

PhD Position Available: Controlled reactivity of sulfoxides on insulating substrates

- **Context :**
 - Host laboratory: [Institut Matériaux Microélectronique et Nanosciences de Provence \(IM2NP, UMR 7334 CNRS\)](#)
 - Research team: [Nanostructuration \(leader: Ch. Loppacher\)](#)
 - Host university: Aix-Marseille Université, France
- **Funding:**
 - Beginning / Duration : September 2022 / 3 years
 - Gross salary : 90.756 k€ for three years
- **Thesis directors:** Christian Loppacher (christian.loppacher@im2np.fr) and Laurent Nony (laurent.nony@im2np.fr)

Over the past ten years, "on-surface synthesis" has emerged as an important topic in the field of surface physics. It concerns the study of new approaches to reaction mechanisms between organic molecules as they are adsorbed on the surface of a sample of interest⁽¹⁾: metal, semiconductor, or dielectric. The combination between: (i)- low dimensionality of the environment induced by the surface, (ii)- intermolecular and molecules-substrate interactions, (iii)- deposit conditions, (iv)- temperature of the surface, as well as (v)- the contribution of external elements to the reaction (e.g. UV light), make it possible to control the reaction conditions. The resulting intermolecular bonds, often covalent, lead to the formation of two-dimensional organic polymers, the structural quality of which depends on the fineness of the control of the preceding elements. But the important point is that these organic nanostructures are impossible to synthesize using regular methods of synthetic in-solution chemistry.

In this context, dielectric substrates, including the surfaces of single crystals of alkali halide salts (KCl (001), NaCl (001), KBr (001), etc.) are of particular interest. Indeed, their low reactivity combined with their dielectric nature limit the modification of the intrinsic electronic properties of the adsorbed molecules and thus promote the anticipated reaction mechanisms. The added benefit of these materials is that they can either be used in a solid state, or prepared in thin layers that are deposited on a metallic substrate.

In order to characterize the resulting organic nanostructures as well as their properties (electronic, optical, etc.), studies must be carried out from the nanostructure, down to the individual molecule. This requires the use of an ultra-vacuum environment coupled with probe microscopy techniques (tunneling microscopy, STM, atomic force microscopy in noncontact mode, nc-AFM) operated both at room temperature and at low temperature (<10K), as well as in situ optical spectroscopy.

Regarding organic precursors, sulfoxides ($R_2S=O$) are compounds carrying a sulfinyl functional group ($S=O$, cf. fig. 1) and exhibit an important reactivity in solution featuring deoxygenation, or controlled extrusion (cf. fig. 2), of the sulfinyl group under UV irradiation. The transposition of these in-solution properties to surface synthesis has never been studied so far.

The topic of this thesis concerns the study of sulfoxides organic precursors with a view to initiating new reaction mechanisms for on-surface synthesis on alkali halide substrates, primarily by deoxygenation and / or controlled extrusion of the sulfinyl group.

The choice and the nature of the sulfoxide precursors will be established in consultation with chemist colleagues, Claire Kammerer from CEMES (Toulouse) and David Madec from LHFA (Toulouse), involved in the ANR project funding the thesis, the CROSS project (Controlled Reactivity Of Sulfoxides on insulating Surfaces).

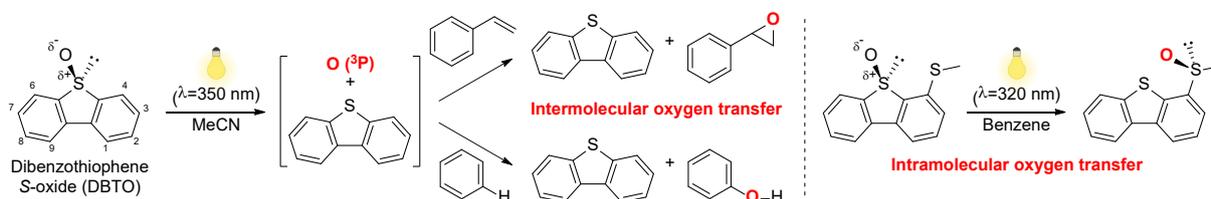


Figure 1: Prototypical sulfoxide precursor, dibenzothiophene S-oxide, which can be deoxygenated under UV irradiation in solution, yielding inter- or intra-molecular oxygen transfer

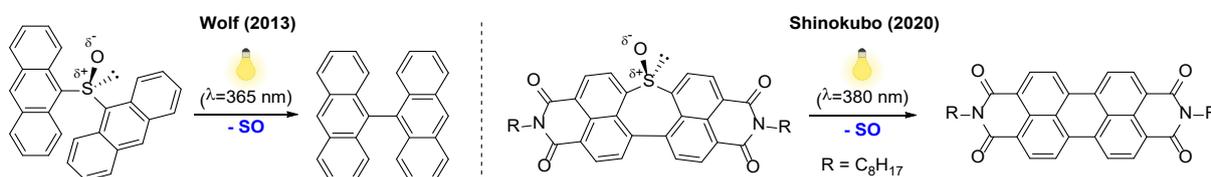


Figure 2: Photo-induced SO extrusion in diarylsulfoxides in solution, yielding the formation of C-C bonds

The surface studies will be carried out within the Nanostructuration team of IM2NP on two ultra-vacuum setups, one featuring an STM / nc-AFM operating at room temperature, the other featuring an STM / nc -AFM operating at low temperature (9K). The resulting nanostructures will be characterized down to the individual molecule scale with advanced STM and nc-AFM techniques (multidimensional spectroscopy). The team has expertise in CO tip-functionalization allowing intramolecular resolution (see fig. 3). The optical properties of the nanostructures will be characterized by two in situ differential reflectance spectroscopy setups implemented on each UHV setup.

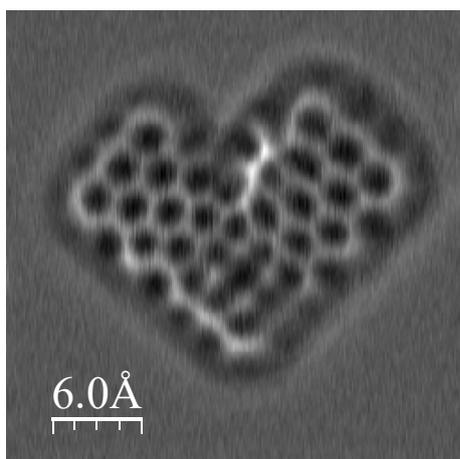


Figure 3: Constant height nc-AFM image of an isolated porphyrinoid-like molecule on Au (111) imaged with a CO tip. The intramolecular resolution is clearly visible. The image was taken on the low temperature apparatus of the Nanostructuration team at IM2NP.

- (1) Clair, S.; De Oteyza, D. G. Controlling a Chemical Coupling Reaction on a Surface: Tools and Strategies for On-Surface Synthesis. *Chem. Rev.* **2019**, *119*, 4717-4776.

The candidate should hold a master's degree in physics and have a pronounced interest in nanosciences, surface science and physical chemistry. She / he must have strong motivation for experimental physics and instrumentation (already established during her/his M2 internship), as well as skills in signal processing (LabVIEW and / or Matlab programming desired).

Keywords: Surface Science, Physical Chemistry, Scanning Probe Microscopy (STM/AFM), Differential Reflectance Spectroscopy, Ultra-high vacuum

Interested candidates are invited to send CV, motivation letter, diploma with transcripts and contact details of two referees to Christian Loppacher (christian.loppacher@im2np.fr) & Laurent Nony (laurent.nony@im2np.fr).