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Herstellung und Eigenschaften selbstorganisierter Monolagen
Preparation and Properties of Self-Assembled Monolayers

*"Molecular self-assembly is a strategy for nanofabrication that involves designing molecules and supramolecular entities so that shape-complementarity causes them to aggregate into desired structures. Self-assembly has a number of advantages as a strategy: First, it carries out many of the most difficult steps in nanofabrication--those involving atomic-level modification of structure--using the very highly developed techniques of synthetic chemistry. Second, it draws from the enormous wealth of examples in biology for inspiration: self-assembly is one of the most important strategies used in biology for the development of complex, functional structures. Third, it can incorporate biological structures directly as components in the final systems. Fourth, because it requires that the target structures be the thermodynamically most stable ones open to the system, it tends to produce structures that are relatively defect-free and self-healing. […]**Self-assembled monolayers, SAMs, represent one type of structure that is using molecular self-assembly to build structure and function on the nanometer scale.** They are not a general solution to the problem of building functional nanostructures, but the lessons learned from them will be valuable in building more versatile systems. They also are among the first of the self-assembled systems to move into technology, and there are lessons that can be learned from them about technology transfer and nanotechnology."*

George M. Whitesides,
Department of Chemistry, Harvard University, Abstract for the Fourth Foresight Conference on Molecular Nanotechnology, 1995

Introduction

A SAM consists of a single layer of organized organic molecules bound to a surface. SAMs offer a unique combination of physical properties that allow fundamental studies of interfacial chemistry, solvent-molecule interactions and self-organization. Their well-ordered arrays and ease of functionalization make them ideal model systems in many fields. SAMs are invaluable substrates in nanotechnology, for example in
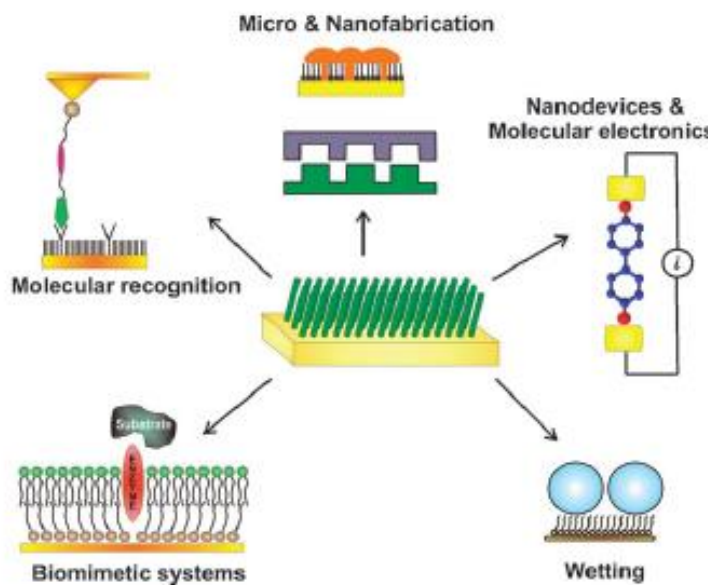

Figure **1**. Some applications of self-assembled monolayers in nanotechnology. (The Royal Society of Chemistry 2010).

the fields of material protection, biosensing and device fabrication[1] (Figure 1).

One of the most widely studied systems of SAMs are gold-alkylthiolate monolayers[2] (Figure 2). Self-assembly of thiols and dithiols on gold is, in principle, easy to perform and can be done both in the gas phase and in liquid environments (from solutions of different solvents), the latter being by far the most popular method because of its simplicity and accessibility in most laboratories. In general, adsorption is performed in 10–1000 mM solutions of thiols, dithiols, dialkyldisulfides (in general S–S bonds break upon adsorption and thiolate SAMs are obtained) and dialkylsulfides in different solvents, depending on the nature of the molecule. Adsorption times also depend on the nature of the molecule: while 2–12 h are enough to form a well-ordered SAM in the case of long chain alkanethiols, at least 24 h are necessary for short chain alkanethiols or thiols with certain end-groups different from –CH_3. Mixed monolayers may be formed if the solution contains two or more different thiols.

