Macromol. Symp. **2010**, 288, 87–94 DOI: 10.1002/masy.201050211

Photon Trapping and the Enhancement of Electronic Excitation Energy Transfer Efficiency Caused by Colloidal Crystals

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Summary: The efficiency of electronic excitation energy transfer from photoexcited fluorescein to rhodamine 6G is enhanced by 2.26 times in an exhaustively deionized colloidal silica suspension. This enhancement is caused by the photon trapping effects due to the Bragg reflection of colloidal crystals formed in the suspension. The lower enhancement efficiency of 1.41 times observed for rhodamine B as an acceptor is attributed to the inefficient spectral overlap between donor fluorescence and acceptor absorption bands.

Keywords: bragg reflection; colloidal crystals; excitation energy transfer; fluorescence spectra; photon trapping

Introduction

Colloidal crystals are an ordered crystalline array structure, consist of mono-dispersed colloidal spheres.[1–3] They are formed by the electronic repulsive force of expanded electrical double layers around the colloidal spheres and the Brownian motion of the spheres in exhaustively deionized suspension.[4,5] Because the lattice spacing of the colloidal crystals matches with wavelength range of visible light, the crystals show bright iridescent colors when irradiated with white light. Therefore, reflection spectroscopy is quite effective in analyzing the lattice structure of colloidal crystals, since the Bragg diffraction wavelength locates in the range of visible wavelength. The nearest-neighbor interparticle distance of colloidal spheres in colloidal crystals is clearly and easily determined from the wavelength at the reflection peaks. We have reported the optical properties of colloidal crystals caused by electro-optic[6–8] and rheo-optic[9] effects of the crystals.

Recently, much attention has been paid to the colloidal crystals for the application of photonic crystals. Photonic crystals are two- or three-dimensional periodic structures in which the refractive index changes with the length in the order of the optical wavelength.[10–15] Photonic crystals hold the promise of important technological applications, e.g., optical switching and computing. Previously, we reported the photon trapping effects of colloidal crystals in aqueous suspension of colloidal silica spheres.[16] The trapping efficiency strongly depended on the thickness and alignment of the crystal layers; the efficiency increased from ca. 40 to 60% according to the increase in thickness of observation cell from 1 to 10 mm. However, a part of photon energy trapped in the crystals is deactivated by non-radiative processes in every reabsorption cycle. Therefore, we attained an enhancement of electronic excitation energy transfer efficiency by the photon trapping within the colloidal crystals.[17] The efficiency of electronic excitation energy transfer from photoexcited rhodamine 110 (R110, energy donor) to rhodamine

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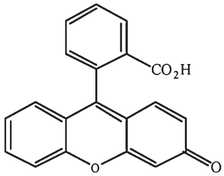
B (RB, energy acceptor) in an exhaustively deionized colloidal silica suspension has been enhanced more than 20% by the photon trapping effects. The colloidal suspension shows Bragg reflection and when the Bragg-peak wavelength matches with the fluorescence band of R110, a depletion was observed in the R110 fluorescence spectrum. This means the fluorescence of R110 is partially trapped due to the Bragg reflection inside the crystal lattice. In the coexistence of RB, the enhancement of RB fluorescence intensity was observed. These facts clearly indicate the trapped photon energy of R110 is efficiently transferred to RB within the colloidal crystals. Recently, Kolaric et al. showed that resonance energy transfer efficiency from 3-indocyanine (energy donor) to 5-indocyanine (energy acceptor) chromophores linked by oligonucleotides, when they are embedded in close-packed silica colloidal crystals, is enhanced by 45%.[18] In the present report, we attained the enhancement of the electronic excitation energy transfer efficiency by 2.26 times (126% enhancement).

