Photochromic Reaction of a Diarylethene in Langmuir-Blodgett Films

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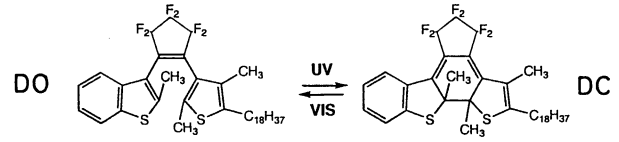
Photochemical properties of a diarylethene with a thiophene and a benzothiophene ring in Langmuir-Blodgett (LB) films have been examined. The diarylethene, which exhibited a highly effective photochromism in fluid solution, was found to show a similar photochromism in LB films. The quantum yields of coloring and breaching reactions have been determined to be 0.27 and 0.10, respectively.

Photochromic reaction has received much attention in view of fabrication of optical memories and molecular devices. Irie et al.[1] developed highly effective photochromic molecules, 1,2-diarylethene derivatives containing heterocyclic rings. Among these compounds, a non-symmetric diarylethene exhibits a photochromic reaction:



By irradiating a ring-open form (DO) with UV light, it is converted to a ring-closed form (DC). Inversely, DC returned to DO by irradiating with VIS light. Irie et al.[2] have found that this photochromic reaction in solution exhibits a high repeatability of reversible conversion, and that the reaction yields no bi-product which may arise from an irreversible reaction. It is of importance to investigate photochromic properties of this molecule in Langmuir-Blodgett (LB) film as a molecular monolayer or multilayer, since the molecular environment in LB film should be different from those in solution. We will report here on the photochromic properties of DO and DC in LB films, and discuss its applicability to a 2D optically switching molecular device which was proposed recently by Yamazaki et al.[3]

The non-symmetric diarylethene was synthesized by an elimination reaction of perfluorocyclopentene with organolithium compounds. The detail of synthetic procedure is described in Ref. 1. A mixture of diarylethene (DO) and tripalmitine dissolved in chloroform was spread on a surface of water subphase in the Langmuir trough (Joyce-Loebl). The subphase containing $CdCl_2$ (3×10^{-4} M) was kept at 20 °C and at pH 6.7 by adding $NaHCO_3$ buffer solution. Figure 1 shows the surface pressure-area isotherm of monolayers in various concentrations of DO. Sharp increases of the surface pressure are seen at a molecular area of 0.6 nm^2 corresponding to the calculated area of tripalmitine, indicating the formation of compressed monolayer. The compressed monolayer was deposited on a quartz plate under surface pressure at 22.5 mN/m. Usually fifteen layers were deposited by repetitive raising and dipping of substrate to form the Y-type multilayer. The structure of the LB multilayer is illustrated schematically in Figure 1b.

Absorption and fluorescence spectra of diarylethene are shown in Figures 2 and 3, respectively for EPA solution and for LB film. In EPA solution, DO shows absorption bands only in the ultraviolet region shorter than 350 nm, but after UV irradiation it exhibits a spectrum with absorption maxima at 540 and 412 nm. At room temperature, no fluorescence was detected for both forms of the diarylethene with the conventional steady-state fluorescence spectrometer. At 77 K, however, both forms emit fluorescences with peaks at 435 nm for DO and at 658 nm for DC. In LB film, the absorption spectrum is similar to those in solution. By UV irradiation, the absorption bands appeared at 550 and 420 nm due to the DC form. The absorption intensity at this band increased upon UV irradiation, and decreased upon VIS irradiation. An extremely weak fluorescence was detected only for DO by means of a ps time-resolved fluorescence spectrometer (Figure 3).[4]

Figures 4 and 5 show the time-evolution of absorption intensity of LB films obtained by monitoring at 550 nm (DC) upon UV (300 nm) and VIS (550 nm) irradiations, respectively. Intensities of the monochromatic light were changed in the range between 0.01 and 0.5 mW/cm^2. Under UV irradiation, the absorbance of DC increased with time, fast at earlier time but slowly at later time, and it decreased with time under VIS irradiation. The changing rate depends on the light intensity.

