

Selective Electrostatic Binding of Ions by Monolayers of Mercaptan Derivatives Adsorbed to Gold Substrates

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A single, self-assembled monolayer of organic material is used to impart pH-dependent electrostatic-based recognition capability to an Au electrode. The results show that 4-aminothiophenol and related mercaptans change the surface characteristics of naked Au toward the adsorption of positively and negatively charged ions as a function of pH. For example, anthraquinone-2,6-disulfonate irreversibly adsorbs to naked Au surfaces over a broad range of pH. However, a preadsorbed monolayer of 4-aminothiophenol prevents adsorption of anthraquinone-2,6-disulfonate at high pH but electrostatically binds it at low pH. The principle of pH-dependent binding is general for a number of amine-, carboxylic acid-, and pyridine-terminated mercaptan derivatives adsorbed to Au surfaces.

Introduction

In this paper we report that a single monolayer of organic material can be used to impart pH-dependent molecular recognition capability to an Au electrode. Our results show that 4-aminothiophenol (4-ATP) and related mercaptans change the surface characteristics of naked Au toward the adsorption of positively and negatively charged ions as a function of pH. For example, anthraquinone-2,6-disulfonate (2,6-AQDS²⁻) irreversibly adsorbs to naked Au surfaces over a broad range of pH. However, a preadsorbed monolayer of 4-ATP prevents adsorption of 2,6-AQDS²⁻ at high pH but electrostatically binds 2,6-AQDS²⁻ at low pH. The principle of pH-dependent binding is general for a variety of mercaptan derivatives adsorbed to Au surfaces.

Electrodes are often intentionally modified with thick layers of organic polymers to perform specific tasks such as catalysis or passivation. However, the morphology of polymers is difficult to control, and therefore the function of polymer-modified electrodes is often erratic and nonreproducible. Many mercaptan derivatives undergo self-assembly to form organized, surface-confined monolayers that do not suffer from ill-defined or nonreproducible morphological characteristics.¹⁻³ These and other advantages of ultrathin films have prompted us to design monolayer structures that impart desirable functions to electrode surfaces.

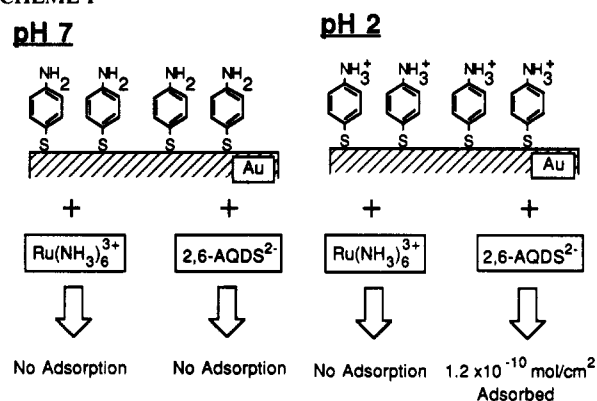
The results reported here relate to our interest in using modified surfaces as molecular recognition membranes for chemical sensors. Molecular recognition is best implemented by creating sites that exhibit both physical and chemical interactions with target analytes.^{4,5} However, to simplify initial experiments we have chosen to explore these two elements separately; the preliminary results discussed here deal only with molecular discrimination by electrostatic interactions between an adsorbed monolayer and a dissolved redox species. Subsequent publications will focus on aspects of physical recognition and integration of chemical and physical recognition elements into a single, surface-confined monolayer structure.

Experimental Section

Anthraquinone-2,6-disulfonic acid, disodium salt, was used as received from Aldrich Chemical Co. Ru(NH₃)₆Cl₃ was used as received from Strem Chemicals, Inc. 4-Aminothiophenol (4-ATP) was obtained from Aldrich and vacuum-sublimed prior to use. Buffer solutions were made from analytical reagents. pH 2.1 and 7.2 phosphate buffers, nominally pH 2 and 7, had an analytical phosphate concentration of 0.1 M and were made from equimolar mixtures of H₃PO₄ and NaH₂PO₄ or NaH₂PO₄ and Na₂HPO₄, respectively. Water was purified by a Milli-Q filtering system (Millipore). All solutions were degassed with N₂ prior to use.

