

# Direct Observation of Photo Switching in Tethered Spiroyrans Using the Interfacial Force Microscope

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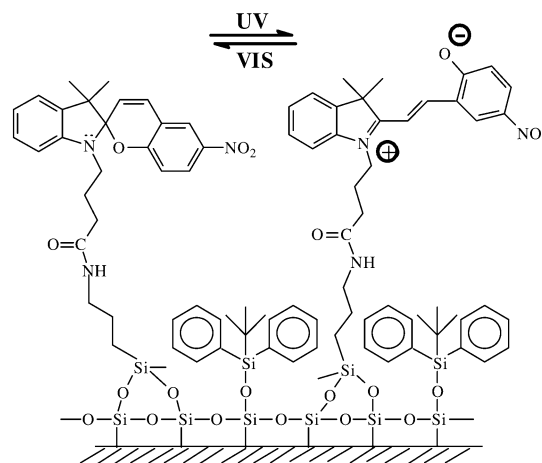
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## ABSTRACT

The interfacial force microscope has been used to establish the changes in the surface chemistry that accompany photoactivated opening and closing of rings in tethered spiropyran monolayers. Contact potential measurements show that ring opening via ultraviolet light creates a more polar surface, while exposure to visible light closes the rings and resets the surface. Normal force measurements show that open ring structures are protonated in electrolyte solutions, amplifying the switching of electrical double-layer forces.

Reversible switching of interfacial properties is a promising tool for applications to microfluidic systems, including analytical chemistry, chemical processing, biothreat detection, fluidics in space, and biomedical devices.<sup>1</sup> A wide range of stimuli, including heat, light, and applied voltage, are being investigated for reversibly changing either the wetting characteristics of a surface or its ability to adsorb or desorb species in the contacting fluid.<sup>2</sup> For biological applications, the use of light offers unique opportunities, as light fluxes are easy to control temporally and are less likely to perturb delicate biological structures than most other stimuli. Recently, we have demonstrated that tethered films of spiropyran molecules respond to optical stimulation, resulting in significant reversible changes in water contact angle.<sup>3</sup> Here, we report on the use of a scanning probe system called the interfacial force microscope to investigate nanoscale interactions between the spiropyran and model surfaces and further elucidate the changes in surface chemistry induced by light.

The optical switching of spiropyrans has been studied extensively in solution using techniques such as NMR and optical spectroscopies.<sup>4</sup> In its “native” state (Figure 1, left), the oxygen-containing ring in the spiropyran is closed. Exposure of spiropyran solutions to UV light (<400 nm) opens this ring (via scission of the C–O pyran bond) to produce an open, highly polar colored isomer (Figure 1, right). The light-induced isomerization can be reversed by



**Figure 1.** Schematic of spiropyran monolayer on a glass surface shown in both the closed (left side) and open (right side) state. The spiropyran is attached to 3-aminopropylmethylsilyl groups with the TBDS molecules acting as spacer units.

using visible light (450–600 nm) or by heating the solution. We have tethered the photochromic spiropyran 1'-(3-carboxypropyl)-3',3'-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2'-indoline to a glass surface to investigate the extent to which such switching can be used to modify surface chemistry. The tethering is accomplished by allowing the carboxylic acid end group of this functionalized spiropyran to react with a self-assembled monolayer created using 3-aminopropyltriethoxymethylsilane (ADES) to form a covalent amide linkage. Previous studies have shown that the extent and kinetics of photoactivation of tethered spiropyrans

