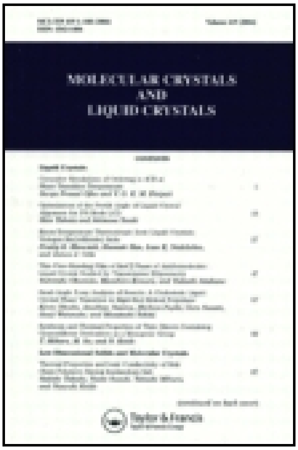

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Efficient Photoisomerization of Hybrid Langmuir-Blodgett Films of Amphiphilie Anionic Azobenzene and Alkylammonium with Long Alkyl Chains

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EFFICIENT PHOTOISOMERIZATION OF HYBRID LANGMUIR-BLODGETT FILMS OF AMPHIPHILIE ANIONIC AZOBENZENE AND ALKYLAMMONIUM WITH LONG ALKYL CHAINS

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We fabricated stable hybrid monolayers of an anionic azobenzene and alkylammonium, while pure azobenzene did not form a stable monolayer. Efficient photoisomerization of azobenzene proceeded in the Langmuir-Blodgett films due to salt formation of the two components, allowing azobenzene to have free volume with alkylammoniums as spacers.

Keywords: alkylammonium; anionic azobenzene; Langmuir-Blodgett film; photoisomerization

INTRODUCTION

Photochromic organic compounds have attracted wide attention for the fabrication of optical switching and storage devices [1,2]. Azobenzene is a typical photochromic compound and is promising for the applications to various optical materials owing to the ease of synthesis and toughness against photoirradiation. *Trans* isomer of azobenzene is thermodynamically more stable than *cis* one. In the liquid states, *trans* azobenzene isomerizes easily to *cis* isomer by ultraviolet (UV) irradiation. However, in many cases, photoisomerization does not proceed efficiently in the solid states due to the close packing of molecules. Free volume is considered to be necessary for azobenzene to photoisomerize because the cross-sectional area of the molecule increases with the isomerization to *cis* isomer [3–5]. Many researches have aimed at improving the efficiency of

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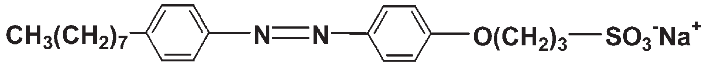
isomerization. The strategies are as follows: (1) ion-complex formation of amphiphilic azobenzene and polyion dissolved in the subphase [3–6], (2) inclusion of azobenzene in the cavity of amphiphilic cyclodextrins [7], (3) tethering of azobenzene as side groups to polymers [8], and (4) coupling with bulky hydrophobic moieties [9] or bulky hydrophilic moieties [1].

On the other hand, we have reported that a fatty acid and alkylammonium [10,11], and an anionic merocyanine and alkylamine [12] are homogeneously mixed with each other in the Langmuir-Blodgett (LB) films owing to salt formation of the molecules having the opposite charges, whereas phase-separated structures are commonly observed in mixed multicomponent LB films. By the application of this method, mixing of amphiphilic counterions is promising for endowing azobenzene with free volume in the LB films.

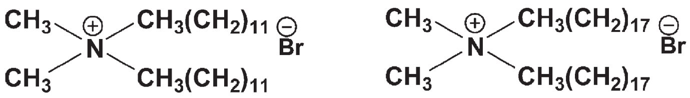
In this paper, we report the formation of stable LB films of anionic amphiphilic azobenzene and alkylammoniums. Reversible *cis-trans* isomerization of azobenzene proceeds efficiently in the LB films.

EXPERIMENTAL

The materials used in this study are shown in Figure 1. A mixed methanol-chloroform (4:6) solution containing Az(8-3) and alkylammonium (mixing ratio of 1:1) was spread on pure water on a Lauda FW1 film balance at 17°C. The concentration of the spreading solution was 0.25 mM for each component. The films were deposited at 20 mN m^{-1} by vertical dipping method on quartz or mica substrates. Photoisomerization of azobenzene in the LB films was performed by the alternate illumination of monochromated UV (365 nm) and visible (436 nm) light from a 500 W high-pressure mercury



Sodium 3-[4-(4'-octylphenylazo)phenoxy]propanesulfonate(Az(8-3))



Didodecyldimethylammonium bromide **Dimethyldioctadecylammonium bromide**

FIGURE 1 Compounds used in this study.

lamp. Atomic force microscopic (AFM) images were taken by a SPA300 (Seiko Instruments) with an SPI3800 probe station operated in noncontact mode using silicon cantilevers.

