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Photoisomerization of azobenzene in the interlayer space of magadiite†

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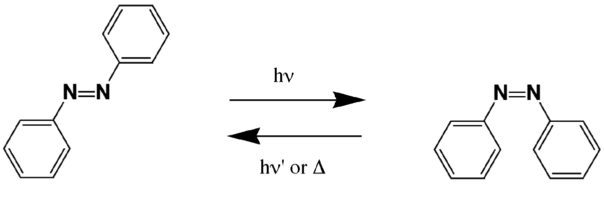
The intercalation of a cationic azobenzene derivative into the interlayer space of magadiite was conducted by the ion exchange reactions between magadiite and *p*-[2-(2-hydroxyethyldimethylammonio)ethoxy]azobenzene bromide. X-Ray diffraction and elemental analysis confirmed the formation of the *p*-[2-(2-hydroxyethyldimethylammonio)ethoxy]azobenzene magadiite intercalation compound. The spectral properties, as well as the X-ray diffraction results, reveal that the adsorbed azo dye cations form head-to-head aggregates in the interlayer space. The intercalation compound exhibited a novel photomechanical effect; the basal spacing changed reversibly upon photoisomerization of the intercalated azo dye.

Introduction

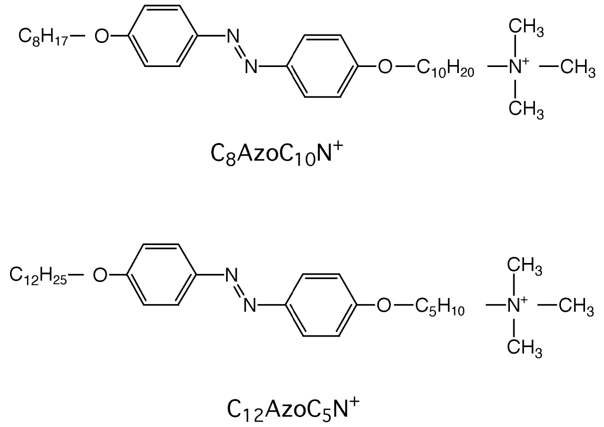
Organization of organic compounds on inorganic solid surfaces has been extensively investigated in order to control the surface properties of the solids as well as to control the functions of the adsorbed species.[1] Functional supramolecular assemblies have been obtained by controlling the states of the adsorbed organic species at the surface of inorganic solids. Intercalation of organic 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.[2] Recently, the photochemistry of intercalation compounds has been investigated. The introduction of organic and organometallic photoactive species into layered solids, in order to construct photofunctional intercalation compounds, has been extensively investigated.[3]

We are interested in the photochemistry of azobenzenes in the interlayer spaces of layered silicates,[4–10] with the aim of constructing photoresponsive inorganic–organic nanocomposites. Azobenzenes are well-known photochromic dyes which show *trans*–*cis* isomerization (Scheme 1) and their photochromic reactions in various heterogeneous systems have been reported previously.[11–16] In order to introduce azobenzene into the interlayer space, the hydrophobic modification of the surface properties of montmorillonite and synthetic swelling mica by the intercalation of surfactants has been carried out.[4–6] Although the intercalated azobenzenes photoisomerize effectively in the hydrophobic interlayer space of the organoammonium silicates, it is difficult to evaluate and control the location and the orientation of the intercalated azo dyes in the hydrophobic interlayer space. In the case of the dialkyldimethylammonium–montmorillonite system, the temperature dependence of the photosiomerization of the intercalated azo dye was investigated.[6] The *trans*-to-*cis* photoisomerization was restricted at lower temperatures, reflecting the change in the states (gel-to-liquid crystal phase transition) of the intercalated dialkyldimethylammonium ions.

Amphiphilic cationic azobenzene derivatives (Scheme 2) have also been used as guest species for intercalation into layered silicates (magadiite and montmorillonite).[7–9] The dye orientation in the interlayer spaces was discussed with reference to the spectral shifts and the gallery heights of the products. In the molecular assembly, the chromophore interacts to give aggregated states and the dye–dye interactions cause both bathochromic and hypsochromic spectral shifts, depending on the interlamellar structure. The spectral shifts reflect the orientation of the dipoles in the aggregates; smaller spectral red shifts are expected for aggregates with larger dipole tilt angles.[17] Depending on the layer charge density (cation exchange capacity) of the host materials and the molecular structures of the amphiphilic azo dyes, aggregates (J- and H-aggregates) with different microstructures (tilt angles) are formed in the interlayer spaces of layered silicates.[7–9] It is worth noting that the azobenzene chromophore photoisomerizes effectively in the interlayer space of silicates, despite the fact that the azobenzene chromophore aggregates in the interlayer space. It has been pointed out that the isomerization of azobenzene chromophores in the molecular assembly is restricted due to geometrical constraints.[18,19]



