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Photon-Modulated Wettability Changes on Spiropyran-Coated Surfaces

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A coating of photoresponsive spiropyran molecules covalently bound to a glass surface along with a mixture of organosilanes to control the surface environment was prepared. The relatively nonpolar spiropyran can be reversibly switched to a polar, zwitterionic merocyanine isomer that has a much larger dipole moment by UV light, and back again by visible light. The contact angle was 11°−14° lower for dry, spiropyran-coated surfaces after irradiation with UV than that for dry, spiropyran-coated surfaces after irradiation with visible light. The light-induced changes observed in the surface energy were correlated to the switching of the surface-bound spiropyran molecule between polar and nonpolar forms by means of fluorescence spectroscopy and epifluorescence microscopy. Water in capillary tubes coated with the photosensitive layer was observed to rise when the wavelength of incident light was switched from visible to UV. The UV-induced rise was of the order of 2.8 mm for a 500 μm diameter capillary. This microfluidic actuation of water in an enclosed capillary or microchannel using light is termed “photocapillarity”. Contact angle hysteresis prevented the water from flowing back down the capillary when the light was switched from UV back to visible.

Introduction

Recently there has been much interest in the general field of microfluidics for a number of emerging applications in analytical chemistry,[1−4] medicine,[5−7] space,[8] and chemical processing.[9−11] This miniaturization of fluid processing poses many unique challenges requiring new methods and materials. Tasks essential to the operation of all microfluidic devices are the ability to move small volumes of fluid through microchannels and to control fluid flow. With decreasing scale, pumps and valves with moving parts become less attractive from an economic perspective and create daunting manufacturing challenges. For applications needing only occasional use or when sterility is required, single-use microfluidic devices face even greater economic pressure. These concerns have stimulated research into the control of fluid flow in microchannels using systems with no moving parts that can be scaled down to very small volumetric flows.

Manipulation of microchannel or capillary surface properties using a readily controlled external stimulus holds promise as a means for developing new modes of liquid transport for very small volumes. At these small characteristic dimensions, intermolecular and interfacial forces dominate over the force of gravity. Researchers have proposed the use of a variety of means of changing the interfacial properties of materials to induce or control surface wetting by liquids, including electrical potentials and fields,[12−18] temperature,[19−21] light,[22−31] and chemical means.[32]

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The use of light offers unique opportunities. Advances in the integration of LED sources in micro-total analysis systems (μ-TAS) hold promise for the production of low-cost miniaturized systems.[33−35] Also, light fluxes are easily controlled temporally, and the action of light can be independent of the liquid properties. But perhaps most importantly for biological solutions, conditions for photoactuation may be relatively mild. For biological applications, extremes in temperature, the use of nonaqueous solutions, and the use of aqueous conditions differing radically from physiological norms must be avoided. In addition, deleterious interactions of biological molecules with the surface should be minimized by avoiding high surface densities of reactive or denaturing molecules. The latter concern becomes more important upon miniaturization, since surface area-to-volume ratios increase dramatically. The work described in this paper is not only centered upon the use of light wavelengths compatible with biological solutions but also centered on the idea that the actuating molecule should be chemically unreactive and present at low surface densities to minimize interference with labile molecules.

Our research explores the design of a photosensitive surface whose wetting characteristics may be changed by the use of light. This coating, when applied to the inside walls of capillaries, allows the flow of water to be induced by light of specific wavelengths. We have termed this microfluidic actuation of water in an enclosed capillary or microchannel using light "photocapillarity". While there has been substantial work using light to control surface properties, a summary of the literature reveals that demonstration of aqueous photocapillarity has not previously been achieved.

Reports of systems involving photochromic molecules or copolymers used to demonstrate the changing of contact angles of liquid drops on flat surfaces[22,23,28,30,31,36,37] have appeared since the early 1980s. Much attention has been given to various means of copolymerization or immobilization of photochromic molecules from the spiropyran[31,38−40] or azobenzene families.[22,27−30] Other molecules that undergo photoreversible reactions such as dimerization have also been used in contact angle[23] or droplet release[41] experiments.

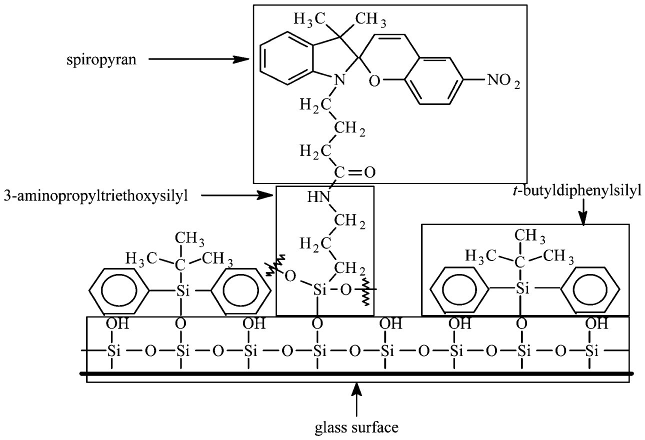

Figure 1. Schematic of the surface chemistry of spiropyran-coated glass.

Translation of contact angle changes on surfaces to liquid movement in capillaries minimally requires three conditions. First, the immobilization method must be amenable to treatment of the inner walls of capillaries. Second, the capillary material should not absorb an amount of light that would reduce the photon flux at the surface to subactuation levels. Finally, the liquid/solid contact angle should change appreciably and within a reasonable period of time in order to establish the capillary pressure driving force needed to move the liquid. One or more of these conditions appears to have limited the investigation of photoresponsive surfaces in capillaries or microchannels. In fact, the only work reported using capillaries or microchannels is that of Ichimura and colleagues,[27] who limited their approach to a binary liquid mixture of 4-propyl-4′-ethoxy- and 4-propyl-4′-butoxyphenylcyclohexanes. They used a surface tension gradient induced by shining light on a capillary coated with a tethered azobenzene monolayer.

In this research, glass slides and capillaries were modified by derivatizing their surfaces with a mixture of organosilane groups using (3-aminopropyl)triethoxysilane (ATES) and *tert*-butyldiphenylchlorosilane (TBDS) and then linking the photochromic spiropyran 1′-(3-carboxypropyl)-3′,3′-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2′-indoline (SPCOOH) to the free amino groups via an amide bond. The result was a dilute layer of spiropyran on a silanized surface (Figure 1).

