STUDY OF A NOVEL TYPE OF WATER-SOLUBLE NON-LINEAR PHOTO-INITIATORS FOR MULIPHOTON INDUCED EMULSION PHOTPOLYMERIZATION ; APPLICATIONS IN MICROFABRICATION.

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Context:

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]….

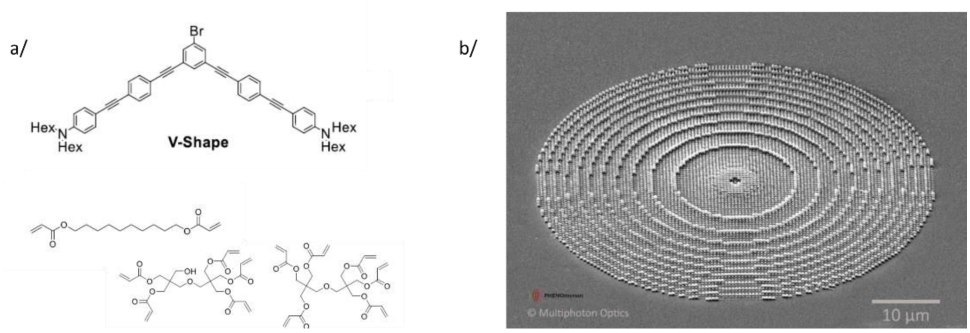

Figure 1. a/ Typical structure of a photoinitiator (top) and monomer mixture(bottom) used in our two-photon photoresists formulations b/ Example of realization (with project partner Multiphoton Optics) achieved with this formulation: this meta-lens can be used as a micrometric sized lens in miniaturized cameras

More recently, the development of ultra-sensitive photoinitiators of low-threshold multi-photon polymerization has been a major achievement of our group (Figure 1).[3]

Project:

Grounding on these preliminary successes, our group now envisions to adapt the nature and structure of these multi-photon polymerization photoinitiators to the aqueous environment, with the ambition to provide a new tool for emulsion polymerization of hydrophobic monomers using near-infrared photo-initiation, especially for DLW microfabrication purposes. A key step towards this achievement is the synthesis of water-soluble polymer appended derivatives of our photoinitator (**VS2-PHEA**) owing to a technology previously described and patented by our laboratory. Recent preliminary studies have shown that 1/ the water soluble macrophotoinitiator **VS2-PHEA** could be readily obtained by photoATRP starting from **VS2-In** (Figure 2a) 2/ **VS2-PHEA** could be successfully used as a one photon water soluble photoinitiator (upon 455 nm irradiation) to initiate the emulsion polymerization of Methyl Methacrylate.

[1]a/ M. Galland, T. Le Bahers, A. Banyasz, N. Lascoux, A. Duperray, A. Grichine, R. Tripier, Y. Guyot, M. Maynadier, C. Nguyen, M. Gary Bobo, C. Andraud, C. Monnereau, O. Maury, *Chemistry – A European Journal* **2019**, *25*, 9026-9034; b/ B. Mettra, Y. Y. Liao, T. Gallavardin, C. Armagnat, D. Pitrat, P. Baldeck, T. Le Bahers, C. Monnereau, C. Andraud, *Physical Chemistry Chemical Physics* **2018**, *20*, 3768-3783.

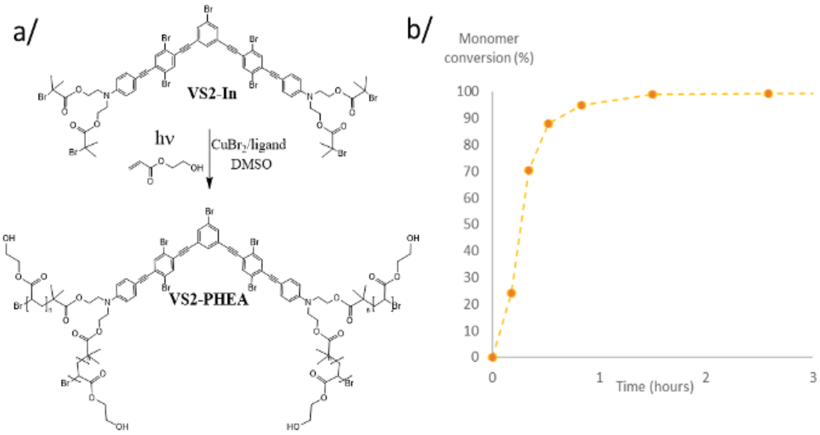

*Figure 2. a/ Structure of macrophotoinitiaor **VS2-PHEA** and its precursor **VS2-In**, with associated photo ATRP process b/ MMA conversion upon continuous irradiation of a Water/MMA/SDS/VS2-PHEA (80/16/0.5/2,5 %wt.) emulsion with a 455 nm LED.*

In this context we are looking for a candidate with a solid background in photopolymerization, especially in the context of microfabrication, hydrogel structuration or emulsion polymerization. The candidate will be involved in a postdoctoral project aiming first at optimizing the operating conditions of this photopolymerization reactions and studying its applicability for 1/the fabrication of microstructured objects from monomer emulsions in water and 2/ the microstructurations of hydrogels thereof.

This technique could be a groundbreaking advancement in the versatility of microfabrication approaches, currently limited to standard radical or anionic chain polymerization in the bulk.

Local Environment:

This postdoctoral project will be funded by an ANR grant (ANR-20-CE06-0009 IR-emulsion) and will benefit from the collaboration of researchers with recognized expertise in the fields of radical chemistry (Dr. Emmanuel Lacôte, LHCEP, Université Claude Benard Lyon I,) and emulsion polymerization (Dr Muriel Lansalot, Dr Elodie Bougeat-Lamy, CP2M, Université Claude Bernard Lyon I).

It will thus benefit from a highly interdisciplinary working environment bringing together molecular and polymer chemists, materials scientists, laser physicists and spectroscopists. State of the art spectroscopy and laser equipment, including laser optical setups operating in the NIR and SWIR, and microfabrication setups operating in the visible (532nm) as well as NIR (750-1000 nm)

Details:

We are looking for a graduate candidate (ideally 0-2 years postdoctoral experience) with a PhD in polymer chemistry/ photochemistry/ materials microstructuration. Experience in the use of LASER sources, although not compulsory, would be an asset; 18 months contract; Monthly stipends (gross) *ca* 2.5 kE, depending on postdoctoral experience

For further details, other practical information and applications, please contact **chantal.andraud@ens-lyon.fr; cyrille.monnereau@ens-lyon.fr.**

[2]a/ C. Ghiazza, L. Khrouz, C. Monnereau, T. Billard, A. Tlili, *Chemical Communications* **2018**, *54*, 9909-9912; b/ C. Ghiazza, V. Debrauwer, C. Monnereau, L. Khrouz, M. Médebielle, T. Billard, A. Tlili, *Angewandte Chemie International Edition* **2018**, *57*, 11781-11785.

[3]a/ C. Arnoux, T. Konishi, E. Van Elslande, E.-A. Poutougnigni, J.-C. Mulatier, L. Khrouz, C. Bucher, E. Dumont, K. Kamada, C. Andraud, P. Baldeck, A. Banyasz, C. Monnereau, *Macromolecules* **2020**, *53*, 9264-9278. b/C. Arnoux, L. A. Pérez-Covarrubias, A. Khaldi, Q. Carlier, P. L. Baldeck, K. Heggarty, A. Banyasz, C. Monnereau, *Additive Manufacturing* **2022**, *49*, 102491.