SANDIA REPORT

SAND2006-7632
Unlimited Release
Printed January 2007

Nanostructured Surfaces for Microfluidics and Sensing Applications

Nelson S. Bell, Dongqing Yang, Marcin Piech, Devens Gust, Sean Vail, Antonio Garcia, John Schneider, Mark A. Hayes, and S.T. Picraux

Sandia National Laboratories

Nanostructured Surfaces for Microfluidics and

Sensing Applications

Nelson S. Bell,[⊕] Dongqing Yang,[†] Marcin Piech,[⊗] Devens Gust,[§] Sean Vail,[§] Antonio A.

Garcia,[⊥] John Schneider,[⊥] Mark A. Hayes,[§] S.T. Picraux,[†,*]

Electronic and Nanostructured Materials
Sandia National Laboratories
P.O. Box 5800-1411
Albuquerque, NM 87185

Abstract

The present work demonstrates the use of light to move liquids on a photoresponsive monolayer, providing a new method for delivering analyses in lab-on-chip environments for microfluidic systems. The light-driven motion of liquids was achieved on photoresponsive azobenzene modified surfaces. The surface energy components of azobenzene modified surfaces were calculated by Van Oss theory. The motion of the liquid was achieved by generation of a surface tension gradient by isomerization of azobenzene monolayers using UV and Visible light, thereby establishing a surface energy heterogeneity on the edge of the droplet. Contact angle measurements of various solvents were used to demonstrate the requirement for fluid motion.

---

[*] To whom correspondence should be addressed. E-mail: picraux@lanl.gov.
[⊕] Sandia National Laboratories, Albuquerque, New Mexico, 87185
[†] Department of Chemical and Materials Engineering, Arizona State University, 85287
[⊗] United Technologies Corporation, CT, 06424.
[§] Department of Chemistry and Biochemistry, Arizona State University, 85287
[·] Harrington Department of Bioengineering, Arizona State University, 85287
[*] Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545

This page intentionally left blank

Table of Contents

Table of Figures

Table of Tables

Introduction

Microfluidic systems are of interest for a variety of potential applications, such as delivering samples in lab-on-chip environments, bio-assays in drug discovery, and chemical analyses where reducing sample size produces decreases in assay time and minimization of reagent volume. The processing of increasingly smaller volumes of liquids creates a challenge for transporting, storeing, mixing, reacting or analyzing unit liquids in these miniaturized analytical systems. However, the physics of scaling does not permit a simple miniaturization of macroscopic pumps for liquid transport due to the increasing importance of interfacial forces relative to volume. Alternative methods to control droplet motion are attractive. Over the past several years, many researchers have worked on various methods to change interfacial properties of materials to induce or control surface wetting of liquids including thermal, chemical, electric and optical potentials and by control of surface morphology. The use of light as a driving force offers unique opportunities such as remote access and lithographic control of surface properties sans lift off template methods. A solid surface modified with photochromic azobenzene derivatives is a promising route to control surface free energy with light. In this paper, we describe an optical approach to liquid transport based on photo-induced wetting/dewetting of azobenzene modified surfaces.

Azobenzene is a well-known photochromic organic molecule, which can be switched from trans to cis by UV/Visible irradiation. A solid surface modified with photochromic azobenzene was able to control the surface free energy with light, because the conformational change of azobenzene results in a change in the molecular dipole moment. The reversible switching behavior of azobenzene upon exposure to visible light or heat allows for the optical control of surface wetting properties, and thereby control over fluid motion.

In this study, an azobenzene molecule was covalently bound to a Si surface through aminopropylmethyldiethoxysilane. Fluid transport of a droplet was achieved by creating a gradient in surface tension using controlled exposure of UV/visible light, thereby inducing isomerization of the azobenzene monlayer.

Experimental Section

Synthesis

Synthesis of the azobenzene-acid chloride compound is described in Figure 1.
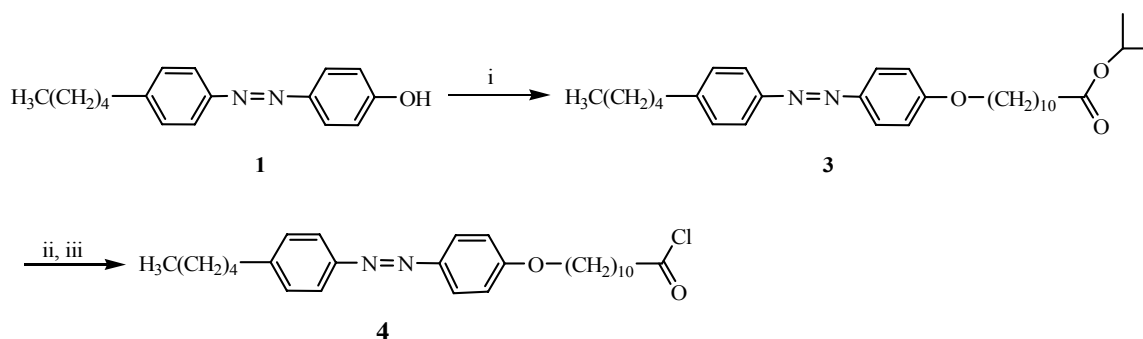
Figure 1. Synthetic route of azobenzene - acid chloride.

