ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 92 (1995) 111–116

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Polarized photoelectrochemical reaction of an azobenzene derivative in Langmuir–Blodgett films

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Abstract

Anisotropic photoisomerization and photoelectrochemical interconversion of an azobenzene derivative in a Langmuir–Blodgett film were investigated using polarized UV–visible spectroscopy. At short irradiation times, in-plane selective photoelectrochemical interconversion of *trans*-azobenzene → *cis*-azobenzene → hydrazobenzene occurred exclusively along the polarization plane of the linearly polarized UV radiation. With prolonged irradiation times, reorientation of the azobenzene moiety was induced during photoisomerization by successive polarized UV excitations. The reorientation was attributed to steric hindrance due to the different molecular configurations of *trans*-azobenzene and *cis*-azobenzene.

Keywords: Polarized reaction; Photoelectrochemistry; Azobenzene derivative; Langmuir–Blodgett films

1. Introduction

In recent years, the development of azobenzene derivatives in ordered monolayer and multilayer films has received increasing interest for application as storage media or switching elements in optoelectronic systems [1–4]. Particular interest has focused on the uniform, ultrathin film structure and the photochemical and electrochemical properties which can be varied reversibly.

The use of linearly polarized light offers a fundamentally new approach to induce optical anisotropy in assembled photochromic films. Recent reports have shown that azobenzene moieties undergo trans → cis photoisomerization in such a way that desirable physical and chemical properties, such as the dichroism of homeotropic and planar oriented films of liquid crystalline polymers [5–7], linear photopolymerization [8], birefringence [9,10] and in-plane anisotropic photobleaching [11], can be modified by polarized light. Thus far, linearly polarized irradiation has been confined to trans → cis photoisomerization.

The electrochemical and photoelectrochemical properties of azobenzene moieties in solution have been investigated during the past few decades [12,13]. A novel photoelectrochemical hybrid "one-way" process, i.e. *trans*-azobenzene → *cis*-azobenzene → hydrazobenzene(HAB) → *trans*-azobenzene interconversion, has been observed in azobenzene derivatives contained in Langmuir–Blodgett (LB) films [2,14]. Recently, we have developed a new type of in-plane selective interconversion system, by the use of successive polarized UV irradiations, incorporating the photoelectrochemical hybrid technique [15]. The interconversion is induced successively and exclusively along distinct polarization directions at the same position in the LB film. This provides a prospective storage process for improving storage density. In this paper, we present further insight into this interconversion system. Polarized in situ difference absorption spectroscopy allows for the detailed and uninterrupted investigation of the in-plane selective photoelectrochemical reaction. Moreover, reorientation of the azobenzene moieties in the LB film is observed after prolonged linearly polarized UV irradiation due to photoisomerization. Together with the electrochemical investigation, it is found that reorientation is predominantly due to steric hindrance caused by the disparity in the molecular configurations of *trans*-azobenzene and *cis*-azobenzene.

2. Experimental details

The studies were performed with 4-octyl-4′-(5-carboxy-pentamethylene-oxy)-azobenzene (ABD), which was purchased from Dojindo Laboratory (Kumamoto, Japan). The

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SSDI 1010-6030(95)04152-4

chemical was of reagent grade and was used without further purification.

The monolayer was spread from a 1.8 mM chloroform solution onto a standard LB trough (Kyowa Kaimen, HBM-AP). A 0.2 mM $CdCl_2$ aqueous solution was used as the subphase and kept at 20 °C. By the conventional vertical dipping method, monolayer and multilayer films were deposited onto SnO_2 glass and CaF_2 substrates respectively, with a dipping speed of 5 mm min^{-1} at a constant surface pressure of 25 mN m^{-1}. LB film fabrication was carried out under dim red light to ensure that all the azobenzene moieties were trans isomers.

