Surface Multi-functionalization: Can Intermolecular Interactions Influence the Structure of Organic Monolayers?

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Project: Surface functionalization with simple and independent molecules offers a promising approach to impart new properties to a substrate. This strategy has various advantages, ranging from diluting active species to exploiting intermolecular cooperative properties, finding potential applications in various fields such as (bio)sensors, catalysis, molecular electronics, or artificial photosynthesis.

In most cases, the targeted objectives require precise control of the molecules distribution on the surface to adjust its chemical and physical properties. This surface distribution can strongly influence the reactivity of a species or the communication between two complementary species.

Among the many existing surface modification strategies, the reduction of aryldiazonium cations stands out as a preferred method, known for the stability of the layers it produces. However, it also presents significant disadvantages related to the complexity of controlling layers in terms of thickness and composition. To address this challenge, we have recently developed a simple, reproducible, and generalizable electrochemical methodology, allowing controlled and durable multi-functionalization of (semi-)conductive surfaces using a mixture of functionalized aryldiazonium cations.

The objective of this doctoral project is to exploit this methodology based on the reduction of aryldiazonium salt to functionalize (semi-)conductive surfaces with mixed monolayers composed of two distinct organic motifs with specific electrochemical and spectroscopic properties. The molecules composing these monolayers will be specifically designed to exhibit intermolecular interactions (Van der Waals interactions, hydrogen bonds, π-π interactions, or electrostatic forces). The impact of these supramolecular interactions between species in solution on controlling their distribution on the surface will be explored (Figure 1).

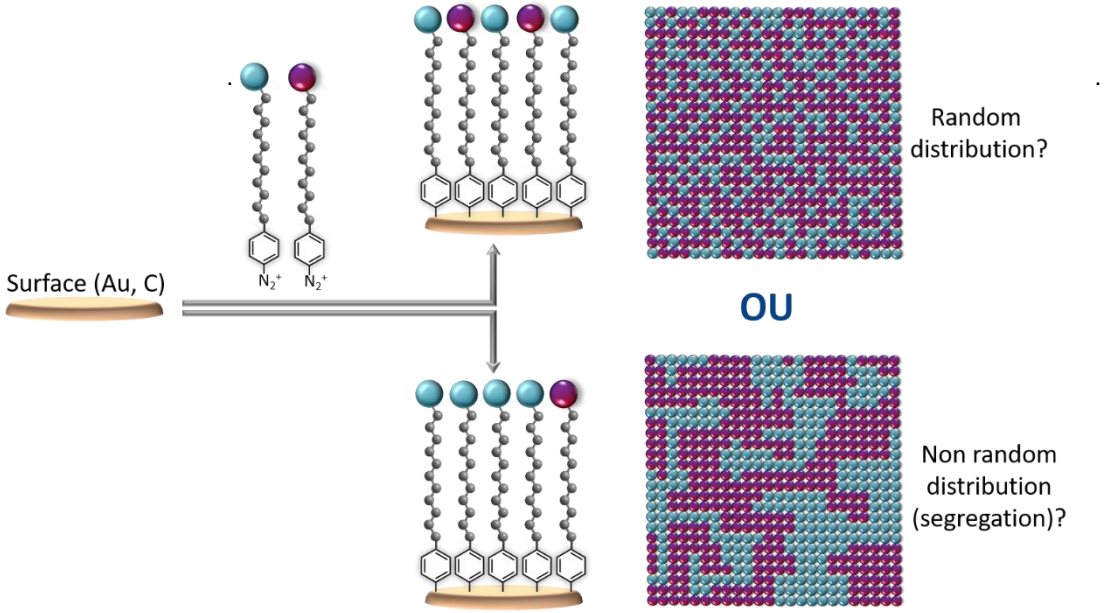

Figure 1. Surface bi-functionalization with a mixture of diazonium salts.

Profile of the applicant: The first part of the research project will focus on the synthesis of target molecules. Subsequently, mixed organic monolayers will be prepared, and physicochemical characterizations will be conducted on functionalized surfaces (electrochemical, spectroscopic, gravimetric, or microscopic characterizations). The candidate should hold a master's degree in chemistry and have a strong affinity for organic synthesis, electrochemistry, spectroscopy, and surface characterization techniques.

Applications must be completed online on the 3MG doctoral school website: https://theses.doctorat-bretagneloire.fr/3mg. They should include a motivation letter, a CV, marks from M1 and the first semester of M2, and at least one letter of recommendation.