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Supplementary Material for:

Thiol Modified Pyrrole Monomers: 3. Electrochemistry of 1-(2-thioethyl)-pyrrole and 3-(2-thioethyl)-pyrrole Monolayers in Propylene Carbonate

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DETAILED EXPERIMENTAL

Determination of Surface Roughness

The roughness of the evaporated gold surfaces was determined electrochemically by chrono-Coulometry. The geometrical area of the samples was fixed to 0.2 cm^2 by pressing the gold-covered silicon pieces against a Viton O-ring surrounding a hole in a Teflon electrochemical cell. The cell was filled with a de-aerated aqueous solution of 0.1 M KNO_3, buffered to pH 7 with 1 mM phosphate, containing 1, 2, or 4 mM $Fe(CN)_6^{3-}$. The voltage was stepped between +0.6 V and -0.2 V. Charge was plotted against the square root of time and the slope of the line used to calculate the active area:[1,2]

$$Q = \frac{nFAc\sqrt{Dt}}{\sqrt{\pi}} + B$$

where n is the number of electrons, F is Faraday's constant (96,485 C/mol), A is the electrochemical area sought, c is the concentration of $Fe(CN)_6^{3-}$, D is the diffusion coefficient of $Fe(CN)_6^{3-}$ and equals 6.3 x 10^{-6} cm^2/sec in this electrolyte,[3] t is time in seconds, and B is a constant. Three different concentrations were used to obtain a good average value of the electrochemical area, which was found to be 1.3 times the geometrical area.

Different means of measuring the active surface area of an electrode can yield different results.[4] Also, different evaporation equipment and batches yielded surfaces of variable roughness. The value of 1.3 for our evaporated gold films compares with: 1.6 found by Uosaki et al.[5] determined by the charge required for the formation and reduction of gold oxide; 1.2 found by Schneider et al.[6] by the same method; 1.2 calculated by Widrig et al.[7] for annealed evaporated gold films on mica found by scanning tunnelling microscopy; and 1.7 for Au on mica determined by Schlenoff et al.[8] using radio-labelled alkanethiols.

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Competitive Adsorption

Monolayer affinity for the surface was examined by competitive adsorption. Monolayers of 1-TEP and 3-TEP were deposited from chloroform solutions. Two samples of each monolayer and two clean gold pieces were immersed half-way in the electrolyte and cycled electrochemically (two times at 100 mV/sec between 0 and 1.2 V for 1-TEP and between 0 and 1.4 V for 3-TEP and clean gold).

Samples were stored in air and analyzed within 24 hours. The surfaces were initially cleaned by sonication in ethanol (99% spectroscopic grade) for 1 minute, followed by rinsing with ethanol and drying under a stream of nitrogen. Then 2 μl of a 1 mM solution containing the long chain thiol $SH(CH_2)_{15}COOH$ (made according to [9]) in ethanol, prepared immediately before use, was dotted onto the surface and spread by capillary action. After 15 minutes the dry surfaces were rinsed and sonicated in ethanol for 1 minute, rinsed with ethanol, and dried with nitrogen. The surfaces were placed face-down over 10 μl of an activation solution (1-ethyl-3-(3-dimethylaminopopyl)carbodiimide : N-hydroxysuccinimide ester, 0.4:0.1 M final concentration in water, Sigma, USA) for 60 minutes at room temperature and then rinsed with water and blown dry. The surfaces were immediately placed on 10 μl of an amino-biotin solution (1mg/ml in 0.1M carbonate, pH 8.5, Molecular Probes, USA) and incubated for 4 hours, after which they were rinsed with water and then buffer (150 mM NaCl, 0.05% Tween 20, 10 mM HEPES, pH 7.4, Sigma, USA). Streptavidin was radio-labelled (Amersham S35 protein labeling reagent SLR "sulfur labeling reagent") according to the instructions provided by the manufacturer. The surfaces were placed face-down on 10 μl spots of the labelled streptavidin (the 10 μl contained 10 μg streptavidin, 20,000 counts per minute); after a 30 minute incubation, the surfaces were rinsed repeatedly with buffer and finally with water and blown dry. The surfaces and standards were exposed to a Fuji phosphor-imaging imaging plate for 2 hours that was subsequently read on a BAS2000 Fuji Phosphorimager. The amount of bound material was quantitated using the analysis software. Uncycled gold-coated Si and mica surfaces underwent the same treatment and were used as references for the binding studies.

XPS OF 1-TEP

The N1s and S2p XPS spectra of 1-TEP are shown below. The amounts of nitrogen and sulfur decrease upon cycling past the three monolayer oxidation peaks. Cycling to 2 V causes the monolayer to desorb: only trace amounts of S and N remain.
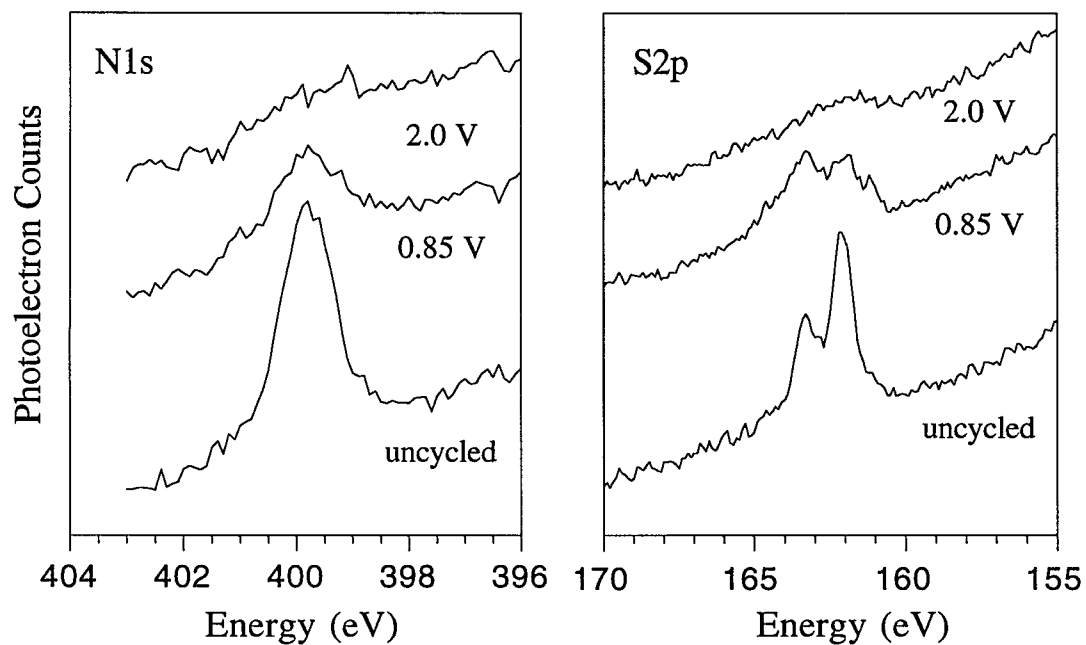
REPLACEMENT BY LONG-CHAIN THIOLS

Thiolate moieties in self-assembled monolayers can react with oxygen and come off the surface.[10] Because this is a defect-mediated process, short-chain thiols like the TEPs, which do not pack perfectly (see paper 2), are especially vulnerable to attack[11]; for long-chain molecules, strong interactions between the alkyl tails hinder desorption[12] and prevent diffusion of oxygen to the thiol-gold interface. Therefore, short-chain thiols are rapidly displaced on the time scale of minutes in a solution of long-chain thiols. Were the thiol-modified pyrrole monolayers to be polymerized during electrochemical oxidation, they would be stabilized and thus resistant to displacement. [13] Cycled monolayers were compared with uncycled ones to see if there was any increase in stability.

