# Photoinduced Reversible *trans–cis* Isomerisation of an Azobenzene Amphiphile Bearing Dialkyl Side Chains in Langmuir–Blodgett Membranes

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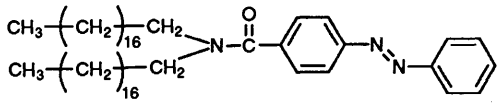
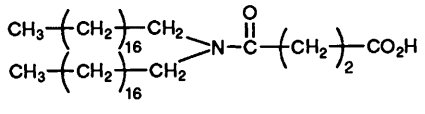
Reversible *trans–cis* isomerisation is induced by UV and visible-light irradiation for Langmuir–Blodgett (LB) membranes composed of an azobenzene amphiphile bearing bulky dialkyl side chains.

The photoresponse of Langmuir–Blodgett (LB) membranes composed of long-chain azobenzene derivatives has been studied extensively for the development of molecule-based optical and electronic devices.[1,2] The photoisomerisation of azobenzene residues from the *trans*- to the *cis*-form is generally suppressed or prohibited in LB membranes owing to the close packing of the azobenzene amphiphiles in the membranes and the resulting lack of free volume available for the geometrical changes accompanying the isomerisation.[2–4] If we want to prepare photosensitive LB membranes, the molecular complexes of azobenzene amphiphiles with cyclodextrin (CD),[3] poly(arylamine) (PAA)[4] or tetracyanoquinodimethane (TCNQ)[5] have to be built in the LB membranes. In such LB membranes, the azobenzene amphiphiles isomerise reversibly to some extent. These LB membranes are endowed with adequate free volume for the *trans–cis* isomerisation to occur reversibly, because of the bulkiness of the CD, PAA and TCNQ moieties. These observations have stimulated us to synthesise azobenezene amphiphiles which exhibit *trans–cis* isomerisation in LB membrane by themselves without complexation. For this purpose, we have prepared an azobenzene amphiphile substituted with bulky dialkyl chains, *N*,*N*-dioctadecyl-*p*-phenylazobenzamide **1**. The present communication reports the photoresponse of the LB membranes composed of **1**.



**1**



**2**

Compound **1** was synthesised by coupling *N*,*N*-dioctadecylamine and *p*-phenylazobenzoyl chloride in $CHCl_3$ in the presence of pyridine at room temperature, followed by purification by silica gel column chromatography. Compound **2** was prepared by the reaction of *N*,*N*-dioctadecylamine and succinic anhydride in pyridine, and was recrystallised from acetonitrile. The amphiphile **1** formed a monolayer on a water subphase, but unfortunately, the monolayer **1** by itself was not stable in its condensed phase. Therefore, the mixed monolayers of **1** and **2** were used in this study. The measurement of surface pressure–area isotherms and the deposition of LB membranes were carried out with a Langmuir trough with an electric microbalance (Kyowa Kaimen Kagaku Co.).

The mixed monolayers of **1** and **2** (**1** content 10, 25 and 50% mol fraction) were prepared on an aqueous subphase containing $3 \times 10^{-5}$ $BaCl_2$ and $4 \times 10^{-4}$ $KHCO_3$ at 12 °C. The monolayers were compressed at the rate of 8.0 $cm^2$ $min^{-1}$ up to a surface pressure of 25 mN $m^{-1}$, whence the monolayers formed a condensed phase. The occupied area per molecule extrapolated to zero pressure ($A_0$) of the mixed monolayers was *ca.* 0.45 $nm^2$, irrespective of the ratio of **1** to **2**. The observed $A_0$ value is consistent with values reported for the monolayers composed of dialkyl chain-substituted amphiphiles such as *N*,*N*-dioctadecylamine derivatives[6] and biological phospholipids,[7] confirming the formation of well packed monolayer membranes of **1** and **2**. The monolayers were deposited on a hydrophobic quartz plate. All monolayers tested gave Y-type deposition, with deposition ratio of unity. The photoisomerisation of **1** in a LB membrane and in solution was monitored by measuring the absorption spectra in air. The *cis*-form percentage of the irradiated sample was calculated from the decrease in absorbance at the $\pi$–$\pi^*$ absorption maximum, assuming that the absorbance of the *cis*-isomer at this wavelength is negligibly small compared with that of the *trans*-isomer.[3–5] A 500 W xenon lamp was used as a light source, with glass filters for isolating UV ($320 < \lambda < 380$ nm) and visible ($\lambda > 450$ nm) light. All measurements were carried out at *ca.* 23 °C.

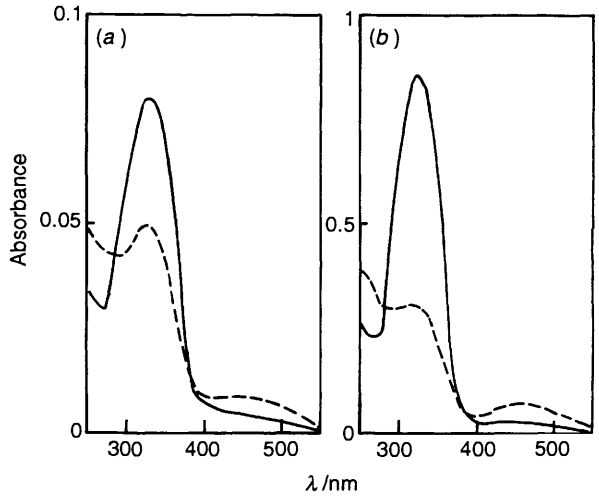



**Fig. 1** Absorption spectra of **1** (*a*) in LB membrane and (*b*) in chloroform solution before (——) and after (– – –) UV irradiation [content of **1** in (*a*) in LB membrane (20 layers) is 25% mol fraction; concentration of **1** in (*b*) is $5.0 \times 10^{-5}$ mol $dm^{-3}$]

