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Communications

Preparation of a Cationic Azobenzene Derivative−Montmorillonite Intercalation Compound and the Photochemical Behavior

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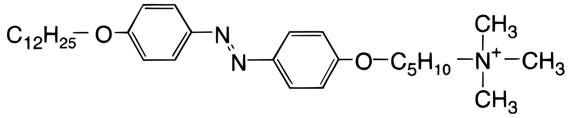
Introduction

The construction of ordered molecular assemblies is of much current interest from a wide range of scientific and practical viewpoints.[1,2] Intercalation of guest species into layered inorganic solids is a way of producing ordered inorganic−organic assemblies with unique microstructures controlled by host−guest and guest−guest interactions.[3,4] Among possible layered solids, the smectite group of layered clay minerals provides attractive features such as large surface area, swelling behavior, and ion-exchange properties for organizing organic guest species.[3−5]

The organization of photoactive species on silicate surfaces is a way to construct novel photofunctional supramolecular systems.[6,7] Since the characteristics of the photoprocesses are sensitive to the environment where the photoactive species are adsorbed,[8] various important information about the nature and the microstructures of the host−guest systems have been clarified. Along these lines, the photochromic reactions of viologens,[9] fulgide,[10] spiropyrans,[11−13] and azobenzene[14] in the interlayer space of montmorillonite has been studied previously, and the photochromic behavior has been found to be different from that observed in solutions or other solid matrixes. Besides the scientific interest in the properties of these supramolecular systems, the organization of the guest species is a possible way to control practically important photochromic reactions.[15]

Scheme 1



p-(ω-(trimethylammonio)pentyloxy)-p'-(dodecyloxy)azobenzene cation

In this paper, the intercalation of a cationic azobenzene derivative, *p*-(*ω*-(trimethylammonio)pentyloxy)-*p*′-(dodecyloxy)azobenzene bromide, abbreviated as C_{12}-AzoC_5N^+ (the molecular structure is shown in Scheme 1) into montmorillonite is reported. Photochromism of azobenzene and its derivatives due to cis−trans isomer-

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ization has widely been investigated. Photocontrol of chemical and physical functions of crown ethers,[16] LB films,[17] cyclodextrins,[18] etc., has vigorously been studied by using photochemical configurational change of azobenzene derivatives. A series of amphiphilic azo dyes with variable alkyl chain length have been synthesized and the formation of self-assembled bilayer structures have been observed in aqueous solutions and in cast films.[19,20] The spectral properties as well as the X-ray diffraction results of the supramolecular systems have revealed that the intermolecular interactions of the azobenzene chromophore were strongly affected by the chemical structure. In the present system, it seems possible to control the orientation of the chromophore on the negatively charged silicate surface of swelling layered silicates through electrostatic attractions.

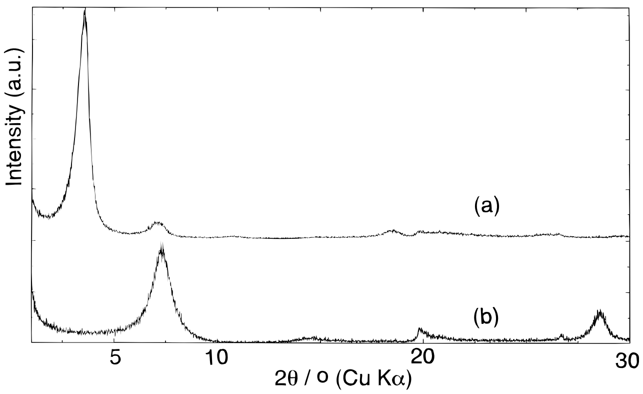

Figure 1. X-ray powder diffraction patterns of (a) C_{12}-AzoC_5N^+−montmorillonite intercalation compound and (b) sodium montmorillonite.

Experimental Section

Sodium montmorillonite (Kunipia F, Kunimine Ind. Co.; reference clay sample of The Clay Science Society of Japan) was used as the host material. The cation-exchange capacity of Na montmorillonite is 119 mequiv/100 g of clay. Intercalation of C_{12}AzoC_5N^+ into montmorillonite was carried out by the conventional ion-exchange method in which an aqueous suspension of montmorillonite was mixed with an ethanol solution of C_{12}Azo$C_5N^+Br^-$ (Sogo Pharmaceutical Co.) and the mixture was allowed to react for 1 day at 70 °C. After centrifugation, the resulting yellowish solid was washed with ethanol and dried.

