

Structure Induced Ion Recognition of Self-Assembled Monolayers on Gold

Z. Jiang, S. Liu and Z. Gao^{1*}

Department of Chemistry, Wuhan University, Wuhan, 430072, China.

¹Institute of Bioengineering and Nanotechnology, 51 Science Park Road, Singapore 117586 Republic of Singapore, *Corresponding author: zqgao@ibn.a-star.edu.sg

ABSTRACT

Self-assembled monolayers of anthraquinone-polyethers on gold electrodes were prepared and characterized by various spectroscopic and electrochemical techniques. The monolayers exhibited better thermal stability in wet environments, suggesting that multi-anchoring effect of the molecules improve the integrated adhesion and the binding stability of the monolayers. In contrast to solution electrochemistry, the unique structure and packing of the monolayer lead to selective ion binding to ions with the right size and charge, such as potassium and sodium.

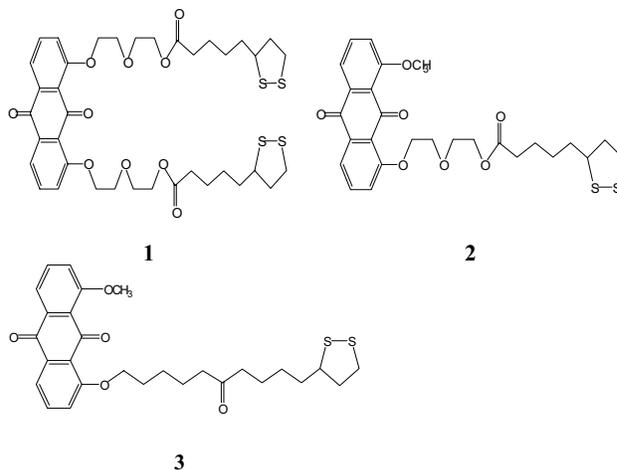
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INTRODUCTION

Interest in self-assembled monolayers/multilayers (SAMs) arises largely from their excellent microstructural definition, which provides a useful platform to probe the relationship between molecular microstructure on electrode surface and macroscopic electrochemical properties such as electron tunneling, electrocatalysis and sensing.^[1] Film durability and stability of these organic monolayers, however, are limited as a result of the relatively easy removal of single organosulfur atoms from solid substrates such as gold.^[1] One way to increase the stability of the SAMs is through the use of a multi-anchoring and/or chelating effect.^[2-4] For example, extremely stable monolayers of bis-thioctic ester derivatives are easily prepared on gold electrodes.^[3,4] No obvious changes are observed for these SAMs after numerous potential scan cycles in the range of 0 - 1000 mV.

Our group has been using self-assembly technique as a means of manipulating molecules with multi-anchoring sites into highly stable monolayers on gold electrodes and exploiting possible ion recognition of these monolayers.^[4-6] In two recent reports,^[5,6] we described the preparation, self-assembly and electrochemical properties of polymeric self-assembled monolayers. In another paper,^[4] crown-ether annelated tetrathiafulvalene derivatives were successfully self-assembled on gold electrodes and the monolayers showed unambiguous ion recognition properties.

In the present work, we report the construction and characteristics of SAMs of the following compounds:



on gold bead electrodes. Surprisingly and in contrast to the behavior of the anthraquinone-polyether compounds in solution, the SAMs showed very high affinity towards alkali metal ions, as evidenced by electrochemical potential shifts of the anthraquinone, even though the molecule contains no polyether macrocycles.

EXPERIMENTAL SECTION

Unless otherwise stated, reagents (analytical-grade or better) were obtained from Sigma-Aldrich (St Louis, MO, USA) and used without further purification. Compounds **1**, **2** and **3** were synthesized via two-step reactions.^[7] Gold bead electrodes were prepared from ultrapure gold wire according to the procedure proposed by Schneir *et al.*^[8] Anthraquinone-polyether monolayers were formed by immersing freshly prepared gold bead electrodes in a tetrahydrofuran (THF) (or dimethyl sulfoxide) solution containing 0.20 - 1.0 mM of the corresponding compounds. The adsorption time was usually 20 - 24 h. Soaking the gold electrodes for a longer time did not affect the characteristics of the resulting monolayers. After adsorption, the electrodes were copiously rinsed with THF and dried under a nitrogen gas stream. Potentials in this work are referred to a non-aqueous Ag/Ag⁺ (0.010 M AgNO₃ in acetonitrile) reference electrode.

