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PAPER

Realization of highly photoresponsive azobenzene-functionalized monolayers†

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We report the successful fabrication of azobenzene-functionalized self-assembled monolayers (SAMs) exhibiting high and reversible photoswitching between *trans* and *cis* states on a flat gold surface. Azobenzene thiols (MeSH and EtSH) containing *meta* and/or *ortho* substituents were chosen based on the occupied area per molecule as well as intermolecular interactions between the azobenzene aromatic rings (formation of H-aggregates). Theoretical predictions of the geometrical structures were performed to clarify the correlation between the molecular structure and photoisomerization characteristics in monolayer systems. The striking difference in absorption spectra of a *trans*-EtSH SAM and a *cis*-EtSH SAM by alternating UV and visible light irradiation was in good agreement with that in their contact angles for water, strongly indicating that the structural changes were controlled by light wavelength. By contrast, despite there being sufficient free space for each MeSH molecule, the strong tendency of the planar azobenzene units to generate H-aggregates even during *cis*-MeSH SAM formation lessened the *trans*-to-*cis* photoisomerization yield in a monolayer.

Introduction

Manipulating the surface properties of organic thin films in response to light wavelengths has attracted a great deal of interest for fundamental research as well as for practical applications.¹ A self-assembled monolayer (SAM) system utilizing the adsorption of sulfur head groups onto metal surfaces is a versatile method for fabricating a supported organic film, since the chemical properties of the topmost surface layer can be adjusted by simply modifying the functional tail group of organic thiols and disulfides.^{2,3}

Photochromic azobenzene molecules undergo *trans*-to-*cis* isomerization upon irradiation with UV light, which can be reversed by either heating or irradiation with visible light.^{4,5} The rod-shaped planar *trans* form is thermodynamically more stable by about 12 kcal mol⁻¹ than the bent-shaped nonplanar *cis* form. The lifetime of the *cis* form is mainly influenced by the molecular structure as well as the surrounding environment (including such factors as solvent properties, temperature, polymer matrix,

packing density of the molecules in the solid state, *etc.*).^{6,7} Understanding the correlations between the molecular structure and *trans/cis* photoisomerization characteristics of azobenzene may open up applications in a wide range of fields, such as molecular motors,⁸ photoswitching,^{9,10} optical data storage,^{11,12} and optoelectronic devices.¹³

Efforts to extend reversible photoisomerization of azobenzene to a flat gold surface have commonly encountered a problematic lack of photoresponsiveness due to the too-dense molecular packing caused by van der Waal interactions between the long alkyl chains and π -stacking interactions between the azobenzene aromatic rings.¹⁴ To promote the *trans*-to-*cis* photoconversion yield in monolayers, several investigations have been performed so far, mainly from the viewpoint of molecular free space.¹⁵ Even though photoresponses of the azobenzene units could be monitored *in real time* by surface plasmon resonance and ellipsometry measurements,^{15b,16} there still remain significant challenges associated with improving the *trans*-to-*cis* photoisomerization yield and controlling the lifetime of the two states without phase separation.¹⁷

In this investigation we have employed EtSH and MeSH azobenzene thiols (Scheme 1) to consider the following three points. First, the respective single-component azobenzene thiols are expected to generate a rather homogeneously distributed monolayer and not a phase-separated system. Second, sufficient free space (more than 0.45 nm² of a critical free space¹⁸) required for photoisomerization can be secured through the introduction of sterically bulky alkyl substituents into the azobenzene unit. Third and most importantly, steric hindrance arising from the bulky alkyl groups at the *ortho* position with respect to the azo group^{19,20} leads to significant distortion from the typical planar

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Scheme 1 (A) Molecular structures and optimized structures (long alkyl chains are omitted for clarity) of EtSH, MeSH, and H-C10. (B) Schematic representation of self-assembled systems prepared from respective *trans*-azobenzene (*trans* SAM[†]) and *cis*-rich azobenzene thiol (*cis* SAM[‡]) solutions and their reversible photoswitching. Unlike *ortho*-alkylated EtSH SAMs exhibiting high and reversible photoisomerization, and despite there being the increased free space between individual MeSH molecules, a strong tendency to aggregate suppressed reversible photoswitching between the *trans*-rich and *cis*-rich states.

trans-azobenzene structure, which would influence π -stacking interactions. Our systematic investigation emphasizes that both free space and suitable regulation of the intermolecular interaction between the planar *trans* azobenzene units are essential prerequisites for creating an azobenzene-functionalized monolayer exhibiting highly efficient photoswitching between the two states.

