Adsorption of a Spiropyran on a Layered Clay Mineral

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Abstract. Adsorption of a photochromic dye, spiropyran, on a layered clay mineral, a synthetic hectorite, was investigated. Spiropyrans are well-known photochromic molecules due to its fast and reproducible color change resulting from the photoisomerization between hydrophobic closed-ring spiropyran and hydrophilic open-ring merocyanine. The photochemical reaction of the adsorbed spiropyran in the modified hectorite was also examined.

1. Introduction

Several research topics on encapsulation of photochromic dyes into nanospaces have been done not only to study the effects of the confinement on the reactions as well as to construct photochromic hybrid materials,[1-8] although the stability of photochemically formed species is largely affected by molecular environment. Closed-ring spiropyrans transform into open-ring, zwitterionic merocyanines by UV irradiation showing the color change from colorless to blue. The open-ring merocyanine forms return to the closed-ring spiropyran forms by heat or visible light irradiation. In polar environments, the merocyanine forms are stabilized through the interactions of the indole cation and phenoxyl anion and show negative photochromism.[9] It was also reported that the open merocyanine forms were protonated in acidic conditions and the protonated merocyanine forms exhibited yellow color. [9]

Among many examples of the successful introduction of spiropyrans into nanospace materials, photoinduced adsorption is a unique behaviour, which uses light irradiation to trigger photochemical reaction and changes in the molecular structures to accommodate a photochemically formed molecules into the nanospace. The first introduction on the photoinduced adsorption phenomena was reported for a spiropyran (SP) in a toluene solution suspended mesoporous silica particle. [2] The thermal equilibria between SP and its isomer, a merocyanine (MC), are dependent on the polarity of the molecular surrounding. In the system of the toluene solution of the SP with the suspended mesoporous silica, the SP was dissolved in the organic solvent but not adsorbed onto the mesoporous silica. On the other hand, the MC was spontaneously adsorbed and stabilized in the mesoporous silica. The MC was expected to be stabilized by the interactions with hydrophilic nanospace materials.

As a group of 2:1 clay mineral contains readily exchangeable interlayer cations and the negatively charged silicate layers, smectite can be a great candidate as the host of intercalation of various guest species. The photoinduced adsorption of the MC onto a smectite was reported [4] in addition to the case of mesoporous silica. The MC formed from the SP by UV irradiation was adsorbed on the smectite with simultaneous decreasing the concentration of the SP in the solution. The visible light irradiation induced the desorption of the MC from the smectite.
Three different colors of retinal Schiff base confined in three montmorillonites suggested that clays of different origins contributed to the variation of the states of the adsorbed dye molecules. [11] Therefore, the systematic study using various nanospace materials including clay minerals to find the precise design of the photochemical reactions (yields and kinetics) is worth investigating. In this study, a synthetic hectorite was used as the support to examine the effects of the interlayer cations on the photochromic reactions of the SP.

2. Experimental Section

2.1. Materials

1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran (SP) was purchased from TCI Co., Ltd. A synthetic hectorite (Sumecton SWF) was kindly donated from Kunimine Industries Co., Ltd. Toluene was purchased from Merck. All the chemicals were used without further purification.

2.2. Proton Exchange of the Hectorite

A synthetic hectorite (Na+-SWF, 2 g) was dispersed in 750 ml of deionized water and stirred by magnetic stirring for 1 day. An aqueous HCl solution was added to adjust the pH of the suspension to 5 and further stirred for 1 day. The sediment was collected by ultracentrifugation at 20,000 rpm for 30 min. The sediment was washed with DI water until a negative silver nitrate test was obtained. The resulting powder was dried at room temperature in vacuum for 1 day. The exchanged hectorite was designated as H+-SWF.

2.3. Photoinduced Adsorption

Hectorites (Na+-SWF and H+-SWF, 10 mg) were added to a solution containing 0.13 mg of SP in 5 mL of toluene (8.07 × 10⁻⁵ M). The suspensions were sonicated for 1 min and transferred to the optical cuvette (10 mm optical length). A UV light was irradiated to the suspensions under magnetic stirring, and the suspensions were stored for 15 min in the dark, and then absorption spectra of the supernatant were measured. The irradiation process was repeated until the suspension reached a photostationary state. The colored suspensions were centrifuged 10 min (3,000 rpm) to obtain sediments. The sediments were dried under ambient conditions overnight in the dark. The red and yellow sediments were designated as H+-SWF/MC and Na+-SWF/MC, respectively and were used to investigate the effect of exchangeable anion on the negative photochromism of the MC.

