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A "Smart" Ultrathin Photochromic Layer

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We present evidence of persistent dichroism in a monolayer which consists of azosilane molecules self-assembled on a quartz glass slide. This dichroism is shown to depend on the irradiation time. Furthermore, it could be both written and erased by irradiation with light of an appropriate wavelength. In addition, the sign of this dichroism can be inverted by choosing the appropriate polarization of the irradiating light, thus exhibiting a "smart communication" between the photochromic layer and the light polarization.

Induction of photochemical birefringence or dichroism in certain materials, on irradiation with polarized light (the Weigert effect), has been known since the beginning of this century.¹ In the 1960s, this effect was widely studied in viscous solutions containing azo dye molecules which are known to undergo cis-trans photoisomerization upon light irradiation,² while during the 1980s, the Weigert effect was used for polarization holography applications.³ Recently a great deal of interest has arisen in azo dye containing materials, because of their possible application in the areas of optoelectronics, photonics, and optical signal processing.⁴⁻¹¹ In azo dye functionalized bulk polymer films, photoisomerization has been used for producing optical channel waveguides,⁴ writing/erasing optical memories,⁵ and stable second-order nonlinear-optical effects.⁶ Langmuir-Blodgett-Kuhn (LBK) multilayer assemblies of azobenzene containing polymeric materials have been used for all-optical modulation,⁷ optical image recording,⁸ and molecular switching.⁹ However, despite this activity, the Weigert effect has rarely been reported for organized molecular structures.⁹⁻¹¹ In this paper, we unambiguously report on dichroism that has been induced in a monomolecular layer of azosilane molecules self-assembled on a quartz glass substrate. Furthermore, we show that this dichroism can be written, erased, and rewritten for several (e.g., 20) cycles without the appearance of any fatigue in the monolayer. Additionally the sign of this dichroism could be switched

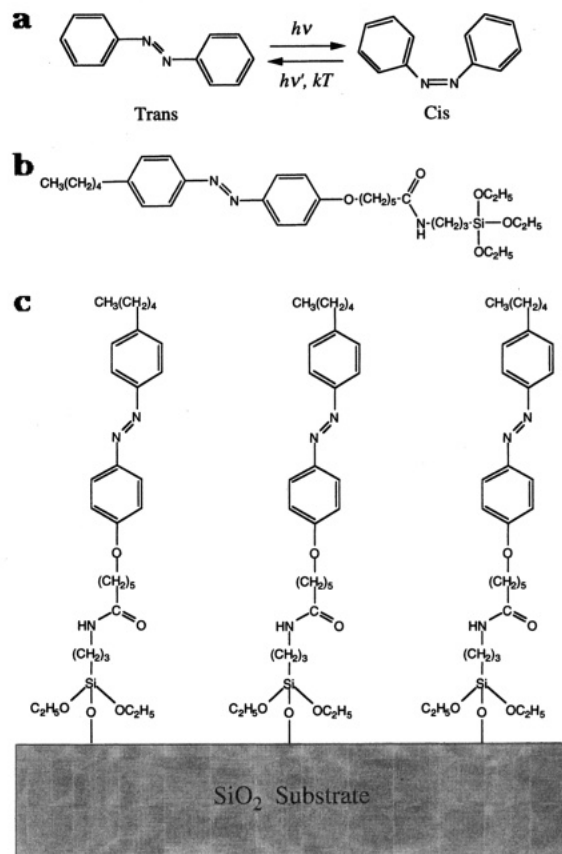


Figure 1. (a) Trans-cis isomerization. (b) Chemical structure of 4-(6-carboxy(3-amidopropyl)triethoxysilane)-4'-pentylazobenzene, referred to in the text as azosilane. (c) An idealized schematic drawing of a self-assembled layer on a SiO₂ substrate.

from positive to negative (and back again) by rotating the polarization of the irradiating light.

