

Potential-Dependent Wetting of Aqueous Solutions on Self-Assembled Monolayers Formed from 15-(Ferrocenylcarbonyl)pentadecanethiol on Gold

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Aqueous solutions of 0.1 M NaClO₄ (pH 1.5, 10 mM KH₂PO₄) show potential-dependent wetting on self-assembled monolayers (SAMs) formed from 15-(ferrocenylcarbonyl)pentadecanethiol (FcCO(CH₂)₁₅SH; Fc = [η^5 -C₅H₅]Fe[η^5 -C₅H₅]) adsorbed on Au surfaces. Contact angles (θ) decreased from 71° to 43° ($\Delta \cos \theta = -0.40$) when the electrical potential of the SAM was increased from 0.3 to 0.5 V (vs a Ag wire reference electrode) and then increased from 43° to 58° when the potential of the SAM was returned to 0.2 V. Repeated cycling between these values of the potential leads to a progressively decreasing response, as the Fc groups were destroyed by side reactions. Contact angles of aqueous solutions on SAMs formed from CH₃(CH₂)₁₇SH decrease by only 2° (from ~115° to 113°, $\Delta \cos \theta = 0.05$) over the same range of potentials (Sontag-Huethorst, J. A. M.; Fokkink, L. G. J. *Langmuir* 1992, 8, 2560–2566). The contrast between the wettability of SAMs terminated with Fc and CH₃ groups suggests that potential-dependent wetting of the former is caused primarily by the electrochemical oxidation of the electrically neutral, surface-confined Fc to the more polar and plausibly more wettable Fc⁺ cation. Linear sweep cyclic voltammetric measurements support this hypothesis. Surfaces of gold patterned with SAMs formed from FcCO(CH₂)₁₅SH and CH₃(CH₂)₁₅SH were used to construct a micrometer-scale “gate” that controls the flow of liquid down a surface.

Introduction

Contact angles of liquids on surfaces of gold covered with self-assembled monolayers (SAMs) of organosulfur molecules have been widely used to characterize the physical chemistry underlying the wetting of liquids on organic interfaces.^{1,2} Self-assembled monolayers of redox-active organic molecules on gold surfaces are also well-defined model systems for the study of interfacial electron transfer between Au and a molecular acceptor or donor.^{3–6}

In this paper, we report electrochemical control over the wettability of organic surfaces using SAMs formed by adsorption of FcCO(CH₂)₁₅SH on gold (Fc = ferrocenyl). We believe that the potential-dependent changes in the wetting of aqueous solutions on Fc-terminated SAMs result from the transfer of electrons to and from the surface-confined redox species, and the interconversion of the less-polar, less-wettable Fc group and the more-polar, more-wettable Fc⁺ group.⁷

Electrical control over the wettability of organic interfaces is, we believe, useful for both fundamental studies of wettability⁸ and potential applications such as electro-optical devices; optical switches based on control of the potential-dependent, interfacial tension between a drop of mercury and an aqueous solution of electrolyte have already been demonstrated.⁹ We illustrate potential uses of electrowetting on organic surfaces by changing the shapes of drops of water on surfaces of gold patterned with areas of SAMs formed from either FcCO(CH₂)₁₅SH or CH₃(CH₂)₁₅SH. Micrometer-wide grooves of gold covered with SAMs formed from FcCO(CH₂)₁₅SH were also used to construct a micrometer-scale “gate” that controls the flow of water down an inclined surface of gold.

Experimental Considerations. We studied potential-dependent wetting of aqueous solutions of electrolyte on ferrocene-terminated SAMs because (i) surface-confined ferrocenes formed by the self-assembly of ferrocene-terminated alkanethiols on gold surfaces undergo reversible oxidation at ~0.5 V (SCE)^{4–6} and (ii) we hypothesized that formation of Fc⁺ from Fc at the surface of the SAM would result in an increased wettability and that this increase could be reversed by electrochemical reduction.

