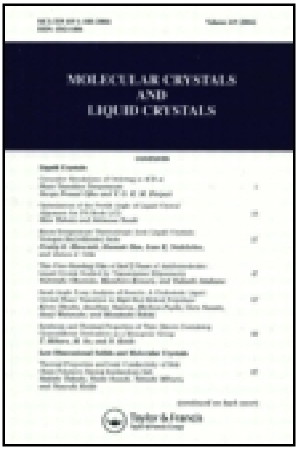

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Electrochemical Recognition of Ions with Self-assembled Monlayers of Calixarenes

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Electrochemical Recognition of Ions with Self-assembled Monlayers of Calixarenes

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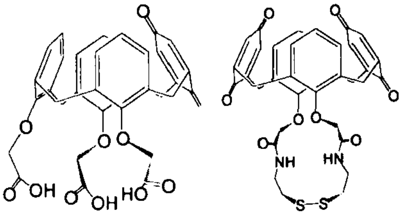
Quinone-functionalized calix[4]arenes with carboxylic acid groups or disulfide group were prepared and their spontaneous adsorption respectively on silver and gold surface was studied. Since the cavity-like structure of calixarenes was immobilized, they exhibited selective affinity towards specific metal ions in aqueous media. Voltammetric as well as EQCM and spectroscopic studies showed the well-ordered deposition of organic receptors and entrapment of metal ions. And it also was found that the repeated capture and removal of metal ions reversibly with chelating agents such as ethylenediaminetetraacetic acid (EDTA) was possible. This is the first example, in our knowledge, of voltammetric detection of metal ions in aqueous media using a chemically modified electrode with redox-active macrocyclic receptors.

Keywords Calix[4]arene disulfide; Electrochemical recognition; Self-assembled monolayers; Voltammetry.

INTRODUCION

Calix[4]arenes with ester groups have been known as selective ionophores especially for Na^+ ion [1]. Properly synthesized calixarenes exhibit excellent ion-binding property due to its rigid three-dimensional cavities for the selective inclusion of inorganic ions or organic cations in aprotic solvents [2,3]. In addition to its physical pore size, distinct electrochemical activity is observed by simple derivatization with quinone. However, not enough solubility of these compounds in water prevents them from wide application. Calix[4]arene with carboxylic acid groups in the lower rim has been prepared as water-soluble calixarenes [4,5]. In addition, quinone moiety was replaced with one of phenol ring members in order for more sensitive voltammetric recognition of alkali and alkaline earth metal ions. These quinone-functionalized calix[4]arenes showed very interesting characteristics such as well-defined redox behavior and selective complexation with Ca^{2+} [6]. The carboxylic acid groups (Fig. 1, **L1**) adsorb spontaneously on silver surface and the presence of Ca^{2+} ions in aqueous media causes a new peak at a positively shifted potential. Instead of carboxylic acid group, disulfide in the lower rim (Fig. 1, **L2**) can also act as rigid legs which are able to anchor on gold surface by two thiolates bondings. This paper reports the physical and electrochemical property of self-assembled monolayer of quinone-functionalized calixarenes and the potential application for metal ion analysis.



L1 **L2**

FIGURE 1. Structure of calixarenes used in the study.
L1: Calix[4]arene-triacid-monoquinone
L2: Calix[4]arene-diquinone-disulfide

EXPERIMENTAL

1. Electrochemical Measurements

Electrochemical experiments were performed with a Windows-driven electrochemical analyzer (BAS100B/W, Bioanalytical Systems, West Lafayette, IN). The surface of a glassy carbon (area = 0.071 cm^2) was polished with 0.05 μm alumina (Buehler, Lake Bluff, MN) and then rinsed with deionized water. The silver electrode was used immediately after the Ag film was coated on glass substrate and its electrode area was 1.04 cm^2. A Pt wire counter electrode and a

Ag|AgCl (in KCl 3 M) reference electrode were used for voltammetric experiments. Dissolved oxygen was removed by bubbling purified nitrogen or argon gas. The voltammetry with modified working electrodes was carried out in 0.1 M 4-(2-hydroxyethyl)-piperazine-1-ethanesulfonic acid (HEPES) buffer of pH=7.4. Synthesis and identification of the calix[4]arenes were described in our previous paper [6]. All reagents were purchased from Aldrich and were used without further purification.

2. Formation of Self-assembled Monolayers

The self-assembled monolayer was obtained by immersing the silver- or gold-deposited glass substrate into a 10^{-4} M solution of L1 or L2 for 12 h or 20 min., respectively. The mass change during the adsorption of L2 was monitored by EQCM.

3. Preparation of Silver and Gold Substrates

The substrate was prepared by evaporating silver and gold (2000 Å) at 10^{-5} - 10^{-6} torr in a thermal resistive evaporator on batches of previously sonicated 2.5 x 3.7 cm slide glasses. For rigid adhesion between glass and silver/gold, a titanium layer of 50 Å thick was deposited. Slide glasses were cleaned carefully before metal deposition.

4. Infra-red Measurements

For infrared reflectance-absorption (IRA) of adsorbed layer, a specular reflection attachment (Harrick VRA, Harrick Scientific Co., NY) was used in conjunction with a Harrick wire grid polarizer. The incident angle for the p-polarized light was 80°. Each spectrum was obtained by averaging 2048 interferograms at 4 cm^{-1} resolution. All IRA spectra are reported as - $\log(R/R_0)$, where R_0 is the reflectivity of the calix[4]arene-modified substrate for the s-polarized light.

