Preparation of a Novel Luminous Heterogeneous System: Rhodamine/Coumarin/Phyllosilicate Hybrid and Blue Shift in Fluorescence Emission

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R6G/coumarin/phyllosilicate hybrids were prepared by incorporation of rhodamine 6G (R6G) molecules into the interlayer space of a coumarin/Mg−phyllosilicate hybrid (a host hybrid). Deintercalation of the coumarin moiety and segregation of two different functional organic dyes are eluded using the host hybrid, in which the coumarin moiety is anchored to the Mg−phyllosilicate moiety with an inorganic/organic covalent bond. TG−DTA, XRD, UV–vis, and fluorescence measurements revealed that novel heterogeneous systems, i.e., the R6G/coumarin/phyllosilicate hybrids, are obtained. The amount of R6G loaded into the hybrids increases as the R6G/host hybrid ratio in the starting mixtures increases. The interlayer spacing of the hybrid is expanded because of intercalation of R6G. Most of R6G is in the monomer state, although aggregates coexist. Fluorescence emission was observed over a wide wavelength range of 350−750 nm. Both the coumarin moiety and R6G fluoresce. The fluorescence intensities from both the coumarin chromophore and R6G decrease as R6G incorporated into the hybrids increases, supporting the coexistence of the two different dyes within the same two-dimensional nanospace. Furthermore, the fluorescence emission from the coumarin moiety is blue-shifted, indicating that the local environment around the coumarin chromophore is changed by construction of the heterogeneous systems.

Introduction

The interlayer space of phyllosilicates provides a two-dimensional nanoscaled gallery. This two-dimensional nanospace is very attractive for constructing organized heterogeneous systems comprising several functional organic molecules and/or metal complexes. It is expected that properties of the chemical species are changed by constructing such supramolecular systems in solid media. For example, the fluorescence emission maxima of laser dyes would be shifted. Construction of such heterogeneous systems is also expected to provide luminous solid-state materials, including two different laser dyes with a very broad fluorescence emission, solid-state photoinduced electron-transfer,[1,2] and energy-transfer systems[3] that are elemental systems of artificial photosyntheses and so on. However, it has been reported that construction of such heterogeneous systems is difficult in many cases because co-intercalates are stratified into individual interlamellar spaces; i.e., the cointercalates are segregated.[1]

Phyllosilicates consist of two-dimensional Si tetrahedral and octahedral sheets. Individual Si tetrahedrons are linked with neighboring tetrahedrons by sharing three corners, i.e., basal oxygen, to form a hexagonal mesh pattern.[4] Phyllosilicates related to clay minerals are classified conventionally into eight major groups on the basis of layer types (1:1 or 2:1), layer charges, and interlayer types. One of the groups is the smectite group. The layer type of smectites is the 2:1 layer; i.e., smectites consist of two Si tetrahedral sheets and one octahedral sheet sandwiched by the Si tetrahedral sheets. Because diadochy isomorphous substitutions occur in the octahedral sheets in smectites, the phyllosilicate layers are negatively charged. To compensate the negative charge, exchangeable cations are intercalated between the layers of smectites. Phyllosilicates belonging to the smectite group are further classified into subgroups according to octahedral sheet types, chemical compositions, and geometry. Smectites with divalent cations in the octahedral sheets are classified as trioctahedral smectites. Typical trioctahedral smectites are hectorite ($M_x(Mg_{3-x}Li_x)Si_4O_{10}(OH)_2$), stevensite ($M_x(Mg_{3-x}\square_x)Si_4O_{10}(OH)_2$), and saponite ($M_{y-x}(Mg_{3-x}(Al, Fe)_x)(Si_{4-y}Al_yO_{10}(OH)_2)$, where M indicates exchangeable cations between layers and □ indicates vacancy. Phyllosilicates with the octahedral cations of Mg are called Mg−phyllosilicates in some cases.

We have reported syntheses of organic/Mg−phyllosilicate hybrids, in which Mg−phyllosilicates and organic moieties

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covalently bond with each other.[5–7] One of them is a luminous layered inorganic/organic nanocomposite, a coumarin/Mg−phyllosilicate hybrid, synthesized by a reaction of a mixture of silylated coumarin, silica sol, and inorganic salts.[7] Coumarin dyes are attractive functional organic molecules and are put to practical use in dye lasers in a liquid state. The dye lasers are very useful because of their wide variable wavelength. It has been reported that laser dyes are incorporated into SiO_2 xerogels,[8–11] zeolites,[12] layered silicates,[6,13–24] and so on. The coumarin/Mg−phyllosilicate hybrid has an interlayer space with the organic moiety and a covalent bond between the coumarin and Mg−phyllosilicate moieties, which are advantageous in constructing a heterogeneous system as follows. The coumarin/Mg−phyllosilicate hybrid is swelled in organic solvents, and another functional organic molecule can be incorporated into the interlayer space of the hybrid even in the organic solvents because the organic moiety is located between the layers. Deintercalation of the coumarin chromophore is considered not to proceed because of the covalent bond between the coumarin and Mg−phyllosilicate moieties. Deintercalation should have proceeded if the covalent bonds were absent. The covalent bonds would suppress stratification of the coumarin moiety and the guest functional organic species into different interlayers. Consequently, the coumarin/Mg−phyllosilicate hybrid is a promising host for construction of heterogeneous systems, in which two different functional organic species are integrated within the two-dimensional nanospace.

Rhodamine 6G (R6G) is also a laser dye and is used in dye lasers in a liquid state. Several aggregations of R6G have been reported.[14–21] A perfect H-type dimer has a sandwich structure with optical transition moments oriented in parallel, and an absorption band for this dimer is placed at higher energies (H band) with respect to an absorption band by the R6G monomer. The perfect H-type dimer is well-known to be nonfluorescent. The transition moments of a perfect J-type dimer are aligned, and absorption band for this dimer is placed at lower energies (J band) than the absorption band by the R6G monomer. Fluorescence from an excited perfect J-type dimer is observed at a longer wavelength than an emission from an excited R6G monomer. Arbeloa and Martínez et al. have reported orientations and absorption and fluorescence bands of the R6G dimers and the aggregates as well as the monomer in R6G/laponite films studied in detail by vis absorption and fluorescence with polarized light.[20,21] They have identified a long displaced coplanar dimer by an absorption J band and a short displaced coplanar dimer by an absorption H band. They have revealed that the long displaced coplanar dimer fluoresces at the longer wavelength than the monomer and that the short displaced coplanar dimer is not fluorescent. Sasai et al. have reported that an emission is observed around 610 nm as well and that this emission could be caused by the J band of a distorted sandwich R6G H-type dimer species,[14] whereas the perfect sandwich H-type dimer is not fluorescent. Higher order aggregates have been reported as well. Absorption and fluorescence bands of the higher order J aggregates are placed at the longer wavelengths than those of the J-type dimers, and absorption bands of the higher order H aggregates are placed at the shorter wavelengths than the H-type dimers. Construction of the integrated interlayer space with two different fluorophores, i.e., R6G and coumarin, is expected to provide a novel heterogeneous system as well as a luminous solid-state material with very broad fluorescence emission.