Because chloride ions react irreversibly with ferrocene under oxidative conditions,^{5,10} we used a silver wire reference electrode rather than a calomel (Hg/Hg₂Cl₂/KCl) reference electrode. We measured the reference potential of a calomel electrode and silver wire in 0.1 M NaClO₄ (pH

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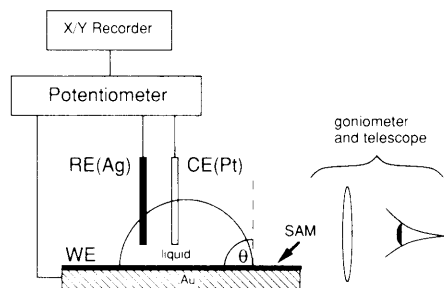


Figure 1. Diagram of the experimental setup used to measure cyclic voltammograms and contact angles of aqueous solutions on Au surfaces supporting SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$. The working electrode (WE) was a gold film covered with a SAM; the counter electrode (CE) was a platinum wire; the reference electrode (RE) was a silver wire.

1.5, 10 mM KH_2PO_4) to be $V(\text{SCE}) = V(\text{Ag wire}) + 0.13$ V. All potentials are reported relative to a silver wire reference electrode.

Figure 1 is a diagram illustrating the experimental arrangement of electrodes used to measure cyclic voltammograms and contact angles of aqueous solutions on gold surfaces supporting SAMs. The contact angles of liquids on the SAMs were measured using a telescope and goniometer. Other experimental considerations are detailed in the Experimental Section.

Results

Cyclic Voltammetry. Figure 2 shows linear sweep cyclic voltammograms of gold films supporting SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$ measured in (a) 0.1 M NaClO_4 (pH 1.5), (b) 0.1 M NaClO_4 (pH 1.5, 10 mM KH_2PO_4), and (c) 0.1 M NaClO_4 (pH 1.5, 10 mM Na_2SO_4). Between each scan the potential of the SAM was held at 0.5 V for either 1 or 5 min (indicated on the graphs). The peaks of the oxidizing and reducing waves of current were observed initially at +0.37 V. The initial shapes of the waves were asymmetric and spiked around the peak potential; this type of shape has been suggested to reflect a distribution of environments within the monolayer⁵ and/or cooperative changes in the structure of these interfaces during the oxidation of the ferrocene.⁶ Figure 2a–c shows a time-dependent, irreversible decrease in the size of the waves of current corresponding to the oxidation/reduction of the surface-confined ferrocene/ferricenium. The shapes of the waves also changed with time; they became more symmetric and the peak potential decreased by ~50–70 mV. The rate of decrease in the electrochemical activity of the SAM does not appear to be influenced by the presence of either 10 mM KH_2PO_4 or 10 mM Na_2SO_4 in the aqueous solution. Figure 2d shows cyclic voltammograms for SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$ that were held at a potential of 0.0 V between scans. SAMs held at 0.0 V did not show a significant time-dependent decrease in the size of the waves of current corresponding to the oxidation/reduction of the surface-confined ferrocene/ferricenium. From these measurements, we infer that the decomposing species is Fc^+ and not Fc and that the rate of decomposition of Fc^+ is approximately independent of the type of electrolyte (for NaClO_4 , Na_2SO_4 , and KH_2PO_4).

Contact Angles. Figure 3 shows the influence of electrical potential on contact angles of aqueous solutions of 0.1 M NaClO_4 (pH 1.5, 10 mM KH_2PO_4) on SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$. Because we observed an irreversible time-dependent and potential-dependent change in the wettability of SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$ (see Figure 2 and discussion above) each datum in Figure 3 was measured using a freshly prepared SAM

