Reversible Photoswitchable Wettability in Noncovalently Assembled Multilayered Films

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Reversible and irreversible photoinduced changes in surface wettability were observed in noncovalently assembled multilayered films. The multilayered films studied were fabricated from a self-assembled monolayer (SAM) consisting of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid on gold, Cu(II) ions complexed to the pyridine head group of the SAM, and either *cis*- (film 1) or *trans*- (film 2) stilbene-4,4′-dicarboxylic acid complexed to the Cu(II) ions. Irradiation of film 1 at wavelengths corresponding to the absorption band of the *cis*-stilbene isomer resulted in an irreversible chemical change and an irreversible increase in wettability, as indicated by surface contact angle and grazing incidence IR measurements. However, no evidence for cis-/trans-photoisomerization was observed. Films 3 and 4, similar to films 1 and 2 in that they consist of an underlying SAM, an intermediate layer consisting of Cu(II) ions, and either *cis*- or *trans*-stilbene-4,4′-dicarboxylic acid as the capping ligand, were fabricated with a mixed SAM that contained both 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid and 4-*tert*-butylbenzenethiol. Irradiation of these films at wavelengths corresponding to stilbene isomer absorption bands resulted in reversible cis- to trans- (film 3) and trans- to cis- (film 4) photoisomerization and reversible switching of the surface wettability between a low wetting state (*cis*-stilbene) and a high wetting state (*trans*-stilbene). The difference in observed behavior between films 1 and 2 and films 3 and 4 is attributed to the greater surface spacing afforded by the mixed monolayer, which allows greater conformational flexibility and lowers the steric barriers to isomerization.

Introduction

Self-assembled monolayers (SAMs) of alkanethiols on gold surfaces have been studied extensively for a wide variety of applications since their initial report by Nuzzo and Allara in 1983.[1] A strong sulfur−gold interaction allows for the rapid generation of well-ordered films with uniform surface properties.[2−9] Monolayers on gold have been shown to be stable under a variety of conditions, including elevated temperatures, immersion in different solvents, and exposure to ultraviolet light.[3,5,8] These systems also offer the ability to chemically modify the alkanethiols to tailor surface properties, providing a facile way to exercise molecular level surface control for the desired application.[3,6,7]

Multilayered films constructed by the step-by-step deposition of individual layers can increase the complexity and functionality of the surfaces compared to SAMs alone. Such films can be fabricated by the sequential deposition of organic molecules and metal ions, where noncovalent metal−ligand interactions provide the "glue" that binds the successive molecular layers into the film. In addition to our own work,[10,11] several examples of such multilayered films have been reported previously. For example, Ulman et al. fabricated multilayered films of mercaptoalkanoic acid and copper ions,[12] and Brust et al. used alkanedithiols acid and copper ions.[13]

We previously reported the fabrication of stable, noncovalently bound multilayer films on gold surfaces using 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid as the SAM. The pyridine head group of this SAM was used as a ligand to bind a layer of copper ions [Cu(II)], which subsequently was complexed to another organic ligand. This noncovalent approach was used with a variety of ligands to fabricate photocurrent-generating films and films exhibiting photoswitchable wettability.[10,11]

The development of controlled surfaces with properties that can be regulated in response to external stimuli such as changes in light, solvent, pH, temperature, or electric potential provide a great deal of interest.[14−17] Systems with switchable surface wettability have potential utility in a variety of areas, such as information storage, microfluidics, biosensing applications, and other fields,[18,19] and for this reason have been studied by several groups. Ralston et al. showed that a SAM of long-chain thymine-terminated thiols exhibited a contact angle change of 26° after irradiation with UV light at 280 and 240 nm.[20] Liu et al. reported

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reversible conformational behavior of 16-mercaptohexadecanoic acid under positive and negative applied potentials that resulted in a change in wettability.[21]

As mentioned above, we have studied photoswitchable wettability in multilayered films.[10] In these films a SAM consisting of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid was complexed with Cu(II) ions which were themselves capped by *cis*-2,2′-dipyridylethylene to produce a relatively hydrophobic surface. UV irradiation resulted in a decrease in hydrophobicity as deduced from a 19° reduction in contact angle. Spectroscopic studies indicated that this reduction in contact angle was due to cis- to trans-photoisomerization of the capping pyridylethylene ligand. For this system, the isomerization and therefore the change in surface wettability was irreversible, thus limiting its utility for most applications.

Irreversible cis-/trans-photoisomerization on surfaces has been reported previously. Fox et al. showed that a *trans*-stilbene isomer could not be converted to *cis*-stilbene when the compound was deposited as a SAM, and is believed to be due to organization of the trans-ligand on the surface, which creates a steric barrier to the trans- to cis-isomerization process.[17] In effect, the trans-isomer packs on the surface in an orientation that provides insufficient space to allow isomerization to the cis-conformation. Reported here are the results of our attempts to create multilayered films that undergo *reversible* wettabilty changes.