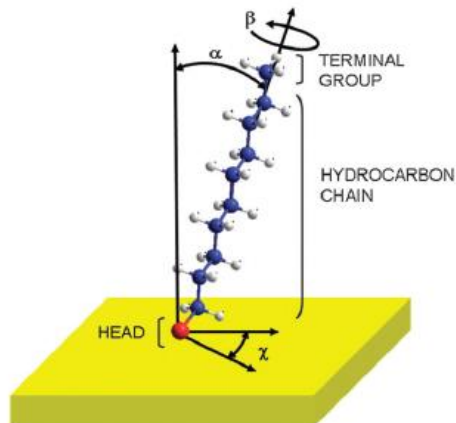Figure **2**. Formation of a SAM on a gold surface via sulfide bridges.

Figure **3**. Scheme of a decanethiol molecule adsorbed on Au(111) (yellow) in a standing up configuration. Typical angles are α = 30°, β = 55°, and χ = 14°. Red: sulfur atom; blue: carbon atom; white: hydrogen atom (The Royal Society of Chemistry 2010).

Each of the molecules that constitute the building blocks of the system can be divided into three different parts (Figure 3): the head-group (linking group), the backbone (main chain), and the specific terminal (active) group. The head-group guides the self-assembly process on each type of substrate, linking the hydrocarbon chain (of variable length) to the metal surface through a strong bond. The interactions among backbone hydrocarbon chains (involving van der Waals and hydrophobic forces) ensure an efficient packing of the monolayer and contribute to stabilize the structures with increasing chain length. The terminal group confers specific properties to the surface (hydrophilic, hydrophobic), and can also be used to anchor different molecules, biomolecules, or nanostructures by weak interactions or covalent bonds.

[1] Wei Lu and Ann Marie Sastry, Self-Assembly for Semiconductor Industry, *IEEE Transactions on semiconductor manufacturing*, **2007**, *20*.

[2] C. Vericat, M. E. Vela, G. Benitez, P. Carro and R. C. Salvarezza, Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system, *Chem. Soc. Rev.*, **2010**, *39*, 1805–1834.
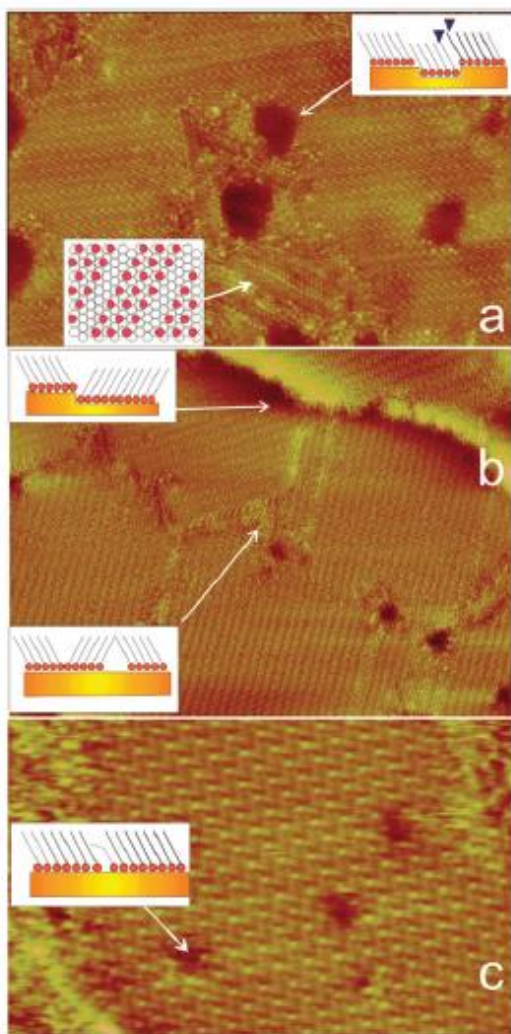
For many SAM applications the quality of SAMs prepared under "standard" conditions is enough, but, for others, defects are a serious problem, and the control of the SAM quality is a crucial point (Figure 4). Several characterization methods are useful for verifying many aspects of the packing and phase behavior of SAMs. In general, the combination of several local and average surface analysis techniques, together with theoretical techniques, can provide a thorough description of the SAM structures[2]. One commonly used technique to observe how the quality of the chemical modification can affect dramatically the properties of a solid surface is the measurement of the angle a liquid droplet makes with the surface.

In this lab training, SAMs will be created by depositing (reacting) long chain hydrocarbon molecules on planar gold substrates. Monolayers of alkyl or aromatic thiol molecules containing different end groups will be deposited. We expect that depositing SAMs on the relatively hydrophilic gold surface should change the properties of the surface in respect to its wettability. The main goal of this lab is to verify this simple hypothesis, by contact angle measurements.

