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Excellent Reversible Photochromic Behavior of 4-Octyl-4'-(5-carboxyl-pentamethyleneoxy)-azobenzene in Organized Monolayer Assemblies

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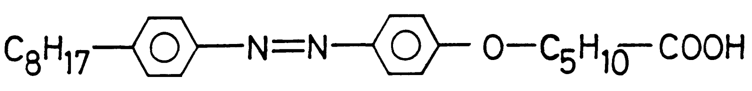
We report the first observation of a photochromic behavior of an amphiphilic azobenzene derivative in the close-packing LB films on a solid support. The excellent reversibility was achieved only after the LB films were 'pretreated' with UV irradiation.

Photochromism in azobenzene system has received considerable attention because of its potential applications in areas such as high density optical memories and molecular switching devices.[1-4)] One of the limitations which has impeded its utilization has been that photochromic reversibility, occurring in solutions, is usually suppressed in a rigid matrix due to a spatial inhibition.[5,6)] The cis ⟷ trans isomerization process in azobenzene system, which is responsible for its observed photochromism, is accompanied by a change in the molecular area. In the presence of a rigid matrix, the molecular area change does not proceed as easily as that in a liquid state which consequently results in irreversibility in its photochromic behavior. In this letter, we show that the pure LB films of 4-octyl-4'-(5-carboxyl-pentamethyleneoxy)-azobenzene) (ABD, whose molecular structure is shown in Fig. 1) can be made to exhibit excellent reversible photochromic behavior after they have been 'pretreated' with UV irradiation.

The LB film was fabricated onto a quartz glass substrate by the conventional Langmuir-Blodgett (LB) method. The number of the deposited monolayers was calculated from the total area change of the Langmuir film at the air-water interface during film fabrication.



ABD

Fig. 1. Molecular structure of azobenzene amphiphile used in the present work.

The quartz glass substrate was hydrophilically pretreated by immersing it in hot sulfuric acid (50% by volume) for about 10 min. All of the film preparation was performed at a surface pressure of 25 mN m^{-1}, at which a close-packing arrangement in the LB film would be expected, and at a constant temperature of 20 °C. A 500-W xenon lamp was used as the excitation source for the experiments. All absorption measurements were done with an UV-visible spectrometer.

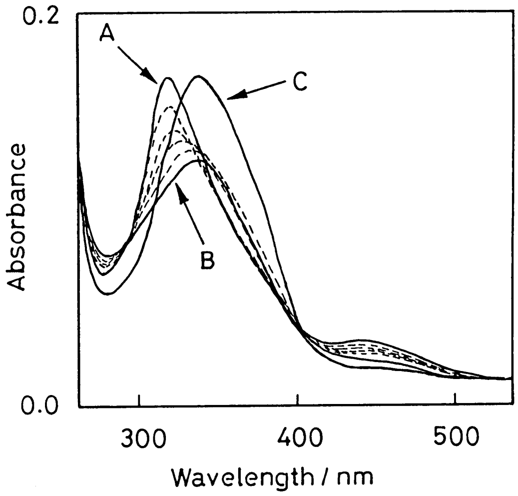


Fig. 2. Absorption spectra of 14-layered ABD LB film on a quartz glass support. (A) before irradiation; (B) after 45 min UV irradiation; (C) after 5 min visible irradiation.

Figure 2 shows the spectral responses of a 14-layered LB film of ABD. When the film was irradiated with an UV light centered at 356 nm with a bandpass of 60 nm, the transition band at 318 nm (curve A, called state 'A') gradually red-shifted with a concurrent decrease in the corresponding absorbance. This behavior lasted for 45 min with the UV irradiation. After which, no further changes in the peak position and absorbance were observed, and the system has reached a steady state (state 'B'), represented by curve B of Fig. 2. It is known that azobenzenes undergo a trans to cis isomerization with UV irradiation, and cis to trans with visible light or heat.1-4) The more stable trans isomer of ABD in the organized film has an intense $\pi-\pi^*$ absorption band7) at 318 nm, compared to the same at 352 nm in chloroform solution. The blue-shift is attributed to a strong coupling between the '-N=N-' chromophores in the organized LB film.6) Conversion of the trans isomer to the cis in the photostationary state 'B' was estimated to be ca. 30% from a calculation based on the difference spectra.8) That it took a considerable length of time for the 14-layered LB film of trans ABD to convert to the photostationary state 'B' is reconcilable with the fact that spatial inhibition exists in the organized film. In a similar experiment with 94 μM (M = 1 mol dm^{-3}) trans ABD in chloroform solution, the photostationary state was easily achieved after irradiated for about a minute with the same UV irradiation.

