

Fabrication and Efficient Photochromism of the Mixed Langmuir–Blodgett Films of a Water-miscible Azobenzene Amphiphile and Long-chain Alkylammoniums

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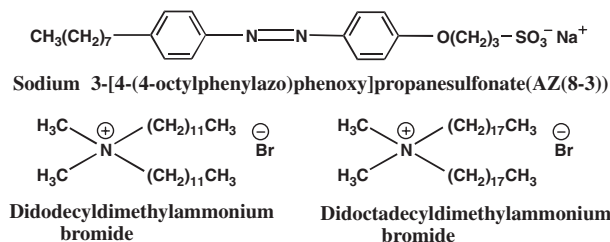
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The fabrication and efficient photochromism of the mixed Langmuir–Blodgett films of a water-miscible azobenzene amphiphile and long-chain alkylammoniums are demonstrated. Long-chain alkylammonium can serve as a counterion to stabilize the anionic azobenzene amphiphile on the water surface, and also as a spacer around the azobenzene amphiphile to prevent the aggregation, enabling the efficient photoisomerization of azobenzene.

Azobenzenes have been one of the most promising compounds for photochromic data storage systems because of the ease of synthesis and their toughness against photodecomposition. The color changes reversibly by the alternate illumination of UV and visible light, which arises from the *cis*–*trans* isomerization of the molecule.

In many cases, however, the isomerization of azobenzene does not proceed efficiently in the solid state, including Langmuir–Blodgett (LB) films, due to the stacking of the molecules. Several attempts have been applied to improve the photoisomerization efficiency in LB films. The reported methods to separate each azobenzene moiety are categorized as follows: (1) incorporating an azobenzene into the cavity of cyclodextrin,¹ (2) introducing bulky substituents in the hydrophilic moiety,² (3) fabricating the ion-complex of amphiphilic azobenzene molecules and a polyion dissolved in the water subphase,^{3–5} or utilizing a branched polymer with azobenzene moieties at branches,⁶ increasing the distance of neighboring azobenzene, and (4) mixing with another component in the spreading solution.^{7,8} The disadvantage of the fourth method is that phase separation often takes place in the film when two components are mixed, where the second component will not work as a spacer.

Based on our previous work on the mixtures at the molecular level (i.e. without phase separation) of counterionic amphiphile pairs such as a fatty acid and a long-chain alkylammonium,^{9,10} and an anionic merocyanine and a long-chain alkylamine¹¹ in LB films, the application of an ionic azobenzene amphiphile with a counterionic spacer molecule is promising for the homo-



Scheme 1.

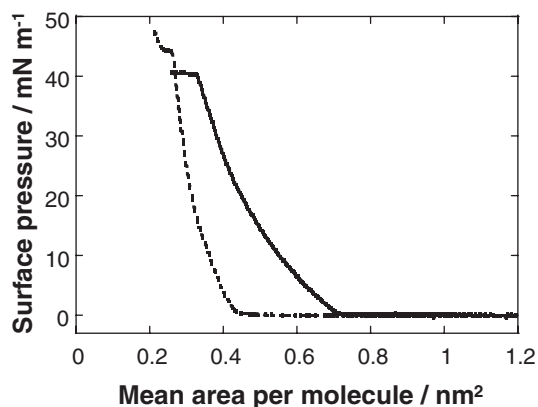


Figure 1. Surface pressure-area isotherms of the mixed monolayers of AZ(8-3) and long-chain alkylammoniums at the air/pure water interface. (solid line) Mixed monolayer with didodecyldimethylammonium, (dotted line) mixed monolayer with didoctadecyldimethylammonium.

geneous mixing, resulting in the efficient photoisomerization. Moreover, counterions can stabilize the monolayers of compounds that alone do not form stable monolayers. In this paper, we report the formation of stable monolayers of a water-miscible anionic azobenzene amphiphile and its reversible photoisomerization in the LB films by mixing with long-chain alkylammoniums.

An anionic amphiphilic azobenzene, AZ(8-3) (Scheme),¹ is used in this study. A chloroform–methanol mixed solution (6/4) of the 1/1 mixture of AZ(8-3) and alkylammonium bromide (0.25 mM for each) was spread onto a pure water at 17 °C. Figure 1 shows the surface pressure-area isotherms of the 1/1 mixed monolayers of AZ(8-3) and alkylammoniums with two long alkyl chains. While the surface pressure does not rise for pure AZ(8-3), the 1/1 mixture of AZ(8-3) and alkylammonium form stable monolayers. The 2/1 mixed monolayer of AZ(8-3) and didodecyldimethylammonium showed a rise in surface pressure at very small mean surface area per molecule, suggesting that around a half of AZ(8-3) molecules were dissolved into the subphase water. The results suggest the formation of a water-insoluble 1/1 ion complex of AZ(8-3) and alkylammonium in the monolayer. The mixture of AZ(8-3) and didodecyldimethylammonium forms a denser monolayer than that of AZ(8-3) and didodecyldimethylammonium, suggesting the stronger hydrophobic interactions between the molecules. Both of these mixed monolayers were successfully transferred onto solid substrates.

