Electrochemical Stability of Self-Assembled Monolayers on Gold

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Most applications of functionalized self-assembled monolayers (SAMs) are based on changes in electrochemical properties. Such applications require electrochemical stability. This study reveals that there is only a limited potential window from −0.8 to +0.4 V_{MSE} where self-assembled monolayers of sulfur-containing adsorbates (thiols and alkyl sulfides) on gold are electrochemically stable. A sensitive parameter describes the quality/stability of the monolayers (viz. the charge-transfer resistance). The substitution pattern of the adsorbates influences the window. Highly ordered monolayers, like that of tetrasulfide-based cavitand (**10**), are more resistant to extreme potentials. The stability window from −0.9 to +0.5 V_{MSE} for this sulfide-based monolayer is comparable to that for a decanethiol monolayer.

Introduction

The self-assembly process of sulfur-containing adsorbates forming monolayers on a gold substrate[1] offers the unique possibility to position and align synthetic receptor molecules close to a transducer and this has led to a number of applications of self-assembled monolayers. Previously, we have reported that self-assembled monolayers of tetrasulfide resorcin[4]arene **10** interact with neutral molecules in the gas phase, like perchloroethylene.[2] Transduction of the interaction was accomplished by surface plasmon resonance[3a] or quartz crystal microbalance measurements.[3b] Electrochemical transduction of interactions with self-assembled monolayers have also been reported. Crown ether monolayers can be used for the selective complexation of alkali cations. Complexation results in a large change in the charge-transfer resistance of the monolayer.[4] Monolayers of β-cyclodextrin complex a wide variety of guests such as ferrocene, 8-anilino-1-naphthalenesulfonic acid (ANS), and 6-(*p*-toluidino)-2-naphthalenesulfonic acid (TNS). This type of interaction was monitored by cyclic voltammetry[5a,b] or impedance spectroscopy.[5c] In other studies, voltammetric measurements showed the complexation of divalent cations such as Pb^{2+} and Cu^{2+} by monolayers of bidentate receptors.[6] Electrochemically active ferrocene monolayers were used as a mediator for an electrical signal from the solution to the electrode in the oxidation of glucose to gluconic acid by glucose oxidase.[7]

The use of self-assembled monolayers in such electrochemical applications requires electrochemical stability of monolayers. To the best of our knowledge, there are no systematic investigations on the electrochemical stability of self-assembled monolayers in contact with aqueous solutions.[8] Here, we report our results on the electrochemical stability of a variety of self-assembled monolayers. We have found that monolayers are stable in a window from −0.8 to +0.4 V_{MSE}. The substitution pattern of the adsorbates (mode of attachment: thiol vs sulfide, and number of attachment points) has a large effect on this window.

Experimental Section

Materials. Synthesis and purification of decanethiol (**1**),[9a] decyl sulfide (**3**),[9a] calixarene **9**,[9b] and resorcinarene **10**[9c] has been described elsewhere. 1-Undecene-11-bromide was prepared by literature procedures.[10] All other chemicals were used as received, unless otherwise stated. Solvents were purified according to standard laboratory methods.[11] All reactions were

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(8) The stability of self-assembled monolayers in organic solvents such as acetonitrile,[a,c] dichloromethane,[a,b] dimethyl formamide,[c] and propylene carbonate[d] has been investigated. However, all electrochemical applications described above were performed in aqueous solutions, and furthermore, organic solvents induce desorption of the monolayer.[e] (a) Everett, W. R.; Fritsch-Faules, I. *Anal. Chim. Acta* **1995**, *307*, 253−268. (b) Everett, W. R.; Welch, T. L.; Reed, L.; Fritsch-Faules, I. *Anal. Chem.* **1995**, *67*, 292−298. (c) Schneider, T. W.; Buttry, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 12391−12397. (d) Groat, K. A.; Creager, S. E. *Langmuir* **1993**, *9*, 3668−3675. (e) Schlenoff, J. B.; Li, M.; Ly, H. *J. Am. Chem. Soc.* **1995**, *117*, 12528−12536.

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carried out in an inert atmosphere. Thin-layer chromatography was performed on aluminum sheets precoated with silica gel 60 F_{254} (E. Merck). Chromatographic separations were performed on silica gel 60 (E. Merck, 0.040−0.063 mm, 230−240 mesh). Melting points are uncorrected. For FAB-mass spectrometry *m*-nitrobenzyl alcohol was used as a matrix. ^{1}H NMR and ^{13}C NMR spectra were recorded at 250 and 63 MHz, respectively, using residual solvent protons as the internal standard.