Let us consider the reaction kinetics following excitation of DO or DC on the basis of the reaction scheme generally accepted for the photochromic reaction.[5]

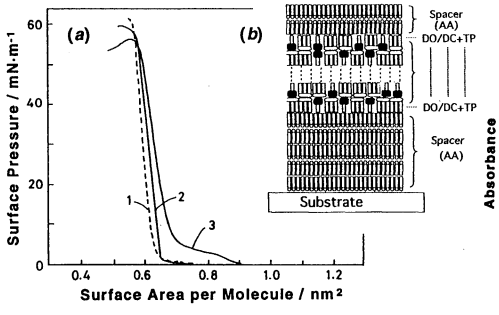


Figure 1. (a) Surface pressure-area isotherms of diarylethene-tripalmitine mixture; The concentration of diarylethene is 0 (1), 5.0 (2) and 20 mol% (3). (b) The structure of diarylethene LB multilayer film.

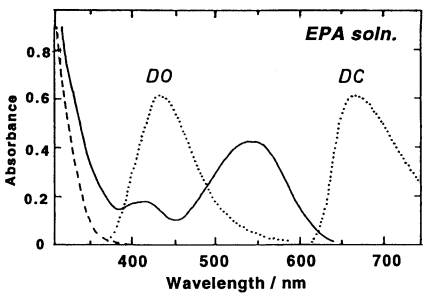


Figure 2. Absorption spectra of diarylethene in EPA solution at room temperature; DO form (– – –) and DC form (——), and fluorescence spectra of the two forms (·····) in EPA rigid glass at 77 K.

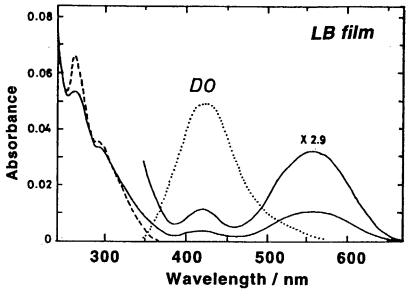


Figure 3. Absorption and fluorescence spectra of diarylethene in LB film at room temperature; DO form (– – –) and DC form (——) in absorption. The fluorescence (·····) was observed for DO.

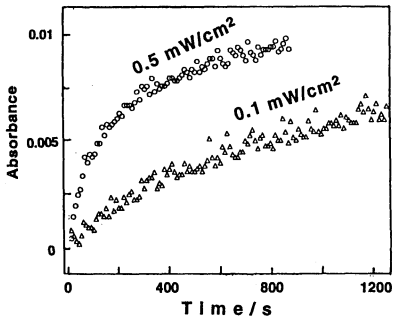


Figure 4. Absorbance changes at 550 nm in DO-LB film under irradiation of UV (300 nm) light.

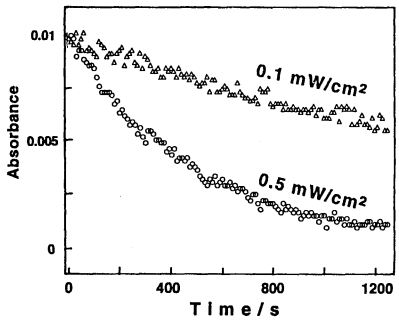


Figure 5. Absorbance changes at 550 nm in DC-LB film under irradiation of VIS (550 nm) light.

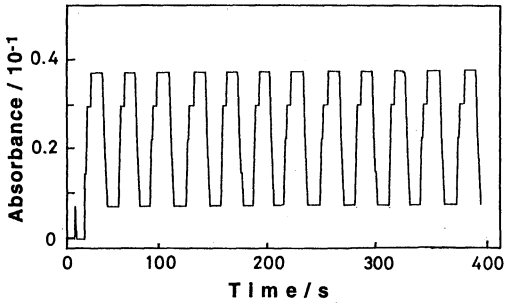
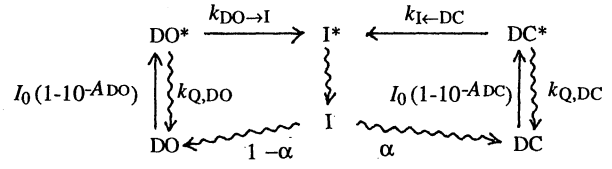


