

Control of the Shape of Liquid Lenses on a Modified Gold Surface Using an Applied Electrical Potential across a Self-Assembled Monolayer

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Electrochemical desorption of a patterned, self-assembled monolayer (SAM) of an organothiol on a gold surface can be used to control the shape of drops of liquid hexadecanethiol (HDT) on the surface. The contact angle of HDT drops on a thin, transparent film of gold (100 Å thick) under an aqueous electrolyte solution could be varied from $128 \pm 2^\circ$ when the gold was held at -1.7 V (vs Ag pseudoreference) to $37 \pm 2^\circ$ when the gold was held at 0.0 V. Switching between these two limiting contact angles could be performed rapidly, reversibly, and reproducibly using this system. These drops could act as lenses and could be used as an optical switch which focuses/defocuses light. An array of 1-nL drops could be formed by differential wetting of a gold surface patterned with methyl- and carboxylic acid-terminated organothiol, and the contact angles of drops in this array could be switched in ca. 50 ms. Alternatively, drops could be confined to an array of gold pads on a conducting glass and switched in a similar fashion.

Introduction

This paper describes the controlled electrochemical desorption of patterned self-assembled monolayers (SAMs) on gold recently described by Porter et al.¹⁻⁴ as a method to control the shape of drops of hexadecanethiol (HDT) present on the patterned surface. When the gold was transparent, these drops acted as lenses for transmitted light. In a system consisting of liquid HDT drops resting on a gold surface and surrounded by aqueous electrolyte, these lenses, displayed large, fast, reversible, and reproducible changes in shape (and thus focal length) as the result of a change in the potential applied to the substrate supporting the lens. Potential-dependent changes in wetting of surfaces due to the presence of an electric field are small.⁵ If the change in surface potential results in an electrochemical reaction and a large change in the species on the surface, however, the effect of potential on wettability can be large.⁶⁻⁸

Results and Discussion

A drop of a liquid alkanethiol resting on a gold surface under water formed a planar convex liquid lens. We have studied the behavior of hexadecanethiol, $\text{HS}(\text{CH}_2)_{15}\text{CH}_3$ (HDT),⁹ on polycrystalline gold substrates held under aqueous electrolyte at different electrical potentials to establish conditions that caused electrodesorption of the SAM formed by contact of gold with HDT. We exploited

these conditions to control the area of contact, and therefore the shape, of drops of HDT on the surface of "transparent" gold (100 Å thick, also polycrystalline but still a continuous metal coating).¹⁰ Previously, we studied the behavior of a drop in air.⁶ Working with hydrophobic hydrocarbon liquids (in this instance, HDT) under aqueous solution was easier, permitted more control over the environment in which the drop resides, and gave more reproducible results.

A drop of neat hexadecanethiol ($\sim 1 \mu\text{L}$) was placed on a "bare" gold surface under 100 mM aqueous sodium perchlorate electrolyte solution. The drop spread reactively¹¹ on gold held at 0.0 V (relative to a silver reference electrode) underwater and formed a hydrophobic monolayer under the drop. The advancing contact angle of this drop reached a value of $37 \pm 2^\circ$. Switching the potential of the gold to -1.7 V versus a silver wire pseudoreference¹² caused electrodesorption of the SAM¹⁻⁴ and retraction of the drop. The receding contact angle of this drop was $128 \pm 2^\circ$. The drop retracted on the surface as the hydrophobic SAM desorbed and water wet the resulting charged gold surface. Retraction of the drop also reduced the interfacial area between the drop and the water (Figure 1, right).

The factors that determine the final contact angle at -1.7 V have not been entirely determined. A drop of HDT placed on the surface when it was held at -1.7 V assumed a contact angle of 128° . This observation indicated that the history of the drop did not play a role in establishing its final contact angle. A drop of hexadecane (a liquid of similar density, dielectric properties, and viscosity) applied to the surface at -1.7 V appeared not to interact with the gold ($\theta = 180^\circ$).

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(9) We selected HDT for this work because it forms excellent SAMs and because the surface of a fully formed SAM of this thiol has a low interfacial free energy: $\gamma_{sv} \sim 20 \text{ erg/cm}^2$. SAMs formed from HDT are hydrophobic: water has a high contact angle on them in air ($\theta_a(\text{H}_2\text{O}) \sim 112-115^\circ$). HDT is a hydrophobic liquid at room temperature with a surface tension of 32 erg/cm^2 and a refractive index of 1.46.