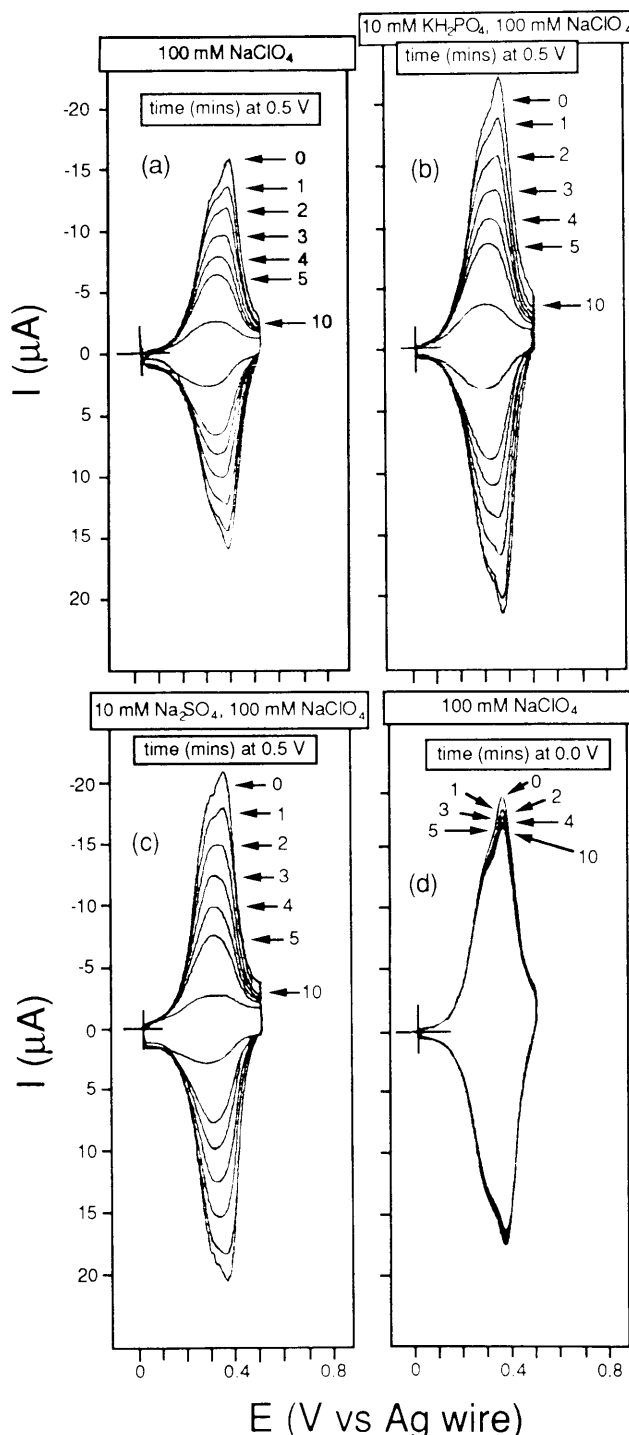


Figure 2. Linear sweep cyclic voltammograms of SAMs formed from $\text{FcCO}(\text{CH}_2)_{15}\text{SH}$ on gold; all experiments were at pH 1.5: (a) measured in 0.1 M NaClO_4 (HClO_4), held at 0.5 V between scans, area = 56 mm^2 ; (b) measured in 0.1 M NaClO_4 (10 mM KH_2PO_4), held at 0.5 V between scans, area = 72 mm^2 ; (c) measured in 0.1 M NaClO_4 (10 mM Na_2SO_4), held at 0.5 V between scans, area = 63 mm^2 ; (d) measured in 0.1 M NaClO_4 (HClO_4), held at 0.0 V between scans, area = 56 mm^2 . Potentials were scanned at 100 mV/s and measured relative to a silver wire. Note the asymmetry in the initial shape of the current waves (see text for details).

and the procedures are outlined below (see also the insets in Figure 3).

(A) Advancing Contact Angles, θ_a (inset at bottom right of Figure 3). First, the contact angle was measured at 0.0 V. Second, the potential was ramped to the desired oxidative potential over a 1 to 5 s interval of time (200 mV/s) and held there. The advancing contact angle was measured after the drop had stopped spreading (typically 15 s). Using this procedure, we measured advancing

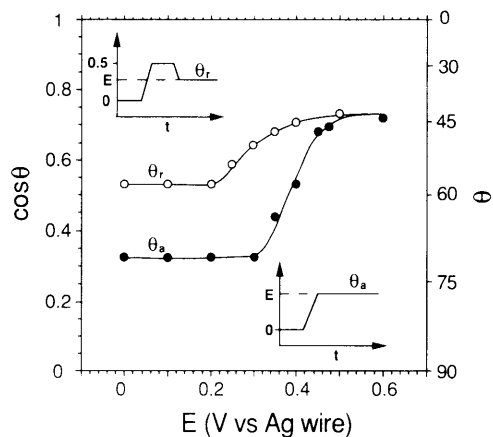


Figure 3. Potential-dependent contact angles of aqueous 0.1 M NaClO₄ (pH 1.5, 10 mM KH₂PO₄) on a gold electrode supporting a SAM formed from FcCO(CH₂)₁₅SH: advancing contact angles, θ_a (●); receding contact angles, θ_r (○). Each datum corresponds to a different sample (see text for details). Potentials are relative to a silver wire reference electrode. The inset shows the potential of the SAM as a function of time used for the measurement of θ_a (bottom right) and θ_r (top left).

contact angles to be invariant (71°) over the range of potentials between 0 and +0.3 V. Contact angles decreased from 71° to 43° as the potential was increased from 0.3 to 0.5 V. Potentials greater than 0.5 V did not result in a further decrease in the advancing contact angle.

