Photo4Future Conference
TWO-DAY EVENT ON PHOTOCHEMISTRY
KEYNOTE TOPICS
PHYSICAL ORGANIC CHEMISTRY,
ORGANIC CHEMISTRY, CHEMICAL
ENGINEERING/FLOW CHEMISTRY,
MATERIAL SCIENCE

BOOK OF ABSTRACTS
NOVEMBER 12-13, 2018

THE PHOTO4FUTURE PROJECT HAS RECEIVED FUNDING FROM THE EUROPEAN UNION'S HORIZON 2020 RESEARCH AND INNOVATION PROGRAM UNDER THE MARIE SKŁODOWSKA-CURIE GRANT AGREEMENT No 641861.
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1. ABOUT PHOTO4FUTURE

The use of visible light energy to induce chemical transformations constitutes an interesting and green activation mode of organic molecules. However, implementation of this energy source in organic synthetic methodologies and in the industrial production of fine chemicals has been challenging. The Photo4Future Innovative Training Network established a training network with five beneficiaries from academia and three beneficiaries from industry to tackle the challenges associated with photochemistry in a coherent and comprehensive fashion. In total 10 Early Stage Researchers have been recruited within the Photo4Future network. The network provided them with opportunities to undertake research with the aim to overcome the current limitations towards the applicability and scalability of photochemical transformations. This was achieved through a rational design of novel photocatalytic methodologies, improved catalytic systems and innovative photoreactors. More specifically, the following topics were pursued in Photo4Future:
- Development of novel photocatalytic methodologies in continuous-flow reactors.
- Development of new heterogeneous photocatalysts.
- Development of new photomicroreactors.
- Study of photocatalytic reaction mechanisms with in situ spectroscopy.
- Study of scalability and transport phenomena of multiphase photocatalytic transformations.

Furthermore, the ESRs were trained in the Photo4Future graduate school, covering training in scientific, personal and complementary skills. Due to the high degree of industrial participation, the Photo4Future network provided an innovation-friendly environment where scientific results can grow and become products or services that will benefit European economies.

The Photo4Future project received funding from the European Union’s Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 641861.
1.1. PHOTO4FUTURE CONFERENCE

Photo4Future is organizing a two-day symposium on **12-13 November 2018 at Strijp-S in Eindhoven**. Young talented researchers who participated in the Photo4Future training program, and international top scientists in the field of photochemistry, will present the latest insight and developments in this field. The program reflects all important aspects of the field including organic chemistry, physical chemistry, solar materials, chemical engineering and spectroscopy.

1.2. GENERAL CONFERENCE INFORMATION

**Conference venue**
To honor the Photochemistry theme of the conference, Eindhoven, The Netherlands is a very well suited place to organise this event. It is an industrial city by origin, where the light bulb was produced by Philips. The Philips factory (known as Strijp -S) is currently used as an artistic hot spot, where many events are organized in an industrial setting. The Photo4Future event will be held at this location.

**Address**
Radio Royaal
Ketelhuisplein 10
5617 AE Eindhoven

**Conference Hotel**
Holiday Inn Eindhoven
Veldmaarschalk Montgomerylaan 1
5612 Ba Eindhoven

Check in time: 15:00 h
Check out time: 12:00 h

Reservations for the hotel can be made via the conference website

**Transport**
Conference participants will be picked up at the hotel on Monday 12 November and 13 November by a Strijp-S host who will accompany them to the bus. The bus will take the participants to Strijp-S and get them back to the hotel at the end of the day.

**Travelling by car**
The nearest parking garage is P1 ‘Klokgebouw’. Generally enough parking spots are available and thus it is not necessary to make a reservation. One-day parking (exit) tickets can be bought via the conference website for 7€. If these tickets are booked in advance, these tickets can be picked up at the registration desk.
Walking Dinner & Glow
On Monday the 12th of November dinner will be served at Radio Royaal. On Tuesday 13th of November, we will be hosting a special ‘GLOW’ dinner in Eindhoven. GLOW is a well-known and internationally acclaimed light-art festival during which the city of Eindhoven is all about light art, ranging from small and interactive projects to large scale art installations and lightshows. All these objects and shows are connected in one walking-tour that will take you all through the city. During our GLOW walk, we will stop at three restaurants where we will enjoy delicious foods and drinks. Make you sure you were comfortable shoes and warm clothes.

More info about GLOW:
https://www.gloweindhoven.nl/en
2. SPONSORS
The **three** best posters will be selected by the Photo4Future Poster Committee and will receive an award sponsored by:

CHEMPHOTOCHEM

&

Reaction Chemistry

& Engineering
### 3. TIME SCHEDULE

#### 3.1. TIME SCHEDULE: NOVEMBER 12TH

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**Session chair: Philipp Jaeker**

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**Session chair: Anca Roibu**
### 3.2. TIME SCHEDULE: NOVEMBER 13TH

#### Morning session

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<tr>
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<td>Daniele Leonori</td>
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*Session chair: Dario Cambie*

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*Session chair: Cecilia Bottecchia*
4. KEYNOTE LECTURES

Tito Scaiano | j scaiano@uOttawa.ca
Department of Chemistry and Biomolecular Sciences and Centre for Advanced Materials research (CAMar), University of Ottawa

4.1. THE MANY FACES OF TITANIUM DIOXIDE: FROM H2 GENERATION AND WATER DECONTAMINATION, TO GREEN CATALYSIS INSPIRED BY CROP ROTATION PRACTICES IN AGRICULTURE

The photochemical splitting of water into H2 and O2 has fascinated photochemists since the OPEC oil embargo in 1973, yet progress has been slow largely due to the challenge of oxidizing water, an energetically uphill reaction. Much of this research has utilized solar light, semiconductor catalysis and "sacrificial electron donors" (SED); that is, molecules that facilitate H2 evolution at the expense of the degradation of valuable chemicals, an approach that has been criticized as it consumes valuable chemicals. Photochemical H2 generation and water treatment are usually considered as orthogonal processes, that is, photocatalytic processes are usually designed with either one of the two outcomes in mind. Instead, we propose them as parallel or concurrent processes that in the future may provide simultaneous solutions to both H2 generation and water decontamination. Whereas alcohols have been the preferred choice for SED, many molecules that can be easily oxidized can fulfill this role, including contaminants that are present in most rivers. In our own research with decorated TiO2 we find that waters from regional river sources generate much more hydrogen than pure water. Preliminary results also show that the bacterial content in water is linked to the amount of H2 generated; indeed, bacterial growth is inhibited under these conditions. We propose that parallel technologies that couple H2 generation and water quality catalysis should be the preferred strategy and that strict water splitting may not be the most practical, valuable or efficient route to H2 generation.

Some of the materials used for hydrogen generation also have interesting properties in the context of synthetic organic chemistry. The use of heterogeneous catalysis has key advantages compared to its homogeneous counterpart, such as easy catalyst separation and reusability. However, one of the main challenges is to ensure good performance after the first catalytic cycles. Active catalytic species can be inactivated during the catalytic process leading to reduced catalytic efficiency, and with that, the loss of the advantages of heterogeneous catalysis. Here we present an unconventional approach in order to extend...
the catalyst lifetime based on the crop rotation system used in agriculture. The catalyst (Pd@TiO$_2$) is used in alternating different catalytic reactions, which reactivate the catalyst surface, thus extending the reusability of the material, and preserving its selectivity and efficiency. As a proof of concept, different organic reactions were selected and catalyzed by the same catalytic material during target molecule rotation.
4.2. LIGHT RESPONSIVE LIQUID CRYSTAL NETWORKS: OSCILLATORY DYNAMICS IN SHAPE AND SURFACES

Introduction
Since their development in the late 80’s of last century, reactive mesogens (RM’s) have find their way to a wealth of applications. The frozen-in molecular order of the polymer networks formed upon polymerization of the aligned reactive monomers brought a new dimension into liquid crystal technologies. Initially developed for their use as low shrinkage, low thermal stress coatings for optical fiber applications, the RM’s demonstrated their function especially in optical applications making use of their optical anisotropy. The large, temperature-stable and adjustable birefringence was adopted by the display industry for many purposes, varying from viewing angle enhancement to optical-retarder based 3D imaging optics. Presently, advanced optical applications for augmented reality and astronomy lenses are drawing much attention as well their use to stabilize special liquid crystal effects for smart windows and dedicated display types.

Light-driven soft-robotic functions
The use of RM’s for soft robotics applications is nowadays studied by many academic and industrial institutes. Triggered by heat, light or humidity the polymers change shape [1], surface structure [2] or porosity [3]. At Eindhoven University, we developed self-sustaining oscillators, cilia based micro-transport devices and haptic surfaces. Films deform from a flat to a complex, but pre-designed, shape with prospects to light-triggered origami and self-folding plastic elements. A completely new development relates to coatings that switch their surfaces from flat to corrugated with a preset topography, thus controlling properties as friction and grip. The lecture will discuss the newest developments in responsive liquid crystal polymer materials, giving a preliminary view on the future of RM’s with advanced applications in the fields of oscillatory films, smart coatings, soft robotics and haptics.

Keywords: Light-driven actuation, oscillatory morphing, soft robotics

References
Burkhard König | burkhard.koenig@ur.de
Faculty of Chemistry and Pharmacy, University of Regensburg, 93040 Regensburg, Germany

4.3. LET THERE BE LIGHT: ORGANIC SYNTHESIS WITH PHOTOCATALYSIS

Introduction
The use of visible light in organic synthesis has received a lot of attention over the last decade, although the idea was promoted already more than 100 years ago.[1] Visible light is easily generated, safe, leaves no trace as a reagent in the reaction mixture and can provide energy to initiate kinetically hindered or even endothermic reactions. However, the use of visible light has also a severe drawback: The energy of visible light photons is small compared to chemical bond energies. Most examples of radical generation by visible light photo-redox reactions use therefore reactive starting materials, such as diazonium, iodonium or sulfonium salts.

