Synthesis of Rhodamine 6G/Cationic Surfactant/Clay Hybrid Materials and Its Luminescent Characterization

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In order to develop the solid-state laser oscillator based on laser dye compound, the intercalation of rhodamine 6G (R6G) together with cetyltrimethylammonium cations (CTA^+) into montmorillonite (Mont) interlayer space was investigated. It was found that the solid material with the light-emitting ability was prepared by cointercalating R6G and CTA^+ molecules into Mont interlayer space at lower molar ratio of R6G to CTA^+ molecules.

Generally, the commercially available dye laser was constructed as dye-solution flow type laser oscillator, but to make a compact laser oscillator, this type laser oscillator has a serious drawback due to a large circulator required to feed laser dye solution. This problem could be solved by developing the solid-state materials with laser oscillation ability. Many researchers have studied on the solid materials with the light-emitting ability to solve this problem.[1–19] Rhodamine 6G (R6G) dye, one of the typical laser dyes, exhibits a high light-emitting ability in a dilute solution, but no fluorescence has been observed in the solid state because of the formation of the *H-type* aggregates.[13–17] Therefore, the development of solid-state laser material will be attained if individual R6G molecules are isolated with each other in the solid state. Some researchers have been studied on the control of dye state in clay interlayer space.[20–22] Endo et al. have reported that the hybridization of rhodamine dye and ethanol molecules with the smectite clay provides solid-state materials with emitting ability.[22] However, this material has still some problem when used as a practical material, because it is difficult to control the amount of the co-intercalated ethanol molecules. In the present study, we used montmorillonite (Mont), which is one of the clay minerals and possesses an ability intercalating and integrating various functional organic cations,[23–29] as host material, and attempted the isolation of the intercalated R6G molecules in the Mont interlayer space by using a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as spacer molecules. Furthermore, the light-emitting ability of the prepared hybrid materials was investigated.

Purified standard sodium Mont (Tsukinuno: ca. 2 wt% of Fe was included) with a cation-exchangeable capacity (CEC) of 1.19 mequiv./g obtained from the Clay Science Society of Japan was used without further purification. CTAB and R6G (laser grade) were purchased from Tokyo Kasei Chemical Industry Co., Ltd and Lambda Phisik, respectively, and they were used without further purification. One gram of Mont powder was added to the prepared CTAB/R6G mixed aqueous solution with appropriate molar ratios ($[R6G]/[CTA^+]$) with keeping the sum of R6G and CTA^+ at ca. 1.19 mmol. The mixed suspension was stirred at room temperature overnight for intercalation reaction. The R6G/CTA^+/Mont hybrid materials were obtained as red powder by the filtration and drying in vacuo. For identifying the layer structure, X-ray analysis of the obtained hybrid powder was carried out with a RINT-2000 diffractometer (RIGAKU) using a Cu Kα radiation source. The FT-IR and fluorescence spectra of the obtained hybrid powder were measured on an FT/IR-610 Fourier transform infrared spectrometer and an FP-750 spectrofluorometer (JASCO), respectively.

Figure 1 shows the FTIR spectra of the prepared hybrid powder. All spectra of the obtained powder exhibited the coexistence of R6G and CTA^+ molecules. This result indicates that R6G and CTA^+ molecules would be cointercalated into the Mont interlayer space. This conclusion is also supported by the observed color of hybrid powder.

The basal spacings, d_{001}, of Mont layer structure estimated from the XRD patterns were plotted against molar ratio between added R6G molecule and cation-exchangeable capacity, [R6G]/[CEC] in Figure 2. The d_{001} values of all hybrid samples were larger than that of Mont. This behavior clarifies that R6G and/or CTA^+ molecules are intercalated into Mont interlayer space by the cation-exchange reaction. The d_{001} values of R6G/CTA^+/Mont hybrids were lager than that of CTA^+/Mont hybrids and smaller than that of R6G/Mont hybrids. Moreover, the d_{001} va-

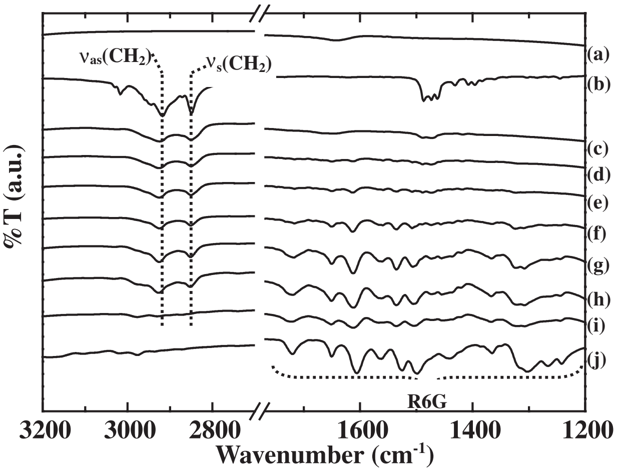

Figure 1. FT-IR spectra of (a) montmorillonite, (b) CTAB, (c)–(i) R6G/CTA^+/Mont hybrid materials, where $[R6G]/[CTA^+] = 0$ (c) , 0.01 (d), 0.1 (e), 0.5 (f), 1.0 (g), 2.0 (h), and ∞ (i), and (j) R6G powders.