(B) Receding Contact Angles, θ_r (inset at top left of Figure 3). First, the contact angle was measured at 0.0 V. Second, the potential was ramped to 0.5 V and the drop was allowed to spread to a contact angle of ~43° (ca. 15 s). Immediately (i.e. after the 15 s, to minimize oxidative damage to the SAM), the potential was decreased at 200 mV/s to the desired value and the receding contact angle was measured after the drop had ceased retracting (typically 30 s). Receding contact angles increased from 43° to 58° as the potential was decreased from 0.5 to 0.2 V (Figure 3).

The hysteresis of 13° in the contact angle ($\theta_a - \theta_r = 71^\circ - 58^\circ$) measured after one cycle of the potential was the same as the hysteresis observed by causing a drop to advance and recede on a SAM of Fc that had not been subjected to applied oxidative potentials. This value of hysteresis (13°) is typical for water on SAMs^{1,2} and is thought to result from factors such as the roughness of the underlying film of gold and chemical heterogeneities within the SAM (although this last factor seems less likely for a SAM formed from one chemical species).¹¹

Figure 4 shows contact angles of aqueous 0.1 M NaClO₄ (pH 1.5, 10 mM KH₂PO₄) as the underlying Fc-terminated SAM was cycled repeatedly between 0.1 and 0.5 V. The initial advancing contact angle at 0.1 V was 71°. After one cycle to 0.5 V (during which time the contact angle decreased to ~43°) the receding contact angle at 0.1 V was 58°. After five cycles between 0.1 and 0.5 V, the receding contact angle at 0.1 V was 48°; this decrease in contact angle was irreversible. The probable cause of the irreversible change in wettability of the SAM is the decomposition of the surface-confined Fc⁺.^{5,6,10} This hypothesis is supported by cyclic voltammetry (Figure 2); the size of the current waves corresponding to oxidation of Fc to Fc⁺ and reduction of Fc⁺ to Fc decreased with increasing exposure of the SAM to oxidative potentials.

Wetting on Patterned, Ferrocene-Terminated SAMs. Figure 5 shows the potential-dependent wetting

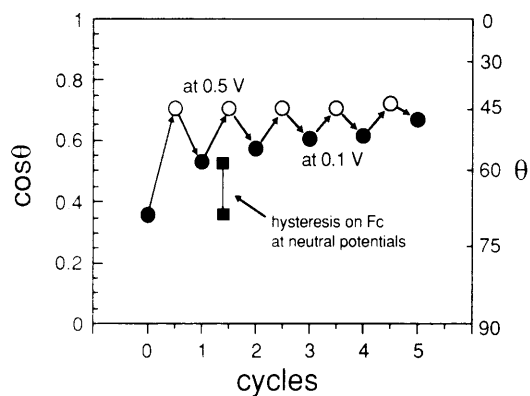


Figure 4. Potential-dependent contact angles of aqueous 0.1 M NaClO₄ (pH 1.5, 10 mM KH₂PO₄) on a SAM formed from FcCO(CH₂)₁₅SH. During each "cycle" the potential of the SAM was increased from 0.1 to 0.5 V, and then decreased back to 0.1 V. The potential of the SAM was cycled 5 times between 0.1 and 0.5 V. The contact angles were measured at 0.1 V (●) and 0.5 V (○), starting at 0.1 V. Potentials are relative to a silver wire reference electrode (see text for details). Also shown (■) is the hysteresis of an aqueous drop of electrolyte on a SAM at neutral potentials without cycling of the potential.