Synthesis of 4-[4'-(Pentylphenyl)azo]phenol (**1**). This compound was prepared according to the procedure previously described. 4-Pentyl aniline (20.2 g, 124 mmol) was dissolved in a mixture of concentrated hydrochloric acid (30 mL) and distilled water (40 mL). Sodium nitrite (8.6 g, 125 mmol) in distilled water (25 mL) was added dropwise to the above solution at 0°C. The resulting solution of diazonium salt was added slowly to a cooled mixture of phenol (1 1.6 g, 123 mmol) and sodium carbonate (21.4 g, 258 mmol) in distilled water (75 mL) at 0°C. Pure 1 was obtained in nearly 100% yield.

Synthesis of isopropyl 11-bromoundecanoate **(2)**. 11-bromoundecanoic acid (25g, 94mmol) was reacted with oxalyl chloride (18g, 141mmol) in dichloroethane (150mL) at 70°C for 30 min under N_2. Dichloroethane and residual oxalyl chloride were removed under reduced pressure. Dichloromethane (90mL), triethylamine (10.1g, 100mmol), and a catalytic amount of N,N-dimethylaminopyridine (DMAP) were added to the reaction. Anhydrous isopropanol (11.3g, 190mmol) was subsequently added to the mixture at 5°C. The reaction was warmed to room temperature and allowed to react for an additional 30 min. The reaction mixture was extracted with 5-10% wt/wt HCl solution and the solvent removed under reduced pressure. Compound 2 was isolated in near 100% yield.

Synthesis of azo-ester **(3).** 4-[4'-(Pentylphenyl)azo]phenol was reacted with isopropyl 1l-bromoundecanoate in the presence of anhydrous potassium carbonate and a catalytic amount of dicylcohexano-18-crown-6 in dimethylformamide (100ml).

Synthesis of azo-acid chloride **(4).** Compound 3 was hydrolyzed using potassium hydroxide in tetrahydrofuran (THF) at reflux. The solution was cooled to 0°C and acidified (pH ~ 2) with 6 M sulfuric acid. The precipitate was filtered, dried and reacted with oxalyl chloride to afford compound 4, which was stored in the dark under nitrogen.

Materials

Silicon (100) n type wafers with an air oxide layer surface were obtained from WaferNet Inc. 3-aminopropylmethyl-Diethoxysilane (ADES) was obtained from Gelest Inc. Toluene was obtained from Mallinckrodt Baker, Inc., and double distilled prior to use. Deionized (DI) water used for contact angle measurement was obtained from a Barnstead nanopure system. All other reagents were purchased from either Aldrich or Alfa Aesar and used as received.

Substrate Functionalization

Si (100) n type substrate (1.5cm×3cm) were cut to rectangular shapes of about 1.5 cm x 3 cm using a diamond-tipped cutter from the original 4 inch circular discs with an air oxide layer surface. Each was cleaned by UV ozone cleaner (UV Ozone cleaner Model 42, obtained from Jelight company Inc.) for 30 min, rinsed extensively with DI water to remove extra charge on the surface, and dried in an oven at 140 °C for 15 min. After cleaning, the substrate was immersed in a solution of 100ul ADES in 10ml double distilled toluene for 30 min at room temperature, then washed well in toluene for 3 times to remove excess reagent, and heated in an oven at 140 °C for 3 hours. The silane-coated substrate was incubated in a toluene solution of azobenzene compound (20mM) in the presence of 4-Dimethylaminopyridine (200mM) for 8 hours in an oven at 80 °C. The substrate was then removed from solution, washed sequentially with toluene, methylene chloride and tetrahydrofuran for 5 min and dried by nitrogen gas. Azobenzene is tethered to SiO_2 surfaces through ADES as linker molecules, shown in Figure 2.

Optical measurements

UV-Visible spectra of azobenzene were recorded on UV-Vis NIR scanning spectrophotometer in order to correlate the observation of contact angle changes on azobenzene modified surface. Because the surface concentration of the azobenzene modified surface is lower than the limit of the absorption spectrophotometer, the absorption of azobenzene acid solutions was used to measure the UV-Visible spectrum. Azobenzene acid was prepared from azobenzene acyl chloride compound. The azobenzene acid toluene solution was illuminated with either UV or
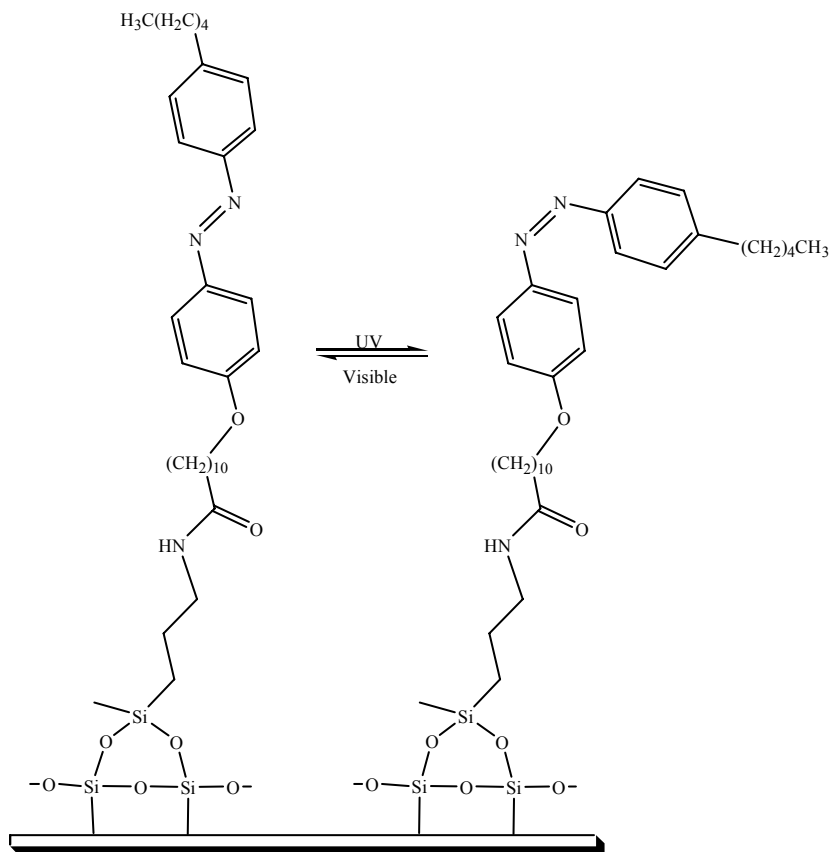
Figure 2. Molecular structure of azobenzene surface

