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Controlled microstructures of amphiphilic cationic azobenzene-montmorillonite intercalation compounds

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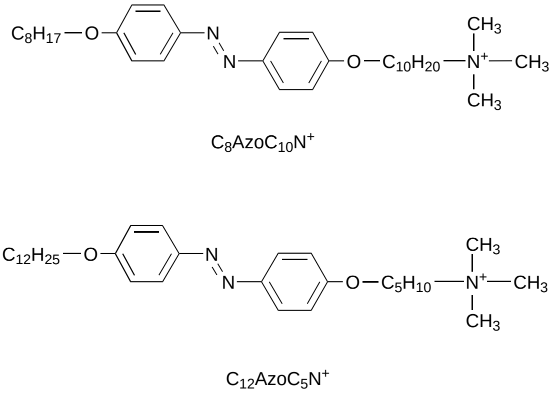
The intercalation of two amphiphilic cationic azobenzene derivatives into the interlayer space of montmorillonite has been conducted by the ion exchange reactions between sodium montmorillonite and *p*-(ω-trimethylammoniopentyloxy)-*p*′-(dodecyloxy)azobenzene bromide or *p*-(ω-trimethylammoniodecyloxy)-*p*′-(octyloxy)azobenzene bromide. X-Ray diffraction and elemental analysis results indicated that the dye cations were intercalated into the interlayer space of montmorillonite. The spectral properties as well as the X-ray diffraction results have revealed that the adsorbed azo dye cations form so-called J-like aggregates with mono- and bi-layers in the interlayer space of montmorillonite. The orientation of the chromophore was controlled by host–guest and guest–guest interactions. The intercalated azo dyes exhibit reversible *trans–cis* photoisomerization by UV and visible light irradiation.

Intercalation of guest species into layered inorganic solids is a method of producing ordered inorganic–organic assemblies with unique microstructures controlled by host–guest and guest–guest interactions.[1,2] 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.[3,4] The organization of photoactive species on the surface of smectites has been investigated to probe the surface properties of smectites as well as to construct novel photofunctional supramolecular systems,[5,6] since the photoprocesses of the photoactive species are environmentally sensitive.[7,8] Along this line, photochromic reactions of organic dyes in the interlayer space of smectites have been reported.[9–17]

We have been interested in the photochemistry of azobenzenes in the interlayer spaces of layered silicates.[14–17] The construction of photoresponsive supramolecular systems based on the photochemical isomerization of azobenzene has been intensively studied.[18] The photoisomerization of azobenzene in the interlayer space may lead to novel photoresponsive inorganic–organic nanocomposites.

The hydrophobic modification of the surface properties of smectites by the intercalation of surfactants[11–16,19,20] has been conducted for the introduction of azobenzenes into the interlayer spaces of smectites.[11–16,19,20] Although the intercalated azobenzenes isomerize effectively in the hydrophobic interlayer space of organoammonium silicates,[14–16] it has been difficult to evaluate and control the location and the orientation of the intercalated azo dyes in the hydrophobic interlayer space.

In order to overcome this limitation, a cationic azobenzene derivative has been used as the guest species.[17] In this paper, we report the intercalation of two amphiphilic azobenzene derivatives *p*-(ω-trimethylammoniopentyloxy)-*p*′-(dodecyloxy)-azobenzene bromide ($C_{12}AzoC_5N^+$) and *p*-(ω-trimethylammoniodecyloxy)-*p*′-(octyloxy)azobenzene bromide, ($C_8AzoC_{10}N^+$) (molecular structures are shown in Scheme 1) into montmorillonite and the photochemical reactions of the azo dyes in the interlayer spaces are reported. A series of amphiphilic azo dyes with variable alkyl chain length have been synthesized and the formation of self-assembled structures has been observed in aqueous solutions and in films.[21–25] In the present system, it seems possible to control the orientation of the chromophore in the interlayer space of swelling layered silicates through electrostatic attractions between the negatively charged surface of the silicate layer and the cationic dyes as well as dye–dye interactions.



