Journée organisée par le Grand Programme de Recherche Post-Petroleum Materials

PPM Thematic Day

Future Trends in Light-driven Processes

Thursday May 25th 2023, 8h30-17h30

Domaine du Haut Carré,

Auditorium de l'Agora

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Organisation

Prof. Yannick Landais, Prof. Thierry Toupance,
Dr. Dario Bassani (ISM)

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Grand Programme de Recherche PPM | Post-Petroleum Materials / université de BORDEAUX

8h30-8h55 **Coffee reception**

8h55-9h00 Introduction
Prof. Yannick Landais, ISM, WP1 coordinator

Chair – Prof. Yannick Landais, ISM-ORGA, Bordeaux University

9h00-10h00 Better organic synthesis with light !
Prof. Burkhard Koenig, University of Regensburg

10h00-10h20 Photo-oxidation by Near-Stoichiometric Amounts of $^{*}O_2$ Generated Ex Situ From Endoperoxides: A Mild and Efficient Access to ^{18}O- and ^{17}O-Labelled Compounds with High Isotopic Enrichment
Ms. Alexandra Doussot, ISM-CSH, Bordeaux University

10h20-11h00 **Coffee break**

Chair – Prof. Thierry Toupance, ISM-C2M, Bordeaux University

11h00-11h30 Electrochemiluminescence: An Electrochemically-Triggered Redox-Mediated Light Emission Process
Dr. Laurent Bouffier, ISM-NSYSA, Bordeaux University

11h30-12h30 Producing fuels from sunlight and water: the Holy Grail of artificial photosynthesis
Dr. Murielle Chavarot-Kerlidou, CEA Grenoble

12h30-14h00 **Lunch buffet**

Chair – Dr. Dario Bassani, ISM-NEO, Bordeaux University

14h00-14h30 **Copper(II), benzophenone and sun: A useful combo for photocatalyzed functionalization of alkynes and alkenes**
Dr. Jean-Marc Vincent, ISM-NEO, Bordeaux University

14h30-14h50 **Thiochromane Formation via Visible-Light Mediated Intramolecular δ-C(sp^3)–H Bond Arylation of Sulfonamides**
M. Shuai Liu, ISM-ORGA, Bordeaux University

14h50-15h20 **Sorption mechanism in heterogeneous photocatalysis. The enlightening example of laser-deposition of metals onto bare TiO_2 nanoparticles**
Dr. Jean-Pierre Delville, LOMA, Bordeaux University

15h20-15h40 **Light trapping within 3D macrocellular ceramics towards environmental remediation**
Ms. Elodie Layan, CRPP, ISM-C2M, Bordeaux University

15h40-16h20 **Coffee break**

Chair – Dr. Aline Rougier, ICMCB, Bordeaux University

16h20-17h20 **Visible light-driven reduction of CO_2 with molecular and hybrid catalysts**
Prof. Marc Robert, University Paris Cité

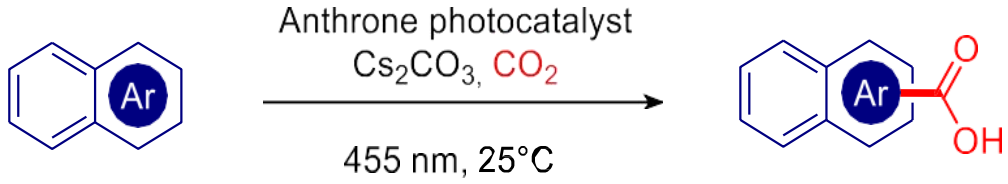
17h20-17h30 **Closing remarks**

Abstract-Book

Better organic synthesis with light !

Burkhard König

University of Regensburg, Regensburg, Germany.