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(11) "Reactive spreading" across a surface describes the forward movement of liquid caused by its reaction with the surface and the spread of this liquid as a film over the modified surface. The contact angle of the leading edge of the drop of reacting liquid with the modified surface is low when reactive spreading occurs: Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1994**, *10*, 4581-4587.

(12) The potential established by a silver wire in a solution containing HDT is undetermined since the wire would undoubtedly be covered with a monolayer of HDT. The behavior described here, however, was reproducible when silver wire that had been freshly cleaned in nitric acid (ca. 30 s immersion in concentrated nitric acid followed by rinsing with water) was employed.

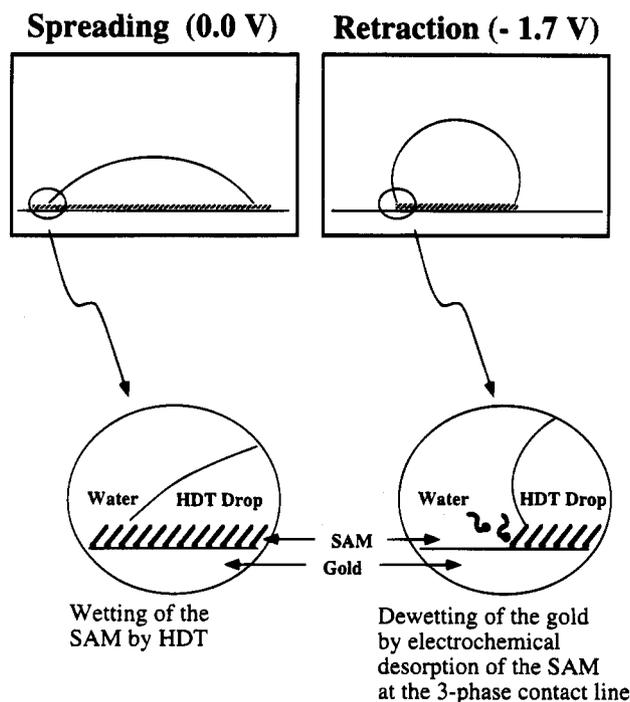


Figure 1. Schematic of the behavior of a drop of HDT on a gold surface at 0.0 V (left) and at -1.7 V (right) [versus Ag wire pseudoreference] under 100 mM sodium perchlorate electrolyte solution. At 0.0 V, the HDT reacted with the gold surface and formed a monolayer that is wet by the HDT liquid. At -1.7 V, the monolayer reductively desorbed as RS^- ,¹⁻⁴ and the drop of HDT retracted.

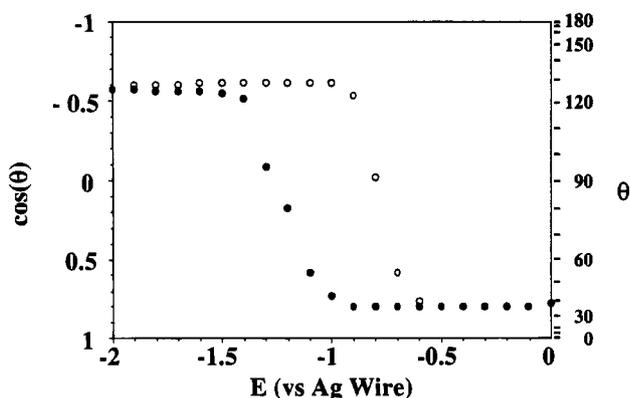


Figure 2. Contact angle of a drop of HDT ($\sim 1 \mu\text{L}$) on a gold surface under 100 mM aqueous sodium perchlorate changed with the potential of the gold. The potential was ramped at 50 mV/s with respect to a silver wire pseudoreference electrode. Solid circles denote data obtained as the electrical potential was scanned in the negative direction and the drop was observed to retract from the surface. Open circles denote data obtained as the electrical potential was scanned in the positive direction and the drop was observed to spread on the surface.