Scheme 1 Molecular structures of the amphiphilic azo dyes used

Experimental

Materials

Sodium montmorillonite (Kunipia F, Kunimine Industries Co.; reference clay sample of The Clay Science Society of Japan) was used as the host material. The cation exchange capacity (c.e.c.) of the Na-montmorillonite is 119 mequiv./100 g of clay. The two amphiphilic azo dyes $C_{12}AzoC_5N^+Br$ and $C_8AzoC_{10}N^+Br$ were purchased from Sogo Pharmaceutical Co. and used without further purification.

Sample preparation

Intercalation of $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ into montmorillonite was carried out by a conventional ion exchange method in which an aqueous suspension of montmorillonite was mixed with an ethanol solution of $C_{12}AzoC_5N^+Br^-$ or $C_{12}AzoC_5N^+Br^-$ (0.014 M) and the mixture was allowed to react for one day at 70 °C. The amount of the added dye was 1.2 times excess of the cation exchange capacity of the clay, since excess amounts of amphiphilic species may be adsorbed as a salt (intersalation). After centrifugation, the resulting yellowish solid was washed with ethanol and dried under reduced pressure at room temperature. The intercalation compounds were dispersed in toluene with sonication and casted on quartz substrates, so that thin films were obtained. The thin films are used for the photochemical studies.

Characterization

X-Ray powder diffraction patterns of the products were recorded on a Rigaku RAD-IA diffractometer using monochromatic Cu-Kα radiation. Absorption spectra of the films were recorded on a Shimadzu UV-3100PC spectrophotometer. The composition of the products were determined by the CHN analysis (Yanaco MT-3).

Photochemical reactions

The photochemical reaction of the intercalated azobenzene was conducted by UV and visible light irradiation with a 500 W super high pressure Hg lamp (USHIO USH-500D). A band-pass filter, Toshiba UV-D35, with transmittance centered at 350 nm, was used to isolate the UV light. For the *cis–trans* reverse reactions, a sharp cut filter, HOYA L42 (cut-off wavelength 420 nm) was used to obtain visible light. The reactions were monitored by the change in the absorbance of the *trans*-isomer of the azobenzene. A sample film was set in a cryostat with optical windows (Oxford DN-1704), and the photochemical reactions were performed at constant temperatures between 100 and 400 K for a single sample.

Results and Discussion

In the reaction between $C_{12}AzoC_5N^+Br^-$ and Na-montmorillonite, a yellowish solid was obtained. The XRD pattern of the product is shown in Fig. 1(b), together with that of Na montmorillonite [Fig. 1(a)]. The basal spacing of the product was 2.4 nm, indicating an interlayer expansion of 1.4 nm. (The thickness of the silicate layer of montmorillonite is 9.6 Å.) A yellowish solid was also obtained by the reaction between $C_8AzoC_{10}N^+Br^-$ and Na-montmorillonite. The XRD pattern of the product [Fig. 1(d)] shows a basal spacing of 2.5 nm, which indicates an interlayer separation of 1.5 nm. The difference in the basal spacings between the two compounds is ascribable to the difference in the size of the dye cations as well as the amounts of the adsorbed dyes.

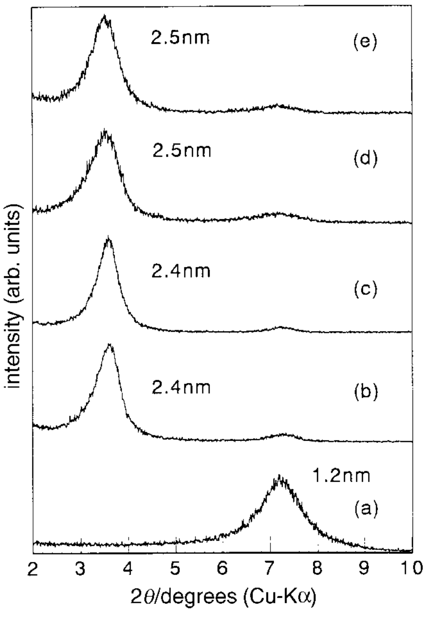


Fig. 1 The X-ray powder diffraction patterns of (a) sodium montmorillonite, (b) and (c) $C_{12}AzoC_5N^+$ montmorillonite intercalation compound: powder (b) and cast film (c); (d) and (e) $C_8AzoC_{10}N^+$ montmorillonite intercalation compound: powder (d) and cast film (e)