Reactions using more than one photon and/or electron
The energetic barrier for photoreduction and radical generation can be overcome using more than one visible light photon. By consecutive photoinduced electron transfer (conPET) a colored and persistent radical anion of the photocatalysts is generated, which is subsequently again excited gaining additional redox energy.[2] Transfer of the electron to a substrate closes the catalytic cycle. Our first generation of conPET catalysts, perylene diimides (PDI), suffered from low solubility and strong aggregation. Rhodamine 6G, a second-generation conPET catalyst, is commercially available, highly soluble and provides upon visible light excitation a reduction power of up to -2.4 V vs SCE.[3] The redox power of the catalysts depends on the excitation wavelength allowing chromo-selective transformations in organic synthesis. However, a sensitized electron transfer yielding the highly reactive radical anion of pyrene upon blue light irradiation achieves much faster photocatalytic transformations with quantum yields of up to 12 %.[4] We also discuss recent findings in dual photo-metal catalysis, which allow the visible light driven utilization of carbon dioxide as a C1 building block in synthetic organic chemistry.[5]

Keywords: photoredox catalysis, conPET,

References
Geraldine Masson | geraldine.masson@cnrs.fr
Institut de Chimie des Substances Naturelles, ICSN-CNRS, France

4.4. VISIBLE LIGHT PHOTOREDOX CATALYSIS AS A TOOL FOR FUNCTIONALIZATION AND PREPARATION OF COMPLEX ORGANIC MOLECULES

Visible light photoredox catalysis has emerged as a powerful strategy for the selective formation of new C-H, C-C and C-heteroatom bonds.[1] Indeed, this useful synthetic tool allows chemists to make reactions which cannot be done with already known processes (or under harsh conditions) under mild and eco-friendly conditions. For the past five years,[2] we have been interested in the development of novel photoredox-catalyzed transformations: (1) activation of sulfidic C-S bonds,[3] and (2) tandem difunctionalization of olefins.[4] This lecture will detail our contribution to this field by presenting the synthesis of a wide variety of complex organic molecules. Learning and understanding the catalytic processes and mechanism involved in our transformations are an important part of our research program and lead us to new developments.

KEYWORDS: Photoredox catalysis, Desulfitative transformations, Perfluoroalkylation

REFERENCES
4.5. MATERIALS DESIGN FOR THIRD GENERATION
SINGLET FISSION SOLAR CELLS

Organic materials offer a rich palate to be decorated with functional units in order to tune various properties. For example, the ability to generate multiple excitons from a single photon (singlet fission in molecular materials) has the potential to significantly enhance the photocurrent in single-junction solar cells, and thus raise the power conversion efficiency from the Shockley–Queisser limit of 33% to 44%. However, there is a paucity of materials that undergo efficient singlet fission. Our group is interested in designing building blocks that are capable of generating triplet pairs in modular small molecules and polymers. This talk will provide an overview on our approach to the design, synthesis, and evaluation of the materials.

Keywords: Solar, Polymer Solar Cells, Singlet Fission
Sophia Haussener | sophia.haussener@epfl.ch
Institute of Mechanical Engineering, EPFL, Lausanne, Switzerland

4.6. MODELLING AND EXPERIMENTATION OF PHOTO-ELECTROCHEMICAL FUEL PROCESSING DEVICES

The realization of a functional photo-driven electrochemical device requires a detailed understanding of the complicated and coupled multi-physics processes, taking place on multiple temporal and spatial scales. Specifically, such approaches involve complex interactions between multi-mode heat transfer, multiphase flow, charge transfer, and chemical reaction. Device-scale experimentation and modelling is required to identify relevant challenges and to actively and efficiently supports the choice of the most interesting conceptual design pathways, material choices, and operating approaches, all dependent on the chemistry targeted.

First, I will discuss approaches to develop relevant modeling frameworks at multiple scales and how these models can be coupled. The frameworks include i) macroscopic device models [1], ii) mesoscopic (photo)electrode models [2], and iii) atomistic-scale material and interface models [3]. Macroscopic device models (centimeter to meter scale) account for the coupled charge, mass, and heat transport and provide information on heterogeneities of the scalar and vector fields in a functional device. Mesoscale component models (micrometer to nanometer scale) can be based on the exact mesostructured of the component obtained by combined experimental-numerical approaches (such as nano-tomography coupled to direct pore-level numerical simulations). Such models can provide detailed understanding of the effect of (un)intentional morphology of photoelectrodes on their performance, and subsequently provide guidance for tailored morphologies with enhanced performance. Atomistic-scale models (nanometer to angstrom scale) can estimate material properties and interface characteristics of photocatalysts or electrocatalysts and can be used to better understand the relevant interfaces in a functional PEC device.

Second, I will discuss how the knowledge gained from computational modeling can be used to support the design of dedicated photoelectrochemical (PEC) components’ experiments, the design of PEC devices, and the scaling towards PEC systems. For example, the meso-scale models provide insight into the variations of the reactant and product concentration to which a meso-structured photoelectrode surface is exposed, providing an understanding of the kinetic variation expected within the electrode and consequently the conclusion drawn from such experiments. Macro-scale models can provide an understanding of the limitations of a PEC device design and subsequently ensure that the operating conditions chosen ensure that transport limitations are circumvented and only material limitations are observed. PEC system experimentation will provide realistic operating conditions and open new routes for more practical and relevant PEC device designs and operating conditions (for example flow devices or high pressure operation).

Keywords: solar fuels, solar hydrogen, photoelectrochemistry, thermal integration
References


4.7. PHOTOINDUCED GENERATION OF C–N BONDS

Introduction
Nitrogen-containing compounds are a privileged class of molecules, which have applications in medicines, agrochemicals, dyes and materials. As a result, the construction of C–N bonds is an extremely active area of research. Nitrogen-radicals are a versatile class of synthetic intermediates however, the difficulties associated with their generation have thwarted their use in chemistry [1].

Research
We have developed two classes of hydroxylamine derivatives as nitrogen-radical precursors that can be activated upon visible light-promoted single electron transfer [2]. Owing to the nature of the electrophore installed on the O-atom both oxidative and reductive quenching cycles can be exploited. This has enabled aminofunctionalization [3], remote functionalizations [4] and N-arylation reactions [5]. The mechanistic aspects and the synthetic potential of these processes will be discussed.

Keywords: nitrogen radical, aminofunctionalization, arene amination, photoredox catalysis

References
Gonzalo Cosa | gonzalo.cosa@mcgill.ca
Department of Chemistry, McGill University, 901 Sherbrooke Street West, Montreal QC, H4A 0B8, Canada

4.8. CHEMI-CONTROLLED ACTIVATION OF BODIPY BASED FLUORESCENT PROBES

Chemoselective fluorogenic probes rely on the induction/enhancement of fluorescence upon activation of an otherwise dimly emissive fluorophore in the presence of a chemical cue [1]. A number of photophysical/photochemical processes may be exploited in designing this type of probes, where judicious choice of the mechanism may enable monitoring real-time in a non-invasive manner where and when reactive intermediates are formed, thus enabling reaction screening in e.g. biological settings. Provided the probes are capable of undergoing order of magnitude fluorescence enhancements following interception of target intermediates, and by applying concepts of single molecule localization microscopy (SMLM) [2], one may be able to count and report single events.

Our ongoing interest on the role of lipid peroxidation and associated byproducts - including lipid derived electrophiles (LDEs) - in cellular physiology and pathology have led to developing a number of fluorogenic probes over the years intended to monitor lipid peroxyl radicals, electron transport in membranes, and how LDE react and evolve within cells. In this presentation I will describe our progress on the preparation of various types of fluorogenic probes relying on modified BODIPY dyes. I will discuss the mechanism of action of the probes providing a rationale for the choices of trap and reporter (BODIPY dyes) segments on the basis of signal sensitivity (and the ensuing photo-physical - chemical processes), chemical selectivity and environment specificity [3]. I will provide recent examples for the use of the probes in bio-analytical assays and in state-of-the-art fluorescence imaging studies including super resolution imaging based on SMLM [3] of reactions in biological milieu [3e]. Imaging studies conducted on E. coli and HeLa cells will provide new insights on the role of reactive oxygen species (ROS) in the lipid membrane and cellular activity [3e].

KEYWORDS: BODIPY dyes, fluorogenic probes, Reactive oxygen species, electrophiles, super resolution, Lipid membranes

REFERENCES
Emiel Hensen | e.j.m.hensen@tue.nl
Eindhoven University of Technology, The Netherlands

4.9. HETEROGENEOUS CATALYSIS FOR PHOTO(ELECTRO)CHEMICAL CONVERSION IN FUTURE ENERGY TRANSITION SCENARIOS

We have far more oil, coal and gas than we can safely burn. Tackling global warming implies that we must leave most of our fossil reserves in the ground. This will require a completely different way of running our economy, shifting away from petroleum-derived fuels for mobility and deriving our chemicals and materials as much as possible from renewable resources. In this lecture, I will discuss the challenges and opportunities that arise from these changes and the enabling role that catalysis can play in the energy transition using examples of our own research including the sustainable production of fuels and chemicals.

Case studies will be presented in the domain of renewable energy storage and the sustainable production of fuels and chemicals. A common aspect of these studies is the use of renewable energy in the form of direct sunlight (photocatalysis) or green electricity derived from sunlight. The working approach is to combine careful spectroscopic investigations of the operation mechanism of well-defined models systems with density functional theory calculations and microkinetics simulations.

In the lecture, I will discuss recent examples of work done in our group [1-5]. The role of computational chemistry will be explained by comparing large-scale kinetic simulations of CO₂ hydrogenation and electroreduction on Cu particles to the Fischer-Tropsch process. Optimization of interface energetics will be highlighted for the development of p-InP towards a highly efficient photocathode. The growth of a thin n-InP layer grown on p-InP results in a buried junction, increasing the valence band with respect to the Fermi level. The stability of InP under realistic conditions is evaluated by online electrochemical mass spectrometry, allowing to distinguish the roles of H₂ evolution and surface reduction in current generation. The InP photocathode can be protected by a thin titania layer. While In is a scarce material, phosphides of first-row transition metals also display interesting hydrogen evolution rates. We investigate the activity and stability of Co₂P and investigate in detail the mechanism of catalytic dissolution.

REFERENCES
Tanja Cuk | tanja.cuk@colorado.edu
Renewable and Sustainable Energy Institute, Department of Chemistry, University of Colorado, Boulder

4.10. RESOLVING THE DYNAMICS OF CHEMICAL BOND FORMATION AT AN ELECTRODE SURFACE

Catalytic mechanisms at electrode surfaces guide the development of energy storing reactions and chemical synthesis. Insight has thus far been dominantly guided by a combination of theory of the intermediate steps of the reaction and the measured rate of product evolution. To further the field, the intermediate steps and how they lead to the chemical bonds of the product should be observed experimentally. My lab employs time-resolved vibrational and electronic spectroscopy to interrogate the molecular and dynamic properties of the meta-stable intermediates and how they reach critical transition states. In order to do so, the highly selective oxidation of H$_2$O to O$_2$ is triggered at the semiconductor (SrTiO$_3$)-aqueous interface by an ultrafast light pulse in an electrochemical cell [1]. The surface vibrational and electronic levels are then probed with mid-infrared and optical light pulses, from picosecond time-scales of charge trapping through microsecond time-scales of bond formation.

Using these techniques, we have captured the birth of charge-trapping intermediates (e.g. Ti-O$^-$ and Ti-O$^-$-Ti) [2-4] from valence band holes on the titania surface. Having captured the charge-trapping intermediates at their formation (picoseconds), my lab has tracked their evolution towards the first chemical bond formation event, O-O, of the water oxidation reaction. In many proposed mechanisms of water oxidation, this step is thought to rate-limit full O$_2$ evolution. In this talk, I will focus on how we reveal the dynamics of this event through a broad mid-gap semiconductor band that averages over the mobile intermediate population of Ti-O$^-$ and Ti-O$^-$-Ti; conversely, site-localized intermediates defined by their molecular vibrations are not sensitive to bond formation dynamics. Two parallel transition state pathways, tuned by pH and ionic strength, are defined by separate activation barriers that are modulated by temperature, ionic strength, and a H/D kinetic isotope effect.