o-Bis((11-undecenyl)oxy)benzene (2a). Catechol (1.00 g, 9.09 mmol) was added to a solution of NaH (1.22 g, 28.0 mmol) in dimethylsulfoxide (DMSO) (250 mL). The reaction mixture colored blue under gas evolution. After half an hour 1-undecene-11-bromide (4.67 g, 20.0 mmol) was added to the reaction mixture, which was stirred overnight. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated. The resulting brown oil was purified by flash chromatography (eluent hexane−CH_2Cl_2 1:1) yielding **2a** as a white solid (2.67 g, 6.45 mmol, 71%). mp 28−29 °C. ^{1}H NMR (CDCl$_3$) δ: 6.88 (s, 4H, ArH), 5.90−5.74 (m, 2H, R−C**H**=CH$_2$), 5.03−4.91 (m, 4H, R−CH=C**H$_2$**), 3.98 (t, 4H, $J = 6.8$ Hz, OCH$_2$), 2.08−1.99 (m, 4H, C**H$_2$**CH=CH$_2$), 1.87−1.75 (m, 4H, OCH$_2$C**H$_2$**), 1.50−1.25 (m, 24H, CH$_2$). ^{13}C NMR (CDCl$_3$) δ: 149.2, 139.2, 121.0, 114.2, 114.1, 69.2, 33.9, 29.8−29.0, 26.2. MS (FAB-MS) *m/z*: 414.3 (M$^+$; calcd. for C$_{28}$H$_{46}$O$_2$: 414.4). Anal. Calcd. for C$_{28}$H$_{46}$O$_2$: C, 81.39, H, 11.17. Found: C, 81.10; H, 11.19.

o-Bis((11-mercaptoundecyl)oxy)benzene (2). A solution of **2a** (1.44 g, 3.48 mmol), thioacetic acid (5 mL, 70 mmol), and azobisisobutyronitrile (AIBN) (trace) in toluene (300 mL) was irradiated with a mercury lamp for 8 h. After the addition of water, the reaction mixture was extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated, yielding a yellowish oil. The intermediate thioester **2b** was purified by flash chromatography (eluent hexane−CH_2Cl_2 1:1) and immediately deprotected. A solution of **2b** (0.89 g, 1.50 mmol) and Zn (1.23 g) in a mixture of toluene and acetic acid (1:1, 600 mL) was stirred overnight. Subsequently, water was added to the reaction mixture and extraction with CH_2Cl_2 yielded a yellowish oil. The crude reaction mixture was purified by flash chromatography (eluent hexane−CH_2Cl_2 4:1), yielding **2** as a white solid (0.18 g, 0.37 mmol, 25%). mp 38−39 °C. ^{1}H NMR (CDCl$_3$) δ: 6.88 (s, 4H, ArH), 3.98 (t, 4H, $J = 7.3$ Hz, OCH$_2$), 2.56−2.48 (m, 4H, CH$_2$S), 1.85−1.76 (m, 4H, OCH$_2$C**H$_2$**), 1.65−1.25 (m, 32H, CH$_2$). ^{13}C NMR (CDCl$_3$) δ: 149.2, 121.0, 114.0, 69.2, 34.1, 29.6−29.1, 28.4, 26.0, 24.7. MS (FAB-MS) *m/z*: 482.2 (M$^+$; calcd. for C$_{28}$H$_{50}$O$_2$S$_2$: 482.3). Anal. Calcd. for C$_{28}$H$_{50}$O$_2$S$_2$: C, 69.65; H, 10.44. Found: C, 69.06; H, 10.09.

11-Bromoundecyl decyl sulfide (4a). To a solution of 1-undecene-11-bromide (62.21 g, 267 mmol) and 9-BBN (9-borabicyclo[3.3.1]nonane, 42.0 mL, 21 mmol) in tetrahydrofuran (THF) (400 mL) was added decanethiol (58 mL, 280 mmol) at 0 °C. The solution was stirred overnight at room temperature. Subsequently, THF was evaporated and hexane and water were added. The organic layer was dried over $MgSO_4$ and concentrated, yielding a yellowish oil. Crystallization from EtOH yielded **4a** as a white solid (78.15 g, 192 mmol, 72%). mp 25−26 °C. ^{1}H NMR (CDCl$_3$) δ: 3.41 (t, 2H, $J = 6.8$ Hz, CH$_2$Br), 2.49 (t, 4H, $J = 7.3$ Hz, CH$_2$S), 1.90−1.79 (m, 2H, C**H$_2$**CH$_2$Br), 1.45−1.18 (m, 32H, CH$_2$), 0.89 (t, 3H, $J = 6.5$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 34.0, 32.8, 32.2, 31.9, 29.7−28.7, 28.1, 22.7, 14.1. MS (FAB-MS) *m/z*: 407.2 ([M+H]$^+$; calcd. for C$_{21}$H$_{44}$SBr: 407.2). Anal. Calcd. for C$_{21}$H$_{43}$SBr: C, 61.89; H, 10.63; S, 7.28. Found: C, 61.83; H, 10.87; S, 7.28.

