

Formation of Azobenzene-Containing Self-Assembled Monolayers and Alkyl Chain Length Dependence of the Photoreactivity

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Azobenzene-containing self-assembled monolayers were prepared on gold-deposited substrates from unsymmetrical disulfides with an alkyl group of different lengths and an azobenzene moiety. The photoresponse was detected by contact angle measurement and observation of surface-induced liquid crystal (LC) alignment. The SAMs of 4-[12-(dodecylthio)dodecyloxy]-4'-hexylazobenzene and 4-hexyl-4'-[12-(octadecylthio)dodecyloxy]azobenzene showed decrease in contact angle on irradiation with UV light. Homogeneous alignment of LC was observed only in the nematic LC cell which was fabricated using a SAM of 4-[12-(dodecylthio)dodecyloxy]-4'-hexylazobenzene irradiated with linearly polarized light. The director of the LC layer was in perpendicular to the electric vector of actinic light, indicating that a polarization-selective photoreaction of the azobenzene moiety took place. A SAM of 4-[12-(docosylthio)dodecyloxy]-4'-hexylazobenzene showed no photo-response, presumably due to little free space around azobenzene arising from the presence of long alkyl chains.

Key words: SAM, Gold, Disulfide, LC, Azobenzene.

1 INTRODUCTION

Self-assembled monolayers (SAMs) which consist of thiol or disulfide compounds on gold¹ have been noticed as a simple method of giving a monolayer. We have attempted to make a photoreactive well-ordered molecular layer for an application to high-density photorecording materials by introduction of an azobenzene chromophore into a SAM system. Azobenzene is well known as a photoisomerizable compound which isomerize from *trans*- to *cis*-form and from *cis*- to *trans*-form upon irradiation with ultraviolet (UV) light and visible light respectively. First, 12-[4-(4-hexylphenylazo)phenoxy]dodecanethiol was synthesized, and its monolayer was fabricated on the gold. As a result, we observed well-ordered molecules in the SAM with AFM measurement.² However, less reactivity of azobenzene groups is anticipated because there is no free space in the molecular film arising from their densely packed structure. Wang et al. actually clarified using the electrochemical technique that the azobenzene molecule gave *cis*-form of only 5% or less even after irradiation of such a kind of SAM with UV light.³ A relation between photoreactivity and a molecular occupied area of azobenzenes has been reported on monolayers of azobenzene macrocyclic amphiphiles on a glass substrate and water.^{4,5} The

regulation of a two-dimensional concentration of chromophores is important for formation of a photoreactive surface, because sweep volume is necessary for isomerization of azobenzenes.⁶ Evans et al. used mixed films comprised of alkanethiol and azobenzene alkanethiol in order to prevent the aggregation of azobenzene moieties and to maintain the photoreactivity.⁷ They confirmed the photoisomerization of the azobenzene moieties by observation of spectral change in the sample in which absorption intensity was earned using colloidal gold particles, and by detection of the slight change of the surface plasmon signal of a planar substrate. In this study, we used unsymmetrical disulfides with an alkyl group of different lengths and an azobenzene moiety, instead of azobenzene alkanethiols. We expect generation of a free space around the azobenzene moieties in the SAM required for photoisomerization because a surface concentration of an azobenzene moiety should be diluted with a simple alkyl chain. The absorption measurement cannot be applied to detection of the photochemical reaction on a sample because of weak absorption intensities of the chromophore. The alkyl chain length dependence of photoreactivity was investigated by contact angle measurement and observation of surface-induced liquid crystal (LC) alignment. These two methods of contact

angle measurement and observation of surface-induced liquid crystal alignment become intriguing tools to evaluate the photoreaction at outermost surface,⁸ because they are sensitive to alteration of physical properties of the surface. Here we describe the surface-induced LC alignment control based on the command surface effect;⁹ photoinduced orientational and structural changes of chromophores bound to a surface brought about alignment of LC bulk contacting with the surface.

