Observation of Nanometer-Level Structural Changes by the Trans−Cis Transition of an Azobenzene Derivative Monolayer with a Radioactive Tracer

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We report direct observation of radioisotopically labeled molecular structural changes in these photochemical processes with the interference effect of electron-capture X-ray emitted by nuclear transformations in radioactive atoms. The azobenzene derivative molecules were specifically reacted with the radioactive atoms (^{111}In) by using ionic bonds between the carboxyl groups in the azobenzene derivatives and the radioactive atoms. The trans−cis isomerization of the monolayer on the substrate was distinctly reflected in the period of the observed interference fringes. We measured the trans−cis photoisomerizations on the same substrate during seven alternations by using UV−visible light irradiation. As a result, we observed irreversible photochromism in the monolayer of azobenzene derivatives on the substrate because of the close packing of chromophores.

1. Introduction

Reversible photochromisms of molecules based on cis−trans isomerization,[1] spiropyran−merocyanine isomerization,[2] and dimerization[3] play an important role in many area, such as molecular systems and their applied fields. The photochemical processes and the characterization of azobenzene derivatives are usually analyzed by UV−visible spectroscopy[1] on the substrate, surface pressure−area isotherms at the air−water interface,[2] and other techniques.[4] Although information about the azobenzene chromophores on the substrate can be obtained by the UV−visible absorption spectra, no direct observation of molecular structural changes in these photochemical processes have been reported so far. We observed the conformational changes of the ^{111}In-labeled azobenzene derivative monolayer by using the interference effect of monochromatic radiation emitted by nuclear transformations in radioactive atoms. This method, interference pattern from radioisotopes (IPR),[5,6] can effectively detect nanometer-level structural changes of radioactively labeled molecules.

2. Theoretical Section

The observed characteristic X-ray interference fringes are generated between the direct monochromatic emissions from the radioactive atoms and the emissions totally reflected by the substrate surface, as shown in Figure 1.[5] The vertical position of a radioactive atom relative to the substrate surface can be determined by analyzing the measured interference fringes, because these fringes depend strongly on the distance between X-ray-emitting atoms and the surface of the substrate.
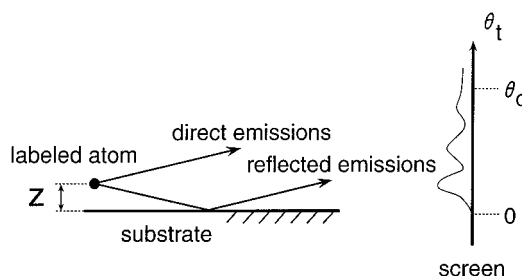

Figure 1. Schematic of the interference phenomenon of monochromatic radiation from a radioactive atom embedded within a sample. Z represents the distance between the radioactive atom and the substrate surface. θ_t is the take-off angle of monochromatic radiations.

We modeled three homogeneous mediums (air, a Langmuir−Blodgett (LB) film containing an azobenzene derivative layer, and a Pt substrate) as stratified media (Figure 2). The theoretical pattern from the stratified media can be obtained on the basis of the optical electromagnetic wave solution of Maxwell's equations on each interface and reciprocity.[7−9] In other words, a calculation of the X-ray intensity from the z coordinate for the take-off angle θ_t is identical to that of the incident X-ray field at coordinate z for the glancing angle (θ_t).[10−12]

When radioactive atoms act as X-ray sources having the distribution N, the yield Y is given by