((11-Undecyl decyl sulfide)oxy)benzene (4). To a solution of phenol (0.60 g, 6.38 mmol) and KOH (0.43 g, 7.6 mmol) in DMF was added **4a** (2.32 g, 5.7 mmol). The reaction mixture was stirred overnight at 90 °C. Subsequently, CH_2Cl_2 was added and the organic layer was washed with alkaline water. The crude reaction mixture was purified by flash chromatography (eluents hexane to hexanes−ethyl acetate 30:1) to give **4** as a white solid (1.12 g, 2.67 mmol, 80%). mp 39−41 °C. ^{1}H NMR (CDCl$_3$) δ: 7.27 (dd, 2H, $J = 8.5$ Hz, $J = 7.5$ Hz, *m*-Ar−H), 6.92 (t, 1H, $J = 7.5$ Hz, *p*-Ar−H), 6.89 (d, 2H, $J = 8.5$ Hz, *o*-Ar−H),

3.95 (t, 2H, $J = 7.0$ Hz, ArO−CH$_2$), 2.49 (t, 4H, $J = 7.1$ Hz, SCH$_2$), 1.84−1.72 (m, 2H, ArOCH$_2$C**H$_2$**), 1.63−1.23 (m, 32H, CH$_2$), 0.88 (t, 3H, $J = 6.8$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 129.4, 120.4, 114.5, 67,9, 32.2, 31.9, 29.7−29.0, 26.1, 22.7, 14.1. MS (FAB-MS) *m/z*: 421.5 ([M+H]$^+$; calcd. for C$_{27}$H$_{49}$OS: 421.3). Anal. Calcd. for C$_{27}$H$_{48}$OS: C, 77.08; H, 11.50. Found: C, 76.39; H, 11.89.

o-Bis((11-undecyl decyl sulfide)oxy)benzene (5). Analogously to the preparation of **4**, catechol (0.16 g, 1.47 mmol), KOH (0.18 g, 3.20 mmol), and **4a** (0.80 g, 197 mmol) yielded after purification (eluents hexane to hexane:ethyl acetate 10:1) **5** as a white solid (0.79 g, 1.04 mmol, 71%). mp 50−51 °C. ^{1}H NMR (CDCl$_3$) δ: 6.88 (s, 4H, ArH), 3.98 (t, 4H, $J = 6.9$ Hz, OCH$_2$), 2.51 (t, 8H, $J = 7.1$ Hz, CH$_2$S), 1.86−1.75 (m, 4H, OCH$_2$C**H$_2$**), 1.65−1.25 (m, 64H, CH$_2$), 0.89 (t, 6H, $J = 6.7$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 149.2, 121.0, 114.1, 69.3, 32.2, 31.9, 29.8−29.0, 26.0, 22.7, 14.1. MS (FAB-MS) *m/z*: 763.5 ([M+H]$^+$; calcd. for C$_{48}$H$_{91}$O$_2$S$_2$: 763.6). Anal. Calcd. for C$_{48}$H$_{90}$O$_2$S$_2$: C, 75.52; H, 11.88; S, 8.40. Found: C, 75.78; H, 12.10; S, 8.30.

m-Bis((11-undecyl decyl sulfide)oxy)benzene (6). Analogously to the preparation of **4**, resorcinol (5.0 g, 4.55 mmol), KOH (0.56 g, 10.01 mmol), and **4a** (2.5 g, 6.15 mmol) yielded after purification (eluents hexane to hexane:ethyl acetate 15:1) **6** as a white solid (0.26 g, 0.34 mmol, 8%). mp 49−50 °C. ^{1}H NMR (CDCl$_3$) δ: 7.16 (t, 1H, $J = 8.4$ Hz, *m*-ArH), 6.50 (m, 1H, *o*-Ar−H), 6.46 (m, 2H, *p*-Ar−H), 3.93 (t, 4H, $J = 7.0$ Hz, OCH$_2$), 2.51 (t, 8H, $J = 7.1$ Hz, CH$_2$S), 1.83−1.72 (m, 4H, OCH$_2$C**H$_2$**), 1.65−1.25 (m, 64H, CH$_2$), 0.88 (t, 6H, $J = 6.6$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 160.4, 129.0, 106.6, 101.4, 68.0, 32.2, 31.9, 29.4−29.0, 26.0, 22.7, 14.1. MS (FAB-MS) *m/z*: 763.5 ([M+H]$^+$; calcd. for C$_{48}$H$_{91}$O$_2$S$_2$: 763.6). Anal. Calcd. for C$_{48}$H$_{90}$O$_2$S$_2$: C, 75.52; H, 11.88; S, 8.40. Found: C, 75.34; H, 12.10; S, 8.34.

