

# Synthesis and Characterization of Simple Self-Assembling, Nanoporous Monolayer Assemblies: A New Strategy for Molecular Recognition

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Composite monolayer films spontaneously adsorb onto the surface of Au from an ethanolic mixture of two mercaptans to form a nanoporous surface. The monolayers consist of an electron-transfer-retarding *n*-alkanethiol framework, which passivates the Au surface, and a much shorter aromatic mercaptan, which induces molecular-sized defects within the passivating framework. Electrochemical experiments indicate that the chemical nature of the template and the template/framework ratio in the deposition solution control the size, number, and chemical characteristics of the defects. For example, 4-hydroxythiophenol/1-hexadecanethiol mixed monolayers yield monolayer assemblies that admit  $\text{Ru}(\text{NH}_3)_6^{3+}$  probe molecules but not  $\text{Fe}(\text{CN})_6^{3-}$ .

## Introduction

We report the synthesis and characterization of two-component, self-assembling monolayers that act as nanoporous molecular recognition membranes. The framework component of these composites prevents probe-molecule penetration through the monolayer membrane, and the template component induces defect sites within the inert framework that permit probe-molecule penetration. The degree of penetration is controlled by the chemical and physical characteristics of the probe and template molecules. The number of the defect sites can be reproducibly varied by changing the relative concentrations of the template and framework molecules in the solution from which the monolayer assembles.

Self-organizing chemical systems represent a versatile approach for the rational modification of surfaces.<sup>1</sup> During the past several years, significant effort has been directed toward the synthesis and characterization of ideal, defect-free mono- and multilayers.<sup>2-7</sup> However, little emphasis has been placed on synthesis and analysis of intentionally formed defect structures.<sup>8-10</sup>

Sagiv was the first to report the intentional perforation of self-assembling, surface-confined monolayers of alkylsiloxanes, and he showed that such membranes could effectively readsorb molecules of approximately the same size and shape as the molecules used to induce the

perforations.<sup>8</sup> More recently, Bilewicz and Majda<sup>10</sup> have shown that Langmuir-Blodgett (L-B) films containing molecules that disrupt the passivating nature of the L-B monolayer can be transferred intact to electrode surfaces. The electrodes thus modified display electrochemical responses which range from that of an unpassivated surface to that of a totally passivated surface depending on the number of "gate" sites originally spread onto the L-B subphase.

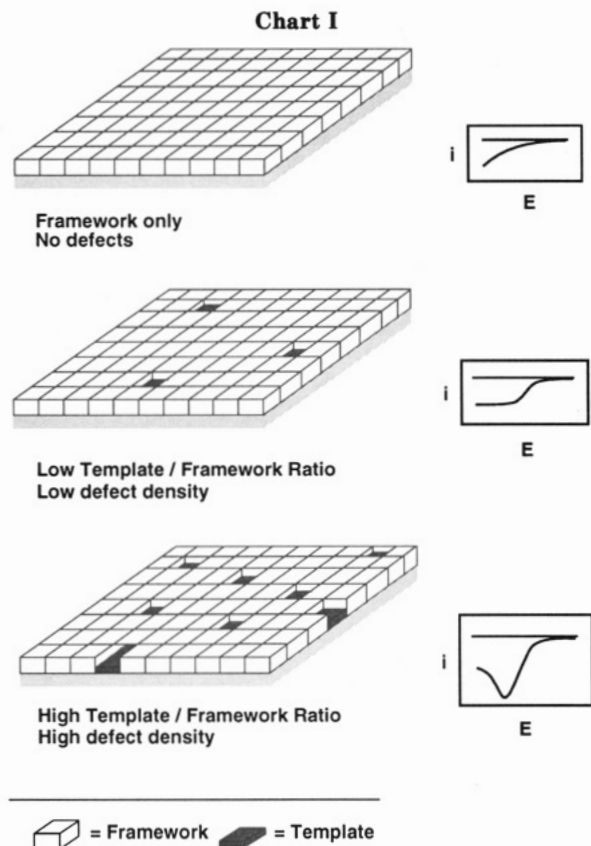
Our approach to synthesizing and characterizing molecular recognition sites is illustrated in Chart I. First, a clean Au substrate is exposed to a dilute solution of two mercaptans. The *n*-alkanethiol molecules act as an inert electron- and mass-transfer-blocking layer,<sup>1-6,11-13</sup> while the functionalized, aromatic organomercaptan molecules act as electron-transfer sites. The number of defect sites on the surface is a function of the relative concentrations of the two mercaptans in the bulk deposition solution.<sup>14</sup> In this paper, we demonstrate that the size, number, and chemical characteristics of defect sites can be reproducibly controlled, and we analyze the electrochemical response of the perforated monolayers in terms of the theory developed by Amatore et al.<sup>15</sup> Within the context of this theory, monolayers that contain either many closely spaced small defects or a few large defects give rise to voltammograms that have shapes defined by linear diffusion of a bulk-phase redox species. Monolayers that contain only a few very small defects spaced sufficiently far apart that their diffusion layers do not overlap give rise to voltammograms that are characterized by radial diffusion. The essential features of the theory are qualitatively summarized by the cyclic voltammetry responses shown on the right side of Chart I.

