J. Am. Chem. Soc. **1995,** *117,* 1845−1846

Photochemistry and Surface Properties of Self-Assembled Monolayers of *cis*- and *trans*-4-Cyano-4′-(10-thiodecoxy)stilbene on Polycrystalline Gold

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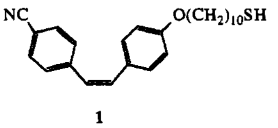
Received September 16, 1994

Self-assembled monolayers of thiol derivatives adsorbed on gold surfaces significantly modify the properties of the metal surface,[1−6] the molecular structures of the adsorbed species being intimately linked to the properties of the resulting derivatized surfaces.[1−4] Recently, both photochemical[5−7] and physical[8,9] techniques have been used to selectively modify surface properties such as contact angle with a probe liquid or interfacial electron transfer rates; however, all of these procedures involve alteration of the chemical composition of the monolayer.

Photopatterning of a monolayer should also be possible using simple photochemical isomerization or dimerization reactions within a monolayer. The photochemical isomerization of stilbene and its derivatives is one of the most thoroughly studied photochemical reactions.[10] The photostationary state is wavelength dependent, and both isomers of most stilbene derivatives are stable toward thermal isomerization. The photochemistry of stilbene derivatives in Langmuir−Blodgett films,[11−14] is analogous to that observed in viscous solution,[15] the photostationary state being determined by steric and electronic factors.

Herein we describe a self-assembled array in which a photochemical reaction within a monolayer results in modification of the surface properties. Irradiation of an ordered monolayer of *cis*-4-cyano-4′-(10-thiodecoxy)stilbene (**1**) on a gold surface with visible light (>350 nm) results in a decrease in the contact angle with water in the irradiated region.



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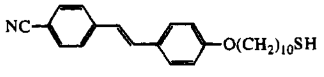

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Significantly, irradiation of a monolayer of the trans isomer (**2**) under identical conditions does not result in any change in contact angle. When the sample is cooled so that atmospheric moisture condenses on the native and isomerized surfaces, these differences can easily be followed by the naked eye; thus, irradiation constitutes a new technique for surface imaging and for differentiation of surface composition.

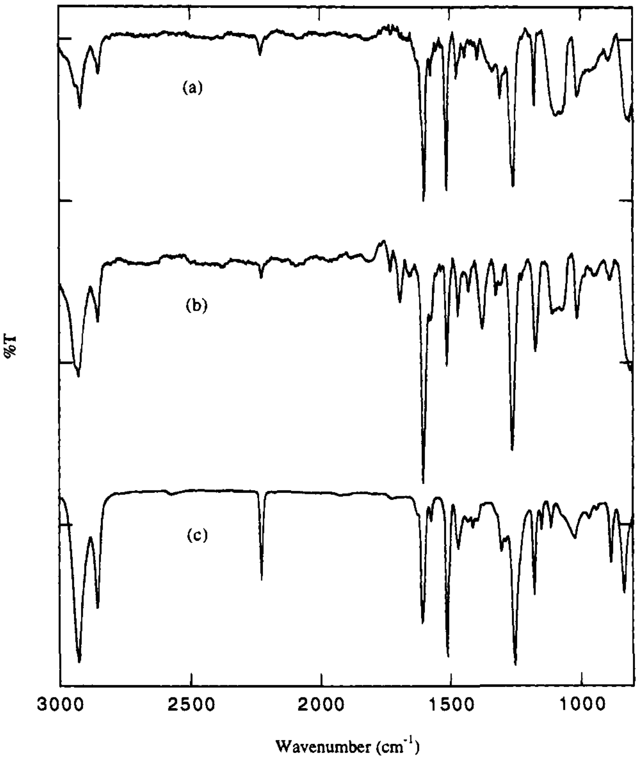

Figure 1. Grazing angle reflectance FTIR spectra of (a) **2** and (b) **1** on gold. (c) Solid-state FTIR spectrum of **1** in KBr.

We prepared monolayers of **1** and **2** on clean gold surfaces[16] by immersion in a 1 mM deaerated ethanol solution of the appropriate thiol for 2−12 h. Monolayers prepared in this fashion were characterized by grazing angle surface FTIR spectroscopy,[17] contact angle measurements, and electrochemistry. The grazing angle FTIR spectra of monolayers of **2** and **1** (Figures 1a and b, respectively) correspond well to those obtained from KBr pellets containing the compounds. The solid-state spectrum of **1** is shown in Figure 1c for comparison.

Sessile drop contact angle measurements are very sensitive to surface composition.[18] Measurements of the sessile drop contact angle of water with surfaces modified by monolayers of **1** or **2** indicate that the monolayer formed from **1** is more hydrophobic ($\theta = 60° \pm 1°$) than that formed from **2** ($\theta = 44° \pm 2°$). The former value is similar to the contact angle reported for a monolayer of 10-cyanodecanethiol on gold ($\theta = 60°$).[2] We attribute this observed difference in contact angles to a conformational difference between monolayers of **1** and **2** that results in a difference in the degree to which the polar CN group is able to interact with the probe liquid.