Stilbene compounds are widely known to readily undergo reversible cis-/trans-isomerization upon exposure to the appropriate wavelengths of ultraviolet light.[22] Therefore, the photoswitching ligands used in these studies were *cis*- and *trans*-stilbene-4,4′dicarboxylic acid. These particular stilbene ligands were shown to undergo cis- to trans- and trans- to cis-isomerization in solution, and given the appropriate surface spacing, they may be expected to exhibit the same behavior in multilayered films. These ligands also were chosen because carboxylic acid groups are known to complex metal ions such as Cu(II),[12,13,23] thereby providing a means to bind the ligand to the film. In addition, the conformational change following isomerization is expected to change the orientation of the carboxylic acid group on the surface, leading to variations in surface wettability from one isomer to the other.

Experimental Details

Materials and Methods. All chemicals and solvents were reagent grade or better and used as received. *cis*-Stilbene-4,4′-dicarboxylic acid (95%) was purchased from Lancaster Synthesis Inc. (Windham, NH). *trans*-Stilbene-4,4′-dicarboxylic acid (95%) was from Frinton Laboratories, (Vineland, NJ). Ethanol (200 proof, absolute) for all experiments was obtained from Pharmco Products (Brookfield, CT).

Attenuated total reflectance (ATR) infrared spectroscopy experiments were carried out on a Thermo Electron (Waltham, MA) Nicolet FT-IR model 6700 spectrometer using a liquid nitrogen cooled, mercury cadmium telluride (MCT) detector. UV/Visible spectra were recorded on a Perkin-Elmer (Wellesley, MA) Lambda 35 UV/vis double beam spectrometer, and a baseline correction (solvent vs solvent) was performed prior to each experiment.

Preparation of Self-Assembled Monolayers. Gold surfaces were obtained commercially from evaporated metal films (EMF) (Ithaca, NY). The float glass slides (25 mm × 75 mm × 1 mm) are coated with 50 Å of a chromium adhesion layer followed by 1000 Å of gold. Prior to monolayer formation, the slides were cut to the desired size and cleaned by immersion in a piranha solution (70% concentrated sulfuric acid, 30% concentrated hydrogen peroxide) at 90 °C for 10 min. The slides were then washed thoroughly with distilled water, followed by absolute ethanol, and then blown dry in a stream of nitrogen. Cleaned slides were then immediately placed in the desired monolayer solution. Monolayers were prepared by immersion of the gold slides in a 1 mM solution of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid in ethanol for 18 h. Mixed monolayers were prepared by immersing the clean gold slides in a solution containing a mixture of 0.5 mM 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid and 0.5 mM 4-*tert*-butylbenzenethiol in ethanol (for mixed monolayers, the total concentration of thiol was 1 mM). Copper(II) bromide was used as the source of Cu(II) ions. The SAM-covered gold slides were immersed in a solution of 2 mM copper bromide in ethanol for 2 h. Capping of the copper ions with the *cis*- and *trans*-stilbene-4,4-dicarboxylic acid was carried out by immersing the copper-capped gold slides in 5 mM solutions in ethanol. Coverage was completed after 36−48 h of exposure. In the mixed monolayer systems following deposition of Cu(II), the gold slides were submersed in a solution of 2 M HNO_3 for 30 min and then rinsed with water followed by ethanol to remove any copper ions that may have physisorbed on the CH_3 head group. Control experiments showed no monolayer degradation following exposure to 2 M HNO_3. After each layer deposition, and prior to any characterization, the films were removed from solution, rinsed with ethanol, and dried with nitrogen. New films were prepared for each characterization experiment.

Irradiation. Slides were irradiated using a Rayonet reactor equipped with mercury arc lamps with maximum distributions of light centered at 254 and 350 nm. Exposure to 254 nm light was performed with the slides in ethanol with no filter; for irradiation at 350 nm, a Pyrex filter was used, which cuts off light below 305 nm.

Computational Modeling. Molecular structures of the *cis*- and *trans*-stilbenes were minimized for energy using Molecular Operating Environment (MOE) software, version 2005.06 (Chemical Computing Group Inc., Montreal, Canada). Structures were minimized first using the AMBER94 potential control under a solvent dielectric of 24. Minimized structures were then subjected to a 30 ps molecular dynamics simulation employing the NVT statistical ensemble. Dynamics calculations on structures were heated to 400 K, equilibrated at 310 K, and cooled to 290 K at a rate of 10 K/ps. The lowest energy structures obtained from these calculations were reminimized for energy.

Contact Angle Goniometry. Contact angle measurements were obtained using a Rame-Hart (Netcong, NJ) model 100-00 goniometer. Measurements were obtained using 1 μL droplets of deionized water applied to the surface using a calibrated Epindorf pipet, and the angle was then measured using a protractor mounted in the eyepiece.