The photochemical reaction of the intercalated C_{12}AzoC_5N^+ was carried out by UV irradiation with a 500 W super-high-pressure Hg lamp. A glass filter, Toshiba UV-D35, was used for isolating UV light.

Results and Discussion

By the reaction between C_{12}Azo$C_5N^+Br^-$ and Na montmorillonite, a yellowish solid was obtained. The XRD pattern of the product is shown in Figure 1a, together with that of Na montmorillonite (Figure 1b). The basal spacing of the product was 2.6 nm, indicating an interlayer expansion of 1.6 nm. (The thickness of the silicate layer of montmorillonite is 9.6 Å.) The composition of the product was determined by elemental analysis: C 27.3%, N 2.8%. From this value, the C/N ratio was calculated to be 11 which corresponds to the value (11) of the dye itself and the amount of the adsorbed C_{12}AzoC_5N^+ is determined to be ca. 110 mequiv/100 g of clay. These results indicate that the cation exchange between sodium ions and C_{12}AzoC_5N^+ ions occurred almost quantitatively.

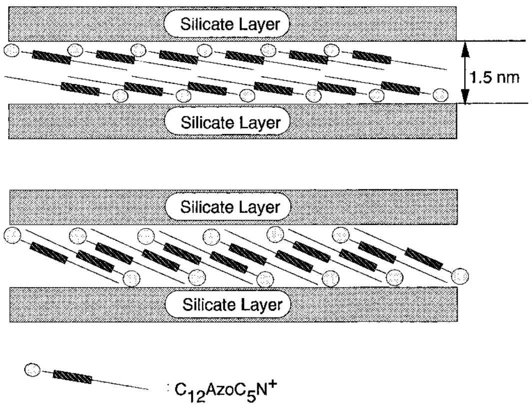

Figure 2. Proposed microstructures of the C_{12}AzoC_5N^+−montmorillonite intercalation compound.

From the observed basal spacing and the size of C_{12}-AzoC_5N^+, the orientation of the intercalated dye cation was discussed. Supposing that the alkyl chains of C_{12}-AzoC_5N^+ were fully extended, two types of orientation can be expected from the observed basal spacing in the present system. The proposed schematic drawing is shown in Figure 2. One is an interdigitated monomolecular layer of the dyes with the alkyl chain inclined to the silicate sheet. The other is a bilayer coverage of the dye with the alkyl chain inclined to the silicate sheet. The intercalation and the arrangements of the alkylammonium ions in the interlayer spaces of layered silicates have extensively been investigated previously.[21] It is well-known that the orientation of the surfactants in the interlayer space is determined by the layer charge density and the size of the organic cation. Judging from the observed basal spacing, the size, and the adsorbed amount of C_{12}AzoC_5N^+, the intercalated C_{12}AzoC_5N^+ ions are densely packed in the interlayer space of montmorillonite. Therefore, the orientation was determined by the layer charge density and the size of the cation in the present system in a similar manner to those of the alkylammonium ions in the interlayer spaces of negatively charged silicates.

Being similar to the long-chain alkylammonium montmorillonites,[22] the C_{12}AzoC_5N^+−montmorillonite intercalation compound swelled in toluene to some extent. By casting the suspension onto a quartz substrate, a thin film was obtained. The basal spacing (2.6 nm) was the same as that of the powdered sample, suggesting that the arrangement of the intercalated C_{12}AzoC_5N^+ did not change during the film preparation. The film-forming ability is worth noting as a merit of the present host−guest systems for photochemical studies. In previous work on the preparation and photochemical reaction of the alkylammonium−montmorillonite−*p*-

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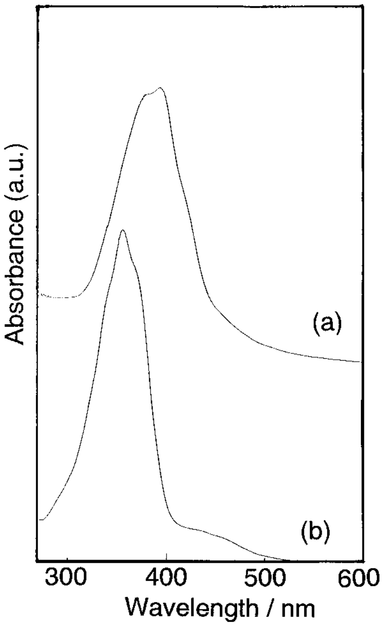

Figure 3. Absorption spectra of (a) the $C_{12}AzoC_5N^+$–montmorillonite intercalation compound and (b) an ethanol solution of $C_{12}AzoC_5N^+Br^-$ (1×10^{-4} M).

