

Swiss Nanoscience Institute – PhD Program

ORACLE

SUPRAMOLECULAR CHARGE AND SPIN- ARCHITECTURES PRODUCED BY CHEMICAL ‘CLIPPING’

*Langmuir Blodgett Assembly and Host Guest Interactions: Towards
functional supramolecular systems.*

Proposers

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1. Introduction

This PhD project aims to develop a novel approach for the design of supramolecular layers with an atomically precise architecture and thickness on solid surfaces. It stems from recent findings achieved by the proposers on the stabilization of Langmuir-Blodgett (LB) films through a self-assembly process, using supramolecular clips.¹

Beyond the established *clipping*, porous layers shall be developed which can then be flexibly equipped with functionalized guest molecules containing donors, acceptors and/or molecular magnets. Thereby a novel toolbox is developed for the design of engineered interfaces by modification of the LB layer assembly and complementary structure/property correlation studies are carried out in close collaboration between PSI and FHNW.

2. State of the art

The assembly of organized monomolecular layers on surfaces represents a foremost research axis in nanotechnology, with a large number of possible applications ranging from biosensing to future information storage. Since the seminal work of Whitesides on self-assembled monolayers (SAMs) of organo-thiolates on metal surfaces,² these systems have become the predominant method for the chemical modification of surfaces. SAMs substantially overshadowed the surface coating technique developed in the 1930s by Irving Langmuir and Katharine Blodgett: the Langmuir-Blodgett (LB) deposition method.²³ Surface coating by the LB technique is more versatile, as it does not require the presence of active chemical functions able to react covalently with the surface. LB transfer can be carried out with a broad variety of non-water soluble amphiphiles on any type of surfaces. Additionally, it provides the possibility to control the surface packing of those amphiphiles. However, this technique suffers from a major drawback that is the poor stability of the produced films.

Lately the two proposers developed a novel strategy that allowed drastic stabilization of LB films using supramolecular clips; *cf.* Fig. 1.¹ It was demonstrated that amphiphiles bearing negative charges at their polar head, self-assembled as Langmuir layers, can be stabilized using small organic “clips” that possess negative charges in a favourable *syn*- position. This allowed the stable transfer of monomolecular films from the assembly trough to solid substrates. In this first case the transferred layers were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and surface ellipsometry.

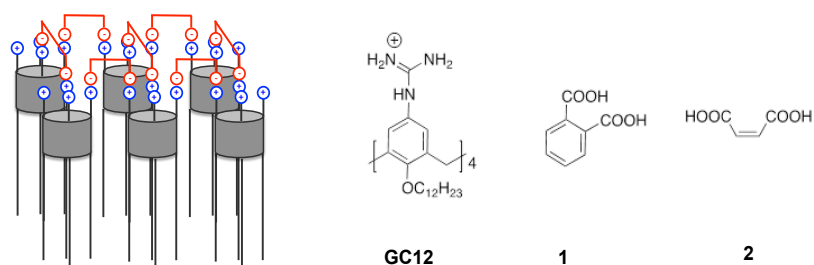


Figure 1. Schematic representation of a LB film stabilized by electrostatic clips (left) and molecular formulas of the amphiphile (GC12) and the two clips that were used for the stabilization strategy (1: *ortho*-phthalic acid, 2: maleic acid).

3. Innovation content of the project

In the present proposal, it is planned to expand the approach of *clip stabilization* to develop a novel approach of surface supramolecular engineering. It is based on the use of macrocyclic amphiphiles bearing several (2-8) metal coordination ligands at their polar side. The building blocks will be produced by chemically “decorating” calixarene macrocycles, a class of molecules widely used to produce designer amphiphiles.⁴ In *ORACLE*, the work will consist in introducing in the calixarene macrocycle, chemical moieties possessing the ability of coordinating the chosen metal ions, *e.g.* carboxylate, pyridine, terpyridine. We hypothesize that the presence of transition metal ions in the

¹ N. Moridi, C. Wäckerlin, V. Rullaud, R. Schelldorfer, T. A. Jung and P. Shahgaldian, *Chem. Commun.* **2013**, 49, 367

² J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.* **2005**, 105, 1103

³ A. Ulman, *An introduction to ultrathin organic films: from Langmuir-Blodgett to self-assembly*; Academic Press: Boston, 1991

⁴ N. Moridi, D. Elend, O. Danylyuk, K. Suwinska and P. Shahgaldian, *Langmuir* **2011**, 27, 9116–9121; K. Helttunen and P. Shahgaldian, *New J. Chem.* **2010**, 34, 2704; P. Shahgaldian, M. A. Sciotti, U. Pielas, *Langmuir* **2008**, 24, 8522

liquid phase, beneath the Langmuir monolayers, will cause the formation of two-dimensional crystalline arrays that can be transferred on a solid substrate, as depicted in Fig. 2. Host guest systems are developed on the basis of this architecture by either including building blocks containing cavities (e.g. calixarenes) or by using the natural pores of the clipped LB film as hosts for guest molecules that can be added either via the liquid or via sublimation after transfer to a solid substrate. The possibility of making a large part of, if not all, the assembly steps from the liquid phase provides a step across a significant hurdle: The majority of molecules, and in particular the components of complex supramolecular architectures are not sublimable (e.g. most molecular magnets) and can only be investigated along the routes to be developed in this project or as bulk crystals.