Redox-neutral photocatalytic C-H carboxylation

Ideal chemical transformations in terms of green and sustainable chemistry convert abundant, low energy starting materials into high value products without losing a single atom.[1] Light-driven catalysis offers tools for such reactions.[2] We discuss in the lecture how key photocatalytic principles can be applied to redox-neutral reactions, such as C-H carboxylations of alkanes and arenes with carbon dioxide.[3] Current scope and limitations are shown and a perspective is given where the use of light may lead to better catalysis.[4] Next we will discuss how photochemistry can improve cross-coupling reactions,[5] with and without transition metal catalysts.[6]

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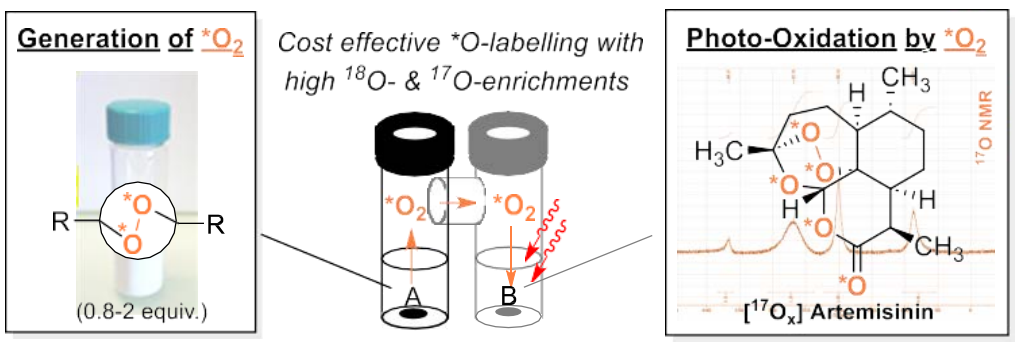
Photo-oxidation by Near-Stoichiometric Amounts of $^*O_2$ Generated *Ex Situ* From Endoperoxides: A Mild and Efficient Access to ^{18}O- and ^{17}O-Labelled Compounds with High Isotopic Enrichments

Alexandra Doussot,[a] Marie-France Bakaï,[b] Eric Fouquet[a] and Philippe Hermange*[a]
[1] *Univ. Bordeaux, ISM, UMR-CNRS 5255, 351 Cours de la Libération, 33405 Talence Cedex, France*
[2] *Université de Kara, BP 404 Kara, Togo*

Among the various elements, oxygen plays a key role in many functional groups, and its isotopic labelling often proves determinant for mechanistic insights. Indeed, [^{18}O] can be easily differentiated by mass analysis from the predominant [^{16}O] and recent advances in NMR instrumentation allows efficient detection of the chemical shift of [^{17}O] (-30 to +1000 ppm).[1] It is however necessary to use isotopically enriched compounds because of the low natural abundance of [^{18}O] and [^{17}O] (0.204% and 0.037%, respectively). Synthetic methodologies for the incorporation of labelled oxygen (*O) have been extensively studied.[2] They generally rely on the use of one of the cheapest isotope precursors: [*O]H_2O, but often require harsh conditions limiting their use to simple synthons, and/or involve reversible isotopic exchange yielding lessened isotopic enrichments. Some examples using gaseous *O-labelled dioxygen were reported, whose *O-atom molar cost is comparable to [*O]H_2O. However, the need to employ large excesses of this gas and the difficulty to manipulate it precisely greatly increase the overall cost of these procedures, which made them under-used. To solve these major drawbacks, we developed solid and stable precursors that can release quasi-stoichiometric amounts of [$^{18}O_2$] and [$^{17}O_2$]. After activation in a two- chamber glassware,[3] these compounds generated quasi-stoichiometric amounts of [*O2]dioxygen that can be photosensitized to oxidise various substrates. This method provided in a single step ^{18}O- and ^{17}O-labelled endoperoxides, quinones and phenols, in moderate to good yields and very high isotopic enrichments (up to 83%). As exemplified by the syntheses of [$^{18}O_x$]artemisinin and [$^{17}O_x$]artemisinin, this strategy is particularly suitable for affordable investigation of the chemical mechanisms involved in dioxygen oxidations using mass spectrometry and ^{17}O NMR.[4]



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Electrochemiluminescence: An Electrochemically-Triggered Redox-Mediated Light Emission Process

