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Self–assembled monolayers of organosulphur molecules bearing calix[4]arene moieties

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Abstract

We investigate the self-assembly of modified calix[4]arene on gold surfaces. Calix[4]arene was modified through a reaction sequence which led to assembling of the crown-5 moiety and to the insertion of two thioether groups into the starting molecule. The so-obtained calix[4]arene-crown-5 bis(7-thiatridecyloxy) (hereafter called calix[4]arene) was in the stable 1,3-alternate conformation. The calix[4]arene/gold interface was investigated by means of spectroscopic ellipsometry (SE), scanning tunneling microscopy (STM) and cyclic voltammetry (CV). SE data indicate a layer thickness compatible with the formation of a monomolecular layer. This result is confirmed by STM imaging which shows the formation of a high density of small pits, one gold layer deep, a typical feature of self-assembled organosulphur monolayers on gold. CV measurements performed in presence of the $[Ru(NH_3)_6^{2+/3+}]$ redox couple indicate a passivation of the metal electrode, resulting in a reduction of the redox current, after the layer deposition.

CV has also been used to investigate the selectivity properties of calix[4]arene-covered gold electrodes by measuring the redox current decrease in the presence of different salt solutions. It is found that calix[4]arene-covered electrodes are able to complex K^+ and Ba^{2+}, while no complexation is observed in the case of Li^+, Na^+, Cs^+, Mg^{2+} and Ca^{2+}.

Keywords: Modified calix[4]arene; Self-assembled monolayers; Spectroellipsometry; Scanning tunneling microscopy; Cyclic voltammetry

1. Introduction

In the 1980s, new technology requirements for chemically active materials led to the development of new techniques to bind organic molecules to the surface of inorganic substrates. The possibility to assemble organic layers exposing different functionalities allows one to tailor the physicochemical properties of the surface and prompts their use for wettability, lubrication and corrosion control as well as for the development of biosensors able to perform molecular/ionic recognition [1]. Organic molecules that covalently bind to either conductor or insulator surfaces can form thin ordered films [self-assembled monolayers (SAMs)]. Among SAMs, large attention has been recently paid to layers formed by organosulphur molecules which bind to transition metals, like gold or silver [2].

Here we focus on the preparation and characterization of functionalized gold surfaces obtained by the self-assembly of calix[4]arene-crown-5-bis-sulfide. This molecule was synthesized as a first step to obtain selective recognition of ions. Calixarenes are ditopic receptor molecules, which have been widely studied in recent years for the selective recognition of ions and neutral molecules [3]. Synthesis was carried out starting from calix[4]arene through a reaction sequence which led to insertion into the molecule of proper chemical functions, i.e. two thioether groups, which serve as anchoring groups to enable the self-assembly of the molecule to the metal substrate, and a crown-5 moiety (Fig. 1). The stiffening of calix[4]arene by introducing a polyether chain bridging two opposite phenolic groups, resulting in a stable 1,3-alternate

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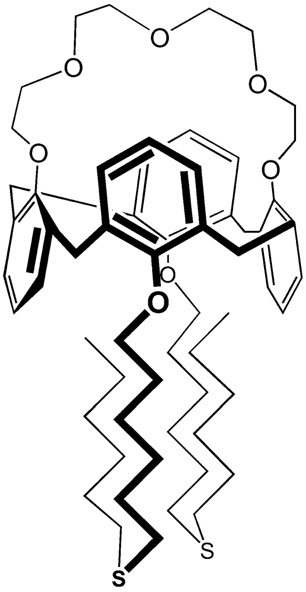

Fig. 1. Structure of calix[4]arene used in this study.

conformation, improves its selectivity and confers significant affinity towards alkaline cations [4].

Since the functional properties (e.g. the selectivity) of a SAM-covered surface critically depend on the SAM molecular order, the structural characterization of the calix[4]arene/gold interface was the first step of our study. In this paper, we report the results obtained by coupling a local probe technique, scanning tunneling microscopy (STM), with a global technique, spectroscopic ellipsometry (SE), in the visible range. SE is a well-established technique to get information on the thickness and the refractive index of thin films [5], with sounding applications to organic and biological films [6–8]. The SE results on calix[4]arene SAMs will be compared with results on *n*-alkanethiols SAMs, model systems whose structure [9,10] and optical behaviour [6] are relatively well known.