The polarized UV–visible spectra of a nine-layer film of ABD on a CaF_2 substrate, before and after polarized UV illumination, were recorded on a Shimadzu UV-3101PC UV–visible spectrophotometer with dichroic sheet polarizers. UV irradiations were carried out using a 500 W xenon lamp, employing two bandpass filters and a polarizer to obtain polarized light with a wavelength of 365 nm for the trans→cis photoisomerization. The polarized irradiations were set with electric fields parallel and perpendicular to the film dipping direction respectively. Identical light intensities of the UV beams were aligned in mutually perpendicular directions.

Polarized photoelectrochemical measurements were carried out using a home-built system as described previously [15]. The SnO_2 glass substrate with an ABD monolayer film was attached to the electrochemical cell and served as the working electrode. A Pt wire and Ag/AgCl (saturated KCl) were used as counter electrode and reference electrode respectively. After UV irradiation, a potential sweep was applied to the film by a potentiostat (Hokuto Denko, HAB-151). Faradaic currents related to cis→HAB reduction and HAB→trans oxidation were detected. Polarized in situ difference absorption spectra corresponding to each step of the photoelectrochemical process were recorded using the same electrochemical cell.

3. Results and discussion

3.1. In-plane selective interconversion

Excitation by linearly polarized UV light allows the structure of the ABD LB film to be designed with characteristic properties due to the change in anisotropy [15]. Polarized UV–visible spectroscopy affords an efficient means of investigation of the in-plane selective character of the azobenzene derivative ultrathin film. The anisotropic nature of the nine-layer as-transferred ABD film on a CaF_2 substrate prior to excitation is shown in Fig. 1. The absorption band around 340 nm, assigned to the π–π^* transition of *trans*-azobenzene [16–18], shows greater absorption for the polarized probe beam set parallel to the film dipping direction ($A_\parallel$) than for the polarized probe beam set perpendicular to the film dipping direction ($A_\perp$). This indicates that the projections of the π–π^* transition moments, i.e. the long axes of the azobenzene moieties, are distributed anisotropically in the surface plane of the as-transferred film, and the *trans*-azobenzene moieties orientate preferentially along the film dipping direction [19,20]. Similar absorption dichroism is also obtained for the monolayer film on the SnO_2 substrate.

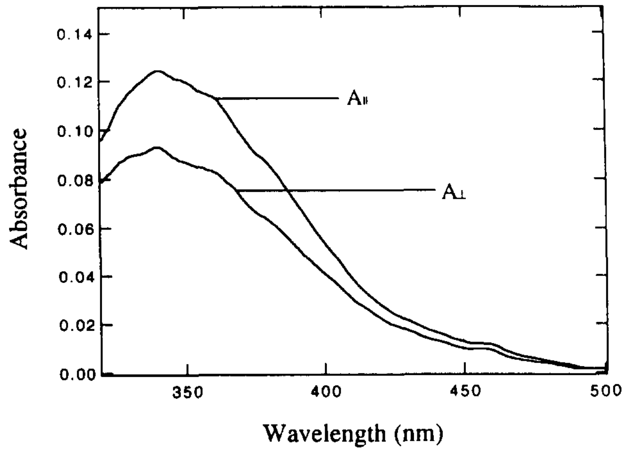

Fig. 1. Polarized absorption spectra of a nine-layer LB film prior to excitation. $A_\parallel$ and $A_\perp$ correspond to the absorbances of the film with polarizers aligned parallel and perpendicular to the film dipping direction respectively.

