Colloid Polym Sci (2006) 285:127–133
DOI 10.1007/s00396-006-1553-0

ORIGINAL CONTRIBUTION

# Enhancement of electronic excitation energy transfer in the colloidal crystals of colloidal silica suspensions doped with fluorescent dyes

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Received: 15 November 2005 / Accepted: 8 July 2006 / Published online: 24 August 2006


**Abstract** The efficiency of electronic excitation energy transfer from photo-excited rhodamine 110 (Rh110, energy donor) to rhodamine B (RhB, energy acceptor) in an exhaustively deionized colloidal silica suspension has been studied. This colloidal suspension shows Bragg reflection due to the formation of colloidal crystals and the Bragg-peak wavelength is controllable by the volume fraction of the silica spheres. When the Bragg-peak wavelength matches with the fluorescence band of Rh110, a depletion was observed in the Rh110 fluorescence spectrum. This means the fluorescence of Rh110 is partially trapped due to the Bragg reflection inside the crystal lattice. In the coexistence of RhB, the enhancement of RhB fluorescence intensity was observed. These facts clearly indicate the trapped photon energy of Rh110 is efficiently transferred to RhB within the colloidal crystals. The quantitative measurements showed that the enhancement of the transfer efficiency is 20% (or slightly more) in the present experimental conditions.

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**Keywords** Colloidal crystals · Photon trapping · Electronic excitation energy transfer · Bragg reflection · Fluorescence spectra

## Introduction

A crystal-like structure is formed when a suspension of mono-dispersed colloidal spheres is exhaustively deionized in polar solvents such as water [1–4]. This structure is called as "colloidal crystals", and the crystals are formed due to the extended electrical double layers around the colloidal spheres and Brownian motion of the spheres. When 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. Reflection spectroscopy is quite effective in analyzing the lattice structure of colloidal crystals, as 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. More than a decade ago, Okubo succeeded in fabricating very large colloidal crystals 2–8 mm in size [5]. Recently, the authors have reported the optical properties of colloidal crystals, including electro-optic [6–8] and rheo-optic [9] effects.

The possibility of a photonic band gap (PBG) was identified recently [10]; since then, many researchers have studied photonic crystals, which are two- or three-dimensional periodic structures in which the refractive index changes with the length in the order of the optical wavelength to use them as practical optical materials [11–15]. Gaponenko et al. observed a dip in the fluorescence spectra of rhodamine 6G (R6G) molecules embedded in an artificial opal [14]. The opal crystal was filled with various

liquids to change the relative refractive index of silica. The position of the dip varied depending on the relative refractive index of silica with respect to the liquid, and the photon trapping effect was reported. Vos et al. reported that in the case of titania doped with R6G, the fluorescence intensity was attenuated independent of the observation angle of photonic crystals made of inverse opals [15].

Previously, we studied the photon trapping efficiencies of colloidal crystals in aqueous suspension of colloidal silica spheres [16]. The trapping efficiencies were strongly dependent on the thickness and alignment of the crystal layers; the efficiency increased from approximately 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. In the present report, an enhancement of electronic excitation energy transfer efficiency is attained for the trapped photons within the colloidal crystal lattice.

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 [17], DNA and RNA helices [18] and microdroplets [19], etc. Nakashima et al. reported an efficient energy transfer for chromophores adsorbed on polystyrene latex surfaces [20–22]. 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 $R^{-6}$ [23]. In our case, the interparticle distance between colloidal spheres of colloidal crystals, and hence the Bragg-peak wavelength, is more than a few hundred 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 (trivial) mechanism [23].

## Experimental

### Materials

An aqueous suspension of colloidal silica spheres (CS91) was donated by Catalyst and Chemical Ind (Tokyo, Japan). The sphere diameter was determined to be 110 (mean diameter)±4.5 nm (standard deviation) by electron microscopy. The suspension was treated in a mixed bed of cation- and anion-exchange resins (AG501-X8(D), Bio-Rad Lab., Hercules, CA, USA) for more than 10 years to eliminate ionic impurities as completely as possible. Rhodamine 110 (Rh110, Aldrich, Milwaukee, WI, USA, dye content >70%) and rhodamine B (RhB, Aldrich, dye content >90%) were used for an energy donor and acceptor, respectively, without further purification. Figure 1 shows the structure formulae of these chromophores. Dye concentrations of Rh110 and RhB in aqueous CS91 suspensions were low, $1\times10^{-5}$ and $2\times10^{-6}$ mol/l, respectively, to avoid dye aggregation, concentration quenching, apparent fluorescence quenching due to reabsorption of the dye, and increase in the critical concentration of crystal melting. On these experimental conditions, the absorbance of Rh110 at the excitation wavelength ($\lambda_{ex}$) was approximately twice as large as that of RhB.