RESULTS AND DISCUSSION

The formation of the monolayers was monitored by various spectroscopic techniques, including ellipsometry and FT-IR. Comparison of the reflection-absorption IR spectra with conventional transmission spectra revealed that weaker absorptions were persistent in all three SAMs for the C=O stretching at 1735 cm^{-1} , -C-O-C- stretching at 1120 cm^{-1} and significant increases in the ratios between the asymmetric and the symmetric C-H stretching in CH_2 at about 2926 and 2850 cm^{-1} indicating that the hydrocarbon chains in the monolayer are oriented approximately normal to the gold substrate. The thickness of the SAMs, estimated from ellipsometric measurements, was found to be in the range of $21 \pm 2.5\text{ \AA}$. All of the above data indicated that the SAMs are densely packed and well-organized with fully extended polyether chains slightly tilted to the surface normal [9]. The surface coverage of the anthraquinone-polyether SAMs was examined by cyclic voltammetry and electrochemical impedance spectroscopy. As illustrated in Fig. 1, the redox response of ferricyanide/ferrocyanide was completely blocked by the anthraquinone-polyether monolayer on gold electrode, suggesting the formation of well-packed monolayers with negligible defects.^[1] As demonstrated by Rubinstein *et al.*,^[10] electrochemical impedance is a more reliable and less perturbing means of evaluating the surface coverage of SAMs. The values of the surface coverage derived from impedance spectra were generally larger than 99.9%, indicating again that densely-packed monolayers were formed on the gold electrodes.

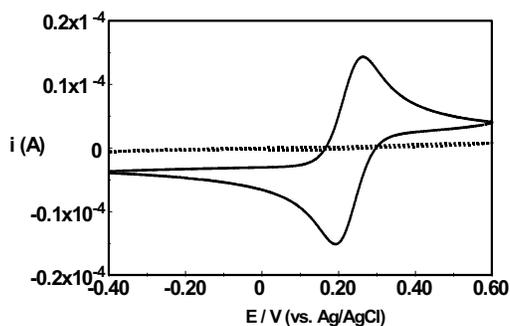


Fig. 1. Voltammograms of $5.0\text{ mM K}_3\text{Fe(CN)}_6$ at a bare gold (-) and an anthraquinone-polyether monolayer coated gold electrode (- -). 0.10 M KNO_3 , scan rate 100 mV/s .

Since the SAMs contain redox-active anthraquinone moieties, surface-confined electrochemical activities are anticipated. The electrochemical behavior of these compounds in solution is similar to that of other previously reported substituted anthraquinones.^[11] For examples, as shown in Fig. 2, the voltammograms of **1** and **2** in THF solution exhibited the usual two quasi-reversible redox waves characteristic of anthraquinones, corresponding to the two one-electron transfer processes leading to the

formation of the dianionic anthraquinone. As can be seen in Fig. 2, the second process, as has been found with other anthraquinone systems, is somewhat chemically and electrochemically irreversible.^[11] Addition of various amounts of alkali metal salts to this solution had no observable effect on the voltammetric behavior of these compounds, implying that no significant complexation occurs in solution. This is not surprising in view of the fact that no cyclic polyether macro-ring is present and only three ether oxygen atoms are present on each of the connected chains.