## Experimental Section

1-Hexadecanethiol ( $\text{C}_{16}\text{SH}$ ),  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$  (Aldrich, 92%), was purified by double distillation. 4-Hydroxythiophenol (4-HTP),  $\text{HS}(\text{C}_6\text{H}_4)\text{OH}$  (Aldrich, 90%), 4-thiocresol (4-TC),  $\text{HS}$ -

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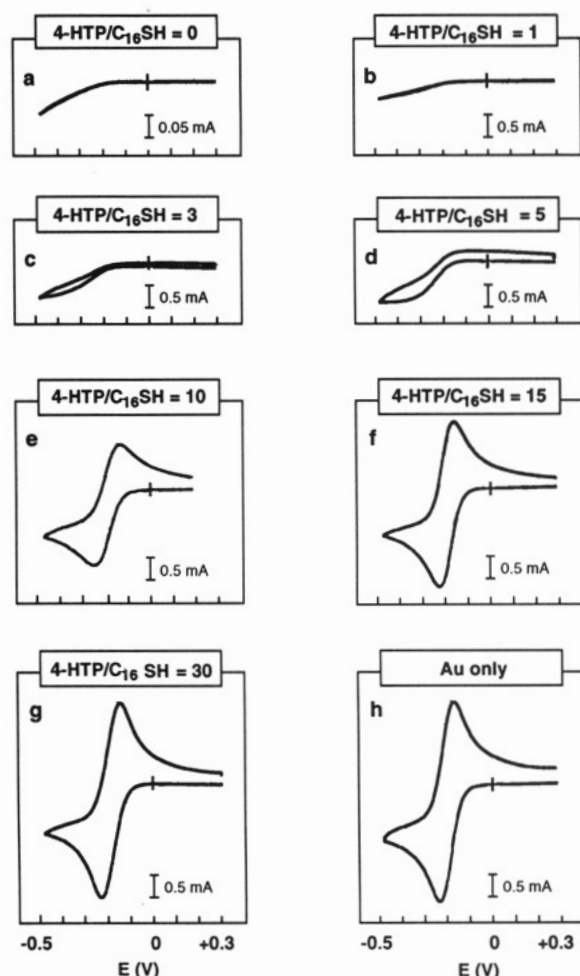
( $\text{C}_6\text{H}_4\text{CH}_3$ ) (Aldrich, 98%), hexaamineruthenium(III) chloride,  $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$  (Strem), and potassium ferricyanide,  $\text{K}_3\text{Fe}(\text{CN})_6$  (Aldrich), were used without further purification; however, we verified that purification of 4-HTP by sublimation did not significantly change the electrochemical results. Water was purified by a Milli-Q System (Millipore).

