**MASTER DE CHIMIE DE PARIS CENTRE - M2S2**
**Proposition de stage 2021-2022**
**Internship Proposal 2021-2022**

**Parcours type(s) / *Specialty(ies):***
☑ Chimie Analytique, Physique et Théorique */ Analytical, Physical and Theoretical Chemistry :*
☑ Chimie Moléculaire / *Molecular Chemistry* :
☐ Chimie et Sciences Du Vivant / *Chemistry and Life Sciences* :
☑ Chimie des Matériaux / *Materials Chemistry :*
☐ Ingénierie Chimique / *Chemical Engineering :*

**Laboratoire d'accueil / *Host Institution***
Intitulés / *Name* : MONARIS (de la Molécule aux Nano-objets : Réactivité, Interactions et Spectroscopies)
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Directeur / *Director (legal representative) :* Pr. Christophe Petit
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**Equipe d'accueil / *Hosting Team :*** Equipe NARCOS (NAnomatériaux et matériaux nanostructurés : Réactivité, Caractérisation et spectrOscopieS)
Adresse / *Address :* 4 Place Jussieu, Barre 43-53, 2ème étage
Responsable équipe / *Team leader* : Prof. Alexa Courty et Prof. Ludovic Bellot-Gurlet
Site Web / *Web site :* http://www.monaris.fr/
Responsable du stage (encadrant) / *Direct Supervisor :* Dr. Gwénaël Gouadec / Dr. Imad Arfaoui
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**Période de stage / *Internship period*** * : 01/02/2022 – 30/06/2022

**Titre / *Title***
**Raman-based characterization of functionalized graphenoid surfaces**

* min. 5 mois à partir du 31 janv 2022 / *min. 5 months not earlier than January 31st 2022.*
Fin de stage au plus tard le 15/07/2022 ou le 30/09/2022 (dates de validation de diplôme). / *End of internship at the latest July 15, 2022, or Sept. 30, 2022 (dates of graduation).*

## 1. Description du projet / *Description of the project*

Self-assembly of molecular networks has emerged as a versatile and promising approach to tune the surface properties of materials.[1,2] The aim of this study is to use Raman spectroscopy to investigate the electronic structure of graphenoid surfaces functionalized with 3D molecular building blocks and confirm the presence of metal-ligand coordination bonding[3]. In this context, an electronically active molecule can be decoupled from a conducting substrate, with a view to develop new molecular electronics and photonics devices.[4,5]

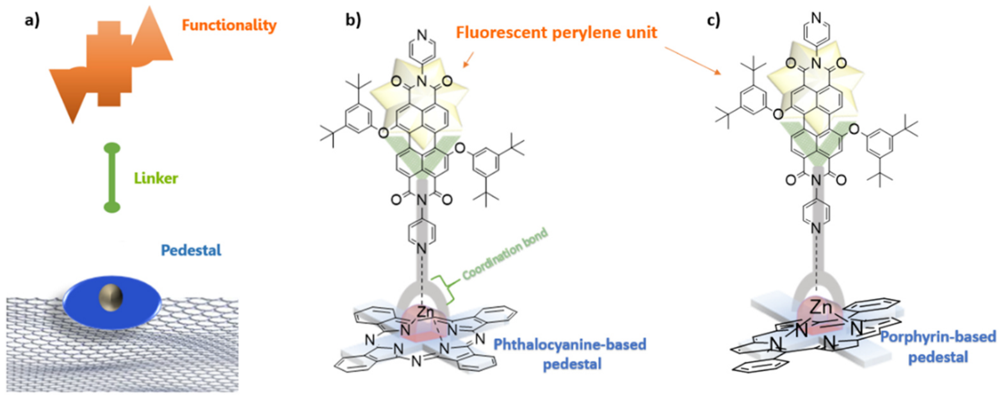


Figure 1 : Graphenoid surfaces functionalization

The surface (graphene on $SiO_2$/quartz or HOPG) is functionalized by drop casting of 3D molecular blocks consisting of a pedestal (zinc phthalocyanine[6] or zinc porphyrin[7]) and a chromophore (perylene-BPDI) – Fig. 1.[8] The blocks are either brought layer-by-layer (first the pedestal molecules, followed by the chromophores) or directly from solutions. In both cases, a host-guest template (1,3,5-tristyrylbenzene, TSB) is used. The roles of the type of substrate/pedestal molecule, the solvent and the solute concentration have already been systematically investigated. The lattice parameters of the formed 2D arrays were also measured at the solid-liquid and solid-air interfaces by Scanning Tunneling Microscopy (STM) - Fig. 2a.