visible light for 5min in order to confirm that azobenzene was switching from trans to cis. The spectrum is shown in Figure 3. The AZOCOOH exhibited its absorption maxima at about 352nm and a weak peak at 440nm, which are related to the π - π^* and n - π^* transitions respectively. After UV light illumination, the trans to cis photoisomerization of AZOCOOH occurs as indicated by a distinctive decrease of π - π^* absorption at 352nm and increase in the n - π^* transition at 440nm. In contrast, the visible light irradiation causes the π - π^* transition to increase and the n - π^* transition to decrease.
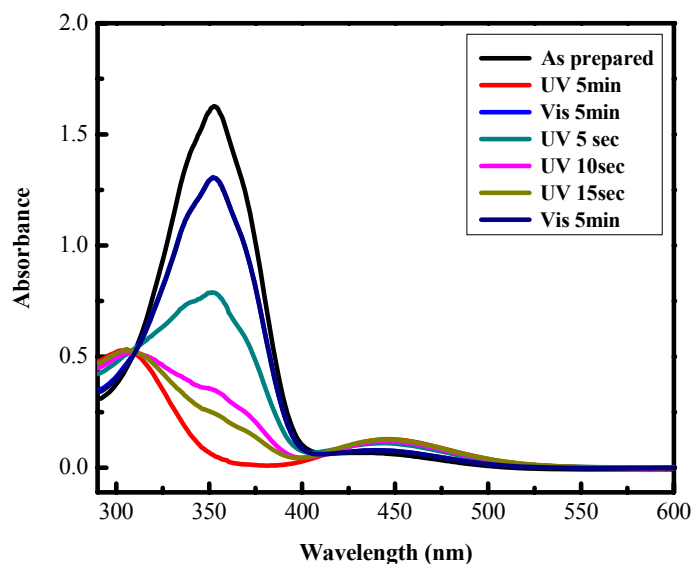
Figure 3. UV-Visible spectral change of the AZOCOOH solution in Toluene under UV and Visible illumination

Contact angle measurements

The contact angle measurement method is shown in Figure 4. The contact angle measurements were performed using a Ramé-Hart Standard Automated goniometer, Model 200-00. This equipment included the DROP image Standard software that uses a curve fitting routine for contact angle calculations. The dynamic advancing and receding contact angles were measured by increasing and decreasing the volume of liquid in the drop with the dispensing needle embedded in the sessile drop. We increase the volume of liquid from t_0 to t_2, and decrease the volume of liquids from t_2 to t_4. An advancing contact angle is measured by averaging the largest possible angles while increasing the liquid volume from t_1 to t_2; A receding angle is measured by averaging the smallest possible contact angle as liquid is removed from the drop from t_3 to t_4.
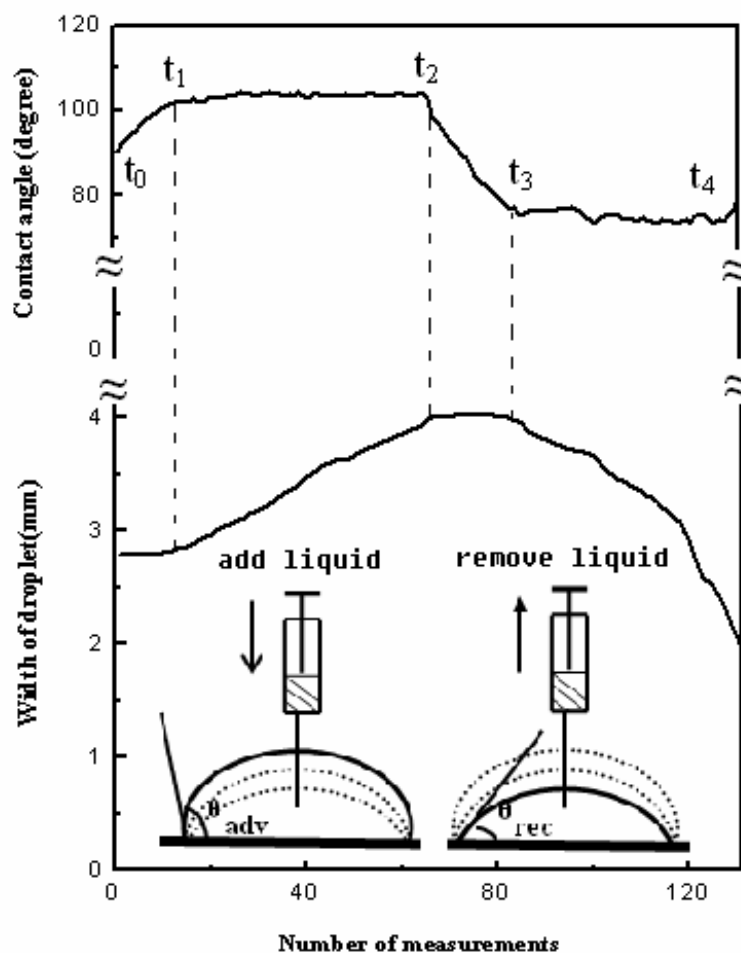
Figure 4. Dynamic advancing and receding contact angle measurement method