of a drop of water (pH 1.5, 0.1 M NaClO₄) on a gold surface patterned with areas of SAMs formed from FcCO(CH₂)₁₅SH and CH₃(CH₂)₁₅SH. Figure 5a is a diagram of the surface; a square area of SAM formed from FcCO(CH₂)₁₅SH is surrounded by a hydrophobic SAM formed from CH₃(CH₂)₁₅SH. The drop of aqueous electrolyte was placed initially on the square area of SAM formed from FcCO(CH₂)₁₅SH and platinum (counter) and silver (reference) wires were inserted into the drop (Figure 5b). Electrical contact with the gold film was made using a "crocodile" clip. Application of a potential of 0.5 V resulted in oxidation of the surface-confined Fc to Fc⁺ and the spreading of the drop (Figure 5c). Because the drop was bounded by the hydrophobic area formed from CH₃(CH₂)₁₅SH, the shape of the three-phase contact line changed from a circle (Figure 5b) to a square with rounded corners¹² (Figure 5c). Reduction of the surface-confined Fc⁺ back to Fc resulted in only a small recovery of the initial shape; the drop retracted slightly from the corners of the square and the three-phase contact line, sections of which are straight in Figure 5c, developed some curvature (Figure 5d). The large hysteresis observed on the patterned surface contrasts to the potential-dependent contact angles measured on homogeneous SAMs formed from FcCO(CH₂)₁₅SH (see Figure 3). On the patterned SAMs, the drops appeared to be "pinned" on the boundary region between the areas of SAM formed from FcCO(CH₂)₁₅SH and CH₃(CH₂)₁₅SH.

An Electrochemical "Gate" That Controls the Flow of Fluid. Figure 6 illustrates the capability of surface-confined redox species to form a micrometer-scale "gate" that controls the flow of liquid down an inclined surface. The figure shows electro-wetting used as a component of a primitive control device; in this instance, an electrically controllable "valve" with no moving parts. The device was constructed from a gold surface covered with a hydrophilic SAM formed from HO(CH₂)₁₅SH and patterned^{12,13} with micrometer-scale grooves supporting hydrophobic SAMs formed from either CF₃(CF₂)₉(CH₂)₂SH or FcCO(CH₂)₁₅SH (Figure 6, top left). At neutral potentials a drop of aqueous 0.1 M NaClO₄ was prevented from flowing down the inclined surface (under the influence

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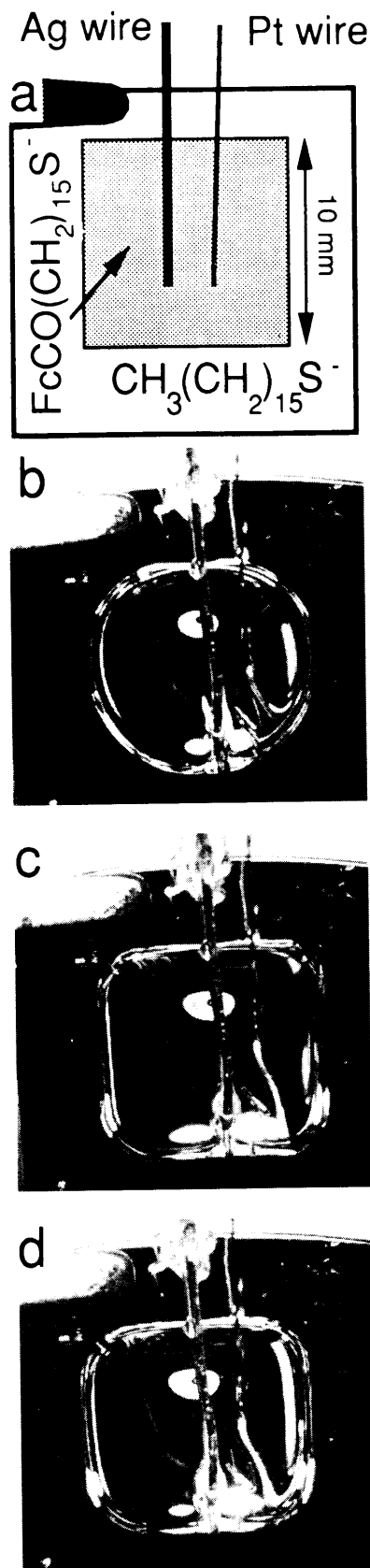


