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X-Ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) have been used to study the interactions between self-assembled monolayers (SAMs) of crown ether adsorbates and metal ions. Both analytical techniques confirmed the selectivities of the 12-crown-4 and 15-crown-5 SAMs that had previously been determined by electrochemical impedance spectroscopy. AFM has also been used to characterize microcontact-printed crown ether monolayers. The electrochemical patterning of monolayers on gold allowed the design of a dual sensor for the electrochemical detection of cations. However, due to cross-contamination of both monolayers during the patterning process a significant selectivity reduction of the layers was observed. Nevertheless, the remaining Na<sup>+</sup> selectivity of the 12-crown-4 SAM and the K<sup>+</sup> selectivity of the 15-crown-5 SAM allowed the unambiguous discrimination between both metal ions.

## Introduction

Studies on interactions between analytes in solution or in the vapor phase and self-assembled monolayers (SAMs) have led to a range of systems that are able to detect (bio)molecules or ions.<sup>1</sup> Although some of the hosts have very remarkable selectivities, many receptor layers suffer from aspecific binding. This lack of selectivity can be solved by the design of better hosts, or by the use of a series of receptor layers with moderate but different selectivities. The use of such sensor arrays then allows the selective recognition of analytes based on the response pattern generated by all receptor layers.<sup>2</sup>

Over the past years, a large variety of methods have been developed for the patterning of self-assembled monolayers on gold. Photolithographical techniques have been investigated by the groups of Gillen and Hemminger.<sup>3</sup> The UV-irradiation of a SAM through a mask oxidizes the exposed thiolates to sulfonates, which can subsequently be rinsed off or replaced by a different adsorbate. Another very simple and effective method for the preparation of patterned monolayers is microcontact printing ( $\mu$ CP).<sup>4</sup> It uses an elastomeric polydimethylsiloxane (PDMS) stamp for the transfer of thiols to the gold surface. The size of the structures that have been produced in this way can have dimensions of less than 1  $\mu$ m.<sup>5</sup> Other methods, like AFM nanoshaving,<sup>6</sup> STM nanolithography,<sup>7</sup> and electron-beam lithography<sup>8</sup> have the advantage of a higher lateral resolution, but are less convenient to use.

In principle, arrays of sensing monolayers can be prepared by any of the above-mentioned patterning techniques. The readout of the individual monolayer responses can be performed with analytical techniques that exhibit a high degree of spatial resolution. For electrochemical transduction, the sensing SAMs should be electrically isolated which allows them to be addressed separately. Recently, Lopez *et al.* have developed an electrochemical patterning method that enables the modification of an array of gold electrodes with different self-assembled monolayers.<sup>9</sup> It is based on the reductive desorption of a SAM from one of the electrodes,<sup>10</sup> and the subsequent deposition of a

different receptor monolayer. In this way, Lopez *et al.* were able to self-assemble three different monolayers on an array of gold electrodes, and monitor their interactions with fluorescein-labeled biomolecules by confocal fluorescence microscopy.<sup>9b</sup>

We have previously shown that self-assembled monolayers of crown ether adsorbates are able to bind cations from a contacting aqueous solution. The use of electrochemical impedance spectroscopy allowed us to monitor the complexation *via* changes of the monolayer capacitance and the charge transfer resistance.<sup>11,12</sup> Furthermore, it was found that the metal ions were bound to the crown ether monolayer as sandwich complexes, which could be prevented by dilution of the receptor layer with heptanethiol. In this paper two non-electrochemical techniques, *viz.* X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM), have been used to study the complexation of metal ions to self-assembled monolayers of crown ether adsorbates **1** and **2** and tris(ethyleneoxy) adsorbate **3** (Chart 1). The feasibility of an array sensor

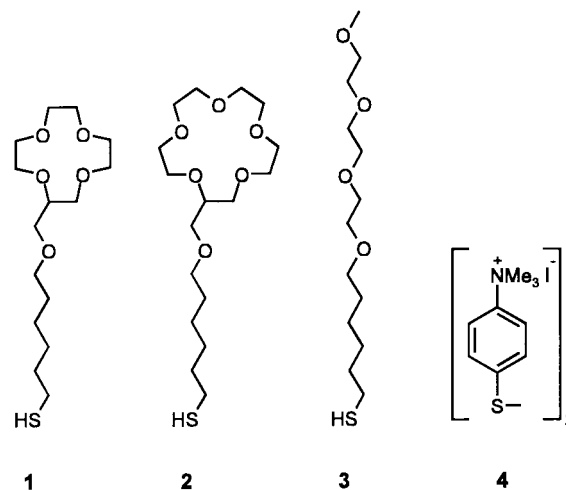


Chart 1

**Table 1** XPS data for monolayers of crown ether adsorbates **1** and **2**, and tris(ethyleneoxy) **3**

SAM	C content (%)	O content (%)	S content (%)
	Calcd/found	Calcd/found	Calcd/found
<b>1</b>	71.4/67.5	23.8/28.4	4.8/4.1
<b>2</b>	70.8/66.4	25.0/29.6	4.2/4.0
<b>3</b>	72.2/72.2	22.2/23.6	5.6/4.2

that uses either of these techniques is discussed. As an alternative to AFM and XPS measurements, electrochemical impedance spectroscopy has been used for the monitoring of host-guest interactions on electrochemically patterned monolayers of crown ethers.