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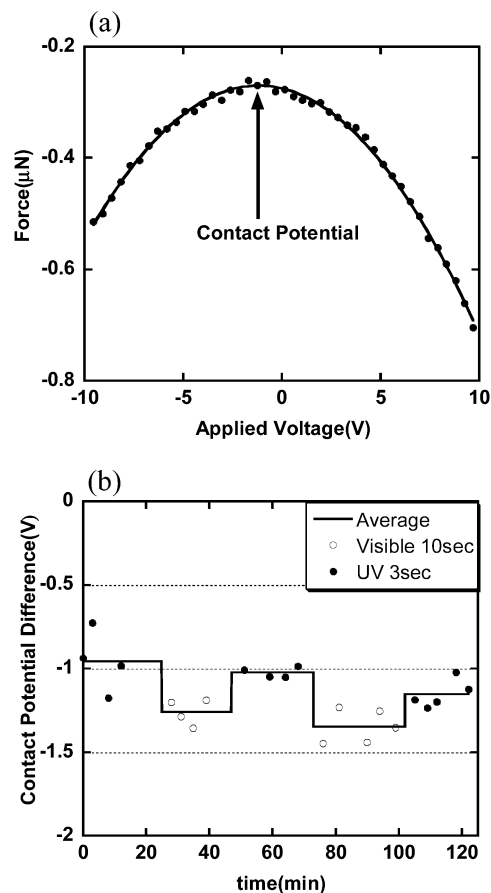
are sensitive to local environmental conditions (polarity, steric constraints, and reactions involving neighboring spiropyran molecules) both in solution and in tethered films.<sup>5</sup> For this reason, the current studies involve monolayers in which the amide-linked spiropyrans are diluted in a base monolayer consisting of *tert*-butyldiphenylsilyl groups (TBDS) (Figure 1). Previous studies<sup>3</sup> have shown that the 20 mol % spiropyran concentration used here promotes the most extensive and reversible photoswitching in these mixed monolayers. In addition, the TBDS provides a hydrophobic background against which the effects of switching of the spiropyran polarity are more readily apparent.

The primary interest in tethered spiropyrans is for photoswitching of surface chemistry. Previous studies on the spiropyran monolayers described above indicate that water contact angles can be switched between 60° and 70°, corresponding to the closed and open ring states, respectively.<sup>3</sup> To obtain more detailed information regarding the switching of interface states, we report here on quantitative measurements of the interaction force between tethered spiropyran and functionalized silica that have recently been obtained using the interfacial force microscope (IFM). The self-balancing force-feedback sensor of the IFM enables the quantitative mapping of the entire force–distance profile as a tip approaches a substrate surface, without the mechanical instabilities that plague other interaction force measurements.<sup>6</sup> Our measurements were performed in liquids using drawn-down optical fibers that were sufficiently long to penetrate the liquid without immersing the IFM sensor. The fiber ends were fire-polished to provide near-atomically smooth tips of known radius. Tips were used as prepared or were functionalized with desired groups using coupling agents such as 3-aminopropyltriethoxysilane. Normal force profiles were obtained by first determining the position of the surface by carefully approaching it with the tip until a light load was detected. The tip was then withdrawn to a selected distance. Measurements were performed by approaching the surface at a fixed tip speed up to a preselected load followed by withdrawal at the same rate.

Information regarding the change in surface states induced by photoactivation of the spiropyran has been obtained using contact potential measurements to probe the polarity of the monolayer. Contact potential measurements were performed by hovering the IFM tip above the surface in air at a fixed distance of 20 nm. The force between the tip and the substrate was then measured as a function of the voltage applied to the tip. The voltage at which the minimum force is measured corresponds to the contact potential difference between the tip and surface (Figure 2a). Observed changes in contact potential difference due to photoinduced activation of the spiropyran can be attributed to the presence of surface dipoles through the expression<sup>7</sup>

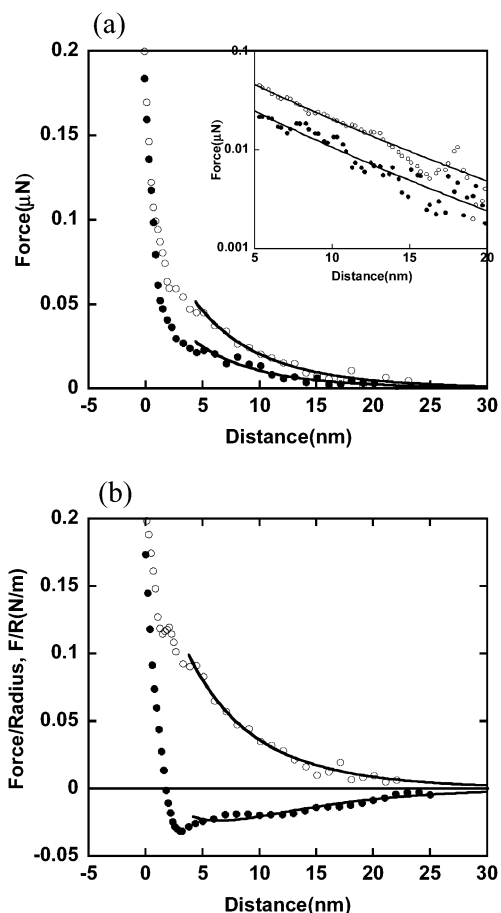
$$\Delta\Phi = -\Delta\mu_n \cos \theta / A\epsilon\epsilon_0 \quad (1)$$