The contact angle of the drop changed continuously as a function of potential between these two limiting values (Figure 2). Hysteresis was observed in the spreading/retraction. The hysteresis in contact angles did not change with the thickness of the gold (and thus its roughness) or with the chain length of the thiol (use of octanethiol and dodecanethiol gave similar results). The changes in contact angle with applied electrical potential were reversible and reproducible: a drop could be cycled for ~ 1 h between -1.7 V and 0.0 V (>50 cycles, 50 mV/s, ~ 1 min/cycle) with no detectable change in its behavior over this period of time.

Switching speeds for drops of this size were determined by changing the potential of the gold (to -1.7 V for

retraction of the drop, or to 0.0 V for spreading of the drop, Figure 3) and observing the time required for the shape to change using a video system. For a drop having a volume of $1 \mu\text{L}$, switching the potential of the gold from 0.0 to -1.7 V resulted in complete retraction of the drop ($\theta_r = 128^\circ$) in 450 ± 40 ms. Switching the potential back to 0.0 V resulted in spreading ($\theta_a = 37^\circ$) in 120 ± 40 ms.

A drop of HDT ($\sim 50 \mu\text{L}$) on transparent gold could behave as a planar convex lens (Figure 3). When the drop was on the surface at -1.7 V, it focused light transmitted through it (Figure 4c). Astigmatism of this lens was minimal presumably because interfacial tension between the two liquids (water and HDT) ensured constant curvature of the lens and because the interior of the lens was free of stress and thus of aberrations. A drop on gold held at 0.0 V also acted as a lens, but one with a longer focal length. The images in Figure 4 demonstrate the ability of the drop to act as an optical switch that focused/defocused light or an image in the far field as a function of applied electrical potential. The drop shown in Figure 4c could be perturbed electrochemically to bring an image repeatedly into/out of focus (>10 cycles).

The focal length of the planar convex lens formed by the drop was proportional to its radius of curvature (eq 1)¹³ where Δn is the refractive index difference between the two media (here ~ 0.1 , for $n_1 = 1.46$ for HDT and $n_2 = 1.35 \pm 0.01$ for the aqueous solution of sodium perchlorate).

$$f = r / \Delta n \quad (1)$$

The drop in Figure 4c had a radius of curvature of $366 \mu\text{m}$, and the focal length of the drop (in aqueous solution) was computed and measured to be approximately 3.5 mm.

The size and shape of HDT drops under aqueous electrolyte could be controlled using gold spatially patterned with SAMs terminated by $-\text{CO}_2\text{H}$ and $-\text{CH}_3$ groups. An array of 1-nL drops formed by differential wetting of a patterned surface¹⁴ was fabricated by the following procedure. First, the gold surface was patterned with HDT using microcontact printing.¹⁵⁻¹⁷ This procedure formed $100\text{-}\mu\text{m}^2$ regions on the surface consisting of SAM terminated with hydrophobic $-\text{CH}_3$ groups. Second, this patterned surface was immersed in a 5 mM ethanolic solution of 11-mercaptoundecanoic acid ($\text{HS}(\text{CH}_2)_{15}\text{COOH}$) for 5 s to fill in the remaining regions of the surface with SAM terminated in hydrophilic $-\text{CO}_2\text{H}$ groups. Moving this patterned surface through a thin (~ 1 mm) layer of HDT on top of the aqueous electrolyte caused drops of HDT to self-assemble on the hydrophobic regions of the patterned SAM. Lowering the potential of the substrate from 0.0 V to -1.7 V changed the shape of the drops in this array and the focal point of light transmitted through each microlens (Figure 5). The array of drops switched between two stable shapes in 50 ms at substrate potentials of 0.0 and -1.7 V.

Patterned SAMs are useful to direct the self-assembly of drops on surfaces. On changing the electrochemical potential to -1.7 V, we expected this entire pattern to desorb reductively from the surface. Although drops were often observed to remain on the regions of the surface originally patterned with HDT (presumably pinned by

