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Preparation of Integrated Coumarin/Cyanine Systems within an Interlayer of Phyllosilicate and Fluorescence Resonance Energy Transfer

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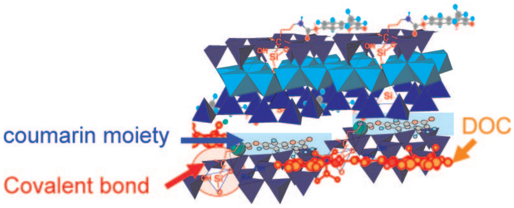
The study of integrated systems in solid media has attracted considerable attention in the field of hybrid nanomaterial chemistry, artificial photosynthesis, photochemistry, and so forth,[1−14] because integrated systems have the potential to exhibit phenomena such as photoinduced electron transfer and energy transfer, which are basic processes in artificial photosynthesis. Integrated systems comprise two or more functional organic molecules and/or metal complexes. An important objective of recent studies has been the determination of how the distances between chemical substances influence reactions in systems of interest.[5,7,8,11,12]

FRET (fluorescence resonance energy transfer) is the transfer of excited-state energy from an excited donor to an acceptor; it results from long-range dipole−dipole interactions between the donor and the acceptor (Förster model).[15,16] The efficiency (E) of FRET is 50% at the Förster distance for pairs of a single donor and acceptor.The Förster distance is typically in the range of 1.5−9.0 nm.[15,17] E depends on the ratio of the number of acceptors to the number of donors (A/D ratio) and the extent of the spectral overlap of the emission spectrum of the donor with the absorption spectrum of the acceptor as well as on the distance between the donor and the acceptor (D−A distance).[15]

Phyllosilicates have layered structures, each layer consisting of two-dimensional Si tetrahedral and octahedral sheets.[18] The interlayer space in phyllosilicates functions as a two-dimensional nanoscaled gallery. This two-dimensional nanospace is very useful for the arrangement of integrated systems.[1−4,7−9,14] However, it has been reported that the preparation of integrated systems is difficult in many cases because of the stratification of cointercalates into separate interlamellar spaces, that is, the segregation of the cointercalates.[14]

Scheme 1. Integrated Coumarin/DOC System within Interlayer Space in Phyllosilicate



We have reported the syntheses of organic/phyllosilicate hybrids, in which phyllosilicate and organic moieties bond covalently with each other,[19−21] including the luminous layered inorganic/organic hybrid—a coumarin/phyllosilicate hybrid (see Supporting Information).[1,21] Coumarin is a widely used functional organic molecule and is used in some dye lasers in a liquid state. The interlayer space in the coumarin/phyllosilicate hybrid functions as a nanoscaled gallery. Another functional organic molecule can be incorporated into the interlayer space in the hybrid. The covalent bonds are expected to suppress the deintercalation of the coumarin moieties and the stratification of the two functional organic species. The deintercalation and stratification would have proceeded if the covalent bonds were absent. Therefore, the coumarin/phyllosilicate hybrid is a promising host for preparing integrated systems. In fact, we have recently reported the preparation of an integrated rhodamine/coumarin system by this technique.[1] Further, we have also reported that the fluorescence emission is blue-shifted by the preparation of the integrated dye system.[1] The coumarin moieties are separated by a distance of the order of several nanometers and cannot move freely. Therefore, the distance between two functional organic substances would be controlled relatively accurately in the range of several nanometers; distances of this order are suitable for some reactions involving energy transfer.[15] DOC (3,3′-diethyloxacarbocyanine) is a fluorescent cyanine dye that absorbs light at approximately 450 nm.[22−24] The integrated dye systems prepared from the coumarin moieties and DOC have the potential to provide solid-state FRET systems.

In this communication, we report the preparation of integrated coumarin/cyanine systems (Scheme 1) within solid-state two-dimensional nanospace. It is expected that the distance between coumarin moieties and DOC molecules would be in the range of several nanometers; distances of this order are suitable for interac-

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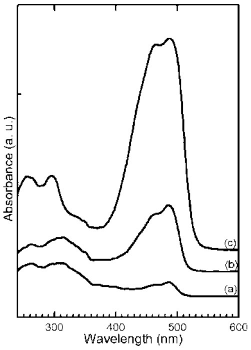

Figure 1. UV−vis absorption spectra for coumarin/DOC phyllosilicate hybrids prepared from starting mixtures with *x* equal to (a) 0.01, (b) 0.10, and (c) 1.0.

tions between the donor and the acceptor involved in energy transfer systems. Furthermore, fluorescence measurement shows that FRET takes place from the coumarin moieties to DOC in the integrated coumarin/DOC systems. These integrated systems are expected to be of significant interest to researchers in the field of hybrid nanomaterial chemistry, artificial photosynthesis, photochemistry, and so forth.