The spiropyrans comprise a group of light-switchable, photochromic organic molecules. The majority of them exist in the dark (in nonpolar solvents) in a colorless, nonpolar "closed" spiro form that absorbs light only in the ultraviolet (UV). When exposed to UV light, the spiropyran undergoes an isomerization that produces an "open" merocyanine form that is colored (absorbing typically at about 530 nm) and highly polar. As shown in Figure 2, this open form is a resonance hybrid of a zwitterionic structure and a neutral structure. Reversion to the stable, closed form occurs on exposure to visible (VIS) light. This reversion may also occur thermally. The zwitterionic structure is a major contributor to the structure of the open form, because, in the neutral structure, the aromaticity of the oxygen-bearing ring is lost. Thus, the molecules may be switched from closed to open with UV light (or thermally in polar solvents) and from open to closed with VIS light (or thermally in nonpolar solvents). Some spiropyrans can withstand repeated light-induced cycling (up to 30 000 in certain cases). They show good quantum yields for isomerization (between 10% and 50%), resulting in efficient energy utilization and few side reactions.[42] They do not generate free radicals, unlike many photochemically active molecules. The photochemical response does not require extreme values of pH and thus should be amenable to biocompatible processing. Most potential applications of the spiropyrans to date involve the light-induced color change. In contrast, the emphasis in this

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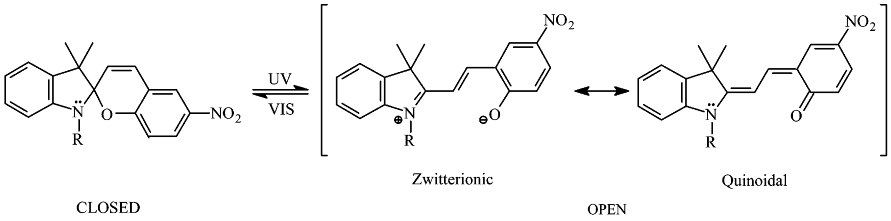

Figure 2. Isomeric molecular structures of a spiropyran upon irradiation with light. Other stereoisomeric forms for the "open" case are also likely to be populated. Solution equilibria due to proton and hydroxyl exchange at low and high pH are not shown.

work is on the light-induced change in hydrophobicity. Photochromism is important only in that it provides a unique, independently controllable mechanism for switching between the two forms.

There are two properties of spiropyrans that make the careful design of the local environment of the attached spiropyran essential for its functionality. First, the switching of spiropyrans from one form to the other is extremely sensitive to steric effects.[26,42] These findings can be explained by the large changes in conformation that the spiropyran undergoes when converting from its nonplanar, closed form to the highly extended, conjugated system of its open form and vice versa. Photoisomerization of the spiropyran could also be hampered at high coverages because of intermolecular interactions.[43] A second issue is that the overall polarity of the environment significantly influences photochromism. A polar environment stabilizes the charged structure of the open, merocyanine form. Tagaya et al.[44,45] found that, for the reversible switching of spiropyrans trapped in a silica matrix, a coexistence of polar and nonpolar regions was essential. Thus, the surface should be designed to possess components of differing polarity. It is for these reasons that this research employs a two-part surface modification approach in which bound spiropyran molecules are separated by nonpolar *tert*-butyldiphenylsilyl groups.

Materials and Methods

An improved synthesis of SPCOOH is reported here.

1′-(3-Carbomethoxypropyl)-3′,3′-dimethyl-6-nitrospiro-[2H-1]benzopyran-2,2′-indoline (SPEST). A 1.78 g (10.7 mmol) portion of 5-nitrosalicylaldehyde was suspended in 32 mL of ethanol. This was followed by a dropwise addition of 3.62 g (10.7 mmol) of the quaternary salt of 1-(3-carbomethoxypropyl)-3,3-dimethyl-2-methyleneindoline[25] in 80 mL of ethanol. The mixture was refluxed (79 °C) for 6 h. After it was cooled to room temperature, the dark purple reaction mixture was further cooled in an ice bath and filtered. The filter cake was washed with cold ethanol, yielding an orange solid (the hydrobromide salt of SPEST) which was dissolved in dichloromethane and washed with 10% aqueous sodium carbonate. The organic layer was dried over sodium sulfate, and the solvent was distilled at reduced pressure. Recrystallization from ethanol yielded 2.14 g of a pale yellow solid (49% yield). ^{1}H NMR (300 MHz, CDCl$_3$) d 1.19 (3H, s, 3′-CH$_3$), 1.29 (3H, s, 3′-CH$_3$), 1.96 (2H, m, N−CH$_2$C*H*$_2$CH$_2$-), 2.37 (2H, m, N−CH$_2$CH$_2$C*H*$_2$-), 3.21 (2H, m, N−C*H*$_2$CH$_2$CH$_2$-), 3.64 (3H, s, COOCH$_3$), 5.88 (1H, d, *J* = 10 Hz, H-3), 6.65 (1H, d, *J* = 8 Hz, H-7′), 6.74 (1H, d, *J* = 7 Hz, H-8), 6.88 (1H, t, *J* = 8 Hz, H-5′), 6.91 (1H, d, *J* = 10 Hz, H-4), 7.09 (1H, d, *J* = 8 Hz, H-4′), 7.20 (1H, t, *J* = 8 Hz, H-6′), 8.02 (2H, m, H-5 and H-7).