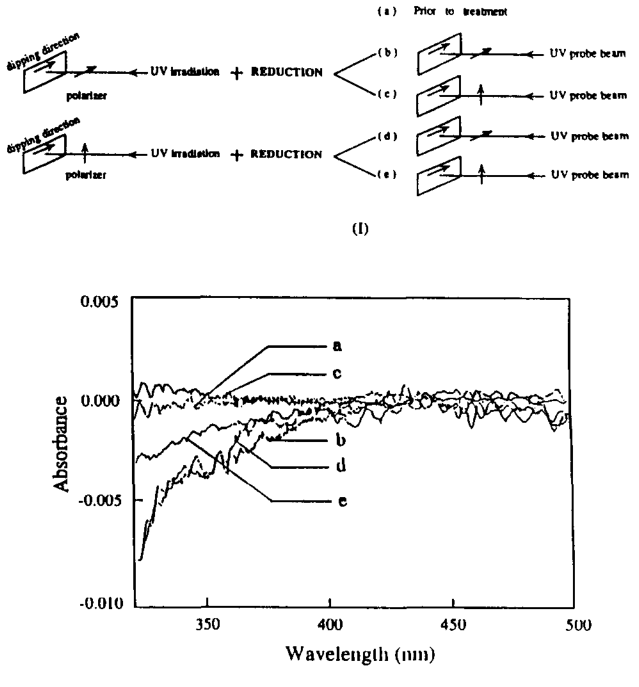

Fig. 2. (I) Schematic illustration of the procedure of measurement of the absorption spectra. (II) Corresponding polarized in situ difference spectra of an ABD monolayer film with respect to the spectrum of the as-transferred film. Irradiation for 20 s in the orthogonal directions.

The polarized in situ difference absorption spectra in Fig. 2 give a direct observation of the in-plane selective interconversion process. The difference spectrum of the ABD monolayer film is measured with respect to the spectrum of the as-transferred film, setting the polarization plane of the probe beams parallel and perpendicular to the film dipping direction, according to the schematic illustration shown in Fig. 2 (part (I)). The film is first treated with 20 s of polarized UV irradiation under −0.34 V cathodic potential. A clear decrease in the π–π^* band is detected along the polarization direction (Fig. 2(b)), whereas little spectral change is detected in the orthogonal direction (Fig. 2(c)). Typically, the occurrence of trans → cis photoisomerization is characterized by a decrease in the π–π^* band of *trans*-azobenzene and an increase in the n–π^* band of *cis*-azobenzene (around 450 nm) [16,18]. Since HAB has no absorption band in the wavelength range of our measurements, no absorption peak appears when photoinduced *cis*-ABD is electrochemically reduced to HAB. The disappearance of the n–π^* band after reduction serves as an indication of the cis → HAB interconversion. As shown in Fig. 2 (part (I)), polarized irradiation of the film at a constant potential bias of −0.34 V results in photoisomerization to the cis isomer, which almost simultaneously transforms into HAB. Therefore the trans → cis → HAB process is marked by only a decrease in the π–π^* band. The anisotropic spectral change between Figs. 2(b) and 2(c) demonstrates that the trans → cis → HAB interconversion occurs with the highest probability along the polarization direction of the UV radiation (parallel to the film dipping direction), while the molecules aligned perpendicular to the film dipping direction are almost unchanged. Whilst maintaining a potential of −0.34 V, another 20 s of polarized UV irradiation with the electric field perpendicular to the film dipping direction was applied to the same film at the same position. The absorption spectrum along the film dipping direction (Fig. 2(d)) remains the same as that after the first irradiation, whereas a clear spectral change is recorded in the orthogonal direction (Fig. 2(e)). This observation indicates that the trans → cis → HAB interconversion is exclusively induced along the polarization direction of the second UV radiation exposure (perpendicular to the film dipping direction), independent of the first photoelectrochemical process.

It is apparent that the decrease in the absorbance of the π–π^* band in Fig. 2 is different for the two orthogonal directions. The decrease induced by irradiation parallel to the film dipping direction ((a) → (b)) is greater than that corresponding to irradiation perpendicular to the film dipping direction ((c) → (e)). In other words, the number of molecules undergoing trans → cis → HAB reaction is different along the mutually perpendicular directions. This is due to the preferential orientation of the azobenzene moieties along the film dipping direction in the as-transferred ABD film (Fig. 1). In addition, a blue shift of the π–π^* transition band is observed in the spectrum of the ABD LB film compared with ABD in solution. This indicates the existence of H-like aggregation in the ultrathin film [21,22]. It should be noted that the aggregate acts as a reaction unit for the successive polarized trans → cis → HAB interconversion. The aggregation effect plays an important role in the in-plane selective reaction [15].