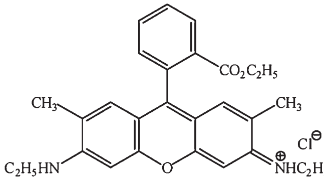
As for the enhancement of energy transfer of electronic excited chromophore dopants in submicrometer-size structures, there are many reports on different systems, e.g. Langmuir-Blodgett films,[19] DNA and RNA helices[20] and microdroplets,[21] etc. Nakashima et al. reported an efficient energy transfer for chromophores adsorbed on polystyrene latex surfaces.[22–24] The theory of electronic excitation energy transfer concerning most of these reports is non-radiative resonance energy transfer by the dipole coupling (Förster) mechanism. This process is major when the distance (R) between energy donor and acceptor is in nanometer range because the rate constant for resonance energy transfer decreases sharply by R^{-6}.[25] In our case, the interparticle distance between colloidal spheres of colloidal crystals, and hence the Bragg-peak wavelength, is more than several tens of nanometer order, and it is too far for the Förster mechanism to participate in. Therefore the enhancement of the transfer efficiency of electronic excitation energy in the present work is considered to be attained by the radiative mechanism.[25]

Experimental Parts

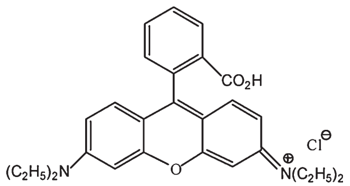
Monodispersed colloidal silica spheres (CS91) were kindly donated by Catalyst and Chemical Ind. Co., Ltd. (Tokyo). The diameter was 110 (mean diameter) ±4.5 nm (standard deviation) as measured with an electron microscopy (TEM, JEM-2000FX, JEOL, Tokyo). Charge density of strongly acidic groups was determined to be 0.48 μC cm^{-2} by conductometric titration with a conductivity meter (DS-14, Horiba, Kyoto). The suspension was treated with a mixed bed of cation- and anion-exchange resins (AG501-X8(D), Bio-Rad Lab., Hercules, CA) for more than ten years in order to eliminate ionic impurities as completely as possible. Fluorescein (FL, Aldrich, Milw, WI, dye content >95%) was used as an energy donor, and rhodamine 6G (R6G, Aldrich, dye content >99%) and RB (Aldrich, dye content >90%) were used as energy acceptors, without further purification. Dye concentrations of FL, R6G and RB in aqueous CS91 suspensions were low, 2×10^{-6}, 4×10^{-5} and 4×10^{-5} mol L^{-1} at the maxima, respectively, to avoid dye aggregation, concentration quenching, apparent fluorescence quenching due to reabsorption of the dye, and to increase in the critical concentration of crystal melting.



FL



R6G



RB

The nearest-neighbored intersphere distance of colloidal crystals can be calculated using Equations 1 and 2.[26,27]

$$l_0 = 0.904\, d_0 \phi^{-1/3} \quad (1)$$

$$l_{\mathrm{obs}} = 0.6124\, \lambda_{\mathrm{p}} n^{-1} \quad (2)$$

where l_0 denotes the distance calculated from the diameter (d_0) and the volume fraction (ϕ) of the colloidal silica spheres, and l_{obs} denotes the distance determined from the Bragg-peak wavelength (λ_{p}) and refractive index of the suspension (n). The value of n is approximated to that of water (1.333). In this study, ϕ of the silica spheres in the suspension was adjusted to be 0.074 in order to match the Bragg-peak wavelength of the crystals with the fluorescence band of donor FL dye ($\lambda_{\mathrm{p}} = 515$ nm). The values of l_0 and l_{obs} are calculated to be 236 nm and 237 nm, respectively, and they are agreed excellently within the experimental error. The size and melting behavior of colloidal crystals can be controlled by adding NaCl to the suspension. Hence, the efficiency of electronic excitation energy transfer was examined at different NaCl additive concentrations. In exhaustively deionized condition with no NaCl additive to the suspension, the size of colloidal crystals formed in the suspension is the smallest ($<100\,\mu$m). When a small amount of NaCl is added to the suspension, the crystal size increases with decreasing nucleation rate, and also with decreasing number of nuclei. At the NaCl concentration slightly lower than the critical concentration of crystal melting, the colloidal crystal size increases to the maximum ($\approx$1 mm). When the NaCl concentration exceeds the critical concentration of crystal melting, all the colloidal crystals are melted away. Ion-exchange resins coexisted were removed before dye solutions were mixed with colloidal suspensions, because the resins adsorb FL, R6G and RB dyes also. Highly pure water obtained from the Milli-Q water system (Milli-RO Plus and Milli-Q Plus. Millipore Ltd., Bedford, MA) was used. Precautions were taken to avoid ionic contamination in the sample preparation.