1′-(3-Carboxypropyl)-3′,3′-dimethyl-6-nitrospiro[2H-1]-benzopyran-2,2′-indoline (SPCOOH). SPEST (109 mg, 0.266 mmol) was dissolved in 4 mL of tetrahydrofuran, and 1 mL of 10% aqueous sodium hydroxide was added. The yellow solution turned blue immediately and then changed back to yellow after several minutes. The reaction mixture was stirred at room temperature for 26 h, during which it turned red. The reaction was quenched with 10% aqueous citric acid and then extracted with chloroform. The organic layer was dried over sodium sulfate and the solvent distilled at reduced pressure, leaving 132 mg of bright red solid SPCOOH (78% yield). ^{1}H NMR (300 MHz, CDCl$_3$) d 1.19 (3H, s, 3′-CH$_3$), 1.29 (3H, s, 3′-CH$_3$), 1.95 (2H, m, N−CH$_2$C*H*$_2$CH$_2$-), 2.41 (2H, t, *J* = 7 Hz, N−CH$_2$CH$_2$C*H*$_2$-), 3.22 (2H, m, N−C*H*$_2$CH$_2$CH$_2$-), 5.88 (1H, d, *J* = 10 Hz, H-3), 6.62 (1H, d, *J* = 8 Hz, H-7′), 6.74 (1H, d, *J* = 9 Hz, H-8), 6.88 (1H, m, H-5′), 6.89 (1H, d, *J* = 10 Hz, H-4), 7.09 (1H, d, *J* = 8 Hz, H-4′), 7.19 (1H, t, *J* = 8 Hz, H-6′), 7.99 (2H, m, H-5 and H-7).

1′-(3-(Propylcarbamyl)propyl)-3′,3′-dimethyl-6-nitrospiro-[2H-1]benzopyran-2,2′-indoline (SPAMD). A 272 mg (0.69 mmol) portion of SPCOOH was dissolved in 50 mL of dichloromethane, giving a red solution. *N*,*N*-Dimethylaminopyridine (30.4 mg) was added, followed by 186 mg of dicyclohexylcarbodiimide. Upon addition of 0.75 mL of propylamine, the solution turned yellow. The reaction mixture was stirred at room temperature for 36 h, quenched with 10% aqueous sodium bicarbonate, and extracted with chloroform. The organic layer was dried over sodium sulfate, and the solvent was distilled at reduced pressure. The remaining red residue was chromatographed on silica gel (1% methanol in chloroform) to yield 62 mg (73%) of red solid SPAMD. ^{1}H NMR (300 MHz, CDCl$_3$) d 1.17 (3H, s, 3′-CH$_3$), 1.27 (3H, s, 3′-CH$_3$), 1.77 (5H, m, N−CH$_2$C*H*$_2$CH$_3$ and N−CH$_2$CH$_2$C*H*$_3$), 1.93 (2H, m, N−CH$_2$C*H*$_2$CH$_2$-), 2.44 (2H, t, *J* = 7 Hz, N−CH$_2$CH$_2$C*H*$_2$-), 3.22 (2H, t, *J* = 8 Hz, −C*H*$_2$CH$_2$-CH$_2$CONH), 3.25 (2H, m, N-C*H*$_2$CH$_2$CH$_3$), 5.85 (1H, d, *J* = 10 Hz, H-3), 6.61 (1H, d, *J* = 8 Hz, H-7′), 6.73 (1H, d, *J* = 9 Hz, H-8), 6.88 (1H, d, *J* = 10 Hz, H-4), 6.90 (1H, d, *J* = 8 Hz, H-5′), 7.09 (1H, dd, *J* = 8, 1 Hz, H-4′), 7.17 (1H, dt, *J* = 8, 1 Hz, H-6′), 7.99 (2H, m, H-5 and H-7); MS (MALDI-TOF) *m*/*z* 435.8 (M$^+$).

Glass Slide Modification. The silane surface derivatization agents, TBDS and ATES, were obtained from United Chemical Technologies, and 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide (EDC) was obtained from Sigma Chemical Co. Methanol, hydrochloric acid, toluene, and ethanol were of reagent grade from Mallinckrodt Baker Inc. Glass slides (precleaned microscope slides, VWR Scientific) were well cleaned by shaking them in a 1:1 volume ratio methanol/concentrated hydrochloric acid solution for 30 min. They were then washed extensively in deionized water from a Barnstead Nanopure system and dried in an oven at 140 °C for 20 min. Toluene was dried by double distillation and stored over 3 Å molecular sieves. Solutions, having concentrations from 0.1 to 0.5 vol % of TBDS in dry toluene and ATES in dry toluene were prepared in airtight glass bottles. The slides were incubated in the TBDS solution for 30 min before being removed from the solution and washed well in toluene to remove excess reagent. The slides were then dried at 140 °C for 20 min and incubated in the ATES solution for about 30 min. The slides were then removed from solution, washed well in toluene and water, and cured in an oven at 140 °C for 30 min to 3 h. The cured, silane-coated slides were incubated in an ethanolic solution of SPCOOH (1 mM) in the presence of EDC (10 mM).[46] This was carried out in an airtight bottle, at room temperature, with gentle shaking for 30 min to 1 h. The slides were then removed from solution, washed sequentially with ethanol and water to remove unbound spiropyran, and dried under vacuum for 20 min.

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Glass Capillary Modification. The procedure followed for coating the inside surfaces of glass capillaries was analogous to that followed for the coating of glass slides. Preliminary experiments showed that soaking the capillary in the coating solutions did not result in effective surface modifications because of low rates of diffusional mass transfer to the insides of the capillaries. This was overcome by pumping the reactant solutions through the capillaries using a peristaltic pump. The pump (P-1, Pharmacia) had a variable flow rate ranging from 4 to 200 mL h^{-1} for tubing of 1.6 mm internal diameter (i.d.). Separate pieces of tubing were used for the pumping of different fluids. Fluran F-5500-A tubing (Norton Performance Plastics) was used to pump methanol, ethanol, hydrochloric acid, and toluene. Tygon tubing (Norton Performance Plastics) was used to pump water. Before use, each piece of tubing was well flushed with its respective solvent in order to avoid possible contamination of the coated capillary with material leached out of the pump tubing. The type of capillary used (Special Glass Thin-Walled capillary tubes, Charles Supper Co.) had an i.d. of 500 μm, a wall thickness of 10 μm, and an overall length of about 80 mm, and it was flared at one end. The flared end was used to couple the capillary to the pumping system tubing. The capillary was dipped into flasks containing the coating solutions through a one-holed Teflon stopper, and the solution was sucked up through the capillary tube and sent to a waste flask.