Figure 5. Potential-dependent wetting of a drop of water (pH 1.5, 0.1 M NaClO₄) on a surface patterned with SAMs formed from FcCO(CH₂)₁₅SH and CH₃(CH₂)₁₅SH: (a) diagram of gold film patterned with SAMs; (b) top view of drop before oxidation of the surface-confined Fc; (c) top view of drop after oxidation (0.5 V) of the Fc to Fc⁺; (d) top view of drop after reduction (0.0 V) of the Fc⁺ back to Fc. The volume of the drop was ~20 μL.

of gravity) by the hydrophobic micrometer-wide grooves (Figure 6, $t = 0$ s). Electrochemical oxidation of the surface-confined Fc to Fc⁺ caused the aqueous solution to wet the groove covered with Fc-terminated SAM and flow

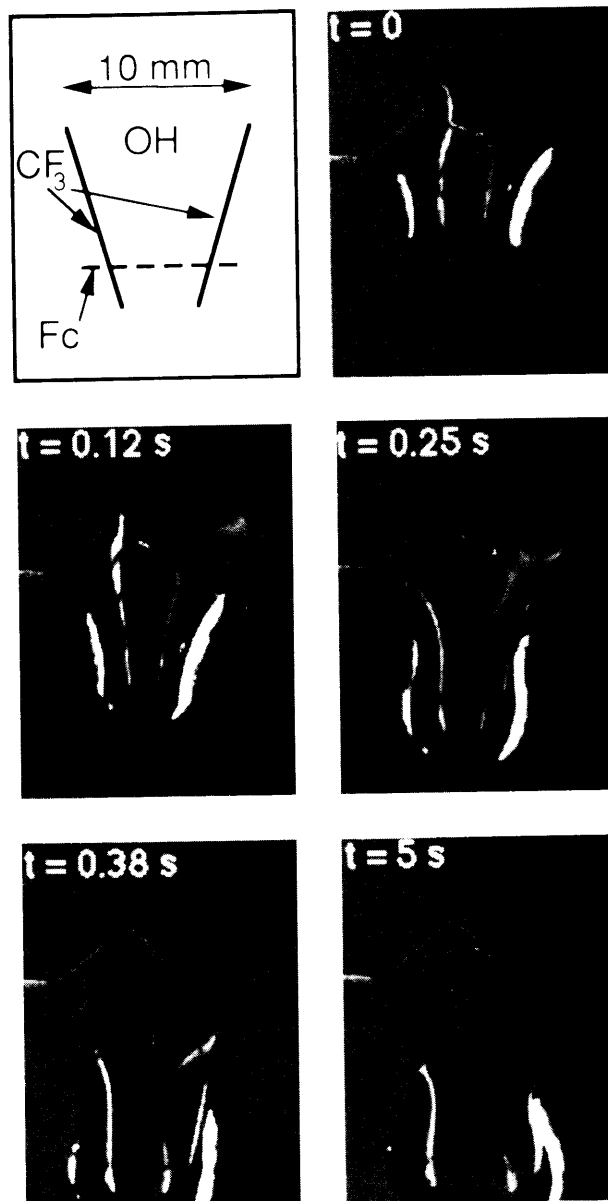


Figure 6. Top views of a drop of water (0.1 M NaClO₄, pH 1.5) on an inclined surface of gold supporting a SAM formed from HO(CH₂)₁₅SH and patterned with micrometer-scale grooves covered with SAMs formed from either CF₃(CF₂)₉(CH₂)₂SH or FcCO(CH₂)₁₅SH. (top left) Diagram of grooves CF₃(CF₂)₉(CH₂)₂SH (solid line) and FcCO(CH₂)₁₅SH (dashed line); ($t = 0$ s) $E = 0$ V. At neutral potentials the drop of water was "contained" by the three hydrophobic grooves and prevented from flowing down the surface of the gold film under gravity; ($t = 0.12$ s) $E = 0.5$ V. The groove covered with a SAM formed from FcCO(CH₂)₁₅SH was transformed from hydrophobic to hydrophilic by the oxidation of the surface-confined Fc to Fc⁺; the water was released from its "container"; ($t = 0.25$ –5 s) $E = 0.5$ V. Following the release of the water from its "container", the water flowed down the surface (between the hydrophobic lines of CF₃(CF₂)₉(CH₂)₂SH) under the influence of gravity.

out of the "container" (Figure 6, $t = 0.12$ s); the solution remained between the hydrophobic lines formed from CF₃(CF₂)₉(CH₂)₂SH as it flowed down the surface (Figure 6, $t = 0.25$ –5 s).