By revealing the dynamics of a bond-formation event exclusively through a mobile population of charge-trapping intermediates, the work identifies surface hopping as a reaction coordinate at electrode surfaces. This necessitates the involvement of a broad distribution of charge-trapping intermediates connected to the transition state(s). Such a reaction coordinate uniquely differentiates catalysis at an electrode surface from its homogeneous counterpart and helps explain its distinctive properties, including robustness to charge-transformation and multiple and tunable pathways.

KEYWORDS: Physical Chemistry, Electrochemistry, Ultrafast Spectroscopy, & Water Oxidation

REFERENCES
4.11. CONTROLLING ENERGY TRANSPORT WITH DNA-CHROMOPHORE ASSEMBLIES

Introduction
Control over the nanoscale spatiotemporal evolution of energy would enable the development of materials with light harvesting, computing, and sensing capabilities. Here, we describe the creation and optimization of DNA-chromophore assembles to produce excitonic circuits, which are devices that prescribe specific spatiotemporal dynamics upon illumination. We leverage the power of DNA self-assembly to introduce nanometer-scale geometric control over structure and site-specifically embed chromophores with control over distance and orientation. We design two unique classes of DNA-templated chromophore aggregates, one enabling superradiant excitations and the other enabling subradiant excitations. The use of chromophore aggregates allows us to harness the remarkable ability of delocalized excitations to drive efficient energy transfer in a way that allows control over mechanisms and interactions with the surrounding environment.

Results
In the first class of aggregates, we demonstrate controlled formation of superradiant (J-) aggregates on DNA nanostructure scaffolds through sequence-specific aggregation of pseudoisocyanine (PIC) within DNA duplexes. By controlling the length and sequence of DNA duplexes, we examined the progression of delocalization of excitations, and demonstrated that delocalization can enhance the efficiency of energy transfer [1,2]. In the second class, we engineer dimers in subradiant (H-) aggregate geometry using covalent attachment of cyanine dyes on DNA. We exploited this control to understand the dependence of energy transport on coupling. These two distinct classes of aggregates offer the eventual use of DNA as a scaffold to engineer excitonic circuitry for solar energy and computing applications.

Keywords: photophysics, energy transfer, DNA origami

References
4.12. MICROFLUIDIC-BASED NANOCRYSTAL SYNTHESIS: TOWARDS ULTRA-FAST PARAMETRIC SPACE MAPPING

Introduction
Recent years have seen considerable progress in the development of microfluidic systems for use in the chemical and biological sciences [1]. At a primary level, interest in such systems has been stimulated by the fact that physical processes can be more easily controlled when instrumental dimensions are reduced to the micron scale. For example, it is well known that when compared to macroscale instruments, microfluidic systems engender a number of distinct advantages with respect to speed, throughput, reagent usage, process control and operational/configurational flexibility. Put simply, microfluidic systems define new operational paradigms and provide predictions about how molecular synthesis could be revolutionized.

Nanomaterials exhibit optical and electronic properties that depend on their size and shape and are seen as tailored precursors for functional materials. These critical dependencies indicate that ‘bottom-up’ approaches for nanomaterial synthesis must provide for fine control of the physical dimensions of the final product. Synthetic routes have attracted significant interest owing to their versatility and ease of use, but for most applications deviations about the mean particle diameter must be <1%. This is beyond the tolerance of standard macroscale syntheses, and it is almost always necessary to post-treat to extract the desired particle size. Conversely, microfluidic systems provide an ideal medium for nanoparticle production. Since both mass and thermal transfer are rapid, temperatures may be defined with precision and reagents rapidly mixed to ensure homogeneous reaction environments.

Content
I will describe how we have utilized microfluidic reactors for highly efficient nanomaterial synthesis. Specifically, I will present autonomous ‘black-box’ systems for the controlled synthesis of nanoparticles, such as CdSe, ZnS, ZnSe, CdSeTe and CuInS$_2$/ZnS [2,3]. Such platforms incorporate microfluidic reactors and real-time optical spectroscopy to monitor the properties of emergent particles. Acquired data are assayed to estimate “experimental success”, with the system intelligently updating reaction conditions in an effort to drive the system towards a desired goal. In this way ‘intelligent’ synthesis of nanoparticles of varying size, shape and size-distribution becomes possible. I will also discuss how droplets (formed spontaneously when multiple laminar streams of aqueous reagents are injected into an immiscible carrier fluid) can be used for the synthesis of high-quality nanomaterials on short timescales [4,5]. Specifically, I will present the use of droplet-based microfluidics for the synthesis of Cesium Lead Halide Perovskite nanocrystals. The combination of online photoluminescence and absorption
measurements and rapid reagent mixing allows the ultra-fast mapping of a wide variety of reaction parameters.

**Keywords:** microfluidics, droplets, fluorescence, perovskite, nanoparticle

**References**

5. PRESENTATIONS

Prasaanth Ravi Anusuyadevi, Cyrial Aymonier and Samuel Marre | samuel.marre@icmcb.cnrs.fr
CNRS, Université de Bordeaux, Bordeaux INP, ICMCB, F-33600, Pessac, France

5.1. SYNTHESIS OF NANOPHOTOCATALYSTS IN SUPERCRITICAL MILLIREACTORS

Introduction
The growing demand of energy production from our contemporary resources and the simultaneous repercussions to the environment from the wastes generated by such sources have pushed the researchers to develop highly efficient systems for photocatalytic processes. The main application concerns the degradation of pollutants, the synthesis of organic compounds (especially drugs in the pharmaceutical industry) and the carbon dioxide conversion to useful fuels. While homogeneous photocatalysts have been extensively studied with efficient but costly noble-metal-based catalysts (Ruthenium, Iridium, etc.), their limited stability and the difficulty to recycle them have somehow reduced the promise of their commercialization at large scale. Oppositely, heterogeneous photocatalysis turns out to be a promising route to address these limitations, in particular by providing facile separation and sustained photocatalytic activity after several runs. Here, semiconductor materials belonging to different families of heterogeneous photocatalysts are synthesized through a continuous supercritical process.

Heterogeneous photocatalysts synthesized using supercritical millireactor
Heterogeneous photocatalysis can be regarded as a cascaded engineering, which involves various processes like optoelectronic conversion, charge transfer occurring on the surface/interface and finally downstream process of separation and recycling of the photocatalysts. The need for the optimization of an advanced photocatalytic system have led to the development of different families of the heterogeneous photocatalysts, which will be first introduced [1]. Then, we will present the processes that have been developed to continuously synthesized advanced nitrides-based semiconductor photocatalysts, taking advantage of the unique properties of supercritical fluids. Specifically, we will describe: (i) the synthesis of binary GaN QDs using a pre-heater tubular supercritical reactor [2], (ii) the elaboration of ternary GaIn1-xN solid solutions with various
compositions at the nanoscale [3] and (iii) the synthesis of GaN/TiO2 hetero nanocomposite photocatalysts.
Some applications of these nanophotocatalysts in two specific heterogeneous photocatalysis domains will be presented, namely: the indirect photochemical excitation (sensitized photoreaction) for degradation of pollutants [2] and the direct photochemical excitation (catalyzed photoreaction) for trifluoromethylation of arenes [3].

KEYWORDS: Heterogeneous nanophotocatalysts, supercritical fluids processes, solid solutions, nanocomposites

REFERENCES
5.2. VISIBLE LIGHT INDUCED CROSS-COUPING REACTIONS BY LIGHT ABSORPTION OF BIMETALLIC COMPLEXES

Abstract

Transition metal cross-coupling reagents have emerged as a powerful synthetic tool for C-C bond construction.\(^1\) Since its discovery, medicinal chemists have broadly used it to build complex new drug molecules otherwise not easily achievable. Negishi reaction is one of the most tolerant functional group transition metal cross-coupling reactions described so far, but its use is limited due to the instability and difficulties in preparation of the organozinc reagents. With our previous experience in preparing organozinc reagents in flow,\(^2\) we studied the behavior of the latter compounds in photocatalytic reactions. We observed that Ni-catalyzed Negishi reactions can be accelerated under visible light irradiation.\(^3\) The presence of both metals Ni and Zn is crucial for the absorption into the visible region. This method provides access to new derivatives with potential value in medicinal chemistry in only 20 minutes of reaction time and 2-5 mol % of nickel loading. As the reaction is carried out in flow, direct scalability is easily achieved, and the overall approach is superior to the batch protocols.

With this new insight in our hands for the combination of transition metal catalysis with visible light, we further busted the scope of Negishi reaction but this time using Pd catalyst.\(^4\) When the reaction mixture was irradiated with blue light palladium catalyst behaved similarly as the nickel catalyst increasing significantly the difference between light and no light reaction. This new photocatalytic process allows the expansion of the scope of zinc enolates in Negishi coupling with deactivated aryl halides. Kinetic, spectroscopic and NMR studies demonstrated the formation of a Pd(0)-zincate complex that allows the absorption of the visible light and accelerates the oxidative addition step of the catalytic cycle.

**Keywords:** photocatalysis, cross-coupling, bimetallic complexes

**References**


5.3. VISIBLE LIGHT DRIVEN BAÉYER-VILLIGER OXIDATION AND KHARASCH-TYPE ADDITION REACTIONS

During the last years, visible light photoredox catalysis has developed as a powerful tool for organic synthesis, especially as being a sustainable alternative for a broad range of different procedures. Herein, we present two such novel visible light approaches: the Baeyer-Villiger oxidation and the photocatalyst free activation of polyhalo compounds for versatile Kharasch-type additions.

The Baeyer-Villiger oxidation is known as an important method for generating esters or lactones from the corresponding ketones. Although certain enzymes (BV mono oxygenases) are capable of performing this transformation, this reaction is normally carried out under harsh conditions (e.g. mCPBA or nitroperbenzoic acid), or using H$_2$O$_2$ and a metal catalyst$^{[1]}$. In this work, a visible light mediated Baeyer-Villiger Oxidation of cyclobutanones is presented. It is suggested that the reaction proceeds via an oxygen superoxide radical anion produced by the reduced organo photocatalyst from molecular oxygen$^{[2]}$. Those mild and inexpensive conditions are proposed as an alternative approach for the currently reported examples.

In previous work in our group the activation of the carbon–bromine bond of CBrCl$_3$ was achieved using blue light and without the use of a photocatalyst.$^{[3]}$ Starting from this point, the activation of various polyhalo compounds and their corresponding C-Br bonds was evaluated under photocatalyst-free conditions. Our test reactions were Kharasch-type additions with non-activated olefins to yield typical ATRA products. In some cases a base is needed as an extra additive, in order to form an electron donor-acceptor complex between the polyhalo compounds and the alkene.$^{[4]}$ Additionally, studies with EPR spectroscopy have been conducted to elucidate the mechanism.