Azobenzene derivatives have two geometric isomers, the "trans" and the "cis" forms (Figure 1a). The photoisomerization reaction begins on elevating molecules to electronically excited states after which nonradiative decay brings them back to the ground state in either the "cis" or "trans" forms. The ratio of cis/trans states is dependent on the quantum yield of the appropriate isomerization reaction. As the azobenzene trans isomer is generally more stable than the azobenzene cis isomer (the energy barrier at room temperature is about 50 kJ mol⁻¹), molecules in the cis form may relax back to the trans form by one of two mechanisms: (1) a spontaneous thermal back reaction or (2) a reverse cis → trans photoisomerization cycle. As a complete cis → trans

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thermal back reaction generally requires several hours at room temperature, the *cis* isomer can be considered as stable on a time scale of minutes.

The molecular structure of 4-(6-carboxy(3-amidopropyl)-triethoxysilane)-4'-pentylazobenzene, henceforth referred to as the azosilane, is given in Figure 1b. Synthetic and characterization details will be published in a forthcoming paper. Spectroscopic characterization of such azobenzene-type molecules is usually performed by the observation of a low energy $n-\pi^*$ band in the visible region of the absorption spectrum and a high energy $\pi-\pi^*$ in the UV region.¹²

Quartz glass substrates were ultrasonically cleaned by immersion in a 2% aqueous solution of RBS 35 (an alkaline detergent obtained from Carl Roth GmbH) for 120 min and then, in succession, ethanol, chloroform, and 20% nitric acid, each for 15 min and finally in saturated sodium bicarbonate solution for 30 min. Between each of the above stages, the substrates were rinsed at least 10 times with ultrapure water (Milli-Q, resistivity higher than 18 M Ω cm) before being sonicated for 15 min immersed in Milli-Q water. Following this cleaning procedure, the glass substrates were dried in an oven at 120 °C before being immersed in a 0.5% solution of the azosilane in ethanol. Two substrates were not placed in the silanating solution (although they were subject to the cleaning procedure stated above) and were kept for use as reference samples in the UV-vis spectroscopic experiments. The other substrates were removed from the silanating solution after 10 min, dried in an oven at 120 °C for 30 min, sonicated in methylene chloride for 15 min, and finally redried in the oven at 120 °C for a further 30 min. The samples were then stored in a sealed vessel prior to the dichroism experiments.

Photoisomerization of the azobenzene units was induced by UV light (360 nm) for the *trans* \rightarrow *cis* reaction and by visible light (blue, 450 nm) for the *cis* \rightarrow *trans* back isomerization. The irradiating light source was a high-pressure mercury lamp (Oriel, 200 W) with a glass filter for UV light and an interference filter for blue light. At these wavelengths the lamp power was adjusted to 2 mW/cm². A Hewlett Packard UV-vis diode array spectrometer (Model 8452A) was used to record linearly polarized absorption spectra of the reference and azosilane substrates. A self-built sample holder enabled us interchange the reference and azosilane substrates (schematically drawn in Figure 1c) without altering sample position or orientation. Dichroism measurements were performed by irradiating the samples with a linearly polarized UV light and immediately recording absorption spectra with the probe light polarization parallel (Abs_{||}) and perpendicular (Abs_⊥) to the initial UV polarization. Ambient red light conditions were employed to avoid the influence of the room light on the isomerization reaction.

Figure 2 shows the absorption spectra recorded with the linearly polarized probe light oriented parallel to the irradiating UV light polarization. Figure 2a shows the absorption spectra of the self-assembled azosilane monolayer, before and after various irradiation times. The change in spectral shape and the existence of the isosbestic points at 310 nm and, less pronounced, at 410 nm clearly demonstrate the *trans* \rightarrow *cis* photoisomerization reaction.