$$I(\theta_t, z, t) = |E_d + E_r|^2 \exp(-\lambda t) \tag{1}$$

and

$$Y(\theta_t) = \int N(z)\ I(\theta_t, z, t)\ \mathrm{d}z \tag{2}$$

where $I(\theta_t, z)$ is the intensity of X-rays due to interference effects

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(a) trans condition

●:^{111}In

azobenzene derivatives: C_8H_{17}—〇—N=N—〇—$O(CH_2)_5COOH$
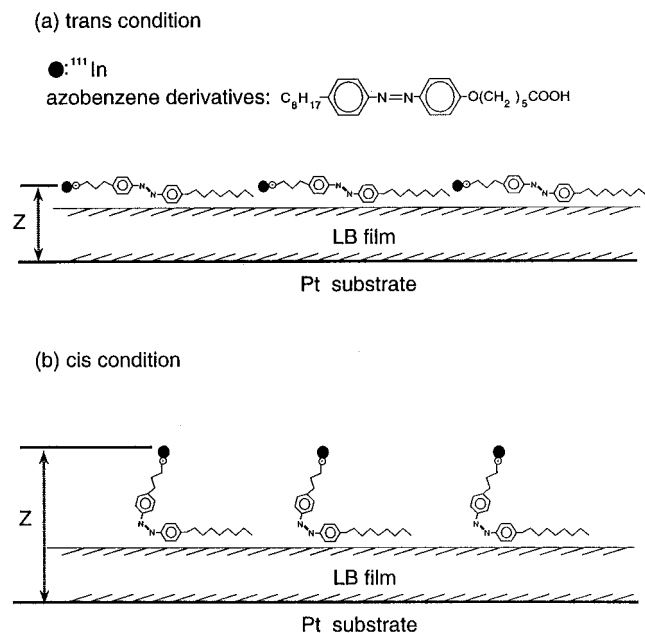

(b) cis condition

Figure 2. Schematic cross-sectional view of the azobenzene derivative monolayer for the (a) trans and (b) cis conditions. This view is one model in which the main axes of the azobenzene derivative molecules in the trans form are horizontal to the surface of the Pt substrate.

between the direct and totally reflected emissions from the z coordinate at the take-off angle (θ_t), E_d and E_r are E-field plane waves of the direct and reflected emissions, and $N(z)$ is the distribution of labeled atoms, in this case, ^{111}In, at a distance z from the substrate surface. The term λ is the proportionality constant known as the decay constant ($=\ln 2/t_{1/2}$), and t is the time from the start of observation of the interference pattern.

3. Experimental Section

3.1. Sample Preparation. We observed the nanometer-level conformational changes of the ^{111}In-labeled azobenzene derivative monolayer by using ionic bonds between ^{111}In atoms and the carboxyl groups in the azobenzene derivatives. Figure 2 shows the cross-sectional view of the sample, which is a ^{111}In-labeled azobenzene derivative (4-octyl-4′-(5-carboxypentamethyleneoxy)azobenzene) Langmuir monolayer deposited on a LB film (four bilayers of cadmium arachidate) on a Pt substrate. The ^{111}In-labeled azobenzene derivative monolayer was obtained by spreading a chloroform solution of the azobenzene derivative molecules on an aqueous subphase solution containing ^{111}In salts. The pH (6.5) of the subphase was adjusted with a 0.5 M sodium acetate buffer and 0.5 M NaOH. One milliliter of ^{111}In solution in the form of indium chloride (InCl$_3$) (Amersham International plc.) was suspended in the subphase and incubated at room temperature for about 10 min. The ^{111}In-labeled azobenzene derivative (trans-type) monolayer was transferred to the surface of the substrate (30 mm × 5 mm) at 10 mN/m by the horizontal dipping method, as shown in Figure 3. We confirmed the photoisomerizations of this film during ten alternations by using the UV−visible absorption spectra. When the azobenzene derivative monolayer was transferred to the substrate at higher pressures, it was difficult to monitor the photoisomerization of this monolayer film because of the close packing of the chromophores. Thus, this monolayer is expanded on the substrate. Figure 4 shows the surface pressure−area isotherms of the azobenzene derivative molecules in the trans condition and one in the cis condition (as reference data). After the azobenzene derivative monolayer was transferred to the substrate, we confirmed the sample surface on the substrate was hydrophilic. Thus, the transferred azobenzene monolayer was rinsed with ultrapure water. We need the thin (LB) film between the ^{111}In-labeled azobenzene derivative layer and the Pt substrate surface in order to observe typical interference fringes. We confirmed that the structure of this LB film (four bilayers of cadmium arachidate) did not change with UV−visible light irradiation.
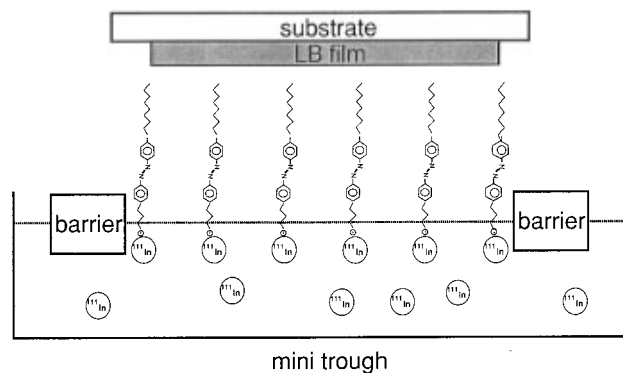