To prepare integrated coumarin/DOC systems, a coumarin/phyllosilicate hybrid (host hybrid, $(C_{14}H_{14}NO_4)_{0.01}(C_5H_{10}O_2N)_{0.2}Li_{0.16}(Li_{0.16}Mg_{2.84})Si_4O_{10}(OH)_2)$[21] is first synthesized by the reaction of organoalkoxysilane, silica sol, and inorganic salts and not by the intercalation of organic molecules into the interlayer of phyllosilicate (see Supporting Information). The DOC molecule was intercalated into the interlayer space in the host hybrid by adding 2 mL of aqueous solutions (2.00×10^{-6}, 2.00×10^{-5}, and 2.00×10^{-4} mol/L) of DOCI (3, 3′-diethyloxacarbocyanine iodide) to 2 mL of an aqueous dispersion of the host hybrid (the host hybrid/H_2O ratio is 0.020 g/mL). The ratios of DOC to the host hybrid ([DOC]/[host hybrid]), abbreviated as *x*, were 0.010, 0.10, and 1.0 mmol/100 g. After stirring the mixtures at room temperature for a week, yellowish precipitates formed and were filtered, washed with water, and dried, yielding the coumarin/DOC/phyllosilicate hybrids.

Very weak absorptions due to the DOC molecules are observed by ultraviolet−visible (UV−vis) measurement of the supernatant after the stir, although strong absorptions due to the DOC molecules are observed at around 480 and 458 nm[22] for the aqueous solutions before the intercalation reaction (see Supporting Information). The ratio of the incorporated DOC molecules to the host hybrid is calculated from the change in the concentration of DOC before and after the intercalation reaction. The calculated ratios ([incorporated DOC]/[host hybrid]) increase with an increase in *x*; the calculated ratios are 0.0095 mmol/100 g (for $x = 0.010$), 0.092 mmol/100 g (for $x = 0.10$), and 0.97 mmol/100 g (for $x = 1.0$). Absorption peaks are observed around 488, 463, 296, and 256 nm for the coumarin/DOC/phyllosilicate hybrids, and these absorption peaks become more intense as *x* increases (Figure 1). These absorption peaks are attributed to the DOC molecules.[23] The absorption peak at around 463 nm is attributable to an *E*-isomer and the absorption peak at around 488 nm is attributable to a *Z*-isomer of the DOC molecules.[25] The UV−vis spectra shown in Figure 1 exhibit a broad absorption peak at around 330 nm due to the coumarin moieties.[26] These results indicate that DOC is included in the coumarin/DOC/phyllosilicate hybrids. XRD patterns show that the interlayer distance space is approximately 1.4 nm for the coumarin/DOC/phyllosilicate hybrids with *x* in the range of 0.010−1.0. The clearance space between the inorganic layers is approximately 0.45 nm because the thickness of the inorganic layer is approximately 0.95 nm.[27] The thickness of the coumarin moieties is approximately 0.4 nm (see Supporting Information). Therefore, it can be considered that the coumarin moieties are aligned nearly parallel to the Si−O−Si surface of the inorganic moieties in the coumarin/DOC/phyllosilicate hybrids with *x* in the range of 0.010−1.0. Further, since the thickness and width of the DOC molecules is approximately 0.3 and 0.8 nm, it can be considered that they are nearly parallel to or oriented with a tilting angle of approximately 30° with respect to the Si−O−Si surface (see Supporting Information). XRD measurement shows that the interlayer distance increases to 1.9 nm for the coumarin/DOC/phyllosilicate hybrid with a large excess of DOC ($x = 100$). The clearance space is approximately 0.95 nm for this coumarin/DOC/phyllosilicate hybrid ($x = 100$). The increase in the clearance space explicitly indicates the incorporation of the guest into the interlayer of the host hybrid. In this large space DOC molecules can adopt any orientation with respect to the silicate surface of the host hybrid (see Supporting Information). The results of UV−vis and XRD measurements indicate that the DOC molecules are intercalated into the interlayer of the host hybrid; that is, the integrated coumarin/DOC systems are prepared within the interlayer. It is considered that the deintercalation of the coumarin moieties and stratification of the coumarin moieties and DOC molecules can be suppressed by the covalent bonds between the coumarin moieties and the inorganic moieties of the host hybrid.

Fluorescence emission is observed around 387 nm when the integrated coumarin/DOC systems are pumped at 320 nm. This emission is due to the coumarin moieties[1,21,28,29] in the integrated coumarin/DOC systems. When the integrated coumarin/DOC systems are pumped at 480 nm, fluorescence emission is observed around 515 nm. This emission is due to the *E*-isomer of the DOC molecules.[22] It is observed that both coumarin moieties and DOC molecules can fluoresce in the integrated coumarin/DOC systems (see Supporting Information).

Fluorescence emission around 520 nm is observed even when the integrated coumarin/DOC systems are pumped at 320 nm (Figure 2a), although DOC molecules do not fluoresce in the reference sample (DOC/hectorite composite) when pumped at 320 nm (Figure 2b).[30] The fluorescence emission at around 520 nm results from an energy transfer from the excited coumarin moieties to the *E*-isomer of the DOC molecules. The emission spectrum of the coumarin moieties overlaps the absorption of both the *E*- and *Z*-isomers

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(30) The DOC molecules in the DOC/hectorite composite fluoresce when the DOC/hectorite composite is pumped at 480 nm (see Supporting Information).