p-Bis((11-undecyl decyl sulfide)oxy)benzene (7). Analogously to the preparation of **4**, hydroquinone (0.50 g, 4.55 mmol), KOH (0.56 g, 10.01 mmol), and **4a** (2.50 g, 6.15 mmol) yielded after purification (eluents hexane to hexane:ethyl acetate 15:1) **7** as a white solid (0.13 g, 0.17 mmol, 4%). mp 75−77 °C. ^{1}H NMR (CDCl$_3$) δ: 6.82 (s, 4H, ArH), 3.90 (t, 4H, $J = 7.2$ Hz, OCH$_2$), 2.51 (t, 8H, $J = 7.3$ Hz, CH$_2$S), 1.81−1.69 (m, 4H, OCH$_2$C**H$_2$**), 1.65−1.25 (m, 64H, CH$_2$), 0.88 (t, 6H, $J = 6.8$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 115.4, 32.2, 31.9, 29.7−29.0, 22.7, 14.5. MS (FAB-MS) *m/z*: 762.5 (M$^+$; calcd. for C$_{48}$H$_{90}$O$_2$S$_2$: 762.6). Anal. Calcd. for C$_{48}$H$_{90}$O$_2$S$_2$: C, 75.52; H, 11.88; S, 8.40. Found: C, 75.18; H, 11.19; S, 8.33.

1,2,3-Tris((11-undecyl decyl sulfide)oxy)benzene (8). Pyrogallol (0.48 g, 3.81 mmol) was added to a solution of NaH (0.85 g, 19.5 mmol) in DMSO (300 mL). After half an hour **4a** (5.35 g, 13.1 mmol), was added to the reaction mixture, which was stirred overnight. The reaction mixture was quenched with water and extracted with CH_2Cl_2. The organic layers were dried over $MgSO_4$ and concentrated. The resulting oil was purified by flash chromatography (eluents hexane to hexane:dichloromethane 1:1) yielding **8** as a white solid (0.44 g, 0.40 mmol, 10%). mp 54−55 °C. ^{1}H NMR (CDCl$_3$) δ: 6.89 (t, 1H, $J = 8.4$ Hz, *m*-Ar−H), 6.54 (d, 2H, $J = 8.4$ Hz, *o*-Ar−H), 3.95 (t, 6H, $J = 7.1$ Hz, OCH$_2$), 2.49 (t, 12H, $J = 7.5$ Hz, CH$_2$S), 1.83−1.67 (m, 6H, OCH$_2$C**H$_2$**), 1.65−1.25 (m, 96H, CH$_2$), 0.88 (t, 9H, $J = 6.8$ Hz, CH$_3$). ^{13}C NMR (CDCl$_3$) δ: 153.4, 138.4, 123.1, 106.7, 73.4, 69.1, 32.2, 31.9, 29.7−29.0, 26.1, 22.7, 14.1. MS (FAB-MS) *m/z*: 1105.9 (M$^+$; calcd. for C$_{28}$H$_{46}$O$_3$S$_3$: 1106.0). Anal. Calcd. for C$_{28}$H$_{46}$O$_3$S$_3$: C, 74.93, H, 12.03; S, 8.70. Found: C, 75.23; H, 12.03; S, 8.82.

Monolayers. Gold Substrates. Gold substrates were prepared by evaporating 200 nm of gold on a glass slide of 25-mm diameter with a 2-nm chromium layer for adhesion. Before use, the gold substrates were cleaned in an oxygen plasma for 5 min. The resulting oxide layer was removed by leaving the substrates for 10 min in EtOH.[12]

Monolayer Preparation. All glassware used to prepare monolayers was immersed in *piraña* at 70 °C for 1 h. **Warning**: *piraña* solution should be handled with caution; it has detonated unexpectedly.[13] Next, the glassware was rinsed with large amounts of high-purity water (Millipore). The cleaned gold

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Chart 1. Adsorbates Used in This Study

$$R = C_{10}SC_{11}-$$
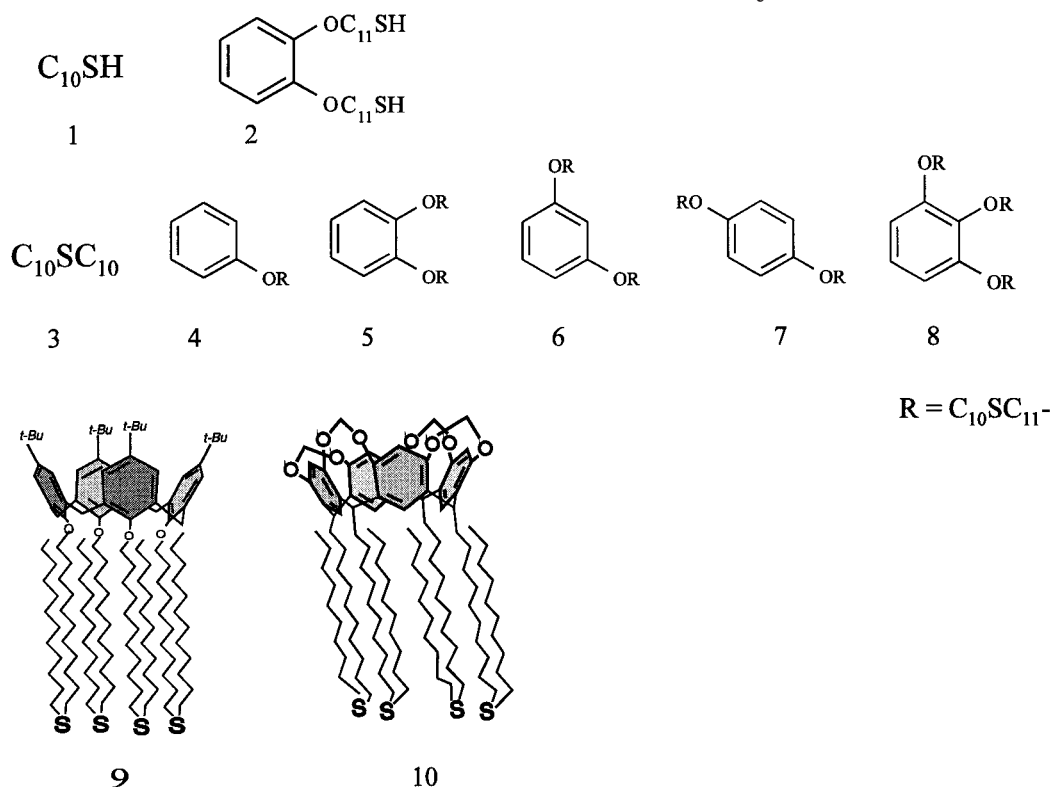
substrates were immersed with minimal delay into a 1 mM adsorbate solution in ethanol:CHCl$_3$ (1:2) for 16 h. Sulfide monolayers were prepared at 60 °C[14] and thiol monolayers at room temperature. Subsequently, the substrates were removed from the solution and rinsed with large amounts of dichloromethane, ethanol, and water to remove any physisorbed material.