The affinity of the long chain thiol $SH(CH_2)_{15}COOH$ to cycled and uncycled halves of 1-TEP and 3-TEP treated surfaces and clean gold was determined within 24 hours of the surface preparation. No significant difference was found between the two halves of each surface or among the three different surfaces in the phoshphor images. If cycling did indeed produce small islands of oligomerized 1-TEP, then they were too small to stabilize the monolayer since the long-chain thiols were able to completely replace the oxidized TEP within 15 minutes.

In contrast with these results, Willicut et al. reported [13] that oxidized short-chain 1-substituted pyrrole monolayers were not readily displaced in competitive adsorption experiments with ferrocenylalkanethiol, whereas unoxidized monolayers were almost completely displaced (>95%) within 90 minutes. The increase in stability was evidence for polymerization of the monolayer. Is it possible that those slightly longer carbon chains (n = 3 to 6) allowed the pyrrole moieties to assume a configuration more favorable to polymerization? In addition to chain length, factors critical in displacement experiments are solvent, temperature, and surface defects.

DEPENDENCE OF CYCLIC VOLTAMMOGRAMS ON SCAN RATE
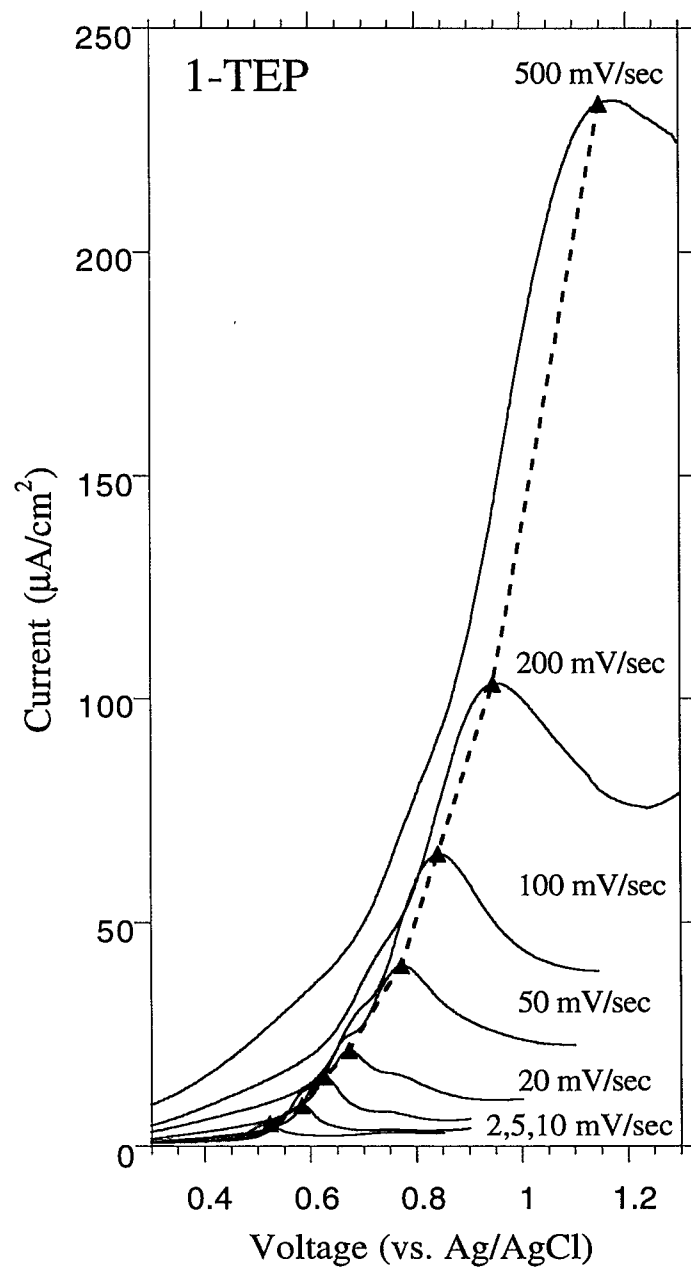
Forward potential excursions for 1-TEP at various scan rates between 2 and 500 mV/sec. The second peak position is marked with a triangle.
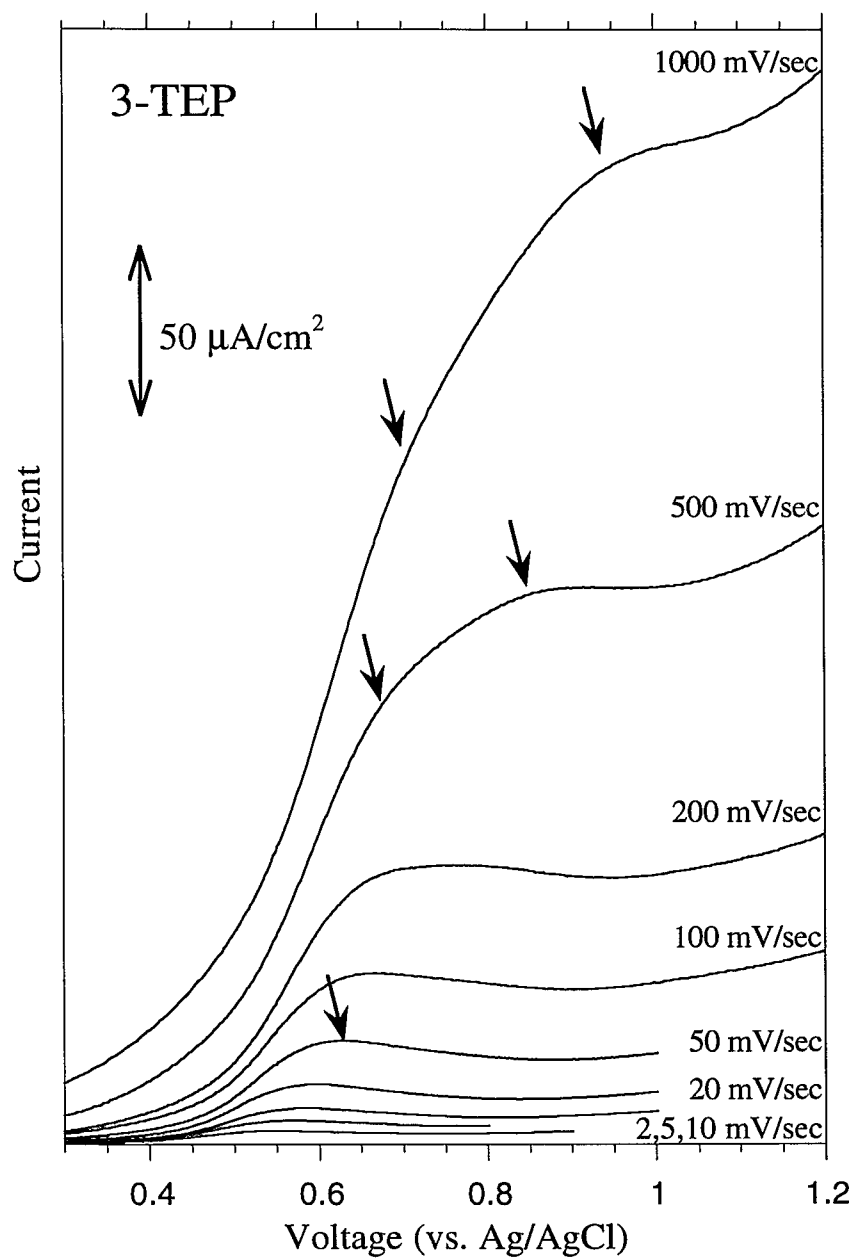
Forward potential excursions for 3-TEP at various scan rates between 2 and 1000 mV/sec.
The peak (indicated by arrow) splits into two at high scan rates.