2 EXPERIMENTAL

2.1 Materials

4-[12-(dodecylthio)dodecyloxy]-4'-hexylazobenzene (C6AzC12SSC12).

0.94 g of 4-(12-bromododecyloxy)-4'-hexylazobenzene was dissolved in 40 ml of DMF, into which an aqueous solution (5 ml) of sodium thiosulfate (0.56 g) was added slowly. The solution was poured to water after stirred for 4 h at 60°C. A precipitation appearing in the solution was filtered out and washed with acetone several times to remove the starting materials. Dodecanethiol (0.40 g) in methanol (6 ml) was mixed with 1 ml of an aqueous solution of sodium hydroxide (0.08 g) and then the mixture was stirred for 1 h at room temperature. A DMF (40 ml) solution of the washed precipitation was added dropwise to the mixture under an Ar atmosphere. After stirred for 6 h, the reaction mixture was poured to water, and the filtered precipitation was purified by silica-gel column-chromatography and by recrystallization from the

mixture of THF and methanol, to give 490 mg of yellow powder (Yield; 26%). Mp; 68.5-69.5 °C. Cal for C₄₂H₇₀N₂O₁S₂: C, 73.84; H, 10.33; N, 4.10; S, 9.39. Found C, 73.80; H, 10.44; N, 4.12; S, 9.37. 4-Hexyl-4'-[12-(octadecylthio)dodecyloxy]azobenzene (C6AzC12SSC18) and 4-[12-(docosylthio)dodecyloxy]-4'-hexylazobenzene (C6AzC12SSC22) were synthesized in a similar manner as mentioned above.

2.2 Sample preparation

Gold deposition. Cleaved mica plates (1x2cm) were set into a chamber in which a pressure was kept at 2.5-3.0 x 10⁻⁷ torr. Gold was evaporated on surfaces of the mica plates whose temperature was controlled at 350°C. After deposition of 1000-1500 Å thickness of gold, the substrates were annealed at 550°C for 2 h to make a gold (111) surface.

SAM preparation. According to the method described in the literature,¹⁰ the prepared gold substrates were exposed to UV/O₃ just before use to remove a contamination from the gold surface and were immersed in ethanol. These plates were put into a 1 mmol/L dichloromethane solution containing each disulfide compound for 12 h. The substrates were immersed into clean dichloromethane for several hours and rinsed twice with dichloromethane to give a SAM

2.3 Physical measurement

Contact angle measurement was carried out on a CA-X contact angle meter of Kyowa Kaimen Kagaku. Photoirradiation was made with ultra-high-pressure mercury arc with color filters, using 365 nm and 436 nm line as UV and visible light, respectively.

2.4 LC cell fabrication

A glass plate was treated with octadecyltriethoxysilane bringing homogeneous LC alignment. An LC cell was fabricated by injecting the LC doped with 1wt % of the dichroic dye between the silane-treated glass plate and a SAM to give a hybrid-type guest-host (GH) LC cell for the determination of an LC director. Spherical glass beads of an 8 μm diameter were suspended in the LC for the adjustment of a cell gap. Cell assembly was carried out at an ambient temperature.

3 RESULTS AND DISCUSSION

3.1 SAM preparation

Bare gold surfaces to be quickly contaminated were observed by a contact angle measurement just after they were cleaned by the ozonization. The cleaned surface showed a contact angle of about 60° for water. Each SAM prepared from solutions of three different disulfides on Au substrates showed contact angles of about 100° for water (Figure 2). Since the disulfide