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SCHEME I



Data were obtained on a BAS 100A cybernetic potentiostat. All potentials are reported vs an Ag/AgCl, KCl (saturated) reference. E° values were obtained from the average of the potentials corresponding to the peak cathodic, $i_{p,c}$, and peak anodic, $i_{p,a}$, currents. About 70–80% of the solution resistance was electronically compensated. A flow-through Kel-F cell was used that allowed all surface modification and adsorption steps to be carried out in the absence of O₂ and without removing the electrode from the solution phase. Electrodes (area = 0.317 cm²) were made by patterning Au onto Si wafers by e-beam deposition; an intermediate molecular glue was used to bind the Au and Si.⁶ Immediately prior to modification electrodes were cleaned by immersion in hot "piranha" solution (3 H₂SO₄:1 H₂O₂) and subsequent electrochemical reduction of any surface oxide that might have been present.

Results and Discussion

4-ATP has been used as the pH-sensitive surface modifier for these experiments. 4-ATP-modified surfaces were prepared by soaking a clean Au electrode in a 10 mM 4-ATP ethanol solution for several hours. Under these conditions, a single monolayer of 4-ATP spontaneously adsorbs to the Au surface through a thiolate interaction,³ and it may self-assemble to form an organized,

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TABLE I: Electrochemical Characteristics of Anthraquinone-2,6-disulfonate (2,6-AQDS²⁻) at Naked and 4-Aminothiophenol (4-ATP)-Modified Au Electrodes

electrode/substrate	pH 2			pH 7		
	$E^{\circ'}$, V	ΔE_p , mV	$\Gamma_0 (\times 10^{10})$, mol/cm ²	$E^{\circ'}$, V	ΔE_p , mV	$\Gamma_0 (\times 10^{10})$, mol/cm ²
Au/2,6-AQDS ²⁻ -bulk	-0.085	290		-0.324	184	
Au/2,6-AQDS ²⁻ -ads	-0.045	30	0.61	-0.340	60	0.80
Au/4-ATP/2,6-AQDS ²⁻ -bulk	-0.050	416		-0.332	268	
Au/4-ATP/2,6-AQDS ²⁻ -ads	-0.060	60	1.20			

close-packed monolayer.⁷ Since the pK_a of 4-ATP should be close to that of aniline, $pK_a = 4.6$, the modified electrode surface will be positively charged at low pH but electrically neutral at high pH. Indeed, we have found that the 4-ATP-modified surfaces selectively bind negatively charged molecules, such as 2,6-AQDS²⁻, at low pH but not at high pH and that positively charged molecules, such as $Ru(NH_3)_6^{3+}$, are not bound at any pH. This pH-dependent function is illustrated in Scheme 1, and the electrochemical characteristics of the Au/4-ATP/2,6-AQDS²⁻ systems are summarized in Table I.

Cyclic voltammograms of 5 mM 2,6-AQDS²⁻ at a naked Au electrode in pH 2 and 7 phosphate buffers are shown in Figure 1, a and b, respectively. Diffusion waves for the reduction and oxidation of bulk 2,6-AQDS²⁻ are present at -0.230 and +0.060 V at pH 2, while the analogous waves at pH 7 are at -0.416 and -0.232 V, respectively. The 47 mV/pH unit shift in $E^{\circ'}$ from -0.085 V at pH 2 to -0.324 V at pH 7 is midway between that expected for a two-electron, one-proton redox process, 30 mV/pH unit, and a two-electron, two-proton process, 59 mV/pH unit.⁸ This behavior can be accounted for by noting that reduction of 2,6-AQDS²⁻ at pH 2 results in formation of a dihydroquinone, while at pH 7 one of the phenolic protons is only partially protonated, $pK_a = 7.35$.⁹ The large potential difference between the cathodic and anodic peaks, $\Delta E_p = E_{p,c} - E_{p,a}$, particularly at pH 2, is primarily the result of slow electron-transfer kinetics, but it also incorporates a significant component of uncompensated solution resistance. Features similar to those shown in Figure 1a,b have been observed previously at Hg electrodes.¹⁰