As stated previously, once the photostationary state is attained, the photoinduced or thermal *cis* \rightarrow *trans* back isomerization can bring the azo molecules back to the initial state. In Figure 2b, the photostationary state was

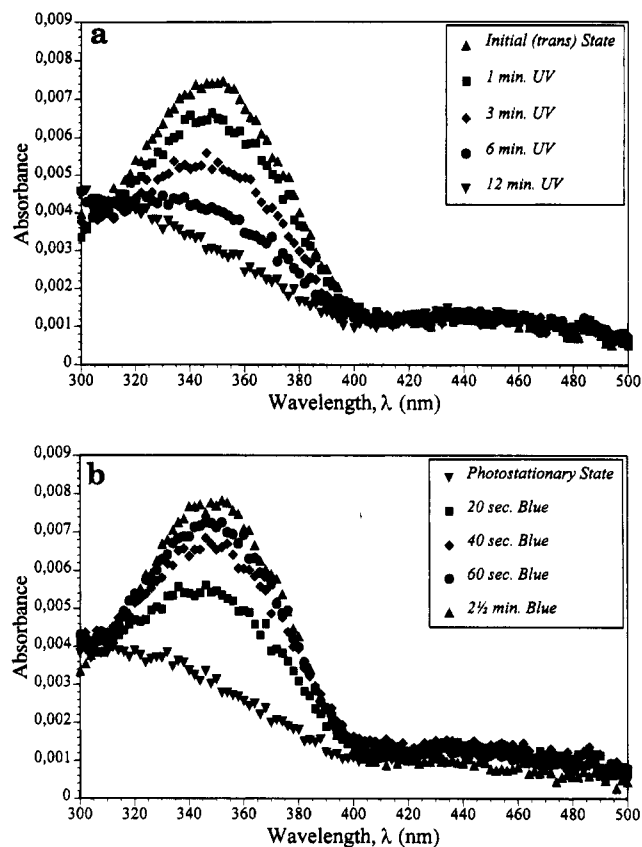


Figure 2. (a) UV-vis absorption spectra of the azosilane layer before (\blacktriangle) and after (\blacksquare , \blacklozenge , \bullet , \blacktriangledown) various timed doses of linearly polarized UV (360 nm) irradiation. The probe light was also linearly polarized and oriented parallel to the exciting UV irradiation. The initial state (\blacktriangle) corresponds to the *trans* state. (b) UV-vis absorption spectra of the azosilane layer before (\blacktriangledown) and after (\blacksquare , \blacklozenge , \bullet , \blacktriangle) various amounts of unpolarized blue (450 nm) irradiation. The probe light was linearly polarized and oriented parallel to the exciting UV irradiation employed in Figure 2a. The initial state (\blacktriangledown) corresponds to the photostationary state.

reached by irradiating the sample with the UV light for 13 min, before commencing a series of irradiations with unpolarized blue light and immediately recording the absorption spectrum after each irradiation. The recovery of the initial, *trans* state, spectra and the existence of the isosbestic points clearly demonstrate the blue light induced *cis* \rightarrow *trans* back isomerization. It can be clearly seen, that after only 20 s of blue light irradiation, an appreciable amount of the azo molecules have already been switched back into the *trans* state. The initial spectra prior to UV irradiation was restored after only 2½ min of blue light irradiation. The difference in switching times required for the UV-induced *trans* \rightarrow *cis* (12 min) and the blue-induced *cis* \rightarrow *trans* (2½ min) isomerizations may be attributed to the much smaller extinction coefficient exhibited by the *cis* state (at 450 nm) than by the *trans* state (at 360 nm).

Additional data (not shown) clearly show the thermal *cis* \rightarrow *trans* back reaction. In this experiment, the azosilane sample was irradiated with UV light until the photostationary state was attained. The sample was subsequently kept in a dark environment and absorption spectra were recorded at various time intervals. After 30 min of relaxation, the spectrum remains unchanged, demonstrating that the thermally activated *cis* \rightarrow *trans* back reaction is very slow. In other words, the *cis* state is stable within this time period. A small, but noticeable, *cis* \rightarrow *trans* relaxation could be observed after 1½ h. Complete thermal recovery required more than 2 days.