EXCURSION TO MORE AND LESS EXTREME POTENTIALS

The oxidation peaks were shown by the spectral data not to be due to simple desorption. Is there a clear desorption peak at higher potential? In order to check for the presence of oxidative desorption peaks at higher potentials, 1-TEP monolayer surfaces were cycled to +2.0 V and the scans compared with those of clean Au surfaces.

Above 1.5 V, Au forms a surface oxide, and at still higher voltages oxygen is evolved. A cathodic dissolution peak is obtained on the return sweep. No additional peaks were evident during the first scan for 1-TEP; in fact, clean Au and 1-TEP scans were indistinguishable after the monolayer oxidation peaks. Since XPS confirmed that the monolayer had desorbed by 2 V, the material remaining on the surface must either come off bit by bit or simultaneously with the gold oxidation. This process does not consume significant current.
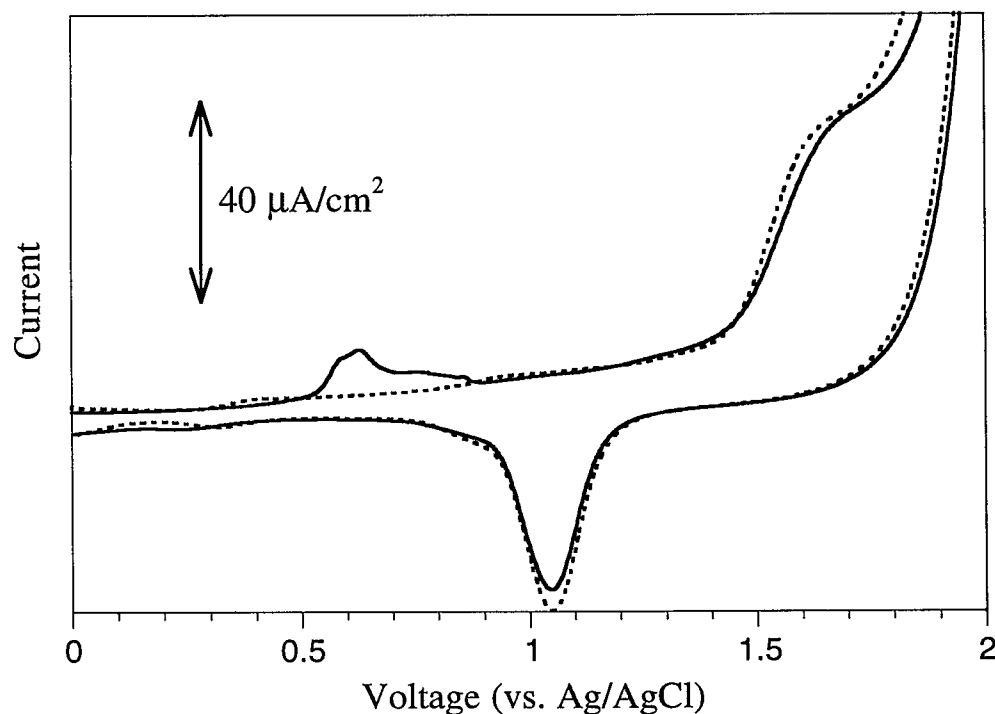

Cyclic voltammograms, first scan, of 1-TEP monolayer (solid line) and clean Au (dotted line).

