

# Adsorption of 1,10-Phenanthroline within a Dodecanethiol Monolayer: An Approach to a Switchable Electrode Surface

Kuang-Yu Hou, Lei Yu, Mark W. Severson, and Xiangqun Zeng\*

Department of Chemistry, Oakland University, Rochester, Michigan 48309

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A simple method was used to prepare a “switchable” electrode surface by using self-assembled monolayers of dodecanethiol on a gold electrode. The dodecane-modified electrode was electrochemically inactive until the monolayer was soaked in solutions of 1,10-phenanthroline or 2,2'-bipyridine. The electroactive form of the electrode could be reverted back to the nonelectroactive form by rinsing the electrode. Surface IR results showed that both dodecanethiol and 1,10-phenanthroline exist in the mixed monolayer.

## Introduction

Self-assembled monolayers (SAMs) prepared from organo-sulfur or organoamine/imine compounds on metals such as gold or silver have been investigated intensively due to their unique chemical and physical properties and their potential for a wide range of applications.<sup>1–3</sup> Alkylthiols, such as 1-*n*-dodecanethiol (C<sub>12</sub>H<sub>25</sub>SH), spontaneously adsorb from solution or the vapor phase onto oxide-free metals to form oriented closely packed monolayers. The ease and flexibility of the self-assembly process provides a convenient method for altering the properties of the metal as an electrode. The alkylthiols are bound to the electrode surfaces via strong gold–sulfur bonds. Once they are adsorbed on the electrode surface, the resulting monolayer is very stable in aqueous or organic solutions within a large range of electrode potentials. The closely packed hydrophobic layer prevents direct contact of most solution species with the metal surface. Consequently, interfacial capacitances are markedly reduced and most electron-transfer reactions are strongly inhibited.

The production of materials with micrometer- or submicrometer-scale patterns is of importance in a range of applications such as photonic materials,<sup>4,5,6</sup> high-density magnetic data storage devices,<sup>7</sup> microchip reactors,<sup>8</sup> and biosensors.<sup>9</sup> Recently, great progress has been made in using monolayers to create chemical patterns on surfaces with microscale masks<sup>10</sup> or microcontact printing techniques.<sup>11</sup> However, to develop such surfaces, a detailed understanding of the structure and stability of multicomponent monolayers on the nanometer scale is needed. One critical aspect of this problem is controlling the state of mixing of adsorbate molecules, which differ greatly in one or more structural elements, e.g., terminal functional group, molecular length, and chain substitution.<sup>12</sup> In monolayers containing alkanethiolate molecules, previous studies have found that films can be constructed in which one component will distribute randomly in a matrix of a second component,<sup>13</sup> segregate into domains,<sup>14,15</sup> or be displaced from the film into solution by the second component.<sup>16</sup>

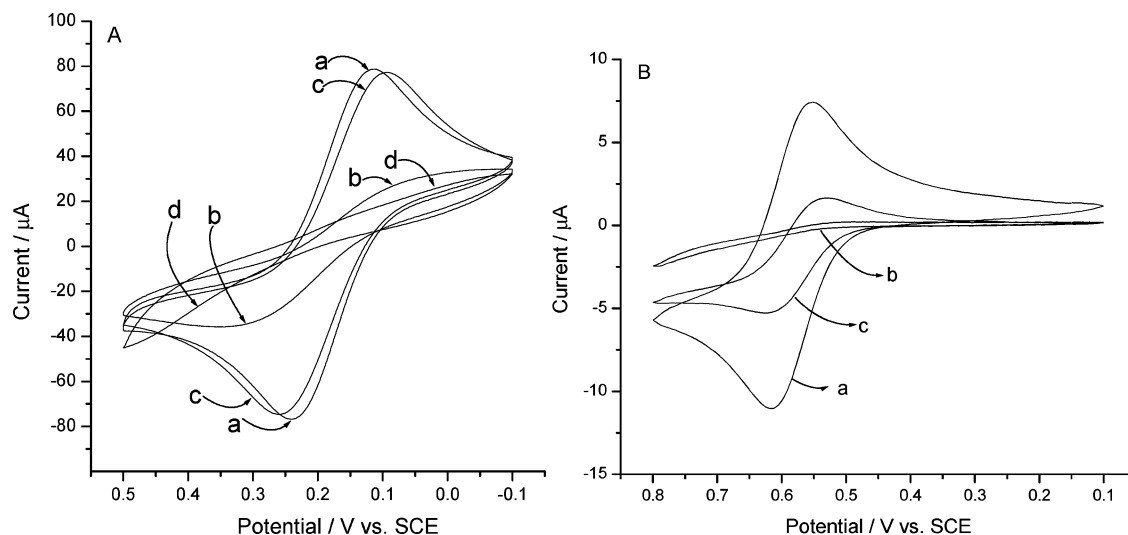
Within the closed compact domain, the alkylthiol monolayer is lattice-like. However, pinholes or defects cannot be avoided at the domain boundaries and the substrate's defect sites, especially on a polycrystalline metal substrate. Taking advantage