where  $\Delta\Phi$  is the change in contact potential,  $\Delta\mu_n$  is the change in the intrinsic dipole moment,  $A$  is the surface area



**Figure 2.** (a) Force response at 20 nm from the surface in air as a function of applied voltage between the Au coated tip (at ground) and spiropyran monolayer on an oxidized silicon surface. Contact potential difference is defined as the potential shift for minimum force and solid line is a parabolic fit to the data. (b) Switching behavior as indicated by the contact potential change after UV (filled circles) and visible light (open circles) exposure due to spiropyran molecules switching between open and closed states. Data points are for different positions on the surface and the solid line is the average value for open and closed states. Results indicate a change in polarity of the surface upon switching, with the spiropyran dipole pointing toward the surface on ring opening.

occupied per active dipole,  $\epsilon$  is the dielectric constant of the medium between the tip and substrate ( $\epsilon = 1$  for air),  $\epsilon_0$  is the permittivity of free space, and  $\theta$  is the angle between the surface normal and the axis of the dipole. Contact potential measurements have been obtained on films of tethered spiropyran after cyclical exposures to UV and visible light for 3 and 10 s, respectively (Figure 2b). The shift in contact potential by  $-0.27$  V ( $\pm 0.1$ ) on exposure to UV light indicates that surface dipoles are created that point toward the surface (the positive end of the dipole is closer to the surface than the negative end). The UV-created dipoles are largely removed on exposure to visible light. Multiple cycling between UV and visible light indicates that the process is reversible. However, the gradual decay in the difference between the UV and visible contact potentials suggests that there may be a gradual deterioration in the photoactivity of the film, possibly induced by the voltage cycling in air.



**Figure 3.** (a) IFM force profiles taken with amine-coated tip after UV (open circle) and visible light (solid circle) exposures to the spiropyran surface under formamide containing  $2 \times 10^{-3}$  M KCl. The solid lines are curves fitted<sup>11</sup> with electrical double layer force (eq 2), providing  $\sigma_{\text{spiro,UV}} = 0.028$  C/m<sup>2</sup> and  $\sigma_{\text{spiro,vis}} = 0.014$  C/m<sup>2</sup>. Inset is log-scale plot of the two curves for the 5–20 nm region; the curves are linear and parallel, confirming surface–charge creation with constant decay length. (b) IFM force profiles divided by tip-radius after UV exposure taken with amine-coated tip (open circle) and bare-silica tip (filled circle). The polarity of force depends on tip-functionalization group, indicating that the surface of spiropyran exposed to UV under formamide is positive.

Estimates of the efficiency of switching of the tethered spiropyrans can be extracted from the contact potential data by starting with the assumption that the dipole moment in the spiropyran is oriented perpendicular to the surface ( $\cos \theta = 1$ ). Both experimental and theoretical estimates indicate that UV activation should increase the dipole moment in the spiropyran unit by around 8 D units (experimental values