Electrochemical experiments were carried out in a single-compartment, three-electrode, glass cell containing a  $\text{Ag}/\text{AgCl}$ ,  $\text{NaCl}$  (3 M) reference electrode and a Pt counter electrode. Working electrodes were prepared as follows: Au flag electrodes ( $1 \times 2$  cm) were cut from 0.1-mm-thick Au foils (Aesar, 99.95%). The Au flags were electrochemically cleaned,<sup>16</sup> polished,<sup>17</sup> and annealed in a calibrated Lindberg Model 55035 tube furnace at  $1055^\circ\text{C}$  for 5 h in flowing Ar (170 mL/min). The cleaning process was then repeated. Just prior to each surface modification, the Au electrodes were cleaned by dipping in freshly prepared "piranha solution" (3/1 concentrated  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2$ ) for 5 min and 6 M  $\text{HCl}$  for 10 s, and then electrochemically cycled two or three times between 0 and +1.5 V in 0.1 M  $\text{HClO}_4$ . (Caution: piranha solution reacts violently with organic compounds, and it should not be stored in closed containers.) Surface modification was carried out by soaking each electrode in an ethanol solution containing two mercaptan derivatives for at least 36 h.

All electrochemical experiments were performed with a Pine Instruments Model AFRDE4 bipotentiostat, and data were recorded on a Kipp and Zonen Model BD-90 X-Y recorder.

### Results and Discussion

The cyclic voltammetry results shown in Figure 1 were obtained from an electrode prepared by soaking Au foils in ethanol solutions containing various ratios of 4-HTP, the defect-inducing organomercaptan  $\text{HS}(\text{C}_6\text{H}_4)\text{OH}$ , and  $\text{C}_{16}\text{SH}$ , the framework *n*-alkanethiol  $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ . We were able to reproduce the data shown in Figure 1 five times in nine attempts to within 10%; in all but one of the remaining trials the voltammograms were of the same general shape, but the peak or limiting cyclic voltammetric



**Figure 1.** Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-HTP/ $\text{C}_{16}\text{SH}$  ( $\text{HS}(\text{C}_6\text{H}_4)\text{OH}/\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ ). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  and 1.0 M  $\text{KCl}$ . The scan rate was 0.1 V/s.

current varied more than 10% from the mean value. For each trial, the same Au foil was used for a particular template/framework ratio, and each electrode was cleaned as described in the previous section prior to remodification with 4-HTP and  $\text{C}_{16}\text{SH}$ . The four trials that resulted in deviations of more than 10% from the average arose from experimental difficulties that we were able to trace to the electrode cleaning or modification procedure. Following modification, the electrode potential was cycled between +0.3 and -0.5 V at 0.1 V/s in an aqueous electrolyte solution consisting of 5 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  and 1.0 M  $\text{KCl}$ . In the presence of defect sites that have the correct combination of size and intermolecular interaction energies, the  $\text{Ru}(\text{NH}_3)_6^{3+}$  probe molecules should penetrate the inert framework and undergo electron exchange with the underlying Au surface. The electron transfer should be facile since the electron-transfer rate constant for  $\text{Ru}(\text{NH}_3)_6^{3+}$  is large.<sup>10a,18</sup> If the probe molecules cannot penetrate the monolayer framework, they can only be reduced by electrons that tunnel through the  $\text{C}_{16}\text{SH}$  layer. Since the distance of closest approach of the probe to the electrode surface is approximately the thickness of the monolayer, about 21–25 Å,<sup>2c,4</sup> the tunneling current should be small relative to that arising from direct electron transfer at defect sites.

