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Photomechanical response of azobenzene/organophilic mica complexes

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Abstract

To clarify whether photomechanical response is limited to the special combination of azobenzene (AzBz)/organophilic tetrasilicic mica (TSM) complexes, another swelling synthetic fluoro-mica, lithium taeniolite, was used as a starting host for AzBz/organophilic mica complexes. Basal spacings of organophilic taeniolites (o-TNs) prepared by the intercalation of trimethylalkylammonium (TMAA) into the TN increased linearly as alkyl chain length in TMAA increased from 2.44 to 2.86 nm. This indicates paraffin-type arrangement of TMAA in the TN gallery. Intercalation of AzBz to o-TN was performed via the gas phase at 100 °C. Photoresponses of AzBz/o-TN complexes were examined by XRD measurement under alternate UV and visible light irradiation. A decrease in basal spacing was observed under UV irradiation, and an increase was under visible light irradiation. Basal spacing change was 0.09–0.18 nm, which corresponds to 3–5% of the AzBz/o-TN basal spacing. These results indicate that reversible photomechanical response is a general phenomenon for AzBz/organophilic mica complexes.

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1. Introduction

Some organic molecules isomerize upon photoirradiation. This phenomenon is called photoisomerization, and when accompanied by a change in the visible absorption spectrum, it is called photochromism [1,2]. Photochromism was successfully applied, for example, to sunglasses by Corning Co. Ltd. in 1964. The change in dimension by photoisomerization has been attempted to be applied to a microactuator [3,4] and liquid crystal control [5,6], and recently, for the formation of surface structures,

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such as a surface relief grating (SRG) [7–10]. For this purpose, azobenzene (AzBz) and its derivatives are commonly used due to their large change in molecular dimension upon photoisomerization. The molecular length of *trans*-AzBz, 1.34 nm, decreases to 0.89 nm (*cis*-form) via isomerization.

Most of the studies concerning photoresponse had been conducted on organic systems from the nanoscopic scale, i.e. isolated molecules [11] and thin films such, as LB films [12], to the visible scale, such as polymer films [13,14], gels [15], or crystals [16]. In most microscopic systems, photoresponse is large and clear [17]. However, the photomechanical changes were reported to be very small, at most only 0.8%, in the bulk system [14].

We have reported clear photoresponse as large as 10% for the AzBz/organophilic layered synthetic mica complex [18,19]. It is the first successful result for achieving a large photoresponse. The microscopic molecular isomerization was directly related to basal spacing change. We also observed photoresponse for micas intercalated with cationic AzBz derivatives [20], though the response was much smaller.

So far, for the preparation of AzBz/organophilic mica complexes, tetrasilicic mica (TSM) was used as the host. Largest photoresponse was recorded for organophilic TSM (o-TSM) with pseudo-trimolecular arrangement of trimethylalkylammonium (TMAA). This arrangement was assumed to help the incorporated AzBz to be arranged perpendicular to the layer of o-TSM, and also to be isolated from the neighboring AzBz, which would enable efficient isomerization [18,19]. Those o-TSMs with bilayer structure also showed reversible response; however, photoresponse was not observed for the complexes with paraffin structure [19].

The purpose of the present study is to examine photoresponse by using other hosts, such as synthetic taeniolite (TN). It is known to form a paraffin structure upon incorporating TMAA [21].

2. Experimental

2.1. Materials and preparation

Synthetic mica, lithium taeniolite (LiTN, Topy Industries) with the composition $\text{LiMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2$ was used as a host. Azobenzene (AzBz, Merck GmbH), TMAA bromides, and $\text{C}_n\text{H}_{2n+1}\text{N}(\text{CH}_3)_3\text{Br}$ ($n = 12, 14, 16, \text{ and } 18$, Tokyo Kasei Kogyo Co. Ltd.) were used as purchased. LiTN was changed to organophilic mica by ion exchange of Li^+ by TMAA^+ in the same manner as previously described [22], and the resulting o-TN was used as host material for AzBz intercalation. For each kind of TMAA, the amount of TMAA was fixed to 0.5 and 2.0 times the cation exchange capacity (CEC) of LiTN (215 mEq./100 g, specification by Topy Industries) for ion exchange reaction. The o-TNs are simply expressed as, for example, C14(0.5), which means o-TN prepared using TMAA having the alkyl chain with 14 carbon atoms, $\text{C}_{14}\text{H}_{29}\text{N}(\text{CH}_3)_3\text{Br}$, at 0.5 times the CEC. Intercalation of AzBz into o-TN was conducted at 100 °C for 2 days, via the vapor phase in an airtight vessel as described in our previous papers [18,19].

2.2. Characterization

The elemental analysis of LiTN was conducted by ICP for Li, Mg, and Si, and F was determined by photometry after steam distillation. The contents of those organic elements, C, H, and N in o-TN were determined using the NCH analyzer, with acetanilide as a standard.

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