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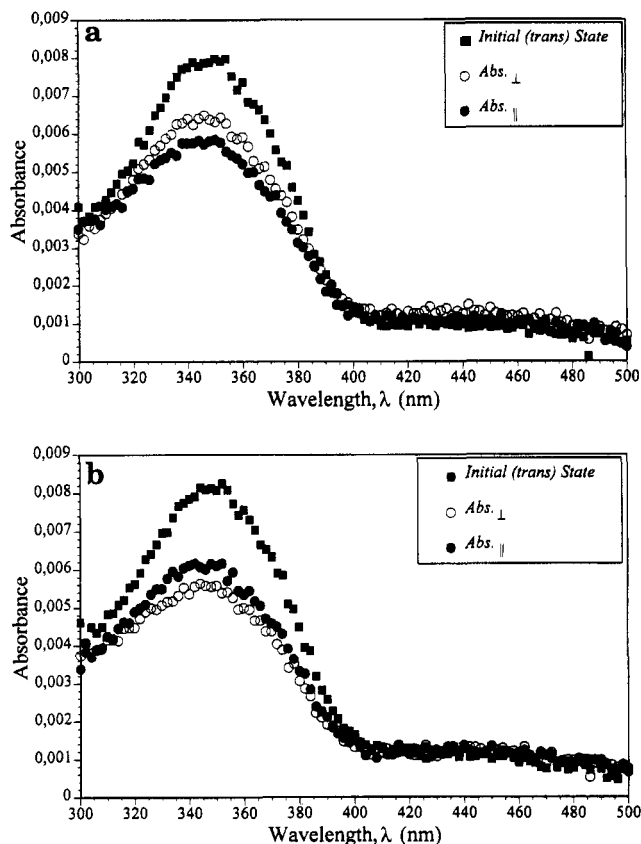


Figure 3. (a) UV-vis absorption spectra of the azosilane layer before (■) and after 3 min (○, ●) of linearly polarized UV (360 nm) irradiation. The probe light was also linearly polarized and spectra were obtained for both parallel, $Abs_{||}$ (●), and perpendicular, Abs_{\perp} (○, ■), orientations. Identical spectra were obtained for both $Abs_{||}$ and Abs_{\perp} prior to UV irradiation. For reasons of clarity, therefore, only Abs_{\perp} (■) is shown. (b) As in Figure 3a, except that the polarization of the irradiating UV light has been rotated through 90°. $Abs_{||}$ and Abs_{\perp} correspond to the same orientations as in Figure 3a.

Figure 3a shows the dichroism observed in our self-assembled azosilane layer. These spectra were obtained after 3 min of irradiation with linearly polarized UV light. It is clear that the absorption, Abs_{\perp} , of the probe light, linearly polarized perpendicular to the initial UV light polarization, is higher than the absorption, $Abs_{||}$, recorded with the probe light linearly polarized parallel to the initial UV light polarization. Identical spectra were recorded for both $Abs_{||}$ and Abs_{\perp} prior to UV irradiation (only Abs_{\perp} shown), demonstrating that the monolayer was optically isotropic at that time. The UV-induced dichroism could be erased on irradiation with unpolarized blue light (2½ min) upon which the initial spectra for both $Abs_{||}$ and Abs_{\perp} were recovered. Further irradiation with linearly polarized UV light restores the initial dichroism, and successive cycles of UV (linearly polarized)/blue (unpolarized) irradiation have shown that this dichroism can be written/erased and rewritten without any fatigue over 20 cycles. Figure 4 shows dichroic spectra ($Abs_{||}$ and Abs_{\perp}) recorded immediately after 3 min of irradiation with linearly polarized UV light and, subsequently, after 2 h of relaxation in the dark. It can be clearly seen that the spectra from the relaxed sample have been shifted to higher absorbance, due to the thermal back reaction, but that the initial dichroism was retained.