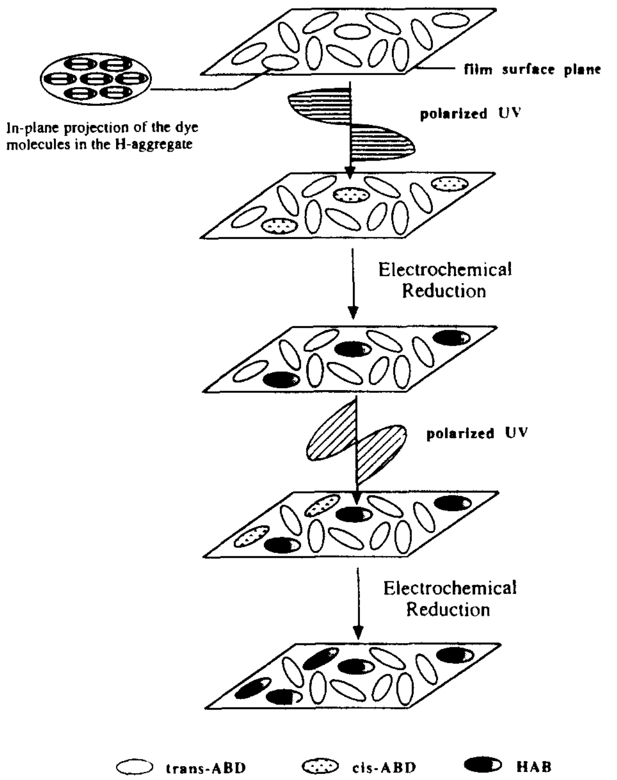

Fig. 3. Schematic diagram of the in-plane selective interconversion in an ABD LB film.

The above results of the spectroscopic investigation are described schematically in Fig. 3. *Trans*-ABD is converted into *cis*-ABD with the highest probability for those aggregates which have transition moments parallel to the polarization plane of the UV illumination beam, whereas the molecules in the other aggregates with different orientations are hardly influenced. The product of in-plane polarized photoisomerization is electrochemically replicated to be HAB, which is thermally stable and, more importantly, insensitive to the actinic light for both trans → cis and cis → trans photoisomerizations. The electrochemical procedure can "freeze" the first photoisomerization event to yield thermally stable HAB in the aggregates with an orientation along the polarization direction. Therefore when the polarized UV beam perpendicular to the original direction irradiates the same position for the second time, trans → cis isomerization is mainly induced along the second direction. The photoisomerization process induced by the second radiation exposure yields HAB, which is fixed in the film along the second direction. This in-plane selective interconversion system provides a prospective storage process for reading and writing information along distinct polarization directions which can improve storage density.

3.2. *In-plane reorientation*

The above in-plane selective photoelectrochemical process was performed using 20 s of UV irradiation, which is sufficiently short a time to ensure interconversion with low yield

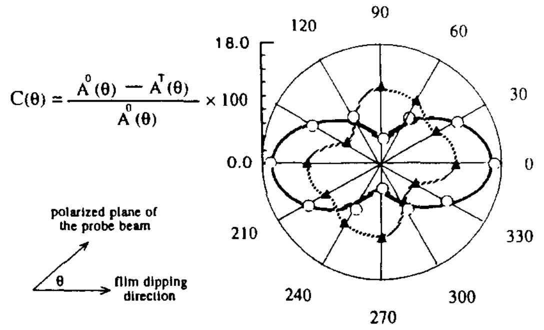

Fig. 4. Polarized photoreaction parameter $C(\theta) = [A^0(\theta) - A^T(\theta)]/A^0(\theta) \times 100$ depicted as the vector length vs. the angle between the plane of polarization of the incident probe beam and the film dipping direction (polarogram) of a nine-layer ABD film. Polarized UV irradiations for 150 s and 300 s with electric fields parallel (full line) and perpendicular (broken line) to the film dipping direction respectively were successively applied to the film.