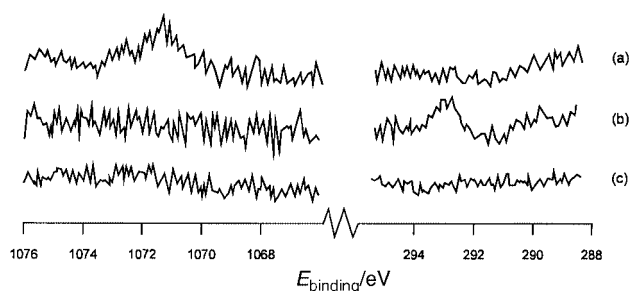
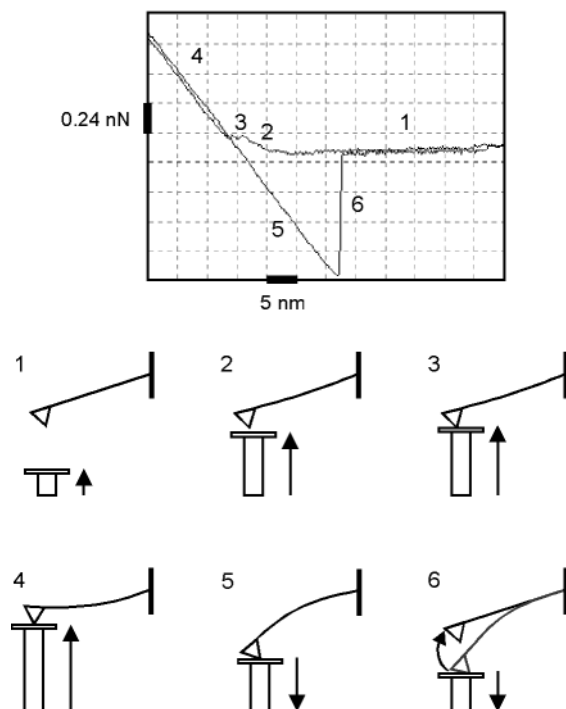
## Results and discussion

### Non-electrochemical detection of metal ions by crown ether monolayers

XPS measurements of the monolayers showed the presence of the elements C, O, and S. The experimentally determined and calculated percentages of the elements in these monolayers are given in Table 1. For all monolayers a clear trend is visible: the determined amount of oxygen is slightly larger than expected on the basis of the elemental composition, whereas the determined amount of sulfur is somewhat smaller than calculated. These observations are attributed to the attenuation of photoelectrons that originate from atoms deeper in the layer. Furthermore, the binding energies of the  $S_{2p}$  electrons ( $S_{2p_{3/2}}$  at 162 eV and  $S_{2p_{1/2}}$  at 163 eV) were shifted by  $-1.5$  eV compared to bulk thiols, which confirms that the adsorbates were bound to the gold surface.<sup>13</sup> These results are in full agreement with a monolayer structure in which the thiols are used to anchor the adsorbates to the gold substrate and in which the receptor part is exposed to the outer interface.

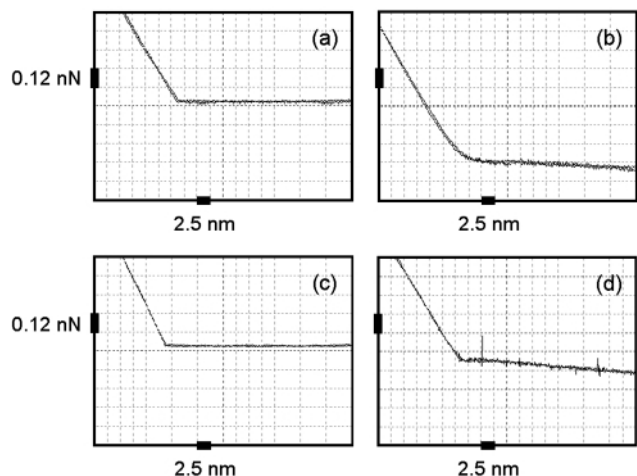
Apart from the elemental analysis of the monolayers, XPS can be used to analyze the reversible binding of ions from solution to the surface.<sup>14</sup> Here, we have applied *ex-situ* XPS to study the selectivity of cation binding to self-assembled monolayers of crown ethers **1** and **2** and tris(ethyleneoxy) **3**. The SAMs were exposed to an aqueous solution of both 20 mM NaCl and 20 mM KCl. After withdrawal of the layers from the solution the surfaces were dewetted completely. The dewetting is essential, since it prevents the deposition of a non-complexed layer of salts during the evaporation of the water, as was confirmed by AFM measurements. XPS analysis showed 12-crown-4 SAM  $Na^+$  (1.2%), while a signal for  $K^+$  was absent (see Fig. 1). The reverse was observed for the 15-crown-5 SAM: 0.5%  $K^+$  and no signal for  $Na^+$ . Finally, the tris(ethyleneoxy) monolayer bound neither sodium nor potassium ions. These findings are in full agreement with the sodium selectivity of 12-crown-4 SAMs and potassium selectivity of 15-crown-5 SAMs.<sup>11,12</sup> By comparing the amounts of sodium and potassium in the crown ether monolayers to the amount of sulfur (Table 1), it was estimated that after withdrawal from the solution 60% of the 12-crown-4 SAM and 25% of the 15-crown-5 SAM are involved in sandwich complexation.