Light Sources. The UV light source was a Model UVGL-25 Mineralight Lamp in the 366 nm wavelength setting. This generated a power of 2 mW cm^{-2} at a distance 2 cm from the source. The VIS actinic light source used for the contact angle measurements was a 50 W Model LS 86/110 lamp from Fiberoptic Specialties, Sarasota, FL. This was coupled to a Fostec diffuser containing an IR filter, resulting in a power of 1.34 mW cm^{-2} at a distance 2 cm from the source. The VIS actinic light source used for the capillary rise experiments was a 50 W High-Intensity Illuminator (Series 180, Dolan Jenner) coupled to a water flow-through IR filter to reduce heat. It illuminated the entire capillary with a measured power of 4.8 mW cm^{-2}.

Contact Angle Measurements. Advancing contact angles were measured using the sessile drop technique. The treated glass plates were placed on a Newport XY Translation Stage (Model 401) and illuminated with the appropriate wavelength of light for at least 30 min from a distance of about 2 cm. A 2 μL drop of deionized water ($pH = 5.5$) was then carefully placed on previously unwetted portions of the plate using a micropipet. The image of the drop on the surface was captured within 5 s of drop deposition in order to minimize error due to evaporation. The drop was observed using a Navitar microscope (magnification range from 250× to 900×) attached to the stage, and a Hitachi digital color video camera (Model VK-C370) interfaced to a computer. The images so obtained were processed using ScionImage1.62c software to obtain values of the contact angles. All measurements were repeated on at least six unwetted areas of a single slide as well as on multiple slide samples to determine reproducibility. The surface was then dried and illuminated with the appropriate wavelength of light, and the next set of contact angle measurements was taken.

Capillary Rise Measurements. The experimental setup used for measurement of capillary rise is shown in Figure 3. The capillary was fixed vertically to a measuring scale and was connected to a two-way valve at its top. During the actual measurement of the capillary rise, the valve was set so that the top of the capillary was open to atmospheric pressure. The water in the capillary could be blown out by switching the valve to connect with the pressure regulating device. The measurement was performed by raising the z-stage with the beaker of DI water to the point where the bottom of the capillary was just submerged in the water, causing the water to rise up in the tube under capillary pressure. It was estimated that the error of measurements taken visually through a magnifying glass was $<\pm 0.5$ mm.

For measurement of equilibrium capillary rise, the tube was first dried under vacuum, illuminated with the desired wavelength of light for a fixed period of time (usually 30 min), and finally dipped into the water to measure the rise. Ensuring that the capillary was dry was essential for reproducible measurements. Each measurement was repeated at least four times. The equilibrium capillary rise of water was also measured in tubes that had been wetted with water and blown out just prior to the measurement. For kinetic measurements, the tube was first dried and illuminated with VIS light for a fixed period of time (usually 30 min) before dipping it into the beaker of water. The water meniscus usually reached a steady-state height within 10 s. After ensuring that a steady-state had been achieved, the capillary was then bathed in UV light and the water height was monitored versus time until a new steady-state height was reached.

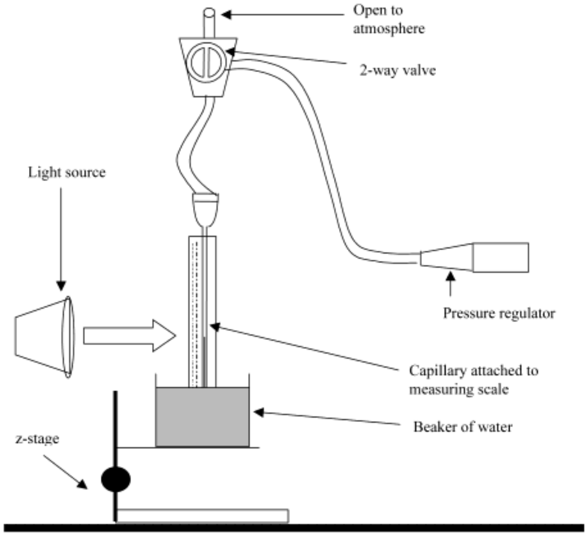

Figure 3. Experimental setup for measurement of capillary rise.

Epifluorescence Microscopy. The fluorescence of the coated slides after treatment with either UV or VIS light was examined using an inverted fluorescence microscope (Leica, model DM IL). The objective lens used (L40×) led to an illuminated area of a specimen plane of about 150 μm diameter. The coated slide was placed on the microscope stage and excited with 515−560 nm light from a high-pressure Hg lamp source. The fluorescent light of wavelength >590 nm was collected from the same direction by the use of an N21 filter cube (excitation filter B.P. 515−560 nm, dichromatic mirror 580 nm, suppression filter L.P. 590 nm). The integration time for a fluorescence image from a single spot was set at 1 min, and the image was captured digitally using MagnaFire software. The fluorescence of each spot was measured over several cycles of alternating UV and VIS irradiation (each of 20 min duration). Spots on several different areas of the sample, as well as on multiple samples, were examined. Measurements were performed in air, or in a water environment, by placing a drop of deionized water over the spot being studied. The fluorescence images so obtained were processed using Image-Pro Plus to plot a histogram of the intensity of fluorescence in terms of an arbitrary scale of 0−256.

Fluorescence Spectroscopy and UV/VIS Absorbance Spectroscopy. Quartz cuvettes (Starna Spectrosil Far UV, 3-Q-10) having a 10 mm path length were used in all measurements. The fluorescence spectra were obtained using a Photon Technology International spectrofluorimeter (model QM-2000-4). The fluorescence of SPCOOH in solution was measured using a 1 nm excitation slit, an 8 nm emission slit, a 2 nm step size, and a 0.2 s integration time. The signal-to-noise ratio of the surface-bound spiropyran fluorescence was increased by using 8 nm excitation and emission slits, a 10 nm step size, and a 10 s integration time. In this case, the coated slide was held in the quartz cuvette at a 45° angle to both the excitation beam and the detector. UV/VIS absorption spectra of SPCOOH solutions were obtained with a Shimadzu UV2100U spectrophotometer using 5 nm slits, a 2 nm step size, and medium speed scans.