of the defects and pinholes, some microscale or submicroscale patterned surfaces have been achieved by inserting thiolated conjugated molecules into the defects or pinholes of the host alkylthiol monolayers.<sup>12,17</sup> Each guest molecular domain is isolated by the two-dimensional matrix of the host alkylthiol monolayer. The guest molecules have a thiol group and bind to the substrate via the Au–S interaction at boundaries between structural domains and at substrate step edges. The defects or pinholes can also be the nucleation sites of the electropolymerization of conducting polymers.<sup>4,18</sup> The deposited conducting polymer islands behave as microelectrodes.

In the present work, a mixed monolayer was prepared by combining alkylthiol-based organic compounds and polypyridine compounds. Heterocyclic molecules such as pyridine, 4,4'-bipyridine (4,4'-bpy), 2,2'-bipyridine (2,2'-bpy), and 1,10-phenanthroline (1,10-phen) have also been found to adsorb onto gold, silver, or copper surfaces to form a compact monolayer in vacuum and in solution<sup>19–26</sup> through the interaction between the nitrogen lone-pair electrons and the metal surface.<sup>3</sup> Due to the aromatic structure of pyridine, bipyridine, and phenanthroline, the monolayers of those heterocyclic molecules are not insulators, and electrochemical reactions can occur directly on such modified electrodes. The aromatic molecules act as electron intermediates or as “shuttles” between the redox species in the solution and the metal electrode.<sup>27–30</sup> One advantage of using pyridine-based compounds is that attachment of an organic structure to a pyridine or 1,10-phen “anchor” is much easier than synthesis of organic compounds containing a thiol linker.<sup>31</sup> Additionally, when organothiols or conductive polymers are used to modify the defects, they cannot be removed from the substrate without destroying the monolayer. In contrast, under some conditions the 1,10-phen and 2,2'-bpy based compounds can be removed without disrupting the alkylthiol monolayer.

Changing the substituent groups in the alkylthiol monolayer can alter the structure and properties of the interface. The range of properties that can be obtained in homogeneous monolayers of a single thiol compound is limited. Formation of mixed monolayers containing two or more components with different structures and properties provides a way to construct an interface with new properties. The properties of the alkylthiol and polypyridine monolayers are very different. The alkylthiol-modified electrode is electrochemically passive, while the poly-

\* Address correspondence to this author. E-mail: zeng@oakland.edu.  
Phone: 248-370-2881. Fax: 248-370-2321.



**Figure 1.** CVs (scan rate 100 mV/s) of (A) 1 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  and (B) 1 mM 4-OH-TEMPO in 0.1 M  $\text{NaClO}_4$  solution on (a) bare gold, (b)  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode, (c)  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrode, and (d)  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode after 1,10-phen was removed.

pyridine-modified electrode is active for electrochemical reactions and charge-transfer processes.<sup>29,32,33</sup>

In this paper, a  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer was formed on a freshly cleaned bare gold surface, which inhibits electron-transfer processes of a redox probe. It was found that this inactive modified electrode could be switched to an electrochemically active form by modification with 1,10-phen or 2,2'-bpy. The passive surface could then be regenerated by simply washing out the absorbed 1,10-phen or 2,2'-bpy. The properties of the electrode can be switched reversibly many times. Thus, great control over the structure and properties of the monolayer by coadsorption of dodecanethiol and 1,10-phen could be obtained.

