a genuine curiosity. I went through the index and checked for the classics. For example: Kasha's rule. I found a hit and was informed correctly about the definition, implications, and the well-known example of azulene. The phenomenon was even nicely illustrated with photophysical data such as rate constants and quantum yields. On the chemical side I located easily the entry "Norrish photoreactions", but no Paternó-Büchi reaction or di-π-methane rearrangement, although both reactions are briefly discussed in Chapter 7. Maybe the index can be further completed in future editions. In general the Molecular Organic Photochemistry chapter (Chapter 7) is informative and provides a first overview which the interested reader can expand with other classical photochemistry textbooks.[1] The "organic world" in Chapter 7 is complemented with Chapter 8 where the fundamental aspects of inorganic photochemistry and photophysics are treated. This underlines the universal utility of the book.

The unquestionable strength of the book is its orientation towards the application side of photochemistry. It gives a very competent introduction into diverse fields ranging from light-powered molecular devices and machines and artificial photosynthetic processes, to bio-relevant implications of photochemical/photophysical process and technological applications (photochromism, solar cells, photopolymerization, etc.). The inclusion of a chapter on "Green (Photo)chemistry" is an interesting idea, especially nowadays where photocatalytic processes are in the focus of modern organic synthetic chemistry. All this is accompanied by a very useful and practical chapter on "Experimental Techniques". The last chapter of the book is entitled "Research Frontiers" and gives the reader a flavor of the current directions of photosciences. I think this is a nice inspiration and challenge for young scientists who wish to contribute to the future success of light-induced processes and phenomena. In some way it also connects again with G. Ciamician who predicted the future implications of photochemistry in his famous Science article " The Photochemistry of the Future" in 1912.[1]

I recommend the Balzani-Ceroni-Juris book as a "must-have" textbook which really embodies the spirit of modern photoscience. From my own experience it is also a very appealing textbook for teaching an introductory course on photochemistry, to be used by both lecturers and students. I hope it makes its way into many book shelves and libraries. It is not simply one more textbook on photochemistry but it complements usefully other books such as the "Turro" or better "Turro-Ramamurthy-Scaiano",[1] the "Klán-Wirz",[3] the "Klessinger-Michl",[4] or the CRC Handbook on Photochemistry and Photobiology (edited by Griesbeck, Oelgemöller, and Ghetti)[5] to name some prominent examples. Its style reminds me a lot of an older, now discontinued book by H. G. O. Becker which I fancy a lot and which unfortunately is only available in German ("Einführung in die Photochemie", 1991).[6] I am glad to have now an up-to-date alternative that I can recommend to my students and colleagues.

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[1] N. J. Turro, V. Ramamurthy, J. C. Scaiano, *Principles of Molecular Photochemistry*, University Science Books, Sausalito, **2009**.
[2] G. Ciamician, *Science* **1912**, *36*, 385-394.
[3] P. Klán, J. Wirz, *Photochemistry of Organic Compounds*, John Wiley & Sons, Chichester, **2009**.
[4] M. Klessinger, J. Michl, *Excited States and Photochemistry of Organic Molecules*, VCH, Weinheim, **1995**.
[5] A. Griesbeck, M. Oelgemöller, F. Ghetti (eds.), *CRC Handbook on Photochemistry and Photobiology*, CRC Press, Taylor & Francis, Boca Raton, **2012**.
[6] H. G. O. Becker, *Einführung in die Photochemie*, Deutscher Verlag der Wissenschaften, Berlin, **1991**.

# ANNOUNCEMENTS

## 21st International Symposium on the Photochemistry and Photophysics of Coordination Compounds

Kraków, Poland
July 5th-9th, 2015

We kindly invite you to the 21st International Symposium on the Photophysics and Photochemistry of Coordination Compounds. This is part of a biannual series of conferences which started in the 1970s. The last meetings of the series were held in Sapporo (Japan), Strasbourg (France) and Traverse City (USA). For the forthcoming symposium we will welcome you in Kraków – the Royal Capital of Poland.

The 21st ISPPCC will cover the following topics:
- photophysics
- light emitting molecular materials
- biosystems
- solar energy conversion and photocatalysis
- coordination photochemistry
- inorganic nanoparticles
- molecular-scale photonic devices

The conference will bring an opportunity of discussions and exchange of ideas for experienced researchers, graduate and undergraduate students.
Plenary lectures, oral communication and two poster sessions will present the cutting-edge problems of photochemistry and photophysics of inorganic systems.