Results and discussion

Both EtSH and MeSH containing alkyl substituents at the *meta* and/or *ortho* positions with respect to the azo group showed good

solubility in organic solvents such as dichloromethane, acetone and DMF to give transparent solutions before and after UV light irradiation. By comparison, H-C10 lacking the meta and ortho substituents (Scheme 1) showed very poor solubility in common organic solvents. Accordingly, the corresponding alkanethiol could not be isolated pure. NMR data of EtSH, MeSH and H-C10 taken before and after 365 nm light irradiation indicated that more than 95% of the cis form was produced in each photostationary state, irrespective of the type and position of substituent introduced. The half-life times of the cis form of EtSH were found to be 380 h, which was about 30-50 times longer than those of comparable MeSH (13 h) and H-C10 (7 h) (see ESI[†]). Slow thermal cis-to-trans isomerization of orthodiethylated EtSH can be explained by steric hindrance originating from bulky ethyl substituents at the ortho position,19d which restrict large-scale distortion of the azo group during isomerization.

The following two important observations can be made on the basis of the spectroscopic data obtained for MeSH and EtSH (Fig. 1 and Table 1). First, in contrast to H-C10 and MeSH possessing strong π - π * absorption bands with maxima at 373 ($\varepsilon = 41\ 000\ L\ mol^{-1}\ cm^{-1}$) and 368 nm, respectively, *ortho*-alkylated azobenzene (EtSH) underwent a substantial blue-shift in the π - π * absorption band to 354 nm, together with a notice-able reduction of about 30-40% in its molar extinction coefficient (ε). Second, whereas the *trans* forms of H-C10 and MeSH displayed weak featureless n- π * bands at around 450 nm,^{4a,21} the shape and intensity of the n- π * band in the *trans* state of EtSH were quite comparable to that of the corresponding *cis* form (inset of Fig. 1).

These observed spectroscopic features can be interpreted in terms of the steric and electronic effects originating from the introduction of sterically bulky ethyl groups at the *ortho* positions. Our density functional theory (DFT, B3LYP/6-31G(d,p)) calculation²² clearly indicates that *meta*-methylated azobenzene (MeSH) adopted a planar structure in the azobenzene unit²³ with the dihedral angles C–C–N=N and C–N=N–C of 179.61° and 179.99°, respectively (Scheme 1A). However, *ortho*-diethylated EtSH was distorted from the coplanarity of the two benzene



Fig. 1 UV-vis absorption spectra of EtSH, MeSH and H-C10 in dichloromethane. Inset: absorption spectral changes of EtSH upon UV light irradiation.

Table 1 Calculated dipole moments, spectroscopic data, contact angles, and photoconversion yields of EtSH and MeSH

Compound	EtSH		MeSH	
	trans form	<i>cis</i> form	trans form	cis form
dipole moment $(\mu)^a$	0.37	5.42	1.00	5.98
$\lambda_{\rm max}/{\rm nm} (\epsilon/{\rm L} {\rm mol}^{-1} {\rm cm}^{-1})^b$	354 (26 000)		368 (37 000)	_
index ()	trans SAM	cis SAM	trans SAM	cis SAM
area-per-molecule ^c /nm ²	0.55	_	0.50	
λ_{max}/nm	350	352 ± 1	343	347 ± 1
$\Delta A = A_{trans rich} - A_{IIV} (\text{at } \lambda_{max})$	0.0040 ± 0.0005	0.0041 ± 0.0005	0.0044 ± 0.0005	0.0052 ± 0.0005
contact angle/° (as prepared \rightarrow UV)	$94 \rightarrow 90$	$89 \rightarrow 89$	$93 \rightarrow 90$	$93 \rightarrow 90$
photoconversion yield/%	88 ± 5	90 ± 5	51 ± 3	65 ± 5