After UV irradiation, the LB film was then exposed to visible light of wavelength longer than 440 nm for 5 min whereby a new steady state (state 'C') was attained (curve C of Fig. 2). The state 'C' was composed predominantly of the trans isomer of ABD. The shift in the peak position of the steady state 'C' from that of state 'A' is due to the film expansion, as will be explained later, and hence the weakening of the '-N=N-' coupling. The weakening effect of the '-N=N-' coupling will be demonstrated later in the ABD-stearic acid mixed film experiments. After the above UV and visible irradiation, the LB film was then found to give an excellent reversibility between state 'B' and state 'C' when irradiated alternately with UV (for 60 s) and visible(for 30 s) lights (see Fig. 3). The reversible switching between state 'B' and state 'C' could be repeated for at least 40 cycles with a 2% deviation in absorbance. This behavior, however, was not observed under identical conditions on LB films which were not 'pretreated' with UV irradiation. Thus, we believe that the 'pretreatment' with UV irradiation provides a favorable environment for the reversible reaction.

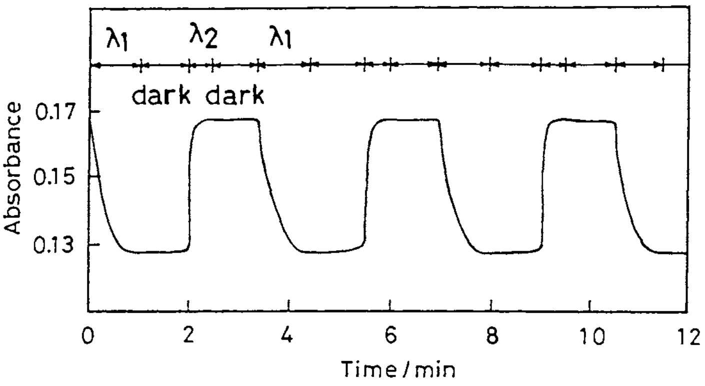


Fig. 3. Changes in absorbance at 338 nm of the ABD LB film on alternate irradiation with UV light (λ_1 = 356 nm) for 60 s and visible light(λ_2 > 440 nm) for 30 s.

The reversible behavior of ABD molecules in the rigid LB films may be explained by the 'film expansion' concept. Our results show that the molecular area of ABD in the Langmuir film of 17 mN m^{-1} is increased by 2.4 $Å^2$ in the trans to cis isomerization process. Hence, it would be reasonable to expect that the trans to cis isomerization (state 'A' to state 'B') would induce a gradual expansion of the LB film and perhaps a partial rearrangement of ABD molecules. Because of a spatial inhibition in the rigid film, it is believed that the area-increasing reaction may occur initially only in the 'hole' or 'defect' regions.9) After a sufficient duration of UV exposure, the film expansion will provide a sufficient free volume for a smooth trans ⟷ cis transitions (state 'C' ⟷ state 'B') in the film. As a result, a reversible behavior was observed. An indirect evidence for the film expansion comes from the observed gradual red-shifts of the $\pi-\pi^*$ band of trans ABD isomers in the LB film under UV irradiation (shown by the dashed curves in between curve 'A' and curve 'B' in Fig. 2). This was due to a gradual decrease in the interaction between adjacent '-N=N-' chromophores of ABD molecules in the film as a result of the film expansion.

A similar reversible behavior was also observed in the mixed LB films of trans ABD and stearic acid. In this case, the blue-shift of the initial

π-π^* transition band of trans ABD isomers in reference to the solution state showed a gradual decrease when ABD molecules in the film were diluted with the inactive stearic acid. Furthermore, compared to the initial state, the π-π^* band of trans ABD isomers in all the mixed films showed a red-shift after the 'pretreatment' of UV irradiation, but the quantity of the red-shift becomes gradually decreased. The results for the mixed LB films were summarized in Table 1. These results have strongly implied the weakening of the '-N=N-' coupling in the LB films because of the presence of stearic acid molecules.

Table 1. Blue-shift of the π-π^* transition band of trans ABD isomers at the initial state($\Delta\lambda_b$) and red-shift of the same band after UV irradiation ($\Delta\lambda_r$). The former was referenced to the solution state

	100% (ABD)	50%	31%	Cast	Soln
$\Delta\lambda_b$ (nm)	34	24	15	12	0
$\Delta\lambda_r$ (nm)	20	5	3	—	0

We have also tried the same experiments on cast films prepared by a spin casting method. The results were shown in Table 1 as well. In this case, no definite stable state was attained in the course of UV and visible irradiation. This may be attributed to a lack of '-N=N-' coupling due to a random arrangement of ABD molecules in the films. The non-cooperative trans to cis isomerization of the randomly arranged ABD molecules in the cast films has prevented the film from a whole expansion though the area-increasing reaction partially occurred.

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