Results and Discussion

Surface Modification. TBDS molecules have been shown to react with silicate surfaces to form Si−O−Si bonds.[47] In this study, one purpose for the TBDS surface

Table 1. Water Contact Angle Measurements of a Glass Surface after Various Stages of Surface Treatment

reaction sequence	contact angle, deg
cleaned	5 ± 1
treated with TBDS	57 ± 2
treated with ATES	72 ± 4
treated with SPCOOH, under VIS light	74 ± 3

derivatization was to dilute the surface coverage of the bound SPCOOH so as to meet the steric demands of the spiropyran−merocyanine photoconversion and avoid intermolecular interactions between the merocyanine forms.[26] Another function was to convert some of the highly polar silicate surface to a more hydrophobic, organic surface. Ring opening and closing of the spiropyran is facile in such a medium. The large size of the phenyl rings on a *tert*-butyldiphenylsilyl group bound to the glass surface is likely to sterically hinder reaction of TBDS at adjacent hydroxyl groups. It has been reported that, on TBDS-treated surfaces, the attached *tert*-butyldiphenylsilyl groups are separated by at least one silicon atom with a free hydroxyl group attached.[48] These hydroxyl groups might be available for reaction with ATES, which has smaller substituents. The ATES could also react with larger areas of underivatized surface resulting from incomplete reaction with TBDS.

The formation of 3-aminopropylsilyl films on silicate surfaces treated with ATES has been widely studied, and it has been reported that parameters such as the degree of water exclusion, concentration, reaction time, and temperature play important roles in determining the characteristics of ATES-treated surfaces.[49−51] The ATES reportedly reacts with both the surface oxygens and adjacent 3-aminopropylsiloxy groups to form cross-linked structures.[52] It was found that the bulk of silane−surface siloxane bonds are formed during the ATES curing step, and without this a majority of the silane is merely physisorbed to the surface.[50,53] This is an important consideration for the construction of photosensitive surfaces, as physisorbed ATES could be leached away by subsequent ethanol and aqueous treatments.

Contact angle measurements were used to characterize the glass slides at different stages of the coating procedure. These measurements give a macroscopic measure of the surface hydrophobicity after each surface modification step and were also used to verify the reproducibility of the procedure. The contact angle of the surfaces during a typical treatment sequence (0.5% TBDS for 30 min, 0.1% ATES for 30 min, 1 mM SPCOOH with 10 mM EDC for 1 h) is given in Table 1. Cleaned glass slides produced very small water contact angles consistent with that of very clean glass as reported previously.[54] Successive modifications with TBDS, ATES, and SPCOOH caused the surface to increase in hydrophobicity, leading to a final value of water contact angle of about 74° for the spiropyran-coated surface under visible irradiation. This is similar to the contact angles of water observed on silicate surfaces derivatized with azobenzene[29,30] or pyrimidine-coated surfaces.[23]

Light-Induced Changes in Contact Angles. The goal of preparing a spiropyran-coated, photosensitive surface was to achieve changes in the surface energy, as measured by the water contact angle, solely through the use of light. It was expected that the large change in dipole moment between the two isomeric states of the spiropyran would lead to measurable changes in the energy of the surface to which it was bound. For the spiropyran-coated surfaces, water contact angles after UV irradiation were different from those after VIS irradiation (Figure 4a). A graph of the results of contact angle measurements after subjecting spiropyran-coated, photoresponsive surfaces and a control surface to sequential irradiation of VIS and UV light is shown in Figure 4b. The control surface was coated with silanes by treatment with TBDS and ATES but was not derivatized with spiropyran. The figure shows that UV irradiation of the photosensitive slides results in lower water contact angles than VIS irradiation. This indicates that the surfaces are more polar under UV irradiation, as would be expected by the opening of the spiropyran, than under VIS light, where the spiropyrans would be in the closed form. These results demonstrate that reversible water contact angle changes of 11°−14° are possible using this surface design. The magnitude of the light-induced water contact angle change achieved at pH 5.5 using this surface compares favorably with that of other systems reported (12°,[28] 9°,[30] 8°[27,29]) despite the expected low surface coverage of spiropyran. Although the focus of the present study is investigation of the nature and magnitude of changes in surface properties as a function of light-induced switching of the spiropyran between isomeric forms, any ultimate practical use of this effect must take into account possible degradation of the spiropyran during irradiation. Studies of spiropyrans closely related to that employed here show that although such spiropyrans are relatively stable to repeated cycling, degradation eventually occurs.[42] We found that the spiropyran-coated surfaces could be put through at least four consecutive cycles of wettability changes, each cycle consisting of first drying the surface, VIS irradiation, contact angle measurement, drying the surface again, UV irradiation, and contact angle measurement. Moreover, since the intensity of light used in our studies is quite low, we expect that many more cycles are possible before degradation reactions begin to interfere with the surface effect. Samples could be stored for at least 1 week without loss of ability to switch between their higher and lower wetting states.

The surface was designed to include *tert*-butyldiphenylsiloxyl groups in order to reduce the coverage of spiropyran molecules. This design was hypothesized to lead to a less restrictive geometry so that the photochromic reaction could take place with minimal steric hindrance due to spiropyran interaction. The design also favors reversible spiropyran photoisomerization by preventing interaction with the highly polar silica surface, which would tend to keep the spiropyran molecule in its open form. If the glass slides were not initially coated by TBDS treatment, a higher concentration of ATES-amine groups would be expected to be available to bind spiropyran to the surface. To test this hypothesis, spiropyran was bound to slides coated only by the ATES treatment. The wettability changes achieved on the ATES-treated, spiropyran-coated slides are compared with those on slides treated with both TBDS and ATES in Figure 5. It was found that the water contact angle could be reversibly