Instrumentation. For X-ray photoelectron spectroscopy (XPS) a VG Escalab 220i-XL instrument was used with a monochromatic Al Kα X-ray source. XPS data were collected from a surface area of (150 mm × 150 mm) with a pass energy window of 20 eV using 10 and 20 scans for carbon and sulfur, respectively. The advancing and receding contact angles with water were measured on a Krüss G10 contact angle measuring instrument, equipped with a CCd camera during the growth and shrinkage of a droplet. Electrochemical measurements (cyclic voltammetry and impedance spectroscopy) were performed on an Autolab PGSTAT10 (ECOCHEMIE, Utrecht, The Netherlands) in a three-electrode system consisting of a gold working electrode (clamped to the bottom of the cell, exposing a geometric area of 0.44 cm^2 to the electrolyte solution), a platinum counter electrode, and a mercurous sulfate reference electrode (+0.61 V$_{NHE}$). Cyclic voltammetric capacitance measurements were conducted in 0.1 M K$_2$SO$_4$ between −0.4 and −0.3 V$_{MSE}$ at scan rates ranging from 0.1 to 2.0 V/s. Heterogeneous electron-transfer measurements were conducted in 1 mM K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ and 0.1 M K$_2$SO$_4$ between −0.7 and 0 V$_{MSE}$ at 0.1 V/s. We report for the heterogeneous electron-transfer measurements the sum in the current of the anodic and cathodic scan at the formal potential of the redox couple (−0.2 V$_{MSE}$). Impedance spectroscopy measurements were performed in 1 mM K$_3$Fe(CN)$_6$/K$_4$Fe-(CN)$_6$ and 0.1 M K$_2$SO$_4$ at −0.2 V$_{MSE}$ with an amplitude of 5 mV using a frequency range from 50 kHz to 0.1 Hz. The capacitance and charge-transfer resistance of the monolayer were obtained by fitting the experimental data to an equivalent circuit consisting of the monolayer resistance parallel to the monolayer capacitance, in series with the solution resistance. Good fits were obtained. Stability measurements were performed by scanning for 1 h in

the potential area of interest (size window, 0.8 V; scan rate, 0.1 V/s; therefore, 225 scans) in 0.1 M K$_2$SO$_4$.

Results and Discussion

The potential window where self-assembled monolayers are stable is important for any future electrochemical application. The goal of this study was to study the influence of the type and number[15] of S-containing linkers in the adsorbates (Chart 1). All the adsorbates are electrochemically inactive. First, we will discuss the synthesis of the adsorbates, second, the characterization of the monolayers by wettability studies, XPS, and electrochemistry, and third, the electrochemical stability of the self-assembled monolayers.

Synthesis of the Adsorbates. The synthesis and purification of decanethiol (**1**),[9a] decyl sulfide (**3**),[9a] calixarene **9**,[9b] and resorcinarene **10**[9c] have been described elsewhere. Bisthiolbenzene **2** was obtained by alkylation of catechol with 11-bromo-1-undecene and subsequent conversion of the double bonds to thiol units by the stereoselective anti-Markovnikov addition of thioacetic acid to the double bonds, and finally hydrolysis of the thioesters under alkaline conditions. Alkyl sulfides **4**−**8** were obtained by alkylation of the corresponding alcohols with 11-bromoundecyl decyl sulfide (**4a**) in the presence of a base. Compound **4a** was obtained by the anti-Markovnikov addition of decanethiol over the double bond of 11-bromide-1-undecene with 9-BBN as a catalyst.[16]

Monolayer Characterization. In this study we have used wettability studies, XPS, and electrochemistry for characterization of the self-assembled monolayers. The monolayers can be divided into three different classes:

(14) Previously, we have shown that for sulfide monolayers an elevated adsorption temperature of 60 °C increases the quality of the monolayer (ref 2a).