X-ray crystal structure,^{19c} CPK model, and absorption spectral data.^{9,29}

rings (the C–C–N=N dihedral angle was 159.14°) as a result of the presence of the bulky ethyl substituents at the *ortho* positions,^{19c} which caused the blue-shift in the π – π * band and the remarkable decrease in ε .^{19,24} In addition, the relatively characteristic n– π * band of *trans*-EtSH can also be closely associated with the distortion of the azobenzene unit. Similar spectroscopic data were observed for macrocyclic compounds containing distorted azobenzene units as well.²⁵ That is, the forbidden n– π * transition for the conventional planar *trans* form becomes partially allowed for the distorted *trans* form.^{4a}

To explore the effect of the molecular structure on both the spectroscopic features and reversible photoisomerization by UV–vis absorption spectroscopy in monolayer systems, we prepared the following two types of azobenzene monolayer systems. Polycrystalline gold films with a thickness of 20 nm were immersed into 0.1 mM *trans*-azobenzene (for preparing *trans*-azobenzene SAMs) and *cis*-rich azobenzene (for preparing *cis*-azobenzene SAMs) solutions, respectively, in the dark. In particular, to keep the azobenzene moiety in the *cis* form, UV light was irradiated for 5 min every two hours. UV light irradiation and dark incubation of the azobenzene monolayers was performed under a nitrogen atmosphere to prevent undesirable photoreaction and contamination.

The N1s and S2p X-ray photoelectron spectra of MeSH and EtSH SAMs on gold surfaces are presented in Fig. 2, together with the corresponding fits. The respective spectra of *cis* SAMs were almost the same as those of *trans* SAMs.^{9d,26} A single peak



Fig. 2 N1s and S2p X-ray photoelectron spectra of as-prepared *cis*-EtSH and *cis*-MeSH SAMs, together with the corresponding fits (solid line).

occurring at a binding energy of 399.8 eV in the N1s spectra of both *cis*-SAMs is ascribed to the azo group in the azobenzene unit. Characteristic doublet structures at 163.2 and 162.0 eV (with peak area ratio with 1 : 2) arising from the presence of the S2p1/2 and S2p3/2 peaks, respectively, in the S2p spectrum are attributable to thiolate-type sulfur bound to the metal surfaces. These emission peaks are consistent with those acquired for alkanethiol SAMs,^{27,28} responsible for the chemisorption of the azobenzene thiols to the gold surface without chemical contamination.

While an intense π - π * transition at 350 nm and a second π - π * transition at 250 nm were observed for *trans*-EtSH monolayers, as-prepared cis-EtSH monolayers showed a relatively weak absorption band at 352 \pm 1 nm along with an apparent band at 274 nm (Fig. 3a). Irradiation with UV light brought about a prominent reduction in the π - π * band as well as emergence of an absorption band at 274 nm, which is comparable to the spectral changes in solution (inset of Fig. 1). A comparison of the absorption spectrum of the as-prepared cis SAMs with that of the cis-rich state obtained after UV light irradiation demonstrates that a considerable amount of cisazobenzene was present in the as-prepared *cis*-EtSH SAMs. Under our assumption that the molar extinction coefficients of the trans and cis forms do not significantly change before and after the preparation of SAMs,96,90,29 the estimated content of cisazobenzene was ca. $60 \pm 5\%$ in the as-prepared cis SAMs. The ratio of the cis to trans forms was then increased to roughly 90/10 in the photostationary state of UV light, quite similar to the trans-to-cis photoconversion yield (88 ± 5%) in trans-EtSH SAMs (Table 1).

By contrast, there was spectroscopic similarity between the asprepared *trans*-MeSH and *cis*-MeSH SAMs on the gold surface, as clearly seen in Fig. 3c. Strong $\pi - \pi^*$ absorption bands with maxima at 343 and 347 ± 1 nm observed for *trans*-MeSH and *cis*-MeSH SAMs, respectively, were considerably blue-shifted by 25–20 nm with respect to $\lambda_{max} = 368$ nm in solution. These spectral changes can be explained in terms of the formation of Haggregates. Moreover, unlike EtSH, the *cis* SAMs prepared from *cis*-rich MeSH solutions were comprised not of *cis*-azobenzene, but rather *trans*-azobenzene as the major component. This conclusion was based on the following observations: (1) the similarity of the absorbance at ~250 nm between the as-prepared *cis* SAMs and the *trans*-rich state obtained after sufficient