It is known that thiolates can be desorbed by reduction as well as oxidation. In 0.5 M KOH, Widrig et al.[7] found that n-hexanethiol monolayers desorbed from Au/mica at -1 V vs. Ag/AgCl and n-octadecanethiol desorbed at -1.3 V. In dimethylformamide with tetrapropylammonium perchlorate, dodecanethiol reductively desorbed at -1.4 vs. Ag/AgCl as seen by Schneider et al.[6] using a combination of electrochemistry and quartz crystal microbalance. Everett et al.[15,16] found that dodecanethiol monolayers were unstable at potentials both positive and negative of 0 V vs. Ag/AgCl in both methylene chloride and acetonitrile with tetrabutylammonium hexafluorophosphate, especially for potentials more negative than -1 V and more positive than +0.5 V. They also showed that the Cr adhesion layer underlying the Au did not affect the stability or electrochemical behavior of these monolayers.
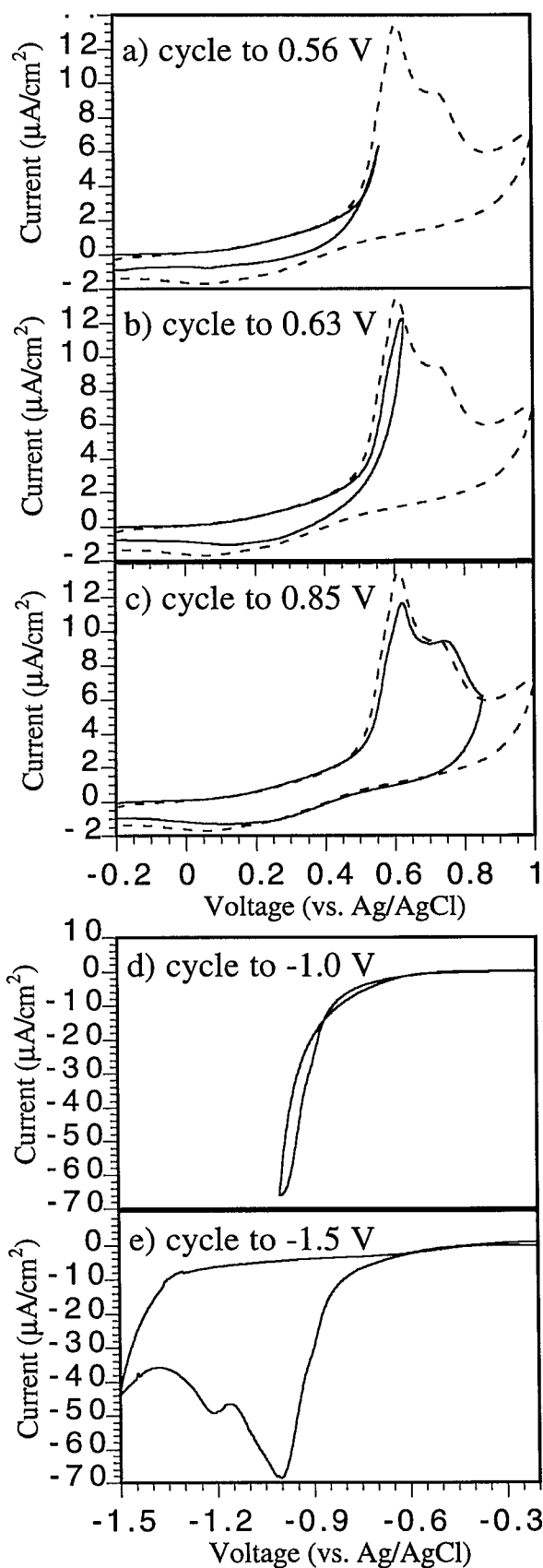
To check for the presence of reduction peaks due to desorption, oxidized surface-bound species, or any products that might have been produced during follow-up reactions, the potential was extended in the cathodic direction. When the TEP monolayers were cycled between +0.3 and -0.90 V, the large Au reduction peak near -0.55 was shifted cathodically, by ca. -0.35 V to -0.9 V, in both the first and second scans. When cycled first to +0.9, past the TEP oxidation peaks, and then to -0.90, no additional reduction peaks were observed due to the TEPs, but the Au reduction peak was no longer shifted. The oxidation of the monolayers thus destroyed their blocking ability. When the monolayers were scanned from 0 V to potentials more negative than the first gold reduction peak at -0.9, peaks near -1.3 V were seen during the first potential excursion before the second large gold reduction peak at -1.6 V (see figure below). After such a negative potential excursion, the monolayer oxidation peak did not appear at positive voltages. These small peaks would thus appear to represent reductive desorption of the monolayer. However, IRAS measurements showed otherwise, as shown below.
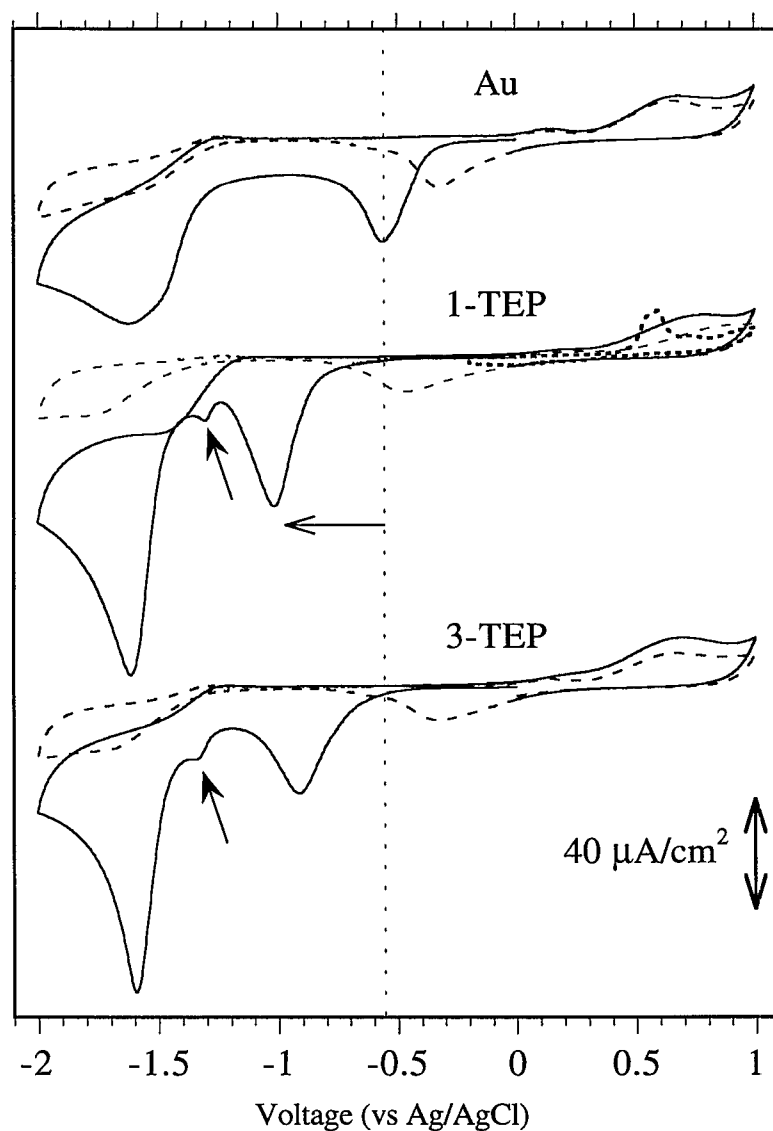
Cyclic voltammograms in PC/LiClO$_4$ at 10 mV/sec from 0 to -2 to 1 V scanning in the negative potential direction first; first scan shown as solid line, second as dashed line. The surfaces were reduced before oxidation, causing a disappearance of the usual monolayer oxidation peak obtained upon scanning first to positive voltages (superimposed as a dotted line over the 1-TEP scans). The Au reduction peak near -0.55 was shifted cathodically, by ca. -0.35 V to -0.9 V. Reductive monolayer peaks are visible near -1.3 V.

To see how the IRAS signal depended on the extent of oxidation, 1-TEP monolayers were cycled at 10 mV/sec to thepotential of the first of the three peaks (0.56 V), to the second peak (0.63 V), and to past the third peak (0.85 V). The IRAS spectra are below and show that at 0.56 V the 1-TEP peaks (1497, 1280, 1090, and 727 cm^{-1}) are reduced in size, and already by 0.63 V, none remain.