A short introduction to the wettability of functional nanostructures.

The topic of wetting has received tremendous interest from both fundamental and applied points of view. It plays an important role in many industrial processes, such as oil recovery, lubrication, liquid coating, printing, and spray quenching. In recent years, there has been an increasing interest in the study of superhydrophobic surfaces, due to their potential applications in, for example, self-cleaning, nanofluidics, and electrowetting.

Figure **4**. Scanning tunneling microscopy (STM) images of alkanethiolate SAMs on Au(111) showing different types of surface defects (sketched in the insets) (a) vacancy islands and missing rows, (b) domain boundaries and step edges (c) molecular defects (pinholes) (The Royal Society of Chemistry 2010).

Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. Small contact angles (<<90°) correspond to high wettability, while large contact angles (>>90°) correspond to low wettability. Contact angle and the wetting behavior are influenced by many physical and chemical factors such as surface roughness and heterogeneity and it is often difficult to find reproducible results.

Hence, a variety of contact angles has been defined to address different situations and some of these are outlined below[3].

The Young equation

The relationship between surface tension and contact angle was first recognized by Young. In principle, the contact angle of a liquid drop on a solid surface in aqueous solution, as shown in Figure 5, is determined by the mechanical equilibrium under the action of three interfacial tensions, i.e., solid–vapor surface "tension", solid–liquid interfacial "tension", and liquid–vapor surface tension. The contact angle determined by balancing the surface tension forces is known as Young's contact angle and the relationship describing the balance of surface forces is known as Young's equation
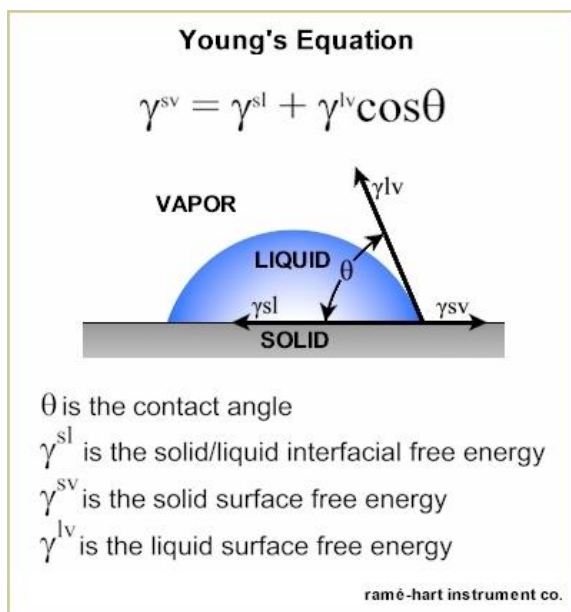

Young's Equation

$$\gamma^{sv} = \gamma^{sl} + \gamma^{lv}\cos\theta$$

θ is the contact angle
γ^{sl} is the solid/liquid interfacial free energy
γ^{sv} is the solid surface free energy
γ^{lv} is the liquid surface free energy

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Figure **5**. Scheme of the relationship between surface tensions and contact angle.

The validity of Young's equation requires that the solid surface is smooth, flat, homogenous, inert, insoluble, nonreactive, non-porous, and of non-deformable quality. These conditions are usually not met by real surfaces. A surface, which meets all the requirements of the Young equation, is referred to as an ideal surface. However, most practical surfaces are non-ideal and the measurable contact angle values on such surfaces are referred to as the apparent contact angles, θ_{app}. As a consequence, this value is not unique but falls into a more or less wide interval between the advancing (largest) and the receding contact angle (smallest). The difference between them is called contact angle hysteresis.

The three main contributing factors relating to non-ideal surfaces are:
- contamination of either the liquid or the solid surface
- surface roughness,
- surface immobility on a macromolecular scale