The coordination geometry of the metal ions will allow for controlling the packing lattice of the monolayer. This phenomenon will be studied, *at the air-water interface* using a Langmuir trough, surface ellipsometry, BAM and synchrotron-based grazing incidence X-ray diffraction (GIXD).⁵

After transfer to a solid substrate and subsequent evacuation of the residual solvent, the transferred film will be imaged on its support by electron microscopy (SEM, TEM, STEM) and scanning probe microscopy (SPM). The chemical and physical structure of the multicomponent layer will be further investigated by photon based spectroscopic tools (X-ray photoelectron spectroscopy XPS, near edge X-ray absorption fine structure NEXAFS) and its electronic or spintronic function by UV-photoelectron spectroscopy UPS and X-ray magnetic circular dichroism XMCD.

Notably, the so-produced LB films will be assessed as host systems for the site-specific introduction of different functional guest molecules in the film. This 2nd stage assembly can be realized at different positions of the clipped LB-film backbone and provides molecular architectures, which can be modified and compared to their analogues with little efforts.

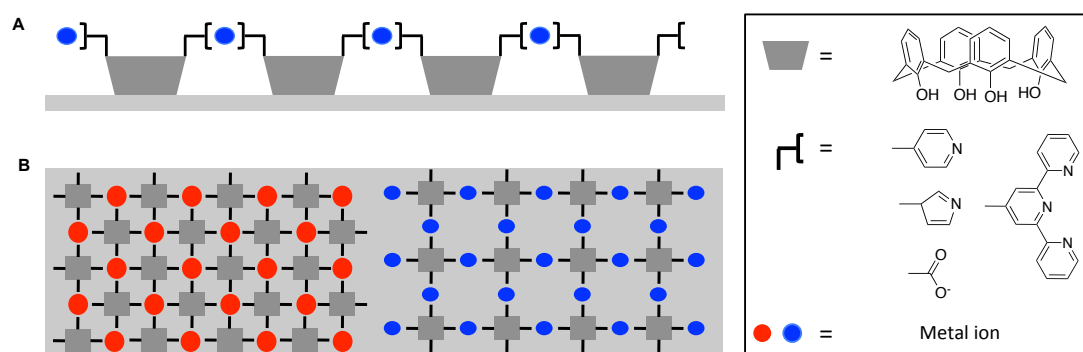


Figure 2. Schematic representation of LB film stabilized by metal ions with different coordination geometries (**A**: side and **B**: top views), and examples of molecules that can be used to produce these supramolecular systems (**C**)

4. Project organization

The project asks for a well-trained nanosciences (UniBS) or natural sciences (ETHZ) graduate with a strong background in physical chemistry and interest in surface physics.

In her/his first year, the candidate will be introduced to the chemical synthesis of calixarene compounds and supervised to learn the preparation techniques in the Shahgaldian group. As soon as first layers are reproducibly available, the two groups shall closely interact to perform physico-chemical investigations. This includes synchrotron experiments for the structural investigation of the layer floating on the Langmuir trough and investigations of the layers after transfer to the solid substrates. Laboratory-based experiments can be performed immediately, while synchrotron-photon based investigations need more preparation time, but provide unique access to complementary information. It is foreseen that experimental sessions at synchrotrons shall be staffed by at least one member from each of the hosting groups in addition to the PhD student requested in this proposal.

The future Ph.D candidate will be jointly supervised by Prof. P. Shahgaldian (Institute of Chemistry and Bioanalytics, FHNW) and Prof. T. Jung (Molecular Nanoscience group at the Laboratory for Micro and Nanotechnology LMN of PSI). In the first year the candidate shall be predominantly, but not exclusively present at FHNW while in the 2nd and 3rd year the foreseen investigations of structure and property of the assembled layers requires more and more presence at LMN. There is already a strain of a first publication and some more results, which can be used to train the candidate in the preparation of manuscripts already in the first year.

⁵ Carried out at the Advanced Photon Source (APS) at Argonne National Laboratory (Chicago, USA) in collaboration with Prof. David Vaknin (Iowa State University)