Laurent Bouffier and Neso Sojic

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Electrochemiluminescence (ECL) involves an interfacial electron-transfer that initiates a sequence of chemical/redox steps during which a luminophore is brought to its excited state. In other words, it is an electrochemically-triggered redox-mediated light emission process. Even if ECL is known for decades, it remains a very active field of research. ECL hot topics encompasses molecular electrochemistry aspects, various analytical applications and also the coupling with optical microscopy to enable space- resolved imaging.[1] After reminding the basics of ECL and the main involved molecular mechanisms, the assessment of new ECL-active chromophores will be discussed. In particular, we will focus on new tunable molecular structures that exhibit comparable or even better ECL properties than the inorganic complex $Ru(bpy)_3^{2+}$ that is considered as the gold standard ECL luminophore.[2] Finally, the molecular engineering of new probes incorporating additional functionalities to confer ECL enhancement capability as well as chiroptical property will be proposed.[3] This will be illustrated with multicolor ECL achieved by competitive electron-transfer processes and also with circularly- polarized ECL emission.

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Producing fuels from sunlight and water: the Holy Grail of artificial photosynthesis

Murielle Chavarot-Kerlidou

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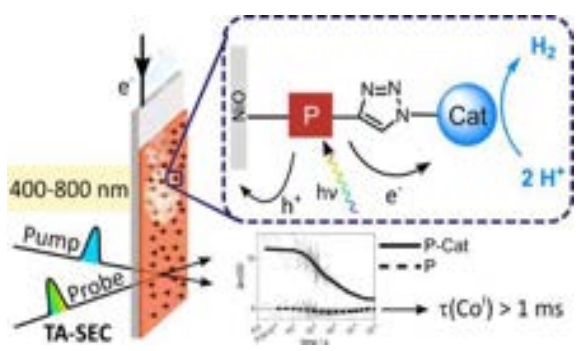
https://www.solhycat.com/

Making fuels and chemicals from sunlight and abundant raw materials such as water and CO_2 represents a major challenge to meet for a clean energy future. To achieve sunlight-driven water splitting, the integration of molecular H_2-evolving catalysts into photoelectrochemical cells is a promising, yet challenging strategy.[1] Our contribution to the field will be highlighted through different examples covering all aspects from catalyst design to the construction of functional water-splitting devices. Photoelectrochemical activity of dye-sensitized NiO photocathodes based on covalent dye – cobalt catalyst assemblies will be discussed in detail,[2-5] together with some key insights into the factors currently affecting their performances, obtained from advanced spectroscopy and post- operando characterizations.[3,4]



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Copper(II), benzophenone and sun: A useful combo for photocatalyzed functionalization of alkynes and alkenes

Jean-Marc Vincent

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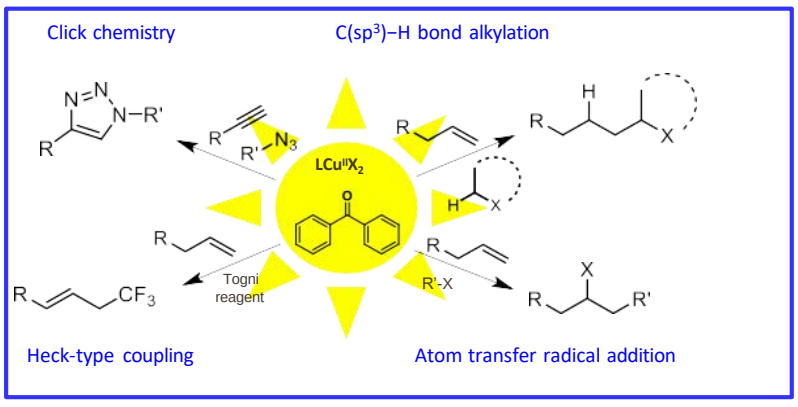
In the research field of catalyst development, a reactivity *versus* stability dilemma exists as extremely reactive catalysts are difficult to store/handle, thus limiting the scope of their use. This is particularly true for catalysis mediated by low-valent M(0/I) species possessing open coordination sites, whose dioxygen sensitivity typically requires storage/handling in a glovebox. To address this key issue, a powerful approach is to develop photoreducible precatalysts. In the lecture, our contribution toward this goal will be presented with a focus on copper catalysis. It will be shown that Cu(II) precatalysts which integrate a benzophenone photosensitizer in their structure could find their place in the chemist's toolbox. After presenting the synthesis of such complexes and their photoreduction properties, their scope and limitation for application in key transformations, including CuAAC,[1] trifluoromethylation of alkenes[2] and C(sp^3)–H bond alkylations,[3] will be described.