Scheme 1



$C_8AzoC_{10}N^+$

$C_{12}AzoC_5N^+$

Scheme 2

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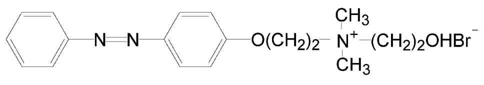
†Basis of a presentation given at Materials Discussion No. 5, 22–25 September 2002, Madrid, Spain.



Scheme 3

Due to the success of the effective photoisomeization of azo dyes in interlayer spaces, we expect that the photoresponsive properties of the resulting intercalation compounds will be developed. For this purpose, studies using various layered materials and photoisomerizable organic dyes are ongoing. Here, we report the intercalation of a cationic azo dye, *p*-[2-(2-hydroxyethyldimethylammonio)ethoxy]azobenzene bromide (Scheme 3), into the layered silicate magdiite, with the nominal chemical composition $Na_2Si_{14}O_{29}$. The dye consists of a photoisomerizable azobenzene unit and a cationic dimethyl(hydroxyethyl)ammonioethoxy group. The resulting intercalation compound exhibited a change in the basal spacing on UV and visible light irradiation, a new type of photomechanical effect.

Experimental section

Materials

Magadiite was synthesized by a hydrothermal reaction described previously.[20] The cationic azo dye, *p*-[2-(2-hydroxyethyldimethylammonio)ethoxy]azobenzene bromide (abbreviated as AZ^+Br^-) was synthesized by reacting phenylazophenol with dibromoethane and subsequent reaction of the product with dimethylaminoethanol. The dye was recrystallized from ethanol and characterized by ^1H-NMR, CHN analysis (calculated for $C_{18}H_{24}BrN_2O_2$: C, 54.83; H, 6.13; N, 10.66; found: C, 54.90: H, 5.93; N, 10.69%) and mass spectrometry.

Sample preparation

Intercalation of the AZ^+ into magadiite was carried out by conventional ion exchange. Magadiite (0.15g) was mixed with aqueous AZ^+Br^- solution and the mixture allowed to react for one day at 70 °C. After centrifugation, the resulting yellowish solid was washed with acetone and dried at room temperature. The intercalation compounds thus obtained were dispersed in solutions of poly(methylmethacrylate) (PMMA) in chloroform and cast on glass substrates, so that supported films were obtained for the photochemical studies.

Characterization

X-Ray powder diffraction patterns were obtained on a Mac Science, MXP[3] diffractometer using monochromatic Cu-Kα radiation. Visible absorption spectra were recorded on a Shimadzu UV-2500PC spectrophotometer. The composition of the products was determined by thermogravimetry (TG) and CHN analysis. TG was performed on a Mac Science TG-DTA 2000S instrument at a heating rate of 10 $°C\ min^{-1}$ using α-alumina as the standard. CHN analysis was performed on a Perkin Elmer 2400 II instrument.

Photochemical reactions

The photochemical reaction of the intercalated azobenzene was initiated by UV and visible light irradiation with a 200 W super high pressure Hg–Xe lamp. (USHIO UVF-203S) A HOYA U-340 band pass filter with the transmittance centered at 340 nm was used to filter the UV light. For the *cis*-to-*trans* reverse reactions, a HOYA L42 sharp cut filter (cut off wavelength 420 nm) was used for visible light irradiation. The reactions were monitored by the change in the absorbance of the *trans*-isomer.

Results and discussion

Cation exchange of magadiite with AZ^+Br^- yielded yellow–orange solids. The amount of AZ^+Br^- solution used was varied in order to control the AZ^+ content of the products. When 264 mmol AZ^+Br^- per 100 g of magadiite was added, the amount of the intercalated AZ^+ was determined to be 190 mmol per 100 g host by elemental analysis (C, 25.69; H, 2.96; N, 3.56%). The loaded AZ^+ cations were quantitatively intercalated into the interlayer space of magadiite as revealed by the absence of dye remaining in the supernatant when the amount of AZ^+Br^- added was less than the cation exchange capacity of magadiite. Hereafter, the products are denoted as AZ^+-magadiite(*n*), where *n* denotes the amount of AZ^+ adsorbed (mmol per 100 g host).