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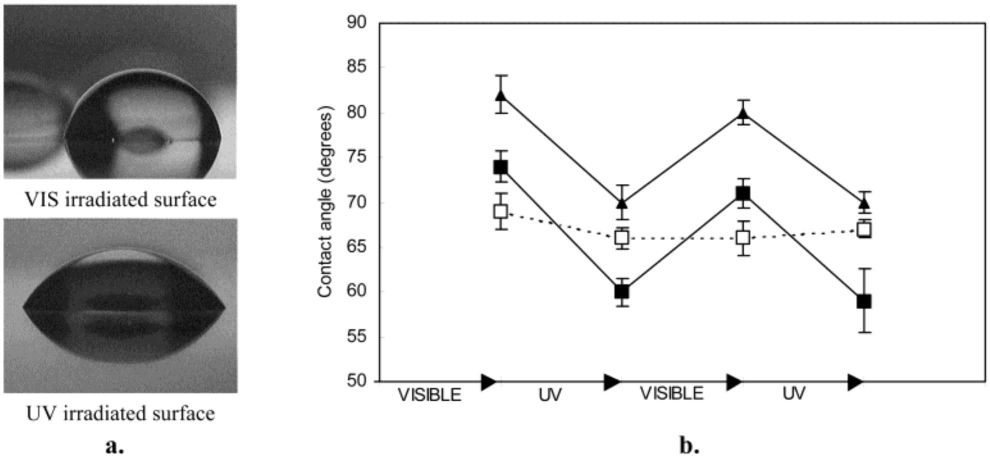


Figure 4. (a) Examples of water drops on a photosensitive surface after visible and UV irradiation. (b) Light-induced change in water contact angle on coated slides (the broken line represents a control slide modified only using TBDS and ATES; each solid line represents a slide modified with TBDS, ATES, and spiropyran molecules). Error bars represent one standard deviation.

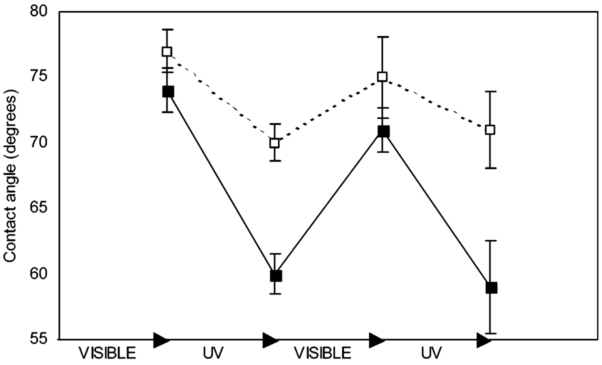


Figure 5. Comparison of light-induced water contact angle changes on photosensitive slides with and without TBDS treatment. The broken line represents a spiropyran-coated slide treated with ATES. The solid line represents a spiropyran-coated slide treated with TBDS and ATES.

changed with light on a slide for which TBDS treatment had been omitted. However, the magnitude of this change was only about 5° compared to 13° for a surface that had been treated with TBDS. It appears that while the ATES-treated surface is sufficiently hydrophobic to enable some of the spiropyran molecules to open and then reclose, the surface treated with both TBDS and ATES produces a much larger effect. It may be that the *tert*-butyldiphenylsiloxyl groups favor a less dense packing of spiropyran molecules on the surface, allowing a higher percentage of the molecules to convert between the open and closed forms.

Fluorescence and UV/Vis Absorption Spectroscopy. Fluorescence spectroscopy was performed on the coated slides in order to correlate the surface energy changes observed via the contact angle technique with the changes in chemical structure of the spiropyran bound to the photosensitive surfaces. Spiropyrans are known to exhibit luminescence only in their colored, merocyanine form and not in their closed form. From the absorption and fluorescence emission spectra of SPCOOH in water at pH = 5.5 (Figure 6), it is seen that, in the dark when thermally equilibrated, the spiropyran equilibrium features a significant amount of the open form. Under visible illumination, it is almost entirely in the closed, spiro form. Under UV (366 nm) illumination, a photostationary state featuring both the open and closed forms is reached, resulting in an intermediate degree of fluorescence. This occurs because irradiation at 366 nm excites both the open and closed forms. The absorbance spectra of SPCOOH in water show that the open form absorbs light in the 500 nm region of the spectrum, but the closed form is virtually transparent in this region. On the basis of these spectra, it can be concluded that ~10% of the spiropyran is in the open form in water at pH = 5.5 under 366 nm irradiation.

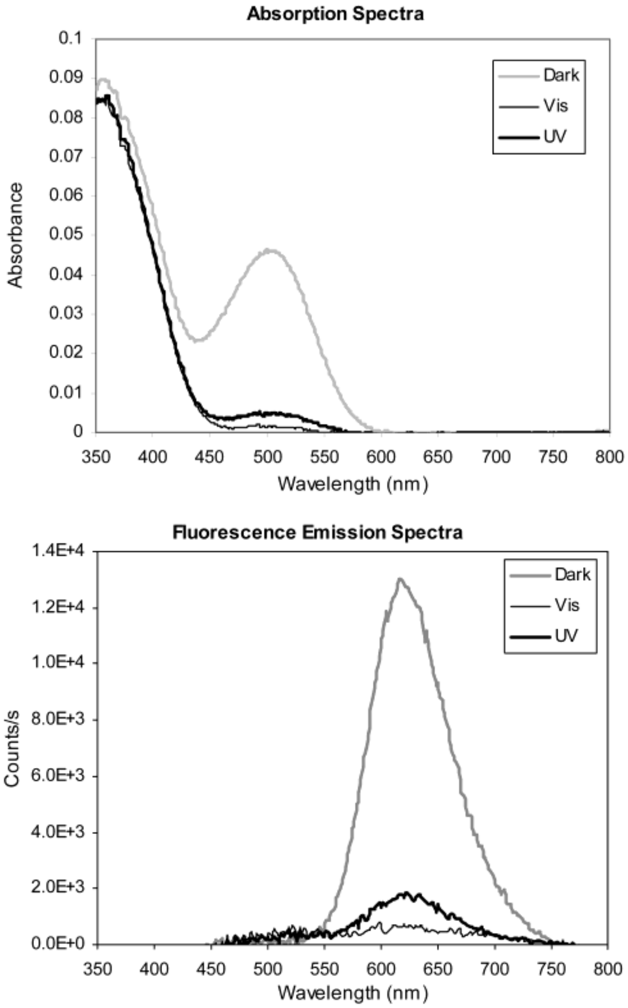


Figure 6. Absorption and fluorescence emission spectra of a solution of SPCOOH in water under visible or UV illumination or in the dark.