### Preparation of colloidal suspensions

The volume fraction ($\phi$) of the silica spheres in the suspension was adjusted to be 0.0701 to match the Bragg-peak wavelength of the crystals with the fluorescence band of donor Rh110 dye ($\lambda_{max}$=525 nm). The nearest-neighbored intersphere distance of colloidal crystals is calculated using Eqs. 1 and 2 [24, 25].

$$l_0 = 0.904\, d_0\, \phi^{-1/3} \tag{1}$$

$$l_{obs} = 0.6124\, \lambda_p\, n^{-1} \tag{2}$$

where $l_0$ denotes the distance calculated from the diameter ($d_0$) and $\phi$ of the colloidal silica spheres, and $l_{obs}$ denotes the distance determined from the Bragg-peak

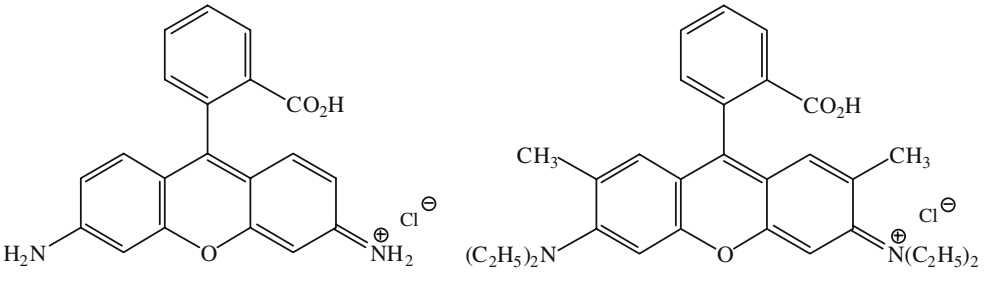


**Fig. 1** Molecular structures of Rh110 and RhB

wavelength ($\lambda_p$) and refractive index of the suspension ($n$). In this study, the value of $n$ is approximated to that of water (1.333). In the case of CS91 crystals with $\phi$=0.0701, the Bragg peak was determined to be at $\lambda_p$=535 nm by measuring the reflection spectrum. The values of $l_0$ and $l_{obs}$ are calculated to be 241 and 246 nm, respectively. Both $l_0$ and $l_{obs}$ agreed excellently within the experimental error. The CS91 suspension with $\phi$=0.0370 was also prepared for a reference experiment. In this case, the Bragg-peak appeared at 650 nm, and the wavelength is mismatched with that of the Rh110 fluorescence band peak.

It is possible to control the size and melting behavior of colloidal crystals by adding slight NaCl to the suspension. Hence, the efficiency of electronic excitation energy transfer was examined at three different NaCl additive concentrations. For the first, in exhaustively deionized condition with no NaCl additive to the suspension, the size of colloidal crystals formed in the suspension is the smallest. Secondly, at the NaCl concentration slightly lower than the critical concentration of crystal melting, the colloidal crystal size increases to the maximum. Finally, when the NaCl concentration exceeds the critical concentration of crystal melting, all the colloidal crystals are melted away.

Before dye solutions were mixed with colloidal suspensions, ion-exchange resins that coexisted were removed, because the resins adsorb Rh110 and RhB chromophores also. Highly pure water obtained from the Milli-Q water system (Milli-RO Plus and Milli-Q Plus. Millipore, Bedford, MA, USA) was used. Precautions were taken to avoid ionic contamination in the sample preparation.

### Spectroscopic measurements

Quartz rectangular cell [inner size=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, Japan) 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, Japan). Absorption spectra were obtained using a spectrophotometer (U-3500, Hitachi, Tokyo, Japan) by using a rectangular cell. Fluorescence spectra were measured using a spectrofluorophotometer (U-4500, Hitachi, Tokyo, Japan) at the right-angle direction of the excitation light. The fluorescence lifetime of Rh110 was measured using single-photon counting technique (NAES-700D, Horiba, Kyoto, Japan).