Quartz rectangular cell (10 mm (optical path lengths) ×10 mm (width)) was used in the measurements. For the reflection spectra measurements, a light beam from a halogen light source (PHL-50, Sigma Koki, Saitama) was introduced perpendicular to the observation cell wall through a Y-type optical fiber; the incident light beam was focused on the inner cell wall (diameter <1.5 mm). The reflection spectra were recorded on a photonic multichannel analyzer (PMA-50, Hamamatsu Photonics, Hamamatsu). Absorption spectra were obtained using a spectrophotometer (U-3500, Hitachi, Tokyo) by employing a rectangular cell. Fluorescence spectra were measured using a spectrofluorophotometer (U-4500, Hitachi, Tokyo) at the right angle direction of the excitation light. Excitation wavelengths (λ_{ex}) were 460 and 480 nm for FL (donor) + R6G (acceptor) and FL (donor) + RB (acceptor) systems, respectively. For measurements using colloidal crystals, the colloidal suspensions were first stirred and then allowed to stand for more than 30 min at $25 \pm 1\,^{\circ}$C in an air-conditioned room to attain as high a degree of crystallinity as possible.

Photon Trapping of Colloidal Crystals

When a suspension of colloidal crystals is irradiated with an external white light source, a peak is observed in the reflection spectrum. This reflection peak is due to the Bragg reflection from the crystals. On the other hand, when light is emitted by photo-excited fluorescent dyes inside the colloidal crystals of colloidal suspension, a depletion is observed in the fluorescence spectrum.[16] This depletion is caused by photon trapping inside the crystals due to Bragg reflection. When a second dye, which acts as an energy acceptor, is added to the suspension, the efficiency of electronic excitation energy transfer will be enhanced by the photon trapping of the crystals.

Figure 1 shows absorption and fluorescence ($\lambda_{\mathrm{ex}} = 460$ nm) spectra of FL and

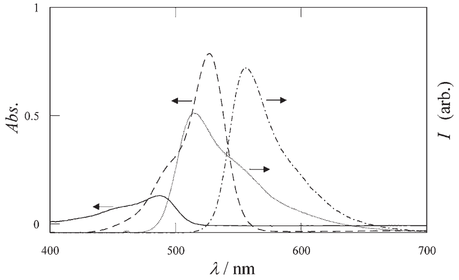


Figure 1.
Absorption (solid line for FL, broken line for R6G) and fluorescence ($\lambda_{ex} = 460$ nm, dotted line for FL, dashed-dotted line for R6G) spectra in water. [FL] = 2.0×10^{-6} mol L^{-1} and [R6G] = 1.0×10^{-5} mol L^{-1}.

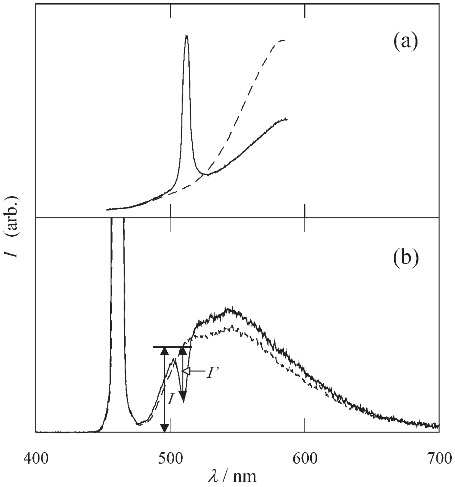


Figure 2.
(a) Reflection and (b) fluorescence ($\lambda_{ex} = 460$ nm) spectra of CS91 ($\phi = 0.074$) suspension added with FL (2.0×10^{-6} mol L^{-1}). [NaCl] = 0 mol L^{-1} (solid lines), 9.0×10^{-5} mol L^{-1} (broken lines).