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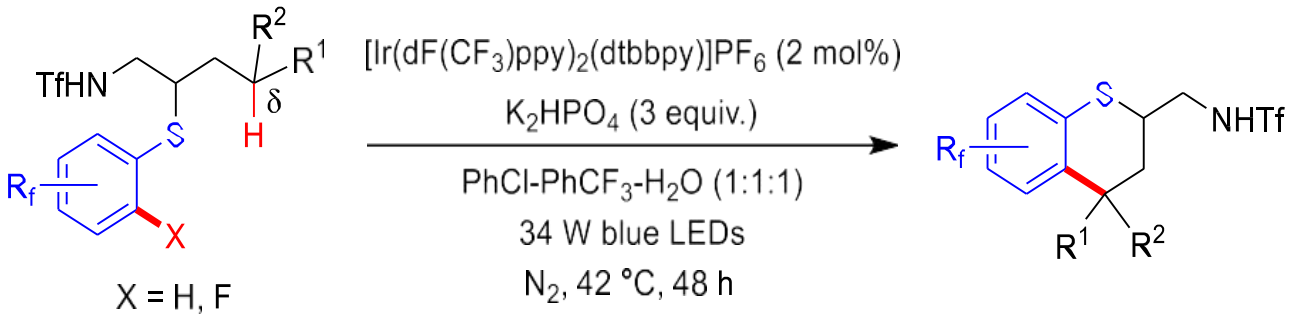
Thiochromane Formation via Visible-Light Mediated Intramolecular δ-C(sp^3)–H Bond Arylation of Sulfonamides

Shuai Liu, Nivesh Kumar, Frédéric Robert and Yannick Landais University of Bordeaux, CNRS, Bordeaux INP, ISM, UMR 5255, F-33400, Talence, France.



Visible light-mediated intramolecular site-selective δ-C(sp^3)H bond arylation of aliphatic trifluoromethanesulfonamides was developed. The reaction proceeds through a radical cascade including the generation of a sulfonamidyl radical,[1,2] which triggers a 1,5-hydrogen atom transfer, affording a -C-centered radical, which finally cyclized onto a neighboring thiopolyfluoroaryl moiety[3] to deliver a range of synthetically useful thiochromanes.[4] The cyclization process occurs through two distinct pathways depending on the nature of the substituent X, *ortho* to the native C-S bond. DFT calculations were carried out which rationalize the different pathways.[5]

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Sorption mechanism in heterogeneous photocatalysis. The enlightening example of laser-deposition of metals onto bare TiO_2 nanoparticles

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Adsorption mechanisms of reactants are at the heart of heterogeneous photocatalysis efficiencies, and remain the subject of intense discussions.[1, 2] Schematically, on the one hand, the Langmuir-Hinshelwood kinetic model (chemisorption),[3] where reagents are supposed to be pre-adsorbed on the photocatalyst surface prior to photo-reaction, is systematically used for bare photocatalysts, such as TiO_2, despite some inconsistencies in photon flux dependence of reaction rate.[4] On the other hand, Eley- Rideal-like models (physisorption),[5] where reagents diffuse toward the photocatalyst and further react with photoactivated surface states, were advanced to discuss these inconsistencies. We propose to tackle this debate using the much larger range of photon fluxes accessible from lasers, as compared to classical lamps and LEDs, and investigating the kinetics of photodeposition of single metallic (Au, Ag, Pd) nanodots onto bare TiO_2 anatase nanoparticles.[6] Quantitative rescaling of the data sets in laser intensities confirms that a Langmuir-Hinshelwood description leads to inconsistent orders of reaction with respect to light intensity, while the photoactivation of surface states solves these difficulties and then, is much more likely at work.