### Accessibility and accommodation

Kraków is easily accessible by plane. There is an international airport (www.krakowairport.pl) with several direct connections with major European cities (Munich, Frankfurt, Paris, London, Berlin, Warsaw, Rome, Vienna and many others). The airport is localized 12 km from the city center. Kraków has also a good train connection with Warsaw (*ca.* 3 h) and bus connection with Katowice airport (*ca.* 1.5 h).

The city offers numerous hotels of various standards, giving a choice between luxurious and economic rooms. This flexibility of choice should enable participation of a broad society of photochemists and photophysicists (students, post-docs, professors). The list of hotels will be available at the conference's webpage. Furthermore, there will be a limited number of rooms in student dormitories accessible, at very affordable prices (*ca.* 15 €/night).

**Early Registration until 31.03.2015**
**Abstract submission: 15.05.2015**
**Late Registration until 15.05.2015**

**e-mail: isppcc@chemia.uj.edu.pl**
**homepage: isppcc2015.pl**

# Attention Early Career Photochemists

The Gordon Research Seminar on Photochemistry is approaching! The seminar is an opportunity for advanced graduate students and postdocs to give oral presentations, posters, and to network with their peers. The Seminar will take place July 18-19th 2015 at Stonehill College in Easton, Massachusetts, USA in conjunction with the Photochemistry Gordon Research Conference. The application deadline for oral presentations is April 30th, and for posters it is June 20th. For more information, and to apply, please visit the website: https://www.grc.org/programs.aspx?id=14809

# Countdown to the XVI Congress of the European Society of Photobiology

September is approaching, and the Organising Committee is making the final arrangements for the XVI ESP Congress, which will commence on Monday evening 31st August and will end on Friday afternoon 4th September.

The exciting programme comprises 27 symposia distributed over four days of scientific schedule, which span the fields of photodermatology, molecular and cellular photobiology, phototechnology, environmental photobiology, photosensory biology, and photodynamic therapy. Each symposium features a minimum of 4 invited talks and a number of shorter communications selected amongst the submitted abstracts.

With the help of Doug Learn from Charles River Laboratories, a bespoke symposium on the theme Photobiology in Industry has been organised, to take place on the morning of the 1st September. This gives an overview of the manifold applications of photobiology in the industrial environment, and includes regulatory matters, research collaborations and insights to career pathways.

Alongside the traditional lecture delivered by the Young Investigator Awardee, the programme offers 7 Keynote lectures, which are scheduled independently to allow attendance from all delegates, as the first sessions of the morning or afternoon on 1st-4th September. A 2.5 hours poster session is scheduled for the 2nd September and includes a lunch-box to encourage conference delegates' attendance and lively discussions.

In keeping with past editions of the ESP congress, the Society offers travel fellowships to encourage attendance of PhD students and early career researchers. The closing date now having past, a record number of applications have been received, confirming our junior colleagues' eagerness to attend the meeting. The results of the applications will be announced shortly.

The Congress will be the opportunity to pay a tribute to our sorely missed friend and colleague Giulio Jori, who left us at the end of December 2014. The tribute will start with a Memorial presented during the opening ceremony of the Congress, and will continue on Friday the 4th of September, with two sessions dedicated to Giulio: a morning Symposium on environmental PDT chaired by Amparo Faustino and Tim Maisch, and a series of short presentations in the afternoon by former students of Giulio's who pursued independent careers in photobiology, organised by Francesca Giuntini.

The OC does not forget that the ESP congresses are also a moment for members to enjoy each other's company on social as well as scientific fronts: our social programme features a welcome buffet post-registration on the 31st of August, and the gala dinner on the 3rd of September after the ESP General Assembly.

Abstract submission is open and will remain open until Wednesday the 20th of May. The OC is looking forward to receiving your contributions to make our XVI congress as successful as ever.

## TECHNICAL NOTE

## The Future of Photochemistry

Vapourtec (Cambridge, UK) has recently launched the UV-150, a pioneering photochemical reactor that will lead to more efficient, precise, consistent, safe and scalable photochemical synthesis offering potential routes for novel compounds and building blocks together with possible new manufacturing processes.

Two years in development, the plug and play reactor offers a wide range of features that makes it an industry first. With no intensive set up required, it is unique within the field of flow chemistry and is designed to complement Vapourtec's existing R-Series and E-Series flow chemistry systems used in hundreds of laboratories around the world.