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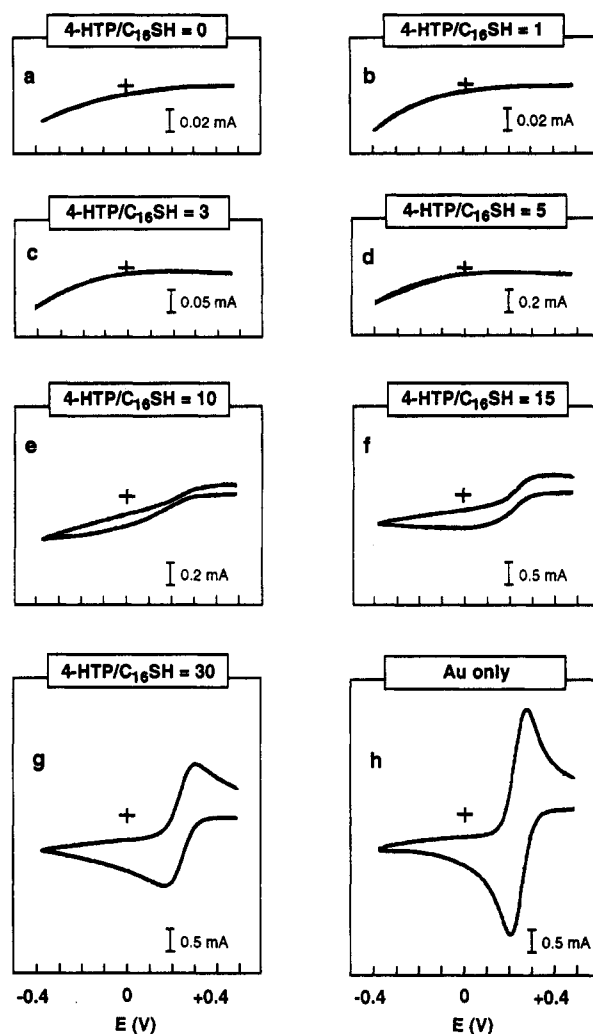
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Figure 1a shows the result obtained for a nominally defect-free  $C_{16}SH$  monolayer surface. The roughly exponential shape of the cyclic voltammogram and the magnitude of the maximum cathodic current are consistent with electron tunneling through the film.<sup>3b,5,10,11</sup>

Figure 1b shows the behavior of an electrode modified in a solution containing 4-HTP and  $C_{16}SH$  present in a 1/1 ratio. Several points are noteworthy. First, the maximum cathodic current is about 5 times higher than that of the completely passivated electrode, Figure 1a. Since, we have reproduced the data in Figure 1b four times in five attempts using different Au foils, we ascribe the current increase to surface defects induced by the template molecules; the defects permit  $Ru(NH_3)_6^{3+}$  to penetrate the monolayer framework. Second, the shape of the cyclic voltammogram is approximately sigmoidal, rather than exponential, and similar to that expected for an array of microelectrodes.<sup>10,15,19</sup> This suggests that the template-induced defects are small and widely spaced relative to the diffusion layer thickness, since either large defects or closely-spaced small defects will result in peak-shaped cyclic voltammograms that are characteristic of linear diffusion.<sup>10,15,19,20</sup> Third, since the concentrations of template and framework molecules in the deposition solution are identical, and since it is clear that only a very small fraction of the molecules on the Au surface are template molecules, it follows that the much longer framework molecules compete more effectively for surface adsorption sites than the template molecules. This is consistent with results reported by Whitesides and co-workers,<sup>14</sup> and it arises principally from the greater van der Waals interaction potential between framework molecules.

Parts c and d of Figure 1 are consistent with the qualitative interpretation of part b. The shapes of these voltammograms arise from radial diffusion of  $Ru(NH_3)_6^{3+}$  to small, widely dispersed defect sites on the electrode surface. This conclusion is confirmed by the scan rate dependence of the data shown in Figure 1d: scan rates between 10 and 1000 mV/s result in only a doubling of the maximum limiting current,  $i_{lim}$ , which is not consistent with the result anticipated for linear diffusion to a macroscopic electrode. As the concentration of the template molecules in the deposition solution is increased relative to the framework molecules,  $i_{lim}$  increases, and there is a clear departure from pure radial diffusion to a mixed linear/radial regime.<sup>10,15,19</sup> Mixed diffusion behavior is especially evident in Figure 1e, and when 4-HTP/ $C_{16}SH = 15$ , nearly ideal linear diffusion obtains, Figure 1f.<sup>20</sup> When 4-HTP/ $C_{16}SH = 30$ , the cyclic voltammetry obtained using the modified surface, Figure 1g, is indistinguishable from that of a naked Au surface, Figure 1h. The voltammetry shown in Figure 1 does not change significantly even after 10 voltammetric cycles.