The Wenzel and the Cassie equations

Wenzel may have been the first scientist to investigate the effect of surface roughness on the static contact angle. He observed that surface roughness caused a hydrophobic fluid to behave as if it were more hydrophobic and a hydrophilic fluid to behave as if it were more hydrophilic. Wenzel also suggested that the geometry of the surface had a greater effect on the static contact angle than did the chemistry. On a rough surface, the apparent contact angle is related to the ideal contact angle according the Wenzel equation:

$$cos\ \theta_w = r\cos\theta_Y$$

[3] T.T. Chau , W.J. Bruckard, P.T.L. Koh, A.V. Nguyen, A review of factors that affect contact angle, *Advances in Colloid and Interface Science* **2009**, *150*, 106–115.
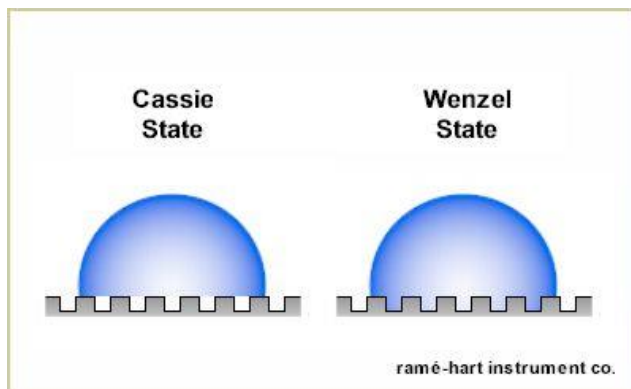
Figure **6**. Scheme of the Cassie and the Wenzel model.

This modification is required when the drop size is sufficiently large compared to the roughness scale, and if the liquid completely penetrates into the roughness grooves on the solid surfaces (Figure 6). In this equation, θ_w is the Wenzel contact angle (the apparent contact angle on a rough surface), θ_Y is the ideal Young contact angle on a smooth surface and r is the average roughness ratio, defined as the ratio between the true and the apparent surface area of the solid. It is implicitly assumed that the surface features of the substrate are insignificant compared to the drop dimensions and that their geometry is of no consequence as long as it does not affect the surface area. On a heterogeneous surface, the apparent contact angle is related to the ideal contact angle by the Cassie equation. Cassie derived an equation describing contact angle changes for two component surfaces as follows:

$$\cos \theta_C = f_1 \cos \theta_1 + f_2 \cos \theta_2$$

Here f_1 is the fractional area of the surface with contact angle θ_1, f_2 is the fractional area of the surface with contact angle θ_2, and θ_c is the Cassie contact angle. The Cassie equation is reduced to Cassie-Baxter equation for a porous surface, such as a mesh or screen surface:

$$\cos \theta_C = f_1 \cos \theta_1 - f_2$$

In this case, f_2 is the fraction of air spaces (open area) which makes $\cos\theta_2=-1$, as $\theta=180°$ for a non-wetting situation. Originally, the Cassie-Baxter equation was proposed to described wetting phenomena at porous surfaces, it can also be used for rough hydrophobic surfaces when liquid does not penetrate the surface structure. The advantage of the Cassie-Baxter model over Wenzel's approach is that it describes real systems more accurately. However, in the Cassie-Baxter equation, it is difficult to accurately determine the parameters f_1 and f_2 for randomly roughened surfaces. The theories proposed by Cassie and Wenzel have been widely used to predict the real (rough and heterogeneous) surface behavior, especially in the past 5 years with the new area of research in "super-hydrophobic" surfaces.

In the frame of this lab-training the simple Young's Model will be applied.

Experimental instructions

Solution-Based Self-Assembly. (This procedure was adapted from Sigma-Aldrich).

Self-assembled monolayers (SAMs) of thiols are prepared by immersing a clean gold substrate into a dilute solution of the desired thiol. For this lab-training two different thiols and a mixture of both will be used (3 samples). The exact chemical structure will be revealed at the end of the

training, after discussion of the characterization by contact angle, in order to stimulate a deeper analysis of the data obtained.

Although self-assembly takes place rapidly, good experimental procedures are needed to produce consistent, highly ordered films.

Reagents and Equipment:

• Gold coated substrates
• Thiol compound(s)
• 200 mL ethanol • Calibrated micropipettes
• Container for mixing thiol solution
• Tweezers for sample handling
• A dedicated ethanol solvent bottle
• Parafilm® for sealing
• Containers for sample preparation
• Petri dishes for transporting and storing SAMs
• Dry nitrogen gas
• Analytical Balance
• Ultrasonic bath

Environment - A clean environment is key to prepare high-quality SAMs. Even low levels of contaminants can affect monolayer quality. Avoid rooms or hoods in which silanes or poly(dimethylsiloxanes) (PDMS) have been used. These compounds easily cross contaminate a variety of surfaces. All thiols should be handled in a fume hood.