Atomic force microscopy is a rapidly developing analytical technique that allows the study of surfaces with high resolution and has for instance been used to determine the molecular packing of self-assembled monolayers.<sup>15</sup> The modification of AFM tips with self-assembled monolayers influences their interactions with the sample, which can be used in the chemical mapping of surfaces (chemical force microscopy, CFM).<sup>16,17</sup> Furthermore, it has been shown that even interactions between single molecules can be detected by CFM.<sup>18</sup> The combination of chemical sensitivity and spatial resolution stimulated the investigation of the binding of metal ions to self-assembled monolayers of crown ether adsorbates with AFM.

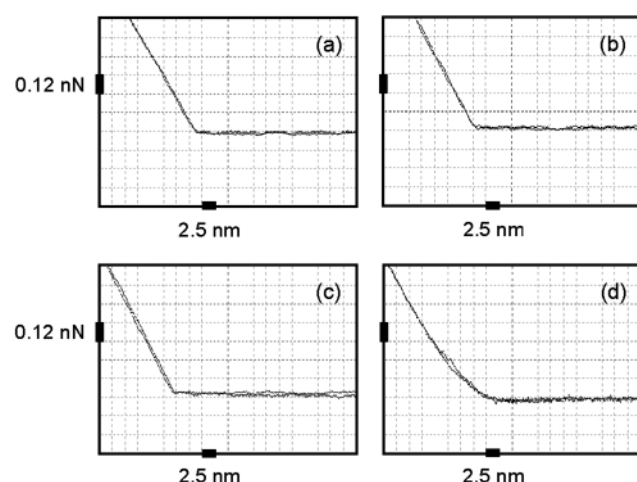
**Fig. 1** XPS spectra of self-assembled monolayers of 12-crown-4 (a), 15-crown-5 (b), and tris(ethyleneoxy) (c). Left side:  $Na_{1s}$  signal; right side:  $K_{2p_{3/2}}$  signal.**Fig. 2** Force-distance curve measured between a  $Si_3N_4$  AFM tip and a 12-crown-4 SAM in an aqueous solution of 10 mM NaCl.

The interactions between an unmodified silicon nitride tip and self-assembled monolayers of 12-crown-4 adsorbate **1** and 15-crown-5 adsorbate **2** in aqueous solutions resulted in force-distance curves that were dominated by the adhesive forces between the hydrophilic tip and the monolayer (see Fig. 2). Pronounced hysteresis was observed. During the approach of the monolayer towards the tip (1), no forces are experienced until at a certain distance (2) the tip experiences a weak repulsive force that results in the deflection of the cantilever. This might indicate that the AFM tip is (slightly) positively charged and hence a repulsive force is experienced between the AFM tip and the positively charged self-assembled monolayer. By further movement of the sample, the gradient of the adhesive force will overcome the spring constant and the repulsion; this is when the tip contacts the surface (3). When the sample continues its upward movement, it causes a deflection of the cantilever (4). During retraction of the monolayer, adhesive forces between the monolayer and the tip cause the cantilever to remain in contact with the monolayer (5). During this movement the cantilever is bent until the spring constant overcomes the force gradient and the tip snaps off (6).

In order to reduce the adhesive force between the tip and the monolayer, AFM measurements were performed in acetonitrile solutions (Figs. 3 and 4). In 0.1 mM solutions of  $NaClO_4$  or  $KClO_4$ , no long range interactions between the AFM tip and the 12-crown-4 or 15-crown-5 SAMs were observed. This resulted in force-distance curves that displayed no hysteresis

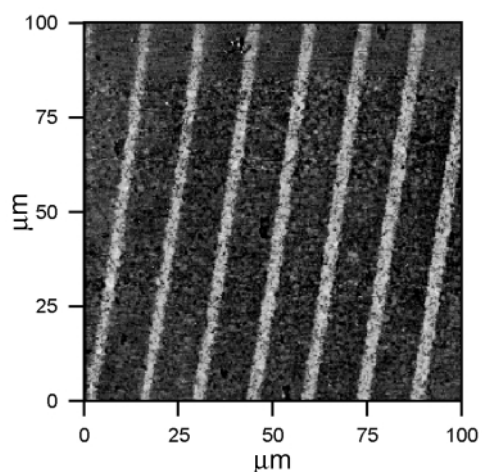


**Fig. 3** Force–distance curves measured between a  $\text{Si}_3\text{N}_4$  AFM tip and a 12-crown-4 SAM in MeCN solutions containing 0.1 mM  $\text{NaClO}_4$  (a), 10 mM  $\text{NaClO}_4$  (b), 0.1 mM  $\text{KClO}_4$  (c) and 10 mM  $\text{KClO}_4$  (d).



**Fig. 4** Force–distance curves measured between a  $\text{Si}_3\text{N}_4$  AFM tip and a 15-crown-5 SAM in MeCN solutions containing 0.1 mM  $\text{NaClO}_4$  (a), 10 mM  $\text{NaClO}_4$  (b), 0.1 mM  $\text{KClO}_4$  (c) and 10 mM  $\text{KClO}_4$  (d).