Photo irradiation

The UV light source was a Model UVGL-25 Mineralight Lamp with 254/365nm wavelength, 115V, and 60Hz. We use 365nm wavelength for UV irradiation. The visible light source was a Model LS 87/110 lamp with 50W Lite source from Fiberoptic Specialties, Sarasota, Fl. We use a UV filter to block the wavelengths smaller than 520nm.

Solvents

All probe solvents for contact angle measurements were obtained from Alfa Aesar. Diiodomethane, 1-bromonaphthalene, 1-methylnaphthalene, dimethylformamide, acetonitrile, benzontirile, formamide and ethylene glycol were used in this study as received.

Results and Discussion

Wettability of Azobenzene Surface

Figure 5 shows reversible wettability transition under visible and UV irradiation. The advancing contact angle in water changes from 100º-102º under visible light to 88º - 89º under UV light. The difference in advancing contact angle or the switching angle was around 11-12 degrees. The trans has a small dipole moment and a low surface free energy, therefore it exhibits a higher contact angle. The cis conformation possesses a higher dipole moment and surface free energy, and thereby exhibits a lower water contact angle. The switching angle of this azobenzene surface was larger than other reports. Oh et al. use an O-octacarboxymethylated calyx resorcinarene with pendent p-octylazobenzene units as a photo-responsive adsorbate (H-CRA-CM).[8] The switching angle is 8 degrees on H-CRA-CM-modified surface by UV/Visible illumination. Siewierski et al. prepared monolayer assemblies on silicate substrata by the direct deposition of alkyltriethoxysilanes and covalent attachement of azobenzene derivatives to functionalized SAMs.[6] The switching angle varied from 4 to 9 degrees in these films.
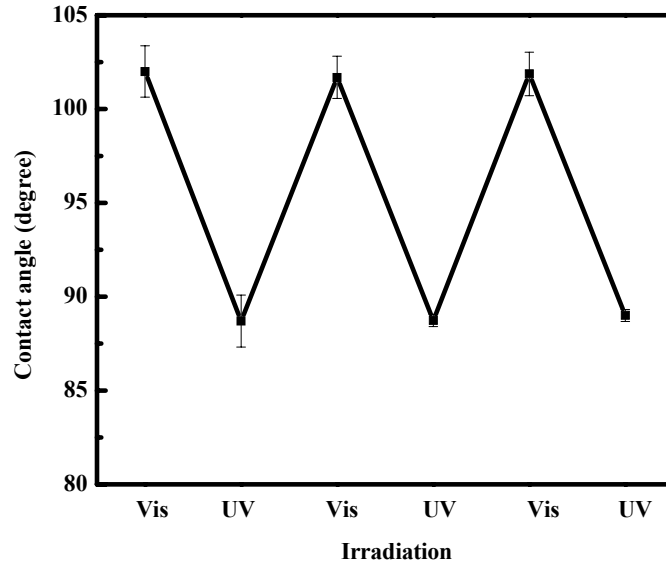
(a) Reversible water advancing contact angle under UV/visible illuminations

(b) Advancing contact angle under visible light **(c)** Advancing contact angle under UV light

Figure 5. Reversible advancing contact angle changes on azobenzene modified Si surface by UV and visible irradiations

Contact Angle Measurements with Different Solvents

To evaluate liquid-solid interactions, we measured the advancing (θ_{adv}) and receding (θ_{rec}) contact angles for various liquids on the azobenzene-modified surface both before and after UV irradiation. The solvents include diiodomethane, 1-bromonaphthalene, 1-methylnaphthalene, dimethylformamide, acetonitrile, benzonitrile, formamide, and ethylene glycol. We prepared 2-3

samples for each solvent and measured 5 points for each sample. Table 1 shows the contact angle results on the azobenzene surfaces using various solvents.

Table 1. Contact angle (degree) on azobenzene surface with various solvents

Solvents	Switching Angle	Surface Tension	Trans		cis	
			θ_{adv}	θ_{rec}	θ_{adv}	θ_{rec}
benzonitrile	15	38.65	32.0 ± 2.0	26.2 ± 1.25	17.0 ± 0.76	--
acetonitrile	15.5	27	27.0 ± 0.55	19.4 ± 1.41	11.5 ± 0.87	--
DI water	11	72.8	101	75	88.5	67
formamide	10.7	58.2	82.2 ± 1.36	62.8 ± 1.18	71.5 ± 0.66	58.2 ± 1.01
ethylene glycol	9.3	48	73.2 ± 0.73	49.0 ± 1.15	63.9 ± 0.71	41.5 ± 0.49
diiodomethane	12	50.8	54.1 ± 0.49	43.7 ± 0.58	42.1 ± 1.08	33.1 ± 1.28
dimethylformamide	10.7	36.8	37.5 ± 1.74	29.6 ± 1.47	26.8 ± 0.53	19 ± 1.34
1-methylnaphthalene	10	40.5	33.3 ± 1.09	23.5 ± 0.77	23.3 ± 0.34	13.5 ± 0.56
1-bromonaphthalene	8.3	44.4	38.0 ± 0.67	33.5 ± 0.5	29.7 ± 0.40	24.6 ± 0.51