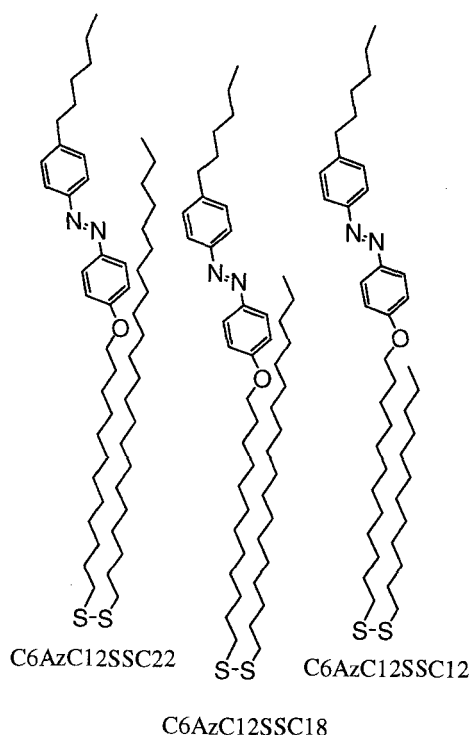


Figure 1 Structures of disulfides

bond tethered to Au surfaces, it is likely that molecular terminals far from the disulfide bond dominate wetting property on the SAM. In all samples, it is anticipated that outermost surfaces are occupied by methyl groups of the hexylazobenzene moiety. Accordingly, the contact angles that we observed here should reflect hydrophobicity arising from terminal groups.

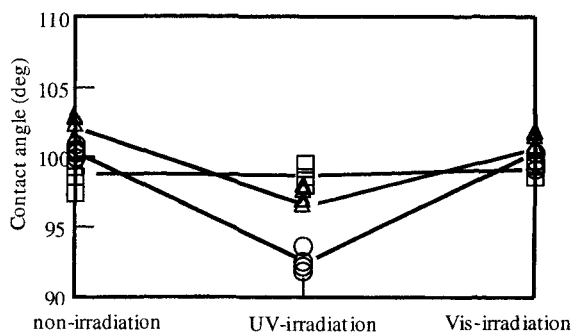


Figure 2 Water contact angles of SAMs formed from C6AzC12SSC12 (○), C6AzC12SSC18 (△) and C6AzC12SSC22 (□), which were irradiated with UV and visible light.

3.2 Photoresponse in contact angle

After each SAM was irradiated with UV light or visible light, contact angles for water on the SAM were measured. Figure 2 shows the contact angles before and after the irradiation. UV irradiation with SAMs of C6AzC12SSC12 and C6AzC12SSC18 resulted in the distinct decrease in contact angles, indicating that some kind of photoreaction can proceed even in the SAMs. On subsequent irradiation with visible light, contact angles recovered, with a slight decrease, when compared with the initial values. This behavior is well consistent with the photoisomerization behavior of azobenzenes on UV and visible irradiation. When azobenzene compounds photochemically change from *cis*- to *trans*-form, some portion of *cis*-isomer usually remains even after sufficient exposure of visible light in the solution. Both *cis*- and *trans*-isomer have an absorption band in the visible region, so that *cis* to *trans* and *trans* to *cis* photoisomerizations occur at same time. In solutions azobenzene absorbed visible light and reached to a photostationary state at a ratio of *trans*:*cis*-isomers = 80-90:20-10%. A contact angle is generally considered to be determined by several parameters such as dispersion force, dipole-dipole interaction, hydrogen-bond interaction and so on. Therefore, the behavior observed here could be explained to be alteration of physical property or orientational change of outermost hexylazobenzene moieties resulting from photoisomerization. For example, dipole moments of model compounds for C6AzC12SSC12 calculated with molecular mechanics followed by MOPAC (AM1)

indicated a clear difference between two isomers. *Trans*-4-butoxy-4'-hexylazobenzene has 1.21 debye due to oxygen atom of the ether bond, and while its *cis*-isomer has 4.92 debye, which is owing to a bend structure.