Figure 2 shows the UV–vis absorption spectra of the single-layer mixed LB film of AZ(8-3) and didodecyldimethylammoni-

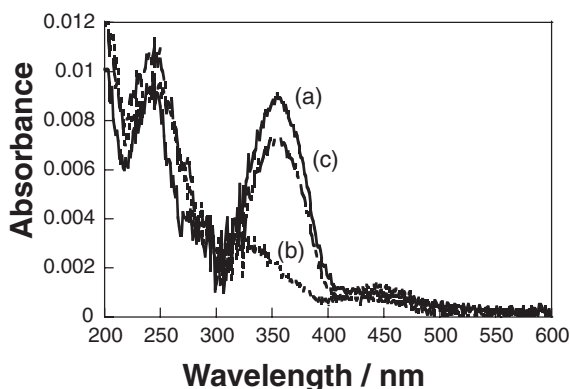


Figure 2. UV-vis absorption spectra of the mixed LB film of AZ(8-3) and didodecyldimethylammonium. (a) The spectrum before light irradiation, (b) after UV light irradiation, (c) after the following visible light irradiation.

um on a quartz substrate before and after photoirradiation. The absorption peak due to *trans*-azobenzene is located at ca. 355 nm. When the LB film is irradiated with UV light (monochromated light from high-pressure mercury lamp, $\lambda = 365$ nm), the absorption due to the *trans*-isomer decreases with time. On the other hand, the small absorption peak at ca. 440 nm that corresponds to the *cis*-isomer appears. The conversion is estimated to be 80–85%.¹² Subsequent irradiation with visible light (436 nm) restores the absorption due to the *trans*-isomer. These results show that reversible *cis*–*trans* isomerization proceeds efficiently in the mixed LB film.

In the case of the mixed LB film of AZ(8-3) and dioctadecyldimethylammonium, the absorption peak due to *trans*-azobenzene is located at ca. 340 nm, suggesting slightly different circumstance of azobenzene moiety due to the denser molecular packing than the case of the mixed LB film with didodecyldimethylammonium. The smaller absorption intensity of the *trans*-isomer than the case of the mixed LB film with didodecyldimethylammonium indicates the more oblique orientation of the longer molecular axis of the azobenzene moiety with respect to the film surface. Similar photoisomerization was observed, but to a lesser extent (conversion: 45–60%).

In our previous work on the mixed LB films of counterionic amphiphile pairs (fatty acids and long-chain alkylammoniums,^{9,10} and an anionic merocyanine and a long-chain alkylamine¹¹), we showed, through several evidences such as infrared spectra, that these two components are mixed at the molecular level. This is due to the electrostatic interaction of an anion derived from a fatty acid or an anionic merocyanine and a cation derived from an alkylammonium or an amine. Considering the

above, we assume homogeneous mixing of AZ(8-3) and an alkylammonium at the molecular level due to the oppositely charged head groups. The resulting efficient photoisomerization of the azobenzene moiety also suggests that the ammonium molecules are located close to the AZ(8-3) molecule and serve as a spacer. The less efficient photoisomerization in the case of the mixed LB film with the longer alkylammonium is probably due either (or both) to the denser packing of azobenzene moiety owing to the longer spacer molecule, or to the difference in orientation of azobenzene moieties with respect to the substrate surface, which affects the efficiency of light absorption.

In summary, the Langmuir and the LB films of a water-miscible anionic azobenzene are successfully prepared by mixing with long-chain alkylammoniums, the counter cations. We suggest homogeneous mixing of the two components at the molecular level due to the oppositely charged head groups of the two components. Photoisomerization proceeds efficiently in the mixed LB films. Long-chain alkylammonium molecules serve as a spacer around the azobenzene amphiphile to prevent the aggregation, facilitating the photoisomerization of azobenzene.

References and Notes

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- 12 Conversion from the *trans*-isomer to *cis*-one is estimated from the change in absorbance at the absorption peak due to the *trans* isomer.