The fluorescence emission spectra of a glass slide modified with the spiropyran coating and immersed in water at pH = 5.5 were obtained after irradiating it with

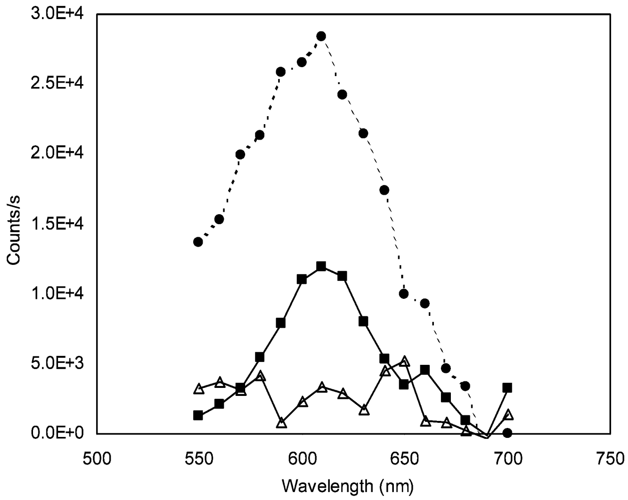


Figure 7. Fluorescence emission spectra of a slide modified with spiropyran coating and irradiated with different wavelengths of light in an aqueous environment (triangles, squares, and circles represent VIS irradiation, UV irradiation, and dark condition, respectively).

different wavelengths of light (Figure 7). The emission spectra were roughly similar to those of the spiropyran molecule in aqueous solution. The surface-bound spiropyran was cycled between its closed and open light forms multiple times reproducibly. As was seen in the fluorescence spectra of SPCOOH in solution, only a fraction of the spiropyrans on the surface open under 366 nm irradiation. This was ascribed to the establishment of a photostationary state, as discussed above.

The emission spectrum of the surface-bound spiropyran was compared with that of a model spiropyran, 1′-(3-(propylcarbamyl)propyl)-3′,3′-dimethyl-6-nitrospiro[2H-1]benzopyran-2,2′-indoline (SPAMD). The emission spectra of an aqueous solution of SPAMD and the surface-bound spiropyran in water are very similar, with the emission peak for SPAMD being 614 nm compared to ~615 nm for the surface-bound fluorophore. The similarity in the emission peaks implies that the microenvironment experienced by the spiropyran on the surface is comparable to that it experiences in aqueous solution. Studies of the effect of solvent composition upon the absorption and emission characteristics of the surface-bound spiropyran are currently in progress.

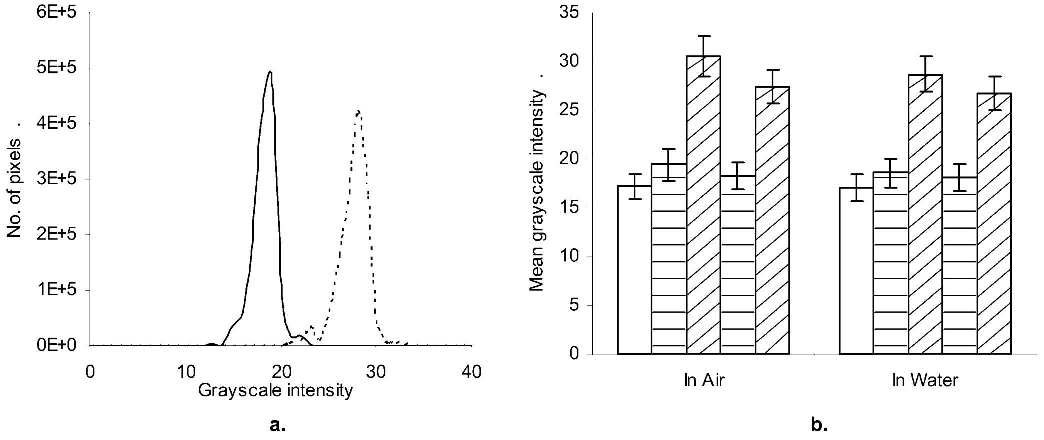
Table 2. Water Capillary Rise in 500 μm Diameter, Coated Glass Tubes after UV and Visible Irradiation[a]

	average water capillary rise (mm)		
illumination	control tube—dry	photosensitive tube—dry	photosensitive tube—wet
VIS	22.6 ± 0.1	33.9 ± 0.2	57.1 ± 0.1
UV	22.8 ± 0.2	36.7 ± 0.1	57.5 ± 0.1
VIS	23.2 ± 0.2	34.1 ± 0.1	56.8 ± 0.1
UV	23.0 ± 0.1	36.8 ± 0.2	57.8 ± 0.1

[a] Each value is the average of four readings.

Epifluorescence Microscopy. Epifluorescence microscopy was used to obtain quantitative information on surface homogeneity and the degree of switching between open and closed forms of the surface-bound SPCOOH. This was achieved by integrating the fluorescence over a wide range of wavelengths, resulting in an improved signal-to-noise ratio compared with that of the fluorescence spectroscopy measurements. These measurements are presented as histograms of the mean fluorescence intensity of areas on the slide surface in terms of an arbitrary scale in Figure 8a. Slides treated only with TBDS and ATES were used as controls and showed no change in fluorescence intensity after being irradiated with either UV or VIS light. The spiropyran-coated slides exhibited large changes in their fluorescence at wavelengths > 590 nm (Figure 8b). Under visible irradiation the intensities of fluorescence of the photosensitive slides are very close to that of the control slides, as would be expected from the emission spectra in Figure 7. These results confirm the switching of the surface-bound spiropyran between the open, fluorescent forms and the closed, nonfluorescent form in both air and water environments. The similarity between the degree of switching in the air and water environments may be due to the presence of a layer of adsorbed water on the slides used in the air measurements. It was also noticed that the maximum fluorescence intensity was obtained from samples that had been left in the dark overnight, just as was seen in the emission spectra in solution (Figure 6) and on the surface (Figure 7).

Light-Induced Changes in Capillary Rise. We have also investigated whether the surface energy changes observed in the contact angle measurements on the coated plates could be translated into changes in the equilibrium rise of water in vertical, coated capillaries. Table 2 shows the results for two cycles of a typical equilibrium capillary rise experiment. Each cycle consisted of drying of the capillary, VIS irradiation, a dry capillary rise measurement, wetting of the capillary, a wet capillary rise



a.

b.