The aims of this study are construction of a novel luminous heterogeneous system, i.e., an R6G/coumarin/phyllosilicate hybrid, and to examine whether fluorescence behavior can be changed and controlled by construction of the heterogeneous system or not. To achieve this, the coumarin/Mg−phyllosilicate hybrid was employed as a host hybrid. The R6G/coumarin/phyllosilicate hybrid was prepared by incorporation of R6G molecules into the interlayer space of the host hybrid. Because the intercalation of cationic dye (R6G) is easier than intercalation of the neutral coumarin, the coumarin moiety was first anchored to the inorganic moiety of the host hybrid. Construction of the heterogeneous system was revealed by thermogravimetric and differential thermal analyses (TG−DTA), X-ray diffraction (XRD), and ultraviolet–visible (UV–vis) measurements. Fluorescence measurements showed wide fluorescence emission spectra over 350−750 nm, and both coumarin and R6G fluoresced in the R6G/coumarin/phyllosilicate hybrid. Furthermore, fluorescence emission was blue-shifted by constructing the heterogeneous system. This study provides a new sound method for constructing the heterogeneous systems and presents the fact that the properties of functional organic substances can be changed and would be controlled by construction of the heterogeneous systems. The strategy reported here can be applied widely.

Experimental Section

Materials. LiF, $MgCl_2 \cdot 6H_2O$, NH_4OH, and 7-hydroxy-4-methylcoumarin ($C_{10}H_8O_3$) were purchased from Wako Pure Chemical Industries, Ltd. Isocyanatopropyltriethoxysilane ($C_9H_{20}NO_4$) was purchased from Shin-Etsu Chemical Co., Ltd. Silica sol (Ludox

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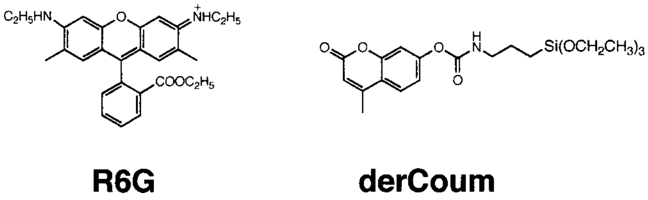
Scheme 1. Rhodamine 6G (R6G) and 7-(3-Triethoxysilylpropyl)-*O*-(4-methyl-coumarin)urethane (derCoum)



HS-30, Du Pont) was kindly purchased from Maruwa Bussan Co., Ltd. Rhodamine 6G dye (R6G, Scheme 1, laser grade) was purchased from Exciton, Inc. All reagents were used without further purification, unless otherwise noted.

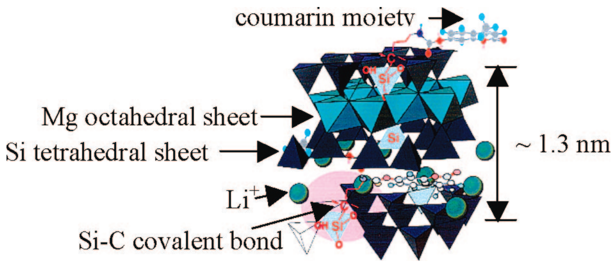
7-(3-Triethoxysilylpropyl)-*O*-(4-methyl-coumarin)urethane ($C_{20}H_{29}NO_7Si$, Scheme 1), abbreviated derCoum, was synthesized from 7-hydroxy-4-methylcoumarin and isocyanatopropyltriethoxysilane according to the method reported by Suratwala et al.[8] The structure of the synthesized derCoum was confirmed by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. derCoum was used for the synthesis of a host hybrid. $Mg(OH)_2$ gel was prepared from $MgCl_2 \cdot 6H_2O$ and NH_4OH[25,26] and was used for the synthesis of the host hybrid.

Synthesis of a Host Hybrid, Coumarin/Mg−phyllosilicate Hybrid. The host hybrid was synthesized by a reaction between derCoum and inorganic reagents, as we had previously reported.[7] derCoum, LiF, $Mg(OH)_2$ gel, and silica sol were mixed in water at room temperature to obtain a starting slurry. The molar ratio of $[Si]/[Mg(OH)_2]/[LiF]$ was 1.5:1.0:0.2, and the [derCoum]/[Si] molar ratio was 0.02. The chemical formula of silica sol was assumed to be SiO_2 in calculating the molar ratios. NH_4OH aqueous solution was dropped into this slurry with stirring. The slurry was refluxed in a round-bottom flask for 4 days. Because derCoum has ethoxysilyl groups, both the hydrolysis reaction and the condensation reaction with silanol groups of the silica sol surface proceed under the reaction condition. The obtained mixture after the reflux was washed in tetrahydrofuran to remove free coumarin dye molecules and then washed in water. The precipitate was filtered and then dried under a reduced pressure. The structure of the synthesized coumarin/phyllosilicate hybrid was characterized by XRD, elemental analysis, IR spectra, high-resolution solid-state ^{29}Si NMR, and so on.

Preparation of R6G/Coumarin/Phyllosilicate Hybrid. The coumarin/Mg−phyllosilicate hybrid was used as the host hybrid for preparing R6G/coumarin/phyllosilicate hybrids. The host hybrid (0.060 g) was added to ethyl alcohol (2 mL). The mixtures were then stirred at room temperature for several hours, and suspensions were obtained. R6G was dissolved in ethyl alcohol. The concentrations of these R6G ethyl alcohol solutions were from 2.94×10^{-3} to 1.42×10^{-2} M. The R6G ethyl alcohol solutions (2 mL) were added to the ethyl alcohol suspensions (2 mL) of the host hybrid. R6G/host hybrid ratios, abbreviated x, were from 0.10 to 0.48 mmol/g in these starting suspensions. After the starting suspensions were stirred at room temperature for a week, the precipitates were filtered, washed with ethyl alcohol and water, and then dried.