Containers should be easily sealable. For the highest quality films, oxygen exposure should be minimized during the assembly process. This is achieved by reducing the headspace above the thiol solution and backfilling with an inert gas. Each substrate is placed in its own container to avoid interactions that would be detrimental to film quality.
Containers can be re-used, as long as they are rinsed well with solvent after each use and dedicated to the same thiol to avoid cross-contamination.

Sample Slides – Gold-coated slides must have an adhesion layer of chromium (Cr) or titanium (Ti) under the gold layer. If this layer is missing, the gold will delaminate and ruin the monolayer during sonication.

A. Determine necessary amounts and concentration of thiol solution.

1. Calculate the total volume of thiol solution needed to make the number of samples desired:

2. Calculate the total amount of thiol needed to prepare desired amount of thiol solution.

$$Mass\ of\ thiol = Total\ Volume\ \cdot Concentration\ \cdot molecular\ weight$$
$$m\ [g] = V\ [l] \cdot\ c\ \left[\frac{mol}{l}\right] \cdot MW\ [\frac{g}{mol}]$$

Where MW is the Molecular Weight of the thiol, and c is the concentration (typically 1–5 mM). If the thiol is a liquid, convert the mass to a volume using the density. Use a calibrated micropipette to measure and dispense liquid thiols.

B. Prepare Thiol Solution - Prepare enough solution for all samples to ensure the solution concentration is constant across the sample set. When preparing mixed thiol solutions, prepare a stock solution of each thiol separately, then mix them at the proper proportions for the final stock solution.

1. Rinse all assembly containers with 3–5 mL of solvent. Repeat 2–3 times and re-cap each container. Also rinse all beakers, tweezers, etc., to be used in the experiment.

2. Measure the appropriate volume of solvent into a clean solution container.

3. Dispense the mass (or volume) of thiol into the solvent.

4. Sonicate solution for 5–10 minutes to dissolve.

5. Once dissolved, dispense the planned volume of solution into each sample container.

C. Sample Self-Assembly

1. Immerse gold substrate in container containing thiol solution. Handle gold substrates with tweezers and minimize exposure to air.

2. Backfill each container with dry nitrogen gas, seal the cap and wrap with Parafilm.

3. Incubation time around 24 hours. Longer assembly times tend to result in a better packing of the monolayer. Samples prepared from the previous group will be used to continue the process.

D. Terminate Self-Assembly

1. For simple alkane thiols, hold sample with clean tweezers and rinse with solvent for 10–15 seconds using a clean solvent bottle.

2. Dry sample with a stream of dry nitrogen gas.

3. Place each sample in a container with fresh solvent,

4. Sonicate the samples for 1-5 minutes.

5. Remove the samples individually and rinse again for 10–15 seconds under a steady stream of ethanol.

6. Dry sample with a stream of dry nitrogen.


E. Sample Storage

1. Place in clean Petri dish or desiccator.

2. Backfill Petri dish with dry nitrogen.

3. For long-term storage - Place Petri dishes in a jar backfilled with dry N2 and sealed with Parafilm. If you are going to use the monolayers for further experimentation, plan your experiments so you can rinse the samples right before use. Minimize time between preparation and use, since SAMs can oxidize over time.

Contact Angle

The most widely used technique of contact angle measurement is a direct measurement of the tangent angle at the three-phase contact point on a sessile drop profile. The equipment consists of an in x-, y- and z-direction movable stage to place the sample, a syringe with a needle to form a liquid drop, an illumination source and an integrated camera to take photographs of the drop profile in order to measure the contact angle at leisure. The use of relatively high magnifications enables a detailed examination of the intersection profile. The measurement is achieved by simply aligning the tangent of the sessile drop profile at the contact point with the surface and applying the Laplace-Young equation.

