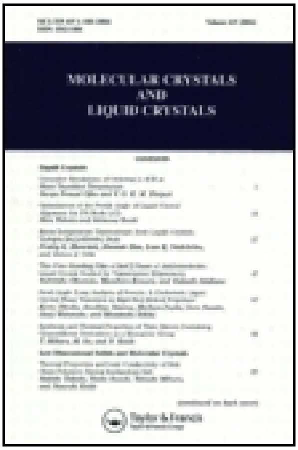

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Intercalation and Photochromism of Monocationic Diarylethenes Incorporated in Clay Layer Surfaces

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Intercalation and Photochromism of Monocationic Diarylethenes Incorporated in Clay Layer Surfaces

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*The intercalation of the colorless open (**1O**) and the blue-colored closed forms (**1C**) of monocationic diarylethene into cation exchange clays and the photochromic reversibility of these hybrid materials was investigated. Both the **1O**/clay and **1C**/clay hybrid powders exhibited reversible color changes upon alternative irradiation of UV and visible light, however, the photochromic durability was found to be strongly influenced by the form upon intercalation, i.e., open or closed, as well as by the coverage degrees. The blue-colored, closed **1C**/clay was found to exhibit higher photochromic durability than the **1O**/clay.*

Keywords: photochromism, diarylethenes, cations exchange clays, hybrid materials

INTRODUCTION

Organic photochromic compounds have attracted much attention for applications in such photofunctional devices as light-stimulated

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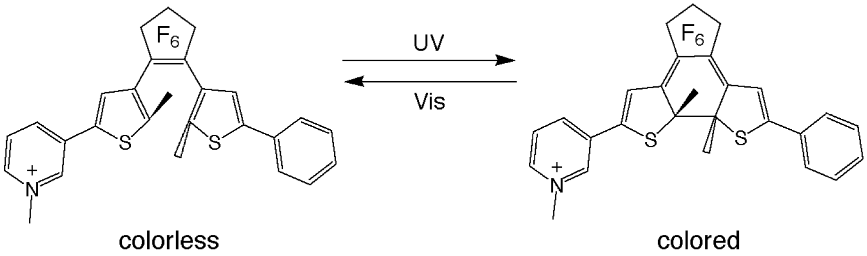
recording, optical or display systems [1]. Among these, diarylethene-type compounds, developed by Irie et al, exhibited efficient photochromic performance during the on/off iteration of the coloring which excluded any thermal influence [2]. An urgent and important point that needs to be resolved in the use of such diarylethene hybrids is the stable and continuous repetition of the photochromism in solid or solid-like states. Previously, we have reported on the hybridization of layered clay minerals [3] with dicationic diarylethene molecules [4]. These dicationic diarylethene/clay hybrid materials exhibited reversible photochromic behavior under UV/visible light irradiation even in the solid state. However, they had rather low durability and low regeneration of the open and closed forms. The degree of orientation and mobilization of the diarylethene chromophores on the clay surfaces were considered to affect the photochromic durability, as the diarylethene molecules themselves are reported to be quite stable photochromic compounds. In the present article, we report on the intercalation of monocationic diarylethene compounds in cationic clay and their photochromic reversibility between the colorless open form (**1O**) and the colored closed form (**1C**), as shown in Scheme 1.



1O **1C**

SCHEME 1 Photochromic reaction of the monocationic diarylethene.

EXPERIMENTAL

A purified standard sample of sodium montmorillonite clay (Tsukinuno) with a cation exchange capacity (CEC) of 1.19 mequiv/g was used as the host material without further treatment, as supplied by the Clay Society of Japan. A colorless monocationic diarylethene compound (**1O**) was synthesized according to modified procedures described in previous literature [5,6]. The colored form (**1C**) was obtained by UV irradiation of **1O** in methanol (1 mmol/L) in the range of 280–340 nm. The **1O** and **1C**/clay hybrid powders were synthesized by mixing a clay aqueous suspension (84 mg/100 mL) with an appropriate amount of 1 mmol/L methanol solution of **1O** or **1C** [4]. The molar ratios between the added amounts of the monocationic diarylethene **1O** or **1C** and the amount of clay were adjusted at 10–300% against the CEC of the clay. After stirring overnight, these mixed suspensions were filtered, washed several times with water, and then dried to powder *in vacuo* at room temperature.

X-ray diffraction (XRD) analysis was carried out with a RINT-2000 diffractometer (Rigaku) using CuKα radiation ($\lambda = 0.154$ nm). The photochromic changes were monitored by UV (280–340 nm) as well as visible (>500 nm) light irradiation using a 300 W Xe lamp through glass filter systems.