Naked Au electrodes irreversibly bind 2,6-AQDS²⁻ over a wide range of pH. To illustrate this, clean Au electrodes were dipped into pH 2 and 7 buffer solutions containing 5 mM 2,6-AQDS²⁻ for 10 min, rinsed, and then immersed in pure buffer solutions containing no bulk 2,6-AQDS²⁻. The cyclic voltammetric response of these electrodes (Figure 1c,d) shows that irreversible adsorption of 2,6-AQDS²⁻ takes place at both pH 2 and 7. Figure 1e,f shows the corresponding voltammetry for identically treated Au electrodes that were not soaked in the 2,6-AQDS²⁻ solutions. For thermodynamically reversible surface waves ΔE_p is 0, the width of the waves at half-height is equal to 45.3 mV for a two-electron process, and the cathodic and anodic peak current, $i_{p,c}$ and $i_{p,a}$, are proportional to the scan rate.⁸ The waves shown in Figure 1c,d deviate from the ideal values: $\Delta E_p = 30$ and 60 mV at pH 2 and 7, and the half-wave widths of the cathodic and anodic waves are about 100 mV. However, $i_{p,c}$ and $i_{p,a}$ are proportional to the scan rate and $E^{\circ'}$, -0.045 at pH 2 and -0.340 V at pH 7, is close to that of bulk 2,6-AQDS²⁻. These features are consistent with those expected for a quasireversible electron-transfer reaction to irreversibly adsorbed 2,6-AQDS²⁻. The integrated current under the reduction waves for 2,6-AQDS²⁻ corresponds to an average surface coverage, Γ_0 , of 0.61×10^{-10} and 0.80×10^{-10} mol/cm² at pH 2 and 7, respectively.

Our results for the adsorption of 2,6-AQDS²⁻ onto naked Au are comparable to those previously obtained for adsorption onto Pt and Hg electrodes. Soriaga and Hubbard^{11,12} found that

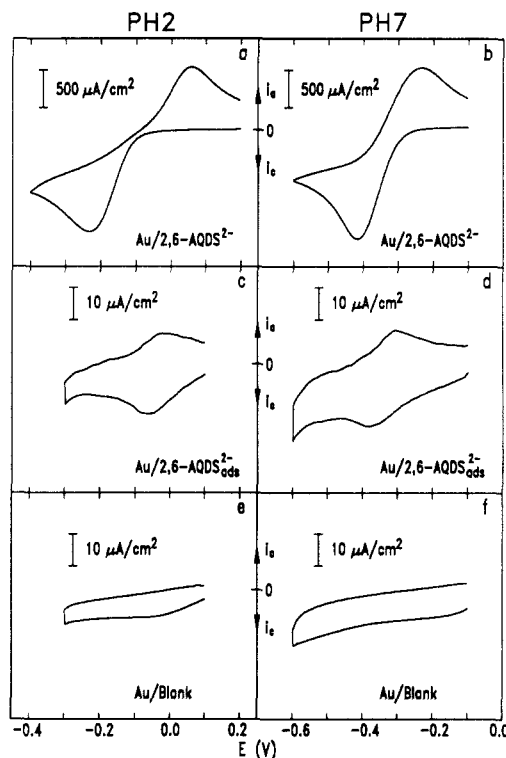


Figure 1. Cyclic voltammetry obtained at naked Au electrodes (area = 0.317 cm²) in pH 2 and 7 phosphate buffers ([PO₄³⁻] = 0.1 M). Scan rate = 0.10 V/s. (a) pH 2, 5 mM 2,6-AQDS²⁻, $E^{\circ'} = -0.085$ V. (b) pH 7, 5 mM 2,6-AQDS²⁻, $E^{\circ'} = -0.324$ V. (c) pH 2, surface-confined 2,6-AQDS²⁻ obtained by dipping the electrode into 5 mM 2,6-AQDS²⁻ for 10 min and rinsing with pH 2 buffer, $E^{\circ'} = -0.045$ V, and $\Gamma_0 = 0.61 \times 10^{-10}$ mol/cm². (d) pH 7, surface-confined 2,6-AQDS²⁻ obtained by dipping the electrode into 5 mM 2,6-AQDS²⁻ for 10 min and rinsing with pH 7 buffer, $E^{\circ'} = -0.340$ V, and $\Gamma_0 = 0.80 \times 10^{-10}$ mol/cm². (e) pH 2 phosphate buffer only. (f) pH 7 phosphate buffer only. Potentials vs Ag/AgCl, KCl (saturated).