Keywords: Baeyer-Villiger oxidation, superoxide, ATRA, visible light

References

Cecilia Bottechia | c.bottecchia@tue.nl
and Timothy Noël | t.noel@tue.nl

Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Netherlands.

5.4. PHOTOREDOX CATALYSIS IN CONTINUOUS-FLOW: AN ENABLING TOOL FOR BIOMOLECULE MODIFICATION & AUTOMATION

In the last decade, visible-light photoredox catalysis emerged as a powerful strategy enabling novel transformations in organic synthesis [1]. Compared to other catalytic approaches, photoredox catalysis offers the advantage of enabling the activation of organic substrates under mild reaction conditions, while making use of visible-light irradiation as a sustainable source of energy. Due to the possibility to achieve an efficient and uniform irradiation of the reaction mixture, performing photochemical reactions in continuous-flow reactors is highly beneficial.

Applications in chemical biology
Owing to the aforementioned mild reaction conditions (i.e. room temperature, use of visible light) and to the high functional group tolerance, photoredox catalysis could represent an ideal strategy for chemoselective biomolecule modification [2]. In this talk, the development of novel photoredox-based methodologies aimed at cysteine modification will be presented. In all cases, the implementation of continuous flow technology resulted in increased yields and shorter reaction times. Finally, the application of these photocatalytic strategies to the chemoselective modification of model peptides under biologically relevant conditions will be discussed.

An automated continuous-flow platform for Stern-Volmer analysis
Fluorescence quenching studies and Stern-Volmer analysis are effective tools in the context of reaction discovery and for the elucidation of reaction mechanisms in photoredox catalysis.
We recently reported the first fully automated continuous-flow platform capable of performing these experiments in an automated fashion. [3] The development and calibration of such automated platform will be presented, together with the application to relevant cases studies showcasing its potential in reaction discovery and mechanistic studies.

Keywords: Photoredox catalysis, flow chemistry, bioconjugation, automation, fluorescence quenching studies

References
**Dario Cambie | d.cambie@tue.nl, Michael G Debije and Timothy Noël | t.noel@tue.nl**

**Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Netherlands.**

### 5.5. ENERGY-EFFICIENT SOLAR PHOTOCHEMISTRY WITH LUMINESCENT SOLAR CONCENTRATOR PHOTOMICROREACTORS

**INTRODUCTION**

The use of solar light to promote chemical reactions holds significant potential with regard to sustainable energy solutions [1]. The number of visible light-induced transformations has recently increased significantly with the introduction of photoredox catalysis. Thanks to its mild activation conditions, photocatalysis is destined to become the most versatile manifold for single-electron transfer chemistry. Yet, the use of abundant solar light to promote chemical reactions has been extremely limited [2].

**Luminescent Solar Concentrator-based PhotoMicroreactors (LSC-PMs)**

We have recently introduced a novel reactor design, called Luminescent Solar Concentrator-based PhotoMicroreactor (LSC-PM) as a merger between light-collecting technology and a microflow photoreactor [3]. With such a device the concentration of the dilute solar radiation was achieved, resulting in a high photonflux to the reaction mixture. However, the major practical barriers hampering a wider use of solar energy to promote photochemical reactions are the variations in sunlight intensity at different times of the day as well as the fluctuations caused by passing clouds.

**Addressing solar irradiance fluctuations in the solar production of chemicals**

Now, we present an automatically responsive reaction control system enabling solar photochemistry under vastly changeable irradiance conditions [4]. While the luminescent solar concentrator photomicroreactor (LSC-PM) design converts solar light into a narrow and steady spectral distribution, this reaction control system, inspired by the Quality by Design approach, maintains the reaction conversion constant at a set target value by dynamically changing the residence time in the reactor. The superior efficiency of an LSC-PM equipped with this reaction control system is shown both with artificially generated light fluctuations and in outdoor experiments using sunlight.

**Keywords:** Solar photochemistry, flow chemistry, luminescent solar concentrators, photoredox catalysis

**References**

Xiaojing Wei and Timothy Noël | t.noel@tue.nl

5.6. VISIBLE-LIGHT PHOTOCATALYTIC DIFLUOROALKYLATION IN BATCH AND FLOW VIA DECARBOXYLATION AND 1, 2-HETEROARENE MIGRATION

Introduction
The introduction of fluorinated moieties into organic compounds has resulted in a dramatic enhancement of their physical, chemical, and biological properties, rendering medicinal and agrochemical compounds to be more potent. Benefitting from the flow technology, different stereoselectivity was observed between batch and flow experiments and exothermic reactions was realized in flow to allow for scaling up.

Visible-Light Photocatalytic Decarboxylation of α,β-Unsaturated Carboxylic Acids
A simple yet effective photocatalytic decarboxylative protocol to prepare difluoromethylated styrenes and phenylacetylenes is described. By changing the reactor, having access to both stereoisomers is a unique and powerful approach and provides opportunities for other photocatalytic transformations. Compared with previously described methods, this procedure does not require additional metal catalysts or hypervalent iodine reagents to facilitate CO₂ extrusion. The generality of our protocol is demonstrated by the broad substrate scope. Ortho-substituted cinnamic acids give the less stable Z-selective products. The thermodynamically favored E-stereoisomer could be readily obtained in continuous-flow through accurate control of the reaction time. Having access to both stereoisomers simply by changing the reactor is a unique and powerful approach and provides opportunities for other photocatalytic transformations.

Visible-Light Photocatalytic Difluoroalkylation-Induced 1, 2-Heteroarene Migration of Allylic Alcohols
A convenient method for the preparation of sp³-rich heterocycles comprises a photocatalytic difluoroalkylation-induced 1,2-heteroarene migration of allylic alcohols. Here we describe for the first time the benefits of using flow to facilitate such migration reactions, including shorter reaction times, higher selectivities, and opportunities to scale the chemistry.

Keywords: E/Z selectivity, flow chemistry, difluoromethylation, photoredox catalysis

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KU Leuven, Belgium

5.7. SCALABILITY OF GAS-LIQUID PHOTOOXIDATIONS FROM THE MICRO- TO THE MILLI-SCALE

A photoreaction of increasing interest is the photosensitized addition of singlet oxygen, as it is an atom-economic method of functionalization and is applied in the synthesis of commercial chemical products as fragrances and pharmaceuticals [1]. Many singlet oxygen oxidations were applied to organic substrates in flow photo microreactors due to their small penetration depth and the presence of segmented flow which leads to enhanced interfacial mass transfer [2]. However, scale-up is usually preceded by an extensive parameter study (e.g. variation of the light source intensity, concentration of the sensitizer, transport gas fraction) realized for each reaction system on the small and large scale [3]. If the light absorption and scattering phenomena in the employed gas-liquid photoreactors are understood at a fundamental level, they can be predicted and the scale-up procedure becomes faster and cost efficient.

This study aims to investigate the photon transport in gas-liquid flows on the micro- and milli-scale. The microreactor consists of a glass plate with a serpentine channel and the milli-scale reactor is a Corning® Advanced-Flow™ G1 Photo Reactor. Both reactors are irradiated by green Light-Emitting Diodes (LEDs). Firstly, the photon flux and the optical pathlength are experimentally determined by visible-light actinometry following a methodology previously reported [4]. The actinometric measurements are performed in single liquid phase and in gas-liquid two-phase flows. Secondly, a modelling tool based on the ray tracing technique implemented in Matlab is used to support the experimental results.

As application, the gas-liquid photooxidation of 2-methoxyfuran in the presence of molecular oxygen and Rose Bengal in ethanol is scaled-up from the microreactor to G1 Photo Reactor. The optimal concentration of the photosensitizer on micro- and milli-scale is correlated to the optical pathlength determined by actinometry. This study will contribute to the understanding of the light absorption and scattering phenomena in different gas-liquid flow patterns at the micro- and milli-scale. This knowledge is crucial for making the scale-up process more efficient, but also for designing improved multiphase flow photochemical systems.

Keywords: gas-liquid flow, photooxidation, actinometry, microreactor, millireactor

References
Sztella Murényi¹ | stella.murenyi@gmail.com, Timothy Noël², György Dormán³ and Péter Kormos¹


5.8. ‘FROM BENCHTOP TO LAPTOP’. GENERATION AND UTILITY OF A PHOTOCHEMICAL FLOW CHEMISTRY DATABASE

The application of flow within photochemistry has become the most popular flow application in recent years. [1] [2] PhotoFlowReact Search database is the world’s first online database of flow chemistry reactions. It is an on-line database for considering the specific feature of flow chemistry (not searchable by any other databases).

A searchable database of flow photochemical reactions would represent a high value for the organic chemists helping them to shorten the reaction path or leading to novel biologically active molecules that are not accessible by any other ways. A recent, excellent review (Cambié, D., Chem. Rev., 17 (2016) pp10276-10341) was selected as the initial source of the PhotoFlowReact database, in association with the Photo4Future Grant and the authors belong to the partner institutes.

The main features of the test version of the PhotoFlowReact Database: 53 articles, 425 photochemical reactions, 47 different types of photoreactions. Altogether, 49 data fields were generated and filled with appropriate data available in the articles. We have extracted the data into an xls sheet, which was prepared to allow an automatic uploading into the searchable database environment. The reactions have been drawn by Marvin Sketch. Photo4Future partner institutes were requested to test the PhotoFlowReact database involving their PhD students.

The sustainable organic synthesis via sunlight-induced photoactivation of organic molecules has attracted much attention in the last decade, and visible light photoactivation is considered as a “green process”. [3] Many researchers attempted several thermally initiated catalytic reactions under light-induced conditions using photocatalysts. Minisci reaction [4] was also investigated under photochemical conditions and the initial results were promising using various photocatalysts.

We have started to collect and review papers about these reactions, and inserting them into the PhotoFlowReact database. Also, during my secondment in Eindhoven at the TU/e University, my research plan is to attempt photo-induced Minisci reactions under flow conditions, hoping that the conversion and selectivity could be improved. Such research is justified by the potential broad applications of the reaction in many fields of the chemical industry.

