PHOTOCHEMICAL REACTIONS THROUGH ELECTRON TRANSFERS INDUCED BY MULTIPHOTONIC EXCITATION: STUDY AND OPTIMIZATION OF PHOTOREDOX PROCESSES FOR NEW APPLICATIONS IN THE SHORT WAVE INFRA-RED (SWIR).

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Context

In 1911, in a now famous column published in the journal "Science", italian physico-chemist Giacomo Luigi Ciamician drew the attention of the scientific community on the potentialities associated with the use of light as an energy source suitable for inducing chemical reactions:

« if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!»

With the constant development of ultra-short pulse power lasers, the field of photochemistry has widened to the use of non-linear optical processes, such as multi-photon excitation, extending the range and technicity of possible applications (nonlinear microscopy, phototherapy, and micro-scaled patterning of surfaces, for instance).

The Chemistry for Optics team at the ENS de Lyon laboratory, founded by Chantal Andraud, has been a major actor in the development of molecular tools for non-linear optics for over twenty years. Over the past ten years, in particular, the team's contribution has extended to the study and optimization of non-linear photochemical processes: molecular and hybrid materials for dynamic two-photon phototherapy,[1] studies of photo-induced molecular processes applied to the synthesis of molecules of interest[2]….

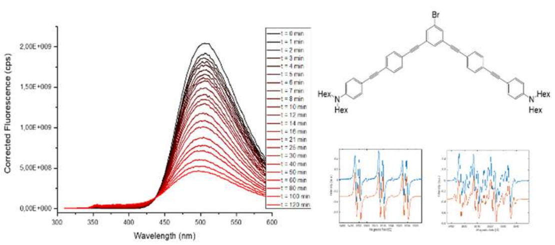

Figure 1 (left) kinetic monitoring of photo-induced radicals generation by spectrofluorimetry (right) RPE signature of radicals formed with free radical trap of DMPO and PBN type

More recently, the development of ultra-sensitive photoresits for the low-threshold multi-photonic micro-fabrication of functional micro- and nanostructures (for diverse applications ranging from ultra-flat optics to catalysis) has emerged as a major objective of the team, being the object of several important funding (ANR, Horizon2020…).[3]

Successful design of such resins requires understanding and optimizing the electron transfer processes that are consecutive to the multi-photon excitation of the "photosensitizing" molecules used in the formulation. In that framework, we contributed to the development of different techniques (coupling of fluorescence spectroscopy to RPE, electrochemistry or even NMR) and tools (radical traps possessing a characteristic RPE or NMR signature, chemical actinometry techniques) allowing to carry out this type of study, initially under mono-photonic excitation, and to quantify the kinetics and quantum yields associated with these processes (Figure 1).

Objectives

Through this thesis proposal, we plan to diversify these techniques (DSC under irradiation, IR or Raman monitoring of photo-induced processes) and to extend them to multi-photon absorption by using dedicated light sources, in particular in a wavelength range called SWIR (Short Wavelength Infra Red: 900-1700nm). This range is of particular interest, since it covers in particular the second (1000-1300 nm) and third (1500-1800 nm) windows of biological transparency, as well as the wavelengths of telecommunications. It is therefore particularly suitable both for applications in biological tissues or more generally in dense and diffusing media, but also for security and defense applications.

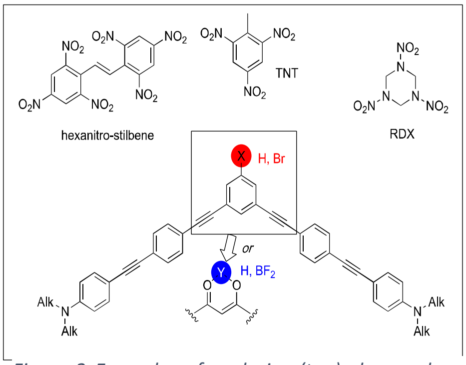

Figure 2 Examples of explosive (top) chromophore (bottom) pairs considered in this work

A major application objective of this thesis will be to develop and optimize pairs of photosensitizers and molecules presenting a highly exothermic decomposition (Figure 2). These systems, capable of generating a shock wave on micrometric scales, may be of major interest for various applications ranging from biomedical (new generation contrast agents for photoacoustic imaging) to digital optical storage of information. (etching of polymer layers). Systems developed within the framework of this project may also find an application in a separate project, led by a partner laboratory (LHCEP, UMR5278, University of Lyon), relating to the design of new generation secure optical detonators, which benefits from LABEX funding.

This multidisciplinary work will therefore cover the design, synthesis and spectroscopic and spectro-electrochemical study of photosensitizers optimized for multi-photon absorption around telecom wavelengths, the study of their photo-induced electron transfer properties with different highly energetic molecules (primary explosives), and the study of the decomposition reaction on microscopic scales (nanocrystals photo-irradiated under a two-photon microscope, for proof of principle, doped polycarbonates, etc.).

Environment

This thesis will take place in the chemistry laboratory of ENS de Lyon, where most of the research concerning the development of photosensitizers and mechanistic spectroscopic studies aimed at their characterization will be carried out, in close collaboration with our partner lab in Lyon, LHCEP that will provide the detonating molecules.

References

[1] a/ M. Galland et al , *Chemistry – A European Journal* **2019**, *25*, 9026-9034; b/ B. Mettra et al. *Physical Chemistry Chemical Physics* **2018**, *20*, 3768-3783.

[2] a/ C. Ghiazza et al.*Chemical Communications* **2018**, *54*, 9909-9912; b/ C. Ghiazza et al. *Angewandte Chemie International Edition* **2018**, *57*, 11781-11785.

[3] C. Arnoux et al. *Macromolecules* **2020**, *53*, 9264-9278.