If a drop is placed on a solid surface, there will certainly be some interaction between the fluid and the solid substrate upon which it rests, even if this is due only to van der Waals forces. Some type of surface interaction, such as adsorption or ionization of surface groups is likely in many cases. The interaction between solvents and a solid surface with photo-switching molecules can arise from different reasons. The photo-conversion mechanism of azobenzene is conformational change from trans to cis across the -N=N- bond. This geometrical change leads to in a change in the molecular dipole moment based on the orientation of the lone electron pairs of each nitrogen atom. Most solvents exhibit the same magnitude of the switching angle, which correlates to the conversion mechanism of azobenzene.

However, benzonitrile and acetonitrile have larger switching angles than DI water. Benzonitrile and acetonitrile are chemically similar, and they have a relatively large dipole moment and dielectric constant. Their basic character might play a role in neutralizing carbonium (HCO_3, H_2CO_3) species from dissolved CO_2 molecules, or acidic conditions may

hinder the azobenzene cis-trans isomerization due to attachment of an H$^+$ ion to one or both of the azobenzene nitrogen. Another explanation is that acetonitrile is a small, highly polar molecule also having an organic group, and compared to water it might be able to solvate azobenzene to a better extent than water while at the same time offering stabilization of the cis form due to dipole-dipole interactions. A definitive study of this phenomenon was beyond the scope of this investigation.

Surface Energy of Azobenzene Containing Surface Films

The contact angle on the azobenzene modified surfaces increases with an approximately linear relationship to the surface tension of the probe liquids, shown in Figure 6. The form of this
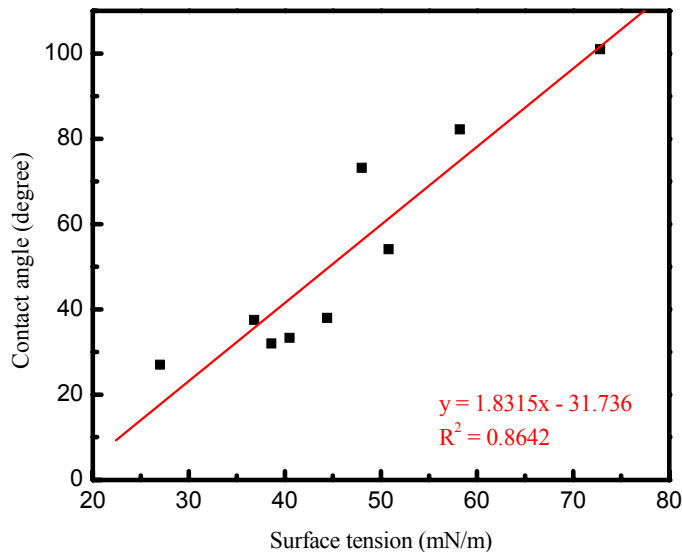

Figure 6. Contact angle on azobenzene surface as a function of surface tension of probe liquids

relationship suggests that the azobenzene surface properties can be modeled using probe liquids to gain a reliable estimate of the surface energetics of the azobenzene interface with fluids.

Parameters describing the wetting parameters of these films have value for predicting fluid transfer, which will explored later in the report.

Van Oss Theory

The surface free energy determined from the wetting properties of the surface is an important surface parameter and plays a very important role in various physicochemical processes occurring at interfaces. The Lifshitz – van der Waals/acid-base (LWAB) approach to determine solid surface free energy proposed by Van Oss and colleagues presents a very useful method for surface free energy calculation. Accordingly, the surface free energy can be expressed by eq.1.

$$\gamma_S^{TOT} = \gamma_S^{LW} + \gamma_S^{AB} \tag{1}$$

$$\gamma_S^{AB} = 2\sqrt{\gamma_S^- \gamma_S^+} \tag{2}$$

where the superscript LW is the apolar Lifshitz-van der Waals, AB is the polar electron-donor/electron-acceptor (or Lewis acid-base) components of the energy, and + and - denote the electron-acceptor and electron-donor parameters of the surface energy, respectively. Using this approach, the work of adhesion W_A for a liquid/solid system can be expressed as,

$$W_A = \gamma_L(1 + \cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^- \gamma_L^+} + \sqrt{\gamma_S^+ \gamma_L^-}) \tag{3}$$

where subscripts s and L denote solid and liquid.

Eq. 3 (called the van Oss-Chaudhury–Good equation) provides a simple way to predict a solid surface free energy using contact angle measurement with three probe liquids, two of which have to be polar and one of which is apolar. By using three different liquids on the solid to measure contact angle, then solving three simultaneous equations, we can predict the three unknown solid parameters.