Characterization. XRD measurements were performed at room temperature at ambient humidity using a Rigaku Rint 2000S diffractometer with Cu Kα radiation. XRD patterns under a stream of nitrogen were also recorded at room temperature using Cu Kα radiation on a Rigaku Rint 1200. High-resolution solid-state ^{29}Si NMR spectra were measured using a Bruker ASX400 spectrometer at room temperature. Larmor frequency was 79.49 MHz. The ordinary cross-polarization (CP) pulse sequence was used together with magic angle spinning (MAS) of the sample. The chemical shift was referenced to neat tetramethylsilane. TG−DTA were carried out using a MAC Science TG-DTA 2000 in O_2 flow with a ramp of 10 °C/min to 1000 °C. Elemental analyses were performed by an inductively coupled plasma (ICP) atomic absorption. A CHN analysis was performed by a Perkin-Elmer CHNS/O analyzer Series II 2400. UV–vis spectra were measured by the reflection method using a Shimadzu UV–vis−NIR scanning spectrophotometer UV-3100PC with an integrating sphere for the host hybrid. UV–vis spectra were also measured using a Jasco V-570 UV/vis/NIR spectrophotometer with an integrating sphere for the host hybrid and the R6G/coumarin/phyllosilicate hybrid diluted with $BaSO_4$ (barium sulfate) because of strong absorptions by R6G. Fluorescence emission spectra were recorded with a Shimadzu spectrofluorophotometer RF-5300.

Scheme 2. Schematic Representation of the Host Hybrid



Results and Discussion

Structure of the Host Hybrid. Coumarin chromophore is located between layers of Mg−phyllosilicate moiety and is covalently bonded with the inorganic moiety in the host hybrid (the coumarin/Mg−phyllosilicate hybrid) as illustrated in Scheme 2. In this section, the structure of the host hybrid is outlined because it is a key point of this study, although we have already reported the synthesis and characterization of the host hybrid.[7]

The ethoxysilyl group of derCoum is hydrolyzed, and subsequently, the condensation reaction proceeds between the generated silanol group of derCoum and silanol groups of silica sol surface under the reflux condition. The hydrolysis and condensation reactions and formation of the Mg−phyllosilicate structure occur in one pot.

The Mg−phyllosilicate moiety has a layered structure analogous to Mg−trioctahedral smectites, such as hectorite and stevensite, which are clay minerals having 2:1 layers. They consist of two Si tetrahedral sheets and one Mg octahedral sheet sandwiched by the Si tetrahedral sheets. A part of the Mg octahedral site is substitute by Li^+ ion, and the Mg−phyllosilicate layer is negatively charged. The Li^+ ion is located between the layers and compensates the negative charge. The latter Li^+ ion between the layers is an exchangeable cation. The inorganic structure was revealed by XRD, IR, ^{29}Si NMR, and so on.[7] The XRD pattern of the host hybrid is similar to that of Mg−trioctahedral smectites (see the Supporting Information), as shown in Figure 1. All peaks in the XRD pattern are attributed to the Mg−phyllosilicate structure. An asymmetrical peak at about $2\theta = 35°$ ($d = 0.26$ nm) is indexed as 13 and 20; a reflection

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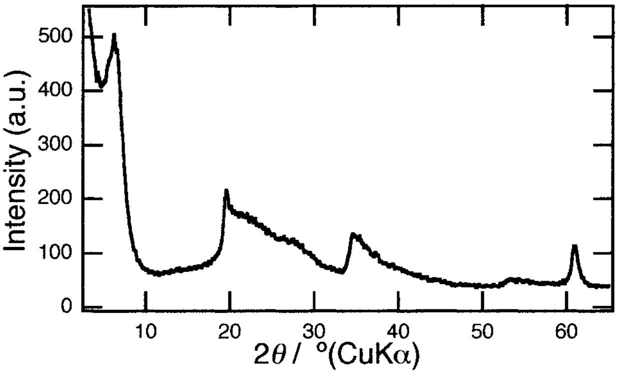

Figure 1. X-ray diffraction patterns for the host hybrid under an ambient atmosphere.

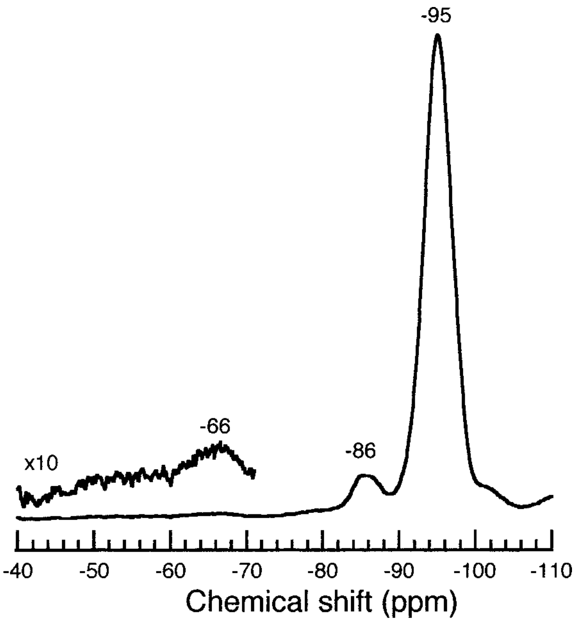

Figure 2. ^{29}Si CP/MAS NMR spectrum of the host hybrid (coumarin/Mg−phyllosilicate hybrid). An enlarged spectrum (10 times) is inserted. A MAS rate was 4.5 kHz.

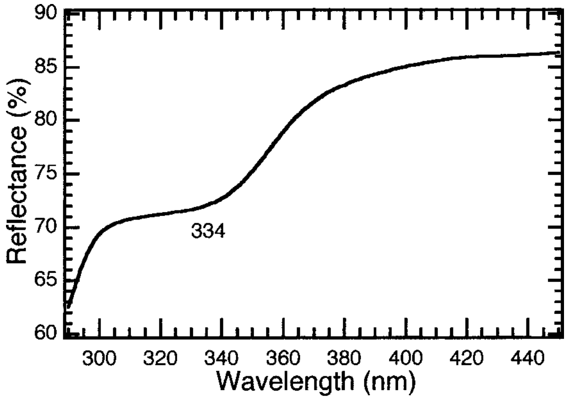

Figure 3. UV–vis reflection spectrum for the host hybrid.

peak at about $2\theta = 20°$ ($d = 0.45$ nm) is indexed as 02 and 11; and a reflection peak at about $2\theta = 60°$ ($d = 0.15$ nm) is indexed as 06 and 33.[4] There are no peaks indexed to brucite, LiF, or other unknown materials. Si, Mg, and Li were detected by ICP analysis. IR absorption peaks are observed at 3680 and about 1000 cm^{-1}, and these absorptions are due to the OH group of the Mg−phyllosilicate structure and Si−O−Si vibration, respectively. Furthermore, a ^{29}Si NMR signal is observed at −95 ppm, as shown in Figure 2, which is assigned to $(MgO)\underline{Si}(OSi)_3$ in the Mg−phyllosilicate structure.[27] The intensity of the signal at −86 ppm is very high in comparison to the spectra of Mg−trioctahedral smectites.[27] This signal is attributable to $(SiO)_2(MgO)Si(OH)$. The signal around −66 ppm is assigned to $(SiO)_2CSi(OY)$ (Y is Mg and Li in this study). The signals around −86 and −66 ppm increase as the [derCoum]/[Si] molar ratio in the starting slurry increases (see the Supporting Information). Because the $(SiO)_2CSi(OY)$ is located in the tetrahedral sheet, one of the SiO_4 tetrahedron adjacent to the $(SiO)_2CSi(OY)$ species cannot share one of corners. Consequently, a $(SiO)_2(MgO)Si(OH)$ species is formed, although the ideal smectite structure has no surface silanol group.