(Fig. 3(a), (c) and Fig. 4(a), (c)). During the approach and retraction of the sample, the tip did not experience any forces that led to adhesion or repulsion. Only when both were in direct physical contact was the movement of the sample reflected in a force that was required for the bending of the cantilever. The absence of hysteresis indicates a thermodynamically controlled experiment.<sup>19</sup> When the concentration of  $\text{NaClO}_4$  was increased to 10 mM, the force–distance curve for the 12-crown-4 exhibited a small, but distinct curvature. This curvature is attributed to weak repulsive forces between the tip and the substrate (Fig. 3(b)). Since for identical concentrations of  $\text{KClO}_4$  no repulsion was detected, the interaction is probably caused by dipole–cation interactions between the silicon nitride tip and the cations that are bound to the 12-crown-4 monolayer.<sup>20</sup> From the curvature of the force–distance plot it was determined that the AFM tip is experiencing a repulsive force at distances of less than 5 nm from the surface. The relatively weak repulsion experienced by the tip is related to a low density of cations bound to the crown ether SAM. These observations are in accordance with the sandwich complexation of the monolayer that requires two crown ether adsorbates, which limits the maximum number of surface-bound metal ions. The sodium selectivity of the 12-crown-4 SAM<sup>11</sup> could be confirmed by the AFM measurements: no effects were observed for  $\text{KClO}_4$  (Fig. 3(c), (d)). Moreover, the 15-crown-5 monolayer, which is highly potassium selective,<sup>11</sup> only showed a repulsive interaction with the AFM tip in 10 mM  $\text{KClO}_4$  (Fig. 4).



**Fig. 5** Friction force micrograph obtained with an unmodified  $\text{Si}_3\text{N}_4$  AFM tip on a microcontact printed SAM in air. Dark lines (low friction) correspond to microcontact printed SAM of triethylene glycol adsorbate **3**, and bright lines (high friction) correspond to filled SAM of 12-crown-4 adsorbate **1**.

In an attempt to increase the observed repulsive forces, the AFM tip was modified with a self-assembled monolayer of a quaternary ammonium salt. This was achieved by coating the cantilever with 2 nm of titanium and 75 nm of gold, and subsequent modification of the gold by self-assembly of 4,4'-disulfaneyldiphenylbis(ammonium) diiodide (**4**) (see Chart 1). Unfortunately, the modified tips showed no improvement of the repulsive force compared to the silicon nitride tip. Instead, the relatively strong adhesive forces between the tip and the monolayer resulted in a pronounced snap inwards, which interfered with the detection of the repulsion. The increased adhesion between the modified tip and the sample is probably caused by a change of its interfacial energy and the larger radius of the modified AFM tip.

The deposition of self-assembled monolayers in a two-dimensional pattern, for the potential application in array sensors, was achieved by microcontact printing.<sup>4</sup> The structures of the PDMS stamp (lines of 15  $\mu\text{m}$  width, separated by 5  $\mu\text{m}$ ) were transferred onto the gold substrate, using a 1 mM solution of the tris(ethyleneoxy) adsorbate **3** as ink. Subsequently, the substrate was exposed to a solution of 12-crown-4 thiol **1** to modify the remaining areas of bare gold. The produced pattern could be visualized by friction force microscopy, which showed that the stamped triethylene glycol SAM had a significantly lower friction than the subsequently assembled layer of 12-crown-4 (Fig. 5). This can be explained by differences in order for the SAMs of adsorbates **1** and **3**. We have previously shown by wettability studies and electrochemical measurements that the molecular structure of the tris(ethyleneoxy) adsorbate **3** allows a more ordered packing of the monolayer than the crown ether **1**.<sup>11</sup> As a result, the disorder in the crown ether regions of the microcontact printed SAMs gives rise to rotational and vibrational modes and thus to an increased magnitude of friction.<sup>21</sup>

Friction force microscopy showed that microcontact printing was successfully employed for the production of patterned SAMs. Unfortunately, the limited signal to noise ratio of laterally resolved pull-off force measurements was insufficient to unequivocally detect the weak repulsive forces that accompany the complexation of metal ions.

#### Electrochemical patterning of SAMs and their use in array sensing

Both XPS and AFM confirmed the highly selective complexation of metal ions to self-assembled monolayers of crown ethers. However, the signal to noise ratio of these analytical techniques was not sufficient to allow the monitoring of metal

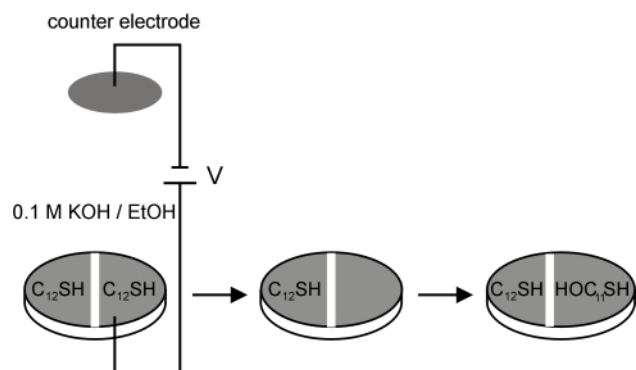


Fig. 6 Electrochemical patterning of SAMs on gold.