2.4. Photochromism

UV-Visible spectrophotometer (PerkinElmer, LAMDA 1050) was used to obtain absorption spectra of the samples. Visible light and UV irradiation were carried out with a Xe lamp (ABET technologies, Sunlite solar simulator, 100 W) and UV spotlight (LED, 365 nm) at room temperature.

3. Results and Discussion

The photoinduced adsorption of the MC by the UV irradiation to the hectorite suspensions was followed by change of the absorbance of the SP in supernatants before and after UV irradiation. The UV-Vis absorption spectra of the supernatants are shown in Figure 1. The supernatants displayed no absorption in the visible light region, meaning that the MC has not remained in the solutions thanks to a short lifetime in toluene (15 s), and the hectorites were sedimented. The decrease of the SP by the UV irradiation was followed by the change of absorbance at 333 nm. The absorbance became constant (photostationary state) after UV irradiation for 12 min and 24 min for Na+-SWF and H+-SWF, respectively.
At the photostationary state, the adsorbed amounts of the MC were estimated by the change in the absorbance at 333 nm due to the SP in the supernatant before and after the UV irradiation. The decreases of the SP concentration were 56% (from 0.94 to 0.41) and 67% (from 0.98 to 0.32) from the initial concentration, given that the adsorbed amounts of MC were 7.33 mg/(g of hectorite) and 8.75 mg/(g of hectorite) for Na⁺-SWF and H⁺-SWF, respectively.

The adsorption of the MC under UV irradiation was followed by the absorbance at 333 nm, which is due to the absorption of the SP. The time profiles of the absorbance at 333 nm was not fit with the single-exponential equation (eq. 1), but they fitted with double-exponential equation (eq. 2).

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[A] = [A]_0 e^{k_1 t} 
\]

\[
[A] = [A]_0 (\alpha e^{-k_1 t} + \beta e^{-k_2 t})
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where, \([A]\) is the concentration of SP at time \(t\), \([A]_0\) is the initial concentration of SP, \(k_1\) and \(k_2\) are first-order rate constants (min⁻¹), and \(\alpha\) and \(\beta\) are amplitude of the two single exponential reactions. The rate constants of the photoinduced adsorption of the MC are summarized in Table 1.

**Table 1. Rate constants of the photoinduced adsorption of the MC on Na⁺-SWF and H⁺-SWF.**

| Adsorbent | \(k_1\) (min⁻¹) | \(k_2\) (min⁻¹) |
|-----------|-----------------|-----------------|
| Na⁺-SWF   | 0.186           | 2.26            |
| H⁺-SWF    | 0.054           | 2.66            |

Figure 1. Changes of the absorption spectra of the supernatants of (a) Na⁺-SWF and (c) H⁺-SWF and the changes of the absorbance at 333 nm by the UV irradiation for (b) Na⁺-SWF and (d) H⁺-SWF.
The fittings with double exponential equation suggested that the adsorption of the MC contained two first-order reactions, which were thought to be the adsorption of the MC and the protonated MC, respectively. Because the protonated MC was thermodynamically stable compared to the MC in a bentonite [14], it was expected that the high amounts of proton in H-SWF/MC led to the formation of the protonated MC and the stability of the protonated MC suppressed the diffusion of the MC (or the protonated MC) into the nanospace, taking longer time to reach the photostationary state in H-SWF (24 min) than in Na-SWF (12 min). The relatively weak interaction between the MC and Na accelerated the adsorption.

The visible light irradiation was done to examine the negative photochromism of the MC in the hectorites. Figure 2 shows the red color of Na-SWF/MC turned orange after visible light irradiation. After visible light irradiation for 1 min, the absorption spectra at the wavelength of 515 nm of Na-SWF/MC was dramatically decreased from 1.63 and became constant at 1.06 after irradiation for 2 min. On the other hand, in H-SWF/MC system, the yellow color has remained after irradiated by visible light for 10 min. The absorbance at 515 nm decreased from 0.50 to 0.45, suggesting that the MC transformed into the SP or the protonated MC. The absorbance at 410 nm indicated that small amounts of protonated MC in both samples were increased after visible light irradiation for 10 min. Therefore, it was confirmed that the protonated MC is generated by visible light irradiation to the MC in both hybrids.

Figure 2. Photographs of Na-SWF/MC and H-SWF/MC (a,c) before and (b,d) after irradiated by visible light for 10 min and (e,f) UV-Vis absorption spectra during irradiated by visible light.