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Light Trapping Within 3d Macrocellular Ceramics Towards Environmental Remediation

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Photochemistry and photocatalysis have been the subject of numerous studies in the past decades. In particular, gas phase photocatalysis is of promising interest when considering air remediation, especially indoor air pollution. To favor higher efficiencies, novel hierarchical oxide-based architectures have been designed while combining sol-gel chemistry and complex fluids, leading to multiscale porous self-standing catalysts [1,2]. The association of silica scaffolds with various oxides (TiO_2, WO_3, ...) resulted in the formation of materials acting as photonic sponges. This feature is of high interest regarding the miniaturization of existing devices, in which light penetration does not exceed a few hundred of µm at best. In this context we overcome one major drawback of gas photocatalysis i.e. the number of layers efficiently activated by light irradiation. Through a colloid approach, by introducing TiO_2 nanoparticles into the silica matrix, catalysts exhibiting efficient VOCs (acetone) photo-oxidation were designed while acting in volume [3,4]. These results will be discussed in terms of environmental remediation offering "out of the box" efficient and robust monolithic self-standing heterogeneous catalysts.

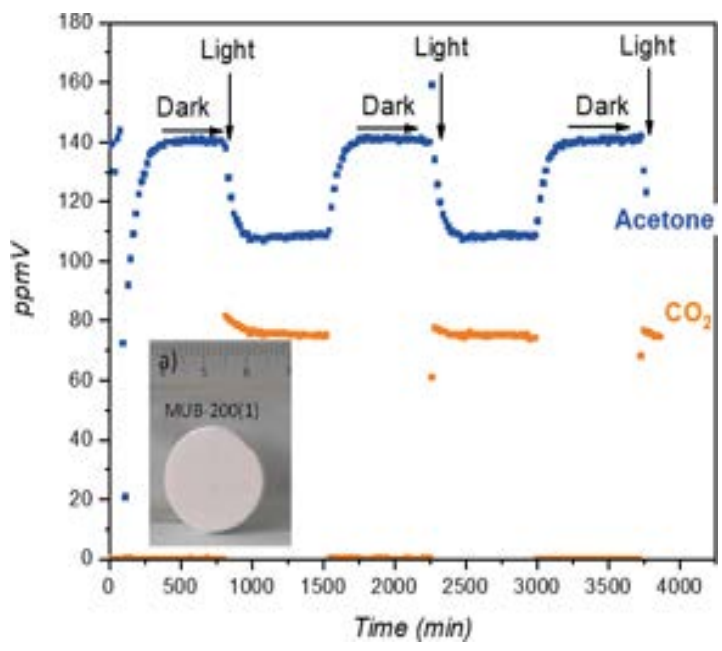

Figure 1. TiO_2@SiO_2 ceramic and acetone/CO_2 concentrations during a photocatalytic test (dark periods correspond to the material's saturation with acetone).

References:

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4 R. Backov et al., **2021**, *Patent*, FR21-13537, (B121-12922).

Visible light–driven reduction of CO_2 with molecular and hybrid catalysts

Marc Robert[1,2]

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[2] Institut Universitaire de France (IUF), F–75005, Paris, France

Reduction of carbon dioxide has as main objective the production of useful organic compounds and fuels - *renewable fuels* - in which solar energy would be stored. Molecular catalysts can be employed to reach this goal, either in photochemical or electrochemical (or combined) contexts. They may in particular provide excellent selectivity thanks to easy tuning of the electronic properties at the metal and of the ligand second and third coordination sphere. Recently it has been shown that such molecular catalysts may also be tuned for generating highly reduced products such as formaldehyde, methanol and methane, through multiple PCET reactions. Our recent results will be discussed, using earth abundant metal (Fe, Co) porphyrin, phthalocyanine and quaterpyridine catalysts.[1-7]

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