

Intercalation of Spirooxazine Induced by Zinc Cation Chelation in Montmorillonite and Its Photochromic Behavior

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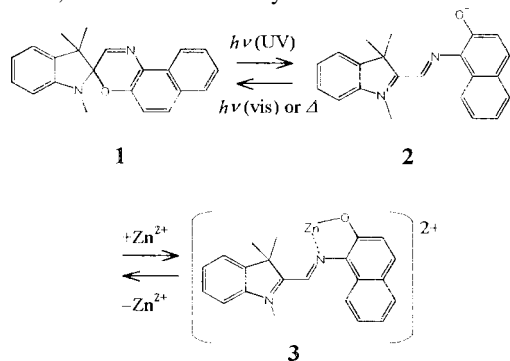
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Spirooxazine (SPO) was introduced into hydrophobically modified montmorillonite dispersed in acetone under UV illumination in the presence of zinc ions. The fluorescence spectra of the samples exhibited photochromic behavior arising from the photo-induced interconversion between the original species of SPO and the Zn-chelated complex of the SPO-derived merocyanine.

Organic-inorganic composites made by exchanging sodium ions in interlayers of montmorillonite with cationic dyes enable the preparation of photo-functional materials. Studies on the photochromism of cationic spiropyran¹ and azobenzene² and viologen³ intercalated in such clays have been attempted. Non-ionic dyes can be intercalated into the interlayers of the clays made hydrophobic by ion exchange of organic surfactants. In fact, it has been reported that non-ionic spiropyran⁴ and azobenzene⁵ were adsorbed in the hydrophobic montmorillonite to control the photochromic behavior of the dyes.

Spirooxazine (SPO) exhibits photochromic behavior by a heterolytic bond cleavage between the spiro carbon and oxygen.⁶ The original colorless SPO (**1**) is transformed into the colored merocyanine (**2**), and then coordinated to specific metal ions (e.g., Zn²⁺) in the solution, forming the fluorescent metal complex (**3**) (Scheme 1).⁷ The species **2**, which, otherwise, quickly reverts to **1**, becomes stabilized by the chelation of the metal ion.



Scheme 1.

First, sodium ions were exchanged with zinc ions in the interlayers of the montmorillonite. The zinc ions were efficiently chelated with **2** formed by UV light irradiation of **1** in the interlayers. The resulting **3** was, however, too stable to exhibit any photochromic behavior. Therefore, the present study has been taken to realize a circumstance to adsorb both the SPO molecules and zinc ions and stabilize **1** as well as **3** by the surfactant-modified montmorillonite clay. In this way, measuring the fluorescence spectra of **3** was more informative for an analysis of the photochromic behavior rather than its absorption spectra since the coverage of SPO is low.

SPO,⁸ ZnCl₂ (Wako Chemicals, extra pure grade), acetone (Dojin Chemicals, spectro-grade), and hexyl-, octyl-, decyl-, and cetyltrimethylammonium bromides (Tokyo Kasei) were used without further purification. Deionized and distilled water was also used. Purified standard montmorillonite clay (Na_{0.33}(Al_{1.67}Mg_{0.33})Si₄O₁₀(OH)₂·nH₂O) with a cation exchange capacity (CEC) of 119 m mol / 100 g was purchased from the Clay Science Society of Japan.

Suspensions of montmorillonite (Mont) were stirred for 40 h in water containing the surfactant molecules, i.e., hexyl (Hex), octyl (Oct), decyl (Dec), and cetyl (Cet)-trimethylammonium bromides in amounts of 100% CEC of the montmorillonite were used in order to form composites containing surfactant monolayers, as reported previously.⁹ The hydrophobic clay modified by one of these surfactants was suspended in acetone containing SPO and ZnCl₂ in excess amounts of the montmorillonite CEC. The Hex-Mont suspensions were stirred in order to adsorb the SPO and Zn²⁺ as **3** onto the hydrophobic clays under UV light irradiation (Hg lamp, $\lambda = 350 \pm 50$ nm) for 0, 4, 12, 24, and 48 h. The other homologs-Mont suspensions were also stirred during irradiation for 48 h. These SPO samples included in the Hex-, Oct-, Dec-, and Cet-Mont were dried at 60 °C for a sufficient length of time and referred to as Hex-, Oct-, Dec-, and Cet-Mont(SPO), respectively.

The fluorescence spectra of the hydrophobic montmorillonite including the SPO and Zn²⁺ were observed as a function of time with UV (350 ± 10 nm) or visible (450 ± 10 nm) light irradiation in order to monitor the photochromic behavior with a JASCO FP-750 fluorescence spectrophotometer.

Figure 1 shows the fluorescence ($\lambda_{\text{ex}} = 450$ nm) and excitation ($\lambda_{\text{em}} = 540$ nm) spectra of the Hex-Mont(SPO) obtained by the adsorption of SPO and Zn²⁺ under UV light irradiation for 48 h. The shape and peak position of the spectra of this sample are essentially coincident with those observed in acetone without montmorillonite, indicating that **3** was adsorbed into the interlayers of Hex-Mont.^{7a,7b}

Figure 2 shows the fluorescence spectra ($\lambda_{\text{ex}} = 450$ nm) of the same sample as shown in Figure 1 observed during the reaction by

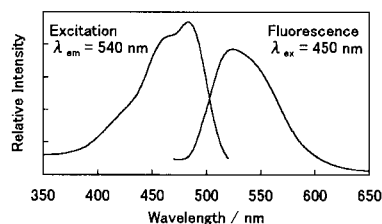


Figure 1. Fluorescence and excitation spectra of Hex-Mont(SPO) obtained by the adsorption of SPO molecules and zinc ions under UV light irradiation for 48 h.