To see whether the TEP monolayers had been desorbed by the reduction described above, 1-TEP monolayers were deposited for 2.5 hours in ethanolic solutions, sonicated, and electrochemically reduced. One sample was cycled twice from -0.2 to -1.0, to the first gold reduction peak. The second was cycled once from -0.2 to -1.5 V, past the second, small monolayer reduction peak and part-way down the third, Au peak. Instead of finding clean, laboratory air-contaminated surfaces, however, we obtained both 1-TEP peaks (at 1497, 1280, 1090, and 727 cm^{-1}) and large, very broad carbonate peaks (near 1530, 1450, and 870 cm^{-1}, the latter a narrower peak). The monolayer cycled to -1 V had 1-TEP peaks only somewhat smaller than an uncycled monolayer and carbonate peaks that were 3-4 times that size. The larger negative potential gave much larger carbonate peaks and slightly smaller 1-TEP peaks, the ratio of their heights being approximately 10:1. These electrochemical reduction peaks are therefore *not* due to desorption, but probably to reaction with the propylene carbonate electrolyte. (We did not look at the IRAS signal of monolayers cycled to more negative potentials.) Even though the 1-TEP IRAS peaks were present, it was shown in the figure above that the usual electrochemical oxidation wave was suppressed after reduction. The large amount of carbonate on the surface may block or interfere with the oxidation.

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a) cycle to 0.56 V

b) cycle to 0.63 V

c) cycle to 0.85 V

Current (μA/cm^2)

Voltage (vs. Ag/AgCl)

d) cycle to -1.0 V

e) cycle to -1.5 V

Current (μA/cm^2)

Voltage (vs. Ag/AgCl)

Cyclic voltammograms of 1-TEP to various positive and negative potentials (solid lines). A usual cyclic voltammogram is shown for comparison (dotted line). Corresponding IRAS scans are below.
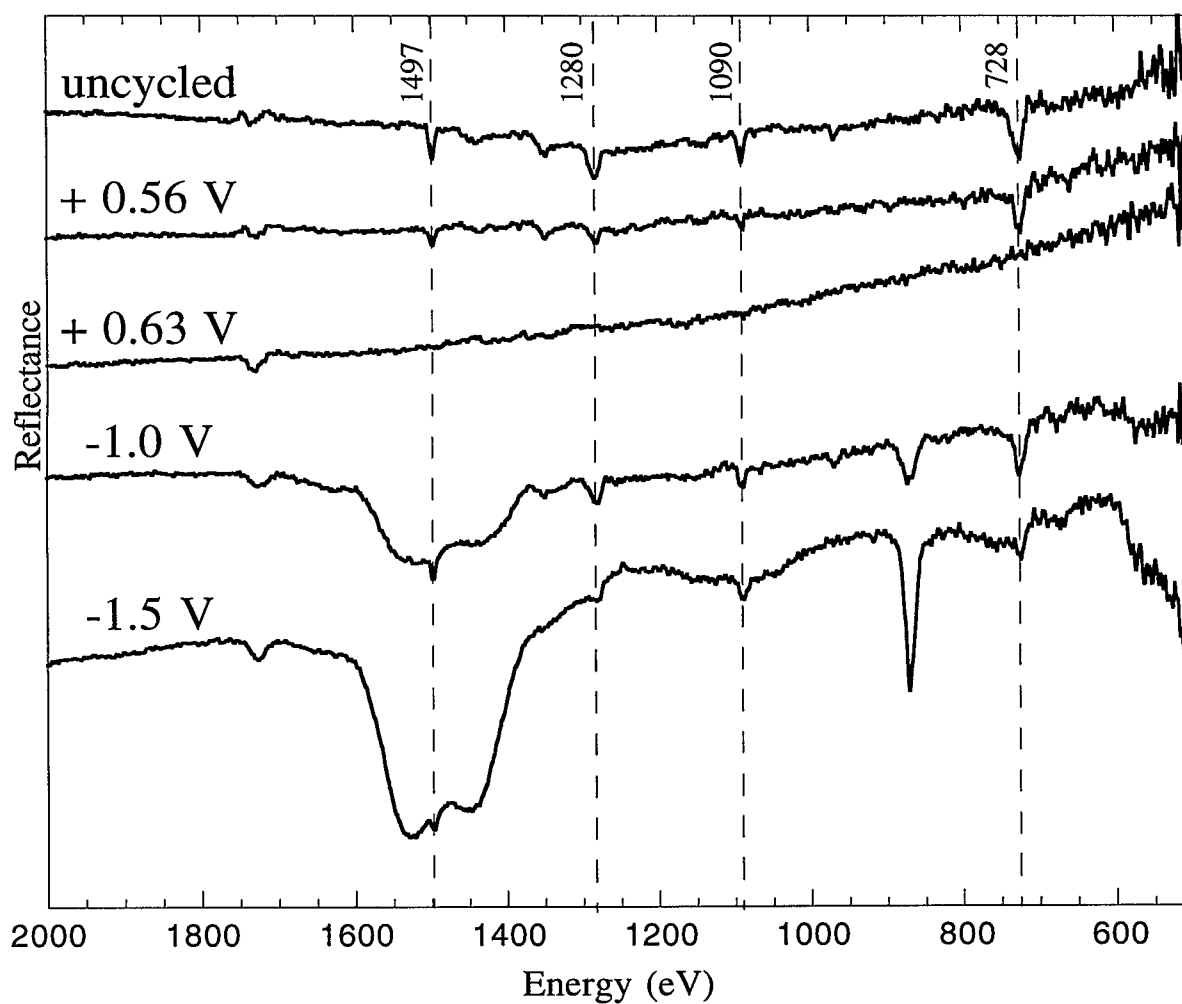
IRAS spectra of 1-TEP monolayers cycled as above to various positive and negative potentials.

GRADUAL INCREASES IN THE UPPER POTENTIAL LIMIT

Electrochemical scans were normally taken to a potential above all the oxidation peaks of the monolayer. The spectral data showed that this caused extensive damage: opening of the pyrrole rings, loss of sulfur and nitrogen from the surface, formation of carbonyls, etc. The electrochemical data showed these surfaces to be inert after the first cycle. We wondered whether lower potential limits would also result in inert monolayers. To help answer this question, the upper voltage limit was raised in steps of 0.1 V starting from 0.2 V and cyclic voltammograms were taken of 1-TEP monolayers at 10 mV/sec until they stabilized. Between 0 and 0.2 V, the first two cycles were the same, as they were between 0 and 0.3 and between 0 and 0.4 V. Therefore, the monolayer is stable and unreactive in this window.

However, with an upper limit of 0.5 V or higher the voltammograms evolved. The first eight cycles for a sample deposited from a PC/1-TEP solution for 5.5 hours are shown in the figure below. The voltammograms stabilized after eight to ten cycles. After that, when the upper limit was raised further, the first and second cycles were the same. In addition, they were the same as those of a typical 2nd scan to a potential above the oxidation peaks. The surface can thus be completely oxidized to electrochemically inactive compounds at only 0.5V. From an applications perspective, this is detrimental because it takes a potential at least that high to deposit PPy (see paper 4).