The compositions of the products were determined by elemental analyses as C, 27; N, 3% for the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound and C, 26; N, 3% for the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound. From the elemental analyses, the amounts of the adsorbed azo dyes were determined as *ca.* 110 and 100 mequiv./100 g clay for the $C_{12}AzoC_5N^+$ and the $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds, respectively. These values indicate that the cation exchange between sodium ions and $C_{12}AzoC_5N^+$ or $C_8AzoC_{10}N^+$ ions occurred almost quantitatively. As observed for the intercalation of long chain alkylammonium ions into smectites, the two amphiphilic azo dyes preferred to occupy the interlayer space of montmorillonite to replace the interlayer sodium ions effectively.

From the observed basal spacings and the sizes of $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ ions, the orientation of the intercalated dye cations can be discussed. Supposing that the alkyl chains of the two amphiphilic azo dyes were fully extended, two types of orientation can be expected from the observed basal spacings. One is an interdigitated monomolecular layer of the dyes with the alkyl chains inclined to the silicate sheet. The other is a bilayer coverage of the dyes with their alkyl chains inclined to the silicate sheet. Note that the tilt angles are different in the two models.

The intercalation of the amphiphilic azo dyes alters the surface properties of montmorillonite to strongly organophilic as has been observed for the long chain alkylammonium smectites.[26–28] Consequently, the $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds swell in organic solvents such as toluene and chloroform. Thin films were obtained by casting the suspension in toluene onto a quartz substrate. The X-ray diffraction patterns of the films are shown in Fig. 1(c) and (e) for the $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds, respectively. The basal spacings of the films (2.4 and 2.5 nm for the $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds, respectively) were same as those observed for the powdered samples, indicating that the arrangements of the intercalated azo dyes did not change during the film preparation and the solvents employed for the films preparation are completely removed. Although the films are slightly turbid, they are still useful for photochemical studies.

The visible absorption spectrum of the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound film is shown in Fig. 2(a). In the absorption spectrum, a band due to the *trans*-azobenzene chromophore was observed at *ca.* 385 nm, which is shifted towards longer wavelength relative to that (355 nm) of monomeric $C_{12}AzoC_5N^+$ in a dilute ethanol solution of

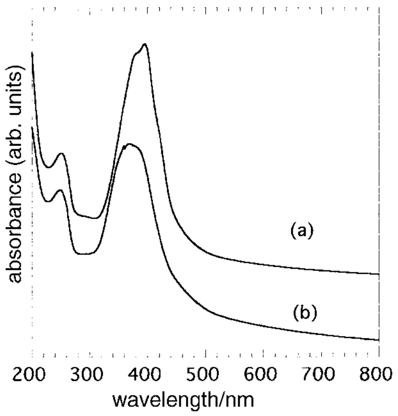


Fig. 2 The absorption spectra of (a) the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound and (b) the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound

$C_{12}AzoC_5N^+Br$. The absorption spectrum of the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound film is shown in Fig. 2(b). A broad absorption band centered at 373 nm was observed in the absorption spectrum. Compared to that of the dye solution (the absorption maximum of a dilute $C_8AzoC_{10}N^+Br$ solution appeared at 355 nm), the absorption band due to the π–π^* transition of *trans*-azobenzene shifted to longer wavelength. It should be noted that the absorption band of the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound film was observed at a shorter wavelength than that of the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound film. A $C_{12}AzoC_5N^+$ montmorillonite intercalation compound with a $C_{12}AzoC_5N^+$ loading of 0.1 of the c.e.c. showed a basal spacing of *ca.* 1.3 nm, indicating the adsorbed dyes arranged parallel to the silicate layers. This intercalation compound was orange, different from that (yellow) of the intercalation compound in which the interlayer cations were replaced almost quantitatively. The adsorbed dyes interact with the surface of silicate layer when the adsorbed amount is low, while the dye–dye interactions are dominant at high loading.