RESULTS AND DISCUSSION

Intercalation of 1O and 1C into the Clay Interlayers

The adsorbed amounts of **1O** and **1C** were estimated from measurements of their absorbance in the filtrate solution. The added diarylethenes (**1O** and **1C**) were intercalated quantitatively, although the intercalated amounts did not exceed the CEC of the clay, indicating that the monocationic diarylethenes were accommodated in the clay layers by electrostatic interactions [3]. The layer distances, i.e., the clearance spaces (CLS), estimated by the subtraction of the layer thickness of the clay (9.6 Å) from the d(001) values obtained from XRD studies, are shown in Table 1. The CLS values steadily increased with an increase in the adsorbed amounts of **1O** and **1C**. In the case of a low coverage (~10%), the diarylethenes tended to be adsorbed parallel to the clay layer surfaces. When the coverage increased to more than ~50%, however, the diarylethenes gradually began to stand upright on the layer surface due to the mutual steric hindrance of

TABLE 1 Relationship Between Loading Amount (L.A.; vs CEC), Adsorbed Amount (A.A.; vs % CEC), and Clearance Space (CLS; Å) for **1O** and **1C**/Clay Hybrids

	1O		**1C**	
L.A.	A.A.	CLS	A.A.	CLS
0	0	1.22	0	1.22
10	0.10	1.46	0.10	1.42
50	0.50	2.31	0.50	2.30
100	0.94	2.46	0.94	2.43

the guest molecules. The CLS values of **1O** and **1C** were, interestingly, almost the same at any coverage stage, implying little effect of the chemical structures of the monocationic guest molecules and the coverage degree on the aggregated conformation.

Photochromism of the Monocationic Diarylethene/Clay Hybrids

Alternative irradiation of UV (280–340 nm) and visible (>500 nm) light was carried out on the **1O** or **1C**/clay hybrid powder sample (*ca.* 10 mg) after spreading over a silica glass substrate (2 cm ϕ). The diffuse reflectance absorption spectra of the **1O**/clay hybrid are shown in Figure 1. Upon UV light irradiation of the colorless starting **1O**/clay hybrids, a blue coloration began to appear and became more pronounced at around 625 nm (Fig. 1b), indicating the photoisomerization from **1O** to **1C** in these clay minerals. Moreover, the resulting blue-colored closed **1C** was then confirmed to revert back to the original open **1O** by irradiation at visible light regions (Fig. 1c). In the next run, the **1C**/clay hybrid powder was used in place of the **1O**/clay as the starting guest diarylethene. Similar reversible absorption spectral changes between the blue-colored **1C** and colorless **1O** could be observed under repeated and alternative UV-visible light irradiation.

Durability of the Color Change by Alternate UV/Visible Light Irradiation

Repeated and alternative UV/vis light irradiation confirmed a reversible color change in the photochromism of the **1O** or **1C**/clay hybrid powders, where a photostationary state (pss) could be attained, leading to constant ratios by irradiation of **1O** for 30 sec and **1C** for 30 min. The reversibility between the colorless **1O** and blue-colored **1C** was then measured as a function of the alternate irradiation cycles. The relative intensities of the absorption maximum of the colored **1C** at 625 nm was normalized by dividing the values with the absorbance intensities before irradiation, (A_n/A_0), and then plotted against the number of alternative UV-visible light cycles (n) for the **1O**/clay and **1C**/clay hybrids, as shown in Figures 2a and b, respectively.

Figure 2 shows that the photochromic reversibility of both the **1O**/clay and **1C**/clay hybrids decreased with alternative UV and visible light irradiation. However, the reversibility was considerably affected by the coverage degree of either **1O** or **1C**. In other words, the reversibility gradually improved with an increase in the coverage of **1O** or **1C**. The results of XRD analysis showed that the