**Keywords:** photo-flow reactions, PhotoFlowReact database, Minisci reactions

**References**

**P. Jäker**¹,² | philipp.jaeker@mat.ethz.ch, **D. Aegeter**¹, **T. Kyburz**¹ and **D. Koziej**²

1. ETH Zurich, Laboratory for Multifunctional Materials, 8093 Zurich, Switzerland; 2. University of Hamburg, Institutes of Nanostructure and Solid State Physics, Center for Hybrid Nanostructures, Luruper Chaussee 149, 22607 Hamburg, Germany

### 5.9. UNDERSTANDING HOW (PHOTO)ELECTROCHEMICAL THIN FILM DEVICES OPERATE USING X-RAY ABSORPTION SPECTROSCOPY

**Energy storage by artificial photosynthesis**

Inspired by natural photosynthesis hydrogen can be directly produced from water and sunlight by photoelectrochemical water splitting. Semiconducting metal-oxides are commonly used as light absorbers and are implemented into solar energy conversion devices as thin layers onto transparent-conductive oxide substrates [1]. Such an architecture enables precise control of surface area, thickness and optical path lengths. Few studies suggest structural and electronic transformations during photoelectrochemical operation with profound implications [2]. Therefore, operando spectroscopic techniques acquiring information during device operation are regarded as decisive tools. However, they often lack adequate instrumentation to follow material’s dynamics under working conditions [3].

![Figure 1: Exploded view of the operando cell](image)

Within this talk, I will present the design of an operando flow cell for high-energy resolution fluorescence-detected (HERFD) X-ray absorption spectroscopy (XAS) experiments on water-oxidizing metal-oxide thin films as shown in Fig. 1. We showcase the cell’s versatility by example for a series of transition metal oxide thin films and present a study on the electrochromic behavior of praseodymium oxide to illustrate the opportunities provided by the HERFD-XAS technique.

**Keywords:** Photo-electrochemistry, artificial photosynthesis, thin films, operando X-ray absorption spectroscopy

**References**


Weiyi Ouyang¹, Mario J. Muñoz-Batista¹, Anna Kubacka², Rafael Luque¹,³ and Marcos Fernández-García¹

1. Departamento de Química Orgánica, Universidad de Córdoba, Edif. Marie Curie, Ctra Nnal IV-A, Km 396, E14014, Córdoba, Spain
2. Instituto de Catálisis y Petroleoquímica CSIC, Marie Curie 2, 28049, Madrid, Spain
3. Peoples Friendship University of Russia (RUDN University), 6 Miklukho-Maklaya Str., Moscow, 117198, Russia

5.10. RU CO-CATALYST DEPOSITED TiO₂ WITH ENHANCED PHOTOCATALYTIC PERFORMANCE IN H₂ EVOLUTION

Introduction
Photocatalytic production of hydrogen from renewable materials and sources is an attractive and possible solution for the development of sustainable energy. A series TiO₂ deposited with different amount of ruthenium co-catalyst were synthesized in the current work and applied in the photocatalytic hydrogen production from methanol aqueous solution, which exhibited significantly improved photocatalytic performance.

Results and discussion

Fig. 1. XRD pattern (left) and photocatalytic performance (right) of the synthesized materials

The XRD patterns presented in Fig. 1 (left). Indicates that TiO₂ in all as-synthesized materials is in anatase phase while no obvious peak corresponding to ruthenium was observed due to the highly disperse of its fine particles. As seen in Fig. 1 (right), with the presence of co-catalysts – Ru, the photocatalytic performance of TiO₂ was significantly improved. TiO₂ with 3% (wt) Ru exhibited optimal performance in photocatalytic H₂ production from methanol solution, obtaining quantum efficiency values of ca. 3.1% and 0.6% for UV and visible light illumination, respectively. The enhance catalytic capability in visible light region could be attributed to the surface plasmon resonance of the ruthenium oxide.

Keywords: photocatalysis, titania, ruthenium, quantum efficiency, hydrogen production

References
6. POSTERS

Patrick Bayer and Axel Jacobi von Wangelin | axel.jacobi@chemie.uni-hamburg.de
Inorganic and Applied Chemistry, University of Hamburg, Germany

6.1. INSIGHT INTO CONTINUOUS-FLOW PHOTOOXIDATION OF CONJUGATED AND ISOLATED ALKENES IN MICRO-FLOW

Introduction
As reactions of organic molecules with molecular oxygen in its ground state often show poor selectivity, protocols applying singlet oxygen are common. Traditional batch reactions of these quasi tri-phasic reactions (gas, liquid, visible light) typically feature bad repeatability and reproducibility, temperature control, and long reaction times. To overcome these limitations, we use a home-built photo-flow microreactor. [1,2]

Investigations
We investigated the oxidation of phenylcyclohexenes with singlet oxygen towards reactivity and selectivity and contrasted our results with computationally obtained energetic data. Depending on the substitution, conversion and ratio between the two main oxidation products, hydroperoxide 1 and [4+2]-cycloaddition product 2, were investigated in a Hammett study revealing two distinct reaction mechanisms.
Efficient and safe flow reactor technology allows for large-scale oxidation of substrates combined with immediate reduction of the produced allylic hydroperoxides to the corresponding alcohols with PPh₃ or Na₂SO₃ (sat. aq.). In consideration of 10⁶ tons/yr of cardanol arising as waste product in the cashew nut production, we investigated the reactivity and conversion of this industrial waste-product in our reactor environment.

Keywords: Singlet Oxygen, Micro-Flow, Schenck-Ene, Photooxygenation

References
M.M.C.H. van Schie, W. Zhang, I.W.C.E. Arends and F. Hollmann | f.hollmann@tudelft.nl
Department of Biotechnology, Delft University of Technology, Van der Maasweg 9, 2629HZ Delft, The Netherlands.

6.2. G-C3N4: TUNABLE PHOTOCATALYSTS GENERATING H2O2 FOR BIOCATALYTIC PURPOSES

Introduction
Enantioselective oxyfunctionalizations of unactivated C-H bonds are still challenging reactions in organic chemistry. Biocatalytically, P450’s are often the chosen system in order to perform these kind of reactions. [1] However, low stability and complicated electron transfer chains make these enzymes hardly feasible from an industrial point of view. Therefore, we suggest the use of peroxygenases, like AaeUPO from Agrocybe aegerita, for these reactions. [2] Peroxygenases directly use hydrogen peroxide in order to directly obtain the active “compound 1” species in their active site. However, adding hydrogen peroxide in stoichiometric amounts at the beginning of the reaction will destabilize the enzymes. Therefore, a method for the in situ generation of hydrogen peroxide is needed. We are investigating the formation of hydrogen peroxide from oxygen and small organic compounds using photo-excited semiconductors. Recently, we have showed a proof of principle for this scheme when using gold-doped titanium dioxide as the photo-catalyst. [3] We now have put our focus on the use of graphitic carbon nitrides as a photocatalyst. [4] These semiconductors are easily prepared from poly-condensation of carbon – nitrogen sources. Furthermore, by doping these catalysts, we can further enhance their properties. Next to peroxygenases, this method of peroxide formation can also be used to drive vanadium chloroperoxidases. [5]

Keywords: Biocatalysis, Peroxygenase, Water oxidation, Graphitic carbon nitrides

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xwang21@bics.bwh.harvard.edu; wangxiao@sari.ac.cn  

1. CAS Key Lab of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute  
2. Eindhoven University of Technology  
3. ShanghaiTech University  
4. Harvard NeuroDiscovery Center, Harvard Medical School and Brigham & Women’s Hospital  

6.3. OXIDATIVE CLEAVAGE OF C= C BONDS UNDER VISIBLE-LIGHT PROMOTED BY OLEFIN-DISULFIDE CHARGE-TRANSFER COMPLEX

Oxidative Cleavage of Olefins  
The oxidative cleavage of olefins (OCO) is widely applied for introducing oxygen-containing functional groups. Old-fashioned ozonolysis [1], the use of metal or non-metal oxidants with strong oxidizing properties are often toxic and harsh [2]. So, simple and practical and mild oxidative cleavage methods is a long-term goal pursued by chemists. In our studies [3], inexpensive aromatic disulfide compounds were used as photocatalyst, and typical mono- or poly-substituted aromatic olefins could be converted into corresponding aldehydes and ketones under visible-light at room temperature.

With the optimal disulfide confirmed as bis(4-methoxyphenyl) disulfide, we set out to explore more olefinic substrates. At room temperature, a diverse set of aromatic olefins could be converted into corresponding ketones and aldehydes with 1 bar of O\textsubscript{2} and catalytic amount of disulfide. We found that charge transfer complexes formed from disulfides and olefins may be the key to initiating co-oxidation of aryl olefins. We envisioned that a similar effect of TOCO/CTC might exist between disulfide and olefin, which could lead to a more feasible S–S bond photolysis by visible light in the presence of an olefin. By analyzing a series of \textsuperscript{1}HNMR of a fixed amount of disulfide mixed with increasing amounts of a-methylstyrene, we found that the chemical shift of the disulfide methoxy group distinctly drifted upfield, which indicated that the electron density on the disulfide had increased.

Keywords: disulfide catalysts · donor–acceptor complexes · olefin oxidation · visible-light photocatalysis

Reference
**6.4. LIGHT-DRIVEN ENZYMATIC REGENERATION OF THE NADH COFACTOR USING A FLAVOENZYME**

**Introduction**

Oxidoreductases are currently being established as valuable tools in organic synthesis for redox reactions. To supply the redox equivalents necessary for the reaction, oxidoreductases require cofactors, for instance NAD(P)H. The high cost for these cofactors make their application in catalytic amounts together with *in situ* regeneration of the catalytically active form inevitable. Next to well-established enzymatic methods, also photo-enzymatic methods may be interesting alternatives [1,2]. Light can excite a photosensitizer to a higher energy level, enabling reactions otherwise impossible. The photosensitizer is reduced while a sacrificial electron donor is consumed. Subsequently, the reduced photosensitizer reduces a catalyst, in this case the flavoenzyme putidaredoxin reductase (PdR). The PdR reduces the cofactor NAD$^+$ to NADH. Furthermore, the regeneration system is coupled to a redox reaction catalysed by the alcohol dehydrogenase from *Rhodococcus ruber* DSM 44541 (ADH-A) [3]. The scope and the limitations of this approach will be discussed.

![Scheme 1: The proposed photo-chemo-enzymatic cascade](image)

**Keywords:** Photocatalysis, Enzymatic NADH regeneration, Biocatalysis

**References**

6.5. REDUCTION OF C=C DOUBLE BONDS BY PHOTOREGENERATED OLD YELLOW ENZYMES

Introduction

Old Yellow Enzymes (OYEs), like YqjM from *Bacillus subtilis*\(^1\), are interesting catalysts for the reduction of conjugated C=C-double bonds.\(^2\) These nicotinamide-dependent flavoproteins have been studied intensively over the past ten years.\(^3,4\) Many stereoselective reductions of activated alkenes, like \(\alpha,\beta\)-unsaturated aldehydes and ketones, nitroester and nitroaromatic compounds have been reported. NAD(P)H-independent direct regeneration approaches for OYEs are interesting for us. Photocatalytic systems wherein excited photocatalysts, such as flavins, mediate the direct transfer of electrons from sacrificial electron-donors, such as EDTA, to the enzymes are investigated (Scheme 1).\(^5\)

\[\text{Scheme 1. Photochemoenzymatic reduction of conjugated C=C double bonds. A photoexcited flavin oxidizes sacrificial electrons donors such as EDTA and delivers the electrons to the enzyme.}\]

Using this regeneration system instead of a traditional nicotinamide cofactors regeneration circumvents issues of chemoselectivity. The scope and the limitations of this photobiocatalytic system will be discussed.