The coumarin moiety was confirmed by IR, UV–vis, and fluorescence spectroscopy.[7] The IR spectrum of the host hybrid shows absorption peaks around 1700 cm^{-1} because of the carbonyl group, 2990−2880 cm^{-1} because of C−H stretching vibrations, and so on. The UV–vis reflection spectrum shows an absorption around 334 nm, as shown in Figure 3. This absorption can be ascribed to overlap the absorption of the neutral and cationic forms[7] of the coumarin chromophore in the host hybrid. The fluorescence emission maximum is observed around 385 nm when the coumarin chromophore in the host hybrid is pumped at 320 nm, and this maximum agrees with the neutral form of the coumarin chromophore. When the coumarin chromophore is pumped with an excitation wavelength of 380 nm, a fluorescence emission is observed around 450 nm. This emission is attributed to the cationic form of the coumarin chromophore, and the emission is red-shifted. This red shift is caused by an interaction of the coumarin chromophore with the inorganic moiety. These results confirm the presence of the neutral and cationic forms of the coumarin chromophore in the host hybrid. The elemental analyses of the host hybrid demonstrate that the atomic ratio of [Si]/[C]/[N] is 1:0.08:0.01. The [C]/[N] ratio obtained is much smaller than that in derCoum (14). This discrepancy suggests that a part of urethane linkage of derCoum decomposes during the synthesis of the host hybrid, whereas the absorption and fluorescence emission spectra demonstrate the existence of the coumarin chromophore for the host hybrid after removing free coumarin dye molecules by a wash with tetrahydrofuran, as described above. The concentration of the coumarin moiety is estimated as 0.01 ± 0.005 per 1 unit of the host hybrid from the elemental analyses (see the Supporting Information).

The interlayer spacing is about 1.6 nm for the host hybrid, as shown in Figure 1. The *d* value becomes shorter to 1.3 nm under N_2 stream. This change suggests the existence of H_2O molecules between layers.

Because the thickness of the 2:1 Mg−phyllosilicate layer is about 0.96 nm, a clearance space (an interlayer separation) is about 0.34 nm for the host hybrid under N_2 stream, viz., for the host hybrid without intercalated H_2O molecules. This

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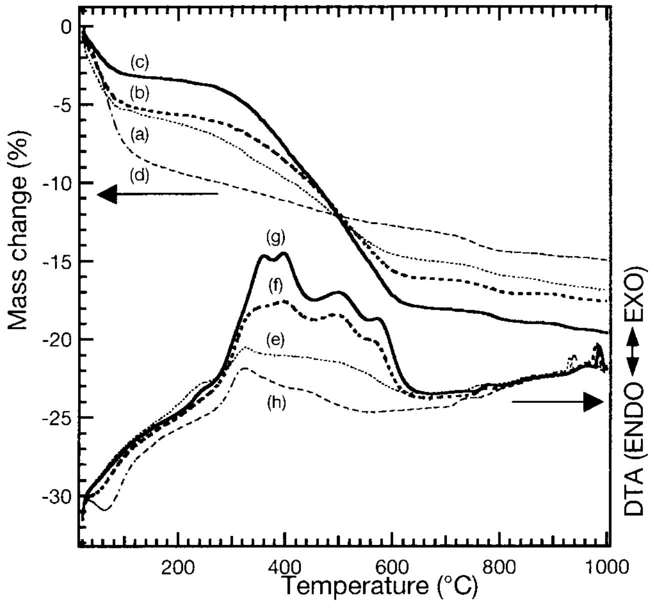


Figure 4. TG−DTA curves in an O_2 gas flow for the R6G/coumarin/phyllosilicate hybrids. Weight loss (curves a−d) is given on the left vertical axis, and DTA (curves e−h) is given on the right vertical axis. The hybrids were prepared from the starting mixtures with *x* of (a and e) 0.10, (b and f) 0.20, and (c and g) 0.48 mmol/g. The weight loss (d) and a DTA curve (h) for the host hybrid are also shown for reference.

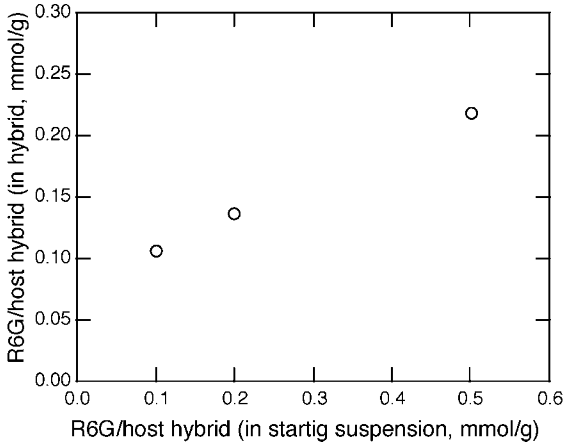


Figure 5. Relation between the content of R6G incorporated in the R6G/coumarin/phyllosilicate hybrids and the R6G/host hybrid ratios (*x*) in the starting mixtures.

value is almost equal to the thickness of the derCoum molecule. The coumarin chromophore is lying nearly in parallel to the Si−O−Si surface.