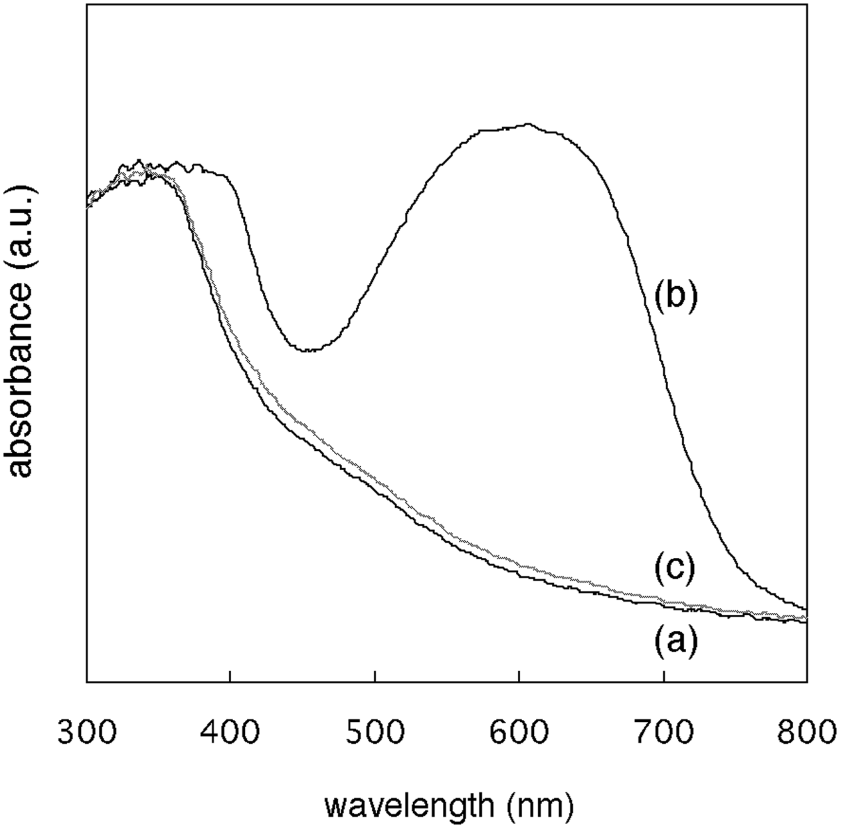


FIGURE 1 Diffuse reflection absorption spectra of the **1O**/clay hybrid with the adsorbed amount = 100% CEC: the as-prepared sample before irradiation (a); after UV-light irradiation (b); and after UV and then visible light irradiation (c).

conformation of the diarylethene aggregates changed from parallel to upright on the layer surface with an increase in the intercalation degrees of the guests molecules. This can be well understood by considering the formation of a compact packing arrangement. In an aggregated conformation, there are two factors controlling the photochromic behavior in aggregated conformation: (1) a change in the layer surface from a polar to less polar condition; and (2) the more likely occurrence of an intermolecular reaction of the diarylethenes. Regarding the effect of the polarity, little difference in the photochromic reversibility of similar diarylethene analogs dissolved in a solvent with a wide range of dipole moments has been reported [7]. Moreover,

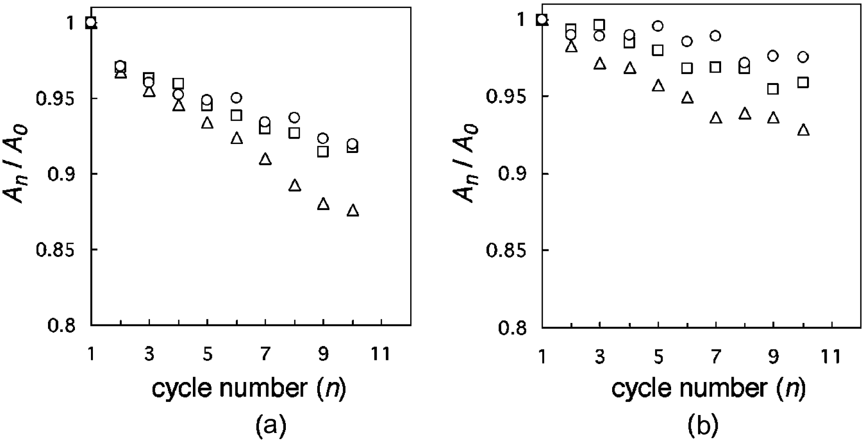


FIGURE 2 The absorbance ratios, A_n/A_0, of the **1O**/clay (a) and **1C**/clay (b) hybrids at 625 nm were plotted against the number of cycles (n) of repeated UV/visible light irradiation, after each UV irradiation. The symbols, (△), (□), and (○), denote the adsorbed ratios of diarylethene against the CEC of clay, i.e., **1O** or **1C**/clay = 10, 50, and 100% CEC of the clay for (△), (□), and (○), respectively.

regarding the low reversibility due to byproduct formation, although a photoinactive dimer was reported to be formed in solution [6], in the present case, such a possibility is unlikely since low coverage would have induced a decrease in the reversibility.

In the case of restricted reaction conditions as for the present confined interlayer space, an efficient chemical transformation would require the least motion of the substrates with as little influence from steric hindrance as possible. The photochromic transformations between **1O** and **1C** are known to be highly efficient and non-degradative, however, the open form (**1O**) in solution exists as a 1:1 equilibrium mixture of two isomers, *parallel* and *anti-parallel*. Irie et al have observed that the *anti-parallel* isomer is photochemically active and can change into the closed form (**1C**), however, a *parallel* isomer is photochemically inactive and remains unchanged [8]. Hence, although rapid interconversions between **1O** and **1C** are necessary for efficient and facile photochromism, such transformations are unfeasible due to the restricted reaction space. The diarylethene compounds were intercalated by means of electrostatic interactions of the cationic sites of **1O** (or **1C**) with the anionic sites of the surfaces, and therefore, not so mobile on the clay surface, especially when they are so compactly packed as molecular aggregates. These results corresponded with our experimental observations in which the reversibility was much more efficient when diarylethene was incorporated in a closed form than in an open form, as shown in Figure 2. Thus, the closed form, **1C**, was seen to convert into the open form, **1O**, with the least motion during isomerization. The development of such hybrid materials with good photochemical reversibility in solid states is much desired for applications in efficient photofunctional systems.

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