Cyclic voltammetry (CV) has been used to obtain information on both the passivation properties of the calix[4]arene SAM and on its selectivity. SAMs bearing ionophore groups can be regarded as ion selective electrodes. To evaluate the selectivity, we monitored the evolution of the electrical response of the SAM-covered electrodes as a function of the ionic composition of the contacting liquid phase. The different voltammetric curves were attributed to the different affinity of the ions to the crown cavity.

2. Experimental

2.1. Chemicals and synthesis

Salts, Bu_4NCl (tetra-*n*-butylammonium chloride, Fluka), $[Ru(NH_3)_6]Cl_3$ (hexammine ruthenium (III) chloride, Aldrich), LiCl (Sigma), NaCl (Sigma), KCl (Sigma), CsCl (Sigma), $MgCl_2$ (Sigma), $CaCl_2$ (Sigma) and $BaCl_2$ (Sigma), were of analytical grade and used as received.

The aqueous solutions were prepared using Milli-Q-water. Absolute ethanol (puriss. p.a. Fluka) was used for preparing solutions for self-assembly.

All reactions were carried out in a nitrogen atmosphere. Dichloromethane was distilled and stored over 3 Å molecular sieves. 5-Bromo-1-hexene and 1-hexanethiol were distilled under reduced pressure. Other solvents and reagents were of analytical grade quality and were used without further purification. When needed, trace amounts of water were removed from solvents through storage over molecular sieves. NMR spectra were recorded with a Varian Gemini 200 spectrometer. Chemical shifts (δ) are expressed in ppm from TMS. Melting points are uncorrected. Analytical TLC were carried out on precoated silica gel plates (Merck, 60 F_{254}); silica gel 60 (Merck, particle size 230–240 mesh) was employed for the preparative column chromatography. Structure of product **3** as well as those of the synthetic intermediates **1** and **2** were assessed by ^1H and ^{13}C NMR spectrometry.

According to general procedures [11], calix[4]arene was prepared in three sequential steps:

- 25,27-Bis(5-hexenyloxy)-26,28-dihydroxycalix[4]arene (**1**). A suspension of calix[4]arene (2 g, 4.7 mmol), 6-bromo-1-hexene (2.28 g, 14 mmol) and finely ground anhydrous K_2CO_3 (1.3 g, 9.4 mmol) in 40 ml in acetone was refluxed under nitrogen for 8 days, until TLC revealed the disappearance of the calix[4]arene reagent. After inorganic salts were filtered off, removal of acetone solvent under reduced pressure afforded an orange oil which solidified on keeping overnight under vacuum. Repeated recrystallization from dichloromethane-methyl alcohol yielded white needles which melted at 124 °C (1.54 g, yield: 56%).
- 25,27-Bis(5-hexenyloxy)calix[4]arenecrown-5 (1,3-alternate) (**2**). A suspension of anhydrous cesium carbonate (3.32 g, 10.2 mmol), calix[4]arene derivative **1** (1.50 g, 2.55 mmol) and tetraethyleneglycol ditosylate (1.41 g, 2.8 mmol) in anhydrous acetonitrile (510 ml) was kept at reflux under stirring in a nitrogen atmosphere for 24 h. After this period of time, inorganic salts were filtered off, and the clear solution was rotoevaporated. Then the residue was dissolved in dichloromethane (100 ml), and the organic phase was washed with 4% HCl and twice with brine. Recrystallization from methanol of the residue obtained after dichloromethane solvent was rotoevaporated gave crystals melting at 105 °C (0.85 g, yield: 45%).
- 25,27-Bis(7-thiatridecyloxy)calix[4]arenecrown-5 (1,3-alternate) (**3**). A solution of compound **2** (0.85 g, 1.14 mmol) and 1-hexanethiol (0.35 g, 2.97 mmol) in anhydrous tetrahydrofuran (2 ml) was put into a Pyrex tube, and, after addition of a few milligrams of azobisisobutirronitrile (AIBN), it was photoirradiated in