so that the unreacted *trans*-azobenzene moieties keep their in-plane orientation during consecutive polarized excitations [15]. A similar in-plane selective photochemical process is also feasible at short irradiation times [15]. With prolonged polarized illumination, trans → cis photoisomerization is always combined with a reorientation of the dye moieties perpendicular to the polarization plane of the radiation beam [4,23]. Reorientation of azo dyes is sufficient to manipulate the orientation of liquid crystals [6,7,24]. As described later, steric hindrance plays a significant role in the occurrence of the reorientation of ABD in LB films.

Polarized absorption spectroscopy of a nine-layer film of ABD on a CaF_2 substrate was investigated using prolonged polarized UV illumination. As reported previously [25], the yield of trans → cis photoisomerization can be estimated by the decrease in the absorbance of the π–π^* band after UV irradiation. On polarized UV illumination, a parameter [11]

$$C(\theta) = [A^0(\theta) - A^T(\theta)]/A^0(\theta) \times 100 \qquad (1)$$

is used to characterize the conversion process. Here θ is the angle between the polarized plane of UV measurement and the film dipping direction. The absorbances of the π–π^* band before and after polarized UV irradiation as a function of the irradiation time T are expressed as $A^0(\theta)$ and $A^T(\theta)$ respectively. During linearly polarized UV irradiation of the ABD LB film, with the polarization planes of irradiation aligned parallel and perpendicular to the film dipping direction, the dependence of C on the angle θ is illustrated in Fig. 4, in which $C(\theta)$ is depicted as the length of the vector vs. the angle θ between the polarizer and film dipping direction.

After the first polarized light exposure of the film (full line in Fig. 4), with the electric field parallel to the film dipping direction, the value of $C(\theta)$ is anisotropic with maxima at 0° and 180°. According to Eq. (1), $C(\theta)$ represents the yield of trans → cis photoisomerization in the direction with angle θ relative to the film dipping direction. Fig. 4 explicitly demonstrates that trans → cis photoisomerization is selectively induced with the highest probability along the polarized plane of the prolonged (150 s) UV irradiation ($\theta = 0°$). This result is consistent with that discussed in Fig. 2. However, when the second 150 s radiation exposure, with the polarization plane aligned perpendicular to the film dipping direction, is applied to the same position, no remarkable spectral change is detected in any direction. Along the same direction, when the irradiation time is prolonged to 300 s (broken line in Fig. 4), the value of $C(90°)$ increases together with a decrease in $C(0°)$, which is very different from the observations after short UV irradiation times. The increase in $C(90°)$ corresponds to the anisotropic trans → cis photoisomerization along the polarized irradiation direction. If the second polarized UV illumination only caused preferential trans → cis photoisomerization in the $\theta = 90°$ direction, $C(0°)$ would retain its value after the first radiation exposure. The decrease in $C(0°)$ in Fig. 4 indicates that the amount of *trans*-ABD in the film dipping direction increases after the second radiation exposure relative to the amount after the first radiation exposure. It is inferred that reorientation occurs together with the second selective trans → cis photoisomerization in the $\theta = 90°$ direction.