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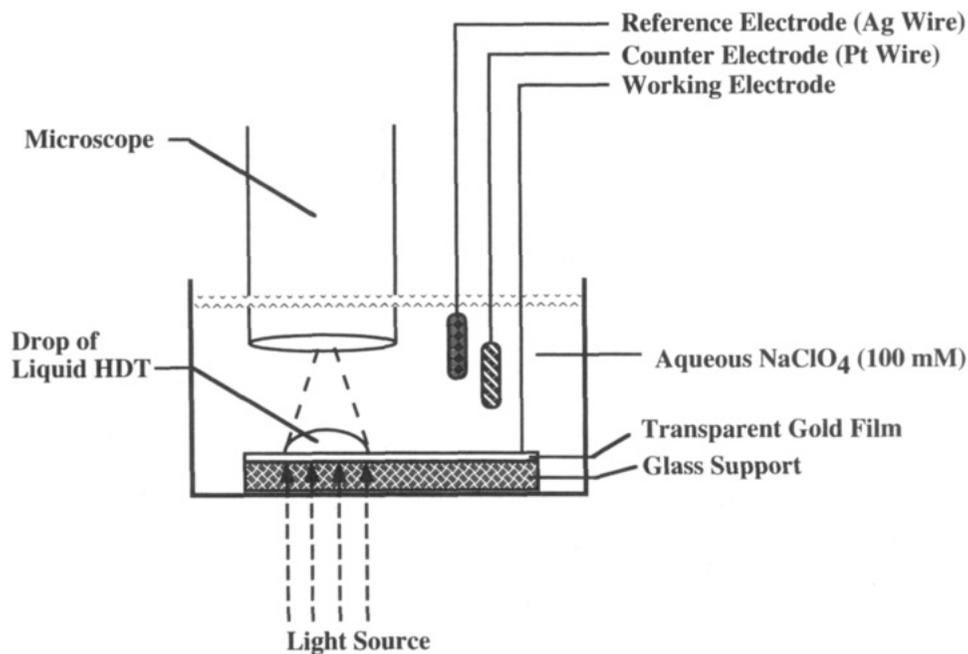


Figure 3. Schematic of the procedure for the electrochemical control of the shape of an HDT drop. The solution could be translated so that the microscope objective focused on the drop or the image focused by the drop.

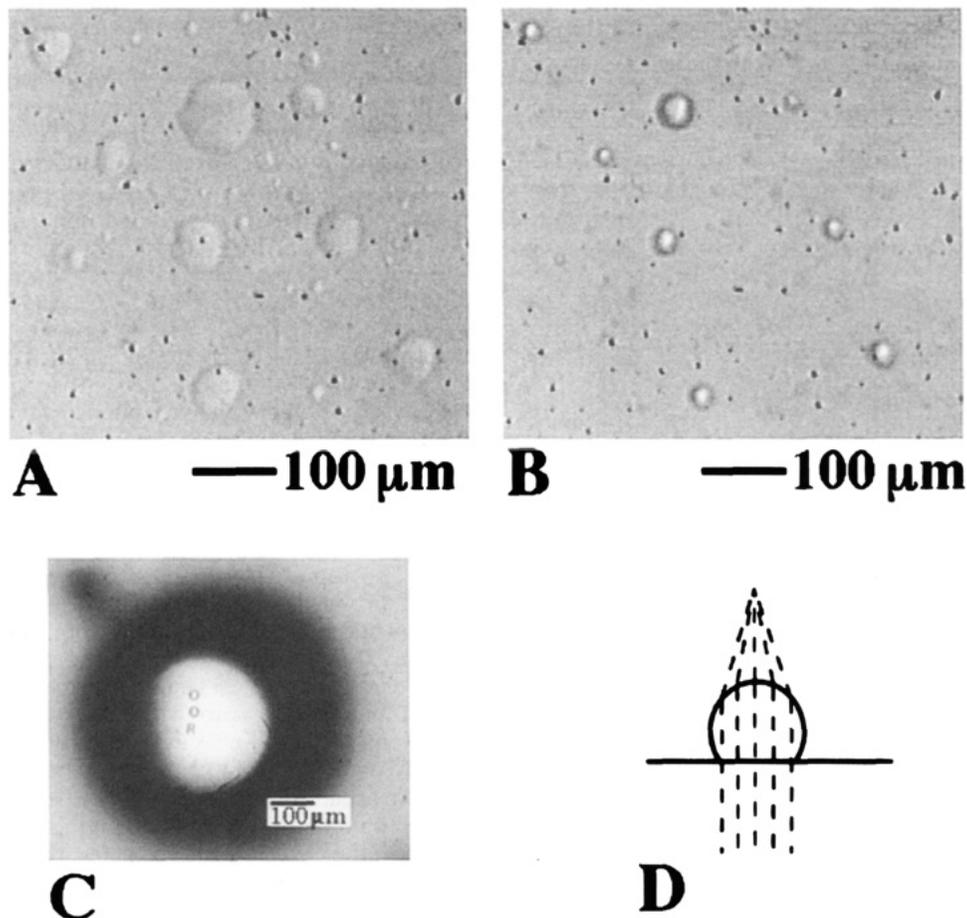


Figure 4. (A, B) Optical micrographs of HDT drops on gold under 100 mM aqueous sodium perchlorate at 0.0 and -1.7 V, respectively. (C) Optical micrograph in which the microscope objective was focused at the focal point of a drop. The drop acted as a lens to focus letters in the far field. (D) Ray trace [not to scale] indicating the focusing of a far field image by a drop.