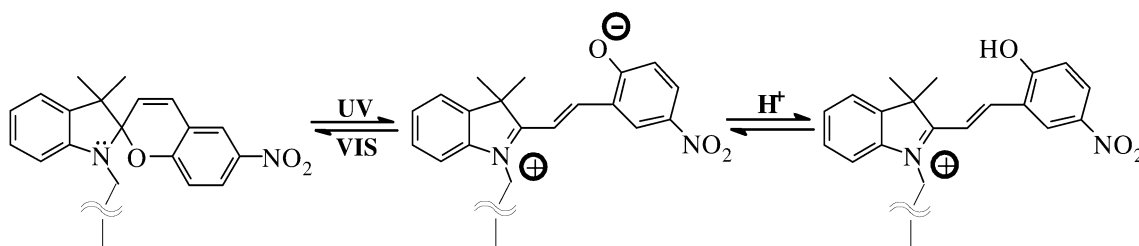
for the closed and open states are 6.4 D and 14.2 D, respectively).<sup>8</sup> Knowing that the surface coverage of active spiropyran units is around  $0.88/\text{nm}^2$  ( $A = 1.14 \times 10^{-18}$  m<sup>2</sup>), the maximum change in contact potential that could be achieved for 100% switching is calculated to be 2.6 V. The observed contact potential change of 0.27 V suggests that at least 10% of the molecules are activated by UV light, corresponding to a surface concentration of the more polar open form of around  $0.09/\text{nm}^2$ . Alternatively, the same contact potential change could be produced if 100% switching were achieved in a film in which the average polar axis of the spiropyran was tilted from the surface normal by  $84^\circ$ .

The contact potential measurements performed in air indicate that tethering spiropyran to the surface does not prevent the pyran rings from opening and closing in response to UV or visible light. However, such results do not reveal the extent to which such switching influences surface interactions of interest in microfluidic systems. To determine how switching mediates interfacial forces, we have performed experiments in the presence of a series of electrolyte solutions. IFM force profiles obtained between polar surfaces in electrolyte solutions are typified by the results obtained for the approach of a bare silica tip to a silica surface in formamide salt solutions ( $2 \times 10^{-3}$  M KCl). When both surfaces have a like charge (in this case negative), a repulsive force is detected at long separation distances. The repulsion increases exponentially as the surfaces approach each other until the tip is within tens of nanometers of the surface. At close separations, deviations from the electrostatic force are observed due to van der Waals attractions, hydration forces, and (on contact) the mechanical compliance of both tip and substrate materials.

The force component of interest here is the electrostatic repulsion, which is described using classical electrical double layer (DLVO) theory. For a spherical tip approaching a planar surface, the repulsion takes the form<sup>9</sup>

$$F(h) = (2\pi R/\epsilon \epsilon_0 \kappa_d)[(\sigma_t^2 + \sigma_s^2) \exp(-2\kappa_d h) + 2\sigma_t \sigma_s \exp(-\kappa_d h)] \quad (2)$$

where  $h$  is the tip–substrate separation distance,  $R$  is the tip radius,  $\epsilon$  is the dielectric constant of the fluid medium,  $\epsilon_0$  is the permittivity of free space,  $\sigma_t$  and  $\sigma_s$  are the surface charges on the tip and substrate, respectively, and  $\kappa_d$  is the Debye length. At 25 °C, the Debye length for a 1:1 electrolyte such as KCl in formamide is given by the expression



**Figure 4.** Schematic representation of the spiropyran on the surface illustrating the closed state and the open states before and after protonation.

$$1/\kappa_d = 0.354/[\text{KCl}]^{1/2} \text{ (in nanometers)} \quad (3)$$

If the tip and substrate have the same surface charge ( $\sigma_t = \sigma_s$ ), the force profile can be used to extract values for the surface charge density. For bare silica, fits of the above equations to our IFM results give  $0.03 \text{ C/m}^2$  ( $0.19 \text{ charges/nm}^2$ ) at pH 6.5 and  $[\text{KCl}] = 2 \times 10^{-3} \text{ M}$ , consistent with typical charge densities on silica.<sup>10</sup> Knowing the charge on the silica tip, IFM profiles obtained on other surfaces can be used to extract the effective substrate surface charge.