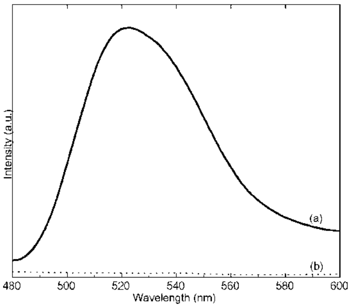

Figure 2. Fluorescence emission spectra in the long-wavelength range for (a) integrated coumarin/DOC system with *x* equal to 0.10 and (b) DOC/hectorite composite (reference sample). Excitation wavelength is 320 nm.

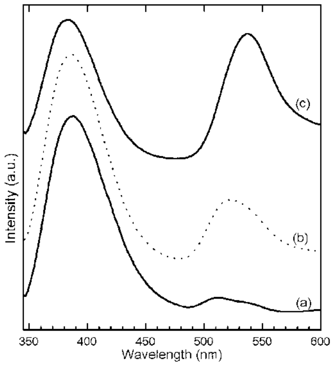

Figure 3. Fluorescence emission spectra for integrated coumarin/DOC system with *x* equal to (a) 0.010, (b) 0.10, and (c) 1.0. Excitation wavelength is 320 nm.

of the DOC molecules (see Supporting Information). It is well-known that FRET can occur when the emission of a donor overlaps the absorption of an acceptor.[15,16] The spectral overlap indicates that energy transfer can occur from the excited coumarin moieties to the DOC molecules. Because the coumarin moieties are anchored by covalent bonds and the distance between them is estimated to be approximately 7 nm, the average D−A distance between the coumarin moiety and the DOC molecule is approximately 3.5 nm or less (see Supporting Information). Such distances are suitable for the occurrence of FRET. It is well-known that an energy transfer can occur across two-dimensional surfaces such as LDH (layered double hydroxide) layers by the Förster mechanism.[31] With regard to the integrated coumarin/DOC systems considered in this study, the average D−A distance is almost the same irrespective of whether the energy transfer across the inorganic sheet is considered. This is because the concentration of the dyes is very low.[32] It is well-known that E is typically measured using the relative fluorescence intensity of the donor according to eq 1.[15]

$$E = 1 - F_{\mathrm{DA}}/F_{\mathrm{D}} \qquad (1)$$

where F_{DA} and F_{D} indicate the relative fluorescence intensities of the donor in the presence and absence of the acceptor, respectively. The main factors that affect FRET are the D−A distance[33] and the A/D ratio.[15] The difference in the relative fluorescence intensities of the coumarin moieties (Figure 3) indicates that E increases with x for the integrated coumarin/DOC system.[34] The increase in E for the integrated coumarin/DOC system can be attributed to the increase in the A/D ratio and/or the decrease in the D−A (coumarin moiety and DOC) distance. Further detailed studies are required to quantitatively clarify the influence of the D−A distance and A/D ratio with increasing x on E.

In summary, this work shows that integrated coumarin/DOC systems can be prepared by the incorporation of DOC molecules into the interlayer of host hybrid (coumarin/phyllosilicate hybrid). The segregation of the coumarin moieties and DOC molecules and the deintercalation of the coumarin moieties are suppressed because the coumarin moieties are fixed to the phyllosilicate moieties by covalent bonds. Fluorescence emission from the DOC molecules is observed even when the integrated coumarin/DOC systems are pumped at 320 nm, whereas fluorescence emission is hardly observed for the reference sample (DOC/hectorite composite). This is attributed to the FRET between the coumarin moieties and the DOC molecules. FRET can occur because the coumarin moiety and DOC molecule are immobilized within a suitable distance (≤3.5 nm) in solid-state integrated coumarin/DOC systems. Furthermore, the efficiency of the energy transfer increases as DOC increases. Through this study, we have shown that this novel strategy can achieve the construction of integrated systems in which interesting reactions occur; furthermore, this strategy can help in controlling interesting reactions such as those involving FRET, electron transfer, and so forth in the solid-state nanoscale gallery. One of the future applications of this technique would be the development of a series of FRET systems with various user-defined FRET efficiencies.

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Supporting Information Available: Chemical structures of the coumarin moiety and DOC; an outline of the synthesis and structure of the host hybrid; UV−vis absorption spectra of DOCI aqueous solutions; fluorescence emission spectra of the integrated coumarin/DOC system, DOC/hectorite composite, and the host hybrid; and an explanation of the orientation of DOC molecules and the average distance between the coumarin moiety and the DOC molecule (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(32) When the concentration of DOC increases and the molar ratio of DOC to coumarin moiety become greater than 1, the difference between the average D−A distance with and without considering the energy transfer across the two-dimensional surfaces will become significant.

(33) It is also well known that E can be given as a function of r for a single pair of a donor and an acceptor:[15] $E = R_0^6/(R_0^6 + r^6)$, where R_0 is the Förster distance and r is the distance between the donor and the acceptor.

(34) The energy transfer can be considered to occur to both the *E*- and *Z*-isomers from the coumarin moiety because of spectral overlap (absorption and emission spectra), whereas only the *E*-isomer can fluoresce intensly.