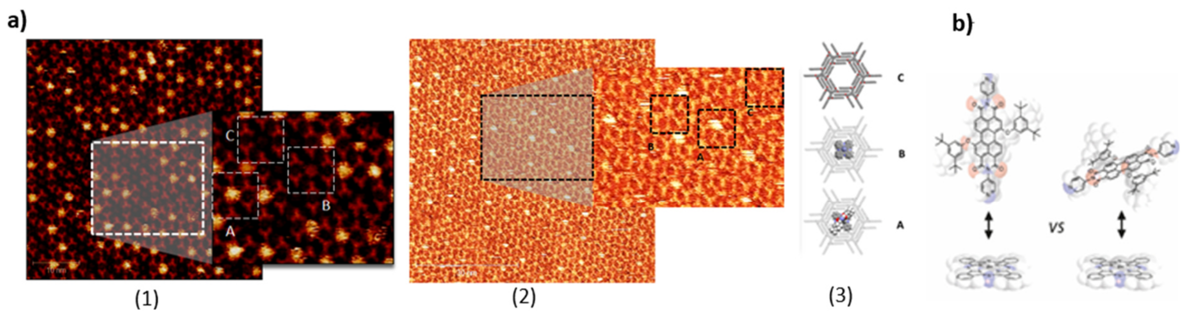


Figure 2 : **a)** STM images of chromophores linked to (1) zinc phtalocyanine and (2) porphyrin pedestals (observations in zones A, B and C are illustrated in (3)) ; **b)** $\pi$-$\pi$ *vs*. Zn-pyridin bonding

## 2. Techniques ou méthodes utilisées / *Specific techniques or methods*

The project will involve the Raman characterization of functionalized surfaces using different excitation wavelengths. Raman Spectroscopy will be used to confirm the metal-ligand coordination between the chromophore and pedestal units and check the integrity of the deposited blocks (Fig. 2b). The trainee will be trained to work in autonomy on the Raman spectrometers.

## 3. Références / *References*

1. Goronzy *et al.*, Supramolecular Assemblies on Surfaces: Nanopatterning, Functionality, and Reactivity. ACS Nano. 2018, 12 (8), 7445-7481 /// 2. Busseron *et al.*, Supramolecular self-assemblies as functional nanomaterials. Nanoscale 5, 7098–7140 (2013) /// 3. Sosa-Vargas *et al.*, Beyond "decorative" 2D supramolecular self-assembly: strategies towards functional surfaces for nanotechnology. Materials Horizons 2017, 4 (4), 570-583 /// 4. Yu *et al.*,. Supramolecular Architectures on Surfaces Formed through Hydrogen Bonding Optimized in Three Dimensions. ACS Nano 4, 4097–4109 (2010) /// 5. Samorì, P. *et al.*, Self-Assembly of Electron Donor−Acceptor Dyads into Ordered Architectures in Two and Three Dimensions: Surface Patterning and Columnar "Double Cables". J. Am. Chem. Soc. 126, 3567–3575 (2004) /// 6. Bottari *et al.*, Phthalocyanine-Nanocarbon Ensembles: From Discrete Molecular and Supramolecular Systems to Hybrid Nanomaterials. Accounts of Chemical Research 2015, 48 (4), 900-910 /// 7. Cook *et al.*, Phthalocyanine analogues: unexpectedly facile access to non-peripherally substituted octa-alkyl tetrabenzotriazaporphyrins, tetrabenzodiazaporphyrins, tetrabenzomonoazaporphyrins and tetrabenzoporphyrins. Chem. Eur. J. 2010, 17, 3136-3146 /// 8. Le Liepvre *et al.*, Fluorescent Self-Assembled Molecular Monolayer on Graphene. ACS Photonics 3, 2291–2296 (2016)