The X-ray diffraction patterns of AZ^+-magadiites are shown in Fig. 1, together with that of untreated magadiite. A new reflection with a *d* value of 2.7 nm appeared and the relative intensity of the (001) diffraction peak due to magadiite (d = 1.56 nm) increased with increasing amounts of intercalated dye. Such phenomena have often been observed for the intercalation of cationic species into smectites and were termed as "segregation". Cationic species such as tris(2,2-bipyridine)-ruthenium(II) complex cations aggregate on smectites even at very low loading (segregation).[21,22] The combination of the guest–guest interactions and the host–guest interactions affects the microstructures of the intercalation compounds. It is thought that AZ^+ is adsorbed into magadiite and subsequent intercalation of AZ^+ occurs with the aid of intermolecular interactions, leading to segregation in the present system.

The interlayer expansion (gallery height) was determined to be 1.57 nm by subtracting the thickness of the silicate layer of magadiite (1.12 nm)[23] from the observed basal spacing. Two possible orientations of the intercalated dye cations were proposed from the gallery height and the size of the AZ^+ ion (1.86 nm for the long axis). One is an interdigitated monomolecular layer and the other is bilayer coverage by the dyes with their long molecular axis inclined to the silicate sheet.(Fig. 2) When semi-quantitative amounts of AZ^+ were adsorbed, some sodium ions remained in the interlayer space, as evidenced by the presence of the peak due to untreated magadiite in the powder X-ray diffraction patterns of such samples.

Visible absorption spectra of AZ^+-magadiites are shown in Fig. 3. The absorption band due to the *trans*-azobenzene chromophore was observed at around 340 nm, which is slightly shifted toward a shorter wavelength relative to that of monomeric AZ^+ in a dilute ethanol solution of AZ^+Br^- (342 nm). The chromophore interacts to give aggregated states

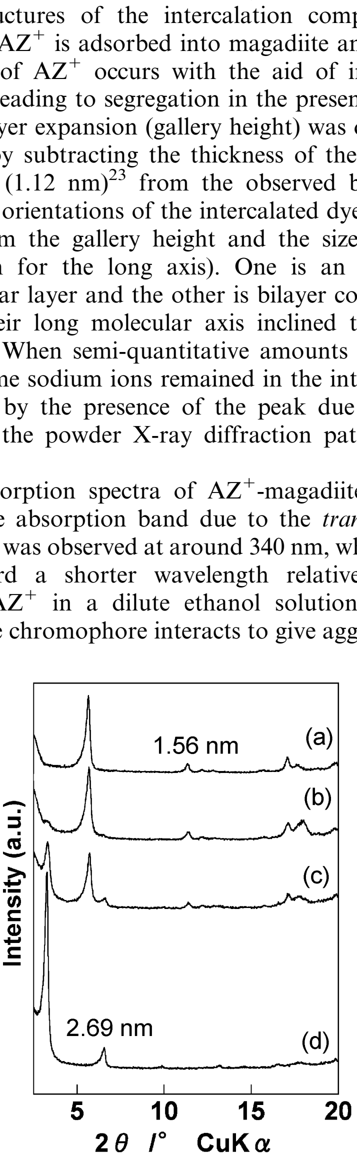


Fig. 1 X-Ray powder diffraction patterns of (a) magadiite and AZ^+-magadiites containing (b) 29, (c) 66, and (d) 190 meq AZ^+ per 100 g host.

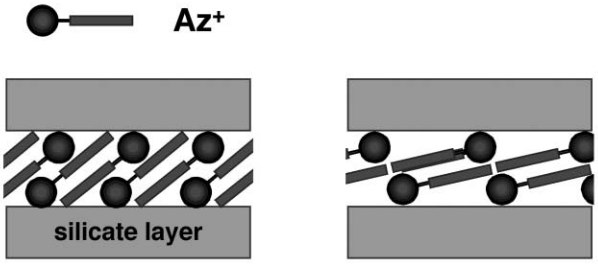


Fig. 2 Proposed interlayer structures of AZ^+-magadiites. (Left) interdigitated monolayer and (right) bilayer.