Conclusions

Aqueous solutions on SAMs formed from FcCO(CH₂)₁₅SH show potential-dependent wetting. Contact angles decreased from 71° to 43° and returned to 58° as the potential of the SAM was ramped from 0.3 to 0.5 V and back to 0.2 V. Cyclic voltammetric measurements support our hypothesis that, over short times (<1 min), potential-dependent wetting is caused by the reversible oxidation

of the surface-confined Fc to Fc⁺. Over longer periods of time (>1 min), cyclic voltammograms show a time-dependent, irreversible decomposition of the surface-confined ferricenium ion. Irreversible changes in wettability accompanied the decomposition of the ferricenium ion. Our observations are consistent with previous reports; both homogeneous solutions of ferrocene¹⁰ and surface-confined ferrocene⁵ are known to react irreversibly with nucleophiles under oxidative conditions.

We do not believe the long-time irreversible decomposition of the ferrocene influences the observed short-time wetting of the SAM. In the absence of irreversible decomposition of ferricenium ion, we do not expect the short-time wetting behavior of the surface-confined ferrocene to have zero hysteresis; we observed, in the absence of any applied potentials, a hysteresis in contact angle of ~13° on the ferrocene-terminated SAM. We would expect, however, redox-active species that do not decompose under oxidative conditions to show a different long-time wetting behavior than the ferrocene/ferricenium couple examined.¹⁴

We have demonstrated the use of surface-confined ferrocenes to manipulate the shapes of drops on Au surfaces and control the flow of a liquid down an inclined surface. This type of *active* control over the wettability of organic surfaces may, we believe, be useful for a range of problems in materials science and manufacturing where external control over the shape and position of liquids on a surface is required (such as electrochemical valves and pumps for the preparation and operation of diagnostic assays and microreactors, control of adhesion, and for "directed" self-assembly of chemical components in parallel syntheses on, for example, surfaces).

Experimental Section

Materials. Titanium (99.999+%), gold (99.999+%), tetrahydrofuran (THF), NaClO₄, KH₂PO₄, Na₂SO₄, HClO₄, and CH₃(CH₂)₁₅SH were obtained from Aldrich. Water was distilled and deionized.

Preparation of Gold Films and SAMs. Glass microscope slides (VWR Co.) were cleaned in piranha solution (30% H₂O₂ and 70% H₂SO₄; **WARNING: Piranha solution should be handled with caution; in some circumstances (most probably when it had been mixed with significant quantities of an oxidizable organic material), it has detonated unexpectedly**), rinsed with distilled water and dried in an oven prior to placement in the evaporation chamber. Titanium (~6 Å) was evaporated 1 Å/s and gold (1000 Å) was evaporated at 5 Å/s onto clean glass microscope slides in a cryogenically-pumped chamber (base pressure ≈ 8 × 10⁻⁸ Torr; operating pressure ≈ 1 × 10⁻⁶ Torr) using an electron beam. The resulting gold films are polycrystalline but have a predominant crystallographic orientation that is (111). Self-assembled monolayers were formed on the evaporated films of gold by immersion in solutions of ~1 mM FcCO(CH₂)₁₅SH in THF for 2 h.

Cyclic Voltammetry. All solutions were degassed with argon for 30 min. Cyclic voltammograms shown in Figure 2 were measured by immersing one end of the gold film in an aqueous solution of electrolyte to a depth of ~10 mm. Electrical contact was made with the gold film (the working electrode) using a "crocodile" clip attached to the end of the gold film not immersed in the electrolyte. The area of the working electrode in contact with the electrolyte was measured after the gold film was removed from the electrolyte. Typically, this area was ~100 mm². The reference electrode was a silver wire with a diameter of 0.5 mm.

(14) We also investigated the influence of electrical potentials on SAMs terminated with quinones/hydroquinones (formed from Q(CH₂)₈SH, Q = quinone [Hickman J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science (Washington, D.C.)* **1991**, *252*, 688–691]). Using aqueous solutions (pH 12) and electrical potentials in the range 0.0–0.7 V, we did not observe potential-dependent contact angles. The first pK_a of hydroquinone, which is 9.9 in bulk aqueous solution (In *Lange's Handbook of Chemistry*, Dean, J. A. Ed.; McGraw-Hill: New York, 1992), is plausibly higher than 12 when confined to an interface.