R6G in aqueous solutions to look at the aspects of their spectral overlap. Fluorescence band of FL and absorption band of R6G overlap well each other, and therefore this pair of dyes works as an effective electronic excitation energy transfer system. Absorption and fluorescence bands of FL and R6G are in good mirror images. Though a slight reabsorption by constituent dyes was observed on the blue edge of the fluorescence band in our experimental condition of the dye concentrations, the effect was negligible at $\lambda_p = 515$ nm where the photon trapping and transfer efficiencies of electronic excitation energy were determined.

Fluorescence light emitted from photoexcited FL is partially trapped inside the colloidal crystals. Solid-line spectra of Figures 2(a) and 2(b) show reflection and fluorescence of FL dopant in colloidal crystals of deionized CS91 colloidal suspension, respectively. A sharp peak and a depletion in the FL fluorescence are observed at the Bragg wavelength ($\lambda_p = 515$ nm) of the crystals in the reflection and fluorescence spectra, respectively, as reported previously.[16] Broken-line spectra of Figures 2(a) and 2(b) show reflection and fluorescence of FL when NaCl (9.0×10^{-5} mol L^{-1}) was added to the suspension, and at this NaCl concentration the colloidal crystals were melted out completely. A comparison of reflection and fluorescence spectra shown by solid lines with those of broken lines in Figures 2(a) and 2(b) clearly indicates that the fluorescence depletion at 515 nm is caused by the presence of colloidal crystals. This depletion is attributed to the photon trapping of the Bragg reflection when the fluorescence light is emitted from the center area of the cell.[28]

The photon trapping efficiency, i.e., the valley depth of the depletion is quantified from the fluorescence spectra by a method as shown in Figure 2(b). Two fluorescence spectra of FL dopant in CS91 suspension ($\phi = 0.074$), in the crystal state (without NaCl) and in the liquid state (with 9.0×10^{-5} mol L^{-1} of NaCl), are overlapped with each other at the red-side tail (at ca. 650–700 nm). The difference in the fluorescence intensities (I') is divided by the fluorescence intensity (I) in the liquid state at the Bragg-peak wavelength ($\lambda = 515$ nm). Thus obtained value of I'/I is the photon trapping efficiency; greater the value of I'/I, the higher is the trapping efficiency. The photon trapping efficiency, i.e., the valley depth of the depletion (I'/I) quantified from the fluorescence spectra was 71% at 515 nm. Some percentage of FL dyes may be adsorbed on the silica spheres. In this case, the mean distance between FL dyes on CS91 sphere surface will be shorter than that in aqueous solution. However in this study, the photon trapping efficiency is estimated by the comparison of fluorescence intensities. Therefore the degree of dye adsorption on CS91 spheres is inconsequential because the amount of adsorption is considered to be independent of the suspension structures, crystal or liquid.

In general, exhaustive deionization of the suspension increases the nucleation rate, however, this decreases the discrete crystal size.[5,29] On the other hand, when a high concentration of NaCl (9.0×10^{-5} mol L^{-1} in this system) was added to the suspension, the colloidal crystals were melted out completely, as mentioned above. Therefore, a small amount of NaCl (1.0×10^{-5}–5.0×10^{-5} mol L^{-1} in this system) was added to the suspension in order to increase single-crystal size of the colloidal crystals. The spectra were taken at 30 min after mixing the suspension when the crystallinity of CS91 spheres in the cell was high enough, and the photon trapping efficiency (I'/I) was obtained as a function of NaCl concentration (Table 1). It should be noted that in spite of our expectations the increase in crystal size had an insignificant effect on I'/I in the present system. The highest I'/I value of 0.71 was obtained at the best deionization condition, in other words, at the smallest crystal size. The addition of NaCl to the system increases the amount of colloidal crystals formed by heterogeneous nucleation, whose crystal faces orient along the observation cell wall.[4,5,16,17] Therefore, it is considered that these plane-oriented crystals are less effective to trap FL fluorescence light emitted randomly in different directions.

Table 1.
Photon trapping efficiency (I'/I) for the CS91–FL system.