impurities that might have collected at the $-\text{CH}_3/-\text{COOH}$ boundaries during patterning), an alternate procedure was devised to construct "pads" to hold and confine the drops. In this case, 100 Å of gold deposited on transparent indium tin oxide (ITO) glass was patterned using micro-contact printing, followed by a basic cyanide etch to remove

the gold unprotected by the HDT monolayer.¹⁵⁻¹⁷ For all of the experiments previously discussed, nonconducting glass was used as a substrate. Although the gold coating on the glass was thin (100 Å), it was sufficiently conducting (see Experimental Section). ITO was used in this case because the gold pads required a conducting substrate to

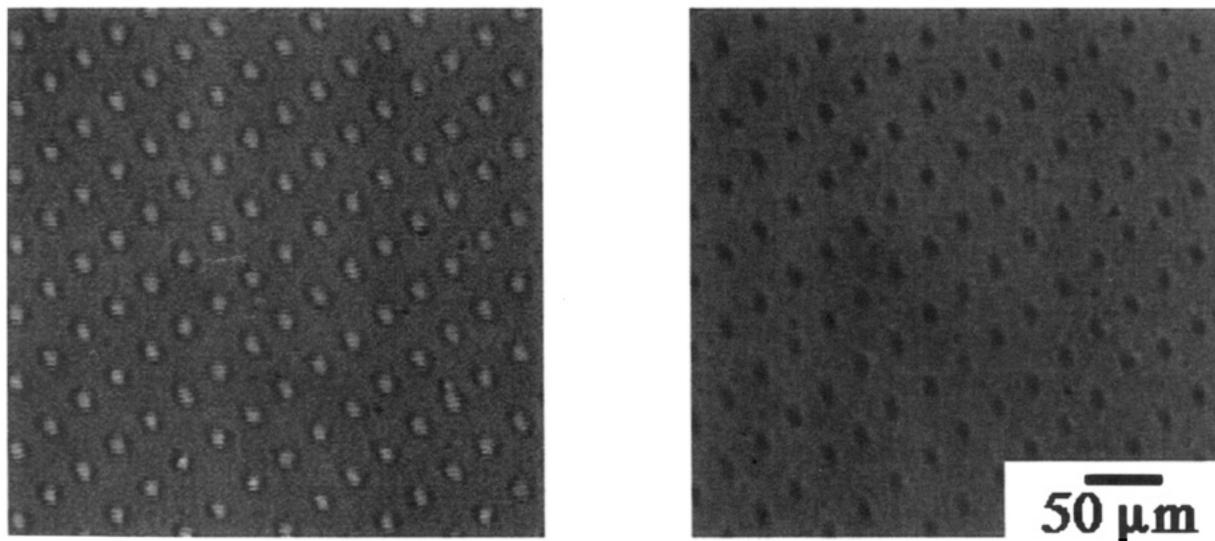


Figure 5. An array of drops (~ 1 nL) switched on a 50-ms time scale.