aminoazobenzene intercalation compound, the sample was embedded in a poly(vinyl alcohol) film to follow the photochemical reaction.[14]

The absorption spectrum of the film is shown in Figure 3 together with that of an ethanol solution of $C_{12}AzoC_5N^+Br^-$ (the dye concentration is 1.0×10^{-4} M). In the spectrum of the intercalation compound, an absorption band due to the *trans*-azobenzene chromophore was observed at around 390 nm, which is shifted toward a longer wavelength region relative to that of the solution. In the molecular assembly, the chromophore interacts to give aggregated states and the dye–dye interactions causes both bathochromic and hypsochromic spectral shifts. According to Kasha's molecular exciton theory,[23] the observed bathochromic shift of the absorption band of the intercalation compound was ascribable to head-to-tail aggregates of the intercalated $C_{12}AzoC_5N^+$. This is consistent with the proposed orientation (Figure 2) speculated from the X-ray diffraction result. At present, the bilayer structure of the intercalated $C_{12}AzoC_5N^+$ in Figure 2 seems to be better model to explain the observed spectral shifts, though it requires further experimental data to determine the detailed microstructure. Thus, the intercalated $C_{12}AzoC_5N^+$ ions are thought to form a J-like aggregate in the interlayer space of montmorillonite.

Shimomura and co-workers have extensively investigated the preparation and organization of a series of azo dyes by changing the alkyl chain length and found that the orientation of the dye can be controlled by changing the molecular structure.[19,20] The approach employed in the present study is another way to control the orientation of the dye cation through electrostatic attractions between the negatively charged silicate surfaces and the cationic dye.

After UV irradiation for 15 min, the band due to the trans isomer (at around 395 nm) decreased (spectrum b in Figure 4). UV irradiation for a longer period did not cause a further spectral change. When the sample was stored in the dark at room temperature after the irradiation, the intensity of the band at 395 nm due to trans isomer did not change significantly. When the sample was heated at 80 °C for a few hours, the adsorption band due to the trans isomer recovered its original intensity (Figure 4c). A reversible spectral change was observed repeatedly. Therefore, the spectral change was ascribed to the trans-to-cis photoisomerization and the thermal cis-to-trans back reaction of the intercalated $C_{12}AzoC_5N^+$. The ratio of the cis isomer formed by the UV irradiation was roughly estimated to be 60% from the difference in the absorption spectra.

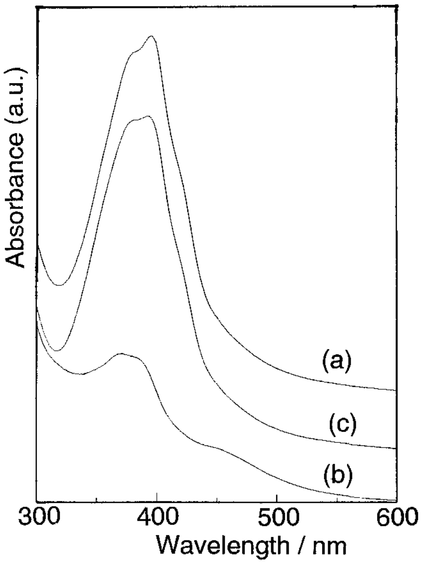

Figure 4. Change in the absorption spectra of the $C_{12}AzoC_5N^+$–montmorillonite intercalation compound. (a) Before and (b) after UV irradiation for 15 min. (c) After subsequent heat treatment at 60 °C for 2 h after UV irradiation for 15 min.

It is worth noting that the azobenzene chromophore isomerized effectively in the interlayer space of montmorillonite, despite the fact that the azobenzene chromophore aggregates in the interlayer space. It has been pointed out that the isomerization of azobenzene chromophore in the molecular assembly was restricted. For azobenzene chromophore to isomerize effectively, efforts have been made by means of the complexation with the cyclodextrin cavity[24] and the polyion complex.[25] $C_{12}AzoC_5N^+$ does not isomerize when it forms bilayer structures. The reason $C_{12}AzoC_5N^+$ isomerizes effectively in the interlayer space of montmorillonite is not clear at present; the physical state of the adsorbates may be concerned.

In summary, the intercalation of cationic amphiphilic azo dye into the interlayer space of montmorillonite has been conducted by the conventional ion exchange method. The intercalated azo dye formed a J-like aggregate in the interlayer space and exhibited reversible trans–cis photoisomerization. Studies on the preparation and properties of intercalation compounds using different hosts and guest ions are now underway in order to understand the nature of the host–guest system and will be reported subsequently.

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