[NaCl]/mol L^{-1}	I'/I
0	0.71
1.0×10^{-5}	0.60
2.0×10^{-5}	0.57
3.0×10^{-5}	0.64
5.0×10^{-5}	0.65
9.0×10^{-5}	0

Enhancement of Electronic Excitation Energy Transfer Efficiency from FL to R6G

Figures 3(a) and 3(b) show reflection and fluorescence spectra, respectively, when both FL and R6G dyes are coexisted in the colloidal suspension. The contribution of FL fluorescence in Figure 3(b) was subtracted for easier comparison. Broken-line spectra were measured when NaCl (8.0×10^{-5} mol L^{-1}) was added to the suspension, and at this NaCl concentration the colloidal crystals were melted out completely. The decrease in NaCl concentration to melt the colloidal crystals from 9.0×10^{-5} mol L^{-1} (Figure 2) to 8.0×10^{-5} mol L^{-1} (Figure 3) is due to the decrease in critical concentration of crystal melting because the additive R6G to the system acts as an electrolyte also. The change in critical concentration of crystal

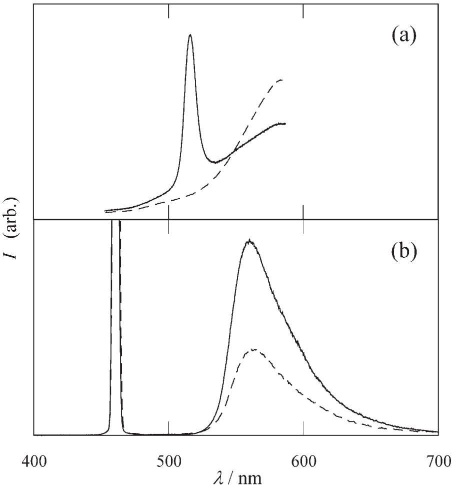


Figure 3.
(a) Reflection and (b) fluorescence ($\lambda_{ex} = 460$ nm) spectra of CS91 ($\phi = 0.074$) suspension added with FL (2.0×10^{-6} mol L^{-1}) and R6G (1.0×10^{-5} mol L^{-1}) in water. [NaCl] = 0 mol L^{-1} (solid lines), 8.0×10^{-5} mol L^{-1} (broken lines).

melting has not quantified because the effect depended on the kind of water-soluble dyes. Figure 3(b) clearly shows that the R6G fluorescence intensity is enhanced by 2.26 times (126% enhancement) in the presence of crystals. This enhancement is caused by the photon trapping of the colloidal crystals in the suspension.

The efficiency of electronic excitation energy transfer from photoexcited FL to R6G in an exhaustively deionized colloidal silica suspension is enhanced in the presence of colloidal crystals when the Bragg-peak wavelength matches with the fluorescence band of FL. In this study, the enhancement of transfer efficiency of electronic excitation energy from FL to R6G was examined at five different NaCl concentrations because the size of colloidal crystals changes according to the NaCl concentration in the suspension (Table 2). In the suspension of exhaustively deionized condition without NaCl, small colloidal crystals fill the measurement cell. When NaCl is slightly added to the suspension, the largest colloidal crystals are formed just before melting. Further addition of NaCl into the cell decreases the critical concentration of crystal melting and all the crystals are melted out due to the shrinkage of the electrical double layers. The concentration of R6G was also examined in Table 2, and the highest electronic excitation energy transfer efficiency was obtained as 2.26 at $[\text{R6G}] = 1.0 \times 10^{-5}\,\text{mol L}^{-1}$ and $[\text{NaCl}] = 0\,\text{mol L}^{-1}$. The fact that the highest electronic excitation energy transfer efficiency was attained at $[\text{NaCl}] = 0\,\text{mol L}^{-1}$ is consistent with the results as shown in Table 1. At an high concentration of R6G ($4.0 \times 10^{-5}\,\text{mol L}^{-1}$), the colloidal crystals were melted out at $[\text{NaCl}] = 4.0 \times 10^{-5}\,\text{mol L}^{-1}$ by the same reason as mentioned above.

Table 2.
Relative fluorescence peak intensity for the FL + R6G system.