a Rayonet Photochemical Reactor equipped with 16 RPR 3500-Å lamps. ^{1}H NMR analysis carried out after 8 h revealed that the reaction was over (as shown by the complete disappearance of the signals of the vinylic protons centered at δ 5.0 and 5.8 ppm). After concentration in vacuo of the reaction mixture, the residue was subjected to column chromatography (eluent: dichloromethane/ethyl acetate 4:1) affording compound **3** as a light yellow viscous liquid (0.78 g, yield: 70%).

2.2. Sample preparation

SAMs for SE measurements were deposited onto commercial gold films evaporated onto chromium-primed glass substrates (Arrandee™, Germany). SAMs for STM and CV measurements were deposited onto gold films epitaxially grown on mica as reported in details elsewhere [12]. Arrandee samples exhibit more homogeneous optical properties and are therefore used for SE measurements, while gold films on mica are characterized by larger (111) terraces and are therefore used for STM and CV measurements. In both cases, before use, the gold films were flame-annealed in a butane flame to red glowing and quenched in ethanol. Flame annealing helps to clean the surface from atmospheric adsorbates and improves the structural order of films producing (111)-textured terraces [12]. Immediately after quenching, the gold substrates were transferred into 0.1 mM calix[4]arene ethanolic solution and therein kept overnight at room temperature. After extraction, they were thoroughly rinsed with ethanol and either dried under a nitrogen stream, in the case of samples for SE and STM measurements, or rinsed in water and immediately transferred to the electrochemical cell, in the case of samples for CV measurements.

2.3. Sample characterization techniques

SE measurements were performed on a rotating compensator spectroscopic ellipsometer (M-2000, J.A. Woollam). The instrument, fully tested in a recent experiment on LB cadmium stearate thin films [13], allows simultaneous measurements at 225 different wavelengths in the range 245–725 nm. Spectra have been collected at several angles of incidence, in the 55–70° range. Samples were characterized by SE after flame annealing, immediately prior to self-assembly and after the layer deposition.

STM measurements were performed in air with a Nanoscope II (Digital Instruments) equipped with a STM A head. Tips were mechanically cut from 0.25 mm in diameter Pt/Ir wire. Typical tunneling parameters were a few tenths of nanoampere as tunneling current and a few hundreds of millivolts as bias.

CV measurements were carried out by using a home-built three-electrode Teflon cell containing a gold working electrode (clamped to the cell to give an exposed electrode area of 0.2 cm^2), a Pt counterelectrode and a Ag(s)/AgCl(s)/Cl$^-$(aq) (3 M) reference electrode. The potential was controlled with a Potentiostat (2059 AMEL, Milano, Italy) and modulated with a Function Generator (568 AMEL); the system was equipped with a Noise Reducer (AMEL). The measurements were carried out in a Faraday cage. CV was carried out in 0.1 M Bu_4NCl aqueous solution containing 1 mM $[Ru(NH_3)_6]Cl_3$. To investigate the response of the system to the different ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}), measurements were performed by adding metal chlorides (MCl_x) to the electrolyte to a final concentration of 1 mM. Working electrode potential was cycled between 0 and − 0.3 V vs. Ag/AgCl/Cl$^-$(aq) (3 M) electrode at a scan rate of 25 mV/s. Electrolytes were degassed with pure N_2. A nitrogen stream was maintained over the solution during the measurements.

All glassware and cell components were cleaned in NOCHROMIX solution (GODAX Laboratories) and thoroughly rinsed with Milli-Q water.