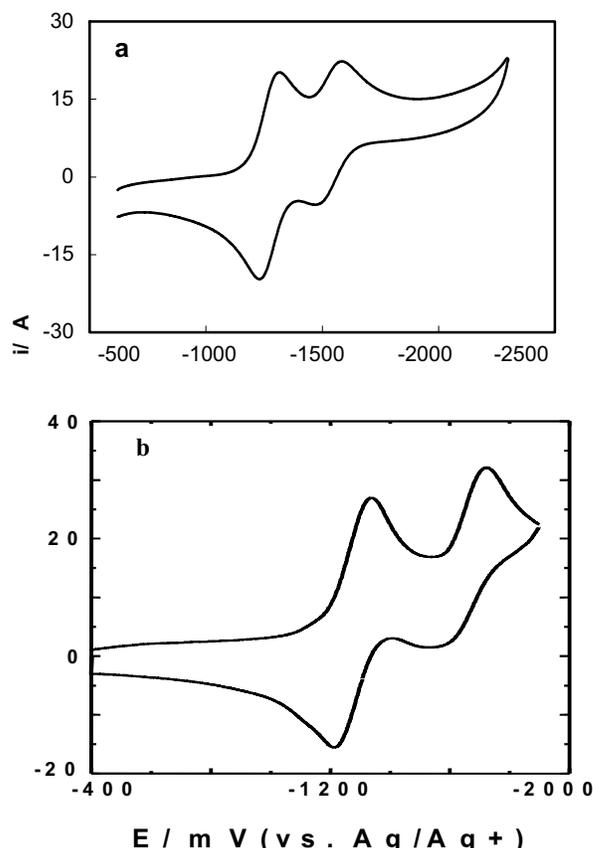


Fig. 2. Voltammograms of 0.20 mM 1 (a) and 2 (b) at 100 mV/s in THF containing $0.10\text{ M TBAPF}_6 + 1.0\text{ mM KPF}_6$.

Fig. 3 shows cyclic voltammograms of monolayer **1** coated gold electrode in THF containing 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF_6). Two pairs of voltammetric peaks appeared at potentials of around -1400 mV and -1600 mV , corresponding to the two one-electron transfer processes of the anthraquinone moieties in the monolayers. Furthermore, unlike the electrochemistry of anthraquinone-polyether derivatives in solution (Fig. 2 and reference 11), both electron transfer processes were clearly resolved and highly reversible. When cyclic voltammetry was conducted at different scan rates, good linearity between the peak currents and the scan rates up to 500 mV/s was obtained, suggesting typical surface-confined voltammetric behavior. Further evidence of the surface-confined voltammetric behavior was obvious

from the Gaussian shapes of the voltammetric peaks and the negligibly small peak-to-peak potential separation, generally in the range of 10 - 20 mV. The surface coverage, calculated from the charge under the first reduction peak of the first scan cycle, was 2.37×10^{-10} mol/cm². However, the charge under the second peak was always much smaller than that of the first peak, suggesting a partial redox process which may be due to the difficulty in getting bulky TBA⁺ counter ions into the monolayer, since the anthraquinone-polyether molecules are highly organized and densely packed on the electrode. Upon repetitive potential cycling in the range of 0 to -1800 mV the monolayer showed little change, implying a very robust monolayer due to the multi-anchoring effect of the disulfides. When the potential was scanned to a more negative value than -1800 mV, considerable amounts of the anthraquinone polyether monolayers were removed from the gold electrode, presumably due to the electrochemical reduction of the sulfur-gold bonds. For example, after 20 cycles between 0 and -1900 mV at a scan rate of 100 mV/s, only a small fraction (< 30%, estimated from the loss of charge under the first reduction peak) of the electrode was covered with the anthraquinone-polyether molecules. Similar behaviors were obtained for SAMs of **2** and **3**.

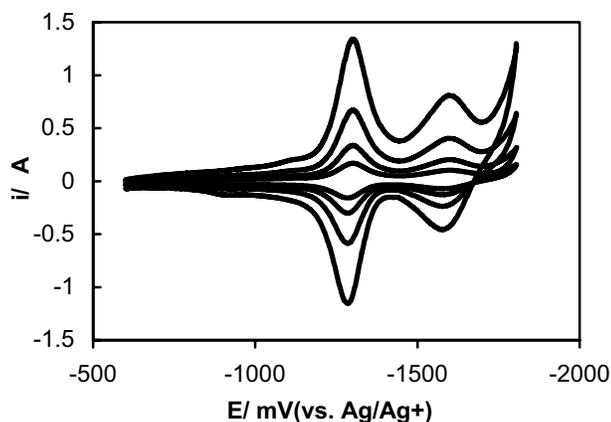


Fig. 3. Cyclic voltammograms of SAMs of **1** in THF solution of 0.10 M TBAPF₆. Potential scan rate, from the innermost, 10, 20, 50 and 100 mV/s.