The blocking effects of monolayers toward solution redox species have been previously used to characterize the homogeneity of the monolayer and to exclude the presence of pinholes.[2,19] Cyclic voltammograms of 1.2 mM Fe(CN)$_6^{4+}$ in

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(16) Surfaces were prepared by argon plasma sputtering of ~100 Å Cr followed by ~2000 Å Au onto single crystal Si wafers (Silicon Sense). Surfaces were either used immediately or cleaned by immersion in freshly prepared 3:1 30% H_2O_2−H_2SO_4 prior to derivatization.

(17) Monolayer spectra were acquired using a Spectra-Tech FT-80 grazing angle reflectance accessory on a Nicolet 550 or 510P FTIR spectrometer. In each case, 256 scans were averaged.

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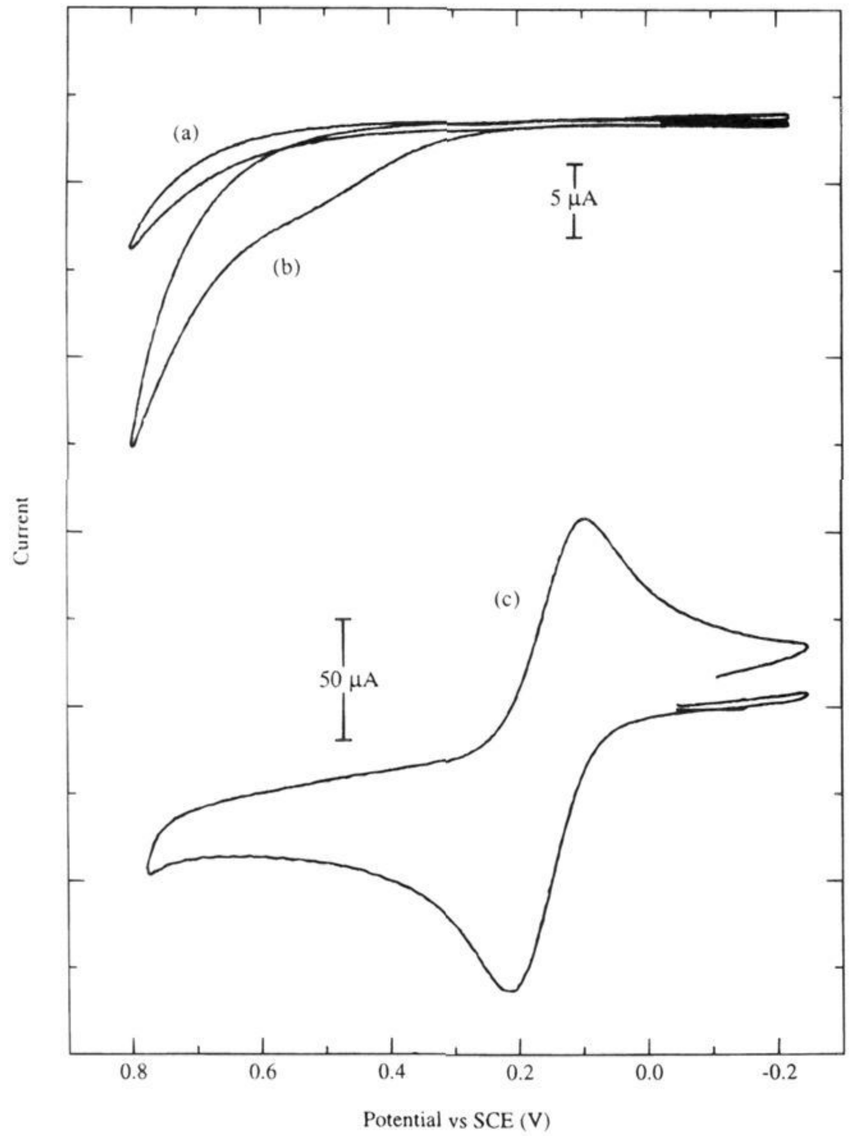

Figure 2. Cyclic voltammograms of 1.2 mM $Fe(CN)_6^{4+}$ in 0.1 M KCl at 25 °C at (a) **2**- and (b) **1**-derivatized gold electrodes. (c) Cyclic voltammogram of 1.2 mM $Fe(CN)_6^{4+}$ in 0.1 M KCl at 25 °C at bare gold (note different current scale). Scan rate was 100 mV/s.