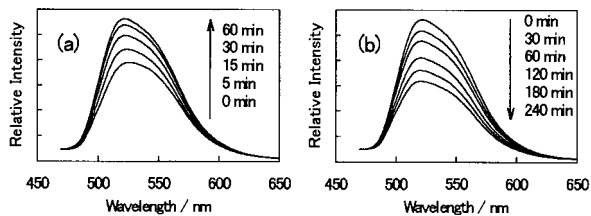


Figure 2. Fluorescence spectra of Hex-Mont(SPO) observed with the time of (a) UV (350 nm) or (b) visible (450 nm) light irradiation.

(a) UV (350 nm) or (b) visible (450 nm) light irradiation. The intensities of the fluorescence band assigned to **3** increased with an increase in the UV irradiation time and reached the saturation point after 60 min. The spectral change indicates that **1** may interact with the Zn^{2+} in the interlayers of Hex-Mont to form a Zn-merocyanine complex (e.g., **3**). This behavior is similar to that in solution (not shown here).^{7a,7b} The results suggested that **1** and zinc ions as well as **3** were intercalated in the Hex-Mont. In contrast to the results in solution, the stability of **3** in montmorillonite was remarkably improved. That is, the intensity of the fluorescence band hardly changed after the sample was kept at room temperature in the dark for a day, whereas the fluorescence disappeared within a day in solution. With prolonged irradiation of visible light, the fluorescence intensity of the sample gradually decreased and reached saturation after 240 min. The fluorescence spectrum of the sample was maintained both in intensity and in the emission maximum when kept at room temperature in the dark for a day. **3** in the clay was dissociated into **1** and zinc ions by the visible light, though not completely.

Figure 3 shows the changes in the fluorescence intensities ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 540$ nm) of the Hex-Mont(SPO)s, which were prepared under different conditions, with the time of UV or visible light irradiation. The present samples of Hex-Mont(SPO) were prepared under UV illumination for 0, 4, 12, 24, and 48 h by stirring the Hex-Mont in acetone containing SPO and Zn^{2+} . In all of the samples, the interconversion between **3** and **1** in the clay was observed by UV or visible light irradiation. A larger amount of **3** was produced in the clay kept under UV irradiation for a longer time in the acetone containing SPO and Zn^{2+} . **3** could hardly be detected after filtration of the intercalated suspensions, so it could be reasonably assumed that the zinc ions were chelated with **2** during UV light irradiation in acetone, and the resulting **3** was mostly intercalated in the Hex-Mont. Consequently, the contents of SPO species and zinc ions in the clays increased with the time of irradiation performed during the adsorption. Upon dissociation of **3** in the clay, the recovered **1** and zinc ions are assumed to be reversibly subject to the photochromic behavior arising from the formation of **3**, remaining close enough to react with each

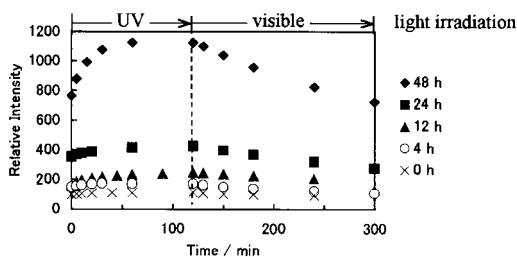


Figure 3. Changes in fluorescence intensities of Hex-Mont(SPO)s with the time of UV (350 nm) or visible (450 nm) light irradiation. The samples were prepared under UV light (350 nm) irradiation for 0, 4, 12, 24, and 48 h.

other. In the samples, the photochromic behavior could be observed despite the small quantity of SPO (< 0.1% CEC).

Figure 4 shows the changes in the fluorescence intensities ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 540$ nm) of Hex-, Oct-, Dec-, and Cet-Mont(SPO) with the time of UV or visible light irradiation. All of the samples were prepared under the continuous irradiation of UV light by stirring in the acetone for 48 h. In all the samples, the changes in the intensities were observed by the interconversion between **1** and **3** despite changes in the surfactant homologs. Larger amounts of SPO could be intercalated in montmorillonite modified by the longer hydrocarbon chain of the surfactants. However, the maximum fluorescence intensity inversely became smaller by modifying the clay by the longer hydrocarbon chained surfactants. Consequently, there is less possibility that the ionic species **3** and zinc ions in the bulk solution are intercalated into the more hydrophobic interlayers of the clay, although the non-ionic species **1** is easily intercalated in the hydrophobically modified clay. Therefore, the formation of **3** could be considered to be controlled by the restricted amounts of zinc ions in spite of enough amount of **1** in the interlayers.

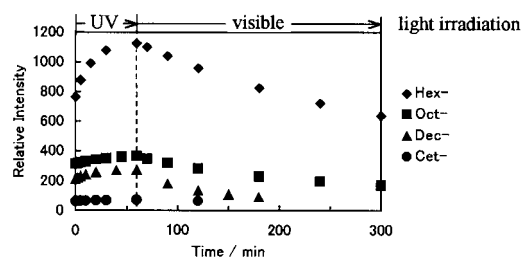


Figure 4. Changes in fluorescence intensities of Hex-, Oct-, Dec-, and Cet-Mont(SPO) with the time of UV (350 nm) or visible (450 nm) light irradiation.

Montmorillonite interlayers were modified by organic surfactants in order to control the hydrophobicity of the interlayers. SPO and Zn^{2+} could both be intercalated into the hydrophobic montmorillonite. As a result, the fluorescence spectra were found to be an effective index for the photo-induced interconversion between **1** and **3**. The preferential intercalation of the SPO species in the clay interlayers proved that **3** was more favorable to the lower hydrophobic circumstance, which was in contrast to **1**.

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