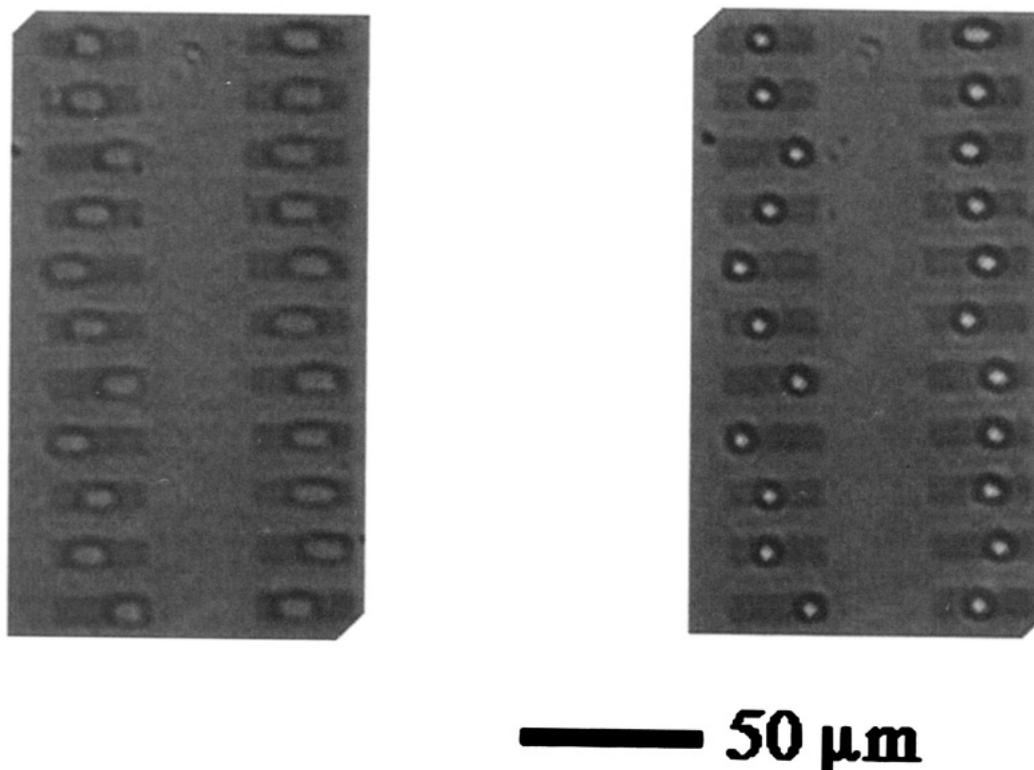


Figure 6. Drops confined in rectangular gold regions patterned on 1 mm of ITO displayed changes in their shape upon switching the potential of the gold.

facilitate electrochemistry upon them. ITO is an electrical conductor, transparent to visible light, hydrophilic, and nonreactive toward thiols. This procedure created hydrophobic gold "pads" upon which HDT drops assembled as the surface was passed through a thin (~ 1 mm) layer of HDT floating on the aqueous electrolyte (see above). Drops were subsequently confined to gold-covered regions on the substrate throughout the experiment (Figure 6). In this demonstration, a potential-induced change in the shape of the drop switched patterned arrays of drops from a focusing (at -1.7 V) to defocusing (at 0.0 V) configuration. With this technique, pads of arbitrary shape, size, and relative placement are easily fabricated, permitting the formation of lenses with more complex shapes.

Conclusions

These experiments demonstrate the use of an electrical potential to influence the shape of a drop reversibly and the application of this change in shape to the formation of liquid lenses and arrays of lenses whose focal length can be changed by changing the potential. Drops of HDT could, in principle, be used as electroactive switches to control the coupling of a light source to a detector. Patterned self-assembly can facilitate the fabrication of arrays of drops of controlled size, shape, and organization. These procedures may have application in areas where control of the shape of a lens is useful (e.g. optical switching, active optics, sensors)¹⁸ and where microlens arrays are employed.¹⁹

Experimental Section

General Procedures. Hexadecanethiol (HDT) and hexadecane were purchased from Aldrich and purified by passage through neutral alumina; 11-mercaptoundecanoic acid ($\text{HS}-(\text{CH}_2)_{10}\text{COOH}$) was available from previous studies. Transparent gold substrates were prepared by evaporation at (1 \AA/s), using an electron beam, of 100 \AA of gold (99.999%) onto titanium-primed (5 \AA) glass¹⁰ or indium tin oxide (ITO, 1 mm on glass, Delta Technologies, Stillwater, MN) at a pressure of 1×10^{-7} Torr. Glass was used for all but the last experiment. Even a 100-\AA gold coating was sufficiently conductive to facilitate electrochemical desorption identical to that observed for thicker gold (1000 \AA) films. Stamps were made of poly(dimethylsiloxane) (Dow-Corning, SYLGARD Silicone Elastomer-184).¹⁵⁻¹⁷

