PhD Position

Covalent 2D organic nanostructures by optically controlled cross-linking of molecular self-assemblies

Keywords: self-assembly, nanophotonics, photophysics, photochemistry

Abstract : The self-assembly of molecules on crystalline substrates leads to non-covalent 2D structures with interesting properties for various fields such as optoelectronics and sensors. The stabilization of these 2D networks into covalent networks, while preserving these properties, is a major challenge and a topical issue. Various demonstrations show that crosslinking can be triggered by thermal processes. Photocrosslinking, on the other hand, is poorly described and the few examples that have been found involve ultra-high vacuum conditions. Building on our previously developed know-how and the additional expertise of chemist collaborators, we therefore propose to carry out photocrosslinking of 2D networks at atmospheric pressure. We will use a model oligophenyl system that will be functionalized to allow photocrosslinking towards the production of a covalent 2D network. The resulting networks will be characterized through the correlation of optical spectroscopy and local probe microscopy to monitor and highlight photo-induced cross-linking processes at wavelength scale.

Location:

The PhD *(starting date: October 2025)* will take place within the CEA/SPEC LEPO group, on the Paris Saclay University campus in France. The LEPO group has carried out different experimental developments in local probe microscopy (AFM, STM) combined with light excitation/optical spectroscopy.

Supervision:

The PhD will be supervised / co-supervised by Dr. Céline FIORINI-DEBUISSCHERT (CEA Research Director), and Dr. Nicolas Fabre who recently joined the CEA/SPEC Nanophotonics group as a permanent scientist. Their expertise ranges from optics/photonics to molecular self-assembly/functional 2D materials and chemical physics/ physical chemistry. These shared skills will be very useful in the framework of the project, which will also benefit from the participation of Prof. David Kreher (ILV/SORG) for the synthesis of the molecules.

Required profile and skills:

The applicant should hold a Master degree and be highly motivated by work on an interdisciplinary subject between physics and chemistry. The expected skills are: a strong background in optics or photophysics, and knowledge in physical chemistry.

Eligibility criteria for PhD candidates:

You must not have lived or worked in France for more than 12 months in the 36 months prior to recruitment.

Details of proposed PhD position

"Covalent 2D organic nanostructures by optically controlled cross-linking of molecular self-assemblies"

Context:

The interaction between a material and its environment first occurs through its surface. Nanostructuring of the surface promotes more selective interactions and can also lead to new optoelectronic properties. The creation of high quality 2D materials is a key objective. One attractive technique is the self-assembly of physisorbed molecules on a crystalline substrate, which offers great flexibility by playing with the molecule/molecule and molecule/substrate interactions to produce a wide variety of networks that can be achieved under ambient conditions.[4,5] However, these non-covalent molecular assemblies are labile and have poor thermal stability. To overcome these limitations, **"custom synthesis" on the surface by cross-linking the molecular network appears to be a potential solution**. One possible preparation method is to deposit molecular building blocks that self-assemble on the surface and then crosslink them directly to form a 2D covalent network.

In this context, several recent demonstrations have been reported in the literature, mainly based on the implementation of thermally activated processes under ultra-high vacuum conditions.[6] However, thermal activation of crosslinking can lead to parasitic reactions with the appearance of defects within the network, which can compromise regioselectivity and reduce the quality of the resulting 2D structures. Therefore, the strategy of light-induced crosslinking is attractive because it allows the use mild chemical reaction conditions, together with offering new parameters to play with: wavelength or polarization. To date, **only a few studies have been reported in the literature describing the possibility of inducing photochemical cross-linking of self-assembled molecular assemblies on a surface** [7,8] using ultra-high vacuum conditions. These are difficult to set up and limit the choice of materials. For future applications, it would be advantageous to carry out photochemical crosslinking in air or at the liquid-solid interface.

Objectives:

The aim of this thesis project is to fabricate for the first time a 2D covalent network and to study its optical properties using specifically designed molecules that self-assemble on a surface via **a cross-linking process controlled by optical excitation under ambient conditions**, either in air or at the liquid/solid interface. This demonstration, carried out on a model system well mastered by SPEC and ILV, would pave the way for a new paradigm in the fabrication of 2D materials with original and innovative optical properties.

Methodology:

At the interface between physics and chemistry, this PhD presents three axes that each represent challenges to overcome:

- **Design and synthesis** of new molecules with functions that enable photocrosslinking and that are able to self-assemble on the surface in a manner compatible with photocrosslinking. This task will make use of the expertise of the ILV and model systems based on previous studies by the partners. It will also benefit from the early work of a post-doctoral student who will start working at ILV in March 2025
- **Characterize** these new assemblies in air or at the liquid-solid interface to ensure that the conditions are right to induce optically controlled chemical cross-linking. This task will benefit from the local probe microscopy resources developed by LEPO.
- **Characterization of the evolution of the assembly after light excitation to highlight the photochemical cross-linking of the illuminated zone**: LEPO's expertise in local probe microscopy (AFM, STM) combined with light excitation will be used to monitor in situ the evolution of assemblies produced under illumination, as depicted in Figure 1.

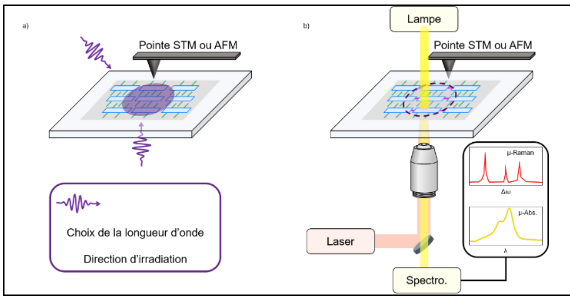

Figure 1. (a) a) Scheme of photopolymerisation monitoring using a local probe (STM or AFM). The purple arrow corresponds to the light stimulus, which can come from below or from the side of the sample. The purple disc represents the irradiated area. The molecules are represented by the blue rectangle and the green lines, various model systems of interest (specifically substituted oligophenyls) having already been defined, drawing on previous studies by ILV and SPEC/LEPO. b) Scheme of the experimental bench coupling local probe and microspectroscopy after photopolymerisation. The dotted violet circle corresponds to the previously irradiated area and the pink lines to the bonds formed.

In summary, the aim of this project is to show the proof of principle of a localized photochemical reaction, at the wavelength scale, in ambient conditions. It presents both a synthesis challenge and the challenge of successfully triggering and characterizing photocrosslinking. If these challenges are met, a number of prospects can be envisaged in both fields.

- This method could be applied to other molecules in the oligophenyl family or to other families of molecules with different geometry of assembly symmetry and different photocrosslinking reactions.
- The light stimulus could also be adapted to achieve selective photocrosslinking. The polarization of the irradiation could also be an interesting parameter to explore for controlling cross-linking: depending on the molecules used and their arrangement on the surface, directional control could be achieved. Similarly, the choice of wavelength could also lead to selective cross-linking of certain chemical functions depending on their absorption. Finally, there is the question of the spatial resolution of the cross-linking, particularly below the wavelength scale that will be considered in this project. This ambitious and longer-term perspective could be implemented by using optical nano-antenna effects (another LEPO area of expertise) towards a localization of the light excitation at nanometer level and, as a result, ultimate cross-linking at the scale of a few molecules..

Références

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