Grazing Incidence Infrared Spectroscopy. Grazing incidence infrared spectra were obtained using a Thermo Electron (Waltham, MA) Nicolet FT-IR model 6700 spectrometer equipped with a Thermo Nicolet grazing angle accessory and a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. The incident IR beam was 75° to the gold substrates. Prior to measurement the optical path was purged with a stream of nitrogen for 30 min, and purging was continued during the experiments. A clean, bare gold slide was used as the background, and a new background was collected immediately prior to each sample run. The scan range was from 4000 to 1000 cm^{-1}, and 64 scans were collected for each sample.

Cyclic Voltammetry. Electrochemistry experiments were carried out using an EG&G Princeton Applied Research (Oak Ridge, TN) model 273 potentiostat/galvanostat. The potentiostat was under computer control using Princeton's model 270/250 Research Electrochemical Software (v. 4.23). A typical three-electrode cell was employed with the SAM functioning as the working electrode, a platinum wire as the counter electrode, and referenced against a standard saturated calomel electrode (SCE). An alligator clip was used to attach the gold slide to the cell, and a surface area of 1 cm^2 was placed in the electrolyte solution. The electrolyte was an aqueous 1 mM potassium ferricyanide solution with 0.1 M potassium chloride as supporting electrolyte. Voltammograms were obtained from −0.3 to 0.7 V at a scan rate of 50 mV/s.

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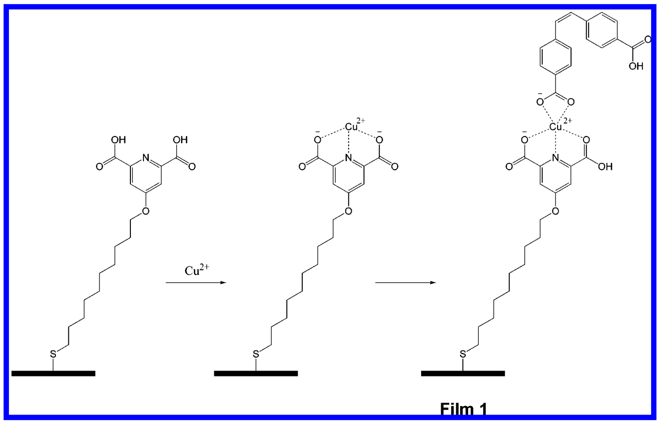
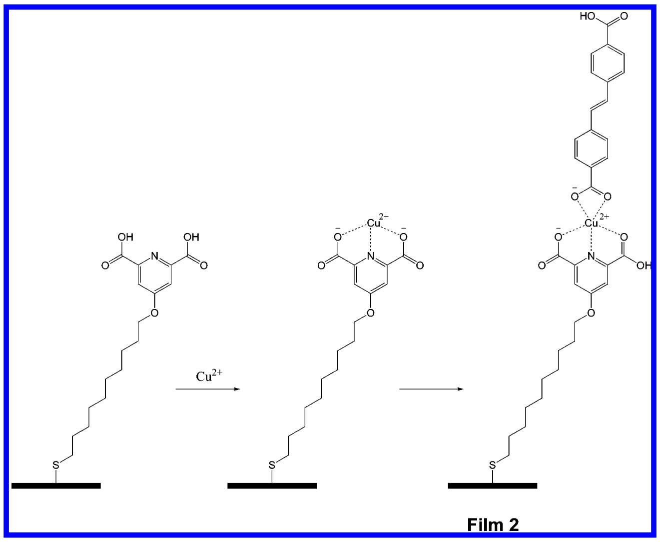
Scheme 1



Scheme 2



Synthetic Details. 4-(10-Mercaptodecyloxy)pyridine-2,6-dicarboxylic acid was synthesized as previously reported.[10,11]

Results and Discussion

1. Multilayered Film Fabrication and Characterization. Multilayered thin films containing 4,4′-stilbenedicarboxylic acid were fabricated by sequential deposition of individual layers that are bound by noncovalent, metal−ligand interactions, as shown in Schemes 1 and 2. These schemes depict an ideal representation of the film structure based on the binding site location and the molecular orientation from modeling studies of cis- and trans-isomers, as described below. Films 1 and 2 consist of a SAM made up of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid deposited on a gold surface. The 2,6-pyridinedicarboxylic acid head group in this SAM acts as a tridentate ligand for a variety of transition metal ions.[24,25] The SAM was subsequently exposed to a solution of Cu(II) ions, which bind to the head group. (Binding constants for this interaction in solution are $> 10^8$.) The metal ion was then "capped" by deposition of the appropriate stilbene isomer. While it is not possible to identify unambiguously the binding mechanism, it is likely that binding occurs between the Cu(II) ion and one of the carboxylic acid groups of the stilbene. Binding between carboxylic acid groups and Cu(II) ions in self-assembled films has been reported previously.[12,13,23] We also note that deposition of the stilbene compounds on the SAM does not occur if the Cu(II) ions are not deposited first.