From the electrochemical data, it cannot be determined whether these oxidation reactions are the same or different from those occurring at higher potentials. In complex reactions, both consecutive and parallel reaction pathways can play a role. The three peaks may or may not represent threshold potentials for different reactions. If they do, then the first reaction may have occurred exclusively in this experiment and produced a different surface than usual, for example one that still contained the pyrrole moiety. Additional spectroscopic studies on these surfaces, outside the scope of this paper, would need to be done to be done to determine the oxidation products corresponding to each peak in the cyclic voltammogram of 1-TEP. (The IRAS spectrum above for a monolayer cycled to the first peak is not directly relevant because that sample was only cycled once.)
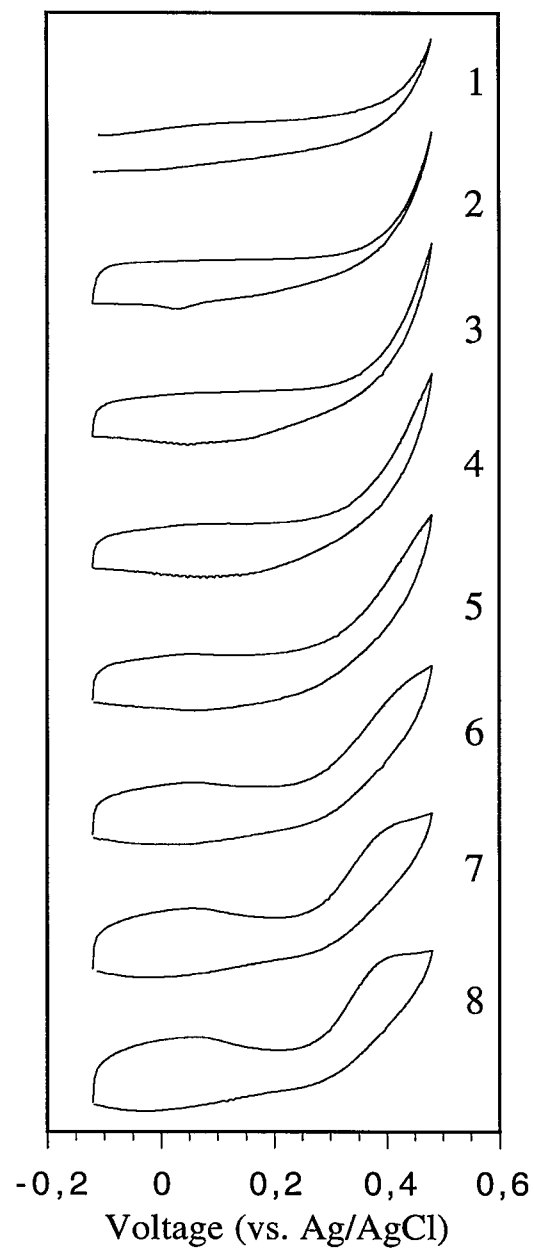
Evolution of cyclic voltammograms of a 1-TEP monolayer cycled at 10 mV/sec between 0 and 0.5 V vs. Ag/AgCl. Scan numbers are indicated.

CYCLED SAMPLES RETURNED TO DEPOSITION SOLUTIONS

We were curious to see whether returning cycled surfaces to the TEP deposition
solutions would result in a re-appearance of the first-scan oxidation peak, and if so, how much
time it would take to recover. A gold surface was put into 1-TEP/ethanol for two minutes,
rinsed thoroughly in ethanol, and, following the usual procedure, cycled between 0 and 1 V.
It was then removed from the electrolyte, rinsed in ethanol, returned to the 1-TEP solution for
some time, rinsed, and cycled again. The oxidation peaks did return, but the first two peaks
were smaller and shifted to more positive potentials. In addition, their relative heights
changed, and after multiple, brief re-immersions the first two peaks could no longer be
distinguished. Part a) of the figure below shows the peaks of a sequence of such scans,
beginning with a freshly deposited 1-TEP monolayer, in which the sample was repeatedly
reimmersed in 1-TEP/ethanol for 45 seconds. The relative change in maximum peak height
vs. cycle number is shown in part b). After a fast initial drop, the maximum decreased slowly
with each cycle. After the sequence of 45-second re-immersions, the sample was re-
immersed for 30 minutes; the peak maximum is represented as a triangle in the inset. The
peak recovered to a higher level when left in solution for a longer time. Another sample was
therefore reimmersed after one cycle for 18 hours to see if the surface could recover fully for
even longer times, but the peak recovered only 72% of its initial height (shown as a square in
the figure), which was approximately the same level as was achieved for only a 45 sec re-
immersion. Therefore, even for the longer immersion time, no more of the original peak
height could be recovered. (As a control, clean Au surfaces were cycled prior to immersion
for the first time in 1-TEP solutions. The peak heights of 1-TEP monolayers on previously
uncycled and cycled gold surfaces were compared and found to be the same.)

These results indicate that in most areas the oxidized (decomposed) 1-TEP residues are
weakly bound to the surface and are rapidly replaced by 1-TEP from solution. If some areas
of the cycled monolayer are organized in some way, then displacement would be hindered in
those regions, resulting in times that must be even longer than 18 hours to reach completion.
Another possibility suggested by the data is that there are two kinds of sites on the gold, one
from which the oxidized thiol can readily come off making up approximately two thirds of the
total number of sites, and one from which the oxidized thiol cannot be easily replaced that
makes up the remaining third (since the peak does not recover to its initial height even for
long re-immersion times). This effect had been seen before by Chidsey et al.[17] and Walczak
et al.,[18] who found that at step defects the thiols are more strongly bound. Schlenoff et al.[8]
also observed that a significant fraction of alkanethiols remained non-exchanged even at long
times (days) when immersed in thiol hexane solutions, possibly as a result of stronger binding