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 microstructures. According to Kasha's molecular exciton theory,[29] the observed bathochromic shifts of the absorption bands of the intercalation compounds were ascribable to J-like aggregates of the intercalated $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ ions in the interlayer space of montmorillonite. The spectral shifts reflect the orientation of the dipoles in the aggregates; smaller spectral red shifts are expected for the aggregates with larger tilt angles of the dipoles.[29] The difference in the wavelength of the absorption maxima observed for the $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds suggests two different orientations of the intercalated azo dyes. For the $C_{12}AzoC_5N^+$ montmorillonite system, a greater spectral shift is observed, indicating the smaller tilt angle of the azobenzene dipoles in the intercalated dye aggregates. The absorption band observed for the $C_8AzoC_{10}N^+$ montmorillonite system showed the smaller spectral shift compared to that observed for the $C_{12}AzoC_5N^+$ montmorillonite system, suggesting a greater tilt angle of the azobenzene dipoles in the interlayer space of montmorillonite.

As discussed previously, two possible orientations of the intercalated species are proposed from the gallery height and the size of the dye; one is a monomolecular layer and the other is a bimolecular coverage in the interlayer spaces. Since the basal spacings of the two intercalation compounds are similar, the tilt angles in the bilayer assembly must be larger than that in the monolayer aggregate. Consequently, the bilayer structure of the intercalated $C_{12}AzoC_5N^+$ [as shown in Fig. 3(a)] seems to be a plausible model to explain the observed spectral shift. On the contrary, the intercalated $C_8AzoC_{10}N^+$ ions are thought to form an interdigitating monomolecular layer in the interlayer space of montmorillonite as shown in Fig. 3(b).

The differences in the microstructures of the $C_{12}AzoC_5N^+$ and $C_8AzoC_{10}N^+$ montmorillonite systems are ascribed to the location of the azobenzene chromophore in the amphiphilic ions. The $C_8AzoC_{10}N^+$ ions are able to adopt an interdigitating monolayer without producing void spaces. On the contrary, for the $C_{12}AzoC_5N^+$ ions to form an interdigitating monolayer, the distance of adjacent azobenzene chromophores must be larger than that expected for the interdigitating $C_8AzoC_{10}N^+$ monolayer to weaken the dye–dye interactions [as schematically shown in Fig. 3(a′)]. As a consequence, the $C_{12}AzoC_5N^+$ ions form a bilayer in the interlayer space of montmorillonite as shown in Fig. 3(a).

Shimomura and co-workers have extensively investigated the preparation and the organization of a series of amphiphilic azo dyes with variable alkyl chain length and found that the microstructures of the dye aggregates varied depending on the molecular structures.[21–23] $C_8AzoC_{10}N^+$ has been reported to form a H-aggregate in cast films as revealed by the X-ray diffraction and the hypsochromic shift of the absorption band in the visible spectrum. On the contrary, $C_8AzoC_{10}N^+$ ions form J aggregates which show a bathochromic shift of the absorption band upon intercalation into the interlayer space of montmorillonite. This observation implies that the states of the dyes in the interlayer spaces are controlled by the electrostatic attractions between the negatively charged silicate surfaces and the cationic dyes as well as the dye–dye interactions.