Preparation of a Heterogeneous System: R6G/Coumarin/Phyllosilicate Hybrid. TG−DTA was performed to study thermal decomposition and the content of R6G that was loaded into the R6G/coumarin/phyllosilicate hybrids. Figure 4 shows TG−DTA curves in O_2 gas flow for the R6G/coumarin/phyllosilicate hybrids and the host hybrid. The DTA curve shows an exothermic peak around 320 °C for the host hybrid, as shown in curve h of Figure 4. This exothermic reaction is caused by decomposition and combustion reactions of the coumarin moiety in the host hybrid. A broad shoulder at the higher temperature suggests decomposition reactions to smaller fragments and stepwise combustion reactions of the organic moiety. The weight loss accompanying the exothermic reaction was observed from about 150 to about 700 °C and indicates the amount of the organic moiety in the host hybrid. For the R6G/coumarin/phyllosilicate hybrids, exothermic peaks appear in the 325–360 °C region and around 400, 500, and 580 °C, as shown in curves e−g of Figure 4. The first exothermic peak shifts from 325 to 360 °C as the R6G/host hybrid ratios in the starting mixtures, *x*, increase. This exothermic reaction is caused by decomposition and combustion of both the coumarin moiety and R6G molecules in the R6G/coumarin/phyllosilicate hybrids. The exothermic peaks around 400, 500, and 580 °C are due to decomposition and combustion reactions of R6G molecules in the R6G/coumarin/phyllosilicate hybrids. The weight loss according to these exothermic reactions is observed from about 150 to about 700 °C and increases as *x* increases. A weight loss is also observed between room temperature and about 150 °C. This weight loss is caused by the release of water. This release will hereinafter be described together with XRD results. The dehydration takes place because of the stream of relatively dried oxygen gas. The weight loss in this temperature region decreases as *x* increases. A very small endothermic peak around 750 °C accompanied by a small weight loss is due to dehydroxylation from the inorganic moiety of the hybrids. The exothermic peak around 950 °C is due to recrystallization of the dehydroxylated inorganic moiety. The bluish emission from the coumarin moiety is not observed for either the supernatant after filtration of the intercalation suspension or washing ethyl alcohol. This indicates that deintercalation of the coumarin moiety did not occur during the preparation of the R6G/coumarin/phyllosilicate hybrids. From the TG−DTA results, the amount of incorporated R6G is determined, as shown in Figure 5. The content of R6G in the obtained hybrids increases from 0.1 to 0.2 mmol/g as *x* increases in the starting mixtures. These values are corresponding from 0.04 (for $x = 0.10$) to 0.08 (for $x = 0.48$) of R6G per 1 unit of the host hybrid. The R6G is incorporated into the R6G/coumarin/phyllosilicate hybrids at several to 20 times as high ratios as the coumarin moiety.

The interlayer space increases from 1.5 to 1.7 nm as the R6G/host hybrid ratio increases, as shown in Figure 6. It is indicated that the interlayer spacing is expanded by intercalation of R6G. For the hybrid with the spacing of 1.7 nm, the clearance space between the inorganic layers is about 0.7 nm because the thickness of the inorganic layer is about 0.96 nm. Therefore, the coumarin moiety and the R6G molecules lie nearly in parallel to the silicate surface,[24–26] as illustrated in Scheme 3. It is considered that R6G molecules are incorporated into the interlayer space of the host hybrid by an ion-exchange reaction with the exchangeable cation, Li^+ ion of the host hybrid, during stirring the starting suspensions. R6G is a cationic dye and can be incorporated into the interlayer with the anchored coumarin moiety. Because the intercalation of the cationic R6G is easier than the intercalation of the neutral coumarin, the host hybrid with the coumarin moiety is applied in this study. The diffraction peaks become relatively sharper and more intense with an increase in the R6G/host hybrid ratio. It is considered that the layer stacking becomes relatively more regular as *x* increases. The interlayer space is shorter under a stream of N_2 in comparison to the interlayer space under ambient

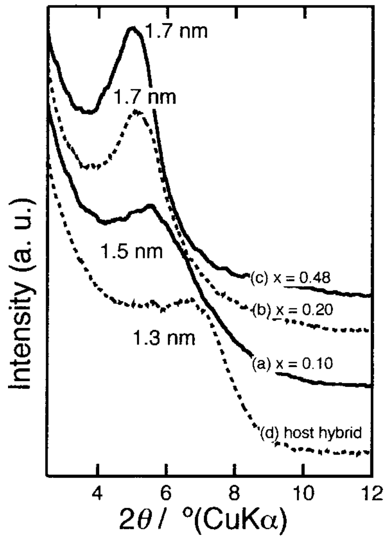
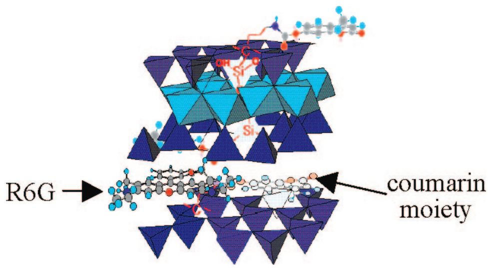


Figure 6. XRD patterns recorded under a stream of N_2 for the R6G/coumarin/phyllosilicate hybrids prepared from the starting mixtures with x of (a) 0.10, (b) 0.20, and (c) 0.48 mmol/g and (d) a profile of the host hybrid for reference.

Scheme 3. Schematic Representation of the R6G/Coumarin/Phyllosilicate Hybrid



atmosphere for each hybrids (cf. the Supporting Information). This is due to the release of water molecules between the layers of the hybrids and is in agreement with the weight loss observed between room temperature and about 150 °C by the TG−DTA measurements, as shown in Figure 4. Although the organic portions are located between the layers of the hybrids, H_2O molecules can be intercalated into the interlayer space of the hybrids. This phenomenon would be ascribed to relatively low organic densities in the hybrids.