$[\text{NaCl}]/\text{mol L}^{-1}$	relative fluorescence intensity		
	1.0×10^{-5} [a]	2.0×10^{-5} [a]	4.0×10^{-5} [a]
0	2.26	2.09	1.51
1.0×10^{-5}	1.30	1.33	1.34
2.0×10^{-5}	1.15	1.20	1.02
4.0×10^{-5}	1.17	1.22	1.00[b]
8.0×10^{-5}	1.00[b]	1.00[b]	–

[a] $[\text{R6G}]/\text{mol L}^{-1}$.

[b] Standard values when colloidal crystals are melted completely.

Enhancement of Electronic Excitation Energy Transfer Efficiency from FL to RB

Enhancement of the electronic excitation energy transfer efficiency by colloidal crystals was also observed when RB was used as an energy acceptor instead of R6G. Figure 4 shows absorption and fluorescence ($\lambda_{\text{ex}} = 480\,\text{nm}$) spectra of FL and RB in aqueous solutions. Absorption and fluorescence bands of FL and RB are in good mirror images. Fluorescence band of FL and absorption band of RB overlap each other, however, the degree of overlap is not efficient when it is compared with that of FL and R6G.

Figures 5(a) and 5(b) show reflection and fluorescence spectra, respectively, when RB is used as an energy acceptor. Solid-line spectra were measured with exhaustively deionized condition, whereas broken-line spectra were obtained when NaCl ($4.0 \times 10^{-5}\,\text{mol L}^{-1}$) was added to the suspension to melt the colloidal crystals completely. At the exhaustively deionized condition, Bragg reflection peak was

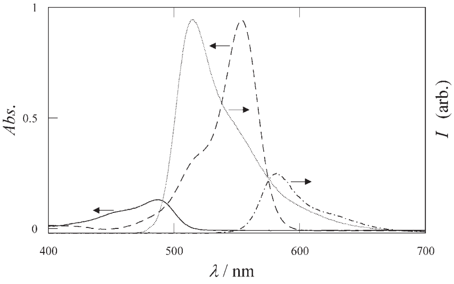


Figure 4.
Absorption (solid line for FL, broken line for RB) and fluorescence ($\lambda_{\text{ex}} = 480\,\text{nm}$, dotted line for FL, dashed-dotted line for RB) spectra in water. $[\text{FL}] = 2.0 \times 10^{-6}\,\text{mol L}^{-1}$ and $[\text{R6G}] = 1.0 \times 10^{-5}\,\text{mol L}^{-1}$.

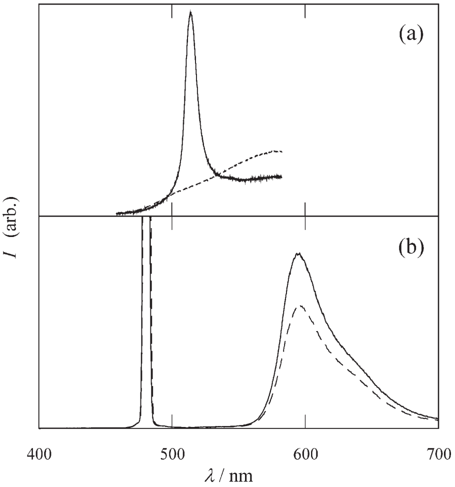


Figure 5.
(a) Reflection and (b) fluorescence ($\lambda_{ex} = 480$ nm) spectra of CS91 ($\phi = 0.074$) suspension added with FL (2.0×10^{-6} mol L^{-1}) and RB (2.0×10^{-5} mol L^{-1}) in water. [NaCl] = 0 mol L^{-1} (solid lines), 4.0×10^{-5} mol L^{-1} (broken lines).

observed as shown in Figure 5(a), and RB fluorescence intensity was enhanced by 1.41 times (41% enhancement) as shown in Figure 5(b). This enhancement is obviously caused by the photon trapping effects of colloidal crystals.