(15) Preliminary studies have revealed that multiple points of attachment increase the *thermic* stability of monolayers. Garg, N.; Lee, T. R. *Langmuir* **1998**, *14*, 3815−3819.

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Table 1. Properties of the Self-assembled Monolayers

	$\theta_{a,H_2O}/\theta_{r,H_2O}$ (°)[a]	C_{ML} (μF/cm^2)[b]	R_{CT} (kΩ)[c]	HET (μA)[d]
1	108/91	1.7	1400	0.18
2	89/73	2.0	1400	0.23
3	103/91	2.5	3	15
4	89/68	4.0	0.3	70
5	91/76	1.9	50	0.60
6	94/81	2.1	40	0.65
7	93/82	2.2	60	0.67
8	92/74	3.5	2	40
9	102/89	2.0	450	0.31
10	105/82	1.9	700	0.25

[a] Advancing and receding contact angle of the monolayer with water. [b] Capacitance of the monolayer determined by cyclic voltammetry at a scan rate of 0.1 V/s. [c] Charge-transfer resistance of the monolayer determined by fitting the impedance data to an equivalent circuit. [d] Sum of the anodic and cathodic current at the formal potential of the ferro/ferri redox couple (-0.2 V$_{MSE}$) determined by heterogeneous electron-transfer measurements.

the thiols **1** and **2**, the sulfides **3**–**8**, and the receptor monolayers **9** and **10**.

Contact angles with water of self-assembled monolayers are an easy first indication of the properties of the monolayer and give information about the hydrophobicity and packing. The advancing and receding contact angles measured for the 10 monolayers indicate hydrophobic monolayers (Table 1).

For the monolayers of adsorbates with multiple attachment points the percentage of sulfur units involved in the binding to the gold substrate was measured by XPS-S$_{2p}$.[1] Unbound sulfur has a binding energy of approximately 163.0 eV, whereas bound sulfur has a 1-eV lower binding energy. Deconvolution of the XPS-S$_{2p}$ signal gives the percentage of bound sulfur. All available sulfurs of bisthiolbenzene **2** (2), calixarene **9** (4) and cavitand **10** (4) are used for binding to the gold substrate. Bipodant **5** (2) uses only ≈ 1.4 of 2 sulfur units (70%). This incomplete use of the available binding sites is probably caused by the mismatch in the area of the (small) aryl headgroup and the supporting sulfide units.[17]

For the electrochemical characterization of self-assembled monolayers, the capacitance and the heterogeneous electron transfer (HET) from cyclic voltammetric measurements, and the charge-transfer resistance (R_{CT}) obtained from impedance spectroscopy, are most frequently used.

The capacitance of a monolayer is an average value of the whole monolayer and provides information mainly about the thickness. The capacitances of the 10 layers indicate monolayer formation, except for the adsorbates **4** and **8** (Table 1). The high values for the capacitance of the latter monolayers suggest submonolayer coverage.

The charge-transfer resistance and heterogeneous electron-transfer measurements show the capability to block a redox couple from solution and are indicative for defects in the monolayer. Such measurements revealed large differences in the properties of monolayers of sulfides **3**, **4**, and **8**, and the other monolayers used in this study (Table 1). The sulfide monolayers **3**, **4**, and **8** are by no means able to block the current from the ferro/ferri couple in solution and are, from the *electrochemical* point of view, not well-packed monolayers.[18] Apparently, one sulfide

(17) Previously, we have shown that well-packed monolayers of the receptor molecules **9** and **10** can only be formed if the area of the headgroup matches the area of the supporting structure (see ref 2).

(18) Previously, we have erroneously reported that decyl sulfide monolayers are *electrochemically* well-packed monolayers (ref 2b). The inability of decyl sulfide monolayers to block the ferro/ferri redox couple from solution was also reported by others: Motesharei, K.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1997**, *119*, 11306−11312.
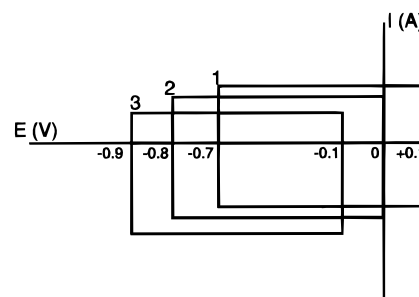

Figure 1. Potential areas used in the electrochemical stability measurements. [0 V$_{MSE}$ = +0.61 V$_{NHE}$].

moiety is not sufficient to form an *electrochemically* well-packed monolayer.[19] The poor electrochemical quality of the tripodant sulfide monolayer **8** might be due to the mismatch between the area of the aryl headgroup and the supporting alkyl chains.