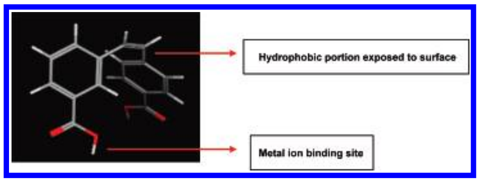


Figure 1. *cis*-Stilbene-4,4′-dicarboxylic acid.

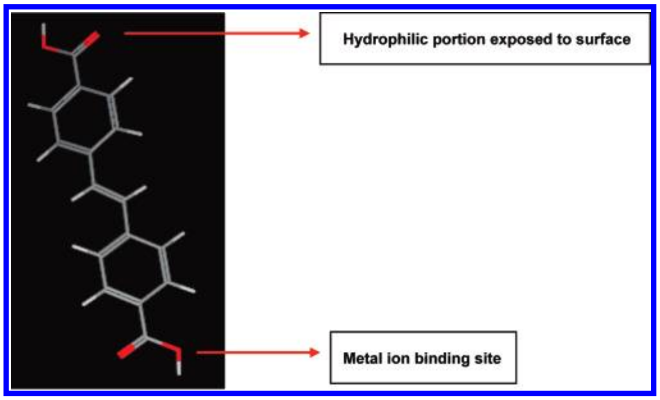


Figure 2. *trans*-Stilbene-4,4′-dicarboxylic acid.

The selection of 4,4′-stilbenedicarboxylic acid as the capping ligand was made for three reasons. First, the cis- and trans-isomers of this compound were shown to undergo reversible photoinduced isomerization in solution based on UV/vis analysis (see Supporting Information). In addition, as pointed out above, the carboxylic acid group is expected to act as a metal-binding ligand and thereby anchor the compound to the film. Finally, isomerization is expected to change the orientation of the nonbound carboxylic acid group relative to the surface and as a result alter the wettability.

Molecular modeling simulations of *cis*- and *trans*-stilbene-4,4′-dicarboxylic acid are shown in Figures 1 and 2, respectively. As demonstrated in Figure 1, *cis*-stilbene-4,4′-dicarboxylic acid will create a hydrophobic surface when bound to a metal ion through one of the carboxylic groups. Conversely, the trans-form (Figure 2) of the compound will generate a hydrophilic surface when noncovalently linked to a monolayer through one end of the molecule. Cis-/trans-isomerization of the stilbene on the surface should provide a marked change in the overall surface wettability.

Following the deposition of each layer (SAM, Cu(II), and stilbene) the films were characterized by a variety of surface techniques, including contact angle goniometry and grazing incidence IR. In addition, since the gold substrate is electronically conducting, cyclic voltammetry was used in order to estimate surface coverage. The results of these characterization studies indicate that the underlying SAM forms a nearly complete layer. This is supported by the characteristic IR bands at 2922 and 2852 cm^{-1} which indicate that the SAM is somewhat ordered,[4,9,26] as shown in Figure 3a. In addition, cyclic voltammetry measurements conducted with the film on gold as the working electrode, using a redox probe, indicate that the SAM is insulating or "blocking"; i.e., there is no current flow detected across the SAM (see Supporting Information).[27]

Subsequent deposition of the Cu(II) ions results in a decrease in contact angle, as shown in Table 1, and also changes in the