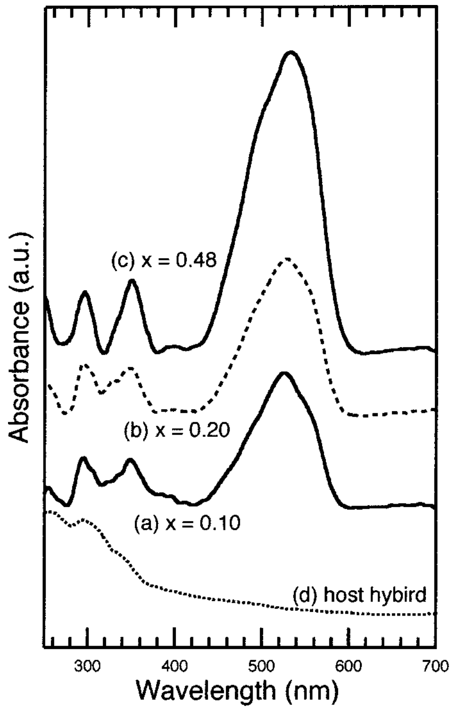
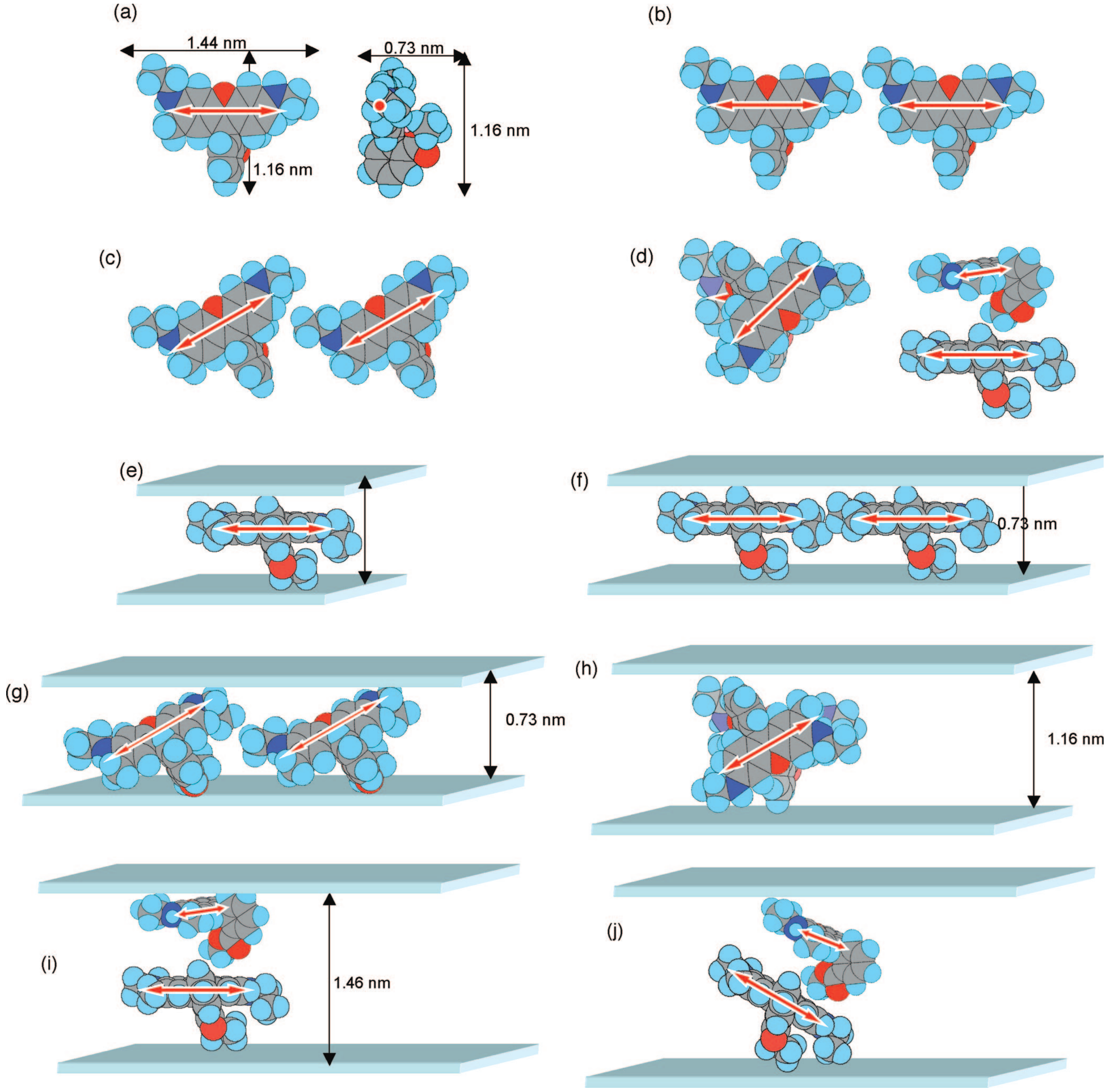


Figure 7. UV–vis absorption spectra for the hybrids prepared from the starting mixtures with x of (a) 0.10, (b) 0.20, and (c) 0.48 mmol/g and (d) a profile of the host hybrid for reference. The samples, except for the host hybrid, were diluted with $BaSO_4$.

The UV–vis spectra show several absorption peaks, as shown in Figure 7. A peak around 530 nm originates from R6G monomer, suggesting that the monomer is the dominant state among several R6G species (the monomer and aggregates). Shoulders are observed around 495 and 560 nm, which are related to the R6G dimer and aggregates. The H- and J-type dimers are well-known as extreme species.[14,20,21] It is known that the absorption by the H-type dimer is observed at the higher energy (H band) than the absorption by the monomer and that the absorption by the J-type dimer is observed at the lower energy (J band). The vibrational shoulder of the R6G monomer might contribute slightly to the absorption shoulder around 495 nm. The transition moments are aligned along the long molecular axis of the monomer units, as shown by an arrow in Scheme 4a. The transition moments are aligned head-to-tail in the perfect J-type R6G dimer, as shown in Scheme 4b. Arbeloa and Martínez et al. have reported orientations and absorption and fluorescence bands of R6G studied in detail by vis absorption and fluorescence with polarized light.[20,21] They have identified a long displaced coplanar dimer as a coplanar J-type dimer with an absorption band placed at the lower energies (J band) and a short displaced coplanar dimer as a coplanar H-type dimer with an absorption band at the higher energies (H band) than the absorption by the monomer. A distance between the monomeric units is long in the long-displaced coplanar dimer and is short in the short-displaced coplanar dimer.[20] In the coplanar dimers, the transition moments are aligned as shown in Scheme 4c. The xanthene planes can lie on the same plane in the coplanar dimers and the perfect J-type R6G dimer, as shown in parts f and g of Scheme 4. On the other hand, the transition moments of the perfect H-type R6G dimer are oriented in parallel, namely, the xanthene planes are stacked, as shown in Scheme 4d. For the R6G/coumarin/phyllosilicate hybrids, the clearance spaces allow for the perfect J-type R6G dimer and the coplanar dimers (parts f and g of Scheme 4), because the interlayer separation corresponds to the thickness of R6G monomer (Figure 6). On the other hand, the perfect H-type R6G dimer is difficult to be placed between the layers in the R6G/coumarin/phyllosilicate hybrids, because the required clearance spaces are about 1.2 nm for a model disposed perpendicularly (Scheme 4h) and about 1.5 nm for a model disposed parallel (Scheme 4i). Because two lengths of R6G contribute to a gallery height required by an inclined model, as shown in Scheme 4j, this model is also difficult. Consequently, the shoulder around 495 nm can be attributed to the H band of the short-displaced coplanar dimer (the coplanar H-type dimer), and the shoulder around 560 nm can be attributed to the overlap of the absorption by the long-displaced coplanar dimer (the coplanar J-type dimer) and/or