Thermal coloration of Na-SWF/MC and H-SWF/MC was followed by absorption spectra of the samples after being stored at room temperature in the dark. In Figure 3, the time profile of the absorbance at 410 and 515 nm of both Na-SWF/MC and H-SWF/MC was plotted to follow thermal coloration processes.
The time profiles of the change in the absorbance at 410 nm was fitted by the single-exponential equation (eq. 1) and the time profiles at 515 nm was fitted by the double-exponential equation (eq. 2) for Na+-SWF/MC, while the profiles for H+-SWF/MC were fitted by the single-exponential equation (eq. 1). The rate constants of the thermal back reaction of Na+-SWF/MC and H+-SWF/MC are summarized in Table 2.

Table 2. Rate constants of the thermal coloration of MC on Na+-SWF and H+-SWF.

| Samples     | 410 nm  | 515 nm  |
|-------------|---------|---------|
|             | k (min⁻¹) | k₁ (min⁻¹) | k₂ (min⁻¹) |
| Na+-SWF/MC  | 6.6×10⁻³ | 43.1×10⁻³ | 6.8×10⁻³ |
| H+-SWF/MC   | 9.1×10⁻³ |         | 5.2×10⁻³ |

The time profiles of the change in the absorbance at 410 nm was fitted by the single-exponential equation (eq. 1) and the time profiles at 515 nm was fitted by the double-exponential equation (eq. 2) for Na+-SWF/MC, while the profiles for H+-SWF/MC were fitted by the single-exponential equation (eq. 1). The rate constants of the thermal back reaction of Na+-SWF/MC and H+-SWF/MC are summarized in Table 2.

The rate constants derived from the change in the absorbance at 410 nm were expected to be from the formation of the protonated MC, which was accelerated under acidic conditions. The rate constant for the change in the absorbance at 410 nm was higher for H+-SWF/MC than that for Na+-SWF/MC, due to higher proton content of H+-SWF/MC than that of Na+-SWF/MC to interacts with phenolate ion of the MC. The protonated MC was expected to be occurred by the reaction with hydroxyl groups at the edges of the clay. [4,12-14] The rate constants at 515 nm for Na+-SWF/MC were fitted with double-exponential equation, suggesting that the thermal coloration was composed of two reactions. Those two components were
expected to be the formation rate of the MC. The first component ($k_1$) was the formation rate of MC, which is only occurred in Na⁺-SWF confirmed the role of Na⁺ to induce the formation of MC even without the UV irradiation. The results can be concluded that the interlayer cation of the hectorite plays important role in stabilizing MC and accelerate the rate of MC formation.

4. Conclusions
The adsorption of the photochemically formed isomers of the SP on the synthetic hectorite and its proton exchanged form was reported. The rate constant of the adsorption for the synthetic hectorite was larger than that for the proton exchanged form, suggesting that the interlayer Na⁺ was thought to play an important role in accelerating the adsorption of the MC on the hectorite. The spontaneous formation and the stabilization of MC on the hectorite were considered to be caused by the interactions between the phenoxyl anion of MC and the interlayer cations of the hectorite.

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6. References
[1] Klajn R 2014 Chemical Society Reviews 43 84-148
[2] Okabe Y and Ogawa M 2015 RSC Advances 5
[3] Yamaguchi T, Maity A, Polshettiwar V and Ogawa M 2018 Inorganic Chemistry 57
[4] Yamaguchi T and Ogawa M 2018 Chemistry Letters 47 91-189
[5] Arieli D, Vaughan D E and Goldfarb D 2004 Journal of the American Chemical Society 126 76-88
[6] Tong Z, Sasamoto S, Shimada T, Takagi S, Tachibana H, Zhang X, Tryk D A and Inoue H 2018 Journal of Materials Chemistry 18 4641-5
[7] Nabetani Y, Takamura H, Hayasaka Y, Sasamoto S, Tanamura Y, Shimada T, Masui D, Takagi S, Tachibana H, Tong Z and Inoue H 2013 Nanoscale 5 3182-93
[8] Umemoto T, Ohtani Y, Tsukamoto T, Shimada T and Takagi S 2014 Chemical Communications 50 31-46
[9] Aiken S, Edgar R J, Gabbutt C D, Heron B M and Hobson P A 2018 Dyes and Pigments 149 92-121
[10] Furutani Y, Ido K, Sasaki M, Ogawa M and Kandori H 2007 Angewandte Chemie International Edition 46
[11] Imwiset K J and Ogawa M 2020 Colloids and Surfaces A: Physicochemical and Engineering Aspects 605 125352
[12] Raymo F M and Giordani S 2001 Journal of the American Chemical Society 123 4651-2
[13] Shimizu I, Kokado H and Inoue E 1969 Bulletin of the Chemical Society of Japan 42 1730-4
[14] Yamaguchi T, Imwiset K J and Ogawa M 2021 Langmuir 37 3702-8