Total surface tension γ_s^{TOT} for azobenzene surface was calculated by Eq. 3. The components of surface tension were determined from advancing contact angles of the following probe liquids: water, ethylene glycol and formamide as polar-containing liquids, and diiodomethane and 1-bromonaphthalene as nonpolar liquids. Table 2 is the surface tension and components of each probe liquid. The total surface tension for a particular solid was expected to depend on the combination of three probe liquids, as well as the kind of the liquids used. Here four different combination of three liquids were used to decrease experimental error, and the surface tension agrees well between the fluid combinations, as shown in Table 3 and Figure 7. The total surface tension under UV light is around 38 mJ/m^2, and is higher than the value of 34 mJ/m^2 measured under visible light. The dispersive and base component increase after the exposure of UV light, because the nitrogen atom lone electron orbital pairs change orientation to increase the molecular dipole moment.

Table 2. Surface tensions and components of probe liquids (mJ/m^2)

Liquid	γ_L^{tot}	γ_L^{LW}	γ_L^-	γ_L^+	γ_L^{AB}
Polar					
DI water	72.8	21.8	25.5	25.5	51.0
ethylene glycol	48.0	29.0	47.0	1.92	19.0
formamide	58.0	39.0	39.6	2.28	19.0
Nonpolar					
diiodomethane	50.8	50.8	--	≈ 0	≈ 0
1-bromonaphthalene	44.4	44.4	0	0	0

Table 3. Calculated solid surface tension components (mJ/m^2) for Si surface with azobenzene based on Van Oss theory.

Calculations	Illumination	γ_L^{LW}	$\gamma_L^{+\,2}$	γ_L^-	γ_L^-
a)	Visible light	32.6	-0.1	0.4	32.6
	UV light	38.6	-0.2	3.2	38.6
b)	Visible light	32.0	-0.70	2.0	32.0
	UV light	38.6	-0.6	4.6	38.6
c)	Visible light	35.5	-0.3	0.4	35.5
	UV light	38.8	-0.2	3.2	38.8
d)	Visible light	35.5	-1.0	2.1	35.5
	UV light	38.8	-0.57	4.58	38.8

a) Using DI water, ethylene glycol, diiodomethane b) Using DI water, formamide, diiodomethane c) Using DI water, ethylene glycol, 1-Bromonaphthalene d) Using DI water, formamide, 1-Bromonaphthalene to calculate
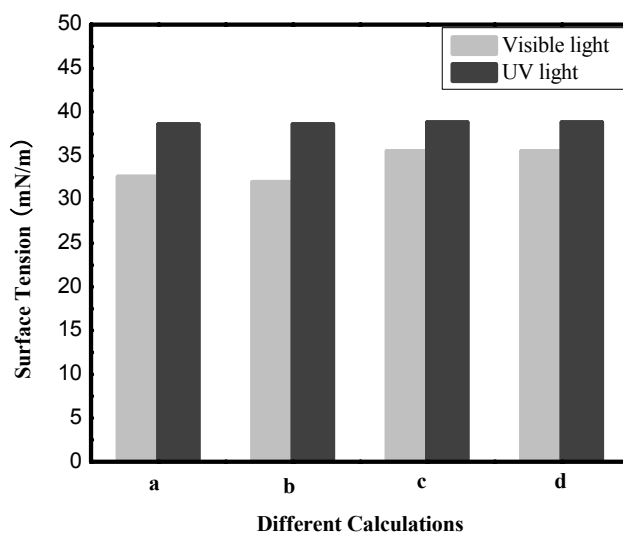

Figure 7. Total surface tension of azobenzene modified surface calculated from LWAB a) Using DI water, ethylene glycol, diiodomethane b) Using DI water, formamide, diiodomethane c) Using DI water, ethylene glycol, 1-Bromonaphthalene d) Using DI water, formamide, 1-Bromonaphtalene.

Light-driven movement of solvents

Figure 8 represents a cross section of a water drop placed on a surface that has a spatial gradient in the surface free energy by UV/visible light. The unbalanced Young's force is given by:

$$dF_Y = [(\gamma_{SV} - \gamma_{SL})_A \quad (\gamma_{SV} - \gamma_{SL})_B]dx \tag{4}$$

Here, γ_{SV} and γ_{SL} are the surface free energies of the solid-vapor and solid-liquid interfaces and dx is the thickness of the section of the drop. If θ_{vis} and θ_{UV} represent the local contact angles at points A and B, then, Eq. 4 can be represented as

$$dF_Y = \gamma_{LV}(\cos\theta_A - \cos\theta_B)dx \tag{5}$$

Visible light
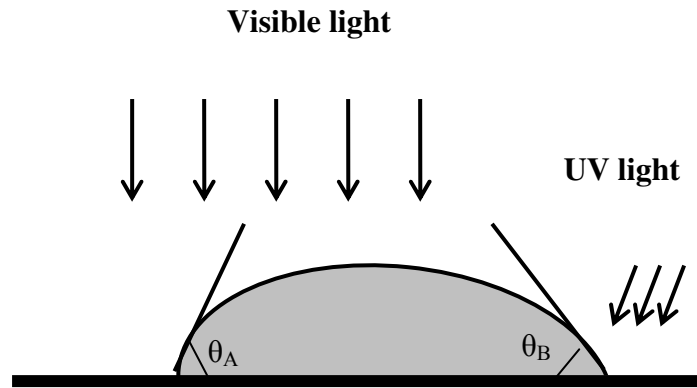
UV light

θ_A   θ_B

Figure 8. Lateral photographs of light-driven motion of liquids on Si substrate with azobenzene

The surface free energy of the liquid-vapor interface is γ_{SL}. The net force (F_Y) experienced by the drop can be obtained by integrating Eq. 5 over the entire width of the drop. If the contact angle at point A is smaller than that at point B, the drop will move in the direction of higher γ_{SV}. This motion has two effects: it decreases the area of the vapor-solid interface having the larger interfacial free energy while increasing that having lower free energy, and it increase the total area of solid-liquid interface. Both changes in free energy, effected over a distance, constitute a

force driving to move the drop. For a surface that exhibits high hysteresis in contact angles however, the receding contact angle at point B may become smaller than the advancing contact angle at point A. Under this condition the drop will not move, the presence of a gradient in surface tension is not by itself sufficient to ensure motion of liquid drops - the surface must also have low hysteresis in contact angles and be free of defects that pin the edge of the drop.