The effect of alkali metal ions on the voltammetric responses of the anthraquinone-polyether monolayers was investigated by cyclic voltammetry in 0.1 M TBAPF₆ solution containing 1.0 mM of the hexafluorophosphate or perchlorate salt of the metal ion. Of all of the ions tested (K⁺, Na⁺, Li⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺ and Ba²⁺), only K⁺ and Na⁺ resulted in distinct voltammetric changes. The voltammograms recorded for the SAMs in K⁺ solution are shown in Fig. 4. For SAMs of **1** (Fig. 4a), both redox waves shifted to less negative potentials, indicating that strong ion binding occurs in solution.^[3] Interestingly, for SAMs of **2**, when the potassium salt was added to the electrolyte, a new pair of redox waves appeared at -730 mV and the peak currents increased gradually with the number of potential cycles. Simultaneously, the original peaks at -1375 mV

diminished after a few cycles (Fig. 4b). These changes were observable even at K⁺ concentration as low as 5.0 M. However, if the potential cycling was conducted between 0 and -1100 mV, i.e. reversing the potential before the first reduction peak, no new peaks were observed after numerous cycles, suggesting that the K⁺-binding is assisted by the negative charges generated during the reduction of the monolayer.

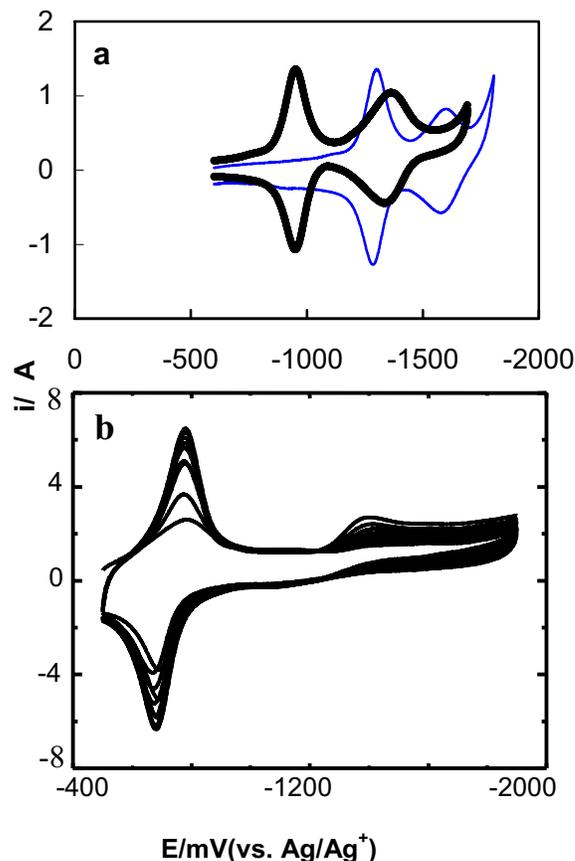


Fig. 4. Cyclic voltammograms of SAMs of **1** (a) and **2** (b) in THF solution containing 0.10 M TBAPF₆ and 1.0 mM KPF₆. Potential scan rate 100 mV/s.

It appears that the peaks at -730 mV correspond to the reduction of the anthraquinone in close association with K⁺. In the presence of K⁺, such anodic shifts of anthraquinone crown ethers due to complexation with Mⁿ⁺ in solution are well documented.^[11] The anodic shift of the redox potential is closely associated with the cation binding interaction. (For example, an anodic shift of 320 mV corresponds to a cation binding enhancement of 2.6×10^5 times in solution^[4,11]). The anodic shift observed here, 645 mV, indicates extremely strong binding of K⁺. Upon addition of 5.0 mM cryptand [2,2,2] to the solution, the effect of K⁺ was eliminated and the current peaks shifted back to the original positions. Similar behavior was also observed for Na⁺, but the anodic shifts of the redox potentials were much smaller. As listed in Table 1, after adding 1.0 mM NaPF₆ to the solution, both the first and the second redox processes were