RESULTS AND DISCUSSION

Figure 2 shows the surface pressure-area isotherms of 1:1 mixed monolayers of Az(8-3) and alkylammoniums with two long alkyl chains. The mixed monolayers are stable at the air/water interface. On the other hand, the compression of pure Az(8-3) does not lead to an increase in surface pressure, suggesting that the Az(8-3) molecules are dissolved (or dispersed) into subphase water. Furthermore the monolayer of a 2:1 mixture of Az(8-3) and didodecyldimethylammonium showed a rise in surface pressure at almost the same area per ammonium molecule with that of a 1:1 mixture, suggesting the formation of a 1:1 mixed monolayer. Based

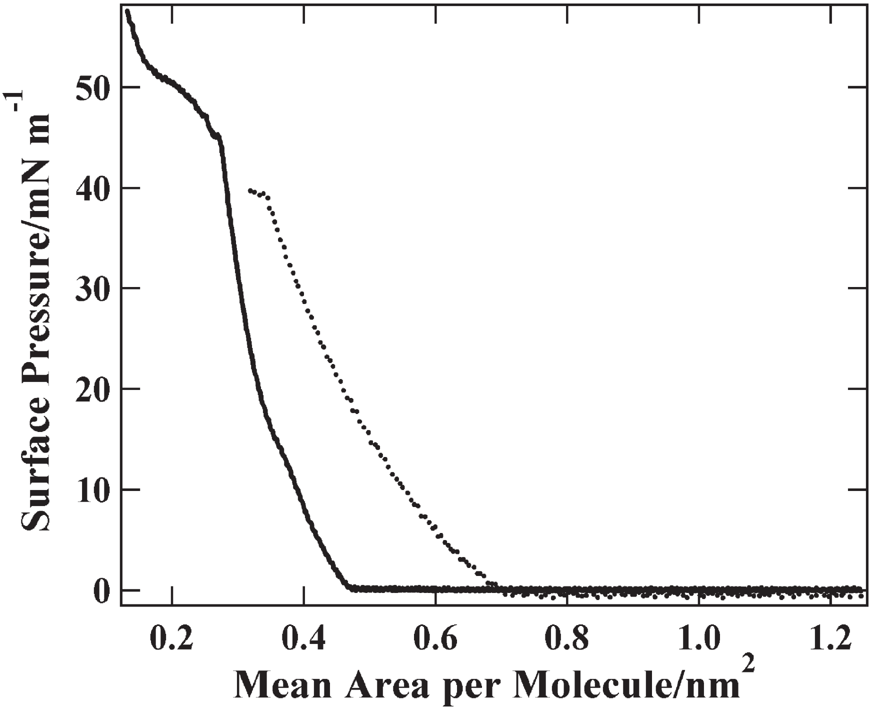


FIGURE 2 Surface pressure-area isotherms of mixed monolayers of Az(8-3) and alkylammoniums having two alkyl chains. Dotted line: didodecyldimethylammonium, solid line: dimethyldioctadecylammonium.

on the above results, we assume that Az(8-3) and alkylammoniums form 1:1 ion complexes in the mixed monolayers. In our previous work on the mixed LB films of fatty acid and alkylammonium [10,11], and on those of anionic merocyanine and alkylamine [12], infrared (IR) spectral measurements reveal that the two components are mixed at the molecular level due to 1:1 salt formation of the anionic and cationic molecules. Considering the above, we further assume that anionic Az(8-3) and alkylammonium are mixed at the molecular level due to salt formation of the molecules with the oppositely charged head groups.

The isotherm of a 1:1 mixed monolayer varies with the chain length of alkylammonium: for example, area per molecule of the monolayer with didodecyldimethylammonium at 20 mN m^{-1} is larger than that with dimethyldioctadecylammonium, indicating the denser packing in the latter film than in the former film. The LB films were transferred onto quartz substrates, in order to investigate the photochromic behavior of azobenzene.

Figure 3(a) shows the UV-vis absorption spectra of a single-layer hybrid LB film with didodecyldimethylammonium before and after photoirradiation. Before irradiation, the absorption peak due to the *trans* azobenzene is located at ca. 355 nm. When the LB film is irradiated with UV light, the absorption peak of the *trans* isomer is replaced by that of the *cis* one at ca. 450 nm. The conversion is estimated to be ca. 85%. After the photostationary state under the UV irradiation was reached, the LB film was irradiated with visible light. By visible irradiation, the absorption peak of *trans* isomer increases. The spectral change on photoirradiation indicates that

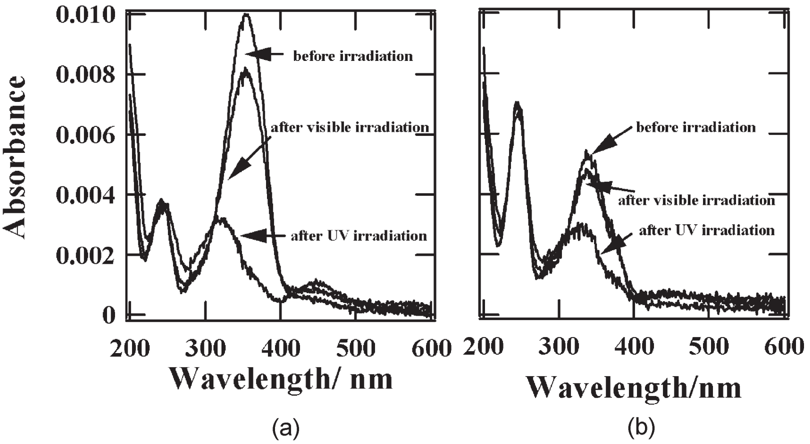


FIGURE 3 UV-vis absorption spectra of single-layer hybrid LB films with (a) didodecyldimethylammonium and (b) dimethyldioctadecylammonium.

cis-trans isomerization of azobenzene proceeds efficiently in the hybrid LB films. The result suggests that mixing of the two components at the molecular level due to salt formation allows azobenzene to have free volume with alkylammonium as a spacer. Similar spectral changes occurred for the LB film with dimethyldioctadecylammonium except that the absorption peak of the *trans* isomer is located at ca. 340 nm (Fig. 3(b)). The conversion is estimated to be ca. 53%, less than that of the mixed LB film with didodecyldimethylammonium.