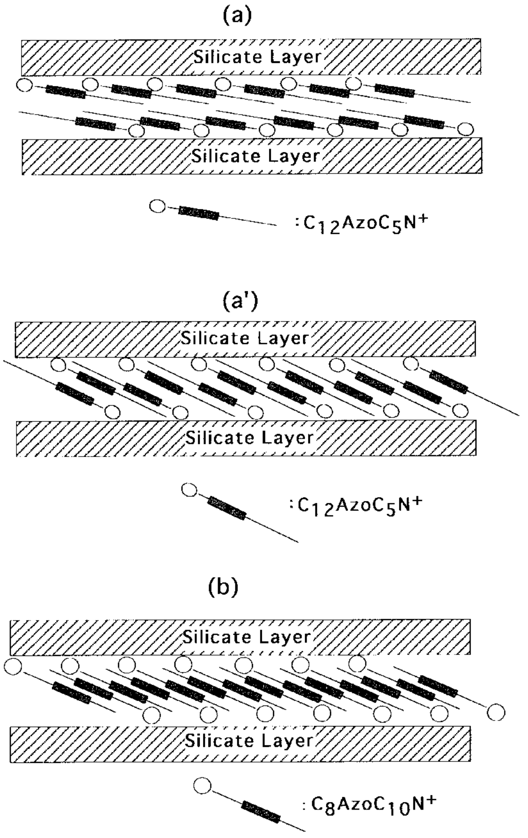


Fig. 3 Proposed microstructures of (a) the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound and (b) the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound. (a′) Less plausible model for the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound, with the $C_{12}AzoC_5N^+$ arranged as an interdigitated monolayer. Note that the distance between the adjacent chromophores is larger in this model.

The photochemical reaction of the intercalated azobenzene has been investigated by UV and visible light irradiation. Fig. 4 shows the change in the absorption spectra of the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound upon UV and visible light irradiation. After UV irradiation, the band due to the *trans*-isomer (at *ca.* 385 nm) decreased [spectra (b) and (c) in Fig. 4 were recorded after UV irradiation for 20 and 50 min, respectively], indicating *trans*–*cis* isomerization. UV irradiation for a longer period did not cause any further spectral change. The absorption band ascribable to the *cis*-isomer appeared at 330 nm. Upon visible light irradiation, the absorption spectrum recovered [Fig. 4(d) shows the absorption spectrum recorded after visible light irradiation for 13 min]. This spectral recovery was also observed thermally. Reversible spectral changes were repeatedly observed. The ratio of the *cis*-isomer formed by UV irradiation at the photostationary state at room temperature was *ca.* 60% from the change in the absorption band due to the *trans*-isomer.

A similar change in the absorption spectra was observed for the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound. Fig. 5 shows the change in the absorption spectra of the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound upon

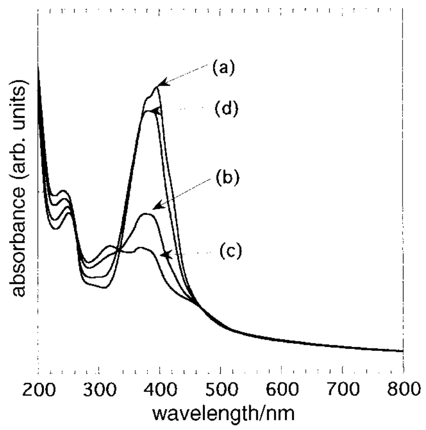


Fig. 4 The change in the absorption spectra of the $C_{12}AzoC_5N^+$ montmorillonite intercalation compound: before (a) and after UV irradiation for (b) 20 and (c) 50 min; (d) after subsequent visible light irradiation for 13 min