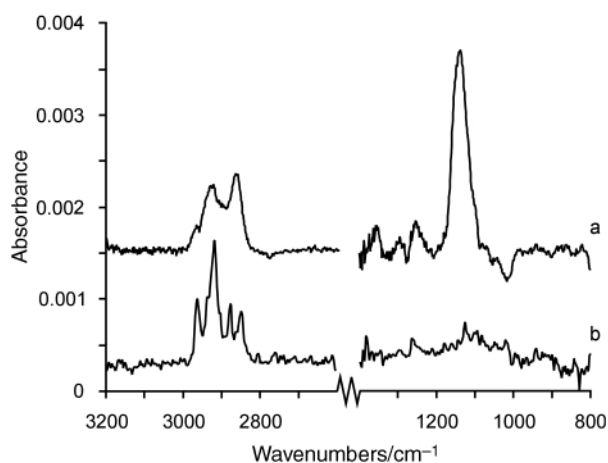


Fig. 7 Grazing-incidence infrared spectra of 15-crown-5 SAM (a) and  $C_{12}H_{25}SH$  SAM deposited after electrochemical desorption of the initially formed 15-crown-5 layer (b).

ions by arrays of sensing layers. Consequently, our attention again focused on the electrochemical transduction that is able to detect the binding of cations very accurately.<sup>11,12</sup> For individual addressing of the different monolayers it is required to use electrically isolated gold electrodes. To test the electrochemical patterning procedure both electrodes were modified with different self-assembled monolayers (see Fig. 6). After the modification of both electrically isolated halves of the gold substrate with a dodecanethiol monolayer, the whole substrate was immersed in an ethanol solution of 0.1 M KOH. By reductive desorption,<sup>10</sup> one of the dodecanethiol layers was stripped from the addressed electrode. Subsequently, the substrate was immersed into a 1 mM ethanol solution of 11-hydroxyundecanethiol to cover the stripped gold electrode with a hydrophilic SAM.

A first indication of the successful patterning of the gold electrodes was obtained by contact angle measurements. The advancing and receding contact angles of the  $C_{12}H_{25}SH$  monolayer were unaffected by the patterning procedure, while the hydroxy-terminated monolayer was completely wetted. However, contact angle measurements are not sensitive enough to detect incomplete desorption of the monolayer. To obtain a more accurate picture of the electrochemical patterning procedure, grazing-incidence infrared studies were conducted. In this case an initially formed monolayer of 15-crown-5 adsorbate **2** was desorbed and a new SAM of dodecanethiol was adsorbed. Incomplete desorption of the crown ether layer would be detected by its strong absorption peak at  $1138\text{ cm}^{-1}$ , the C–O stretching vibration.<sup>12</sup> As shown in the IR spectra in Fig. 7, the electrochemical desorption of the crown ether SAM and the subsequent assembly of dodecanethiol resulted in the complete disappearance of the C–O absorption peak. In view of the sensitivity of the measurement, it is concluded that at

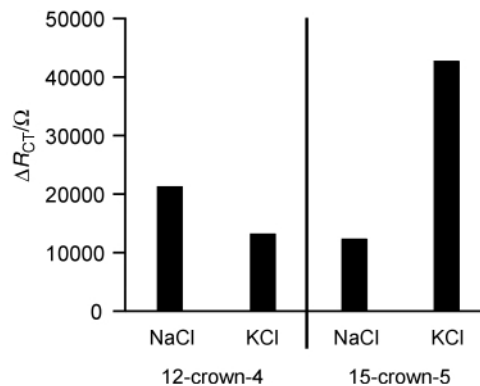


Fig. 8 Change of  $R_{CT}$  at sodium and potassium ion concentrations of 1 mM for electrochemically patterned monolayers of 12-crown-4 and 15-crown-5.

Table 2 Association constants of metal ions with electrochemically patterned and non-patterned crown ether SAMs determined from changes in the charge transfer resistance<sup>a</sup>

	Non-patterned <sup>b</sup>		Electrochemically patterned	
	12-Crown-4	15-Crown-5	12-Crown-4	15-Crown-5
$K_{Na^+}/M^{-1}$	15800	60	7500	4200
$K_{K^+}/M^{-1}$	500	27100	5100	12400

<sup>a</sup> The relative error in the association constants is approx. 10%. <sup>b</sup> The association constants were previously published in ref. 11.

least 95% of the initially formed SAM was removed during the reductive desorption.

Wettability studies and IR spectroscopy both indicated that electrochemical patterning could successfully generate two different monolayers on the same substrate. Therefore, it was used to modify one of the electrodes with a 12-crown-4 SAM and the second electrode with a 15-crown-5 SAM. This was achieved by the assembly of the 15-crown-5 adsorbate **2** on both electrodes, the reductive desorption of one of the layers and the subsequent deposition of a 12-crown-4 SAM. Electrochemical impedance spectroscopy was used to monitor the interactions of both crown ether layers with sodium and potassium ions, utilizing the  $Ru(NH_3)_6^{2+/3+}$  redox couple as reporter ion.<sup>11</sup> From the titration experiments it was evident that the patterned crown ether monolayers were able to bind cations from the aqueous solution, which resulted in a significant increase of the charge transfer resistance ( $R_{CT}$ ). The response of the 12-crown-4 SAM caused by the increase of the  $Na^+$  concentration was higher than for the same  $K^+$  concentration, while the 15-crown-5 SAM showed the opposite trend (see Fig. 8).