RESULTS AND DISCUSSION

Self-Assembled Monolayers on Silver

It has been reported that simple hydrocarbons with carboxylic acid groups adsorb onto silver surface spontaneously through carboxylate anchoring and form self-assembled monolayers [7]. With the aid of carboxylic acid groups in the lower rim, the adsorption of L1 on silver electrode is expected to occur. The experiment indeed shows that L1 is successfully adsorbed onto silver surface by just immersing into the 0.1 mM ethanolic solution of **L1**. The amount of adsorbed compound was checked both by spectroscopic and electrochemical methods. The infrared reflectance absorption spectrum shows that the symmetric stretching band of carboxylate appears at 1400-1420 cm^{-1}, which is in good agreement with the literature [7]. The self-assembled monolayers are formed in the presence and absence of Ca^{2+} in the media. **L1**-modified silver electrode shows similar electrochemical behavior to that of the homogeneous solution as expected. Because of the proton transfer followed by electron transfer, the corresponding oxidation peak is not observed in the potential range as shown in Fig. 2(a) [8].

When the monolayer of **L1** is formed in the presence of Ca^{2+}, new symmetric redox waves appear at a more positive potential compared with that of the reduction wave of **L1** as shown in Fig. 2(b). When the SAM is prepared in Ca^{2+}-free solution, the same symmetric voltammo-gram is obtained by adding Ca^{2+} to the HEPES buffer solution. Accordingly, the same electro-chemical behavior is obtained no matter the complex-ation occurred in the solution or on the surface.

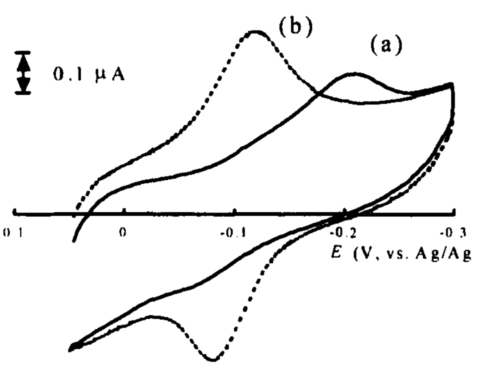


FIGURE 2. Cyclic voltammograms of **L1** film on silver electrode in the absence (a) and presence (b) of Ca^{2+} in HEPES buffer of pH 7.4. The scan rate is 10 mV/s.

One major drawback of the film through carboxylate anchoring is the solubility of SAM towards water. The amount of **L1** decreases gradually as the **L1**-modified silver electrodes are in the aqueous solution for prolonged period, and eventually little is left. This stability problem prevents the electrode from extensive application.

Self-Assembled Monolayers on Gold

On the other hand, **L2** is spontaneously deposited onto gold electrode and almost the same voltammetric behavior is observed when calixarene-diquinone-dicarboxylic acid is on silver electrode. EQCM study shows the maximum anchoring of **L2** on gold surface occurs within 4 minutes and the adsorbed amount corresponds to that of monolayer on the basis of the cross-sectional area of **L2**. The monolayer coverage is well agreed with the electrochemical calculation based on the charges passed for the reduction. Moreover, the IRA spectrum indicates that the adsorbed **L2** forms a well-ordered structure on gold surface. This is evidenced not only by the presence of the characteristic absorption band due to C=O stretching mode in quinone moieties, but also by the disappearance of that of C=O in amide parallel to the gold surface [9].

The electrochemical properties of **L2** in the presence of various metal ions are shown in Fig. 3. The reduction of quinone in the presence of metal ion shifts to the positive direction as expected, but the amount of potential shift is not as big as in the solution. Only a small shoulder for Ca^{2+}, to a broad combination of two peaks for Sr^{2+} and the most shift for Ba^{2+}. At the moment, it is not clear why Ba^{2+} exhibits the strongest complexation with adsorbed **L2**. At any rate, it is possible to utilize this behavior for the determination of Ba^{2+} with the solid state self-assembled monolayer of **L2**. It is the first example of such application utilizing self-assembled monolayers for analysis.

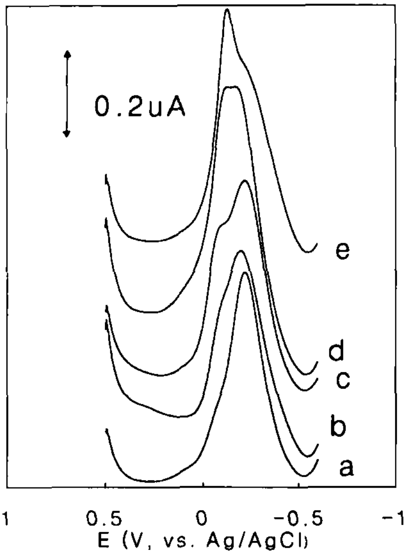


FIGURE 3. Square-wave voltammograms of **L2**-modified electrode in the presence of various metal ions. No metal (a), Ca^{2+} (b), La^{3+} (c), Sr^{2+} (d) and Ba^{2+} (e). Solution; 1 mM of metal ion in 0.1 M HEPES buffer (pH = 7.4), Pulse amplitude; 25 mV, Step potential; 4 mV, Frequency; 15 Hz.

In order for the repeated measurements, once bound metal has to be removed before the next measurement. This can be done either by electrochemically or chemically. The electrochemical treatment is simply applying a positive potential to make the **L2** in fully oxidized state. This removes a good portion of **L2**, but not completely perhaps due to the interaction between **L2** and metal ion through physical entrapping. Chemical treatment with EDTA, however, successfully removes all metal ions from **L2**. Then the renewed surface can be used again without any deterioration.

The present study suggests a few interesting applications, for example, the self-assembled mono-layer surface as a hetero-geneous sensing device for electrochemically inactive metal ions, electrocatalytic surfaces with controllable redox potential and ionswitch-ing by programmed electric signals.

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