## Experimental Methods

**1. Preparation of Self-Assembled Monolayers.** Gold films evaporated on unpolished quartz crystal (ca. 900 Å) (International Crystal Manufacturing Co., Inc., Oklahoma City, OK) or gold bead electrodes were used as the substrate for self-assembly. The geometric area of the working electrode is 0.23  $\text{cm}^2$  for gold on quartz. Since the surface of the electrode was not polished, the "real" area calculated from the  $i_p$  vs  $\nu^{1/2}$  results of the CVs is about 0.28 and 0.058  $\text{cm}^2$  for gold on Quartz and gold bead electrode, respectively. The electrodes were soaked in a 1:1 (v/v) mixture of concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  for 5 min followed by a thorough rinse with deionized water. The freshly cleaned gold electrodes were immersed in 1 mM  $\text{C}_{12}\text{H}_{25}\text{SH}/\text{CH}_2\text{Cl}_2$  solution for 10–12 min. The  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified gold electrodes were immersed in a solution of 3 mM 1,10-phen solution in 70% ethanol for 3 days to form the 1,10-phen coadsorbed monolayer. The absorbed 1,10-phen could be removed by soaking the  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrode in absolute ethanol solvent with stirring for 3 days.

**2. Electrochemical Methods.** All electrochemical experiments were carried out with a one-compartment electrochemical cell. Gold electrodes with or without modification were used as working electrodes. Pt wire and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. Cyclic voltammograms and electrochemical impedance results were obtained with a Parstat 2263 Advanced Electrochemical System (Princeton Applied Research). A 0.1 M  $\text{NaClO}_4$  solution containing 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  and 1 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  or 1 mM 4-hydroxy-2,2,6,6-tetramethylpiperidine (4-OH-TEMPO) was used as the electrolyte solution. The ranges

of potentials scanned for the CV experiments were from  $-0.1$  to  $0.5$  V for  $\text{Fe}(\text{CN})_6^{3-/4-}$  and from  $0.1$  to  $0.8$  V for 4-OH-TEMPO. The frequency range of the impedance study is from 100 kHz to 0.1 Hz. The amplitude of the AC potential was 5 mV and the DC potential was the rest potential, which was 0.16 V vs SCE for experiments shown in Figure 3.

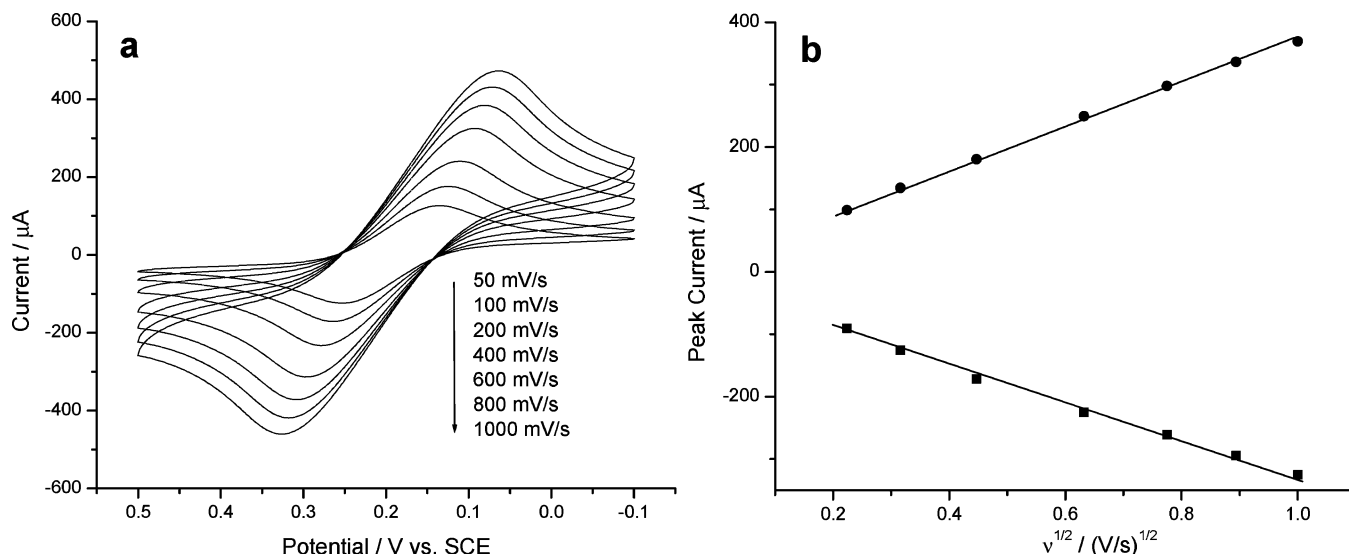
**3. FTIR.** Grazing angle FTIR spectra were recorded with a Bio-Rad FTS 175C FTIR spectrometer equipped with a Harrick Seagull reflection attachment. Gold Arrandee (provided by Dr. Dirk Schröer, Germany; 200–300 nm gold deposited on glass from vapor) was used for the background and substrates for monolayers. The light beam was p-polarized with a Harrick PWG-U1R wire grid polarizer. The angle of incidence was set at  $80^\circ$  for all spectra. Five hundred scans were accumulated for each sample or background. The system was purged with a heavy  $\text{N}_2$  stream for 3 h to remove the  $\text{CO}_2$  and moisture prior to collection of the IR spectra. The resulting spectra were smoothed and the baselines were adjusted with the manufacturer's software.

