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Preparation of Hybrid Organic/Inorganic Luminescent Thin Solid Films with Highly Concentrated Laser-dye Cations

Ryo Sasai,* Takanori Itoh, Nobuo Iyi,† Katsuhiko Takagi,†† and Hideaki Itoh
EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603
†Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba 305-0044
††Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603

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To develop solid materials with high luminescence, the preparation of laser-dye rhodamine 6G (R6G)/clay hybrid thin solid films with surfactant molecules as aggregation suppressors was investigated. Dodecyltrimethylammonium cations were found to be very effective for inhibiting dye aggregation in the clay interlayer space. Consequently, this material showed light emission from the R6G monomer.

The development of a solid-state dye-lasing system has been vigorously investigated by various researchers for reducing lasing instrument size and/or lowering environmental loads. However, a great number of laser-dyes have no lasing ability in the solid state because of the formation of aggregates with less luminescence and/or low luminescent quantum yield. The utilization of various inorganic solid matrixes, such as clay, layered silicate, and mesoporous silica, has been investigated by many researchers.[1–3] Layered clay is one of the effective host materials for solidification because ionic molecules with various molecular sizes can be integrated in its interlayer space. Moreover, the prepared hybrid compounds could have an optical anisotropy originating from layered structure. However, the prepared hybrid compounds cannot exhibit luminescence when laser-dye ions are intercalated in the interlayer space. Thus, it is very important to inhibit the formation of aggregates that lack luminescence ability. Lopez et al. realized the preparation of rhodamine 6G (R6G)/clay hybrid with high luminescence ability in the extremely low concentration range of the intercalated R6G concentration.[4] However, sufficient optical density was not obtained in this hybrid compound. Endo et al. reported that monomeric R6G cations can be intercalated at relative high concentration coexisting with ethanol molecules in the clay interlayer space.[5] However, the efficiency of aggregation inhibitation was still low. In a our previous paper, we found that the co-intercalation of R6G with cationic surfactants into clay interlayer space inhibited the formation of nonluminescent aggregates.[6,7] However, it is important to know which surfactants inhibit the formation of nonluminescent aggregates in order to prepare a hybrid with high luminescence efficiency. In this study, we investigated the effects of alkyl chain length of the surfactant on the aggregation inhibition of R6G cations intercalated in clay interlayer space.

Montmorillonite (Mont) with 1.19 meq./g cation exchangeable capacity (CEC) was used as the solid matrix. Rhodamine 6G, a typical cationic laser dye, was used. Alkyltrimethyl ammonium bromide with various alkyl chain lengths ($C_nH_{2n+1}N^+(CH_3)_3 \cdot Br^-$; $n = 6$, 10, 12, 14, 16, and 18; abbreviated as $CnTA^+Br^-$, hereafter) was used as the aggregation inhibitor. Oriented thin solid films of Mont, prepared by spin-coating 20 g/dm^3 aqueous Mont suspension on glass substrates (film thickness estimated from Atomic Force Microscopy (Nanopics 2100, Seiko Instruments Inc.) was ca. 60 nm), were immersed in 1 mmol/dm^3 of each $CnTA^+Br^-$ aqueous ethanol solution (mol ratio: 0.8) at 60 °C for 6 h. The prepared $CnTA^+$/Mont thin solid films were immersed in 1 μmol/dm^3 of R6G aqueous ethanol solution at 60 °C for 6 h, washed with an aqueous ethanol solution and dried at 60 °C for 2 h in vacuo. Concentration of incorporated R6G molecules in film was ca. 6% vs CEC. Absorbances at peak of all films were ca. 0.05–0.1. Basal spacing values were estimated from X-ray diffraction patterns (RIGAKU, RINT-2500). Absorption spectrum measurements were carried out using a V-550 UV–vis spectrophotometer (JASCO) attached with a film unit (RSH-452). Fluorescence spectra were measured using a fluorescence spectrophotometer F-4500 (HITACHI).

Figure 1 shows the dependence of normalized fluorescence intensity on the carbon number of the alkyl chain. Hybrid thin films without the surfactant ($n = 0$) scarcely exhibited fluorescence. We previously reported that a nonfluorescent R6G aggregate was formed even for low intercalated amount of R6G molecules. Normalized fluorescence intensity slightly increased with an increase in carbon number n of the alkyl chain for values less than $n = 10$. The normalized intensity drastically increased from $n = 10$ to 12. For values greater than $n = 12$, the normalized fluorescence intensity gradually decreased with an increase in carbon number of the alkyl chain. It was found that $C12TA^+$ molecules were most effective for inhibiting nonluminescent R6G aggregation in Mont interlayer spaces.

Figure 2 shows the normalized absorption spectra for the prepared solid thin films. The absorption spectrum of the R6G/Mont without $CnTA^+$ molecules showed an absorption peak at a longer wavelength range than that the monomer

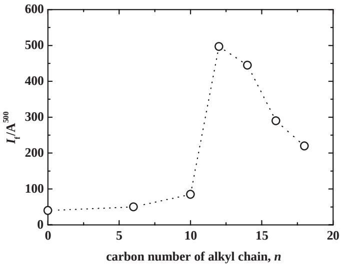

Figure 1. Dependence of normalized fluorescence intensity, I_f/A^{500}, on the carbon number, n, of the surfactant. $n = 0$ means without surfactant. I_f is fluorescence intensity at a peak wavelength, and A^{500} is absorbance at 500 nm. Excitation wavelength is 500 nm.