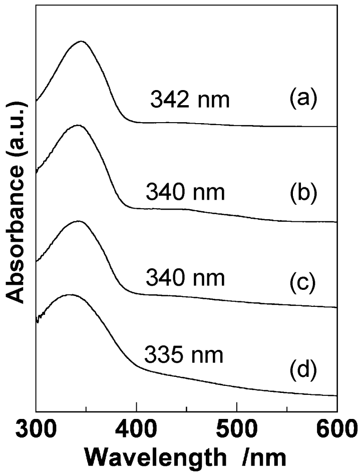


Fig. 3 Asorption spectra of (a) 1.0×10^{-5} M ethanol solution of AZ^+Br^-,(b) AZ^+-magadiite(29), (c) AZ^+-magadiite(66) and AZ^+-magadiite(190).

and the dye–dye interactions cause both bathochromic and hypsochromic spectral shifts, depending on the microstructures.[7–9,24,25] According to Kasha's molecular exciton theory,[17] the observed bathochromic shifts of the absorption bands of the AZ^+-magadiites are ascribable to H-aggregates of the intercalated AZ^+. The intercalated AZ^+ cations are thought to form an interdigitated monolayer to give an H-aggregate in the interlayer space.(Fig. 2, left) In our separate study on the intercalation of AZ^+ into montmorillonite, the intercalated AZ^+ formed J-aggregates, as revealed by the visible absorption spectra and from the gallery heights.[26] Due to the large CEC of magadiite, the intercalated AZ^+ is arranged at a higher tilt angle with respect to the silicate layer if compared to the situation in montmorillonite.

Fig. 4 shows the change in the absorption spectrum of AZ^+-magadiite(190) upon UV irradiation. After UV irradiation, the band due to the *trans*-isomer (at around 342 nm) decreased (spectrum b in Fig. 4 was recorded after 20 min UV irradiation), indicating *trans*-to-*cis* isomerization. UV irradiation for a longer period did not cause a further spectral change. The absorption band ascribable to the *cis*-isomer appeared at around 450 nm. Upon visible light irradiation, the absorption spectrum became identical to the original spectrum [Fig. 4(c)]. Reversible spectral change could be repeated many times over. Similar changes in the absorption spectra upon UV and visible light irradiation were observed for AZ^+-magadiite(29) and (66).

The thermal *cis*-to-*trans* isomerization of AZ^+ in magadiite was followed at 360 K. A first-order plot of the *cis*-to-*trans* reaction (Fig. 5) was based on the following equation:

$$\ln\frac{[t]_\infty - [t]}{[t]_\infty - [t]_0} = -\kappa t$$

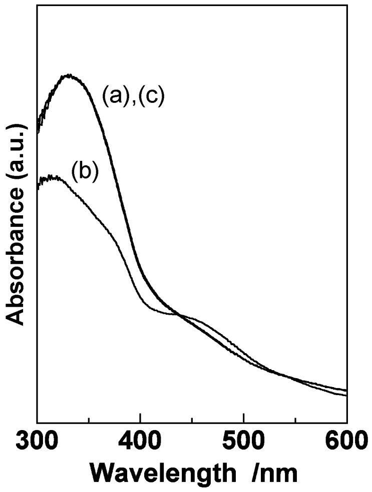


Fig. 4 Changes in the absorption spectrum of AZ^+-magadiite(190) before (a) and after (b) UV irradiation for 20 min. Spectrum (c) was recorded after the visible light irradiation subsequent to UV irradiation.

where κ is the rate constant for the thermal *cis*-to-*trans* isomerization, $[t]$ is the fraction of *trans*-isomer, and $[t]_\infty$ and $[t]_0$ are the fractions of *trans* isomer at the photostationary state and after the completion of the thermal isomerization, respectively. It is known that the thermal isomerization proceeds by first-order kinetics in solution. On the other hand, deviation from first order has been observed for thermal isomerization in solid matrices such as silica gels.[27] The thermal isomerization of AZ^+ in magadiite followed two separate first-order kinetics. Thermal isomerization was faster in the initial stages, but the rate became slower after 20 min. Since the AZ^+ cations are packed densely in the interlayer space of magadiite, the thermal isomerization is thought to be affected by the adjacent dye cations.