Reference

G. Laudadio¹, S. Govaerts¹, Y. Wang², D. Ravelli³, H. Koolman², M. Fagnoni³, S. Djuric² and T. Noël¹ | t.noel@tue.nl
2. AbbVie Inc., USA.
3. University of Pavia, Italy

6.6. PHOTOCHEMICAL CSP³ OXIDATION IN A CONTINUOUS-FLOW MICROREACTOR

Introduction
Decatungstate W₁₀O₃₂⁴⁺, an oligomer usually produced from the non-toxic and inexpensive sodium tungstate, is unique among polyoxometalates for its photocatalytic properties. Due to the possibility of a ligand-to-metal charge transfer under near UV irradiation (λmax = 325 nm), the oxygen atoms of the cluster can acquire partial radical character. [1] As such, the excited state of this polyoxometalate is a potent oxidizer, capable to generate alkyl-centered radicals by hydrogen abstraction on sp³ hybridised carbon atoms. [2] Although the radicals generated by decatungstate are known to be able to react with many electrophiles, a broadly applicable methodology for the oxidation of unactivated C-H bonds using decatungstate as catalyst and oxygen as stoichiometric oxidant has not been developed. This is mainly due to the long reaction times and the practical difficulties encountered when using light irradiation and oxygen gas.

Due to the advantages associated continuous-flow reactors, including enhanced mixing, high surface-to-volume ratio and homogeneous irradiation of the reaction mixture for photochemical transformations, we decided to develop a convenient flow methodology to allow for the selective oxidation of Csp³-H bonds using decatungstate as the photocatalyst and oxygen gas as the oxidant. This presentation will detail on the discovery process, the advantages of flow for gas-liquid photochemistry and the reaction scope. [3]

Reference
Bastien O. Burek\textsuperscript{1,2}, Detlef W. Bahnemann\textsuperscript{2} and Jonathan Z. Bloh\textsuperscript{1}\textsuperscript{*} | bloh@dechema.de
\textsuperscript{1}DEHEMA Forschungsinstitut, Germany | \textsuperscript{2}Leibniz Universität Hannover, Germany

6.7. COATED WIRELESS LIGHT EMITTERS TO SCALE UP PHOTO PROCESSES

The importance of heterogeneous photocatalysis in fundamental and applied science expanded rapidly over the last decades. However, current photocatalytic processes have many engineering limitations such as illumination efficiency and reactor design, hence industrial implementation is still limited to select few cases and only on a small scale.\textsuperscript{[1]} Large scale photocatalysis especially in the case of high catalyst loadings is limited mainly by the penetration depth of light into the reactor, which typically does not exceed a few millimetres.

Besides promising flow techniques for continuous processes,\textsuperscript{[2]} internal illumination is a technique with good prospects to achieve a high illumination efficiency with a more flexible choice of reactor types. Different types of internal illumination such as immersion lamps or optical fibers have been successfully applied.\textsuperscript{[3]} Compared to those methods, wireless coupling of internal light sources, further called Wireless Light Emitters (WLEs),\textsuperscript{[4]} has great advantages for up-scaling photocatalytic processes.

Furthermore, there is the challenge that the photocatalyst needs to be removed from the reaction medium after the reaction, both, to purify the product but also to recover and re-use the often expensive photocatalyst materials, which is technically challenging for very small nanoparticles. For this reason, it is advantageous to immobilize the photocatalyst to larger supporting particles, which in this case can be the WLE itself (cf. Figure 1).

We will present the working principle of the coated WLE, characterization of the coatings and three different model reactions performed with this system: the generation of hydrogen peroxide, the reduction of nitrobenzene and the degradation of methylene blue to demonstrate the wide scope of applications. Finally, we will discuss the future perspective of this technique and the importance of the system for up scaling photocatalytic processes.

Keywords: heterogeneous photocatalysis, upscale, TiO\textsubscript{2}, internal illumination.

References
Various aromatic amines are very important intermediates for the chemical industry. Currently, they are produced by hydrogenation of their nitroaromatic counterparts using platinum-group metals and hydrogen. These reactions are typically not very selective. An interesting alternative is the photocatalytic reduction of nitroaromatic compounds with a suitable electron donor such as alcohols, which is a very efficient and selective reaction [1]. If a primary alcohol is used, the reaction proceeds to form imines and condensed ring systems such as quinolines, making these functionalized compounds directly accessible from the nitroarene in an one-pot reaction [2,3]. In the case of nitrobenzene and ethanol, after the initial formation of aniline and acetaldehyde, the reaction proceeds to form N-ethylideneaniline and finally quinaldine in steps which are thought to be purely acid-catalyzed and independent of the irradiation, Figure 1. The reaction presents a very good example of efficient photocatalytic synthesis as three separate reactions - reduction, oxidation and condensation are realized in one process step. However, there is little information about the kinetics and photonic efficiency of the overall reaction. Herein, we present a detailed study of the photocatalytic nitrobenzene reduction kinetics under different illumination intensities, catalysts loadings as well as the concentration of added acid. The apparent quantum yield of the reaction, typically only a few percent at best for heterogeneous photocatalytic reactions, is observed extremely high. This is true even at very high photon fluxes of up to 0.1 mE/(Ls) which allow the reaction to be completed in only a few minutes instead of the several hours previously reported. Based on detailed studies of the individual reaction steps under different conditions we were also able to determine key intermediates and reaction steps. With this information we were able to devise an updated reaction scheme with knowledge of the necessary conditions to guide the reaction to the desired products and an efficient and selective manner.

KEYWORDS: heterogeneous photocatalysis, TiO$_2$, quinaldines

References
Wei Feng¹,², Dirk Jan Broer¹,²,³ and Danqing Liu¹,²,³*  

² Institute for Complex Molecular Systems (ICMS), Technische Universiteit Eindhoven, Groene Loper 5, 5612 AE Eindhoven, The Netherlands  
³ SCNU-TUE Joint Lab of Device Integrated Responsive Materials (DIRM), South China Normal University, No 378, West Waihuan Road, Guangzhou Higher Education Mega Center, 510006, Guangzhou, China.

6.9. CONTROLLED FINGERPRINT TOPOGRAPHY OF LIQUID CRYSTAL NETWORK COATINGS WITH DICHROIC MOLECULES

Introduction

Functional coatings with switchable surface topographies can be employed in many applications. For instance, previously we developed UV/electrically driven smart coatings for surface friction control using the chiral nematic liquid crystal network (LCN).¹² Chiral-nematic liquid crystal networks are formed by in-situ photopolymerization of chiral reactive liquid crystal mesogens. When the chiral LC mesogens self-assemble on the surface with homeotropic boundary, they spontaneously align in a periodical parallel-perpendicular pattern and form a fingerprint texture with surface topographies within tens of nanometer scale. However, without additional interference, the protruding parts in the coating may be formed by either perpendicular or planar molecules. Here we report a strategy to control fingerprints topographies with the designated molecular configuration forming either hills or valleys using the dichroic initiator and dye. These initiators follow the orientation of the chiral mesogens, hence molecules absorb more UV light when they align parallel to the plane while a small absorption is found when they align perpendicular to the plane, hence the initiation rate is faster in the planar area. Upon polymerization, reactive mesogens are consumed faster in the planar areas leading to monomer diffuse and accumulation in the planar areas. Consequently, a surface corrugation is formed with the planar-oriented molecules standing out. On the other hand, when the polymerization is carried out with a conventional photoinitiator and a non-reactive dichroic dye the opposite occurs where the molecules with perpendicular orientation forming hills. By carefully balancing the material diffusion and anisotropic polymerization shrinkage, relatively flat surfaces are also obtained. These surfaces exhibit distinct topographical deformation processes when subject to external stimuli, e.g., heat.

Keywords: fingerprints, topography, liquid crystal polymer network, dichroic initiator, dichroic dye

References

6.10. NOVEL CO-AXIAL ILLUMINATION TECHNIQUE FOR PHOTOREACTORS FOR ENHANCED PRODUCTIVITY AND EFFICIENCY

Industrial applications of photochemistry are very limited despite the growing interest by academia seen in the increase in publications. The main culprit is the energy inefficient design of current photochemical reactors. In current reactors, the focus is put on mass transfer and mixing and in many cases discarding energy efficiency. This work focusses on significant improvements in energy efficiency by an innovative illumination technique based on the operation principles found in mass and heat transfer equipment. A conceptual scheme is found in Figure 1.

Figure 1 Conceptual scheme of cross-, co- and countercurrent illumination with the terms referring to the relation between flow and light propagation direction.

Crosscurrent illumination (state of the art) has already been modelled and in this work, was used for comparison. The same assumptions as the state of the art were used, which are the use of homogeneously, collimated and monochromatic light and 2 cases with fully developed plug flow and laminar flow. Via non-dimensional analysis followed by a parametric study, 3 important non-dimensional groups were obtained from this mathematical model. These groups are the quantum yield ($\phi$) [mol/einstein], the light/reagent ratio ($\rho$) [(einstein/s)/(mol/s)] and the absorbance ($A$) [-]. For an actual working condition ($A = 5$ (co-axial) and 0.5 (radial); $\phi \cdot \rho = 1$ (as much useful light as reagent)) improvements of more than a factor of 2 were observed regarding conversion of the reagent and light efficiency each, with more significant improvements at lower absorbances. For laminar flow however, the novel technique didn’t show significant improvements. Upcoming experimental evaluation will validate these model results.

The novel co-axial illumination technique already shows promising results and with experimental evaluation has the capabilities of making the photochemical reactors more competitive in the industrial context.

**Keywords:** Photochemical reactor design, modelling

**References**

Sebastian Ponce 1; Jakob Albert 2, Alfons Drochner 1; and Bastian J.M. Etzold* | etzold@tc1.tu-darmstadt.de

1. Technische Universität Darmstadt, 64287 Darmstadt, Germany;
2. FAU Erlangen-Nürnberg, 91058 Erlangen, Germany

6.11. AN OPTICAL MICROREACTOR FOR GAS/LIQUID REACTIONS

Optical micoreactors are particularly interesting for catalysis, as they allow in situ detection, enable precise control of light and liquid sample, and increase the detection sensitivity and photocatalytic activity [1]. However, they face their limits working with gas-saturated liquids, as the presence of bubbles destroys light guidance. Especially, when leveraging the advantage of employing long waveguides, the presaturated reactant depletes. In this contribution, a liquid core waveguide membrane microreactor (LCWM) is presented, bringing the potential of waveguide based optical reactors also for gas/liquid reactions. Basis is a liquid filled Teflon AF tube, which due to its low refractive index (1.29) acts for most liquids (e.g. water) as a waveguide and in parallel allows permeating gas through its wall (Fig. 1).