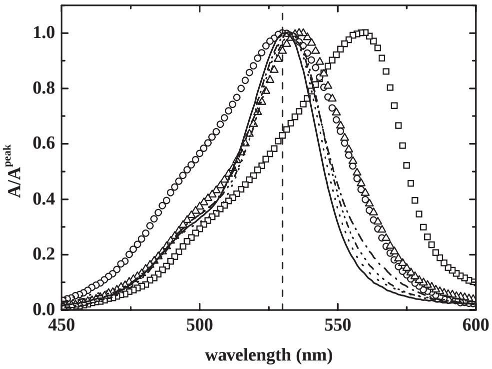

Figure 2. Normalized absorption spectra of solid thin films. R6G/Mont (□) and R6G/ CnTA$^+$/Monts: 6 (○), 10 (△), 12 (solid line), 14 (dotted line), 16 (dashed and single-dotted line), and 18 (dashed and double-dotted line). The dashed line indicates the position of the monomer R6G peak in a dilute aqueous solution.

R6G, which can be observed in a dilute aqueous solution (ca. 1×10^{-6} mol/dm^3). It is well known that this bathochromic shift of the absorption peak is caused by the formation of *J*-type dimers or higher-order aggregates, which have a lower quantum yield of emission.[8] In the case of R6G/C6TA/Mont, the position of the absorption peak corresponded with that of the monomer, however a shoulder with large absorbance also appeared. This hyperchromism at a shorter wavelength range than the monomer peak indicates the existence of *H*-type dimer or higher-order aggregates which have no emitting ability.[6] However, this hyperchromism observed at a shorter wavelength range disappeared for R6G/CnTA/Mont hybrid thin solid films with n values more than $n = 10$. From these results, it is apparent that the co-intercalation of surfactant with n more than $n = 10$ could inhibit the formation of *H*-type aggregate. The R6G/C6TA/Mont exhibited hyperchromism at a longer wavelength range. Thus, this hybrid also has *J*-type aggregates, and weak luminescence could be observed. Since the R6G/C10TA/Mont hybrid has a higher optical density at around 560 nm, this hybrid showed weak luminescence. However, luminescence intensity of the R6G/C10TA/Mont hybrid was slightly larger than that of R6G/C6TA/Mont hybrid. The absence of *H*-type aggregates is responsible for this slight increase in luminescence intensity. Unlike the absorption spectrum of R6G/C6 or 10TA/Mont hybrid, the spectrum for the R6G/C12TA/Mont hybrid almost corresponded with that of the R6G monomer in a dilute aqueous solution. This result supports the conclusion that the fluorescence of the R6G/C12TA/Mont hybrid is derived from the monomer species. Therefore, the co-intercalation of C12TA$^+$ molecules could realize higher dispersion of the intercalated R6G molecules in clay interlayer space. When the carbon number of the alkyl chain, n, became greater than 14, absorbance at around 560 nm slightly increased with increasing n value. This slight increase is favorable for the existence of *J*-type aggregates in the clay interlayer space. For these *J*-type aggregates, the fluorescence intensity decreased with an increase in n. These results lead to the conclusion that the co-intercalation of C12TA$^+$ molecules is effective for inhibiting the aggregation of R6G intercalated in the clay interlayer space. The effective inhibition of C12TA$^+$ molecules for the formation of R6G aggregates can be explained by "*size-matching*" between the R6G molecule and the interlayer space formed by CnTA$^+$ in the clay interlayer (cf. Figure 3). In the case of $n \leq 10$ or $n \geq 14$, the difference between the R6G molecule size and the interlayer size would give rise to a mismatch. The intercalated R6G molecules would then form an aggregate without light-emission ability for eliminating the energetic destabilization due to this size mismatch.

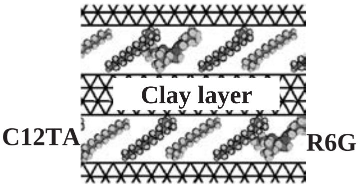

Figure 3. Prospective structure model of R6G/C12TA/ Mont hybrid material.

The molar concentration of R6G molecules in the R6G/C12TA/Mont hybrid was ca. 0.1 mol/dm^3. Usually, the fluorescence of R6G monomer can be observed only in an extremely dilute region, ca. 1 µmol/dm^3, in aqueous media. However, the R6G/C12TA/Mont hybrid with [R6G] = ca. 0.1 mol/dm^3, at which emission quantum yield is extremely low, exhibited monomer fluorescence. This result indicates that the co-intercalation of C12TA$^+$ is an effective method for not only inhibiting aggregation, but also for realizing large accumulation of the R6G monomer in the solid state.

In conclusion, in this study, we successfully prepared organic/inorganic hybrid thin solid films intercalating R6G molecules (ca. 0.1 mol/dm^3) as *monomers* by co-intercalation of alkyltrimethylammonium cations. The hybrid thin solid films exhibited a higher *monomer* luminescence. Moreover, the "*size-matching*" between a R6G molecule and interlayer-space formed by CnTA$^+$ in the clay interlayer was shown to be an essential factor for high dispersion of associative organic molecules, such as a laser dye, in the hydrophobic clay interlayer. The present results provide the necessary impetus to develop organic/clay hybrid solid materials with various functions in the future.

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