Fig. 6 shows the variation of the fraction of photochemically formed *cis*-isomer at the photostationary state at various temperatures. After UV irradiation at room temperature, the fraction was determined to be 49%. We have already reported the photoisomerization of AZ^+ occluded in a mesoporous silica film.[28,29] The pore size of the film was *ca.* 2.5–3 nm, which is large enough for AZ^+ to isomerize. The fraction of *cis*-isomer was *ca.* 70%. The value observed for the present AZ^+-magadiite is smaller in comparison, suggesting that AZ^+ isomerization is restricted by the packing of the dye in the interlayer space. The values decreased with decreasing temperature, suggesting that the motion of the AZ^+ cations is restricted at lower temperatures. For AZ^+-magadiite, the yield of photoisomerization

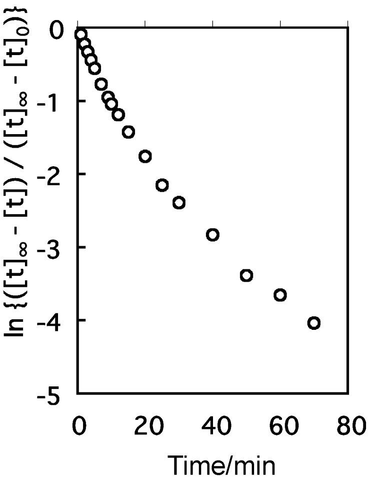


Fig. 5 First-order plot for thermal *cis*-to-*trans* isomerization of AZ^+-magadiite(190) at 360 K.

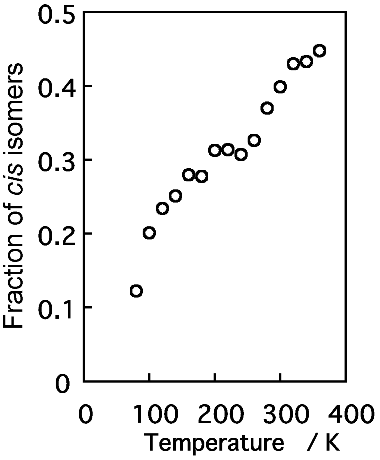


Fig. 6 The temperature dependence of the fraction of *cis*-isomer at the photostationary state.

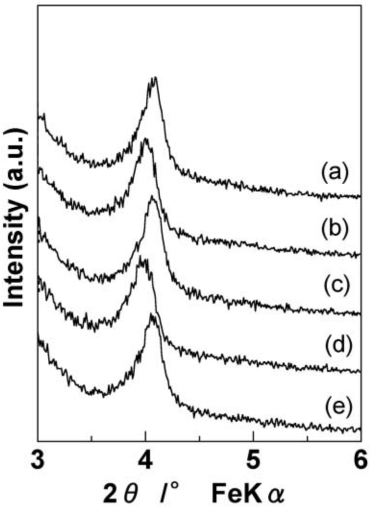


Fig. 7 The reversible change in the XRD pattern of AZ^+-magadiite upon UV and visible light irradiation. (a) Before irradiation, (b) UV irradiated, (c) vis. irradiated, (d) after 2nd UV irradiation, and (e) after 2nd vis. irradiation.

at 100 K was 20% of that obtained at room temperature. In contrast, the photoisomerization took place at lower temperature without significant loss of reaction yield for AZ^+ occluded in a mesoporous silica film. This difference in behavior is also an indication of the dye packing on the surface.

The change in the X-ray diffraction pattern of the film upon photochemical reaction is shown in Fig. 7. The basal spacing changed after UV irradiation from 2.69 to 2.75 nm, and returned to 2.69 nm upon visible light irradiation. Considering the change in the absorption spectrum, the *trans*-AZ^+ cations are thought to form a densely packed aggregate in the interlayer space. Upon UV irradiation, half of the *trans*-form is isomerized to the *cis*-form. It is postulated that a densely packed aggregate is difficult to form in the interlayer space of magadiite at the photostationary state due to the geometric differences between the two isomers, and its formation causes the change in the basal spacing. The adsorption/desorption of water may also be a reason for the reversible change in the basal spacing. The polar nature of the photochemically formed *cis*-isomer compared to the *trans*-isomer may cause the adsorption of atmospheric water, leading to an increase in the basal spacing.

Conclusions

The intercalation of a cationic azo dye into the interlayer space of magadiite has been achieved by ion exchange between sodium montmorillonite and *p*-[2-(2-hydroxyethyldimethylammonio)ethoxy]azobenzene bromide. The intercalated dyes photoisomerize irrespective of the loaded amounts. The photoisomerization of the intercalated dye induces a change in the basal spacing, which can be regarded as a novel photomechanical response.

Acknowledgement

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