SELF-ASSEMBLED MONOLAYERS ON GOLD FOR THE DETECTION OF MOLECULAR INTERACTIONS *VIA* SURFACE PLASMON RESONANCE

Arianna Friggeri, Frank C.J.M. van Veggel, David N. Reinhoudt

Supramolecular Chemistry and Technology, MESA Research Institute,
University of Twente, P.O. Box 217, 7500AE Enschede, The Netherlands.
e.mail: A.Friggeri@ct.utwente.nl

0. Abstract

Self-assembled monolayers, of receptor adsorbates, on gold have been used to detect the presence of small aromatic compounds, in water. Surface Plasmon Resonance (SPR) was used to monitor the *in situ* host-guest interaction processes occuring at the monolayer-water interface.

Keywords: Surface Plasmon Resonance, monolayers, resorcinarenes.

1. Introduction

Self-Assembled Monolayers (SAMs) on gold consist of one layer of molecules adsorbed, via sulfur coordination bonds, onto a gold (111) surface. The scope of this project is to investigate the possibility that SAMs on gold have, to act as detectors for molecular host-guest interactions [1]. So far, several receptor molecules with a variety of functionalities, have been adsorbed on gold substrates and their interactions with a series of aromatic guests has been investigated. These receptors belong to a class of molecules that can be synthesized starting from *resorcinarenes* and will be refered to as cavitands (Fig. 1). The monolayers formed by these adsorbates have been characterized by contact angle, Polarized Infrared External Reflectance Spectroscopy (PIERS), electrochemical measurements and X-ray Photoelectron Spectroscopy (XPS). These techniques show that the adsorbates form well packed monolayers, attached to the gold via the four sulfide moieties and with the head group extending towards the interface between monolayer and the air/water medium.
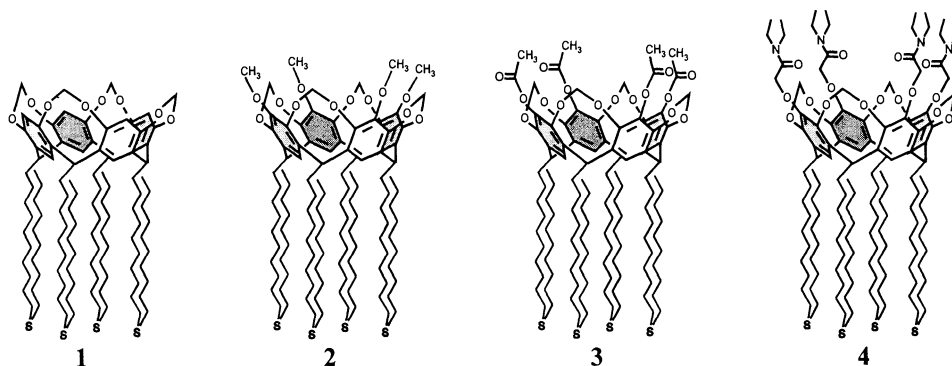

Fig. 1 Cavitand receptor adsorbates

2. Characterization: Results and Discussion

Contact angle results (Table 1) show that all monolayers are relatively hydrophobic. An evaluation of the packing of the molecules in the monolayers can be made by considering the hysterysis values: $\Delta\theta$. Taking into account that decanethiol layers have been reported to have $\Delta\theta$ values of around 17, then, monolayers of **1** can be defined as relatively well ordered, whilst monolayers of compounds **2**, **3** and **4**, are somewhat less well ordered. These results are to be expected considering that the substituents on the upper rim of these cavitand adsorbates are probably arranged in a disordered fashion.

Table 1: Advancing (θ_a) and receding (θ_r) contact angle data for water drops on monolayers of **1**, **2**, **3** and **4**.

	θ_a	θ_r	$\Delta\theta$
Decanethiol	108 ± 1	91 ± 1	17
1	107 ± 1	91 ± 1	16
2	98 ± 2	52 ± 2	46
3	109 ± 2	85 ± 1	24
4	107 ± 3	88 ± 3	19

Capacitance measurements performed on layers **2** and **4** are in the same range as the values reported for **1** and decanethiol layers, whilst **3** gives a slightly higher value. The heterogeneous electron transfer cyclic voltammograms show that all three layers (**2**, **3**, **4**) are able to block the Fe^{2+}/Fe^{3+} redox couple just as effectively as a layer of **1**. Therefore, these types of substituents on the upper rim of cavitands, do not seem to interfere with the overall permeability and packing of the molecules in the monolayers. This is also evident from the resistance values obtained by impedance measurements, shown in Table 2 along with the capacitance values.