3. Results and discussion

In Fig. 2, we show SE data obtained on calix[4]arene SAMs. Results obtained on bare substrates and on dodec-

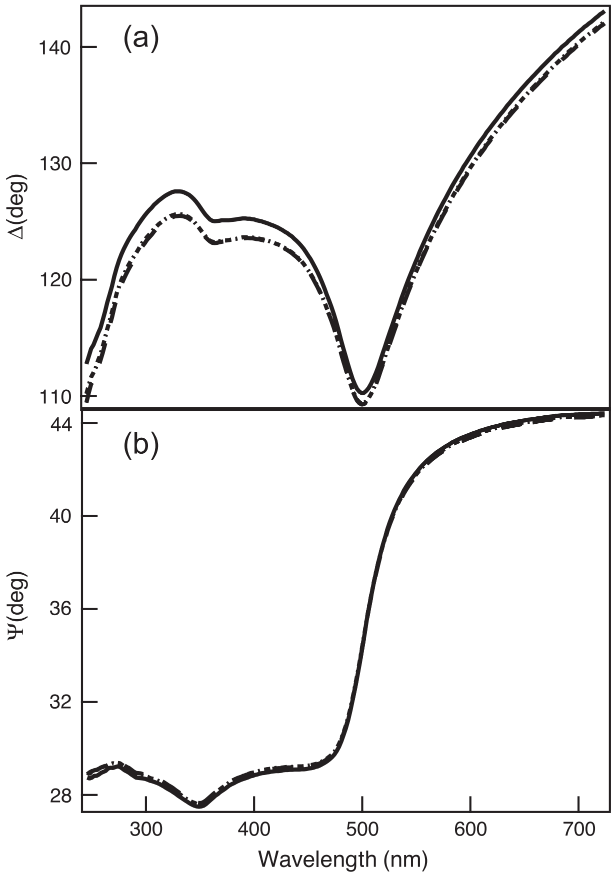

Fig. 2. Ellipsometric spectra of bare gold (solid line), calix[4]arene-covered gold (dash line) and C_{12}-covered gold (dot line) at an incidence angle of 60°. Note that calix[4]arene and C_{12} curves are almost superimposed.

anethiol SAMs (C_{12}) are also reported for comparison. The SE results are conventionally presented reporting the value of the Δ and Ψ ellipsometric angles as a function of the wavelength [5]. Δ and Ψ are defined through the relation $\rho = R_p/R_s = \tan\Psi \exp(i\Delta)$, where R_p and R_s are the complex reflection coefficients for s- and p-polarized light [5], respectively. Δ is the parameter which carries most of the information on the overlayer thickness, while Ψ is mainly related to the near-surface gold electronic structure [6] and is affected by the organic overlayer to a lesser extent (Fig. 2b). Fig. 2a indicates an evident decrease of Δ after the calix[4]arene layer deposition. C_{12}, which is known to form a compact monolayer on gold [14], is characterized by a Δ curve very similar to the calix[4]arene one. Simulations of spectra are necessary for a quantitative analysis. These simulations are based on a stack of laminar model structures with sharp interfaces and need a reliable optical model for the calyx[4]arene layer, not yet available. However, the results of Fig. 1 indicate that the effective thickness of the calix[4]arene layer is closely comparable to the thickness of the C_{12} layer.

Fig. 3 shows an STM image of a calix[4]arene-covered Au(111) sample. Three terraces separated by monoatomic steps can be observed. The terraces are decorated with a high density of pits, a few nanometers in size, one gold monoatomic layer in depth. These depressions, absent on bare gold, are due to the reorganization of the gold topmost layer occurring during the monolayer chemisorption. They are covered by the organic layer which is uniform over the whole surface [15,16]. The formation of these pits, which is well known for alkanethiol SAMs on gold, indicates that SAM has formed.

Fig. 4 compares typical cyclic voltammograms acquired in presence of $[Ru(NH_3)_6]Cl_3$ on bare gold electrodes to those obtained on calix[4]arene-covered gold electrode before and after the addition of 1 mM KCl. The redox peaks observed on bare gold electrodes are heavily reduced in the presence of the calix[4]arene SAM. The reduction of the heterogeneous electron transfer from gold to the ruthenium ions in solution is due to the passivation of the gold surface by the calix[4]arene layer and further confirms the SAM formation. The large reduction of the redox current indicates the deposition of a quite compact layer as inferred also by the SE results and further confirms, as already known for alkanethiols SAM, that pits observed by STM are not holes in the monolayer, but are covered by the organic layer.