Scheme 4. Schematic Representations of (a) R6G with Its Sizes and the Transition Moment (the Arrow) and with a Lateral View, the Orientation of the Transition Moments in (b) the Perfect J-Type R6G Dimer, (c) Coplanar Dimer, (d) Perfect H-Type R6G Dimer with a Horizontal View, and Models of (e) R6G Monomer, (f) the Perfect J-Type R6G Dimer, (g) Coplanar R6G Dimer, and (h) the Perfect H-Type Dimer with the Xanthene Plane Nearly Perpendicular to the Inorganic Layer of the Hybrid, (i) the Perfect H-Type Dimer with the Xanthene Planes Nearly Parallel to the Inorganic Layer of the Hybrid, and (j) the Perfect H-Type Dimer with the Xanthene Planes Inclined to the Inorganic Layer of the Hybrid within the Interlayer Space of the R6G/Coumarin/Phyllosilicate Hybrids



the perfect J-type R6G dimer and absorptions by coplanar higher order aggregates. The J band becomes relatively obvious in the absorption spectra as *x* decreases. As *x* increases, the H band becomes relatively obvious in the absorption spectra. This result suggests that there are the long-displaced coplanar dimer, the higher order aggregates, and/or the perfect J-type R6G dimer, as well as the monomer between the layers of the R6G/coumarin/phyllosilicate hybrid with *x* of 0.10 and that the short-displaced coplanar dimer increases with an increase in *x*. The types of the R6G aggregates will be discussed together with fluorescence behavior in the next section. The very wide absorption of R6G might be attributed to the interaction of the R6G chromophore with the inorganic and coumarin moieties. It is known that CT absorption bands show characteristic band shapes similar to the profile of the UV–vis spectra in the short wavelength region (<420 nm) in Figure 7.[28] Because the same profile is observed for R6G in ethanol, the profile can be assign to an intramolecular CT band of R6G (the xanthene ring). The absorption as a result of the coumarin chromophore should appear around 330 nm, because the absorption is observed around 334 nm for the host hybrid, as shown

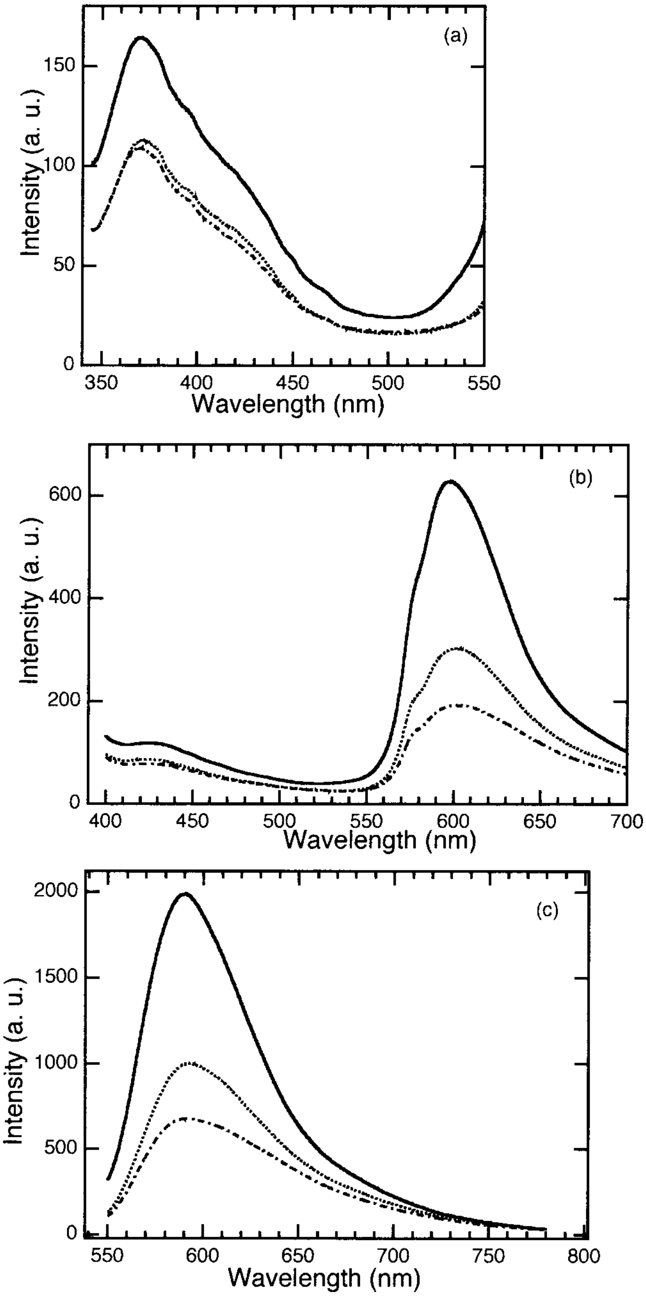


Figure 8. Fluorescence emission spectra for the R6G/coumarin/phyllosilicate hybrids prepared from the starting mixtures with *x* of 0.10 (—), 0.20 (• • •), and 0.48 mmol/g (- • -) when pumped at (a) 320, (b) 380, and (c) 530 nm.

in Figure 3. However, the absorption as a result of the coumarin chromophore is apparently hidden by the relatively strong absorption because of R6G at around 350 nm.

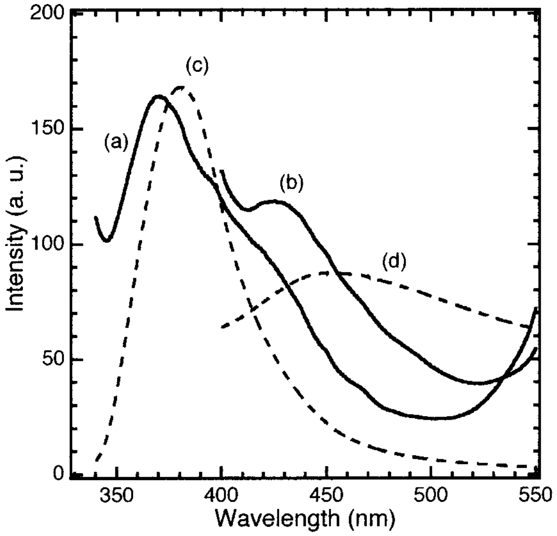


Figure 9. Blue-shifted fluorescence emission (a and b) for the R6G/coumarin/phyllosilicate hybrid with *x* of 0.10 mmol/g and the fluorescence spectra (c and d) of the host hybrid for reference. Excitation wavelengths were 320 nm for a and c and 380 nm for b and d.

Fluorescence Behavior and Blue-Shifted Emission of the R6G/Coumarin/Phyllosilicate Hybrids. Fluorescence emission was observed over a wide wavelength range from about 350 to 750 nm and is composed of several emission bands, as shown in Figure 8. Both the coumarin moiety and R6G fluoresce, although two different dyes coexist in the same layered hybrids. Fluorescence emission peaks around 370 nm (Figure 8a) and 425 nm (Figure 8b) are due to the coumarin fluorophores, and the peak around 590 nm (parts b and c of Figure 8) is attributed to the R6G fluorophore. The peaks around 370 and 425 nm are due to the neutral and cationic forms, respectively. The neutral and cationic forms of the coumarin chromophores coexist in the R6G/coumarin/phyllosilicate hybrids. As R6G incorporated into the hybrid increases, the fluorescence intensity decreases for the emissions from both the coumarin chromophores and R6G because of concentration quenching. This phenomenon supports the coexistence of the two different dyes, i.e., the coumarin chromophores and R6G, within the same two-dimensional nanospace.