## Results and Discussion

The electrochemical properties of  $\text{C}_{12}\text{H}_{25}\text{SH}$  or  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrodes were studied by cyclic voltammetry and electrochemical impedance spectroscopy in the presence of a redox probe,  $\text{Fe}(\text{CN})_6^{3-/4-}$ , in aqueous solution. The CV for the redox couple  $\text{Fe}(\text{CN})_6^{3-/4-}$  on bare gold at a scan rate of 100 mV/s exhibited a pair of reversible redox peaks with  $E^0$  of 0.16 V (Figure 1A, curve a). These peaks show all diffusion-control characteristics. The aromatic molecule, 1,10-phen, is electrochemically inactive in the potential range studied, i.e.,  $-0.1$  to  $0.8$  V.

The cyclic voltammograms for the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox reaction on  $\text{C}_{12}\text{H}_{25}\text{SH}$  and  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified gold surfaces are shown in Figure 1A, curves b, c, and d. The CV curves obtained from the  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode, curve b, show a very small magnitude of current for both anodic and cathodic processes, confirming that the  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer is insulating and inhibits the electron-transfer processes of the redox probe in the solution. The sigmoidal shape of the CV is due to the presence of pinholes and defects in the  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer, which acts as a microelectrode assembly.<sup>34–37</sup>

Curve c is the CV obtained after the  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode was treated with 1,10-phen solution. Redox behavior



**Figure 2.** CVs of Fe(CN)<sub>6</sub><sup>3-/4-</sup> on C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode at various scan rates (a) and peak currents vs square roots of scan rates (b).