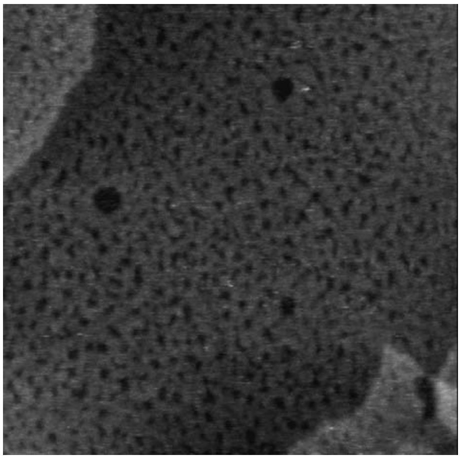

Fig. 3. STM image of a calix[4]arene-covered gold surface. The small pits indicate the occurrence of a layer deposition. Image size (160 × 160) nm^2. Tunneling current 0.15 nA, bias 200 mV.

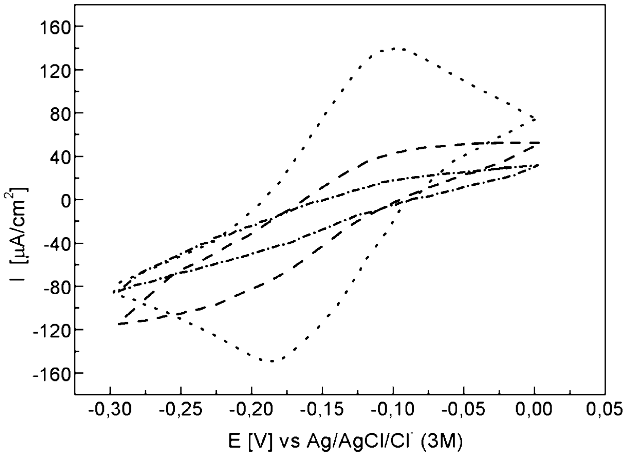

Fig. 4. Cyclic voltammograms in aqueous solutions obtained on: bare gold in 0.1 M Bu_4NCl + 1 mM $[Ru(NH_3)_6]Cl_3$ (dot curve); calix[4]arene-covered gold in the same electrolyte (dash curve) and after the addition of 1 mM KCl (dot dash curve).

To investigate the selectivity properties of the calix[4]arene-covered electrodes, we performed CVs in electrolytes containing both $[Ru(NH_3)_6]Cl_3$ and different mono- and divalent ions (K^+, Li^+, Na^+, Cs^+, Mg^{2+}, Ba^{2+}, Ca^{2+}). The dot-dash curve in Fig. 4 is an example of a CV obtained in the presence of 1 mM KCl. Very similar results are obtained when KCl is replaced by $BaCl_2$. When other mono- and divalent ions (Li^+, Na^+, Cs^+, Mg^{2+}, Ca^{2+}) are used instead of K^+ or Ba^{2+}, no noticeable changes in the CVs can be observed and curves look very similar to those obtained in the presence of $Ru(NH_3)_6^{2+/3+}$ alone. These results give information about the selectivity properties of the calix[4]arene SAM. When the functionalized electrodes recognize and bind the cations, a positive surface charge density forms at the electrodes. As a consequence, the redox couple ions are repulsed by the host–guest system with a charge of equal sign and an attenuation of the redox current is observed. According to this interpretation, the influence of a charged monolayer on the electron transfer to a charged redox couple is ascribed to electrostatic interactions and to the shift of the potential drop across the diffuse layer [17]. Following this interpretation, cyclic voltammetry can be regarded as a tool which enables detection of metal complexation by the calix[4]arene layer. From the analysis of our results, we can conclude that calix[4]arene is selective to K^+ and to Ba^{2+} which have a very close ionic radius.

To summarize, our results indicate that calix[4]arene can be immobilized on gold surfaces and forms compact self-assembled monolayers. SAM-covered electrodes preserve the selectivity properties of the calix[4]arene crown-5 moiety and exhibit a higher affinity towards K^+ and Ba^{2+} compared to other mono- and divalent cations.

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