The resistance changes of both monolayers were used to determine the association constants ( $K$ ) for sodium and potassium cations, using the previously determined relation between the charge transfer resistance  $R_{CT}$  and  $K$  [eqn. (1)],<sup>11</sup> where  $R_0$  is

$$K_C = \frac{R_{CT}}{R_0} - 1 \quad (1)$$

the charge transfer resistance of the monolayer in the absence of metal ions. A comparison of the association constants for the electrochemically patterned layers with the corresponding non-patterned layers is shown in Table 2. It is evident that the patterning has reduced the selectivity of both layers. Neither the primary adsorbed self-assembled monolayer of 15-crown-5, nor the 12-crown-4 layer that was adsorbed after the desorption of the 15-crown-5 SAM had the selectivity of the original layers. The reduced selectivity of the 12-crown-4 layer was attributed to the incomplete desorption or partial re-adsorption

of the 15-crown-5 adsorbates during the reductive desorption of the layer. Consequently, traces of 15-crown-5 might have been incorporated in the subsequently deposited 12-crown-4 SAM. Similarly, during the deposition of a 12-crown-4 SAM defects in the 15-crown-5 SAM can be filled with the 12-crown-4 adsorbate **1**. Since we have shown that the dilution of a 15-crown-5 monolayer with only 10% of heptanethiol leads to a decrease of the  $K^+/Na^+$  selectivity from  $K_K^+/K_{Na^+} = 300$  to 40,<sup>11</sup> we anticipate that the incorporation of small amounts of the 12-crown-4 adsorbate will have an even larger effect on the monolayer selectivity.

In an attempt to prevent the incorporation of adsorbates at monolayer defects, both 15-crown-5 monolayers were sealed with heptanethiol prior to the desorption of one of the SAMs.<sup>22</sup> However, the selectivities of the resulting patterned layers did not improve. Therefore, it is concluded that the defects in the monolayer have been created during the exposure to the ethanol solution of 0.1 M KOH.<sup>23</sup> During the exposure of the defective layer to a solution of a different adsorbate, the defects were filled and cross-contamination occurred.

## Conclusions

The selective complexation of cations to self-assembled monolayers of crown ethers was detected by XPS and AFM measurement. The binding of cations to the receptor layer results in a repulsive interaction with the AFM tip, as measured by AFM force spectroscopy. Friction force microscopy was used to visualize the patterned monolayers, produced by microcontact printing. However, the detected forces that accompany the cation complexation were too weak to use patterned monolayers of receptor adsorbates for array sensing.

Electrochemically patterned monolayers allowed the impedance spectrometric monitoring of metal ion complexations. During the patterning cross-contamination of both SAMs occurred, which influenced the selectivities of the receptor layers. Despite a reduced selectivity, the use of both monolayer responses allows an accurate discrimination between sodium and potassium ions.

## Experimental

### Materials

The syntheses of the adsorbates 2-(6-mercaptohexyloxy-methyl)-12-crown-4 (**1**),<sup>11</sup> 2-(6-mercaptohexyloxymethyl)-15-crown-5 (**2**),<sup>11</sup> 7,10,13,16-tetraoxaheptadecanethiol (**3**),<sup>11</sup> and *N,N,N',N',N',N'*-hexamethyl-*N,N'*-(4,4'-disulfanediyldiphenyl)bis(aminium) diiodide (**4**)<sup>24</sup> have been described elsewhere.

Gold substrates used for AFM measurements were purchased from Metallhandel Schröer GmbH, Lienen, Germany (200 nm gold on 5 nm chromium on glass substrates [ $11 \times 11$  mm<sup>2</sup>]). Prior to use, the substrates were flame annealed with a H<sub>2</sub> flame (H<sub>2</sub>-quality 6). The annealing yielded reproducibly large Au(111) terraces of a few micrometers in size on which the atomic steps, triangular terraces and the Au(111) lattice could easily be imaged by AFM. After annealing, the substrates were allowed to cool to room temperature and used for the monolayer preparation.

Electrochemically patterned SAMs were prepared on gold substrates, prepared by resistive evaporation of gold (200 nm) on glass slides of 25 mm diameter. A layer of 2 nm of chromium was evaporated onto the glass prior to the deposition of the gold layer in order to improve the adhesion of the gold to the substrate. To obtain two individually addressable electrodes, a thin line of gold was removed with a scalpel.

### Microcontact printing

The preparation of elastomeric PDMS stamps with structures in the range of 1 to 100  $\mu$ m has been described by Whitesides

and co-workers.<sup>4</sup> Patterned monolayers were prepared in analogy to published procedures,<sup>4</sup> using 1 mM ethanol solution adsorbates for the wetting of the stamp. After the formation of a patterned SAM by microcontact printing, the remaining bare gold was modified with a different monolayer by immersion into a 1 mM ethanol solution of the corresponding adsorbate for 15 minutes.

### Electrochemical patterning

The modification of two isolated gold electrodes on a glass substrate with different monolayers was performed similarly to the procedure described by Tender *et al.*<sup>9a</sup> After cleaning of the gold electrodes in an oxygen plasma, the gold surface was immersed for 16 hours in a 1 mM ethanol solution of the adsorbate. Subsequently, the electrodes were immersed in an ethanol solution of 0.1 M KOH, and one of the electrodes was contacted for the reductive desorption of the SAM. The desorption of the monolayer was performed in a three electrode cell (gold working electrode, platinum counter electrode, and silver/silver nitrate reference electrode), by applying a voltage cycling between  $-1.0$  and  $-1.5$  V<sub>Ag/AgNO<sub>3</sub></sub> for 15 minutes. After copious rinsing with ethanol and water, the substrate was immersed for 30 minutes in a 1 mM ethanol solution of a different adsorbate to re-modify the second electrode.