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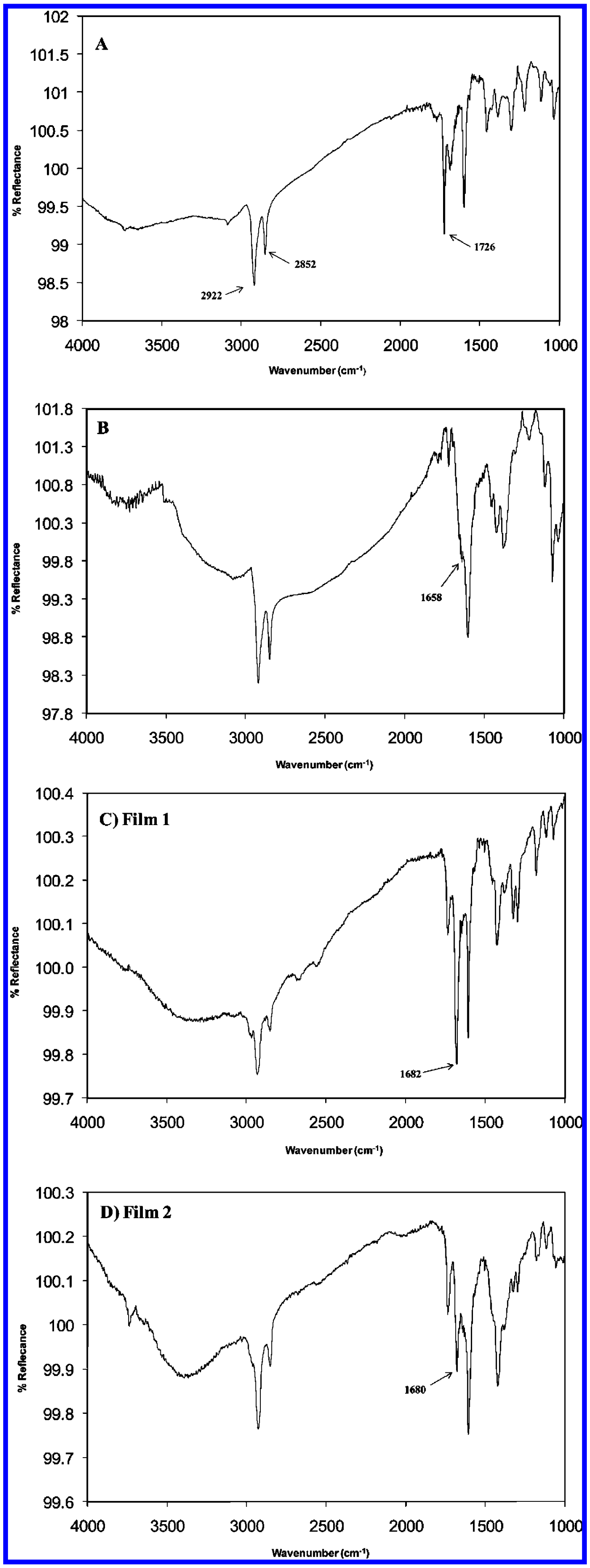

Figure 3. Grazing incidence IR spectra of (a) component 1, SAM of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid; (b) component 2, component 1 + Cu (II) ions; (c) component 3 (film 1), component 2 + *cis*-stilbene-4,4′ dicarboxylic acid; and (d) component 3 (film 2), component 2 + *trans*-stilbene-4,4′ dicarboxylic acid.

Table 1. Contact Angle Measurements for Films 1 and 2

film	contact angle (deg)
bare gold	15 ± 1.0
film 1	
component 1 [4-(10-mercaptodecyloxy)pyridine-2,6 dicarboxylic acid]	74 ± 2.0
component 2 [component 1 + Cu(II) ions]	52 ± 2.0
component 3 (component 2 + *cis*-stilbene-4,4-dicarboxylic acid)	76 ± 2.5
film 2	
component 1 [4-(10-mercaptodecyloxy)pyridine-2,6 dicarboxylic acid]	74 ± 2.0
component 2 [component 1 + Cu(II) ions]	52 ± 2.0
component 3 (component 2 + *trans*-stilbene-4,4-dicarboxylic acid)	50 ± 2.0

IR spectra (Figure 3b). The reduction in the contact angle is attributed to an increase in film hydrophilicity, which is likely caused by the ability of Cu(II) to coordinate water molecules on the surface.

As shown in the IR spectra (Figure 3b), the carbonyl stretching frequency at 1726 cm^{-1} in the SAM shifts to 1658 cm^{-1} in the presence of Cu(II). This shift indicates the presence of a carboxylate group, which is expected to form due to deprotonation of the carboxylic acid of the pyridine head group of the SAM when the metal ion binds to the ligand (deprotonation maintains a charge neutral film). Cyclic voltammetry measurements show that the Cu(II)-capped SAM is no longer insulating, likely indicating that the film is "leaky". Leaky films could be caused by disruption of the SAM structure when the ion binds to the ligand.

Deposition of the stilbene isomers causes further changes in the contact angle that are specific to the isomer deposited, as shown in Table 1. Thus, for the cis-isomer, the contact angle returns to the relatively hydrophobic value observed for the SAM alone, while for the trans-isomer, the contact angle remains low. These results confirm the suggestion that the orientation of the cis-isomer on the surface is such that the unbound carboxylic acid group is not exposed but rather buried in the film. Conversely, the low contact angle for the trans-isomer indicates that in this case the unbound carboxylic acid group *is* exposed, thus producing a hydrophilic surface. IR spectra of stilbene-capped films clearly indicate the presence of the stilbene, as shown in Figure 3c,d. The C═O stretch of the stilbene dicarboxylic acid is seen at 1682 cm^{-1} for the cis-isomer (Figure 3c) and at 1680 cm^{-1} for the trans-isomer (Figure 3d). However, the IR spectra for each isomer are virtually indistinguishable. (We note that the IR absorption of the carbonyl at 1680 cm^{-1} is also seen in solid samples of both *cis*- and *trans*-stilbenedicarboxylic acids examined by ATR, as shown in the Supporting Information).

The results reported above indicate that, should the *cis*- and *trans*-stilbene-capped films undergo isomerization when irradiated at the appropriate wavelengths, the contact angle, IR, and cyclic voltammetry measurements will confirm this process.