Table 2: Capacitance and resistance values for monolayers of compounds **1**, **2**, **3**, **4** and decanethiol

Adsorbates	C ($\mu F \cdot cm^{-2}$)	R (ohm)
2	1.27	2.14e+6
4	1.43	1.08e+6
3	2.64	4.02e+5
1	1.14	3.75e+5
decanethiol	1.24	8.00e+5

Results obtained from Grazing Angle FT-IR are presented in Table 3. It is interesting to note that monolayers of **2** are liquid like, this can be seen from the shifted values of the CH_2 and CH_3 stretching vibrations, whilst monolayers of **3** and **4** are more crystalline.

Table 3: Grazing angle FT-IR data for monolayers of **2**, **3** and **4**.

	ν_{as} CH$_3$	ν_{as}CH$_2$	ν_sCH$_3$	ν_sCH$_2$	ν C-H$_{arom}$	δ CH$_2$
2	2959	2924	2874	2855	3005	1474, 1456, 1423
3	2964	2921	2879	2850	-	-
4	2964	2921	2877	2851	-	-

3. SPR: Results and Discussion

All measurements were carried out in pure water and were repeated at least 3 times. It is important to note that the signals show <u>no</u> memory effect. The SPR [2] set-up used to make the measurements consents simultaneous detection of reflectivity changes on two different monolayers, in contact with the same solution of guest. One of the two layers is a reference layer (monolayer of $C_{18}SH$) used to take into account the change in reflectivity due to changes of refractive index in the bulk solution.

Explaination of some of the results is relatively easy, of others, very difficult, but some interesting conclusions can be made. Reading Table 4 in a vertical fashion (i.e. responses of one adsorbate to several guests) it can be observed that none of the guests show particular affinity for adsorbate **2** and **4.** The most probable explanation for this is the fact that both these layers resemble quite closely the reference layer: they both expose to the aqueous solution, alkyl groups. Furthermore, the shallow aromatic cavity of the adsorbate molecules is not available to the guests, therefore, no particular interaction is present due to the typical cavitand structure. Considering the results obtained for adsorbate **1**, the first observation that can be made is that all guests except *p*-methoxy phenol, show some interaction with the monolayer. Some guests seem to interact more favourably than others, but the reason for this cannot be pinpointed to singular features of the guest. For example, comparing *p*-toluic acid and benzoic acid, it cannot be said that a CH_3 group is necessary for interaction with the monolayer to occur. Of the guests studied, it can be said that the presence of a nitro group seems to favor interactions with receptor surface **1**, although it is not clear how the guest is placed upon the monolayer. Some interesting observations can be made if one considers the <u>solubility</u> and the <u>acidity</u> of the guests. Solubility wise, none of the results show that the more hydrophobic guests interact more strongly with the host monolayers. Looking at the pKa's of the guests, it is also true that there is no particular correlation between the acidity and the responses obtained with layer **1**.

Table 4: SPR results expressed as the difference between the SPR angle change of the receptor layer and reference layer.

*Sol. is the relative solubility in water. 1: insoluble, 2: slightly soluble, 3: soluble.

guests	pKa	Sol.*	SAMs			
			1	2	3	4
p-CH$_3$ benzoic acid	4.36	1	0.06	-	0.05	-
benzoic acid	4.20	2	0.12	-	-	-
p-OH benzoic acid	4.48	2	0.04	-	-	-
p-NO$_2$ benzoic acid	3.41	1	0.08	0.10	-	0.07
p-cresol	10.17	2	0.04	-	-	-
p-NO$_2$ phenol	7.15	3	0.10	0.13	-	0.10
p-OCH$_3$ phenol	>10	3	-	-	-	-

It seems as though functionalization of the upper rim of these cavitand adsorbates leads to selectivity in the recognition of guests in water. Although this might not be a particularly surprising conclusion, it becomes quite important in view of the size of the guests involved and of the experimental medium: water.

4. Conclusions

This study provides *experimental evidence* that, in water, hydrophobic interactions, although present and perhaps the initial driving force of molecular association process, are not the main cause of recognition between host and guest. Unfortunately, because very few studies have been made regarding cavitand host-guest chemistry in water, and none have been carried out on the monolayer/water interface, it is very difficult to extrapolate quantitative data, as well as qualitative information on how the guest is placed with respect to the functionalized layer. From some of the values obtained from the measurements, it seems as though more than one layer of guests is present 'on top' of the adsorbate layer.

5. References

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