### Instrumentation

Details concerning the contact angle measurements, grazing-incidence infrared spectroscopy, and electrochemical impedance measurements have been described elsewhere.<sup>11</sup>

Atomic force microscopic measurements were carried out with a NanoScope III multimode AFM (Digital Instruments (DI), Santa Barbara, CA, USA) with triangular shaped silicon nitride cantilevers (DI) or with functionalized tips that had nominal spring constants of 0.06 N m<sup>-1</sup>.<sup>17</sup> The force-distance curves were measured in acetonitrile or aqueous solutions utilizing a liquid cell (DI). For laterally resolved pull-off force measurements the SFM was operated in the force volume (FV, DI) mode.

### Tip modification

Triangular shaped silicon nitride cantilevers with silicon nitride tips (DI), which were coated with 2 nm Ti and 75 nm Au in high vacuum (Balzers), were functionalized by immersion into a 1 mM ethanol solution of 4,4'-disulfanediyldiphenylbis(aminium) diiodide. After 15 hours the cantilevers were removed from the solution, rinsed with ethanol, and mounted in the liquid cell.

## References and notes

- 1 L. Zhang, T. Lu, G. W. Gokel and A. E. Kaifer, *Langmuir*, 1993, **9**, 786; K.-D. Schierbaum, T. Weiss, E. U. Thoden van Velzen, J. F. J. Engbersen, D. N. Reinhoudt and W. Göpel, *Science*, 1994, **265**, 1413; K. Motesharei and D. C. Myles, *J. Am. Chem. Soc.*, 1994, **116**, 7413; B.-H. Huisman, R. P. H. Kooyman, F. C. J. M. van Veggel and D. N. Reinhoudt, *Adv. Mater.*, 1996, **8**, 561; I. Turyan and D. Mandler, *Anal. Chem.*, 1997, **69**, 894; R. Blonder, S. Levi, G. Tao, I. Ben-Dov and I. Willner, *J. Am. Chem. Soc.*, 1997, **119**, 10467; A. Friggeri, F. C. J. M. van Veggel and D. N. Reinhoudt, *Langmuir*, 1998, **14**, 5457.
- 2 M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaver, R. H. Grubb and N. S. Lewis, *Chem. Mater.*, 1996, **8**, 2298; B. J. Doleman, M. C. Lonergan, E. J. Severin, T. P. Vaid and N. S. Lewis, *Anal. Chem.*, 1998, **70**, 4177.
- 3 M. J. Tarlov, R. F. B. Donald, Jr. and G. Gillen, *J. Am. Chem. Soc.*, 1993, **115**, 5305; J. Huang and J. C. Hemminger, *J. Am. Chem. Soc.*, 1993, **115**, 3342; J. Huang, D. A. Dahlgren and J. C. Hemminger, *Langmuir*, 1994, **10**, 626.
- 4 A. Kumar and G. M. Whitesides, *Appl. Phys. Lett.*, 1993, **63**, 2002; A. Kumar and G. M. Whitesides, *Science*, 1994, **263**, 60; H. A. Biebuyck and G. M. Whitesides, *Langmuir*, 1994, **10**, 4581; Y. Xia and G. M. Whitesides, *J. Am. Chem. Soc.*, 1995, **117**, 3274; Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 550.