The UV-150 allows for safe access to photo chemistry processes that hasn't existed before due to the unique design of the 150 Watt lamp, filters and reactors that deliver enhanced power, analytics and temperature control. The reactor, around 10% of the volume of other reactors that offer similar throughput, operates between -5° and 80°C.

According to Vapourtec Managing Director Duncan Guthrie, the new reactor could have a dramatic impact on the potential of photochemistry within continuous flow processing: "The UV-150 is a truly unique innovation that gives chemists the opportunity to develop 'reagent less' and scalable manufacturing of new and existing compounds and is a far more efficient alternative to traditional batch chemistry approaches.

"Current green photochemistry processes can be hazardous due to the lack of control and scalability inherent within traditional batch systems. The plug and play nature of the continuous processing UV-150 makes it easy to use with a small dedicated power supply and a patented cooling system delivering additional advantages.

"There is real physics behind the UV-150 with a compact high intensity 150 watt lamp, temperature control, wavelength filtering and reflective surfaces all designed to ensure that the photons emitted by the lamp are efficiently absorbed by the reagents. Provision has even been made for mounting an optional spectrometer, this feature allows the absorption by the reagents to be monitored in real time which is yet another unique feature.

"Artemisinin, currently the most effective treatment against malaria, is a perfect example of what can be achieved using photochemistry within a continuous flow synthesis.

"In late 2011 Professor Dr Seeberger and Dr Levesque of the Max Planck Institute reported on a continuous flow conversion of dihydroartemisinic acid, extracted from sweet wormwood (Artemisia annua), into artemisinin with a continuous photochemical transformation central to the reaction.

"There is currently nothing as efficient and easy-to-use as this reactor available in the field of flow chemistry and we are convinced that it will play a pivotal role in many chemical and pharmaceutical breakthroughs in the future.

"Despite still being an underutilised technique, there is growing interest in photochemistry and this is a perfect fit for industry requirements. This is the biggest innovation we have developed so far and there is genuine interest and application within many fields including academic research, pharma, environmental and industrial chemistry," added Duncan Guthrie of Vapourtec.

Vapourtec design and manufacture flow chemistry systems for a wide variety of sectors across the globe including education, pharmaceutical and industry and their technology has been cited as playing a pivotal part in recent major research breakthroughs.

Established in 2003, Vapourtec has developed a flourishing international market for its technology with sales across much of the developed world including USA, China, Japan, Singapore and India.

For more details visit:
www.vapourtec.co.uk/products/photochemicalreactor

*Rob Wilkinson* (Account Director)

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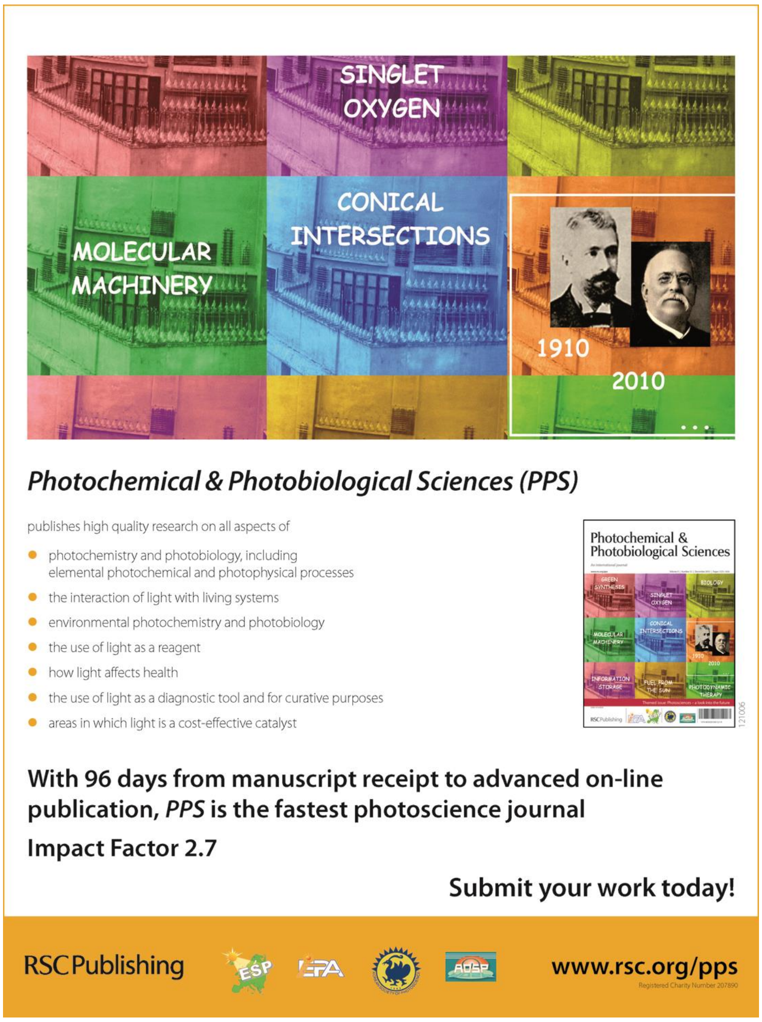
# PHOTOCHEMICAL AND PHOTOBIOLOGICAL SCIENCES