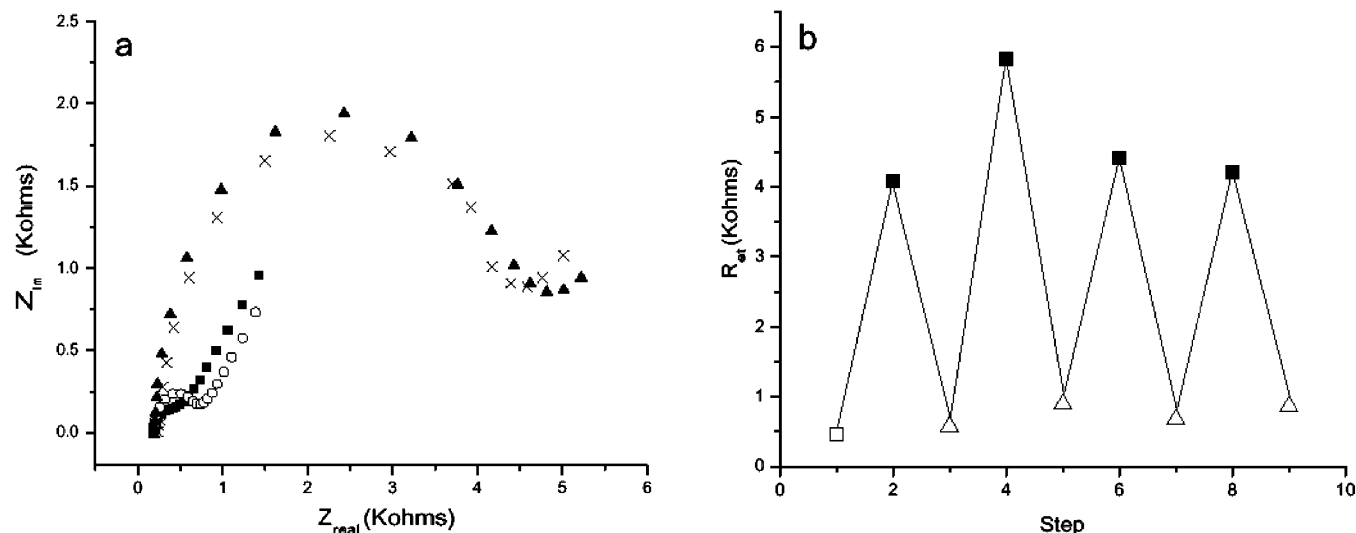
of Fe(CN)<sub>6</sub><sup>3-/4-</sup> on the resulting C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode is qualitatively different from that of the C<sub>12</sub>H<sub>25</sub>SH modified electrode. The CV is peak-shaped, similar to a bare gold electrode (curve a), and is no longer sigmoidal in shape. The current values are much higher than that for the C<sub>12</sub>H<sub>25</sub>SH modified electrode, and both the peak positions and the peak currents are very close to that of a bare gold electrode. These characteristics indicate that the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode facilitates electron transfer. Shown in Figure 1B, when 4-OH-TEMPO neutral radical and its cation were used as redox probes, the blocking effect was also seen on the C<sub>12</sub>H<sub>25</sub>SH modified electrode (curve b in Figure 1B). But a peak-shaped CV (Figure 1B, curve c) was observed on the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode. The similar results from Fe(CN)<sub>6</sub><sup>3-/4-</sup> and 4-OH-TEMPO probes suggest that the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode surface is electrically neutral and facilitates the electron-transfer processes of solution redox probes.

The appearance of redox peaks on the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode surface may originate from two possible mechanisms. In the first, the 1,10-phen molecules are immobilized on the electrode surface in the form of islands formed at existing pinholes and/or defects within the C<sub>12</sub>H<sub>25</sub>SH matrix, and electrochemical reactions take place on these 1,10-phen islands. A second possible mechanism is that the absorption of 1,10-phen or simply the treatment of the modified electrode in 1,10-phen solution creates new pinholes or defects in the C<sub>12</sub>H<sub>25</sub>SH monolayer, into which coadsorption then occurs.

If new pinholes or defects were created, this would constitute a physical change in the structure of the C<sub>12</sub>H<sub>25</sub>SH monolayer. Subsequent removal of 1,10-phen should then result in a surface with much different electrochemical properties compared to those observed prior to 1,10-phen coadsorption. However, this was found not to be the case. When the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode was washed thoroughly with ethanol, the blocking effect was observed again in the CV of Fe(CN)<sub>6</sub><sup>3-/4-</sup>, Figure 1A, curve d, very similar to that seen before 1,10-phen coadsorption, Figure 1A, curve b. This is evidence against the second mechanism, and leads us to prefer the first mechanism, in which 1,10-phen adsorbs into existing pinhole and defect sites within the C<sub>12</sub>H<sub>25</sub>SH monolayer, and subsequent removal of 1,10-phen restores the C<sub>12</sub>H<sub>25</sub>SH monolayer to its original form. The adsorption and removal of 1,10-phen was repeated 4 times, and the resulting CV curves showed similar features.