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at defect sites. However, more data showing the relationship between displacement and re-immersion time would be needed to confirm this reason for the lack of exchange in cycled 1-TEP surfaces.
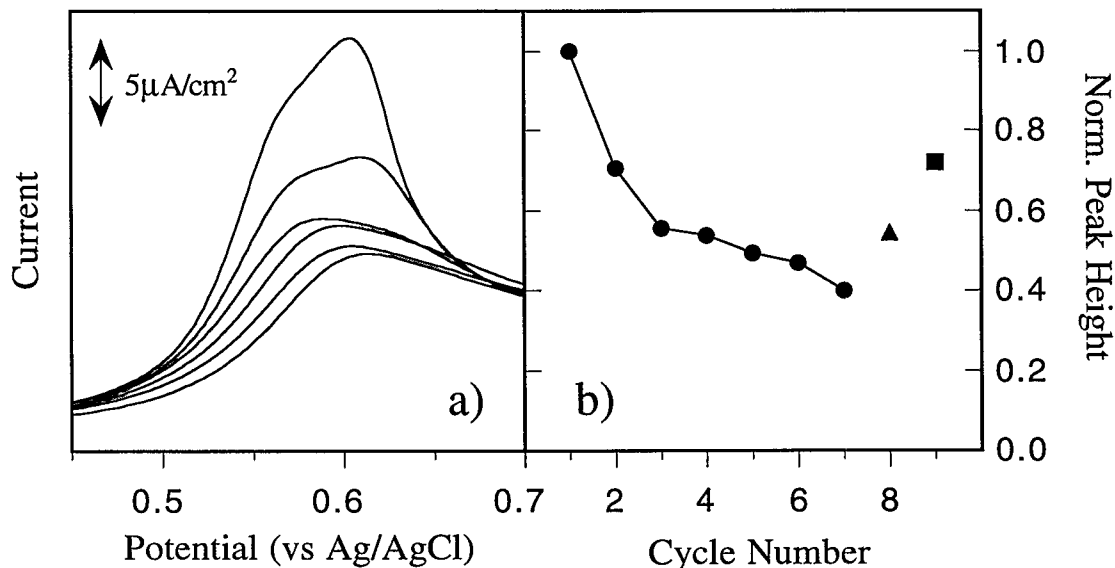

CYCLIC VOLTAMMETRY IN OTHER ELECTROLYTES

It is well known that changing the electrolyte can have a profound influence on redox reactions. [16,19,20] Monolayer films may be more rigid in non-polar solvents, reducing chain motion, or may be poorly solvated. Their stability is also electrolyte-dependent.

Cyclic voltammograms of 1-TEP in various electrolytes were compared, including ethanol/LiClO4, acetonitrile (ACN) with LiClO4 and tetrabutylammoniumperchlorate (TBAP), and water with LiClO4 and dodecylbenzenesulfonate, sodium salt (DBS). There was a wide variability in the number, shape, area, and position of the oxidation waves. In some electrolytes the first-time peaks were essentially absent. Even in the same solvent, changing the salt had a large effect. For example, in water/DBS the oxidation peak did not occur before the gold oxidation. The surfactant might adsorb onto or form a complex with the 1-TEP which could sterically hinder the oxidation reaction, form an insulating barrier over the monolayer, displace the monolayer, or stabilize the pyrrole moiety.

VOLTAMMETRY IN DRY ELECTROLYTE

Willicut et al. reported that ω-(N-pyrrolyl)alkanethiol monolayers could be polymerized in PC only provided that water was rigorously excluded. [13] To see how the exclusion of water would affect the cyclic voltammogram of 1-TEP, it was cycled in a rigorously dried system. Molecular sieves (3Å) were activated, and LiClO$_4$ was dried, by baking them for 16 hours at 180 °C. The sieves were added to bottles that had been flame-dried, and PC was added and sealed under nitrogen. After 6 days, the dry PC was added to the dry LiClO$_4$ and sealed under nitrogen. Tweezers, solution deposition containers, and the electrochemical cell were cleaned in SC1 and dried overnight, together with an Ag/AgCl wire reference electrode, in an oven at 160 °C. Using a flame-dried pipette, 1-TEP was added to dry PC to make an approximately 10 mM solution. Gold-coated silicon pieces were cleaned in SC1, blown dry under nitrogen, dried 5 minutes at 160° (not longer for fear of contaminating the surfaces), and added immediately to the PC/1-TEP deposition solution or used immediately as reference samples.

Cyclic voltammograms made under these conditions did not show significant differences from those made in the usual way. The three peaks were still present, with the same heights and positions. There was no oxidative surface wave during the second scan, nor was there a new anodic peak that would correspond to the reduction of a polymer-monolayer.

Voltage (vs Ag/AgCl)
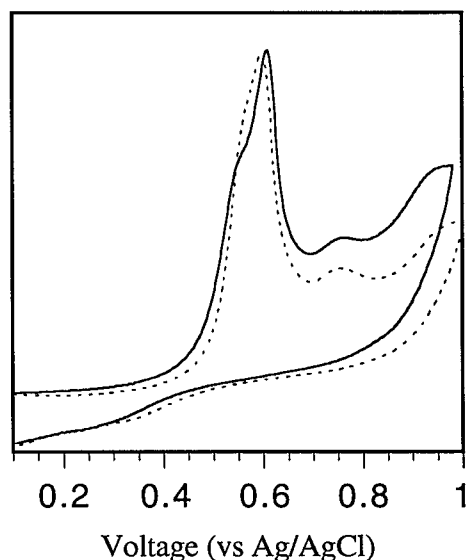
Cyclic voltammogram of 1-TEP in water-free PC/LiClO$_4$ (solid line) and in the usual PC/LiClO$_4$ (dotted line). (An Ag/AgCl wire pseudo-reference was used during the experiments, but values are reported versus Ag/AgCl.)

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Dependence of Cyclic Voltammograms on Deposition Time

In part 2, we found that deposition time made no difference to the spectral data of 1-TEP. Because of the short chains and bulky pyrrole moieties, the molecules never assume a more packed or ordered structure. However, 3-TEP undergoes a surface-catalyzed cleavage in which the pyrrole moiety is lost, and these surfaces become more tighlty packed with deposition time. Was this reflected in the electrochemistry?

Cyclic voltammograms of 1-TEP monolayers deposited from ethanol solutions for 1, 10, 100, 1000, and 10,000 seconds were compared, as well as a monolayer deposited from vapor for 100 seconds. In all cases, the scans were identical: the shape, number of peaks, peak positions, peak heights, and relative peak heights among the three peaks were unchanged with deposition time. These results thus support those in part 2. The initial adsorption is believed to be diffusion controlled and therefore to follow: moles/area = $2C\sqrt{Dt/\pi}$, where C is the concentration, D is the diffusion coefficient (approximately 10^{-6} cm^2/s), and t is time. [6,8] For concentrations of 1 μM, a full monolayer that contains 10^{-9} mol/cm^2 can be formed in one second; at 20 mM, the thiols attach essentially immediately, and no significant further changes take place in the monolayer.