The motion of a droplet can be directed by light if the liquid drop fulfills the following requirement: the receding contact angle (trans-isomer θ_{rec}^{trans}) under visible light must be larger than the advancing contact angle (cis-isomer θ_{adv}^{cis}) under UV light. That is, light induced contact angle changes should be greater than contact angle hysteresis ($\Delta\theta = \theta_{adv} - \theta_{rec}$). By spatially controlling the UV/visible irradiation, the liquid droplet moves toward UV light direction. The driving force arises from a surface tension gradient (contact angle changes). Figure 8 shows the model of optically-directed flow of liquids on surfaces.

To find the solvents that can be moved, we measured advancing and receding contact angles on the azobenzene modified surface before and after UV light irradiation, shown in Table 4. Based on theoretical predictions, 1-Bromonaphthalene has a θ_{rec}^{trans} of 33.5º which is greater than the θ_{adv}^{cis} 29.7º and thus fulfills the motion requirement, as shown in Figure 9 (a). To investigate the light-guided movement of a droplet of 1-Bromonaphthalene, we placed the droplet on the photoresponsive azobenzene modified surface, and focused UV light on one edge of the droplet to generate a gradient in the surface photosiomerization. After 1 minute UV light irradiation, the front edge of droplet contact angle decreased and spread toward the UV light, but the back edge of the droplet remains stationary for 90 seconds, after which transport of the entire droplet occurred, as shown in Figure 10. Video observations also demonstrated the light-induced motion of droplet on the smooth substrate.

However, no motion of droplets on the surface-modified plate was generated by the photoirradiation for some liquids, although their contact angle altered after illumination with visible and UV light. Water, formamide, and ethylene glycol could not be moved using the same irradiation on the azobenzene modified surface. Figure 9(b) is the contact angle of formamide. θ_{rec}^{trans} is around 62.8° is much lower than θ_{adv}^{cis} 71.5°, and the drops can not be moved.
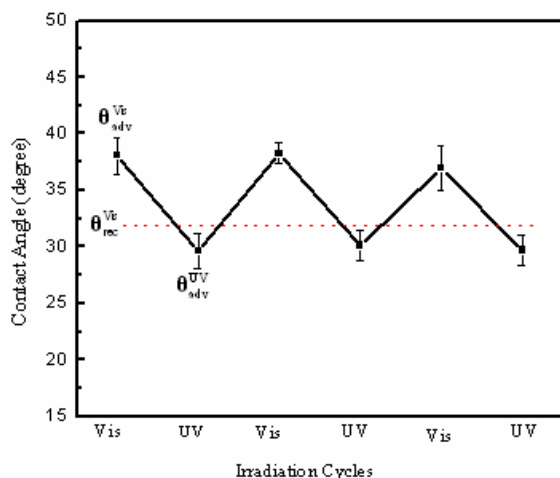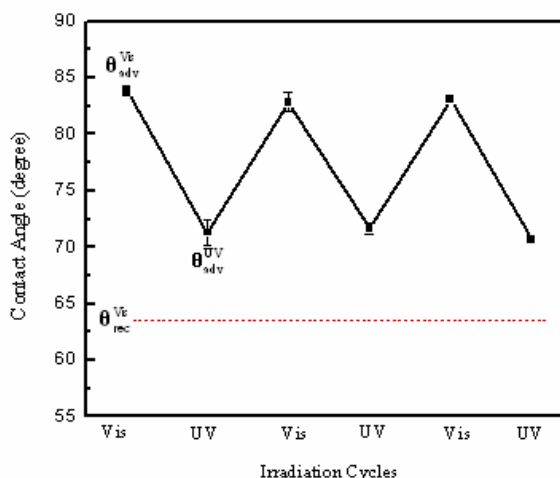
(a) 1-Bromonaphthalene   **(b)** Formamide

Figure 9. Contact angles of solvents on azobenzene modified surface under UV/Visible illumination. (the highlight of this picture was to illustrate the very low hysteresis surface that ensured that the force of the gradient alone was sufficient to move the droplet)