mini trough

Figure 3. Schematic illustration of the azobenzene derivatives at the air−water interface. We used the horizontal dipping method in order to produce the specifically labeled azobenzene derivative monolayer.
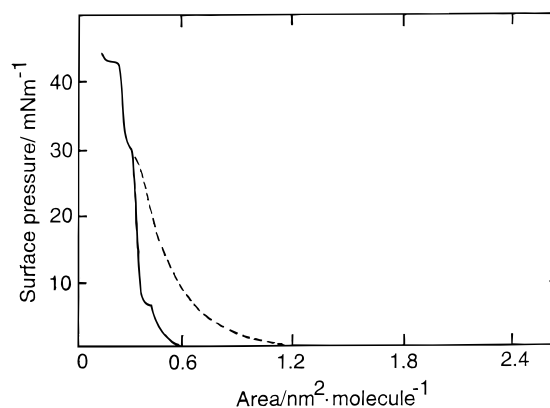

Figure 4. Surface pressure−area isotherms of the azobenzene derivatives for the trans condition (solid curve) and the cis condition (dashed curve) at 20.0 °C.
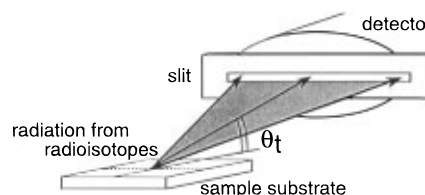

Figure 5. Schematic drawing of the experimental apparatus for an IPR measurement.

The Pt substrate consists of 200 nm of Pt evaporated onto a chromium-coated glass. The specific radioactivity of the ^{111}In atoms (half-life $t_{1/2} = 2.83$ days) was 370 MBq/μg. We measured the total amount (6.0 MBq) of the ^{111}In atoms transferred onto the Pt substrate by counting the γ-ray peak area (245 keV) using a pure Ge detector (EG&G ORTEC).

Irradiation was carried out using a 100 W pressure mercury lamp (UVP Inc., B-100A) through cut filters. We observed the trans conditions of the monolayer after visible light irradiation for 20 min except for the measurement of the first trans conditions, and the UV light irradiation was continued for measurement of cis conditions.

3.2. Instrumentation. Figure 5 is a schematic drawing of the experimental apparatus for the measurement of characteristic X-ray interference. ^{111}In atoms emit cadmium Kα (23.2 keV), Kβ (26.1 keV), γ-ray radiation (171.3 keV, 245.4 keV). In these experiments, we measured electron-capture X-rays (Cd Kα) from labeled ^{111}In atoms. The angular distribution of the electron-capture X-rays was measured by scanning the slit along the transverse direction. The electron-capture X-rays from ^{111}In atoms were monitored by a pure Ge detector through a narrow slit. A slit (30 μm vertical and 10 mm horizontal) was placed before a detector at a distance of 200 mm from the sample in order to determine the take-off angle (θ_t). The angular resolution in the measured region was less than 0.3 mrad. The measured time for one interference pattern was about 12 h.
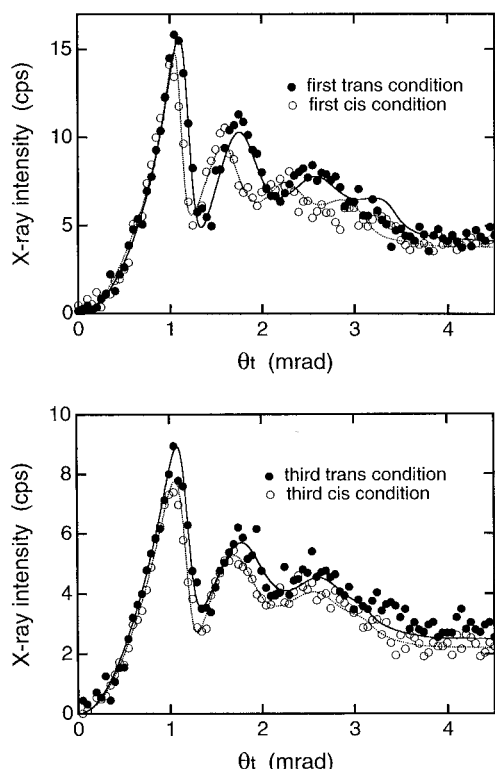
Figure 6. Measured angular distribution (closed circles) and theoretical pattern (lines) of X-rays from ^{111}In for the trans and cis conditions.