- 5 E. Delamarche, H. Schmid, A. Bietsch, N. B. Larsen, H. Rothuizen, B. Michel and H. Biebuyck, *J. Phys. Chem. B*, 1998, **102**, 3324; T. Pompe, A. Fery, S. Herminghaus, A. Kriele, H. Lorenz and J. P. Kotthaus, *Langmuir*, 1999, **15**, 2398.
- 6 S. Xu and G. Liu, *Langmuir*, 1997, **13**, 127.
- 7 C. B. Ross, L. Sun and R. M. Crooks, *Langmuir*, 1993, **9**, 632; J. K. Schoer, C. B. Ross, R. M. Crooks, T. S. Corbitt and M. J. Hampden-Smith, *Langmuir*, 1994, **10**, 615; F. P. Zamborini and R. M. Crooks, *J. Am. Chem. Soc.*, 1998, **120**, 9700; R. Maoz, S. R. Cohen and J. Sagiv, *Adv. Mater.*, 1999, **11**, 55.
- 8 J. A. M. Sondag-Huethorst, H. R. J. van Helleputte and L. G. Fokkink, *Appl. Phys. Lett.*, 1994, **64**, 285; K. Seshadri, K. Froyd, A. N. Parikh, D. L. Allara, M. J. Lercel and H. G. Craighead, *J. Phys. Chem.*, 1996, **100**, 15900.
- 9 (a) L. M. Tender, R. L. Worley, H. Fan and G. P. Lopez, *Langmuir*, 1996, **12**, 5515; (b) L. M. Tender, K. A. Opperman, P. D. Hampton and G. P. Lopez, *Adv. Mater.*, 1998, **10**, 73.
- 10 C.-J. Zhong and M. D. Porter, *J. Am. Chem. Soc.*, 1994, **116**, 11616.
- 11 S. Flink, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Phys. Chem. B*, 1999, **103**, 6515.
- 12 S. Flink, B. A. Boukamp, A. van den Berg, F. C. J. M. van Veggel and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1998, **120**, 4652.
- 13 R. G. Nuzzo, B. R. Zegarski and L. H. Dubois, *J. Am. Chem. Soc.*, 1987, **109**, 733; D. G. Castner, K. Hinds and D. W. Grainger, *Langmuir*, 1996, **12**, 5083.
- 14 D. Hecht and H.-H. Strehblow, *J. Electroanal. Chem.*, 1997, **440**, 211.
- 15 C. A. Alves, E. L. Smith and M. D. Porter, *J. Am. Chem. Soc.*, 1992, **114**, 1222; J. Pan, N. Tao and S. M. Lindsay, *Langmuir*, 1993, **9**, 1556; C. A. Alves and M. D. Porter, *Langmuir*, 1993, **9**, 3507; G.-Y. Liu, P. Fenter, C. E. D. Chidsey, D. F. Ogletree, P. Eisenberger and M. Salmeron, *J. Chem. Phys.*, 1994, **101**, 4301; H. Schönherr, F. J. B. Kremer, S. Kumar, J. A. Rego, H. Wolf, H. Ringsdorf, M. Jaschke, H.-J. Butt and E. Bamberg, *J. Am. Chem. Soc.*, 1996, **118**, 13051; H. Schönherr, G. J. Vancso, B.-H. Huisman, F. C. J. M. van Veggel and D. N. Reinhoudt, *Langmuir*, 1997, **13**, 1567.
- 16 C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton and C. M. Lieber, *Science*, 1994, **265**, 2071; A. Noy, C. D. Frisbie, L. F. Rozsnyai, M. S. Wrighton and C. M. Lieber, *J. Am. Chem. Soc.*, 1995, **117**, 7943; D. V. Vezenov, A. Noy, L. F. Rozsnyai and C. M. Lieber, *J. Am. Chem. Soc.*, 1997, **119**, 2006; A. Noy, D. V. Vezenov and C. M. Lieber, *Annu. Rev. Mater. Sci.*, 1997, **27**, 381.
- 17 H. Schönherr, Z. Hruska and G. J. Vancso, *Macromolecules*, 1998, **31**, 3679; H. Schönherr and G. J. Vancso, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 2486.
- 18 E.-L. Florin, V. T. Moy and H. E. Gaub, *Science*, 1994, **264**, 415; V. T. Moy, E.-L. Florin and H. E. Gaub, *Science*, 1994, **266**, 257; H. Grubmüller, B. Heymann and P. Tavan, *Science*, 1996, **271**, 997; R. McKendry, M.-E. Theoclitou, T. Rayment and C. Abell, *Nature*, 1998, **391**, 566; M. W. J. Beulen, *Supramolecular Interactions at Functional Self-Assembled Monolayers on Gold*, PhD Thesis, University of Twente, The Netherlands, 1999.
- 19 S. N. Mangonov and M.-H. Whangbo, *Surface Analysis with STM and AFM*, VCH, Weinheim, 1996.
- 20 Repulsive interactions between hydroxy-terminated tips and protonated polyallylamine films have previously been detected: H. Schönherr, *From Functional Group Ensembles to Single Molecules: Scanning Force Microscopy of Supramolecular and Polymeric Systems*, PhD Thesis, University of Twente, The Netherlands, 1999; H. Schönherr, Z. Hruska and G. J. Vancso, *ACS Polym. Mater. Sci. Eng. Prepr.*, 1999, 383. Unlike in water, charging of the AFM tip is unlikely in acetonitrile.
- 21 X. Xiao, J. Hu, D. H. Charych and M. Salmeron, *Langmuir*, 1996, **12**, 235; A. Lio, D. H. Charych and M. Salmeron, *J. Phys. Chem. B*, 1997, **101**, 3800.
- 22 I. Rubinstein, S. Steinberg, Y. Tor, A. Shanzer and J. Sagiv, *Nature*, 1988, **332**, 426; S. Steinberg, Y. Tor, E. Sabatani and I. Rubinstein, *J. Am. Chem. Soc.*, 1991, **113**, 5176; S. Steinberg and I. Rubinstein, *Langmuir*, 1992, **8**, 1183; M. T. Rojas, R. Königer, J. F. Stoddart and A. E. Kaifer, *J. Am. Chem. Soc.*, 1995, **117**, 336.
- 23 Partial desorption of self-assembled monolayers on gold during exposure to organic solvents has been shown with radiolabeling experiments, in J. B. Schlenoff, M. Li and H. Ly, *J. Am. Chem. Soc.*, 1995, **117**, 12528, and has been exploited by our group to isolate single metallodendrimers on gold: B.-H. Huisman, H. Schönherr, W. T. S. Huck, A. Friggeri, H.-J. van Manen, E. Menozzi, G. J. Vancso, F. C. J. M. van Veggel and D. N. Reinhoudt, *Angew. Chem., Int. Ed.*, 1999, **38**, 2248.
- 24 H. Z. Sommer, H. I. Lipp and L. L. Jackson, *J. Org. Chem.*, 1971, **36**, 824.