The characterization of the monolayers described above shows that it is important that the structure of the headgroup matches the supporting alkyl chains.

Stability Measurements. Electrochemical applications generally involve cyclic voltammetry or impedance spectroscopy under neutral, aqueous conditions.[20] Therefore, we performed the stability measurements in water with 0.1 M K$_2$SO$_4$ as the electrolyte. The stability measurements were started in the area where self-assembled monolayers are electrochemically stable (vide infra). In this window from -0.7 to $+0.1$ V$_{MSE}$ the potential was scanned for an hour (225 scans). Subsequently, the window was shifted 0.1 V anodically and scanned for another hour (see Figure 1). This renders the total *exposure* time at the extreme potential constant. The same series of experiments was performed at the cathodic site. The capacitance of a monolayer is an inappropriate parameter to monitor the "molecular" quality/stability of a monolayer, as this property is an average of the whole monolayer and unable to accurately detect small changes. Consequently, the quality of the monolayer can be monitored by two other independently determined more sensitive parameters (viz. the charge-transfer resistance (R_{CT}) and the heterogeneous electron transfer (HET)). The decrease in ability of a decanethiol monolayer to block an external redox couple after scanning to the extreme potential of $+0.6$ V$_{MSE}$ for an hour is representative for the whole series (Figure 2).[21] The electrochemical impedance spectroscopy measurements show a drop in R_{CT} of 800 to 1 kΩ. We have chosen the charge-transfer resistance as the parameter to follow the electrochemical stability of self-assembled monolayers.[22] The stability curve for a decanethiol monolayer is shown in Figure 3 (R_{CT}).[23] These

(19) No clear differences between a decanethiol and decyl sulfide monolayer could be observed by other techniques such as IR, XPS, and wettability studies.[9a] Only electrochemistry is apparently sensitive enough to detect differences.

(20) It is well-known that monolayers can be *deliberately* desorbed in the presence of a base or acid in one voltammetric scan at reductive or oxidative potentials; see, for example: (a) Walczak, M. M.; Popenoe, D. D.; Deinhammer, R. S.; Lamp, B. D.; Chung, C.; Porter, M. D. *Langmuir* **1991**, *7*, 2687−2693. (b) Widrig, C. A.; Chung, C.; Porter, M. D. *J. Electroanal. Chem.* **1991**, *310*, 335−359. (c) Weisshaar, D. E.; Lamp, B. D.; Porter, M. D. *J. Am. Chem. Soc.* **1992**, *114*, 5860−5862.

(21) The current at -0.2 V$_{MSE}$ in the heterogeneous electron-transfer measurements has a capacitive and a faradaic component. For curve a, this current (0.18 μA) consists of >80% capacitance current and <20% heterogeneous electron-transfer current of the ferro/ferri redox couple in solution. For curve b, the current (30.0 μA) consists of <2% capacitance current and >98% faradaic current.

(22) The stability of the self-assembled monolayers can also be monitored by heterogeneous electron transfer, leading to the same stability windows.
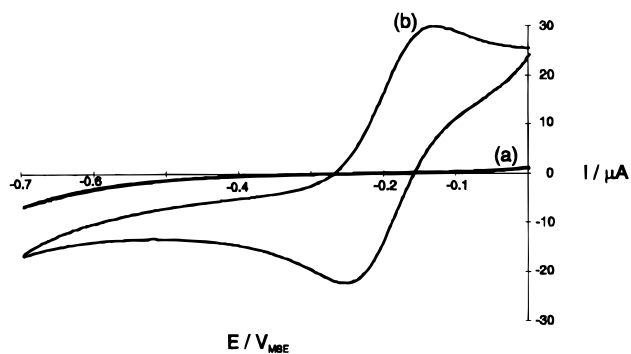
Figure 2. Heterogeneous electron transfer of a decanethiol monolayer: (a) after preparation; (b) after excursion to the extreme potential of $+0.6$ V_{MSE} for an hour. [0 $V_{MSE} = +0.61$ V_{NHE}].
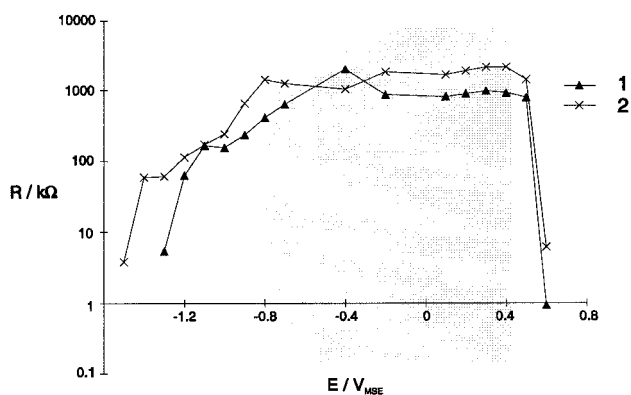

Figure 4. Stability for self-assembled monolayers of the adsorbates **5**–**7**: charge-transfer resistance dependence on the applied potential window. [0 $V_{MSE} = +0.61$ V_{NHE}].

