This exam refers to the pre-announced topic and paper in the box below (paper attached), and related background materials. No materials other than the papers provided may be used during the exam. Whenever possible, use graphs and drawings in your answer.

Science 299 (No. 5605), 371-374, 2003 “A Reversibly Switching Surface”

Please note that the first author of this article, Dr. Joerg Lahann, will be visiting our department as a faculty candidate on Friday April 4.

1.) {15%} Describe what is meant by the “wettability” of a surface and how it is usually quantified. Give some typical numerical values for this parameter used in the quantification of wettability for both highly wettable and highly unwettable surfaces. Give an example of a material that would exhibit these extreme values in the parameter.

2.) {15%} Being as quantitative as possible, and using a diagram, provide a basic thermodynamic explanation of the surface property of “wettability” for a solid surface in contact with a liquid.

3.) {10%} Everyone should get all of these points! I will be very generous in my grading standards here - I am looking for some imagination, not regurgitation of something from the paper. Give one example from the biomedical field of an application in which it would be useful to be able to “switch” the wettability of a surface between two states at will. For your example, explain why the surface would be needed in each state.

4.) {10%} In the paper in question, the researchers were able to produce a lower coverage of the final molecule used in the monolayer than would normally form for 16-mercaptohexadecanoic acid. Write the chemical reactions that allowed the preparation of this surface and explain each reaction step with a sentence or two.

5.) {30%} The researchers claim to be working on a Au(111) surface. 5a.) {10%} Draw a neat diagram of this Au(111) surface, representing each Au atom as an open circle. In the supplementary material for this article (attached here at the end of the paper) the authors state that the Au-Au distance in this surface is 0.29 nm. Show and label this distance on your diagram. 5b.) {10%} The authors state in the supplementary material, and it is widely known from dozens of other papers, that alkanethiolates produce a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. Draw a neat diagram that shows what this means. In your diagram, label the dimensions of the structure. 5c.) {10%} The authors state that in the normal high-density structure (i.e. the one in part 5b) the area-per-molecule is 0.22 nm$^2$. Prove or disprove this in a calculation using the 0.29 nm figure for the Au-Au distance.

6.) {10%} Describe the SFG results in Fig. 3. Make sure that you compare and contrast the polarity of the medium and explain the reasons for the observed intensities of the methylene C-H stretching vibrations. What do the results imply about the ability of the surface to respond to the medium in which it is immersed?

7.) {10%} Criticize the paper by describing a weakness that you perceive. Be specific and detailed. Don’t tell me the paper has no weaknesses.
A Reversibly Switching Surface

Joerg Lahann,1 Samir Mitragotri,2 Thanh-Nga Tran,1 Hiroki Kaido,1 Jagannathan Sundaram,1 Insung S. Choi,1* Saskia Hoffer,1† Gabor A. Somorjai,1 Robert Langer1†

We report the design of surfaces that exhibit dynamic changes in interfacial properties, such as wettability, in response to an electrical potential. The change in wetting behavior was caused by surface-confined, single-layered molecules undergoing conformational transitions between a hydrophilic and a moderately hydrophobic state. Reversible conformational transitions were confirmed at a molecular level with the use of sum-frequency generation spectroscopy and at a macroscopic level with the use of contact angle measurements. This type of surface design enables amplification of molecular-level conformational transitions to macroscopic changes in surface properties without altering the chemical identity of the surface. Such reversibly switching surfaces may open previously unknown opportunities in interfacial engineering.

Interfacial properties, such as wetting behavior, are defined by the molecular-level structure of the surface (1). Diverse modification procedures have been used to permanently alter wettability (2–4). Control of wettability has been recently demonstrated by elegant methods including light-induced (5–6) and electrochemical surface modifications (7–10). These systems require chemical reactions in order to control wettability.

We demonstrate an alternative approach for dynamically controlling interfacial properties that uses conformational transitions (switching) of surface-confined molecules. Polymers have been shown to undergo conformational reorientations when changed from one solvent to another (11) or from one temperature to another (12, 13) because of phase transitions between a well-solvated and a poorly solvated state (14). In contrast, our approach maintains the system’s environment unaltered (including solvent, electrolyte content, pH, temperature, and pressure) while using an active stimulus, such as an electrical potential, to trigger specific conformational transitions (e.g., switching from an all-trans to a partially gauche oriented conformation; see Fig. 1). Amplification of conformational transitions to macroscopically measurable changes requires synergistic molecular reorientations of ordered molecules. In principle, this is attainable with a single-molecular layer, such as a self-assembled monolayer (SAM) of alkane thiolates on gold (15). However, the dense molecular packing in SAMs and the strong interactions between the methylene groups restrict dynamic molecular motions to the outermost atoms (16, 17). All in situ evidence so far indicates that applied electrical potentials have no effect on long-chain alkane thiolates monolayers on gold within the range of chemical stability of the SAM (18). In other words, conventional SAMs are too dense to allow conformational transitions and consequently do not allow for switching. To explore SAMs as a model system for switching, we must establish sufficient spatial freedom for each molecule. Once a low-density SAM is created, preferential exposure of either hydrophilic or hydrophobic moieties of the SAM to the surrounding medium could be exploited for the switching of macroscopic surface properties.