The fluorescence emission peaks around 370 and 425 nm are blue-shifted by 12–15 nm (Figure 9) in comparison to the host hybrid. This blue shift indicates that the local environment around the coumarin chromophore is changed by coexistence with R6G in the two-dimensional interlayer space. Several mechanisms can be proposed for the blue shift, namely, interactions (a formation of the mixed dimer and/or a mutual repulsion) between the coumarin moiety and R6G molecules, an inhibition of stabilizing the coumarin chromophore, and so on. One of the possible mechanisms is that the blue shift is caused by the change in the vibrational behavior accompanying the change in the local environment around the coumarin chromophore. The emission can be shifted when the vibrational levels of the ground and excited states of the coumarin moiety are varied by construction of the heterogeneous system. The local environment around the coumarin moiety becomes more rigid with the increase in the organic density between the layers. This relatively higher rigidity could cause a decrease in the rotation freedom of the coumarin moiety and the blue shift of the emission from the excited coumarin moiety in the same manner as rigidochromism.[29] The mixed dimer and/or mixed aggregates might be associated between the coumarin moiety and R6G. The mixed dimer and aggregates could be one of reasons why the emission is blue-shifted. Shankar and Patnaik have

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reported that a blue shift is observed because of a formation of mixed aggregates associated between rhodamine B and azobenzene derivatives.[30] The (π, π*) excited state is stabilized by the interactions of the cationic coumarin fluorophore with the surface oxygen atoms and silanol groups of the Mg−phyllosilicate moiety in the host hybrid.[7,32] The (π, π*) transition is the lowest energy one of the cationic coumarin chromophore.[7,32,33] In the R6G/coumarin/phyllosilicate hybrids, the interaction and stabilization might be partially inhibited by R6G and the fluorescence emission from the cationic coumarin moiety can be blue-shifted. Further detailed investigation is necessary to clarify the mechanism. The change in the emission suggests that the properties of chemical species would be changed and controlled by constructions of heterogeneous systems in the two-dimensional nanoscaled galleries.

It is well-known that fluorescence emission maximum is observed at about 555 nm for R6G monomer in ethyl alcohol solution, aqueous solution, and so on. Arbeloa and Martínez have reported a fluorescence band placed around 585 nm because of the long-displaced coplanar R6G dimer (the coplanar J-type dimer).[21] The fluorescence around 590 nm (Figure 8c) is ascribed to the long-displaced coplanar R6G dimer in the R6G/coumarin/phyllosilicate hybrids. The fluorescence emission spectra become more asymmetrical as the loaded R6G contents increases. This indicates that there is another fluorescence band at a longer wavelength. Spectral deconvolution produces another component at the longer wavelength region (see the Supporting Information). Those fluorescence bands at the longer wavelength might be attributed to the higher order J aggregates, which fluoresce at the longer wavelength than the J-type dimers. An emission shoulder around 575 nm might be attributed to the R6G monomer (Figure 8b). The emission is weak when R6G is pumped at 380 nm (Figure 8b) and is not observed when R6G is pumped at 530 nm (Figure 8c), whereas the absorption is observed around 530 nm. This might be ascribed to the existence of the dimers and aggregates, because of an energy transfer from the excited R6G monomer to the dimers and/or the higher order aggregates and/or reabsorption of the emission from the monomer by the dimers and/or the higher order aggregates. The emission shoulder from the R6G monomer is red-shifted to 575 nm for the R6G/coumarin/phyllosilicate hybrids as shown in Figure 8b. This red shift can be speculated as follows:

After light absorption at 530 nm by the R6G monomer, internal conversions and relaxation are presumed to be caused in the hybrids. The relaxation can be ascribed to the interactions between R6G and its surroundings, the surface silanol group and surface oxygen atoms of the inorganic moiety and/or coumarin chromophore. This relaxation occurs in a manner similar to solvent relaxations. The solvent relaxations are well-known to occur in dye solutions.[34]

The results of the absorption and fluorescence measurements suggest that R6G exists in the hybrids with the several forms: the monomer, coplanar dimers (long- and short-displaced coplanar dimers), and coplanar higher order J aggregates and that the short-displaced coplanar dimer and higher order aggregates increase with the increase in x. It can be a reason for the decrease in R6G fluorescence intensity with the increase in x that a ratio of the nonfluorescent dimer (the short-displaced coplanar dimer) to the fluorescent dimer (the long-displaced coplanar dimer) increases as shown by the absorption spectra (Figure 7) as well as the concentration quenching.

Conclusions

A novel heterogeneous system, the R6G/coumarin/phyllosilicate hybrid, was prepared by eluding deintercalation of the coumarin moiety and stratification of two different functional organic dyes. R6G was intercalated into the interlayer space of the coumarin/Mg−phyllosilicate hybrid, in which the coumarin moiety was anchored to the Mg−phyllosilicate moiety with the inorganic/organic covalent bond. The R6G/coumarin/phyllosilicate hybrid exhibits the wide fluorescence emission covering from 350 to 750 nm. The fluorescence emission from the coumarin fluorophores is blue-shifted by constructing the heterogeneous system. This study provides a new route for constructing heterogeneous systems by employing host hybrids with inorganic/organic covalent bonds. Furthermore, the properties of functional organic species can be changed and would be controlled by construction of the heterogeneous systems. This sound strategy can be applied widely to constructing various heterogeneous systems in solid-state nanoscaled spaces: photoinduced energy-transfer system, supramolecular systems with designed distances between donors and acceptors, and so on. One of future applications is a dye-sensitized solar cell with suitable and desirable optical properties.

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Supporting Information Available: XRD pattern of Mg−phyllosilicate; ^{29}Si CP/MAS NMR spectra of the host hybrid and another coumarin/Mg−phyllosilicate hybrid with the [derCoum]/[Si] molar ratio of 0.06; chemical formulas for the host hybrid, weight loss, and first-derivative traces for the R6G/coumarin/phyllosilicate hybrid as a function of the temperature; XRD patterns for the R6G/coumarin/phyllosilicate hybrids under ambient atmosphere; and results of spectral deconvolution for fluorescence spectra of the R6G/coumarin/phyllosilicate hybrids. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) There exists a silanol group adjacent to $CSi(OZ)_3$ in the host hybrid because of the covalent bond between the coumarin and Mg−phyllosilicate moieties, whereas smectites have no surface silanol group.

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