anodically shifted by about 195 mV. The effect of Na^+ was also reversibly eliminated by adding 5.0 mM cryptand [2,2,2]. Essentially the same voltammetric responses were observed with anthraquinone-polyether monolayers prepared in the presence of alkali metal ions. To verify the ion binding behavior, the polyethers in the anthraquinone derivatives were replaced by hydrocarbons (compound **3**). SAMs of **3** showed similar electrochemical characteristics to these of **1** and **2**, but alkali ion effect was not observable in solutions containing as high as 5.0 mM of alkali ions.

Table 1. Voltammetric data of monolayers **1** and **2** in THF containing different salts.

Solution	SAM of 1		SAM of 2	
	$E_{1/2}^1$ (mV)	$E_{1/2}^2$ (mV)	$E_{1/2}^1$ (mV)	$E_{1/2}^2$ (mV)
0.10 M TBAPF ₆	-1300	-1590	-1370	-1690
0.10 M TBAPF ₆ 1.0 mM KPF ₆	-950	-1350	-730	-----
0.10 M TBAPF ₆ 1.0 mM NaPF ₆	-1110	-1420	-1180	-1500
0.10 M TBAPF ₆ 1.0 mM LiPF ₆	-1310	-1610	-1375	-1690
0.10 M TBAPF ₆ 1.0 mM RbClO ₄	-1305	-1600	-1375	-1690
0.10 M LiPF ₆ 1.0 mM KPF ₆	-955	-1355	-730	-----

The parameters reflecting the effect of metal ion additions on the voltammetric responses of anthraquinone-polyether monolayers are summarized in Table 1. Note that the K^+ induced response was observed even for solutions containing 100-fold excess of other alkali metal ions, indicating excellent selectivity of the anthraquinone-polyether monolayer towards potassium ion binding. As mentioned previously, solution electrochemistry of **1** and **2** with alkali metal ions showed no sign of ion recognition even in the presence of large excesses of alkali metal ions. The ion-recognizing properties of the anthraquinone-polyether monolayer must thus be originated from the self-assembled architecture. The packing of the molecules in the SAMs is so dense (see above) that intermolecular cooperative binding effects are possible, which cannot occur in solution. Analogous behavior was published recently, showing that strong intermolecular hydrogen bonding occurs within densely packed monolayers.^[12-13] As schematically illustrated in Fig. 5, it is possible that "pseudo crown ether" structures are formed during self-assembly of the anthraquinone-polyether molecules on the gold electrode, and these show very strong affinity towards K^+ and Na^+ . However, in order to form complexes with such structures in the SAMs, alkali metal ions must be of the appropriate size and charge to be able to penetrate into the monolayer. Cyclic voltammetric experiments indicated that the anthraquinone-polyether molecules are highly organized and densely packed on the gold surface and therefore somewhat impenetrable (Fig. 1). On the other

hand, electrochemical reduction of the monolayer introduces negative charges which attract positively charged species from the solution, especially K^+ and Na^+ , and help them access the binding sites in the monolayer where they form very stable complexes with the monolayers. Removal of K^+ or Na^+ ions from the monolayers is only possible by introducing a very strong complexing reagent such as cryptand [2,2,2].

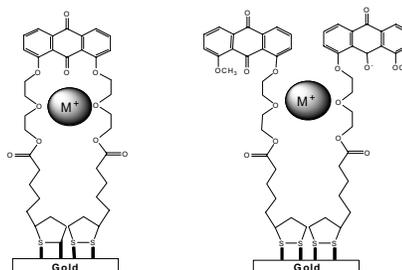


Fig. 5. Illustration of the formation of alkali metal complexes with the monolayers on gold electrodes.

In conclusion, the present work has demonstrated the ability of the anthraquinone-polyether monolayer to bind potassium and sodium ions. The unusually high selectivity is probably the result of the unique structure and packing density of the compound on the surface, which allows cooperative binding to occur but only for ions with the right size and charge to penetrate and fit the monolayer.

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