2. UV-Irradiation of Films 1 and 2. Film 1 (cis-isomer) was exposed to 254 nm irradiation for 60 s in air-saturated ethanol solution. Following irradiation, the film was analyzed using contact angle measurements and grazing incidence IR. Whereas the contact angle of film 1 prior to irradiation was 74°, following exposure the angle dropped to 58°. However, this latter value was quite variable, having a standard deviation of 9°. IR results in Figure 4 show that, upon irradiation, a change occurs in the composition of the film. However, the spectrum of irradiated film 1 is not identical to that of nonirradiated film 2, as would

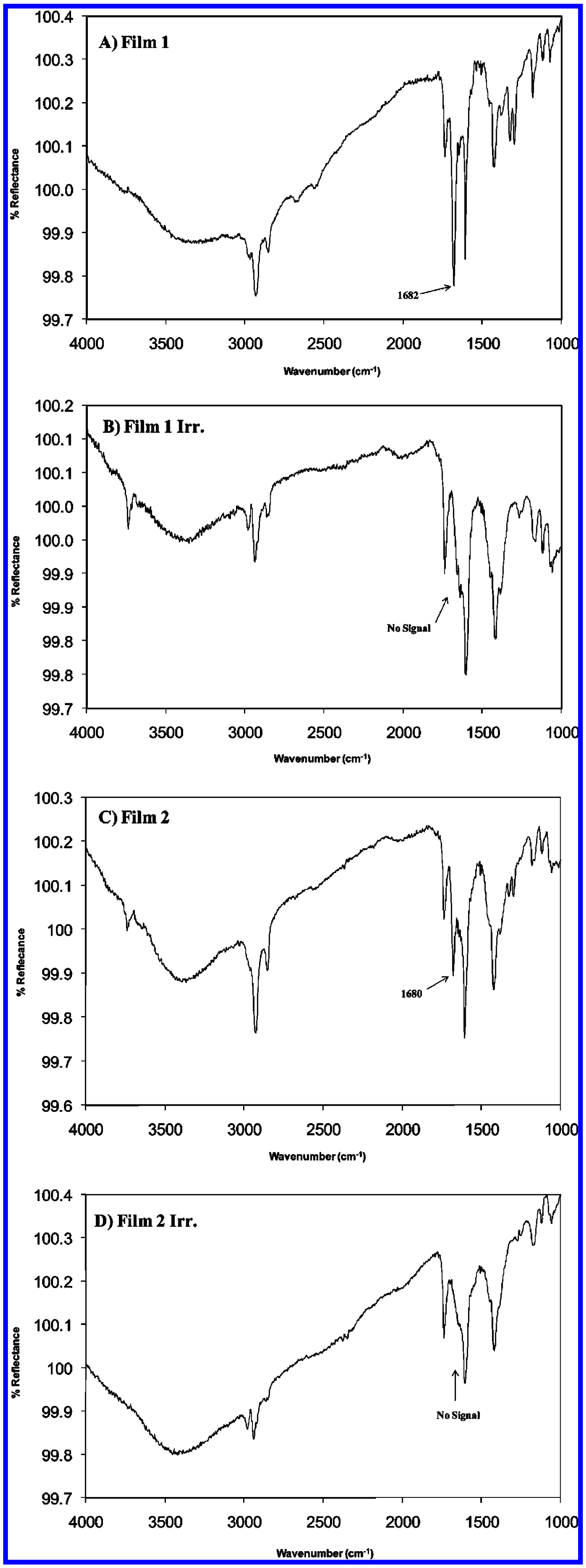

Figure 4. Grazing incidence IR spectra of (a) film 1 (cis-form), (b) film 1 irradiated, (c) film 2 (trans-form), and (d) film 2 irradiated.

be expected had isomerization occurred. Instead, the IR spectra indicate a loss of the stilbene moiety following irradiation. The strong peak at 1682 cm^{-1} due to the C═O stretching vibration of the stilbene is absent in the spectrum of irradiated film 1, as shown when comparing parts a and b of Figure 4. Irradiation of film 2 at 350 nm also leads to a similar change in the film, and the C═O stretching signal is no longer observed, as shown in Figure 4c,d.

This behavior is similar to that in other previously published studies. For example, UV irradiation of films composed of azobenzene-derivatized alkanethiols leads to photodegradation and an associated reduction in water droplet contact angles.[28] In addition, Fox et al. showed that SAMs consisting of *cis*- and *trans*-4-cyano-4′-(10-(acetylthio)decoxy)stilbene do not photoisomerize but instead undergo dimerization. This behavior was attributed to steric barriers to isomerization that result when the SAMs form well-ordered and tightly packed films.[29] The lack of an IR C═O stretching vibration after irradiation suggests that the capping stilbene moiety was either removed from the surface or more likely underwent photodimerization upon exposure to UV light.