Similar experiments were done for 3-TEP monolayers, but in this case the peak position shifted to more positive potentials when samples were left in solution longer, and the peak height and area also increased with deposition time. All these changes appeared to have a logarithmic dependence on time. The increase in the peak size demonstrates that the amount of oxidizable material increases with deposition time, and the shift in peak potential shows that the surface is more difficult to oxidize, most likely because of a tighter packing. Again, these results are consistent with those in paper 2. Unlike the 1-TEP surface, the 3-TEP surface evolves over time.
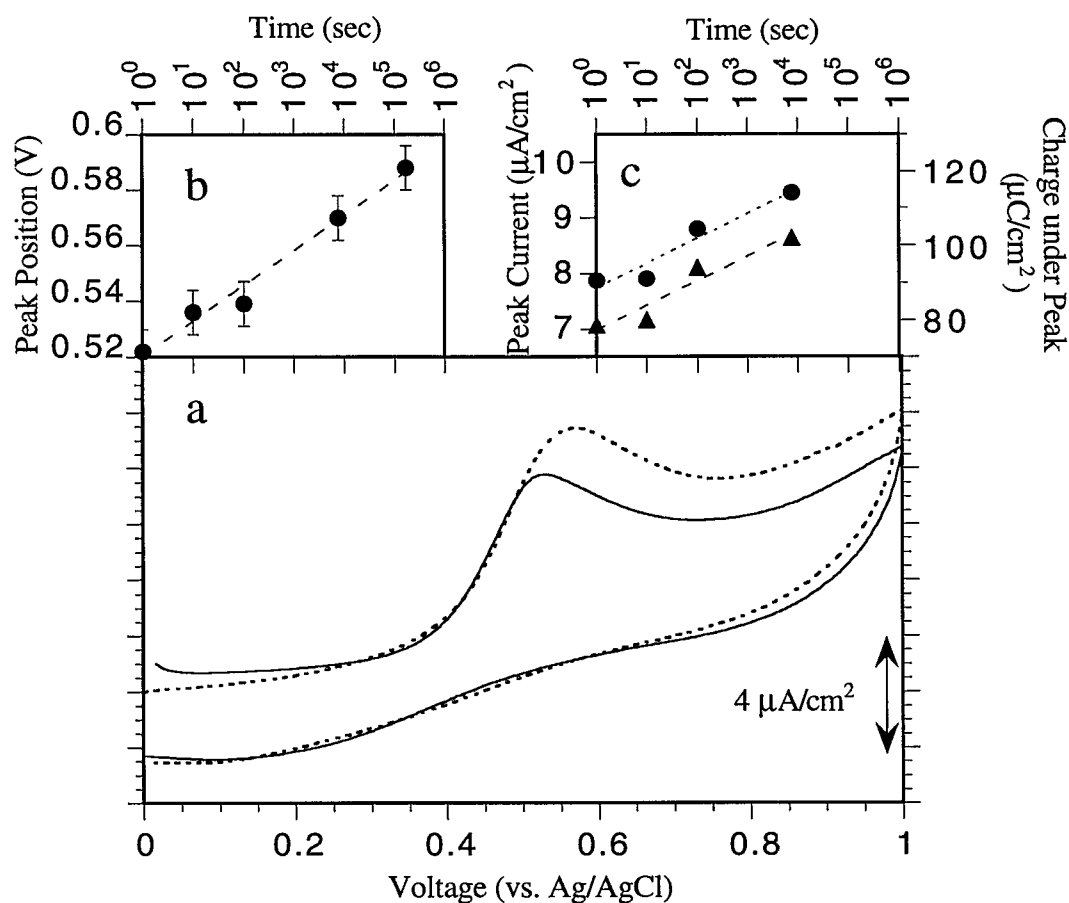
a) Cyclic voltammograms for 3-TEP samples left in solution 1 second (solid line) and 2 hours (dotted line). Dependence of b) peak position and c) peak current (circles) and integrated charge (triangles) on deposition time; all appear to have a logarithmic dependence.

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AU SURFACES CYCLED IN 1-TEP MONOMER-CONTAINING ELECTROLYTE

When clean gold surfaces were cycled in a solution of PC/LiClO$_4$ that contained 1-TEP monomers, the same first-cycle oxidation peaks were observed as for 1-TEP monolayers cycled in monomer-free electrolyte; these peaks were again missing in the second cycle. A set of scans performed at 10 mV/sec between -0.2 and 1 V is shown in the figure below. A monolayer spontaneously forms from the 1-TEP-containing electrolyte, and its oxidation peaks, although small when superimposed on the polymerization current, can be seen near 0.6 and 0.75 V. (The first shoulder at 0.55 is too small to be distinguished.) The absence of these peaks in subsequent scans is further confirmation that they are not due to desorption; otherwise, the 1-TEP in solution would have formed new monolayers and caused the peaks to reappear in each scan. Under these conditions, the oxidation products and are not replaced, unlike the case when the surfaces are rinsed and re-immersed in ethanolic 1-TEP solutions.

During the first scan the current began to rise at approximately 0.5 V due to oxidation of the monolayer, and it continued rising after that peak due to polymerization. On subsequent scans, the polymerization current did not begin until approximately 0.65-0.7 V. The monolayer oxidizes first, before polymerization starts. Further discussion of the polymerization of the TEPs can be found in paper 1 of this series.
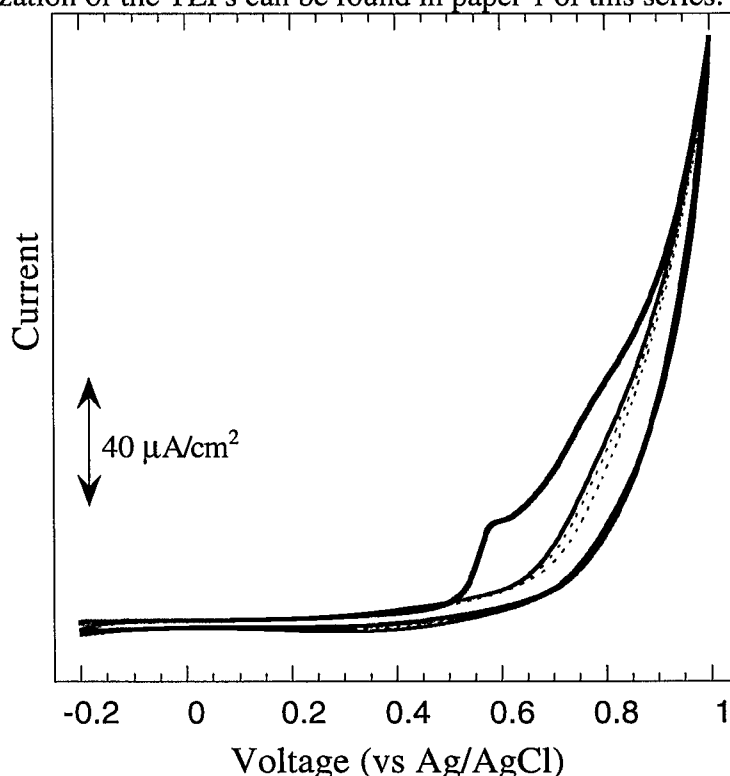
Polymerization by cyclic voltammetry in PC/LiClO4/1-TEP solution at 10 mV/sec. First scan cycle, heavy solid line; second and third cycles, dotted lines; fourth cycle, thin solid line.

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