Prior to illumination, all azobenzene moieties are trans isomers in the LB film. Trans → cis photoisomerization causes an increase in the area per molecule by one-third due to the different molecular configurations of *trans*-ABD and *cis*-ABD [26]. Prolonged UV irradiation stimulates more *trans*-azobenzene moieties to participate in the conversion, so that the molecules in the film are packed more closely than for shorter irradiation times. Although the photoisomerization induced by the first 150 s of irradiation is mainly observed along the polarization plane of the radiation, the resulting steric hindrance strongly blocks the conversion by the second 150 s of polarized irradiation in the perpendicular direction. When the irradiation time is increased further to 300 s, with the polarization plane perpendicular to the film dipping direction, selective trans → cis photoisomerization is finally induced along the polarization direction; however, cis → trans isomerization occurs predominantly due to the steric hindrance caused by the first radiation exposure [26]. The final state of the cis → trans reverse reaction is most likely to be induced perpendicular to the polarization direction of the second illumination due to the continued excitation of the molecules in the parallel direction [24]. This results in an increase in the amount of the trans isomer along the film dipping direction after the second polarized UV radiation exposure (broken line in Fig. 4). In the polarized absorption spectrum of the LB film on prolonged UV irradiation, a slight blue shift of the π–π^* band is observed in the direction with preferential trans → cis photoisomerization. The high yield of photoisomerization induced by prolonged irradiation causes a decrease in the separation between the adjacent azo dyes in each reacted aggregate due to the increase in molecular area accompanying trans → cis photoisomerization. Therefore the angle between the long axes of the azobenzene moieties and the film surface normal tends to decrease [21]. The form of the aggregates in the film is probably transformed through a

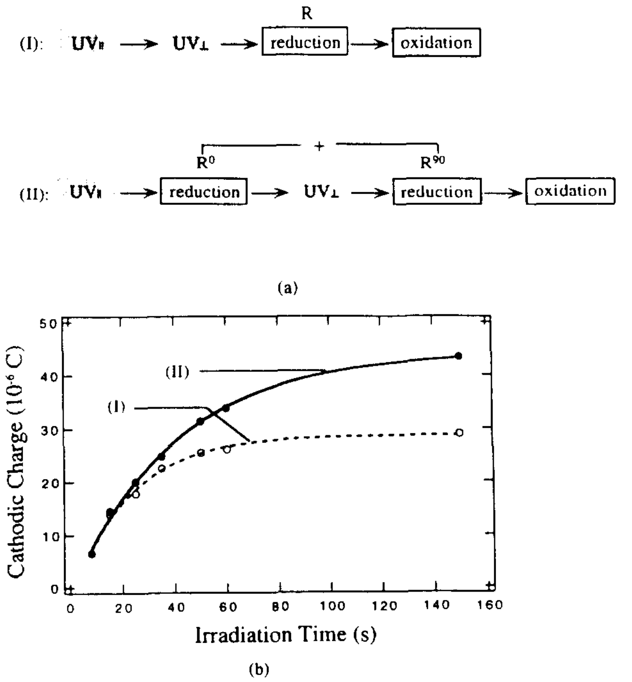

Fig. 5. Dependence of the cathodic charge on the irradiation time (b) for the sequence of polarized photoelectrochemical procedures shown in (a). $UV_\parallel$ and $UV_\perp$ indicate the polarized UV irradiation parallel and perpendicular to the film dipping direction respectively. R^0 and R^{90} represent the electrochemical reductions of photoinduced *cis*-ABD to HAB corresponding to the polarized UV irradiations with the polarization planes parallel and perpendicular to the film dipping direction respectively.

mechanism which is not yet clearly understood. The aggregate is assumed to behave as a reaction unit during successive conversions.