2,6-AQDS²⁻ adsorbed irreversibly onto Pt, $\Gamma_0 = 1.3 \times 10^{-10}$ mol/cm², but that electrochemical reduction of the adsorbed material was chemically and thermodynamically irreversible. He et al.¹⁰ reported that 2,6-AQDS²⁻ adsorbed reversibly onto Hg electrodes and gave rise to nearly ideal, thermodynamically reversible surface electrochemistry. The equilibrium surface coverage was found to be a function of the bulk concentration, obtaining a maximum value of about $\Gamma_0 = 0.8 \times 10^{-10}$ mol/cm². The differences in behavior on Au, Pt, and Hg are probably due to differences in the orientation of the adsorbate on the metal surface.¹³

The cyclic voltammetry of 5 mM 2,6-AQDS²⁻ at 4-ATP-modified electrodes at pH 2 and 7 is shown in Figure 2, a and b, respectively. The shapes of these waves are similar to those obtained at naked Au electrodes except for an increase in ΔE_p that probably arises from a decrease in the electron-transfer kinetics resulting from the presence of the 4-ATP barrier layer.²

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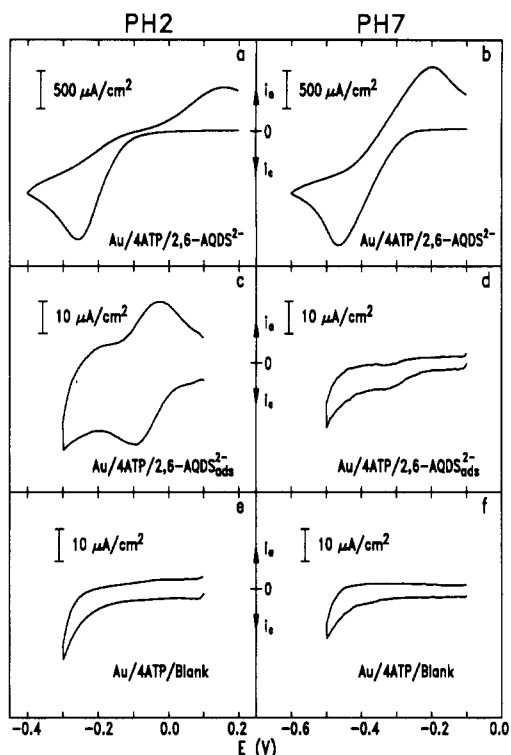


Figure 2. Cyclic voltammetry obtained at 4-ATP-modified Au electrodes (area = 0.317 cm²) in pH 2 and 7 phosphate buffers ([PO₄³⁻] = 0.1 M). Scan rate = 0.10 V/s. (a) pH 2, 5 mM 2,6-AQDS²⁻, $E^{\circ'}$ = -0.050 V. (b) pH 7, 5 mM 2,6-AQDS²⁻, $E^{\circ'}$ = -0.332 V. (c) pH 2, surface-confined 2,6-AQDS²⁻ obtained by dipping the modified electrode into 5 mM 2,6-AQDS²⁻ for 10 min and rinsing with pH 2 buffer, $E^{\circ'}$ = -0.060 V and Γ_0 = 1.2×10^{-10} mol/cm². (d) pH 7, voltammetry obtained by dipping the ATP-modified electrode into 5 mM 2,6-AQDS²⁻ for 10 min and rinsing with pH 7 buffer. (e) pH 2 phosphate buffer only. (f) pH 7 phosphate buffer only. Potentials vs Ag/AgCl, KCl (saturated).