As a proof of concept, the redox chemistry of different heteropolyacids (HPA-n) during the oxidation of biomass to formic acid in semi-batch operation was studied in situ (see Figure 2 as exemplary kinetic study). In good accordance with literature [2], the presence of a higher degree of vanadium in the α-Keggin structure leads to an increment in activity ($k_{\text{red}}$) at similar activation energies ($\approx 70$ kJ mol$^{-1}$). Interestingly, their capacity to be re-oxidized shows to be also strongly related to the V-content in the structure. It confirms the poor performance of vanadium-free catalysts, even at high oxygen partial pressures (30 to 60 bar) applied in common batch reactor experiments. Remarkably, the LCWM reactor required three orders of magnitude less amount of catalyst to obtain reliable kinetic information compared to autoclave experiments.

In summary, this study shows the high potential of our optofluidic setup for fast and low cost catalyst screening. In future contributions, new applications merging intensive light/sample and gas/liquid interaction to combine photo-activation, in situ sensing and gas-liquid reactions will be developed.

Keywords: gas-liquid reactions; in situ spectroscopy; Teflon AF microreactor

References
Sebastien J. Willot, Florian Tieves, Milja Pesic, Elena Fernández-Fueyo, Isabel W.C.E. Arends, and Frank Hollmann*

f.holmann@tudelft.nl

Department of Biotechnology, Delft University of Technology, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

6.12. EXPANDING THE SPECTRUM OF LIGHT-DRIVEN Peroxygenase Reactions

Peroxygenases are very promising catalysts for the selective oxidation of non-activated C–H bonds. They are particularly attractive as they only need H₂O₂ as oxidant for these reactions. However, their robustness, against the latter is also very poor necessitating in-situ generation of H₂O₂ to ensure high activity and stability of the biocatalysts.

Recently, a range of photochemical approaches for the in situ reduction of molecular oxygen to drive peroxygenase reactions using flavins as photosensitizers have been established. Flavins can be excited by blue light, i.e. wavelengths in the range of 400-450 nm. As a consequence, photons of other wavelengths are not utilised in these systems. To improve the photochemical H₂O₂ generation, we have evaluated other possible photosensitizers. Combination of these photosensitizers should allow for a more efficient usage of the photons provided by white light sources (Figure 1).

In this presentation, the setup, characterisation and preparative application of this new approach will be discussed.

Keywords: biocatalysis, hydrogen peroxide, oxyfunctionalisation

References
Ana María Martínez-Gualda\textsuperscript{1}, Rafael Cano\textsuperscript{2}, Leyre Marzo\textsuperscript{1}, Rubén Mas-Balleste\textsuperscript{2}, Alberto Fraile\textsuperscript{1} and José Alemán\textsuperscript{1} | jose.aleman@uam.es

1. Department of Organic Chemistry (module 01), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid (Spain)
2. Department of Inorganic Chemistry (module 07), Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid (Spain)

6.13. PHOTOCATALYTIC ALLYLC C-C BOND FORMATION: ACCESS TO Z- AND E-ALLYLIC INDOLES AND PYRROLES

The palladium-catalyzed Tsuji-Trost allylation [1] is one of the most employed methodologies for the alkylation of allylic systems by nucleophiles such as enolates, silylenolates or enamines. This methodology has been widely used for the alkylation of indoles and pyrroles, being only possible the preparation of the $E$-isomers [2].

Photocatalysis has emerged as a powerful alternative for the generation of new C-C bonds that are difficult to obtain by established methods [3] and several examples have appeared for the arylation of heterocycles [4,5]. In this work, a photocatalytic alternative for the Tsuji-Trost alkylation of pyrroles and indoles is presented, allowing the preparation of the $E$-isomers and, for the first time, the $Z$-isomers. Moreover, a metal-free photo-organocatalyst is employed under smooth conditions to achieve the allylated heterocycles in only 3 hours.

**Keywords**: Tsuji-Trost allylation, heterocycles, photo-organocatalyst.

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**References**

Koen P.L. Kuijpers | k.p.l.kuijpers@tue.nl, and Timothy Noël | t.noel@tue.nl
Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Netherlands.

6.14. AN AUTOMATED CONTINUOUS-FLOW PLATFORM FOR STERN-VOLMER ANALYSIS

Fluorescence quenching studies and Stern-Volmer analysis are effective tools in the context of reaction discovery and for the elucidation of reaction mechanisms in photoredox catalysis.

We recently reported the first fully automated continuous-flow platform capable of performing these experiments in an automated fashion. [1] Figure 1 gives an overview of the design of this automated set-up, which includes a flow cuvette for continuous inline analysis. The development and calibration of such automated platform will be presented, together with the application to relevant cases studies showcasing its potential in reaction discovery and mechanistic studies.

Figure 3: Left) Automated set-up for quenching studies, A) Flow cuvette in set-up, B) Flow cuvette.

Keywords: Photoredox catalysis, flow chemistry, automation, fluorescence quenching studies, inline analysis.

References
6.15. PHOTOCATALYTIC APPLICATIONS OF BISMUTH OXIDE

Chemical transformations promoted by sunlight are at the forefront of research in catalysis.[1] The breathless search for greener, easily accessible, low cost and scalable catalysts has driven the photocatalysis research field to the discovery of new visible-light photocatalysts allowing the replacement of the yet widely used, but economically and toxicologically inconvenient, Ru and Ir-based complexes. In this context, a variety of semiconductors have been used as photocatalysts, such as metal oxides and quantum dots.[2]

Bismuth oxide is an inexpensive, abundant and non-toxic commercially available semiconductor that is usually obtained in large amount as aside product mainly from copper and lead refining. Due to the continuous and increasing interest to develop new catalysts to direct organic photocatalysis, we have explored the photocatalytic activity of bismuth in three valuable organic transformations. In particular, we report the successful application of bismuth oxide, in combination with the chiral amine imidazolidinone, to promote the asymmetric alkylation of aldehydes with α-bromocarbonyl compounds.[3] Also, the feasibility of the Bi₂O₃, as visible light photocatalyst, is successfully demonstrated in classical atom transfer radical addition (ATRA) reaction[4] and in the arylation of heteroarenes[5] under very mild reaction conditions.

Keywords: Photocatalysis, semiconductor, alkylation, bismuth oxide

References
Aloisio A. Bartolomeu$^{1,2}$, Timothy Nöel$^2$, and Kleber T. Oliveira$^1$ | kleber.oliveira@ufscar.br

1. Federal University of São Carlos (UFSCar), Brazil
2. Eindhoven University of Technology, The Netherlands

6.16. PHOTOARYLATION OF QUINOLINES WITHOUT PHOTOCATALYSTS BY USING ARYLDIAZONIUM SALTS: AN EDA COMPLEX APPROACH

Electron-deficient nitrogen heterocycles such as quinoline and pyridine are found as a core structure in natural products, agrochemicals, drug candidates, and in many drugs approved by FDA.$^{[1]}$ Relevant clinical and preclinical drugs such as Pitavastatin, Etoricoxib, Vismodegib, and DDQ107498$^{[2]}$ contain these heterocycles directly linked to aryl groups. Consequently, the development of new and efficient methodologies for the direct C–H arylation of these electron-deficient heterocycles is of great interest. Herein, we report the preliminary results obtained for the direct C–H arylation of quinoline moiety with a diazonium salts using visible light (blue LED) as the light source.

Table 1. Screening of the reaction conditions.$^{[a]}

<table>
<thead>
<tr>
<th>Entry</th>
<th>1 (mmol)</th>
<th>2 (mmol)</th>
<th>Photocatalyst</th>
<th>Lewis Acid</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>2/4$^{[d]}$</th>
<th>Yield 3$^{[e]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{[b]}$</td>
<td>4</td>
<td>0.5</td>
<td>none</td>
<td>BF$_3$·OEt$_2$</td>
<td>CH$_3$NO$_2$</td>
<td>24</td>
<td>38:62</td>
<td>39</td>
</tr>
<tr>
<td>2$^{[c]}$</td>
<td>4</td>
<td>0.5</td>
<td>RFTA</td>
<td>none</td>
<td>MeOH</td>
<td>24</td>
<td>49:51</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>0.5</td>
<td>none</td>
<td>none</td>
<td>MeOH</td>
<td>24</td>
<td>48:52</td>
<td>54</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>0.5</td>
<td>none</td>
<td>none</td>
<td>MeOH</td>
<td>48</td>
<td>47:53</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>0.5</td>
<td>none</td>
<td>none</td>
<td>MeOH</td>
<td>48</td>
<td>43:57</td>
<td>72</td>
</tr>
</tbody>
</table>

[a] Reaction conditions: quinoline hydrochloride (1) (4 and 6 mmol), 4-methoxybenzenediazonium tetrafluoroborate (2) (0.5 mmol) in solvent (3 mL) at r.t. under O$_2$ atm for 24 or 48 h. Reactions were performed in a borosilicate glass tube (ACE pressure tube, 15 mL). [b] With N-BF$_3$-quinoline complex (generated in situ from 4 mmol of quinoline with 2 equiv of BF$_3$·OEt$_2$). [c] In the presence of RFTA (10 mol%). [d] Determined after isolation. [e] Isolated yields.

Initially, we investigated the reaction between N-BF$_3$-quinoline complex and diazonium salt 2 in CH$_3$NO$_2$ at r.t. for 24 h and obtained product 3 in 39% yield (Table 1, entry 1). When the reaction was carried out with quinoline hydrochloride 1 in the presence of RFTA (riboflavin tetraacetate) in MeOH for 24 h, the product 3 was obtained in 48% yield (entry 2). To our delight, the product 3 was obtained in 54% yield even in the absence of RFTA (entry 3), showing that the photocatalyst is not necessary. Notably, when the same reaction was carried out for 48 h, the product 3 was obtained in 61% yield (entry 4) and in 72% yield (entry 5) using 6 mmol of 1. The proof of an EDA-complex formation is under study and the effect of the temperature, different solvents and continuous flow conditions as well.

Keywords: quinoline, aryldiazonium salt, C–H arylation, EDA-complex

References

Julia Patzsch\textsuperscript{1}, Andre Blößer\textsuperscript{2}, Jana Timm\textsuperscript{1}, Fabian Guba\textsuperscript{3}, Roland Marschall\textsuperscript{2}, Dirk Ziegenbalg\textsuperscript{3}, and Jonathan Z. Bloh\textsuperscript{1*} | bloh@dechema.de

\textsuperscript{1} DECHEMA-Forschungsinstitut, Germany
\textsuperscript{2} Bayreuth University, Germany
\textsuperscript{3} Ulm University, Germany

6.17. QUINOLIGHT – DEVELOPMENT OF PHOTOCATALYTIC PROCESSES

Application of heterogeneous photocatalytic reactions can be a key for efficient, “green” processes to overcome energy-intensive conventional thermal approaches. One promising example is the photocatalytic synthesis of quinoline derivatives from nitroarenes that combines photo- and acid-catalyzed steps enabling a photo-induced one-pot reaction.\cite{1} Bringing photoreaction to application requires a holistic approach in development and optimization of photocatalytic processes that includes investigations on reaction kinetics, the photocatalyst and the reactor design.