Table 1. Observed Positions z_0 of ^{111}In Atoms from the Pt Substrate and the Distribution Width δz at Each Stage

sample condition	z_0 (nm)	δz (nm)
first trans	24.4 ± 0.5	4.9 ± 0.4
first cis	30.6 ± 0.5	6.2 ± 0.6
second trans	24.5 ± 0.6	4.9 ± 0.5
second cis	26.8 ± 0.5	5.5 ± 0.5
third trans	24.6 ± 0.5	5.4 ± 0.4
third cis	25.9 ± 0.5	4.9 ± 0.6
fourth trans	24.9 ± 0.5	4.3 ± 0.5

retical curves in Figure 6a were generated by substituting a mean ^{111}In position of z_0 (first trans) = 24.4 ± 0.5 nm and a width of δz (first trans) = 4.9 ± 0.4 nm, and z_0 (first cis) = 30.6 ± 0.5 nm and a width of δz (first cis) = 6.2 ± 0.6 nm, respectively. The theoretical curves in Figure 6b were generated by substituting a mean ^{111}In position of z_0 (third trans) = 24.6 ± 0.5 nm and a width of δz (third trans) = 5.4 ± 0.4 nm, and z_0 (third cis) = 25.9 ± 0.5 nm and a width of δz (third cis) = 4.9 ± 0.6 nm, respectively. The value of δz means the summation of the surface roughness of the Pt substrate, the LB film stacking faults, and the distribution of the azobenzene derivative layer.[10]

Table 1 shows the values of z_0 and δz at each stage. The distance between the ^{111}In atoms and the Pt surface became longer when the azobenzene derivative monolayer was transferred from the trans form to the cis form. However, in the first trans−cis transition, the structural change is about twice the length of the azobenzene derivative molecule. The conformational changes during trans−cis photoisomerization are gradually decreased in the second and third ones. And there is an abrupt increase of the distribution width (δz) for the first cis condition. This result reflects that the first trans−cis conformational change mainly causes the constraints on the closer molecular packing condition. These agree with the fact that the area per molecule (=0.82 nm²/ molecule) for the cis form is larger than that (=0.37 nm²/molecule) for the trans form at the air−water interface.[13] The value of the distribution width (δz) gradually decreased after the second cis condition. These results suggest that the azobenzene derivative monolayer was rearranged on the substrate because of the relaxation of the molecular packing condition on photoisomerization with UV−visible light irradiation.

4. Results and Discussion

We observed both the trans and cis conditions of the azobenzene derivative monolayer for seven alternations (three cycles for the trans−cis−trans transition). As shown in the interference pattern of Cd Kα from labeled ^{111}In atoms (Figure 6), there are three fringes in both the first trans−cis (a) and the third trans−cis (b) transitions of the labeled azobenzene derivative monolayer. The periods of the measured interference fringes for the cis condition were smaller than those for the trans condition at each cycle. These results show that the distance z (Figure 1) for the cis condition was longer than that for the trans condition. The experimental interference pattern is consistent with a model (Figure 2) in which the main axes of the azobenzene derivative molecules in the trans form are horizontal to the surface of the Pt substrate, because if the main axes of the azobenzene derivative molecules in the trans form were perpendicular to the surface of the Pt substrate, the position of the labeled ^{111}In atoms for the cis condition should change to shorter than that for the trans condition.

In addition, the changes of the period in the observed interference fringes between the trans condition and the cis one decreased after the first cycle, as shown in Figure 6. In other words, the vertical conformational change of the azobenzene derivative monolayer in the trans−cis transition reduced after the first cycle.

We calculated the theoretical interference fringes by a χ^2 minimization fitting using eq 2. $N(z)$ was assumed to reach a maximum peak at $z = z_0$ and to have a Gaussian distribution with a standard deviation of δz. The theo-

5. Conclusion

We demonstrated measurements of conformational changes of the trans−cis transition including the rearrangement of the azobenzene derivative monolayer on the substrate. We confirmed that this method or the fluorescent X-ray interference (FXI)[10,11] method will use the measurement of structural changes in liquid crystal films[14,15] and membranes. When the arrangement of the molecules and radioisotope labeling were controlled on the substrate, we could obtain three-dimensional structural information from some interference fringes.

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