(16-Mercapto)hexadecanonic acid (MHA) was chosen as a model molecule because it (i) self-assembles on Au(111) into a monolayer and (ii) has a hydrophobic chain capped by a hydrophilic carboxylate group, thus potentially facilitating changes in the overall surface properties. To create a monolayer with sufficient spacing between the individual MHA molecules, we used a strategy that exploits synthesis and self-assembly of a MHA derivative with a globular end group, which results in a SAM that is densely packed with respect to the space-filling end groups but shows low-density packing with respect to the hydrophilic chains. Subsequent cleavage of the space-filling end groups establishes a low-density SAM of MHA. The spatial dimensions of the precursor molecule to be used were adapted to match the optimum alkane thiolate density for conformational rearrangements.

The equilibrium low-energy conformational state of each of the slowly packed MHA

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1Department of Chemical Engineering, Massachusetts Institute of Technology (MIT), 45 Carleton Street, Cambridge, MA 02139, USA. 2Department of Chemical Engineering, University of California at Santa Barbara, Santa Barbara, CA 93106, USA. 3Department of Chemistry, University of California at Berkeley, Material Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA.

*Present address: Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea. To whom correspondence should be addressed. E-mail: ranger@mit.edu

Fig. 1. Idealized representation of the transition between straight (hydrophilic) and bent (hydrophobic) molecular conformations (kios and solvent molecules are not shown). The precursor molecule MIAE, characterized by a bulky end group and a thiol head group, was synthesized from MHA by introducing the (2-chlorophenyl)diphenylmethyl ester group.
molecules is all trans (all C-C-C torsion angles of the hydrophobic core are 180 degrees) [15]. Upon applying an electrical potential, the negatively charged carboxylate groups experience an attractive force to the gold surface, causing the hydrophobic chains to undergo conformational changes. This chain bending disrupts the all-trans conformational state and causes the aliphatic MHA chains to adopt a mixture of trans and gauche conformations. Thus, the “bent” state of the MHA chains is characterized by an ensemble of molecules in mixed conformations, which maximizes the intermolecular van der Waals contact and exposes the hydrophobic chains of the MHA molecules to the surrounding medium. To obtain a theoretical estimate of the packing density that would provide sufficient conformational freedom for optimal arrangement of the bent states of the MHA molecules, we performed molecular simulations of MHA monolayers, computing intramolecular bonded interactions and inter- and intramolecular nonbonded interactions. Simulations were conducted starting from the states of MHA molecules in bent states. Six assemblies with area-per-molecule values in the range between 0.29 and 2.59 nm² were studied (Materials and Methods). For small area-per-molecule values, relaxation of the highly strained assembly was dominant resulting in a steep decline of the potential energy as S-S spacings were widened. The plot of potential energy versus area per molecule (Fig. 2) shows that steric constraints are reasonably low for area-per-molecule values of 0.65 nm² or higher. On the other hand, the spacing between the MHA molecules for an area-per-molecule value of 0.65 nm² still permits a substantial overlap of MHA molecules, leading to favorable hydrophobic interactions between alkyl chains. Thus, even for the system with the widest S-S spacing of 1.73 nm, sufficient overlap of neighboring chains occurred and prevented the overall energy of the system from approaching zero. We conclude from these simulations that an area-per-molecule of 0.65 nm² is optimum because it supports steric relaxation and allows for substantial chain overlap.

On the basis of these theoretical considerations, we synthesized a MHA derivative with a globular end group [(16-mercapto) hexadecylamine (2-chlorophenyl)triphenylmethane ester, MHAe]. Its space-filling end group (about 0.67 nm²) matched closely with the previously determined area of 0.65 nm². Self-assembly of MHAe on gold and subsequent removal of the acid-labile end groups resulted in a low-density SAM of MHAe (26). The quantitative removal was verified by the absence of the signal of chloroform as detected by x-ray photoelectron spectroscopy (XPS). In addition, the characteristic signal of the triphenylmethyl ester group at 1743 cm⁻¹ in the infrared (IR) spectrum was no longer observed, and the characteristic C==O peak appeared (29). We then exposed a low-density SAM of MHA to a solution of n-butanol immediately after cleavage of the bulky end group and conducted electrochemical desorption. For this mixed SAM, a single desorption peak was detected (orange line in Fig. S1). In contrast, two desorption peaks were found for phase-separated SAMs composed of MHA and n-butanol formed via co-adsorption (blue line in Fig. S1), corresponding to the coexistence of two distinct phases (27). We conclude from this experiment that preparation of a SAM following the previously mentioned strategy resulted in a rather homogeneously distributed monolayer and not a phase-segregated system. These results support the assumption that the low-density SAM consists of molecules that show increased spacing between individual molecules; the formation of MHA clusters is less likely.