Further photoelectrochemical investigation provides strong evidence of reorientation which is principally induced by steric hindrance. Cyclic voltammograms of an ABD monolayer film on an SnO_2 substrate were recorded before and after polarized UV irradiation. Prior to UV irradiation, no reduction or oxidation peaks were observed during the potential sweep from −0.5 V to +0.5 V. This implies that *trans*-ABD is electrochemically inactive in the applied potential range [2,14]. However, after polarized UV irradiation, prominent redox peaks appear in the cyclic voltammogram. The cathodic charge of the reduction peak corresponds directly to the number of molecules converted from photoinduced *cis*-ABD to HAB along the distinct polarization direction, based on almost 100% current efficiency. Fig. 5 shows the sequence of the polarized photoelectrochemical procedure (Fig. 5(a)) and the corresponding graphs presenting the dependence of the cathodic charge on the irradiation time (Fig. 5(b)). When the monolayer film of ABD is consecutively irradiated by polarized UV beams with electric fields parallel and perpendicular to the film dipping direction and a sweeping cathodic potential is applied to the film, a reduction peak is observed. The related cathodic charge corresponds to the total photoinduced *cis*-ABD molecules in the two mutually perpendicular directions. The dependence of the cathodic charge on the irradiation time for this procedure is displayed as curve (I) in Fig. 5(b). However, a different charge dependence is obtained under the following conditions: first, polarized UV illumination parallel to the film dipping direction is applied, followed by a cathodic potential to reduce the photoinduced *cis*-ABD to HAB (R^0); next, a polarized UV beam perpendicular to the film dipping direction is used to irradiate the same film for a second time; the photoinduced *cis*-ABD is similarly reduced to HAB and a reduction peak (R^{90}) is obtained in the cyclic voltammogram. Curve (II) in Fig. 5(b) shows the dependence of the sum of the cathodic charges regarding R^0 and R^{90} on the irradiation time.

As shown in Fig. 5(b), when the irradiation time is less than 20 s, curves (I) and (II) are similar. However, with an increase in the irradiation time, the difference between the two curves becomes obvious. According to Fig. 5(a), (I) represents a similar process to that of the photoisomerization described in Fig. 4. In contrast, process (II) introduces HAB to the isomerization system. HAB possesses a flexible linear configuration and exhibits an area per molecule analogous to that of *trans*-azobenzene. Trans → cis photoisomerization induces an expansion in the area per molecule, whereas the cis → HAB electrochemical interconversion causes a contraction. At short irradiation times, the similarity of curves (I) and (II) in Fig. 5(b) indicates that the resulting yield of trans → cis photoisomerization is limited and that the orientation of unreacted azobenzene moieties along specific directions is unaffected by either photoisomerization or photoelectrochemical interconversion. This is identical with the result obtained in Section 3.1. In the case of prolonged irradiation, the number of photoinduced *cis*-ABD molecules in process (II) is much larger than that in process (I). This presumably results from the similar molecular configuration of HAB and *trans*-ABD. On prolonged UV irradiation with the electric field parallel to the film dipping direction, molecules are packed more closely due to the expansion in area by trans → cis photoisomerization. However, during the subsequent cis → HAB interconversion, the steric hindrance is mostly relieved. Therefore when the second polarized UV radiation exposure in the orthogonal direction is applied to the same film, the photoisomerization is induced with higher yield relative to the case without electrochemical contraction. This confirms that it is the steric hindrance induced by trans → cis photoisomerization which leads to the reorientation of the *trans*-azobenzene moieties in the ABD LB film as inferred according to Fig. 4.

4. Conclusions

The experiments described here show that polarized UV–visible spectroscopy can be used to study efficiently the in-plane selective reactions of ABD LB films. In situ difference absorption spectroscopy demonstrates that, by the use of successive linearly polarized UV irradiations in orthogonal directions, trans → cis → HAB interconversion can be induced consecutively and exclusively along distinct polarization directions in the ABD film. On prolonged UV irradiation with polarized light, azobenzene moieties undergo independent trans → cis isomerization along the polarization plane of the UV radiation during initial excitation. However, selective trans → cis photoisomerization accompanied by reorientation is found after the second radiation exposure in the direction perpendicular to the first irradiation. The incorporation of an electrochemical method confirms that the reorientation can be ascribed to steric hindrance due to the different molecular configurations of *trans*-azobenzene and *cis*-azobenzene.

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