Fig. 3 UV–vis absorption spectral changes of (a) EtSH and (c) MeSH SAMs on gold surfaces. (i) As-prepared *cis*-EtSH and *cis*-MeSH SAMs. (ii) After irradiation with UV light. (iii) After sufficient dark incubation after UV light irradiation. Difference spectra obtained after alternating UV and visible light irradiation of (b) *cis*-EtSH and (d) *cis*-MeSH in SAMs and in dichloromethane.

thermal *cis*-to-*trans* isomerization for 4 h, and (2) the ~10% reduction in absorbance at 250 nm and slightly red-shifted λ_{max} in comparison with that of *trans*-MeSH SAMs. The slight variation in the absorption spectra is likely due to the somewhat loose packing of the azobenzene units in the *cis* SAM,^{16a} as illustrated in Scheme 1B. It is envisaged that the reduction in packing density provided increased free space required for the structural change between the *trans* and *cis* forms. Therefore, the *trans*-to-*cis* photoconversion yield could be somewhat improved in the *cis*-MeSH SAM, when compared with the more densely packed *trans*-MeSH SAM.

Fig. 3d shows the difference spectra taken after alternating UV and visible light irradiation of cis-MeSH SAMs. Such obvious spectral changes are attributed to reversible trans/cis photoisomerization of the azobenzene unit on a gold surface. Moreover, dark incubation of the UV-exposed MeSH SAMs for 1-4 h fully reversed the absorption spectrum as a result of *cis*-to-*trans* isomerization (Fig. 4). Simultaneously the π - π * absorption bands was slightly red-shifted to \sim 351 nm. The difference in absorbance at λ_{max} ($\Delta A = A_{\text{trans rich}} - A_{\text{UV}}$) obtained after sufficient thermal cis-to-trans isomerization and UV light irradiation was found to be ca. 0.0052 ± 0.0005 for cis-MeSH SAMs, higher than ca. 0.0044 ± 0.0005 for trans-MeSH SAMs (inset of Fig. 4 and Table 1). The results support our earlier expectation that the low-density cis-MeSH SAM consists of trans-azobenzene with increased free volume and shows higher trans-to-cis photoconversion.

On the other hand, considering that 0.45 nm² corresponds to the critical two-dimensional free space required for sufficient *trans*-to-*cis* photoconversion,¹⁸ one can expect that both *trans*-MeSH and *cis*-MeSH SAMs securing *ca*. 0.50 nm² and 0.55 nm²



Fig. 4 UV-vis absorption spectral changes of *cis*-MeSH SAMs. Inset: changes in $\Delta A \ (= A_t - A_{UV})$ of *cis*-MeSH and *trans*-MeSH SAMs as a function of thermal *cis*-to-*trans* isomerization time (*t*) after UV light irradiation.

(estimated from the X-ray crystal structure,^{19c} CPK model, and absorption spectral data^{9,29}) as the area-per-molecule value, respectively, would show a high yield of *trans*-to-*cis* photoconversion. However, the estimated *trans*-to-*cis* photoconversion yields for *trans*-MeSH and *cis*-MeSH SAMs remained at *ca*. 51% and 65% levels, respectively. These results imply that in addition to free space, another factor plays a critical role in affecting *trans*to-*cis* photoisomerization of azobenzene molecules in monolayers. That is, despite there being sufficient free volume, strong intermolecular interactions between the planar *trans*-MeSH azobenzene units facilitated the formation of H-aggregates during the SAM preparation, as evidenced by a significant blueshift of the π - π * band in the absorption spectrum. Consequently, favorable π -stacking of the aromatic units restrained *trans*-to-*cis* photoisomerization.

In sharp contrast to MeSH SAMs, for *cis*-EtSH SAMs, $\Delta A (= 0.0041 \pm 0.0005)$ was almost the same as that for *trans*-EtSH SAMs ($\Delta A = 0.0040 \pm 0.0005$), as shown in Table 1 and Fig. 5. The *trans*-to-*cis* photoconversion yield in *cis* SAMs was estimated to be *ca.* 90%, almost identical to that in *trans* SAMs. Even though a considerable amount of the *cis* form existed in the as-prepared *cis*-EtSH SAMs, the average packing density of molecules was not significantly altered in comparison with that of *trans*-EtSH SAMs. Steric hindrance originating from the ethyl groups at the *ortho* positions lessens inordinate intermolecular interactions between azobenzene molecules, and consequently allows for high photoresponse in monolayers. Furthermore, the reversible structural change of the azobenzene unit was



Fig. 5 Reversible switching of (upper) absorbance at λ_{max} and (lower) contact angle for water of photoresponsive *trans*-EtSH SAMs (open circle) and *cis*-EtSH SAMs (filled circle) by alternating UV and visible light irradiation.

successfully maintained without serious deterioration even after more than 1 week of dark incubation.