3. Preparation and Irradiation of Films Fabricated with Mixed Monolayers. Irradiation of films 1 and 2 did not result in isomerization but instead led to permanent chemical change, potentially as a result of photodimerization of the stilbene isomers on the surface. Previous studies have indicated that such behavior may be due to steric crowding in the films, which presents a barrier to isomerization. To alleviate steric crowding and facilitate isomerization, Hu et al.[29] used colloidal gold clusters instead of planar gold surfaces. Film packing on gold clusters is not as ordered as on a planar gold surface and therefore does not lead to steric concerns. Mixed or two-component monolayers have also been used to create separation in monolayer films.[28]

To test the effect of alleviating steric crowding in the multilayered films examined in this study, a mixed SAM of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid and 4-*tert*-butylbenzenethiol was deposited. Mixed monolayers have been used to modify surfaces for a variety of applications.[30−35] The films were deposited from a solution containing an equimolar mixture of the two thiols (this ratio provided the most consistent wettability changes following irradiation cycles). The coadsorption of thiols is the general method for generating mixed monolayer films that can have different chain lengths and also different terminating functional groups.[36] However, factors governing the formation of mixed monolayers are not well understood, and mixed monolayers have been shown to form islands of like molecules on the surface.[37]

As shown in Scheme 3, the stilbene isomers were deposited as before to yield films 3 (*cis*-stilbene) and 4 (*trans*-stilbene) with the only difference being the underlying mixed monolayer (again Scheme 3 is an ideal depiction of the film structure). The

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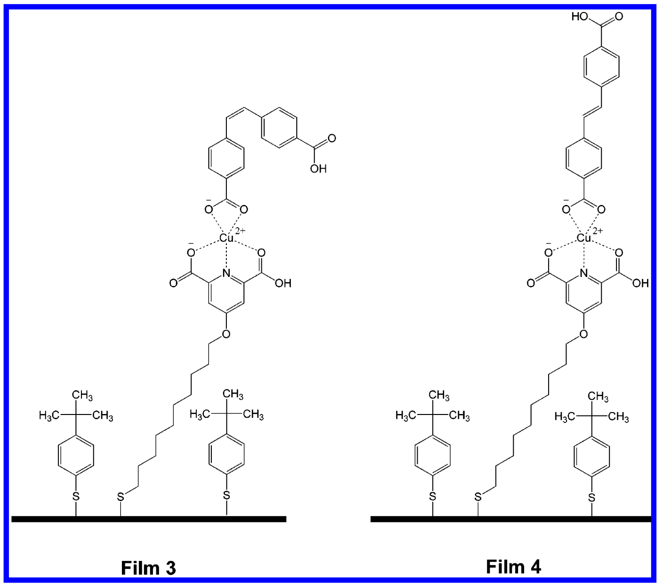
Scheme 3



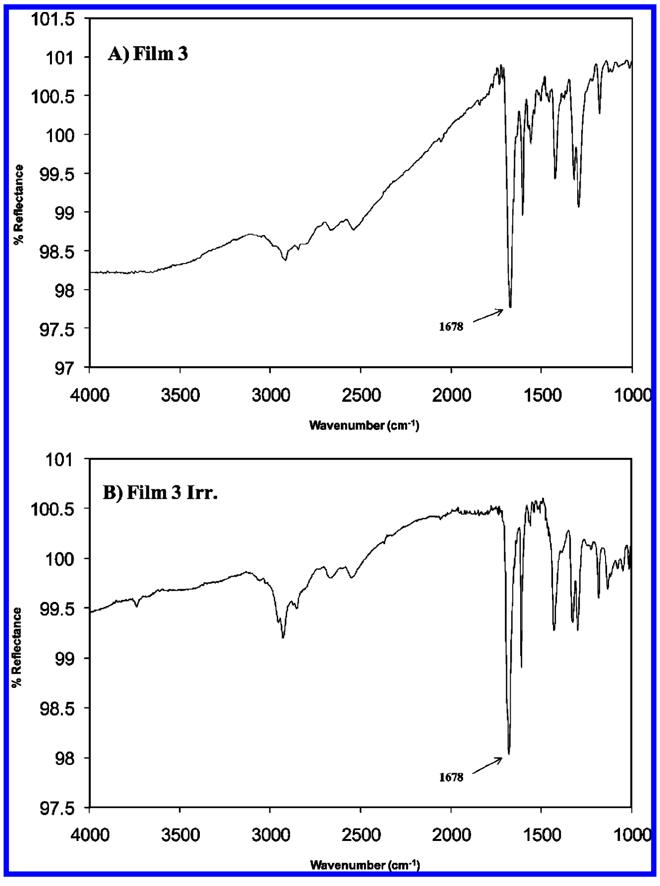


Figure 5. Grazing incidence IR spectra of (a) film 3 (cis-form) and (b) film 3 irradiated.