The project QuinoLight, funded by the AiF program for promoting the Industrial Collective Research (IGF) of the German Ministry of Economic Affairs and Energy (BMWi), aims on addressing these three points in a joint effort.

To optimize the reaction conditions and identify the rate-determining reactions steps, extensive kinetic studies are conducted at the DECHEMA-Forschungsinstitut. These investigations include the variation of photocatalyst loading, reactant concentration, reaction temperature and light intensity.

Today TiO\textsubscript{2} is one of the most favoured photocatalysts due to its low price and good availability. Nevertheless, excitation of TiO\textsubscript{2} requires irradiation in the UV-A range that raises multiple problems for organic syntheses including unwanted side reactions. To address this issue, new ferrite-based photocatalysts are developed at the Justus-Liebig-University Giessen, enabling the absorption and utilization of visible light. By immobilization of the photocatalytic species on a mesoporous acidic support, materials can be synthesized that are able to catalyze both, the photo- and acid-catalyzed steps.\cite{2}

Rapid prototyping procedures are used to cope with the reaction engineering challenges of photoreactors. This includes the use of 3D-printing as a tool to identify advantageous photoreactor designs that are able to handle the special demands of heterogeneous photocatalytic systems. To validate and compare the different designs, an experimental protocol was established including test reactions, actinometry and mixing experiments. This contribution will highlight and discuss the multiple challenges that arise from heterogeneous photocatalytic systems for industrial application. To tackle these challenges this study underlines the importance of synergistic approaches.

**Keywords:** heterogeneous photocatalysis, TiO\textsubscript{2}, reactor design, reaction engineering

**Reference**


Miguel Claros¹ | mclaros@iciq.es, Alicia Casitas², and Julio Lloret-Fillol¹³ | jlloret@iciq.es

¹ Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Avda. Països Catalans, 16, Tarragona, Spain
² Institut de Química Computacional i Catàlisi (IQCC) and Departament de Química, Universitat de Girona, Campus Montilivi, E-17003, Girona (Catalonia, Spain).
³ Catalan Institution for Research and Advances Studies (ICREA), Paseig Lluis Companys, 26, Barcelona, Spain

6.18. DEVELOPMENT OF VISIBLE-LIGHT REDUCTIVE CYCLIZATIONS REACTIONS FROM UNACTIVATED CHLOROALKANES

Recent visible light metallaphotoredox methodologies have allowed the construction of a large variety of C-C and C-heteroatom bonds.[1] Most of these novel photocatalytic protocols are limited to highly active aryl and alkyl iodides and bromides as coupling partners.[2] Although alkyl chlorides are available, economic and bench-stable feedstocks, the chemical inertness of Csp3-Cl bonds hampers their use as electrophilic partners in most of catalytic methodologies, as showcased by the narrow number of transition metal-catalyzed reactions towards this endeavor.[3]

Herein we present an earth-abundant metal-based metallaphotoredox catalytic system (Cu, Co/Ni) that enables the functionalization of Csp3-Cl bonds under visible light irradiation and mild conditions. The in situ photoreduction of cobalt or nickel complexes bearing penta- or tetracoordinate nitrogen-based ligands is a key design element to enable the activation of unactivated Csp3-Cl bonds. This approach unveils a sustainable synthetic protocol towards the construction of carbocycles via intramolecular reductive cyclization of alkyl chlorides that bear tethered alkenes with broad functional group tolerance.

Keywords: Visible Light, Photoredox Catalysis, Dual Catalysis, Cyclizations, Unactivated Chloroalkanes

Reference
Michael Teders¹, Christian Henkel², Lea Anhäuser³, Felix Strieth-Kalthoff¹, Adrian Gómez-Suárez¹, Roman Kleinmans¹, Axel Kahnt², Andrea Rentmeister³, Dirk Guldi² | dirk.guldi@fau.de and Frank Glorius¹ | glorius@uni-muenster.de

¹ Organic Chemistry Institute, University of Münster, Germany
² Department for Chemistry and Pharmacy, FAU Erlangen-Nürnberg, Germany
³ Institute of Biochemistry, University of Münster, Germany


Sulfur-containing molecules participate in many essential biological processes [1]. Of utmost importance is the methylthioether moiety, installed in tRNA by SAM methylthiotransferases [2]. While the photoinitiated thiol–ene reaction for carbon–sulfur bond formation has found widespread applications [3], a biocompatible chemo- and regioselective hydrothiolation of unactivated alkenes and alkynes remains elusive.

The energy-transfer-enabled biocompatible disulfide–ene reaction

Using our luminescence screening approach [4], we designed a novel and general chemoselective anti-Markovnikov hydroalkyl-/arylthiolation of alkenes and alkynes — also allowing the biologically important hydromethylthiolation — by photoinduced energy transfer activation of disulfides [5]. This fast disulfide–ene reaction shows extraordinary functional group tolerance as proven by a broad substrate scope and the functionalization of bioconjugates or drug derivatives. The detailed study of the reaction mechanism, with special focus on the energy transfer sensitization process via transient absorption spectroscopy, led to the development of an improved and more efficient transition-metal-free catalytic system. The biocompatibility of this transformation was intensively investigated by the application of a newly developed bio-additive-based screening approach.

Keywords: energy-transfer, ultrafast spectroscopy, biocompatibility, screening

Reference
G.C. Dubed² | gdubed@iciq.es, S. S. Mondal¹, F.Franco¹, A. Shafir¹, and Julio Lloret-Fillol¹:² | jllloret@iciq.es

¹ Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain.
² Catalan Institution for Research and Advances Studies (ICREA), Passeig Lluís Companys 23, 08010 Barcelona, Spain

6.20. ELECTROCATALYTIC CO₂ REDUCTION IN WATER USING PYRENE BASED COVALENT-ORGANIC FRAMEWORKS DOCKING WITH MN(I)-CATALYST.

Effective large-scale CO₂ conversion to fuels or value-added chemicals is a critical goal to reduce our impact in the environment, and helping to overcome some of the energy crisis problems [1].

Covalent Organic Frameworks (COFs) represent nowadays an interesting alternative to the more classical catalysts, with emergent properties as crystalline porous frames than potentially combine the advantages of the molecular catalysts and the heterogeneous ones [2]. In this work, we present different COFs based on tercarbonyl polypyridyl Mn units anchored to a MWCNTs via π-π stacking to form active electrocatalytic electrodes for CO₂ conversion. The activity of these catalysts were evaluated by electrochemical techniques (CV, CPE) and performing high activity and stability in aqueous solution. Operando UV-vis spectroelectrochemistry has provided information about the formation of two intermediates during catalysis, a Mn-Mn dimer and a five-coordinate Mn species [3, 4].

With these materials we have integrated the Mn(bpy)(CO)₃Br catalyst into a heterogeneous material which clearly enhances the catalytic activity towards CO₂ reduction (FECO~50%) at low overpotentials (~450 mV) in pure H₂O.

Keywords: Electrocatalysis, CO₂ reduction, COF, Mn(bpy)(CO)₃Br.

Reference
A NEW FAMILY OF TETRADENTATED N-BASED NI/CO COMPLEXES FOR THE DEVELOPMENT OF VISIBLE-LIGHT METALLOPHOTOREDOX STRATEGIES

Recent photoredox catalytic methodologies based on the visible-light-induced generation of highly reactive radicals have allowed the construction of a large variety of selective C-C and C-heteroatom bonds.[1] Most of these novel photocatalytic protocols are limited to highly active aryl and alkyl bromides and iodides as coupling partners.[2] The inertness of chloroalkanes has precluded them as prevailing coupling partners in both conventional and photocatalytic cross-coupling reactions.

We have achieved the activation of Csp3-Cl bonds by means of a dual metal catalytic system based on earth-abundant metals (Cu, Co/Ni) and using visible-light as a source of energy. This bimetallic system has been employed to develop sustainable intramolecular reductive cyclization reactions of chloroalkanes that bear tethered alkene or alkyne moieties.[3,4]

Herein we disclose the synthesis and characterization of a family of tetradeptate N-based Co and Ni complexes. The electronic properties of the metal center are modulated by the introduction of several electron-withdrawing and electron-donor substituents at the β- and γ- positions of the pyridine framework. The complexes have been fully characterized by means of X-ray diffraction analysis, accurate mass spectrometry and 1H-NMR spectroscopy at variable temperature. Moreover, we bring to light the catalytic activity of this family of complexes in the aforementioned reactions, taking into account their capability to form hydrogen in presence of protic solvent. The ultimate goal of this project is to obtain the structure/activity relationship in order to develop highly robust and efficient base metals catalysts for the cleavage of strong σ-bonds.

Keywords: photoredox catalysis, visible-light, earth-abundant metals, ligand design, cobalt/nickel

Reference
6.22. REVISITING THE MECHANISM OF REDUCTIVE ELECTRON TRANSFER BETWEEN IRIDIUM BASED COMPLEX AND ELECTRON DONOR

Utilizing sunlight as source of energy to drive current energy scenario into sustainable way is most appealing yet challenging objective to be persuaded in the realm of carbon based energy sources. In this direction, the light has been utilized in tremendous fashion towards producing solar fuels, catalytic transformation of organic molecules and emulating intricate photoinduced electron transfer processes in photosynthesis. Most of these efforts have been relied on transition metal complexes based on Ru and Ir. Although Ru and Ir based complexes were the front-runners as photocatalyst or photosensitizer in photocatalysis, it was often underestimated the clear understanding of its mechanism of excited state photoredox processes over new catalytic reaction methodologies [1]. To this end, the present contribution discusses photoinduced reductive electron transfer between Ir-based polypyridine complex, i.e. [Ir(ppy)$_2$ bipy]PF$_6$ (1) and triethylamine (Et$_3$N) as sacrificial electron donor [2]. Even though the bipyridine based (bipy) Ir complexes are widely known to act as photocatalyst or photosensitizer in photocatalysis and further studied by luminescence quenching studies, core understanding of their excited state molecular properties during reductive electron transfer is still unknown. Here we have observed that the complex 1 pass through two emissive state while undergoing reductive quenching with Et$_3$N. Among this, the second emissive state arise from the excited state radical anion after prompt illumination with an external LED source (1.-*). As radical anions are generally perceived as strong reductants in their excited state, formation 1.-* would demand considering the possibility of two electron transfer from 1 in photocatalytic cycle than the conventional single electron transfer kinetic pathway. Further implication of the second emissive state is exploited in the electron transfer process occurs in the in-situ mixture containing 1, Et$_3$N and other inert substrates.

Keywords: Photo induced electron transfer, mechanistic understanding, transient kinetics.

Reference
Thank you for participating!