We next assessed switching of surface wettability controlled by light wavelengths at which trans/cis isomerization occurs. The contact angles (CAs) of as-prepared cis-EtSH and trans-EtSH SAMs for water were $89 \pm 0.6^{\circ}$ and $94 \pm 1^{\circ}$ respectively (Fig. 5). The lower contact angle of cis SAMs is closely related to the presence of a considerable amount of the *cis* form, as deduced from the characteristic absorption spectral data (Fig. 3a). Further UV light irradiation of the cis-EtSH SAMs under a nitrogen atmosphere did not decrease the CA significantly. However, upon visible light irradiation to induce cis-to-trans isomerization the CA was increased to $92 \pm 0.7^{\circ}$. The CA change on cis-EtSH SAMs was in agreement with that on trans-EtSH SAMs. Explicit photoswitching of the surface wettability for both SAMs is mainly due to the change in the dipole moment between *cis*-EtSH ($\mu_{cis} = 5.42$) and *trans*-EtSH ($\mu_{trans} = 0.37$), accompanied by the reversible structural change controlled by light wavelength. Nevertheless, the CA change on azobenzene SAMs was not so large, only about 3° difference by alternating UV and visible light irradiation. The small changes in the CA may be ascribed to a homogeneously flat surface layer consisting of single-component azobenzene molecules and a relatively smooth surface.30

Conclusions

Both the obvious spectroscopic data and contact angle for water provide convincing evidence for the experimental realization of high and reversible *trans/cis* photoisomerization in singlecomponent azobenzene EtSH SAMs on a flat gold surface. In addition to the high yield of *trans*-to-*cis* photoconversion, the lifetime of the *cis* state was extended on a time scale of hours at ambient temperature. Comparisons of the molecular structure and photoisomerization characteristics in both a *trans* SAM and a *cis* SAM indicated that not only insufficient free space between the individual molecules but also the strong tendency to aggregate during the SAM preparation can be a main disadvantage of photoswitching systems.

Experimental

Preparation of the self-assembled monolayers

For X-ray photoelectron spectroscopy and contact angle measurements, polycrystalline gold films were prepared by thermal evaporation of 100 nm of gold onto clean glass substrates with a 5 m Ti layer as an adhesion layer. For UV–vis absorption spectroscopic measurements, gold films with a thickness of 20 nm were prepared on quartz substrates by vacuum sublimation. The "*trans*-azobenzene SAMs" were prepared by immersion of gold substrates in 0.1 mM *trans*-azobenzene solution in dichloromethane for 6–24 h in the dark. The "*cis*-azobenzene SAMs"^{16a} were formed by dipping gold substrates into UV-exposed (*cis*-rich) azobenzene solution for 6 h in the dark. After immersion, the samples were sufficiently rinsed with dichloromethane, and blown dry with nitrogen gas.

Instrumentation

The chemical composition of the azobenzene SAMs was characterized using XPS measurements (Thermo Fisher Scientific, Theta Probe) by a monochromatized AlKa X-ray source (1486.6 eV). The peak position and area in the spectrum were determined by curve-fitting analysis (Thermo Avantage ver. 3.25). The sessile contact angle method was used to measure the contact angles of a water drop on the gold substrates in air using the Krüss drop shape analysis system DSA10-Mk2. The UV-vis absorption spectrum (Shimadzu UV3150 UV-VIS-NIR spectrophotometer) of each sample was recorded in absorbance mode against air in the reference path. For each spectrum of the azobenzene SAM, the spectrum of the pure gold surface (measured prior to the preparation of the azobenzene SAM) was subtracted. Azobenzene SAMs were exposed to UV light (365 nm, Mineralight lamp, model UVGL-25, UVP, Upland, CA 91786) under a nitrogen atmosphere to induce trans-to-cis isomerization or to visible light (436 nm, high-pressure UV lamp, Ushio Inc., combination of Toshiba color filters, Y-43 + V-44) to induce cisto-trans isomerization.

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