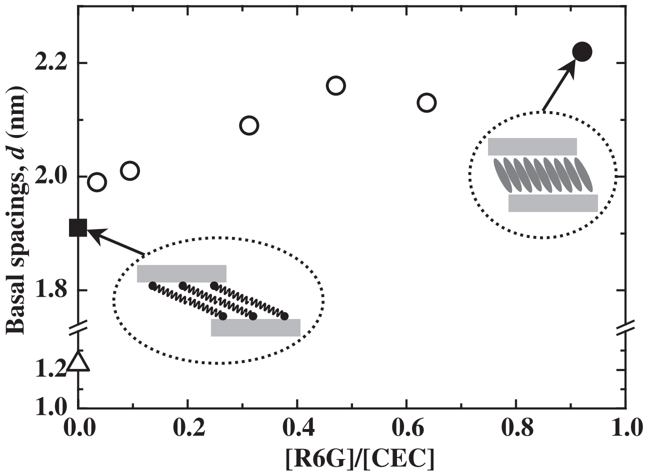

Figure 2. The dependence of basal spacings, *d*, of the Mont layer on the [R6G]/[CEC] value. △: montmorillonite, ■: CTA$^+$/Mont hybrid, ●: R6G/Mont hybrid, and ○: R6G/CTA$^+$/Mont hybrid materials.

lues of R6G/CTA$^+$/Mont hybrids increased with an increase in [R6G]/[CEC] value. These results suggest that the larger and rigid R6G molecule would control layer distance, and the CTA$^+$ molecule with relatively flexible alkyl chain may form the most energetic stable structure in vacant space of Mont interlayer space. Therefore, such behavior could be caused by the change in tilt angle of intercalated R6G molecules. Here, the angle is between the long axis of R6G molecules and the silicate layer.

Figure 3 shows the [R6G]/[CEC] dependence of the fluorescence intensity of hybrid powders excited by 530 nm visible light. In the case of R6G/Mont hybrid materials, its fluorescence intensity was negligibly low, even when [R6G]/[CEC] value was reduced. The intercalated R6G molecules in the R6G/Mont system are considered to form the aggregate without emitting ability at smaller amount of R6G molecules. Since *H-type* aggregate was well known as the aggregate without emitting ability,[13–17,30] the aggregate formed in Mont interlayer space would be *H-type* aggregate. On the other hand, the fluorescence intensity of the R6G/CTA$^+$/Mont hybrid material exponentially increased with decreasing the [R6G]/[CEC] value. This result indicates that the solid material with higher emitting ability can be prepared by cointercalation of R6G and CTA$^+$ molecules at the lower [R6G]/[CTA$^+$] ratio. The high fluorescence intensity clarifies that the interaction among the intercalated R6G molecules is reduced in the presence of the cointercalation of CTA$^+$ molecules with an decrease in [R6G]/[CEC] values, that is, the cointercalated CTA$^+$ molecules may play a role as suppressor for interaction between the intercalated R6G molecules in the R6G/CTA$^+$/Mont hybrid system.

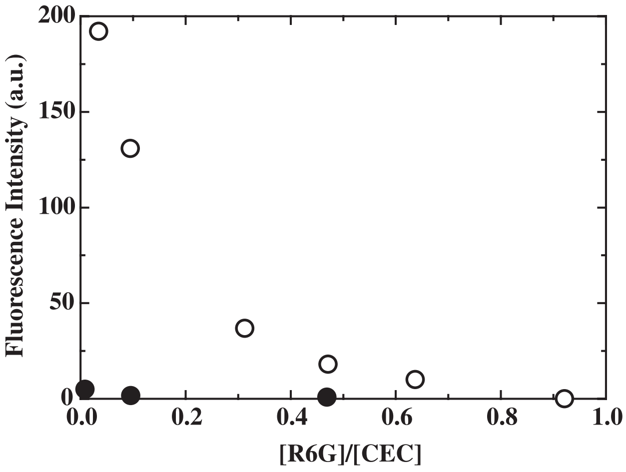

Figure 3. [R6G]/[CEC] dependence of the fluorescence intensity of the R6G/Mont hybrid (●) and R6G/CTA$^+$/Mont hybrid (○) materials. Excitation is by 530 nm visible light.

We succeeded in the synthesis of the solid material with enough emitting ability by encaging together both R6G and CTA$^+$ molecules into the montmorillonite interlayer space. In the present hybrid system, the intermolecular interaction of R6G molecules may be weakened by the cointercalated CTA$^+$ molecules. Therefore, the intercalated R6G molecules were isolated by CTA$^+$ molecules, and the intercalated R6G molecules might generate the fluorescence by the light excitation at the lower [R6G]/[CEC] range. The R6G/CTA$^+$/Mont hybrid solid material prepared in the present study may have a possibility as solid materials for the emitting device and laser device, if the technique for preparing thin-film and bulk modules of the present hybrid is established.

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