Figure 2 presents data analogous to those shown in Figure 1, except that the solution-phase redox probe molecule is  $Fe(CN)_6^{3-}$ . This set of data follows the general trend discussed for  $Ru(NH_3)_6^{3+}$ . For example, there is a clear progression from electron transfer via tunneling through the monolayer film to direct electron transfer at the electrode surface governed first by radial, and then by linear, diffusion as the 4-HTP/ $C_{16}SH$  ratio increases. Qualitatively, the only difference between the cyclic voltammograms shown in Figures 1 and 2 is that the



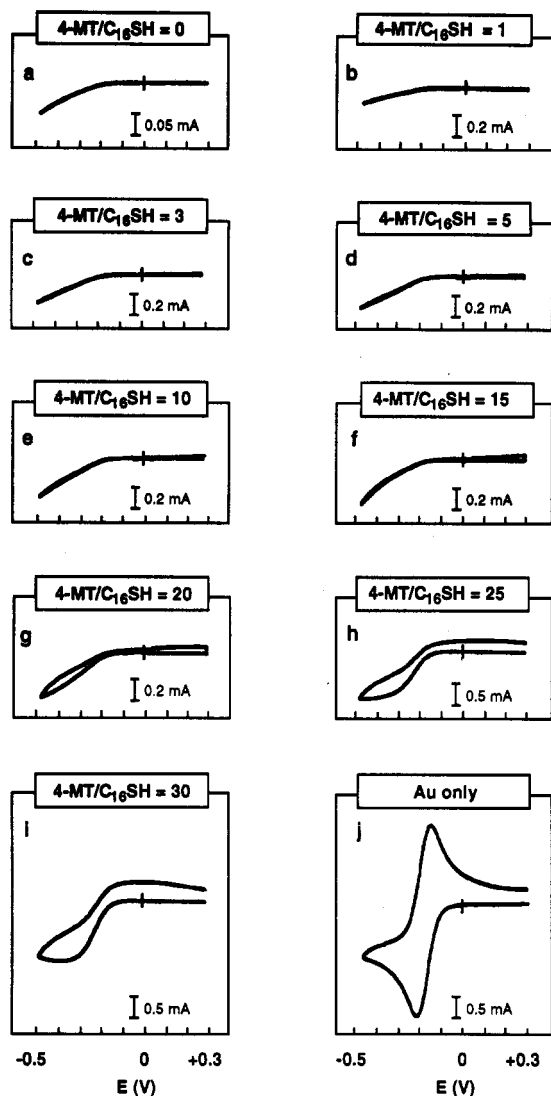
**Figure 2.** Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-HTP/ $C_{16}SH$  ( $HS(C_6H_4)OH/HS(CH_2)_{15}CH_3$ ). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM  $Fe(CN)_6^{3-}$  and 1.0 M KCl. The scan rate was 0.1 V/s.

transition from radial to linear diffusion occurs at a higher 4-HTP/ $C_{16}SH$  value for  $Fe(CN)_6^{3-}$  than for  $Ru(NH_3)_6^{3+}$ . Since the perforated monolayers used to generate Figures 1 and 2 are the same, and since the sizes of the two probe molecules are approximately the same on the basis of their diffusion coefficients,<sup>21</sup> there is only one possible explanation for this behavior: some of the defect sites that admit  $Ru(NH_3)_6^{3+}$  do not admit  $Fe(CN)_6^{3-}$ . That is, although the total number and average size of the defects are fixed, there are differences in the nature of the intermolecular interactions between the probe molecules and at least some of the molecular recognition defect sites. This important observation indicates that the defect sites discriminate between probe molecules on the basis of their chemical nature.