Figure 3. Stability for self-assembled monolayers of the adsorbates **1** and **2**: charge-transfer resistance dependence on the applied potential window. [0 $V_{MSE} = +0.61$ V_{NHE}].

Figure 5. Stability for self-assembled monolayers of the adsorbates **9** and **10**: charge-transfer resistance dependence on the applied potential window. [0 $V_{MSE} = +0.61$ V_{NHE}].

measurements clearly show that a decanethiol monolayer is stable from -0.9 to $+0.5$ V_{MSE}. At potentials more cathodic than -1.1 V_{MSE} and more anodic than $+0.5$ V_{MSE} a rapid decay in quality of the monolayer was observed. The origin of the destruction of the monolayer outside the window is hard to identify but might be caused by hydrogen (cathodic) and oxygen (anodic) evolution.[24] Monolayers of bisthiolbenzene **2** are stable from -0.8 to $+0.5$ V_{MSE}. At more cathodic potentials than -0.8 V_{MSE} a gradual decrease in quality of the bisthiolbenzene **2** monolayer occurs. In general, for this class of monolayers there is a sharp cutoff of the potential window in the anodic domain and a more gradual cutoff in the cathodic domain.

The stability of the monolayers of decyl sulfide (**3**), phenyl sulfide **4**, and trissulfide **8** was not determined, because HET and R_{CT} measurements already indicated that these monolayers are of low quality. Self-assembled monolayers of benzene bissulfide adsorbates **5**–**7** have a lower charge-transfer resistance than those of a decanethiol (**1**) monolayer. The stability window is equal for all three benzene bissulfide monolayers and ranges

from -0.8 to $+0.4$ V_{MSE} (see Figure 4). Also, for these monolayers there is a sharp cutoff in the anodic domain and a more gradual cutoff in the cathodic domain. There is a small but significant increase in quality for these monolayers at potentials between $+0.2$ and $+0.4$ V_{MSE}. The reason for this potential dependent rearrangement of the monolayer is unclear.

The tetrasulfide receptor monolayers of calixarene **9** and cavitand **10** have a much higher quality. The cavitand has a potential window of -0.9 to $+0.5$ V_{MSE}, whereas the calixarene is stable from -0.8 to $+0.4$ V_{MSE} (Figure 5). This difference may be related to the larger rotational freedom of the aromatic rings of the calixarene headgroup than that of the rings of the bridged cavitand, leading to monolayers that are structurally different.[9b]

In conclusion, the stability measurements have shown that self-assembled monolayers are stable between -0.8 and $+0.4$ V_{MSE}. Therefore, all electrochemical applications should be limited to this potential area. The tetrasulfide cavitand **10** monolayers with an exact match between the headgroup and supporting structure leading to highly ordered monolayers has an increased window and is as stable as a decanethiol monolayer.

(23) The values of R_{CT} are assigned to the extreme potentials of the used window. For example, monolayer properties after scanning between -1.3 and -0.5 V_{MSE} are reported at -1.3 V_{MSE}. The starting values, after the monolayer preparation, are arbitrarily assigned to -0.4 V_{MSE} (cathodic scan) and -0.2 V_{MSE} (anodic scan).

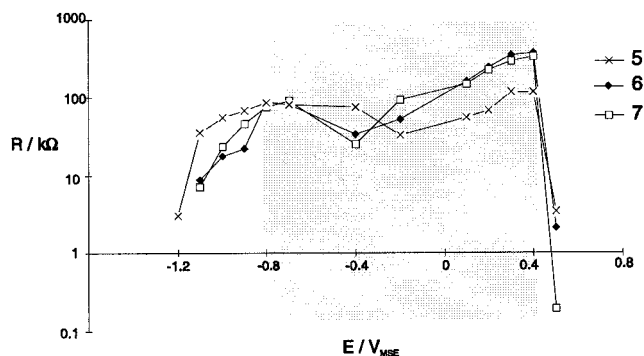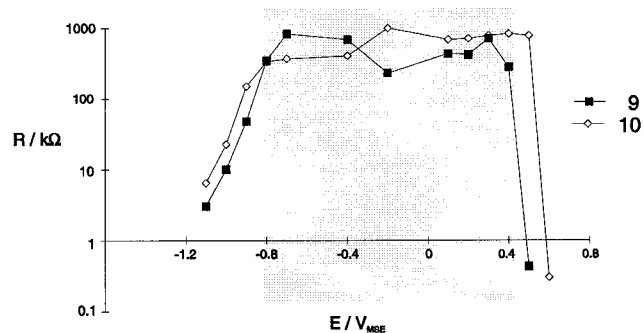(24) Sondag-Huethorst, J. A. M.; Fokkink, L. G. J. *Langmuir* **1992**, *8*, 2560–2566.