Table 2. Contact Angle Measurements for Film 3 (Cis-Form)

film	contact angle (deg)
film 3	
component 1 [mixed monolayer: 0.5 mM 4-(10 mercaptodecyloxy)pyridine-2,6-dicarboxylic acid + 0.5 mM 4-*tert*-butylbenzenethiol]	80 ± 2.0
component 2 [component 1 + Cu(II) ions]	55 ± 2.0
component 3 (component 2 + *cis*-stilbene-4,4-dicarboxylic acid)	70 ± 2.0
film 3 irradiated at 254 nm (5 min)	45 ± 2.0
second irradiation at 350 nm (30 min)	66 ± 1.0

Table 3. Contact Angle Measurements for Film 4 (Trans-Form)

film	contact angle (deg)
film 4	
component 1 [mixed monolayer: 0.5 mM 4-(10 mercaptodecyloxy)pyridine-2,6-dicarboxylic acid + 0.5 mM 4-*tert*-butylbenzenethiol]	80 ± 2.0
component 2 [component 1 + Cu(II) ions]	55 ± 2.0
component 3 (component 2 + *trans*-stilbene-4,4-dicarboxylic acid)	45 ± 2.0
film 4 irradiated at 350 nm (30 min)	65 ± 2.0
second irradiation at 254 nm (5 min)	48 ± 1.0

successful assembly of films 3 and 4 was confirmed by contact angle (Tables 2 and 3) and IR (Figure 5) measurements.

Irradiation of film 3 at 254 nm resulted in a change in contact angle, as shown in Table 2. Following irradiation, the contact angle decreases by ∼25°, indicating a change from a low wetting surface to a higher wetting surface. IR spectra obtained before and after irradiation (shown in Figure 5a,b) indicate that the stilbene moiety is present following irradiation, as demonstrated by the observation of the C=O stretching vibration in both spectra, and this result is unlike that obtained for film 1. When this IR evidence is coupled with the contact angle measurements showing that irradiated film 3 (cis) has the same contact angle as unirradiated film 4 (trans), it is possible to conclude that the *cis*-stilbene undergoes isomerization in the film to the trans-isomer followed by photoinitiated conversion back to the cis-isomer upon exposure to 350 nm light. We note that the observed decrease in the contact angle, ∼25°, is substantially greater than that reported for a variety of photoisomerizable thin films of azobenzenes or spiropyrans that typically exhibit changes of ∼9°.[20] The large change seen in our system compared to previous work is likely due to the high electronegativity of the carboxylic acid portion of the molecule, which results in a significant wettability difference when the molecular orientation changes to expose the acid to the surface.

Film 4 exhibits behavior analogous to that of film 3. Table 3 shows the contact angles obtained for film 4 before and after irradiation at 350 nm and after further irradiation at 254 nm. The contact angle obtained after 350 nm irradiation is nearly identical to that of unirradiated film 3 and following exposure to 254 nm returns to its original value before the first irradiation. Additionally, the IR data (not shown) is similar to film 3, the C=O stretching of the stilbene is still observed following irradiation, supporting the conclusion that the stilbene is undergoing photoreversible isomerization in the film.

We note that further irradiation of either film 3 or 4 beyond a single cycle did not appear to result in complete reversion to the expected contact angles. Instead, further irradiation of both films resulted in a convergence of the contact angles to a value intermediate between those measured for the individual isomers, indicating that the system likely forms a photostationary state of the two isomers (IR analysis indicates that the stilbene moieties are still present on the surface). Further evidence for the formation of a mixture of the two isomers is given by the solution studies of the stilbene isomers that indicate repeated irradiation cycles do not produce complete conversion of one isomer to the other (see Supporting Information).

Summary and Conclusions

Multilayer films of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid + Cu(II) + *cis*-/*trans*-stilbene-4,4′-dicarboxylic acid were fabricated. Irradiation of these films did not result in the photoisomerization of the stilbene moiety. It is believed that photoisomerization was prevented because of steric hindrance arising from tightly packed films. To facilitate photoisomerization, surface space was created by utilizing mixed monolayers. Multilayer films were fabricated with mixed monolayers of 4-(10-mercaptodecyloxy)pyridine-2,6-dicarboxylic acid and 4-*tert*-butylbenzenethiol, allowing for the photoisomerization of stilbene-4,4′-dicarboxylic acid and control over surface wettability. The contact angle data indicates that the photoisomerization was complete for one cycle (cis converted to trans or trans converted to cis) and nearly complete for conversion back to the starting isomer, but that further irradiation gradually resulted in a convergence of contact angles, possibly due to the formation of a photostationary state. These results demonstrate that adequate separation of the surface-bound stilbene moieties is required to achieve isomerization and suggest that a more uniform separation of binding sites may lead to surfaces with better reversible switching behavior.

Supporting Information Available: Additional characterization data, including solution studies of dicarboxystilbene photochemistry, infrared analysis of solid samples, and cyclic voltammetry experiments on multilayered films. This material is available free of charge via the Internet at http://pubs.acs.org.

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