The enhancement values of transfer efficiency of electronic excitation energy from photoexcited FL to RB are tabulated as functions of NaCl and RB concentrations (Table 3). The maximum efficiency of 1.41 was attained at [NaCl] = 0 mol L^{-1} and [RB] = 2.0×10^{-5} mol L^{-1} in this experiments. This enhancement value is small when it is compared with that for FL + R6G system as mentioned above. Furthermore, in the case of R110 and RB as energy donor and acceptor, respectively, the efficiency was reported to be 1.2 times at the minimum.[17] These low enhancement efficiencies for FL + RB and R110 + RB systems are attributed to the inefficient spectral overlap between donor fluorescence and acceptor absorption at present.

As for the mechanism of electronic excitation energy transfer, when R6G or RB dyes are dispersed homogeneously in solution, the average distance between donor and acceptor dyes is calculated to be ca. 50 nm for the dye concentration of 1.0×10^{-5} mol L^{-1}. Non-radiative resonance energy transfer (Förster mechanism) is a distance-dependent interaction between the electronic excited states of two dye molecules in which excitation is transferred from a donor molecule to an acceptor molecule without emission of a photon. The efficiency (E) of electronic excitation energy transfer is dependent on the inverse sixth power of the intermolecular separation (R), can be calculated by using Equation 3.[25]

$$E = 1/[1 + (R/R_0)^6] \qquad (3)$$

where an active sphere (R_0) is the distance at which the energy transfer is 50%, i.e. 50% of excited donors are deactivated by the energy transfer. Typical values of R_0 are in the order of 1–10 nm. Thus, this mechanism is difficult to participate in our experimental condition of the dye concentrations, and the radiative (trivial) mechanism should be dominant in our case. Fluorescence light emitted from photoexcited FL is trapped in colloidal suspension due to the Bragg reflection of the crystals, and the trapped photons are efficiently absorbed by coexisting energy acceptors of R6G or RB. Though the mean distance between dyes may be shorter in the colloidal suspension than that in homogeneous solution due to the adsorption on colloidal spheres, the efficiency of electronic excitation energy transfer estimated in this study is not influenced because the fluorescence spectra are compared at the same adsorption

Table 3.
Relative fluorescence peak intensity for the FL + RB system.

[NaCl]/mol L^{-1}	relative fluorescence intensity		
	1.0×10^{-5} a)	2.0×10^{-5} a)	4.0×10^{-5} a)
0	1.18	1.41	1.26
1.0×10^{-5}	1.07	1.30	1.00b)
2.0×10^{-5}	1.16	1.22	–
4.0×10^{-5}	1.07	1.00b)	–
8.0×10^{-5}	1.00b)	–	–

a)[RB]/mol L^{-1}.
b)Standard values when colloidal crystals are melted completely.

condition; the crystallinity of colloidal crystals does not likely to affects on the adsorption of dyes.

Conclusion

When a suspension of colloidal crystals is irradiated with an external white light, Bragg reflection peak is observed in the reflection spectrum. On the other hand, when fluorescence light is emitted from photoexcited dyes inside the colloidal crystals of colloidal suspension, a depletion is observed in the fluorescence band. This depletion is caused by photon trapping inside the crystals due to Bragg reflection. By the addition of second dye which acts as an energy acceptor to the suspension, the efficiency of electronic excitation energy transfer is enhanced due to the photon trapping effects. When FL and R6G dyes are used as an energy donor and acceptor, respectively, very large enhancement of electronic excitation energy transfer of 2.26 times was attained. This enhancement is considered to be caused by the photon trapping of the crystals. The transfer efficiency was almost the same irrespective of the crystal size. When FL + RB pair is used instead of FL + R6G, the enhancement was 1.41 times. This low efficiency is attributed to the inefficient spectral overlap between FL fluorescence and RB absorption.

Acknowledgements: Drs. M. Komatsu and M. Hirai of Catalyst & Chemical Ind. Co. (Tokyo, Japan) are thanked deeply for providing the sample of CS91 spheres. This research was partially supported by the Japan Society for the Promotion of Science, Grants-in-Aid for Scientific Research (B), (19350110 to A.T. and 18350057 to T.O.), and by the Koshiyama Science & Technology Foundation.

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