Figure 8. (a) Histogram of fluorescence intensity of spiropyran-coated slides after UV (broken line) and VIS (solid line) irradiation. (b) Switching of the mean fluorescence intensity of coated slides in air and water from histograms. Columns with horizontal and diagonal hashes represent spiropyran-coated slides after VIS and UV irradiation, respectively. Columns with no hashes represent control slides treated only with TBDS and ATES. Error bars represent one standard deviation.

measurement, drying of the capillary, UV irradiation, a dry capillary rise measurement, wetting of the capillary, and a wet capillary rise measurement. The water rose 2.8 mm higher on average after UV irradiation than after VIS irradiation of the initially dry, spiropyran-coated capillary. The variation in capillary rise of the control tube (coated only using TBDS and ATES) was within the experimental error of the measurement. The observed light-induced change in capillary rise was similar in magnitude even after four successive cycles of alternating VIS and UV light. Since the equilibrium capillary rise is inversely proportional to the diameter of the tube, it is expected that the use of smaller diameter tubes would result in significantly larger changes in capillary rise.

To estimate the degree of hysteresis present in the system, the light-induced capillary rise changes were also measured in tubes that had been wet throughout their length immediately before taking the reading (Table 2). This resulted in capillary rise values significantly higher than those in the dry tube, indicating the existence of a large value of contact angle hysteresis. Another feature of the large hysteresis is that the capillary rise in the wetted tube changed only slightly with alternating UV and VIS illumination. The magnitude of hysteresis in this system (the average difference between the capillary rise in wet and dry tubes is 22 mm) is much larger than that of the light-induced change (2.8 mm). The contact angle hysteresis of water has been reported to be an issue in other photosensitive systems studied as well. Ichimura et al.[27] obtained a water contact angle change of 8° with a hysteresis of 45°, and Abbott et al.[23] found a water (pH = 5.8) contact angle change of 4° with a hysteresis of 15°−30°. In these cases too, the hysteresis is significantly larger than the light-induced change in contact angle, thus preventing reversible effects. Despite having being studied extensively in the past several decades, the underlying causes of contact angle hysteresis are not fully understood. Different studies have attributed the phenomenon to surface roughness[55,56] and surface heterogeneity.[57] A more recent study[58] on the contact angle hysteresis of well-characterized trialkylsilyl monolayers on silicon found that mobile surfaces with flexible chains and rigid surfaces that pack well exhibit low hysteresis, whereas rigid surfaces that do not pack well exhibit large values of hysteresis. Contact angle hysteresis was also found to decrease with increasing molecular volume of the liquid used.[58,59]

The rate of UV-induced capillary rise was examined by shining UV light on a tube in which water had previously reached its equilibrium capillary rise under VIS light (Figure 9). When the UV light was turned on (at 300 s), it was found that the meniscus in the spiropyran-coated tubes took 300−1500 s to rise 2−3 mm to a new equilibrium position. The rate is believed to depend on the UV light intensity and the nature of the surface coating. Tubes having a more hydrophilic coating exhibited faster UV-induced capillary rise kinetics than those with a more hydrophobic coating. The control tubes did not exhibit the phenomenon of light-induced capillary rise.

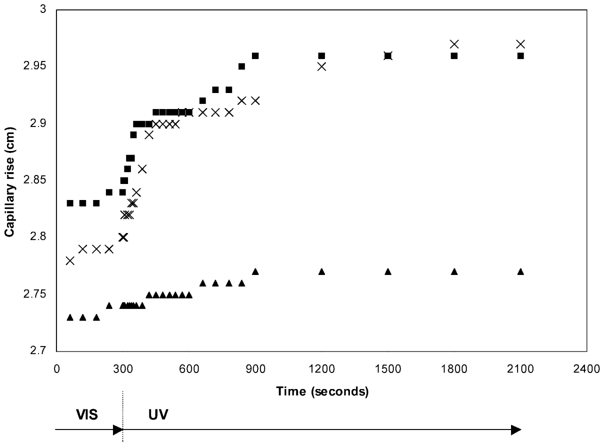


Figure 9. Typical dynamics of water meniscus levels in coated capillary tubes (triangles represent a control capillary modified only by TBDS and ATES; squares and crosses each represent a capillary modified with the photosensitive layer).

This is the first report of the light-driven advancement of water in a capillary tube connected to a reservoir. In the only other example in the literature of light-driven motion of liquids through capillaries,[27] it was reported that water could not be moved through a tube using light because of the unfavorable hysteresis between the advancing and receding contact angles. This problem was overcome in our system by the use of a different geometry. In the capillary rise setup used (Figure 3), only the advancing contact angle in the capillary was significant because of the small diameter of the tube. The receding contact angle would have a negligible effect on the capillary rise because of the relatively large diameter of the beaker. Thus, the use of innovative geometries should also be explored as a means to overcome the negative effects of contact angle hysteresis.

Conclusions

A coating of photoresponsive spiropyran molecules covalently bound to a glass surface along with a mixture of silanes exhibited reversible wettability changes when irradiated with UV and VIS light. The magnitude of the contact angle changes achieved using light was found to be 11°−14° using water of pH = 5.5. The presence of the TBDS in the coating was essential to allow a larger fraction of the molecules to convert between the open and closed forms, possibly by preventing close packing of spiropyran molecules on the surface and/or by affecting surface hydrophobicity. The light-induced changes observed in the surface energy were correlated to the switching of the surface-bound spiropyran molecule between polar and nonpolar forms by means of fluorescence spectroscopy. The fluorescence spectra and photochromic conversion of the spiropyran on the surface in contact with water resembled those of spiropyran in aqueous solution. Water in capillary tubes coated with the photosensitive layer was observed to rise when the light source was switched from VIS to UV. For a 500 μm capillary, the rise due to UV irradiation was 2.8 mm greater than the rise under VIS irradiation. Contact angle hysteresis in the system was found to prevent the water from moving down the capillary when the light was switched from UV back to VIS.

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