Fig. 1 shows the absorption spectra of **1** in (*a*) LB membrane (**1** content: 25%) and (*b*) in chloroform solution before and after UV irradiation. The intensity of the absorption bands around 325 nm, which originate from $\pi$–$\pi^*$ transitions in the *trans*-azobenzene residue of **1**, decreased to reach a photostationary state in 5 min by UV irradiation in the LB membrane and in solution. The original spectra were recovered by visible-light

**Table 1** Effects of content of **1** in the LB membrane on the *cis*-**1** content under UV irradiation and on the $\lambda_{max}$ value of *trans*-**1** in the dark

| | **1** content in LB membrane (%) | | | |
|---|---|---|---|---|
| | 10 | 25 | 50 | **1** content in $CHCl_3$ solution[a] |
| *cis*-**1** content (%)[b] | 54 | 31 | 22 | 71 |
| $\lambda_{max}$(nm) of *trans*-**1** | 326 | 328 | 330 | 324 |

[a] The concentration of **1** is $5.0 \times 10^{-5}$ mol $dm^{-3}$. [b] The LB membranes (20 layers) and the solution were irradiated by UV light for 5 min.

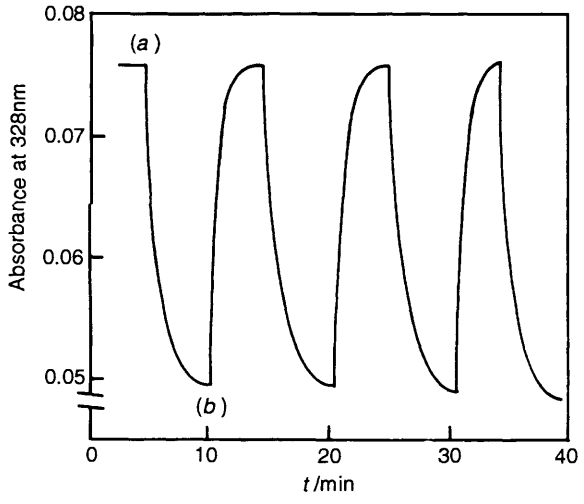



**Fig. 2** *trans–cis* Switching of **1** in LB membrane; the membrane was irradiated alternately with (*a*) UV and (*b*) visible light

irradiation for 3 min or thermally in the dark (half-lives of the thermal decay at 23 °C were *ca.* 5 h in the LB membrane and *ca.* 14 h in solution). The spectral changes were fully reversible during our experimental period. These results demonstrate clearly that the azobenzene amphiphile **1** undergoes *trans–cis* photoisomerisation reversibly in the LB membrane. It seems that the dialkyl side chains of **1** afford adequate free volume for the isomerisation in the LB membrane. This view can be rationalised by the fact that the occupied area of **1** on water ($A_0 = 0.45$ $nm^2$), which is determined by the cross section of the dioctadecyl side chains, is larger than that of the *trans*-azobenzene moiety ($A_0 = 0.28$ $nm^2$).[4]

Table 1 summarises the effects of the ratio of **1** and **2** in the LB membrane on the *cis*-isomer content of **1** at the photostationary state under UV irradiation, and on the absorption maxima ($\lambda_{max}$) of *trans*-**1** in the dark. The *cis*-**1** content increased with decreasing **1** content in the LB membrane, suggesting that much more free volume is available in the LB membrane of lower **1** content than in the membrane of higher **1** content. This is presumably because the cross-section of the carboxylic residue of **2** is smaller than that of the *trans*-azobenzene residue of **1**. It is also suggested that the amphiphile **1** is dispersed uniformly in the LB membranes because the $\lambda_{max}$ values of *trans*-**1** in the LB membranes depend linearly on the content of **1**.[8] The isolation of **1** in the LB membranes may be desirable to the photoisomerisation. It should be noted that the photoisomerisation was prohibited completely for the LB membranes prepared from monoalkyl-chain analogues of **1** and **2**, which were synthesised independently, in any composition. These results strongly support the idea that the photoisomerisation of **1** is ensured by the free volume in the LB membranes which, in turn, originates from the bulky dialkyl side chains of **1**. It is concluded that the cross-section of the side chain of the azobenzene amphiphile must be larger than that of the *trans*-azobenzene moieties (0.28 $nm^2$) for the photoisomerisation to occur in the LB membrane.

Fig. 2 illustrates the photochemical switching of **1** between *trans*- and *cis*-forms in the LB membrane (**1** content: 25%, 20 layers). Though the response time was somewhat slow, the photoresponse was stable and fully reproducible during the experimental period. Such a slow response problem seems to be common to photosensitive organic systems composed of azobenzene derivatives.[9]

Thus, we have demonstrated that the azobenzene amphiphile bearing dialkyl side chains **1** exhibits *trans–cis* photoisomerisation in LB membranes. The present results may be useful for the design and synthesis of azobenzene amphiphiles for the preparation of photosensitive LB membranes.

## Acknowledgements

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