Instrumentation. Optical micrographs were obtained on an Olympus BH-2 microscope. Light was transmitted through the thin gold substrate. The objective lens ($10\times$, numerical aperture of ~ 0.15 , or $20\times$, numerical aperture of ~ 0.22) of the microscope was immersed in water; the image was captured with a charged-coupled camera (NEC model NX18A) through a $15\times$ relay lens at 33 frames/s using a four-head video recorder (Mitsubishi Model 52A). Images were later digitized with a frame grabber (RasterOps, Santa Clara, CA). Electrochemical potential was controlled using a Princeton Applied Research Model 371 potentiostat using the gold surface as the working electrode, a platinum wire as the counter electrode, and a silver wire as a pseudo reference electrode.¹² The surface area of the counter electrode did not limit any of the switching speeds reported. No decrease in switching speeds was observed when a large piece of platinum foil was substituted for the platinum wire counter electrode. Relative placement of these electrodes with respect to the gold surface did not influence switching behavior or speed.

Measurement of Contact Angles. Contact angles were measured on a Ramé-Hart Model 100 goniometer at room temperature. A glass dish with a flat side was used to view the drops from the side. A Micro-Electrapette syringe (Matrix Technologies) equipped with disposable polystyrene pipet tips was used for dispensing liquids onto the SAMs and removing them from the SAMs ($\sim 1 \mu\text{L/s}$). The source of illumination was placed behind the sample. Optical micrographs were obtained using a home-built, horizontal microscope. The objective lens (Olympus $10\times$, numerical aperture of ~ 0.15) was attached to a charged-coupled camera (NEC Model NX18A) through a relay telescope and condensing lens ($10\times$) and the image was recorded at 33 frames/s using a four-head video recorder (Mitsubishi Model 52A). Contact angles were measured directly from digitized images of the profile of drops of these liquids on the gold substrate using IMAGE 1.53 software (National Institutes of Health).

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Fabrication of a Transparent Gold Electrode. The gold (on glass or ITO) was cleaned by brief (ca. 15 s) treatment with "piranha solution" ($7:3$ concentrated $\text{H}_2\text{SO}_4/30\% \text{ H}_2\text{O}_2$), which had cooled to room temperature (ca. 2 h after mixing the two components). **WARNING: Pirhana solution should be handled with caution; it has detonated unexpectedly.**²⁰ The surface was then patterned with thiols (see below) or left "bare". Electrical contact was made by soldering a thin gold wire onto the surface using indium metal (99.999%, Aldrich). As this contact does change the surface, it was made in a region far removed from that where the experiments were performed.

Placement of Single Drops on a Surface. This procedure was accomplished by drawing out a glass pipet in a flame to an outer diameter of $200 \pm 100 \mu\text{m}$. The "bare" gold slide was placed in the electrolyte solution and the drops were dispensed directly onto the surface.

Formation of Microlens Arrays on Gold on Glass. Elastomeric stamps were fabricated according to a published procedure.¹⁵⁻¹⁷ The stamps were inked with an $\sim 1 \text{ mM}$ ethanolic solution of hexadecanethiol and placed in contact with the surface of the gold substrate for 5 s . The derivatized sample was immersed in a solution of $\sim 1 \text{ mM}$ 11-mercaptoundecanoic acid for 5 s to derivatize the remainder of the gold. The sample was rinsed with ethanol ($\sim 20 \text{ mL}$), and dried under a stream of nitrogen. A glass dish was filled with 100 mM aqueous sodium perchlorate solution. Several drops of HDT were added to the top of this solution. The patterned SAM was lowered by hand through the organic phase ($1-5 \text{ cm/s}$) into the aqueous phase. No sensitivity of this procedure to the speed of movement of the sample through the hydrocarbon phase was observed.

Formation of Microlens Arrays Using Gold Pads on ITO. HDT was patterned on the surface of the gold using microcontact printing (see above). The glass/ITO/gold slide was placed into a basic cyanide etch bath (0.1 M KCN , 0.1 M KOH , oxygen bubbled through with vigorous stirring) for ca. 15 min at room temperature.¹⁵ The gold in the non-HDT covered regions was removed. The slide was then transferred through a thin layer of HDT floating on a 100 mM aqueous sodium perchlorate solution as described above.

Acknowledgment. This research was supported in part by the National Science Foundation (PHY 9312572) and in part by ONR and ARPA. We thank Karl Berggren for helpful discussions.

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