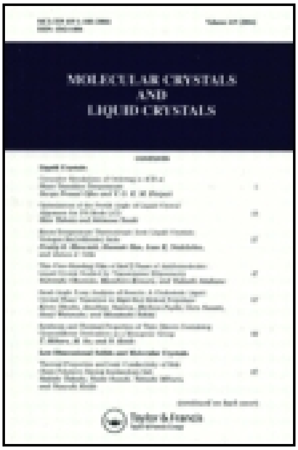

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Photochromism of Diarylethene Intercalated in Clay Interlayers

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The synthesis and photochromism of clay-diarylethene (PyDE) hybrid materials have been investigated. The obtained hybrid materials efficiently exhibited photochromism, but its photochromic efficiency decreased when UV and visible irradiation was repeated. This photochromic degradation could be improved by coadsorbing the cationic surfactant molecules with the PyDE molecules.

Keywords: Photochromism; diarylethene; clay-diarylethene hybrid materials; coadsorption

Diarylethene derivatives, which are thermally stable but photochemically interconvertible with their closed-ring isomers, have been shown to be one of the most promising materials in realizing the development of photon-mode memory devices, a field competitively pursued by many researchers [1, 2]. It is necessary, however, that the materials be constructed to perform facile photochromic behavior in solid and solid-like systems for applications in such memory devices.

In the present article, we have studied the synthesis of photochromic solid materials by the hybridization of diarylethene into clay minerals, which characteristically have a layered structure, by intercalation with ion-exchange reactions [3]. In addition, the effect of coadsorption to improve the photochromic reversibility has been discussed.

EXPERIMENTAL

Synthesized 1,2-bis(2-methyl-5-pyridylthiophen-3-yl)perfluorocyclopentene (PyDE) [4] was used as the photochromic compound and montmorillonite (Mont) with a cation exchangeable capacity (CEC) of 1.19 mequiv./g was supplied by Kunimine Ind., Ltd. Laurylpyridinium chloride (Lpy) was used as the cationic surfactant. The Mont-PyDE hybrid materials were precipitated as a white powder by mixing the Mont with PyDE in a 10% methanol aqueous solution involving 2 N HCl aq. ([PyDE]/[Mont] = 0.2 and 1.0). The

Mont-PyDE-LPy hybrid materials were similarly obtained by mixing Mont, PyDE, and Lpy ([PyDE] : [Lpy] : [Mont] = 0.2 : 0.8 : 1.0) in water. After stirring overnight, these mixture suspensions were passed through a membrane filter to isolate the hybrid powders, which were then washed several times with water, and dried *in vacuo* at room temperature.

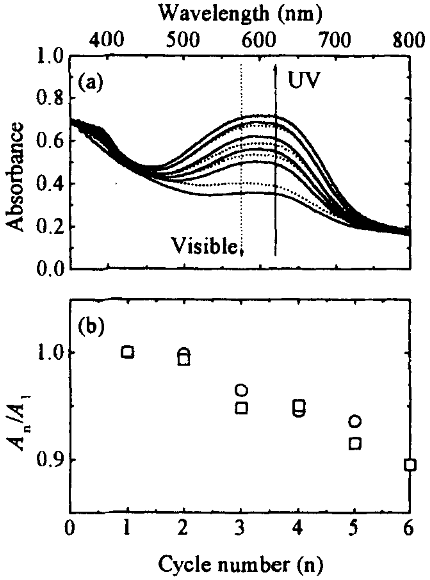

FIGURE 1. (a) Absorption spectra of Mont-PyDE hybrid powders during UV (solid line) or visible (broken line) irradiation at [PyDE]/[Mont]=1.0. (b) Cycle number dependence of the relative amount of closed-ring PyDE molecules. [PyDE]/[Mont] = 0.2 (circles) and 1.0 (squares).

RESULTS AND DISCUSSION

Photochromism of Mont-PyDE Hybrid Powders

FIGURE 1(a) shows the absorption spectra of the synthesized Mont-PyDE hybrid powders at [PyDE]/[SA] = 1.0 obtained by irradiation with UV (solid line) or visible (broken line) light. The increase or decrease in the absorbance at 600 nm was observed by UV and visible light irradiation, showing a characteristic absorption of the closed-ring PyDE. These results indicate that the intercalated PyDE molecules show photochromism in the solid state as efficiently as in solution without Mont. When the PyDE-Mont hybrid powder was alternatively irradiated by UV and visible light, a considerable amount of the converted closed PyDE molecules decreased in number (cf. FIGURE 1(b)). Generally, two types of open diarylethene molecules, *photoactive anti-parallel-* and *photoinactive parallel*, are known to be formed in solution during alternative irradiation procedures [1]. Since the *photoinactive parallel* type PyDE has two cationic nitrogen atoms, both of which adsorb at the anionic sites on the layer surface, it becomes trapped and loses its reversibility, presumably due to restrictions in mobility. The latter photoinactive isomer is believed to be the origin of the decrease in reversibility. It is assumed that the lowering of the reversibility of the photochromism is due to this entrapment of PyDE in the Mont interlayers in a photoinactive form. These trends could typically be observed at [PyDE] /[Mont] = 0.2.

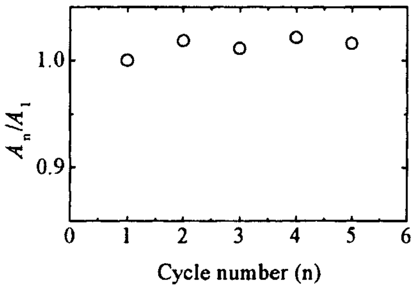

FIGURE 2. Cycle number dependence of the relative amount of closed PyDE involved in Mont-PyDE-Lpy hybrid powders.

The improvement of the reversibility of Mont-PyDE hybrid powders by the coadsorption of surfactant molecules

In order to suppress the formation of *photoinactive parallel* PyDE, Lpy molecules were cointercalated into the Mont interlayers with the PyDE molecules. FIGURE 2 shows the cycle number dependence of the relative amount of the closed PyDE molecules in the Mont interlayers. Compared with the Mont-PyDE hybrid materials, the amounts of the closed PyDE molecules did not change with the increase in the cycle number of alternative UV and visible light irradiation. These results indicate that the coadsorption of Lpy molecules can greatly improve the photochromic reversibility of the Mont-PyDE hybrid molecules. Therefore, it can be rationally assumed that the cointercalated Lpy molecules work to suppress the formation of the intercalated PyDE molecules during visible light irradiation and thus improve the photochromism.

CONCLUSIONS

The intercalation of PyDE as a diarylethene in montmorillonite-diarylethene hybrid materials resulted in efficient and smooth photochromism. The photochromic efficiency of the present hybrid materials, however, decreased by repeated irradiation with alternative UV and visible light. This was attributed to the formation of *photoinactive parallel* open PyDE molecules. However, this degradation could be suppressed and reversibility greatly enhanced by cointercalating Lpy molecules into the clay interlayers with PyDE molecules.

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