0.1 M KCl on bare gold and **1**- and **2**-derivatized gold electrodes of comparable area (Figure 2) reveal suppression of the $Fe^{2+/3+}$ redox couple at +0.19 V vs SCE on bare gold by approximately 2 orders of magnitude at both **1**- and **2**-derivatized surfaces. However, at higher overpotentials, the current at the **1**-derivatized surface rises more quickly than that at the surfaces derivatized by **2**. We attribute this to a lower average thickness in the monolayer of **1**, caused either by conformational differences between the two molecules or a difference in the number of nonpinhole defects.[2]

Irradiation of degassed benzene solutions of **1** or **2** at wavelengths greater than 350 nm at 25 °C under a nitrogen atmosphere results in a photostationary state which is approximately 80% cis, consistent with the differences in extinction coefficients of the low-energy bands of the two compounds.[20] In contrast, irradiation of **1** or **2** in the solid state under nitrogen gave different results. At short irradiation times (2 h), **1** is partially converted to **2**, and **2** remains unchanged. A decrease in molecular volume[14] from cis to trans is likely the most significant factor in determining the product ratio. At longer irradiation times (7 h), both the cis and trans isomers are converted to [2 + 2] cycloaddition products. Such solid-state photochemistry has been previously observed for other derivatives of stilbene.[13,21]

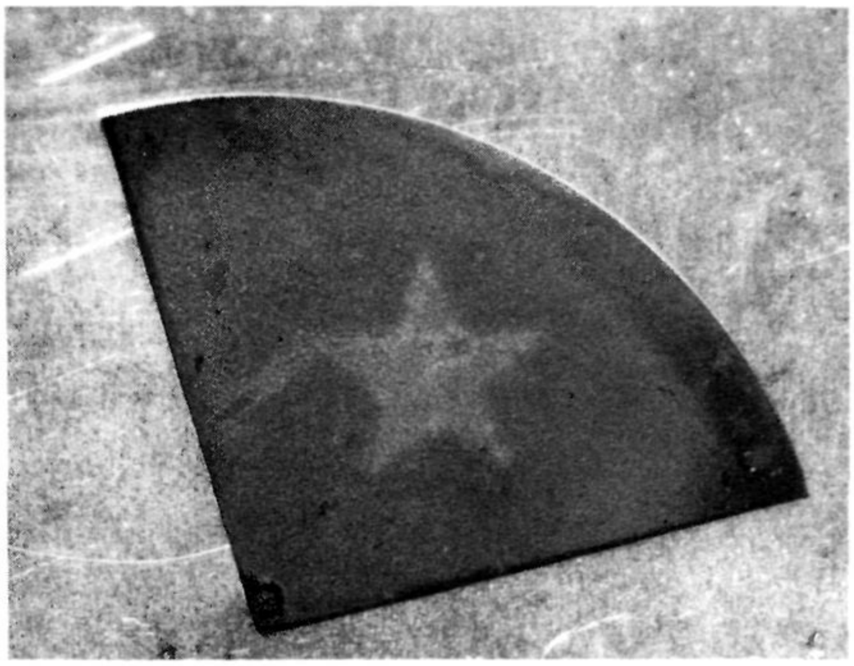

Figure 3. Image of a star produced by condensed water on an irradiated monolayer of **1** on a 100 mm radius silicon wafer, showing the contrast between irradiated and masked (star) regions.

Irradiation of polycrystalline gold surfaces derivatized with **1** or **2** with >350 nm light[22] at 25 °C for 1 h under a nitrogen atmosphere induces very little change in the contact angle of water of the **2**-modified surface, whereas the gold surface derivatized with **1** shows a significant decrease in contact angle (to $\theta = 45°-50°$) in the irradiated area. When the sample is cooled and allowed to condense atmospheric moisture, the difference in irradiated and unirradiated portions of the surface is clearly visible to the naked eye (Figure 3). Comparison of the grazing angle FTIR and XPS spectra of the irradiated and unirradiated surfaces indicates that the observed changes are not due to degradation or removal of the monolayer. The observed changes cannot be attributed to photooxidation of the thiol[5] since irradiation of neither a monolayer of **2** nor a monolayer of 1-octanethiol under identical conditions results in significant changes in the contact angle. Attempts to isomerize a monolayer of **1** thermally by heating under nitrogen at 70 °C for 1 h does not result in any change in contact angle. It is therefore unlikely that the contact angle change induced by irradiation is a purely thermal effect.

These results demonstrate that photoisomerization of **1** may be used to photopattern a self-assembled monolayer on a gold surface. Significantly, changes in the contact angle with water are achieved in the monolayer without any contacting reagent or solvent during the irradiation and without any treatment afterward. We are currently investigating the details of the photochemical reaction and are optimizing the photoinduced changes in contact angle.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences. M.O.W. gratefully acknowledges a postdoctoral fellowship from the Natural Sciences and Engineering Research Council of Canada. We thank Mark F. Arendt for preparation of the gold surfaces used in this work.

Supplementary Material Available: Synthetic procedures and spectral characterization of **1** and **2**; XPS spectra of irradiated and unirradiated surfaces (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[22] Irradiation was carried out using a 450 W Hanovia medium-pressure mercury lamp. The output was passed through a cooled water IR filter and through a Newport Corp. BG.40 color filter.