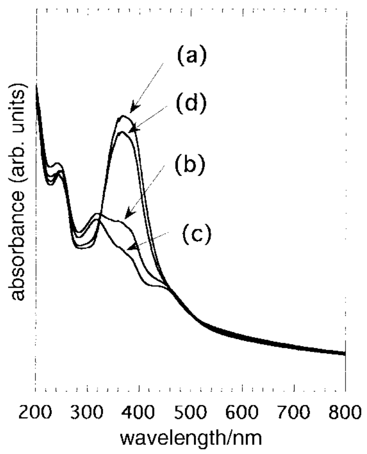


Fig. 5 The change in the absorption spectra of the $C_8AzoC_{10}N^+$ montmorillonite intercalation compound: before (a) and after UV irradiation for (b) 16 min and (c) 32 min; (d) after subsequent visible light irradiation for 8 min

UV and visible light irradiation. After UV irradiation, the band due to the *trans*-isomer (at around 373 nm) decreased [spectra (b) and (c) in Fig. 5 were recorded after UV irradiation for 16 and 32 min, respectively], indicating *trans-cis* isomerization. UV irradiation for a longer period did not cause any further spectral change. Upon visible light irradiation, the absorption spectrum recovered [Fig. 5(d)]. The ratio of the *cis*-isomer formed by UV irradiation at the photostationary state at room temperature was *ca.* 60% from the difference in the absorption spectra.

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 the azobenzene chromophore in a molecular assembly was restricted owing to the lack of free volume. In order for the azobenzene chromophore to isomerize effectively, efforts have been made by means of complexation with a cyclodextrin cavity[30] and with a polyion complex[31] to create sufficient room for photoisomerization.

X-Ray diffraction patterns of the films were recorded during UV irradiation (at the photostationary states). No significant change in the basal spacings was observed upon UV irradiation, suggesting that the interlayer amphiphilic dyes rearrange to minimize the change in the basal spacing during the isomerization. This explanation was supported by the fact the isomerization was significantly restricted at lower temperature. Fig. 6 shows the variation of the fraction of the photochemically formed *cis*-isomer at the photostationary states at different temperatures. These values decreased with decreasing temperature, suggesting that the motion of the azobenzene was restricted at lower temperatures. It has been reported that dialkyldimethylammonium ions in the interlayer space of silicates exhibit a gel-to-liquid crystal phase transition to affect the photoprocess of the intercalated species and the permeability.[11,16,19,32,33] In the present system, the states of the amphiphilic azo dyes might affect the observed temperature dependent photochemical reactions. Upon increasing the temperature above 340 K, the fraction of the *cis*-isomer at the photostationary state decreased as a result of competitive photochemical and thermal processes.

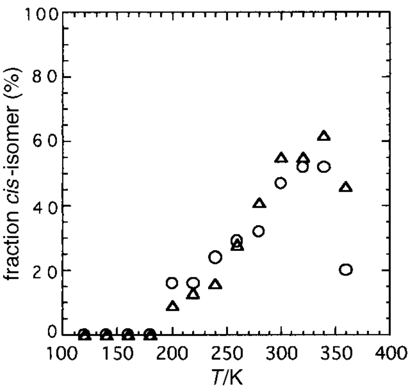


Fig. 6 The temperature dependence of the fraction of the photochemically formed *cis*-isomer at the photostationary states for (O) the $C_{12}AzoC_5N^+$ montmorillonite and (Δ) the $C_8AzoC_{10}N^+$ montmorillonite intercalation compounds

Organoammonium-exchanged clays have been utilized as adsorbents for poorly water soluble species with specific selectivity.[34] The amphiphilic azo dye intercalated montmorillonites may find applications as novel adsorbents with photo-controllable selectivity.

Conclusions

The intercalation of cationic amphiphilic azo dyes into the interlayer space of montmorillonite has been conducted by a conventional ion exchange method. The intercalated azo dyes formed J-like aggregates in the interlayer space of montmorillonite. Although the two dyes gave similar basal spacings, absorption spectra showed differences in the microstructures of the products. Two different models, one a monomolecular the other a bimolecular layer, in the interlayer spaces, have been proposed for the intercalation compounds and this difference has been ascribed to the difference in the molecular structures of the dyes. The intercalated azo dyes exhibited photoisomerization at room temperature.

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