Table 4. Contact angle measurements on azobenzene surface with various solvents

Liquid	trans		cis	
	θ_{adv}(degree)	θ_{rec}(degree)	θ_{adv}(degree)	θ_{rec}(degree)

| **Fulfill motion requirement**				
Benzonitrile	32.0±2.0	26.2±1.25	17.0±0.76	--
Diiodomethane	54.1±0.49	43.7±0.58	42.1±1.08	33.1±1.28
Dimethylformamide	37.5±1.74	29.6±1.47	26.8±0.53	19±1.34
1-Bromonaphthalene	38.0±0.67	33.5±0.5	29.7±0.40	24.6±0.51
Acetonitrile	27.0±0.55	19.4±1.41	11.5±0.87	--
1-Methylnaphthalene	33.3±1.09	23.5±0.77	23.3±0.34	13.5±0.56
Not fulfill motion requirement				
DI water	101	75	88.5	67
Formamide	82.2±1.36	62.8±1.18	71.5±0.66	58.2±1.01
Ethylene glycol	73.2±0.73	49.0±1.15	63.9±0.71	41.5±0.49
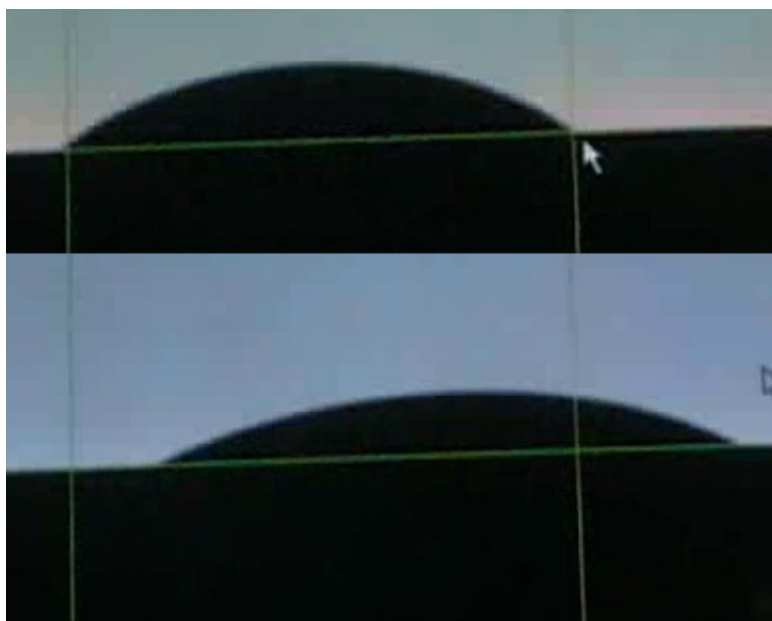
Figure 10. Lateral photographs of light-driven transport of 1-Bromonaphthalene on the Azobenzene surface a) before UV irradiation, b) after UV irradiation

Conclusions

The present work demonstrates the use of light to move liquids on a photoresponsive monolayer, and provides a new method for delivering analyses in lab-on-chip environments for microfluidic systems. A novel surface modification synthetic approach was developed to functionalize substrates with a reversible, photo-switching azobenzene derivative, which exhibited large variation in wetting angle based on UV or visible light exposure. The surface tension of these azobenzene modified surfaces was characterized by Van Oss theory. The factors controlling optically-directed motion of liquids was related to contact angle parameters of the films. Liquid motion was achieved by development of an optical profile which induced a surface energy heterogeneity on the edge of the droplet.

Acknowledgement

References

1. D.Y. Kwok, *Colloids and Surfaces A*, 1999,156, 191-200.

2. H. Radelczuk, L. Holysz, *J. Adhesion Sci. Technol.*, 2002,16,1547-158.

3. D.Y. Kwok, D.Li, A. Neumann, *Langmuir*, 1994, 10, 1323-1328.

4. P.K. Sharma, K. Hanumantha Rao, *Advances in Colloid and Interface Science*, 2002, 98, 341-463.

5. C.J. Van Oss, <u>Interfacial Forces in Aqueous Media</u>, Marcel Dekker, Inc., New York, 1994.

6. L.M. Siewierski, W.J. Brittain, S. Petrash, M.D. Foster, *Langmuir*, 1996, 12, 5838-5844.

7. Wuhui Jiang, Guojie Wang, Yaning He, etc., *Chem. Commun.*, 2005, 3550-3552.

8. S.Oh, M. nakagawa, K.Ichimura, *J. Mater. Chem.*, 2002, 12, 2262-2269.

9. K.Ichimura, S. Oh, M. Nakagawa, *Science*, 2000, 288, 1624-1626.

10. G. Michael, *Science*, 1999, 283, 41-42.

11. R.Rosario, D.Gust, M.Hayes, etc., *Langmuir*, 2002, 18, 8026-8069.

12. C. Feng, Y.Zhang, J.Jin, etc., *Langmuir*, 2001, 17, 4593-4597.

13. T.Vilkner, D.Janasek, A.Manz, *Anal. Chem*. 2004, 76, 3373-3386.

14. R. Rosario, D. Gust, A. Garcia, Mark Hayes, J. L. Taraci, T. Clement, J. W. Dailey, and S. T. Picraux , *J. Phys. Chem. B*, 34 (2004) 12640-12642.

15. J. Berna, D.Leigh, M. Lubomska, etc., *Nature Materials*, 4, 2005, 704-710.

16. Y. Liu, L. Mu, B. Liu, etc., *Chem. Eur. J*. 2005, 11, 2622-2631.

17. M.Chaudhury, G. Whitesides, *Science*, 1992, 256, 1539-1541.

18. L. M. Siewierski, L. M. Lander, A. Leibmann, W. J. Brittain and M. D. Foster, *SPIE Proceedings*, 1005, 2441-2451.

Distribution List

1	MS 1315	S. Tom Picraux, 1131
1	MS 1411	Nelson Bell, 1816
1	MS 1411	James A. Voigt, 1816
2	MS 9018	Central Technical Files, 8944
2	MS 0899	Technical Library, 4536