

# IONIZATION AND MOLECULAR RECOGNITION PHENOMENA IN SELF-ASSEMBLED SURFACES OF BOWL-SHAPED MACROCYCLIC MOLECULES

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## Introduction, Goals, & Motivation

Macrocylic molecules containing molecular sized cavities can act as hosts for recognition of a variety of guest species and are of interest for targeted separations, detection of molecules, and fundamental understanding of molecular recognition.

In this project, self-assembled monolayers (SAMs) of a tetrathiol and tetrasulfide derivatives of the calix[4]resorcinarene cavitand on gold substrates are studied to design chemically selective surfaces. The specific focus here is on ionization of these SAMs for binding charged species.

Two surface analytical techniques, surface plasmon resonance (SPR) technique and contact angle measurements, are used to characterize these SAMs and study ionization with increasing pH. SPR characterization allows measurement of the optical thickness of ultrathin films and to monitor the dielectric changes at a solid-liquid interface in a non-invasive and real-time manner. Contact angle measurement allows a simple characterization of the interfacial energy.

## Self-Assembled Monolayers

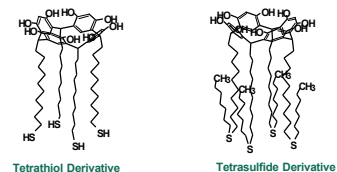
### "Thiol"



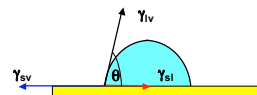
Self-assembled monolayers form spontaneously when a solid substrate is immersed in an organic solution. Commonly, SAMs are formed by chemical binding of S-H (thiol) end of a gold (Au) substrate.

SAMs find many uses such as controlling adhesion and wettability of surfaces, molecular electronic devices, and nanotechnology. The use of SAMs to provide a membrane like microenvironment, useful for immobilizing biological molecules, find many application in biocompatible surfaces and biosensors.

In this project, tetrathiol and tetrasulfide derivatives of calix[4]resorcinarene on thin films of gold (Au) were used for this project. These are large, bowl-shaped molecules with alcohol (-OH) groups. For reference purposes, mercaptopropionic acid was also used to compare the results of ionization of a simple molecule against a more complex one.



## Contact Angle Measurements



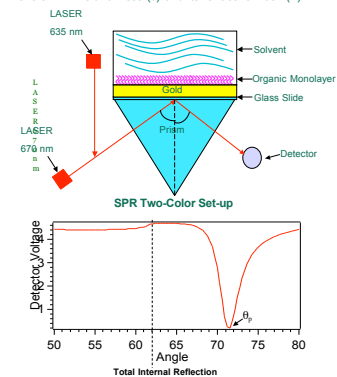
- Young's Equation:  $\gamma_{sv} \cos(\theta) + \gamma_{sl} = \gamma_{lv}$
- Contact angle measurement using a probe liquid is a simple method for characterizing the interfacial properties of a surface.
- The equilibrium contact angle quantifies the interfacial energy and depends on the surface tensions of the solid-liquid interface ( $\gamma_{sl}$ ), the solid-vapor interface ( $\gamma_{sv}$ ), and the liquid-vapor interface ( $\gamma_{lv}$ ).
- Generally for real surfaces, two bounds for  $\theta$  are measured using an advancing drop and a receding drop.

## Surface Plasmon Resonance

Surface plasmon resonance is phenomenon that occurs when a monochromatic, p-polarized light undergoes total internal reflection and the evanescent optical field interacts with a metallic substrate.

SPR technique allows real-time measurement in a non-invasive manner and is highly surface sensitive. SPR angles depend on properties of the metal film,  $n$  of incident light, refractive index,  $n$ , of the dielectric layers.

By monitoring the shift in the angle corresponding to the resonance in reflectivity of incident light, the SPR technique permits measurement of a thin film's thickness ( $d$ ) and its refractive index ( $n$ )



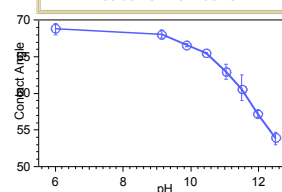
### Optical Modeling

$$\theta_p = f(n_{\text{prism}}, n_{\text{solvent}}, n_{\text{Au}}, k_{\text{Au}}, d_{\text{Au}}, n_{\text{monolayer}}, d_{\text{monolayer}})$$

By measuring the surfaces with multiple wavelengths and solvents, unknowns in the above relation can be found by fitting the experimental data to an optical model based on Fresnel equations.

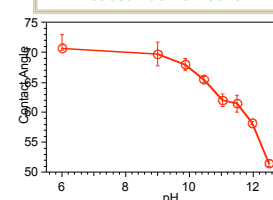
## Results

### Tetrathiol Derivative



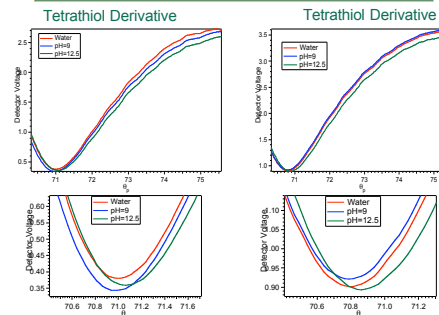
- As the surface becomes de-protonated, it becomes more hydrophilic and a decrease in contact angle is observed
- Ionization occurs at pH=9 and is almost complete by pH=12.5

### Tetrasulfide Derivative



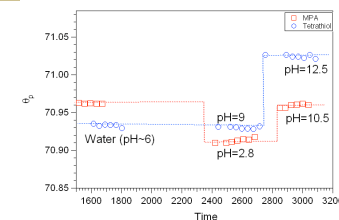
- Similar results as the tetrathiol contact angles were observed also, the methyl groups do not make a notable change

## Ionization of Calix[4]resorcinarene Derivatives



- The results show the angle change of both surfaces from water with a pH=6 to pH=9, there is no notable change
- The results show an increase in  $\theta_p$  when changing from pH=9 to pH=12.5

## Ionization of Tetrathiol and MPA



- Tetrathiol derivative of calix[4]resorcinarene
  - Change from water to low pH shows no change in  $\theta_p$
  - Change from low pH to high pH shows increase in  $\theta_p$  due to ionization
- MPA
  - Change from water to low pH shows decrease in  $\theta_p$  due to protonation
  - Change from low pH to high pH shows increase in  $\theta_p$  due to de-protonation
  - Fender and coworkers (Langmuir, 2002, v18) report opposite trend plusibly due to incomplete monolayer coverages
  - Shift in  $\theta_p$  is larger for the complex tetrathiol molecule compared to the simpler MPA

## Summary

- SPR and contact angle measurements allow probe of ionization at solid-liquid interface
- For tetrathiol and tetrasulfide derivatives of the macrocylic calix[4]resorcinarene, ionization changes are comparable
- Self-assembled interfaces of complex molecules such as the macrocydes show larger shifts in SPR angle upon ionization when compared to simple alkanethiol such as MPA

## Future Work

- Use two-color and multiple-solvent measurements in SPR to determine if ionization changes thickness and/or dielectric properties of the monolayer.
- Use ionized interface to bind organic and inorganic guests to the surface and use SPR to interpret the assembly.

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