The positions of $E^{\circ'}$, -0.050 V at pH 2 and -0.332 V at pH 7, are not significantly different from the corresponding values at naked Au substrates.

pH-dependent adsorption of 2,6-AQDS²⁻ by the 4-ATP-modified electrode is demonstrated in Figure 2c,d. Identical electrodes were modified with 4-ATP and allowed to soak in pH 2 or 7 solutions containing 5 mM 2,6-AQDS²⁻ for 10 min at open circuit. The electrodes were removed, rinsed with buffer solution, and placed in a buffer solution that did not contain any intentionally added 2,6-AQDS²⁻. Figure 2c,d shows the striking pH-dependent adsorption characteristics of the 4-ATP-modified electrode. At pH 2, two persistent waves are present at -0.090 and -0.030 V, but at pH 7 only a single, much smaller wave is observed. The wave at pH 7 might result from adsorption at naked Au defect sites within the monolayer; however, it vanishes after the first scan. The heights of the waves obtained at pH 2 stabilize at about 50% of their initial values after two or three scans. The loss of surface-confined material at pH 2 may be associated with the cathodic background process which occurs at more positive potentials at the modified electrode (Figure 2e) than at the naked electrode (Figure 1e). The waves at pH 2 are centered at $E^{\circ'}$ = -0.060 V and ΔE_p = 60 mV, about the same as for 2,6-AQDS²⁻ adsorbed

to naked Au substrates, and i_{pc} is proportional to scan rate. When the electrode used to obtain the data shown in Figure 2c was briefly dipped into the pH 7 buffer solution and then scanned at pH 2, no waves were observed. These facts are consistent with the presence of a layer of 2,6-AQDS²⁻ electrostatically bound to the electrode surface at pH 2, but not at pH 7.⁸

Integration of the faradaic current associated with the reduction of surface-confined 2,6-AQDS²⁻ (Figure 2c) results in a charge corresponding to an average Γ_0 = 1.2×10^{-10} mol/cm². The results of chronocoulometry are in general agreement with the cyclic voltammetry, but due to the difficulty of obtaining a useful background capacitive current the cyclic voltammetry probably provides a more quantitative estimate of the surface coverage.⁸

For comparison, Figure 2e,f shows the background cyclic voltammograms obtained at 4-ATP-modified electrodes that had not been soaked in 2,6-AQDS²⁻. Interestingly, we noted that potential excursions positive of about 0.6 V result in a large anodic current and apparent loss of all surface-confined 4-ATP.

We also tested the effect of a 4-ATP-modified electrode on the electrochemistry of a positively charged probe molecule, Ru(NH₃)₆³⁺. The reduction of 5 mM Ru(NH₃)₆³⁺ at either naked or 4-ATP-modified Au electrodes is thermodynamically reversible at pH 2 and 7. The cyclic voltammetry of a 4-ATP-modified electrode that had been soaked in a 5 mM solution of Ru(NH₃)₆³⁺ and then transferred to a solution containing only buffer indicated no adsorption at either pH 2 or 7 in accordance with our claim that adsorption primarily results from electrostatic interactions between the adsorbate and the surface-confined 4-ATP.

Conclusions

We have demonstrated that it is possible to modify an electrode surface with a pH-sensitive organic monolayer that discriminates between solution phase redox species on the basis of electrostatic charge. When the solution pH is less than the pK_a of surface-confined 4-ATP, adsorption of negatively charged ions occurs. However, adsorption does not occur if the pH of the solution is raised high enough to fully deprotonate 4-ATP. Moreover, 2,6-AQDS²⁻ adsorbed at pH 2 can be released by increasing the solution pH.

The principle of pH-dependent binding is quite general. For example, results similar to those discussed here have been obtained by using 4-mercaptopyridine as the surface-modifying agent. We have also seen evidence that electrodes modified with carboxylic acid-terminated *n*-alkyl mercaptans bind positively charged ions at high pH but not at pH < pK_a .

We are presently designing more sophisticated mono- and multilayer¹⁴ structures derived from self-assembling molecules and electrostatically bound, redox active ions for applications related to charge trapping¹⁵ and molecular recognition.

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