IFM profiles obtained on UV-activated tethered spiropyran surfaces interacting with a positively charged amine-coated probe tip in the polar solvent formamide (with  $2 \times 10^{-3} \text{ M KCl}$ ) (Figure 3a) reveal that a long-range repulsive force is present. Replacing the amine-coated tip with the negatively charged tip of bare silica reverses the sign on this force from repulsive to attractive (Figure 3b). The observed long-range forces are consistent with the interactions involving electrical double layers generated by a positively charged spiropyran surface. Assuming monovalent point charges, the surface charge density calculated from fits to the long-range repulsion and eq 2 after UV exposure is  $0.028 \text{ C/m}^2$  ( $0.175 \text{ charges/nm}^2$ ).<sup>11</sup> Short-term (10 s) exposure of the tethered spiropyran to visible light (Figure 3a) decreases the measured effective surface charge density to  $0.014 \text{ C/m}^2$  (or  $0.087 \text{ charges/nm}^2$ ). Experiments conducted on other samples show that the surface charge can almost be completely eliminated by longer-term (10 min) exposures to visible light. If UV photoactivation creates one charge per spiropyran ring opened, the IFM results suggest that up to 20% of the spiropyran is switched by the UV exposure. (The total spiropyran surface coverage is estimated to be  $0.88 \text{ molecules/nm}^2$ .) Cycling back and forth between UV and visible light regenerates the two surface charge states for the 4–5 cycles that were investigated.

It is interesting to compare the contact potential results with conclusions drawn from the normal force IFM measurements. The changes in electrical double layer seen in the normal force measurements suggest that short-term exposures to UV and visible light create and eliminate the equivalent of  $0.09 \text{ point charges/nm}^2$  in the spiropyran film. This concentration of added point charges is in excellent agreement with the  $0.09 \text{ open rings/nm}^2$  created by UV activation under similar conditions in air as inferred from the contact potential results. Interestingly, theoretical models indicate that the effective surface charge introduced via opening a spiropyran ring should be much less than one charge per ring. Models of double layers generated by “soft” interfaces such as lipid layers suggest that the effective surface charge density generated by an interface containing both fixed charges and molecular dipoles can be estimated using the expression<sup>12</sup>

$$\sigma_e = \sigma_f + \nu \kappa_d^{-2} l \text{ (if } l \ll \kappa_d) \quad (4)$$

where  $\sigma_e$  and  $\sigma_f$  are the effective and fixed surface charge densities, respectively,  $\nu$  is the effective dipole density (the

product of the surface concentration of dipoles and the component of each dipole perpendicular to the surface),  $l$  is the thickness of the polar region, and  $\kappa_d$  is the Debye length. Although spiropyran has a relatively large dipole moment, the effective charge per dipole calculated using an expression such as eq 4 is on the order of one thousand times smaller than a single point charge. Based on ring opening alone, the change expected in the double layer upon switching should have been negligible.

The key to reconciling the contact potential and normal force measurements is the realization that ring opening need not be the only reaction that occurs when the spiropyran is activated in an electrolyte containing water or other proton sources. When the pyran ring opens up, the phenoxy anion in the open ring can be protonated to form a phenol (Figure 4). In terms of surface charge, protonation of the open ring converts a neutral polar molecule into a positively charged entity. This is consistent with both the sign and magnitude of our normal force measurements. For switching surface interactions, such protonation can be beneficial because it magnifies the impact of ring opening on double layer forces by a factor of around 1000. However, such protonation may also impede the kinetics of ring closure, explaining why surface properties do not completely recover until up to 10 minutes of exposure to visible light.

In conclusion, IFM measurements indicate that a significant fraction (10–20%) of the rings in tethered spiropyran films can be opened and closed by exposing films to UV and visible light, respectively. In air, the ring opening results in the creation of a more polar surface that may exhibit different interactions with atmospheric species. In aqueous solutions and other proton-donating solvents, the ring opening results in the creation of a positively charged surface that can generate large electrical double layer forces. The ability to create and eliminate surface charges and double layer forces could be of significant utility in microfluidic systems. For example, it is much easier to drive fluids through small ( $<100 \mu\text{m}$  diameter) channels using electrokinetic flow than by pressure driven flow. As surface charges in channel walls are required to support electrokinetic flow, the ability to create and eliminate surface charge with light could lead to optically programmable microchannel routing schemes.

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