# CONFERENCE REPORTS

## Italian Photochemistry Meeting 2014

The *Italian Photochemistry Meeting*, traditionally jointly organized every year by the Italian Section of EPA in collaboration with the Interdivisional Photochemistry Group of the Italian Chemical Society (SCI), was held in Cascina Caremma, Abbiategrasso, close to Milano, from November 27th to November 29th, 2014. For the first time, the meeting was co-organized by the Interdivisional Catalysis Group of SCI, coordinated by Rinaldo Psaro (CNR, Milano). Aim of the organizing committee was to provide an opportunity for all Italian scientists working in the field to get in contact, exchange ideas and discuss about photochemistry, photophysics and photocatalysis.

This undoubtedly contributed to the success of the conference and led to a remarkable increase of the number of attendants with respect to previous Italian Photochemistry meetings. The active participants, mainly young scientists working in the field, were more than 100 and contributed with 34 oral communications and 32 poster presentations. The meeting was organized in four sessions focusing on specific topics and each session was preceded by an invited plenary lecture.

The conference was opened by Alberto Diaspro (Italian Institute of Technology, Genoa) who delivered a lecture on three-dimensional fluorescence optical microscopy, an applicative field which had a tremendous development in recent years, as testified also by the 2014 Nobel Prize in Chemistry awarded to E. Betzig, S.W. Hell e W.E. Moerner. In his lecture, entitled *3D Optical Nanoscopy: How the Photo-properties of Fluorescent Molecules Allow to Circumvent the Diffraction Barrier*, Alberto Diaspro presented a fascinating overview on the incredible recent advances in this hot topic, where confocal and multi-photon approaches pushed the optical sectioning ability of getting 3D information to 3D imaging of thick specimens, including organs and tissues, thanks to the understanding and exploiting of the photoproperties of the fluorescent labels being used.

Carlo Alberto Bignozzi (University of Ferrara) presented the opening lecture of the session devoted to homogeneous and heterogeneous photocatalysis. In his lecture on *Molecular Assemblies and Nanostructured Semiconductors for Photoinduced Water Splitting* he outlined the unique advantages that nanostructured materials offer in terms of electroactive surfaces and short hole diffusion path for photoinduced water splitting applications. In particular, he focused on devices based on the coupling between low band gap semiconductors, such as CdS and CdSe, and wide band gap metal oxides, as well as on triple junction photovoltaic cells functionalized with oxygen evolving amorphous iron oxide catalysts.

Visual perception is one of the most fascinating processes devised by nature. In his plenary lecture entitled *Photoinduced Dynamics in Visual Rhodopsin: a Computational Insight* Marco Garavelli (University of Bologna) compared the photophysical and photochemical behavior of retinal chromophores in visual rhodopsins, providing a review of the latest achievements obtained in this field by computational approaches, also in modeling time-resolved bi-dimensional electronic spectroscopy of the primary event of vision.

The last session of the meeting, devoted to artificial antenna systems for solar energy harvesting and conversion, was opened by the plenary lecture of Andrea Sartorel (University of Padova) on *Light Driven Water Oxidation Catalysis for Artificial Photosynthesis.* The recent development of suitable catalysts for water oxidation to dioxygen, which is now recognized as the bottleneck for the construction of an efficient device for water splitting, has been outlined, with specific emphasis to transition metal-based molecular catalysts , in particular cobalt complexes, mimicking the natural machinery of the photosystem II enzyme.

The meeting was characterized by very lively discussions following all oral presentations, which have been mainly delivered by PhD students and post-docs. The prize for the best talk of a young scientist, consisting this year in a copy of the book *Photochemistry and Photophysics*, recently written by Vincenzo Balzani, Paola Ceroni and Alberto Juris, was won by Andrea Cantelli (University of Bologna).