Figures 3a and 4 show that irradiation with vertically polarized UV light induces lower absorbance of vertically polarized ($Abs_{||}$) than horizontally polarized light (Abs_{\perp}). It was of particular interest to see if changing the

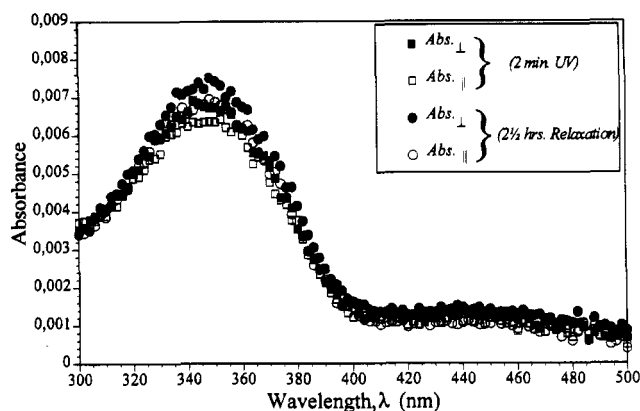


Figure 4. UV-vis absorption spectra of the azosilane layer recorded immediately after 2 min (□, ■) of linearly polarized UV (360 nm) irradiation. The sample was then kept in a dark environment for 2½ h before rerecording the absorption spectra (○, ●). The probe light was also linearly polarized and spectra were obtained for both parallel, $Abs_{||}$ (□, ○), and perpendicular, Abs_{\perp} (■, ●) orientations. Before UV irradiation the sample was in the initial trans state, spectra not shown.

polarization of the irradiating UV light would be mirrored by a change in the absorption spectra. In Figure 3b we show that on irradiating the isotropic ($Abs_{||} = Abs_{\perp}$) monolayer with horizontally polarized UV light, a lower absorbance is recorded using horizontally polarized probing light ($Abs_{||}$) than for vertically polarized probing light (Abs_{\perp}). The amount of observed dichroism is independent of the direction of initial UV polarization. This crossed dichroism could then be erased and rewritten as described previously. The order parameter $S = (Abs_{||} - Abs_{\perp}) / (Abs_{||} + 2Abs_{\perp})$ calculated at 350 nm from the anisotropic spectra in Figure 3 is $S = -0.03$, and is 5 to 10 times smaller than that obtained in azo dye containing bulk polymer films (about 1 μm thick).⁵

The light polarization sensitivity of this photoisomerization reaction originates from the anisotropic shape of the azobenzene molecules. Indeed, considering that the transition dipole moment is along the long principal axis of the molecule, semiempirical LCAO-SCF-CI calculations¹³ have shown that the transition dipole moments for both cis and trans azobenzenes are almost parallel to their $-N=N-$ double bond axes, the probability of an azo unit absorbing a photon and subsequently isomerizing is proportional to the cosine square of the angle between the transition dipole moment and the polarization direction of the exciting light. The molecules aligned parallel to the polarization of the exciting light, therefore, clearly have the highest probability of being excited and isomerized. Consequently, when starting from isotropically distributed trans isomers, linearly polarized UV light burns a hole in this angular distribution due to the selectivity of the molecular excitation (angular hole burning). Furthermore, as the principal axis of the azo unit is reoriented due to the isomerization reaction, the principal axis of the cis state will be tilted with respect to the direction of initial UV polarization (angular redistribution). Both angular hole burning and angular redistribution lead to preferential distribution of the azo molecules perpendicular to the direction of initial UV polarization. It is worth noting that, for high intensities of irradiating light, or for long irradiation times, even the molecules which are aligned perpendicular to the polarization of the irradiating light will be excited. The system will then be saturated and the isotropy will be restored. We have observed this phenomenon in our experiments

by recording that the amount of photoinduced dichroism increases with increasing irradiation times until a maximum value is reached (after 3 min in our study). Longer irradiation progressively produces less dichroism until isotropy is finally regained. A detailed theoretical model accounting for this behavior will be published in a forthcoming paper.

In summary this work reports about persistent photoinduced dichroism in a monolayer which consists of azosilane molecules self-assembled on a glass substrate. We have shown that this dichroism can be written/erased, and rewritten for several cycles without any fatigue appearing in the azosilane layer. Furthermore, we have shown that by rotating the polarization of the irradiating light through 90° , the sign of the anisotropy may be easily inverted. Finally, we believe that this "smart com-

munication" between light polarization and an ultrathin photochromic layer may be useful for anisotropically altering the structural and/or optical properties of ultrathin supramolecular structures containing azobenzene molecules.

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