When an electrode is covered by an insulating monolayer, the pinholes and defects can be regarded as nanoelectrodes or microelectrodes, so that the partially covered electrode now behaves like a nano- or microelectrode assembly.<sup>34-37</sup> The voltametric features of reversible redox species on this kind of electrode depend on the geometrical properties of the pinholes and defects as well as the scan rate.<sup>38-43</sup> Figure 2 shows the effect of varying the scan rates from 50 mV/s to 1 V/s after the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modification. The peak-to-peak separation of the CVs on the C<sub>12</sub>H<sub>25</sub>SH/1,10-phen modified electrode increased, gradually, which is probably due to the uncompensated solution resistance. Shown in Figure 2B, the peak currents are proportional to the square roots of the scan rates. This diffusion-control characteristic further confirmed that the redox species, Fe(CN)<sub>6</sub><sup>3-/4-</sup>, is not confined on the electrode surface. When the microelectrode density is high enough, the diffusion sphere of these microelectrodes overlapped and the CVs on these electrodes show properties such as linear diffusion control.

After 1,10-phen coadsorbs into the C<sub>12</sub>H<sub>25</sub>SH monolayer, the redox reactions of Fe(CN)<sub>6</sub><sup>3-/4-</sup> take place at the sites of 1,10-phen islands, which act as electron pathways. We believe this will facilitate the reactions compared to empty pinholes and defects within the C<sub>12</sub>H<sub>25</sub>SH monolayer, for two reasons. First, the pinholes and defects are recessed microelectrodes. The average electrode depth is approximately the thickness of the monolayer. When 1,10-phen inserts into the pinholes and defects, the electrochemical reactions take place on 1,10-phen covered areas. This will reduce the electrode depth and consequently make the microelectrode areas more accessible. Second, it has been suggested that the Faradaic current at a monolayer covered gold electrode is due to electron transfer at pinholes and electron tunneling at the defects.<sup>36,44</sup> A pinhole is a site at which the electrode surface is exposed to the electrolyte, while a defect, mainly from a collapsed site, is a site at which molecules and ions from the electrolyte can approach the electrode surface at a distance shorter than the thickness of the monolayer.<sup>2</sup> Compared to Fe(CN)<sub>6</sub><sup>3-/4-</sup>, 1,10-phen molecules have a stronger interaction with the gold surface via the nitrogen lone-pair electrons. In addition, 1,10-phen molecules are also less hydrophilic than Fe(CN)<sub>6</sub><sup>3-/4-</sup>. These two effects may cause the 1,10-phen molecules to be bound more closely to the metal surface than the Fe(CN)<sub>6</sub><sup>3-/4-</sup> ions in solution can approach.

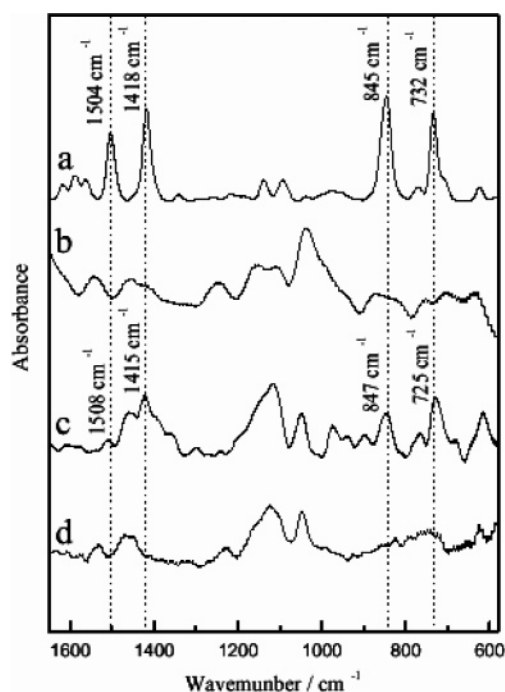


**Figure 3.** (a) Nyquist plots of 1 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox reactions in 0.1 M  $\text{NaClO}_4$  on bare gold (■),  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode (×),  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrode (○), and after the 1,10-phen was rinsed off from the monolayer (▲). (b)  $R_{et}$  of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  redox reactions on bare gold (□), dodecanethiol (■), and  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  (△) modified electrode.

The electron-transfer resistance through the 1,10-phen pathways at the defects would thus be reduced.