Before electrochemical measurements were performed, the surface oxides were removed from the silver wire using an abrasive paper. Either a platinum flag or a platinum wire was used as the counter electrode. Solutions were not stirred measurement of the cyclic voltammograms. Measurements were performed using a signal generator (Princeton Applied Research, Model 175 Universal Programmer) in conjunction with a three-electrode potentiostat (Princeton Applied Research, Model 174A polarographic analyzer).

Potential-Dependent Contact Angles. The experimental setup is shown in Figure 1. Contact angles were measured using a telescope and goniometer (Ramé-Hart) from drops (~10 μL) that were delivered to the surface using a glass syringe. The reference electrode was a Ag wire (diameter = 0.5 mm). A platinum wire was used as the counter electrode. The signal generator and potentiostat are described above. The procedure used to measure the advancing and receding contact angles is detailed in the results section.

Potential-Dependent Wetting on Patterned, SAMs. Preparation of the patterned SAM was as follows. First, we used a Staedtler pen containing neat (liquid) CH₃(CH₂)₁₅SH, clamped to a X-Y micrometer, to "write" the borders of the square on a gold film.¹⁵ Gold outside of the square was derivatized by reactively spreading a 1 mM ethanolic solution of CH₃(CH₂)₁₅SH over its surface; the border of the square, formed from a SAM of CH₃(CH₂)₁₅S⁻, was not wet by the reacting ethanolic solution. The interior of the triangle was derivatized with a monolayer of FcCO(CH₂)₁₅S⁻ by pipetting a 1 mM ethanolic solution of FcCO(CH₂)₁₅SH onto the interior area of the square. After approximately 5 min, the gold film was washed with ethanol and dried under a stream of N₂. Potential-dependent wetting was performed with a drop of aqueous electrolyte (pH 1.5, 0.1 M NaClO₄) that was pipetted onto the square area of SAM formed from FcCO(CH₂)₁₅SH. We used a platinum reference electrode and a silver reference electrode (both were inserted into the drop). Electrical contact with the gold film was made using a "crocodile" clip. The potential of the gold film, relative to the silver electrode, was controlled using the signal generator and potentiostat described above.

Preparation of Electrochemical "Gate". First, a SAM was formed on an evaporated film of gold by immersion in an ethanolic solution of ~1 mM HO(CH₂)₁₅SH for 2 h. Second, two converging (see Figure 6a) micrometer-wide lines of bare gold were micromachined into the SAM using the tip of a surgical scalpel (Feather Industries).¹³ Third, the grooves of bare gold were covered with SAMs by immersion in 0.2 mM CF₃(CF₂)₉(CH₂)₂SH in isooctane for 20 s. Fourth, a third groove was micromachined into the gold film such that the groove intersected the first two grooves at their converging ends (see Figure 6a). Fifth, the third groove was covered with a SAM of FcCO(CH₂)₁₅S⁻ by immersing the gold film in 1 mM FcCO(CH₂)₁₅SH in THF for 20 s. After the gold was patterned with the SAMs, it was inclined to the horizontal with the groove covered with FcCO(CH₂)₁₅S⁻ at the bottom. A drop of aqueous electrolyte, which was placed on the surface of the film within the grooves, flowed down the surface under the influence of gravity until it was contained by the hydrophobic grooves of FcCO(CH₂)₁₅S⁻ (at the bottom) and CF₃(CF₂)₉(CH₂)₂S⁻ (at the sides). A "crocodile" clip was used to make electrical contact with the gold film. Either a reference (Ag wire) and a counter (Pt wire) electrodes or, for simplicity, only a counter electrode (Pt wire) was inserted into the aqueous drop. The "container" was opened by applying an oxidizing potential of 0.5 V. The motion of the drop was recorded using a video camera (NEC) and a Macintosh Quadra 700 with a 24 XLTV digitizing video board (RasterOps). Images were captured using the software MediaGrabber 1.7 (RasterOps) and analyzed using Image 1.47 (National Institutes of Health).

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