Orientation of azobenzene in the hybrid LB films was examined by measuring polarized absorption spectra at an angle of incidence of 45° (data not shown). In the case of the LB film with dimethyldioctadecylammonium, the absorption peak in the p-polarized spectrum was larger than that in the s-polarized spectrum. On the other hand, the two polarized spectra were almost the same in the case of the LB film with didodecyldimethylammonium. The tilt angles of the long axis of azobenzene unit with respect to the film normal are calculated as ca. 43° and 62° in the LB films with dimethyldioctadecylammonium and didodecyldimethylammonium, respectively, using the treatment described in the literature [13].

The difference in the conversion to the *cis* azobenzene in the two hybrid LB films can be explained as follows:

(1) Mean area per molecule at 20 $\mathrm{mN\,m^{-1}}$ is ca. 0.46 and 0.33 $\mathrm{nm^2}$ for the mixed LB films with didodecyldimethylammonium and dimethyldioctadecylammonium, respectively. This shows that free volume is larger in the hybrid LB film with didodecyldimethylammonium.

(2) The peak position of *trans* isomer of azobenzene shows that the azobenzene chromophore is in a monomeric state in the LB film with didodecyldimethylammonium whereas that in the LB film with dimethyldioctadecylammonium forms H-aggregate. Aggregation can hinder the photoisomerization to some extent.

(3) The difference in tilt angle of the azobenzene chromophore may affect the conversion but to a much lesser extent.

The morphology of a single-layer mixed LB film was observed by AFM. Figure 4 represents the AFM image of an LB film of the Az(8-3) and didodecyldimethylammonium deposited on a freshly cleaved mica substrate. The AFM image did not change significantly with UV irradiation and subsequent visible irradiation. This is consistent with our assumption that free volume plays an important role in the photoisomerization in the present study. The results are in contrast to those of the polyion complex LB film of Az(8-3) and poly(diallyldimethylammonium) dissolved in the subphase, where reversible morphological changes of the LB film were observed with photoisomerization of Az(8-3) [6].

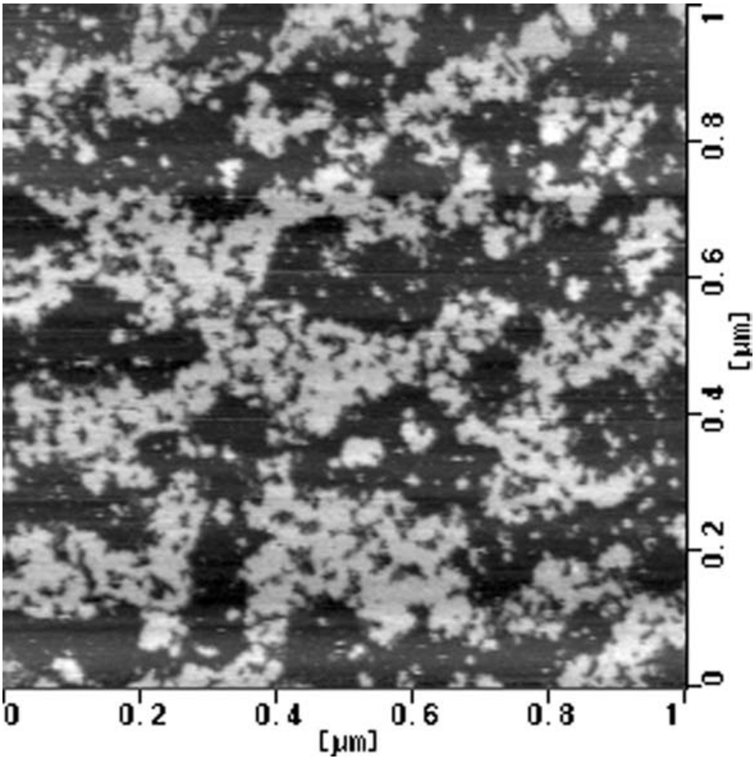


FIGURE 4 AFM image of a single-layer hybrid LB film of Az(8-3) and didodecyldimethylammonium on a mica substrate ($1 \times 1 \mu m^2$).

CONCLUSIONS

We have succeeded in fabricating homogeneously mixed monolayers of azobenzene and alkylammonium owing to salt formation of the two components with the oppositely charged head groups. In addition, in the solid state, photoisomerization of azobenzene proceeds efficiently due to the existence of free volume in the LB films.

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