This direct optical method is advantageous because of its simplicity, as well as the fact that only small and precise amounts of liquids (a few microliters) and small surface substrates (a few square millimeters) are required. On the other hand, there is a relatively higher risk/impact of impurities due to the small size of the liquid and substrate. As for accuracy and reproducibility, the measurement relies on the consistency of the operator in the assignment of the tangent line, which can lead to significant error and inconsistency between multiple users. To establish an advancing contact angle, it is the best to slowly grow the sessile drop until it reaches the drop shape and set it down on the sample surface. The drop on the end of the needle should not splash on the sample, this would affect the measured contact angle. For a relatively large substrate, contact angles should be measured at multiple points to give an average value that is representative of the entire surface.
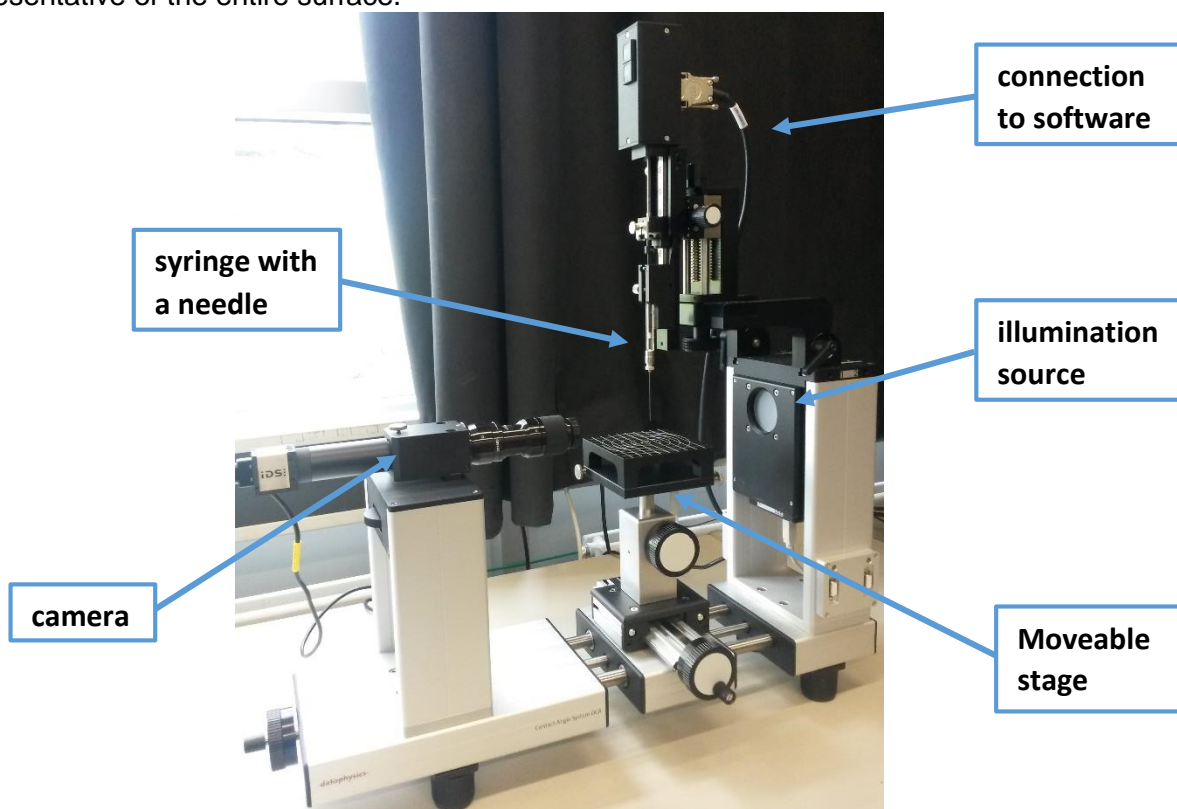
Protocol

General

- **All** the participants should have studied the introduction, before to start the experimental work. Be prepared or you will be not allowed to participate to the experimental training!

- For safety reasons, a clean and safe work with chemicals is mandatory.

- Make notes during the lab training, you will need this information to complete the final report.

- The final report (about 8 pages) should include:
  1) Introduction (SAMs and their applications)
  2) Experimental Part (A detailed description of the experimental work)
  3) Discussion (Evaluation and interpretation of the data collected, estimation of the error)
  4) Short research in the literature about the stability of mixed monolayers

- Hand out the report **not later than 4 weeks** after the completion of the experimental training.

- During the colloquium **all the participants** will be asked about the contents of their final report.

- The persons in charge of the FoPra have the responsibility to deny the certification of participation to the FoPra to all students, who have not fully fulfilled the above mentioned requirements.

Self-Assembled Monolayers:

- Prepare 3 solutions with compounds **A**, **B** and a mixture **C** of both 1:1.

- Use the 3 solutions to prepare 3 samples of self-assembled monolayers on gold.

Contact angle:

- measure at least 5 points on each sample.

- Plot the liquid drop profiles and extrapolate the contact angles.

- Calculate the mean values and the errors.