Before examining whether the low-density MAM of MHA undergoes conformational transitions in response to electric potentials, we confirmed the conformational freedom of the alkaneethioles by studying their response to changes in the chemical environment. Sum-frequency generation (SGF) spectroscopy was used for this purpose because it exploits a highly surface-sensitive nonlinear optical process (22). The intensity of a peak in the SFG spectrum is affected by the orientation of the adsorbed molecules. An ordered monolayer of all-trans oriented molecules is locally centro-symmetric and hence, by rule of mutual exclusion, its methylene modes are sum-frequency inactive. Gauche conformations break the local symmetry and give rise to SFG signals of the methylene groups (23). Figure 3 shows SFG spectra of the low-density SAMs of MHA that were deprotonated. When exposing the low-density SAM to an apolar medium such as air or toluene, the molecules were found to be in disordered conformations. This state was characterized by the presence of gauche conformations as indicated by SFG signals of the methylene groups at wavelengths of 2925 and 2855 cm⁻¹ (Fig. 3, green and black lines). When the same surface was brought in contact with a polar environment (acetonitrile or water), molecules straightened up, presumably by expelling their polar end groups to the solvent. SFG signals associated with the methylene groups were no longer detected. For the dense SAM of MHA, structural reorganizations were far less pronounced and were con-
parable to reported studies (24). On the basis of the detected conformational transitions in response to changes in the polarity of the surrounding medium, we conclude that only the low-density SAM provided sufficient chain mobility to allow conformational reorientations from a hydrophilic (straight chains) to a hydrophobic (bent chains) state.

We next assessed switching induced by an active stimulus, such as application of an electrical potential. Information regarding the prospective range of the electrical potential for switching may be obtained from basic energy considerations. First, alkaneethioles adsorbed on gold and exposed to a surrounding solution show electrochemical stability only in a relatively narrow range of electrical potential [1.046 V to +654 mV with respect to (w.r.t.) the standard calomel electrode (SCE)] (25). Applied electrical potentials must be within this range of stability. Second, the change in Gibbs free energy of the system must be negative for a change in the monolayer structure to occur. With the use of a basic model, we estimated a potential above about +1.30 V (NHE) to be required to satisfy the conditions of molecular reorientation in a low-density SAM (26).

A SFG spectrometer equipped with an electrochemical quartz cell (27) was used to assess the switching of the surface in response to electrical potentials (Fig. 4, A and B). Without applied electrical potential, the SFG spectra recorded in acetonitrile [0.1 M cesium trifluoroacetate (CT)] were featureless in the range between 2820 and 2940 cm\(^{-1}\), signifying straight molecular conformations of an all-trans orientation. Slightly positive polarization of the gold electrodes (+25 mV w.r.t. SCE) did initiate simultaneous switching of the molecules indicated by characteristic methylene modes at wavelengths of 2855 and 2925 cm\(^{-1}\) (Fig. 4A). The presence of gauche conformations in the molecules implies that the molecules bend their negatively charged end groups toward the positively charged gold surface (Fig. 1). After the positive potential was turned off, the low-density SAM returned to an assembly of straight molecules with all-trans orientation, because SFG signals of the methylene groups were no longer detected. Switching was reversible, with intensities of the SFG signals being nearly constant as the electrical potential was repeatedly applied. In contrast, the dense SAM of MHA did not show reorientations induced by an applied electrical potential, because the SFG signals remained unaltered when potential was applied (Fig. 4B).