We have also investigated differences in the electrochemical behavior of perforated, self-assembling monolayers as a function of structurally similar, but chemically distinct, defect-inducing template molecules. Figure 3 presents data that are identical to those discussed for

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**Figure 3.** Cyclic voltammograms for perforated, composite monolayers formed by immersing a Au surface in ethanol solutions containing various ratios of 4-TC/C<sub>16</sub>SH (H<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)CH<sub>3</sub>/HS-(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>). The concentration ratio is given above each cyclic voltammogram. The data were obtained in an aqueous electrolyte solution consisting of 5 mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and 1.0 M KCl. The scan rate was 0.1 V/s.

Figure 1, except that the template molecule is 4-TC (HS-(C<sub>6</sub>H<sub>4</sub>)CH<sub>3</sub>). We chose this compound because 4-HTP may form hydrogen-bonded, phase-separated clusters on the surface. For example, Bain et al. have suggested that hydroxyl-terminated *n*-alkanethiols will tend to form microscopic, hydrogen-bonded clusters a few tens of angstroms across on the Au surface.<sup>14d</sup> This conclusion was supported by the rationalization that the energy required to disrupt hydrogen bonding in an alkane environment is high, and it was further supported by experimental data, which showed that alcohols in alkane solvents exist primarily as tetramers.<sup>22</sup> Since intermolecular hydrogen bonding between 4-TC molecules cannot occur, we anticipate no template aggregation and, therefore, smaller defects within the organic monolayer, compared to the 4-HTP system, for a given template/framework ratio. In addition to differences in the size of the defects, their number is also likely to be a function of the chemical nature of the template molecules. These expectations are borne out; even when 4-TC/C<sub>16</sub>SH = 30,

Figure 3i, radial diffusion obtains, indicating differences in the size and/or number of defects. We hypothesize that non-hydrogen-bonding species do not compete as effectively for the Au surface as their hydrogen-bonding counterparts, since the latter should have several S/Au binding interactions per defect site. Experiments with other templates, such as 4-mercaptopyridine and 4-mercaptobenzoic acid, are consistent with this view.<sup>23</sup>

We have performed a preliminary, semiquantitative analysis of the data shown in Figure 3 using a theoretical model developed by Amatore et al.<sup>15</sup> They have shown a relationship between the average defect radius and distance between defects, and the resulting cyclic voltammetry response to a solution containing a redox probe molecule. The model is appropriate to the chemical systems described here if the perforated monolayers act as arrays of noninteracting ultramicroelectrodes, that is, if diffusion is radial and if the diffusion layers of the individual ultramicroelectrodes do not overlap. This situation corresponds to parts h and i of Figure 3. In these cases,  $i_{\text{lim}}$  is related to the fractional surface coverage of C<sub>16</sub>SH,  $\theta$ , and the average defect radius,  $R_a$ , through the relationship given in eq 1. Here,  $n$  is the number of electron

$$i_{\text{lim}} = nFS c^{\circ} D(1 - \theta)/(0.6R_a) \quad (1)$$

equivalents,  $F$  is the Faraday constant,  $S$  is the geometrically projected surface area of the electrode,  $c^{\circ}$  is the bulk concentration of the redox probe molecule, and  $D$  is its diffusion coefficient.<sup>15</sup>