The unsymmetrical disulfide employed here possesses an azobenzene unit in one side of S-S bond and a linear alkyl unit in another side so that an occupied molecular area of the azobenzene moiety is approximately twice as large as that of the sulfur atoms. It has been reported that the molecular area requisite for isomerization of alkylazobenzene is about 0.45 nm² in a macrocyclic amphiphile system.⁵ Assuming that the sulfur parts of C6AzC12SSC12-22 adsorb on the hollow site of Au (111) which is a stable binding site¹, we can estimate that an average molecular occupied area per azobenzene unit is 0.43 nm², which is adequate for photoisomerization of hexylazobenzene moieties. If the length of alkyl unit is sufficient short when compared with that of a substituent involving the azobenzene moiety, a free space for isomerization might be generated around azobenzene moiety. As mentioned above, larger changes in contact angles were induced by irradiation of SAMs with UV light with a decrease in length of alkyl chains. Moreover, contact angles of SAMs of C6AzC12SSC22 showed no change on UV irradiation. The facts clearly indicate that there was a free volume around the azobenzene moieties in the C6AzC12SSC12 SAM. C6AzC12SSC22 has a docosyl group of enough length to be full with a free space around the azobenzene. To confirm this consideration, a SAM of C6AzC12SSC12 was annealed at 80°C and photoreactivity of the azobenzene moiety was investigated. Ishida et al. reported that the heat induced phase separation of hydrocarbon-fluorocarbon SAM formed from unsymmetrical disulfide on Au.¹¹ According to their paper, after annealing the SAM, domains with a size of 20-200 nm in diameter was observed by a friction force microscopy. From the friction force, they concluded each circular domain consisted of fluorocarbon parts. In our sample, the heat

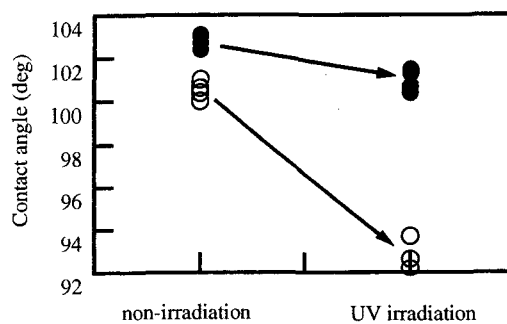


Figure 3 Contact angles of SAMs of C6AzC12SSC12 before (○) and after annealing (●).

treatment at 100°C for 15 h brought about the lowering of the photoresponse, as shown in Figure 3. Therefore, annealed sample has insufficient free spaces for photoreaction in the SAM, due to the formation of domain structure after annealing.

3.3 Liquid crystal alignment

The results on the experiment to investigate the orientation of nematic liquid crystal were summarized at Table 1. In a SAM of C6AzC12SSC12, the liquid crystal orientation induced by a film surface before irradiation was the random and parallel orientation. The film, which was irradiated with polarized UV light, showed the uniform uniaxial orientation of liquid crystal molecules. There is the correlation between orientations of the surface azobenzene and LC molecules.¹² The nematic director of the observed LC alignment was perpendicular to the electric vector of actinic polarized light. Therefore, the anisotropic photo-orientation of LC indicates that photoreaction of the surface azobenzene is selective for the polarization of the actinic polarized light. The liquid crystal showed vertical orientation regardless of optical illumination to the SAM of C6AzC12SSC22 and C6AzC12SSC18. At the present study, it is still unclear whether the azobenzene hardly act as a command molecule or whether the anisotropy due to axis-selective photoreaction was not transferred to liquid crystal molecules, even if the photoreaction is done.

Table 1 LC alignment

	Non-irradiation	Polarized UV
C6AzC12SSC12	=	Homo.
C6AzC12SSC18	⊥	⊥
C6AzC12SSC22	⊥	⊥

=, random planar alignment; ⊥, homeotropic alignment; Homo, homogenous alignment of LC.

4 CONCLUSIONS

In SAMs formed from azobenzene-containing unsymmetrical disulfides, photoisomerization of azobenzene moieties is achieved by irradiation with light due to the presence of a free space around azobenzene moieties. The extent of optical response is markedly dependent on the length of an alkyl chain, and the largest changes of contact angles for water were observed for the SAM substituted with a shorter alkyl chain.

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