Figure 6. Repeated reversible property in the photochromic reaction DO ↔ DC of diarylethene LB film. Change in absorbance of DC at 550 nm is shown.



where I* is an intermediate in the excited state and I is an unstable intermediate in the ground state from where deactivation occurs into DC and DO with a branching ratio of α and 1-α, respectively. $k_{DO\rightarrow I}$ and $k_{I\leftarrow DC}$ are the rate constants of forward and backward reactions; $k_{Q,DO}$ and $k_{Q,DC}$ are the rate constants of deactivation to the ground state (S_0); and I_0 (1 - 10^{-A}) is the number of molecules of DO or DC (mol·cm^{-2}·s^{-1}) excited into the lowest singlet state (S_1) with I_0 being the irradiation light intensity (Einstein·cm^{-2}·s^{-1}) and A being the absorbance of DO or DC. One should note that DO and DC in LB film show weak or no fluorescence indicating a very short S_1-lifetime (the fluorescence lifetime is 30 ps in DO), and that the reaction quantum yields are fairly large, as shown later. This may suggest that the reaction pathways DO*→I*, I*←DC*, and I*→I are fast relative to other deactivation processes. We consider here that the initial state of the sample before irradiation is purely DO or DC, and that the time courses of the reactions DO→DC and DO←DC are examined by monitoring the change of DC concentration which can be measured from the DC absorption intensity at 550 nm. The changes of the DC concentration (mol·cm^{-2}) with time are expressed approximately in the following equations:[5]

$$\frac{d[DC]}{dt} = I_0\,(1-10^{-A_{DO}})\,\alpha\left(\frac{k_{DO\rightarrow I}}{k_{Q,DO}+k_{DO\rightarrow I}}\right) \qquad (1)$$

$$d[DC] = I_0\,(1-10^{-A_{DO}})\,\alpha\,\Phi_{DO\rightarrow DC}$$

for the reaction DO→DC under irradiation of DO at 300 nm, where $\Phi_{DO\rightarrow DC}$ is the reaction quantum yield; and

$$\frac{d[DC]}{dt} = -I_0\,(1-10^{-A_{DC}})\,\alpha\left(\frac{k_{I\leftarrow DC}}{k_{Q,DC}+k_{I\leftarrow DO}}\right)$$

$$d[DC] = -I_0\,(1-10^{-A_{DC}})\,\alpha\,\Phi_{DO\leftarrow DC} \qquad (2)$$

for DO←DC under irradiation of DC at 550 nm. It should be noted that Eq.1 holds only in the initial time region after the irradiation at 300 nm is started, because the irradiation causes excitation of the photoproduct DC. Eqs.1 and 2 show that the DC concentration increases and decreases, respectively, linearly with time in the earlier time region where the concentration change in DO or DC is negligibly small relative to the initial concentration. From the slope of the change, the quantum yields of the photochemical reactions $\Phi_{DO\rightarrow DC}$ and $\Phi_{DO\leftarrow DC}$ can be evaluated with known values for I_0, A_{DO} and A_{DC}. We calculated the initial slopes of the change of DC concentration with time from the absorbance curves shown in Figures 4 and 5. The value of the molar extinction coefficient of DC was taken from the value obtained for benzene solution of DC, ε=8200. The results are $\Phi_{DO\rightarrow DC}$ = 0.27 ± 0.07 and $\Phi_{DO\leftarrow DC}$ = 0.10 ± 0.05 for different light intensities ranging from 0.01 to 0.5 mW/cm^2. These values of quantum yields in LB films are smaller than the value in non-polar solvent (0.41).[1] The smaller values may arise from restriction in molecular space necessary for the conformational change of diarylethene.

To test an applicability of the diarylethene LB film to functional materials, the cyclic behavior of the reversible reaction was examined by the alternating irradiation of UV and VIS light. As shown in Figure 6, a good repeatability is achieved in LB film, and allows one to apply this LB film to optically switching devices.[3]

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References and Notes

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