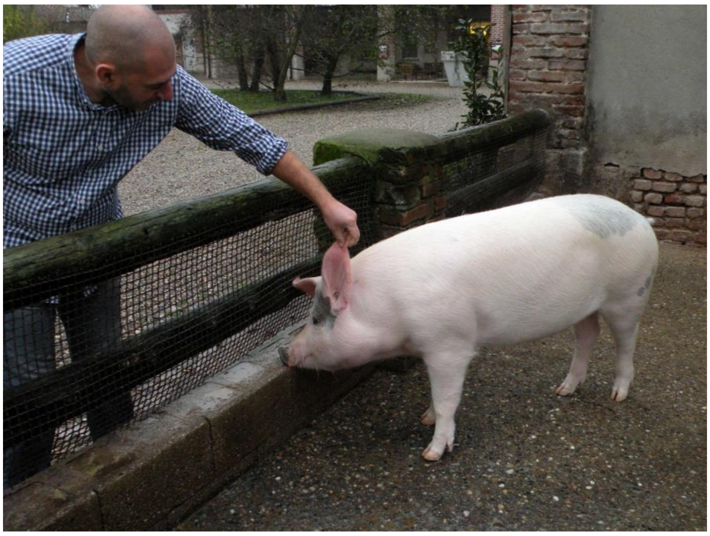
To the success of the *Italian Photochemistry Meeting 2014* also contributed the warm and friendly atmosphere established among the participants thanks to the peculiar location of Cascina Caremma, a rural farm immersed in the rice fields of the *pianura padana* landscape, renowned for the excellent food, typical of this area. As organizers of the conference, we are confident of having provided a useful opportunity to demonstrate how advanced and lively is in Italy the research in photochemistry, photophysics and photocatalysis and to enlighten, once more, the potentialities that investigations in this extremely exciting field have toward a wide range of applications for a sustainable development of our society.

*Elena Selli*
*University of Milano*
*President (2012-2014) of the Italian Photochemistry Group, Italian section of EPA*

A photograph of the participants to the meeting.

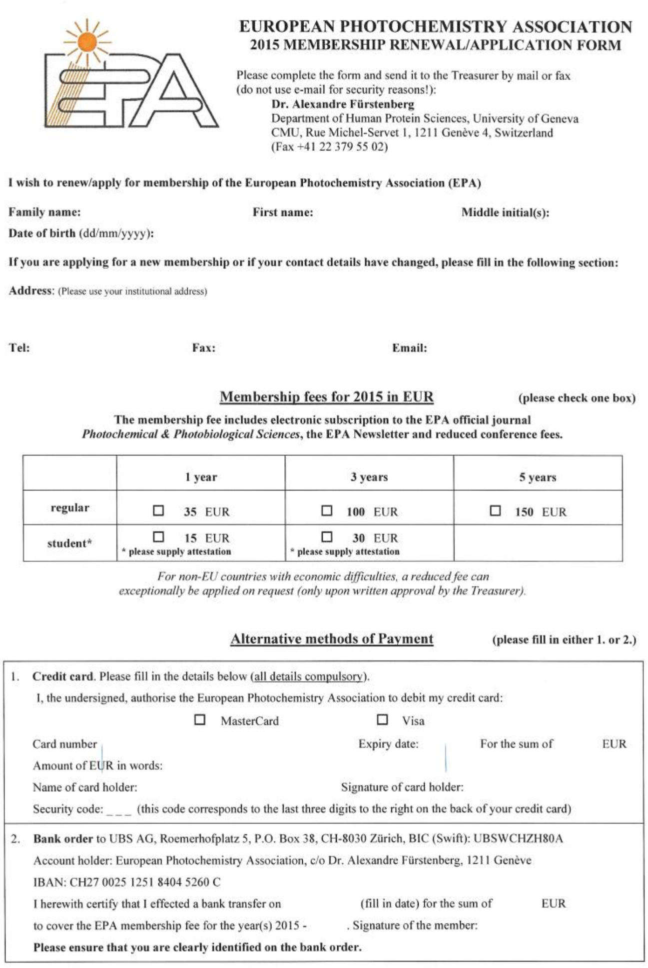
The (very crowded) conference room.

The meeting organizers.



Marco Montalti and a local pig.

# MEMBERSHIP APPLICATION FORM



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