To directly correlate the calculated and experimental values of  $i_{\text{lim}}$ , we must know both the size and number density of the defect sites. Since we do not presently have an independent means for measuring  $\theta$  or  $R_a$ , we must guess the former and calculate the latter on the basis of the experimentally determined value of  $i_{\text{lim}}$ .<sup>24</sup> Here, we have chosen to analyze the data involving the 4-TC/C<sub>16</sub>SH composite monolayer, since we do not anticipate aggregation of the template molecules. This is, we postulate that the minimum radius of a single defect site corresponds approximately to the van der Waals radius of 4-TC, about 3.5 Å on the basis of its liquid density. The maximum defect size induced by a single template molecule might correspond to the maximum number of *n*-alkanethiol framework molecules displaced from their 3-fold coordination sites on a Au(111) surface.<sup>3,5</sup> This corresponds to a maximum displacement of seven C<sub>16</sub>SH molecules, which would open a radius of about 7.5 Å on the surface. For convenience in this approximate calculation, we assume as intermediate average defect radius of 5 Å. Since there are clear differences in the voltammetry of Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> and Fe(CN)<sub>6</sub><sup>3-</sup> obtained at identically prepared electrodes, Figures 1d and 2d, we are confident that the defect sites are of molecular dimensions.

For 4-TC/C<sub>16</sub>SH ratios of 25 and 30, eq 1 yields  $1 - \theta$  values of  $4.4 \times 10^{-6}$  and  $5.7 \times 10^{-6}$ , respectively. Viewed differently, this means there are about  $10^9/\text{cm}^2$  template-induced defect sites on the electrode surface. Although this is an approximate calculation that contains an assumption, it does confirm our expectations and, more

(23) Chailapakul, O.; Crooks, R. M. Unpublished results.

(24) We recently developed a technique, based on scanning tunneling microscopy, that permits us to directly visualize individual defect sites of molecular dimension on surfaces. We are presently evaluating intentionally perforated monolayers of the type discussed here to confirm the tentative conclusion that 4-TC-induced defects are on the order of the van der Waals radius of 4-TC. See: Sun, L.; Crooks, R. M. *J. Electrochem. Soc.* 1991, 138, L23.

importantly, leads to values of  $\theta$  that are on the same order as those obtained by Bilewicz and Majda using L-B methods.<sup>10</sup>

### Conclusions

We have shown that it is possible to use binary mercaptan solutions to prepare functional composite monolayers. The chemical nature of the template and framework and the template/framework ratio of the deposition solution control the size, number, and chemical characteristics of the defects. These in turn control access of probe molecules to the Au surface and are therefore responsible for the molecular recognition function of these monolayers.<sup>25</sup> For example, when 4-HTP/C<sub>16</sub>SH = 15, Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> easily penetrates the monolayer, but Fe(CN)<sub>6</sub><sup>3-</sup> does not. At the present time, we have not unambiguously

(25) We appreciate one of the reviewers suggesting the the selectivity we have observed might arise from differences in the heterogeneous electron-transfer rate constants,  $k^\circ$ , of the two probes ( $k^\circ$  for Fe(CN)<sub>6</sub><sup>3-</sup> is thought to be about 1000 times smaller than  $k^\circ$  for Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>). Three points strongly suggest that electrode kinetics are not a significant factor for the behavior reported in this paper: (1) the theoretical treatment of this chemical system, ref 15, explicitly confirms that electrode kinetics alone cannot change the shape of a voltammogram from peak-shaped to sigmoidal or vice versa; (2) to our knowledge there are no examples of differences in electrode kinetics yielding such a change; (3) another probe molecule, Fe(bpy)<sub>3</sub>(CN)<sub>6</sub> (bpy is bipyridine), yields peak-shaped voltammograms (linear diffusion) under conditions that yield sigmoidal voltammograms (radial diffusion) for the kinetically faster Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> probe.

identified the principal molecule/monolayer interactions that lead to molecular discrimination, but recent experiments suggest that the differences in the sign of the charge, and perhaps attendant differences in solvation energies, for the two probe molecules are at least partly responsible.

To our knowledge, this is the first example of the use of self-assembly chemistry to construct a binary molecular recognition monolayer composed of simple molecular species, and it is intended to complement strategies based on electrostatic binding,<sup>26</sup> covalent bonding,<sup>27</sup> hydrogen-bonding,<sup>28</sup> and complexation<sup>29</sup> that we have previously reported. We are presently engaged in a thorough analysis of the energetic and spatial relationships between the template, framework, and probe molecules, and those results will be presented in future publications.

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