We then addressed the question of whether the observed rearrangements could be amplified into macroscopically detectable changes in surface properties. Advancing (open symbols) and receding (solid symbols) contact angles for the low-density (Fig. 4C) and the dense (Fig. 4D) SAMs were determined while applying either +80 or -300 mV w.r.t. SCE between the underlying gold electrode and a platinum-wire microelectrode. Four subsequent switch cycles were examined, and contact angles with an aqueous solution were measured. Figure 4C indicates switching of the receding contact angles as the surface polarization was alternately changed. Although the advancing contact angle was independent from the applied potential, the receding contact angle showed a sharp step whenever the polarization of the surface was changed (Fig. 4C, solid squares). The large hysteresis in contact angle can be caused by surface roughness or chemical heterogeneity of the surface (28). Because scanning force microscopy did reveal notable differences in surface roughness between systems configured of molecules in bent and straight states (29), the assumption of a chemical discontinuity along the solid-air-liquid contact line best explains the large hysteresis in contact angles and the pronounced sensitivity of the receding contact angle. Following Good and Neumann's wettability model (30), the system reflects the behavior of a smooth but chemically heterogeneous system that is composed of a low-energy area (exposed to air) and a high-energy area (exposed to solution). The observed changes in receding contact angle then signify molecular transitions at the high-energy areas. SFG results support this assumption (Fig. 3). The drop in contact angle was a reversible phenomenon, because the assembly was switched several times between its hydrophilic (straight molecules) and hydrophobic (bent molecules) state (four times for the study shown in Fig. 4C). In contrast, switching was not observed for the dense SAM (Fig. 4D). We excluded the possibility of electrochemically induced protonation, because it would affect both dense and low-density SAMs similarly (in addition, experiments were conducted at pH = 11.5 to avoid protonation). The applied electrical potentials were well above the estimated lower limit of electrical potentials that permit conformational transitions (26) but low enough to be within the potential window of greatest stability for SAMs of alkaneethioles on gold (25, 31). Thus, electrochemical reactions can be excluded as driving forces for the observed changes in surface properties. We conclude that the observed switching in surface properties is microscopically driven by conformational transitions.

This study demonstrates reversible control of surface switching for a low-density monolayer. Because of synergistic molecular reorientations, amplification into macroscopic changes in surface properties is observed. Future research might be directed toward enhancement of macroscopic effects and development of alternative stimuli. The fact that controlled conformational reorientations of single-layered molecules induced observable changes in wettability suggest that these findings may, with further study, have implications in dynamic regulation of macroscopic properties, such as wettablility, adhesion, friction, or biocompatibility. Potential applications might include microfluidics, microengineering of smart templates for bioseparation or data storage, or microfabrication of controlled-release devices.

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**Fig. 4. Microscopic and macroscopic responses of the low-density SAM to an electrical potential as monitored by SFG spectroscopy and contact angle measurements.** Relative SFG intensities (peak areas) of the methylene modes at wavelengths of 2855 cm\(^{-1}\) (solid symbols) and 2925 cm\(^{-1}\) (open symbols) are shown for the low-density (A) and the dense (B) SAMs measured in 0.1 M CT when a potential of +25 mV w.r.t. SCE was repeatedly applied to the system. Coine of the advancing (open symbols) and receding (solid symbols) contact angles for the low-density (C) and the dense (D) SAMs are determined while applying either +80 or -300 mV w.r.t. SCE to the underlying gold electrode. Four switch cycles were conducted, and contact angles were measured with an aqueous solution (0.1 M CT, pH=1.15) at air using a goniometer (VCA-2500XE, Advanced Surface Technology) equipped with an electrometer (6517A, Keithley Instruments) and platinum and carbon fiber microelectrodes (Kantron Scientific). Contact angles averaged at least 100 data points from nine samples with maximum errors of ±3°. The SAMs were examined for chemical integrity and depyrotonation by IR spectroscopy after an electrical potential was applied. The lines are drawn as a guide to the eye.

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We achieved automated optical control over coherent lattice responses that were both time- and position-dependent across macroscopic length scales. In our experiments, spatiotemporal femtosecond pulse shaping was used to generate excitation light fields that were directed toward distinct regions of crystalline samples, producing terahertz-frequency lattice vibrational waves that emanated outward from their multiple origins at lightlike speeds. Interferences among the waves resulted in fully specified far-field responses, including tilted, focusing, or amplified wavefronts. Generation and coherent amplification of terahertz traveling waves and terahertz phased-array generation also were demonstrated.

Ultrafast optical control over electronic and/or vibrational responses of atoms, molecules, and crystals has advanced dramatically in recent years (1–8). Experiments in this field have typically been conducted with femtosecond pulse shaping techniques (9) for generation of complex excitation light fields that yield specified coherent responses or that manipulate complex phenomena such as photochromatic reactions. Typically, these light fields, as well as the material responses generated by them, are specified as a function of time but not of macroscopic spatial location. For ultrafast responses that move coherently across macroscopic distances, more complete optical control over both spatial and temporal evolution requires the use of time- and position-dependent excitation fields. Here we...
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post date 9 May 2003

REPORTS: "A reversibly switching surface" by J. Lahann et al. (17 Jan. 2003, p. 371). Insung S. Choi's "present address" affiliation should be the Korea Advanced Institute of Science and Technology, not the Korean Advanced Institute of Science and Technology.