The results of the electrochemical impedance study were in agreement with the CV results. The heterogeneous electron-transfer resistance,  $R_{et}$ , of the  $\text{Fe}(\text{CN})_6^{3-/4-}$  probe was calculated by fitting the resulting Nyquist plots with the Randle equivalent circuit.  $R_{et}$  of the redox reactions of  $\text{Fe}(\text{CN})_6^{3-/4-}$  depends on the nature of the reaction and the properties of the electrode/electrolyte interface. This value reflects the fact that the electron exchange process between the electrode and a species in the solution is quite facile. As shown in Figure 3,  $R_{et}$  on the bare gold electrode was very low, less than 0.3 K $\Omega$ . The reversible peak-shaped CV in Figure 1A, curve a, indicates a fast electron-transfer process. However, for the  $\text{C}_{12}\text{H}_{25}\text{SH}$  modified electrode, the value of  $R_{et}$  increased to about 4.0 K $\Omega$ , which is attributed to the blocking of the redox probe in solution. When the  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrode was used,  $R_{et}$  decreased to about 0.5 K $\Omega$ , slightly higher than the value for bare gold. This is consistent with the interpretation that the electron transfer is effected through the 1,10-phen pathways. Consequently, when the  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  modified electrode was washed with ethanol,  $R_{et}$  increased again. The increase and decrease of  $R_{et}$  can be repeated several times by absorption of 1,10-phen and subsequent removal.

The results reported here are not unique to 1,10-phen. We also explored the use of another electroactive adsorbate, 2,2'-bpy, in place of 1,10-phen. Use of 2,2'-bpy gave CV and impedance results (not shown) that were qualitatively similar to those obtained from use of 1,10-phen. Our interpretation of the results for 2,2'-bpy is the same as that for 1,10-phen discussed above. Grazing angle FTIR was used to monitor the adsorption and desorption of 1,10-phen. Figure 4a is the absorption spectrum of 1,10-phen on a KBr salt plate. The peaks at 1504 and 1418  $\text{cm}^{-1}$  are the in-plane ( $a_1$ ) vibrations of 1,10-phen; the peaks at 845 and 732  $\text{cm}^{-1}$  are out-of-plane ( $a_2$ ) vibrations.<sup>45</sup> Simulation of the 1,10-phen vibrations by Density Functional Theory (B3LYP/6-31G(d)) agreed with these assignments. After an alkylthiol-modified substrate was treated in 1,10-phen solution, three of these peaks appeared in the reflectance IR spectrum at 1415, 847, and 725  $\text{cm}^{-1}$  (Figure 4c). The peak at 1504  $\text{cm}^{-1}$  was very weak. Since the coverage of 1,10-phen was much less than a monolayer, the absorbance



**Figure 4.** IR spectrum of 1,10-phen on a KBr salt plate (a) and reflection absorbance IR spectrum of  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer (b),  $\text{C}_{12}\text{H}_{25}\text{SH}/1,10\text{-phen}$  mix monolayer (c), and  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer after the 1,10-phen was rinsed off (d).

of the 1,10-phen was very weak, and the small signal/noise ratio makes assignments somewhat uncertain. The observed peaks are due to both in-plane and out-of-plane modes. The selection rule for IR absorption on a metal surface requires an active mode to have a component of its dipole derivative perpendicular to the surface, so the observation of both in-plane and out-of-plane modes indicates that the 1,10-phen molecules are not bound to the surface in purely parallel or perpendicular geometries when coadsorbed into the  $\text{C}_{12}\text{H}_{25}\text{SH}$  monolayer. This could be due to the adsorbed 1,10-phen being tilted with respect to the surface, or from a disordered adsorption in which there are a variety of geometries, possibly including both parallel and perpendicular orientations. As shown by Figure 4d, after thorough rinsing with ethanol, the peaks due to 1,10-phen disappeared, while the peaks due to the alkylthiol remained.



## Conclusions

A switchable electrode was prepared through a very simple procedure. The electrode was blocked for electrochemical reactions when it was modified with a  $C_{12}H_{25}SH$  monolayer. Further modification with 1,10-phen resulted in an electrode surface upon which electrochemical reactions could once again take place. The properties of the electrode could be switched, reversibly, multiple times between the two states. The  $C_{12}H_{25}SH/1,10$ -phen mixed-monolayer modified electrode exhibited features of a microelectrode assembly. IR results confirmed the existence of 1,10-phen in the mixed monolayer at low coverage, and indicated that the 1,10-phen molecules were not adsorbed in purely parallel or perpendicular orientations with respect to the electrode surface.

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