For measurements using colloidal crystals, the colloidal suspensions were first stirred and then allowed to stand for more than 30 min (at 25±1 °C in an air-conditioned room) to attain as high a degree of crystallinity as possible.

## Results and discussion

### Absorption and fluorescence spectra

Absorption and fluorescence spectra of Rh110, RhB, and their mixture were first measured to look at the aspects of their spectral overlap. Figure 2a shows normalized absorption and fluorescence ($\lambda_{ex}$=480 nm) spectra of Rh110 and RhB in aqueous solutions. Absorption and fluorescence bands of Rh110 and RhB 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 $\lambda_p$=535 nm where the photon trapping and transfer efficiencies of electronic excitation energy were determined. Figure 2b,c shows absorption and fluorescence spectra of aqueous solution containing two dyes (Rh110 + RhB),

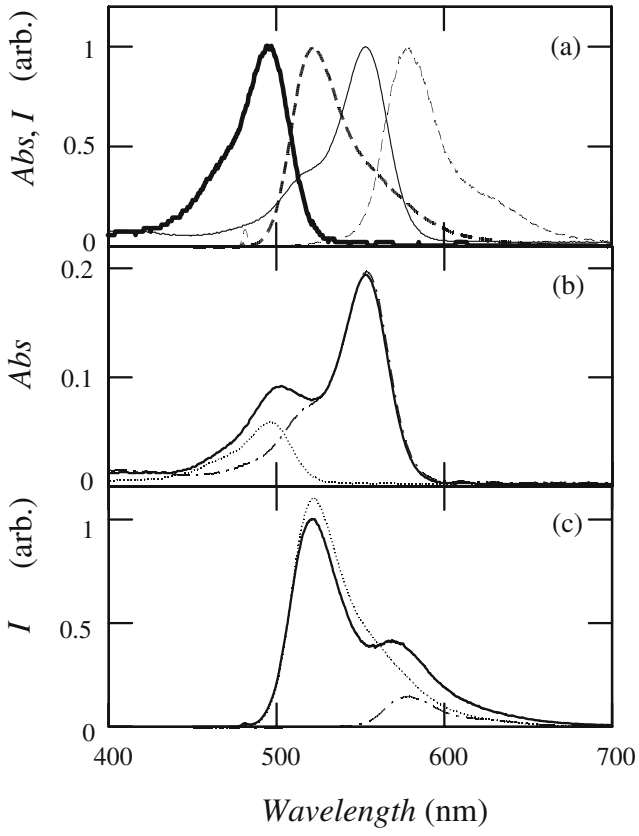


**Fig. 2** Absorption and fluorescence ($\lambda_{ex}$=480 nm) spectra of Rh110 ($1\times10^{-5}$ mol/l) and/or RhB ($2\times10^{-6}$ mol/l) in aqueous solutions. **a** Normalized absorption (*solid curve*) and fluorescence (*broken-line curve*) spectra of Rh110 (*bold*) and RhB (*fine*); **b** absorption spectra of Rh110+RhB (*solid*), Rh110 (*dotted*) and RhB (*dash-dotted*); **c** Fluorescence spectra of Rh110+RhB (*solid*), Rh110 (*dotted*) and RhB (*dash-dotted*)

respectively. Two peaks corresponding to Rh110 and RhB dyes appeared in absorption and fluorescence spectra.

## Photon trapping of colloidal crystals

Fluorescence light emitted from photo-excited Rh110 is partially trapped inside the colloidal crystals. Figure 3a,b shows reflection and fluorescence spectra, respectively, of Rh110 dopant in colloidal crystals of CS91 colloidal suspension. A sharp peak and a depletion in the Rh110 fluorescence are observed at the Bragg wavelength ($\lambda_p$=535 nm) of the crystals in the reflection and fluorescence spectra, respectively, as reported previously [16]. NaCl ($2\times10^{-5}$ mol/l) was added slightly to the suspension to increase single-crystal size of the colloidal crystals. In general, exhaustive deionization of the suspension increases the nucleation rate; however, this decreases the discrete crystal size [5, 26]. Therefore, the spectra were taken with slight NaCl concentration of $2\times10^{-5}$ mol/l, and at 30 min after mixing the suspension when the crystallinity of CS91 spheres in the cell was high enough. Figure 3c shows the fluorescence spectra of Rh110 when $4\times10^{-5}$ mol/l of NaCl was added to the suspension and the crystals were melted out.

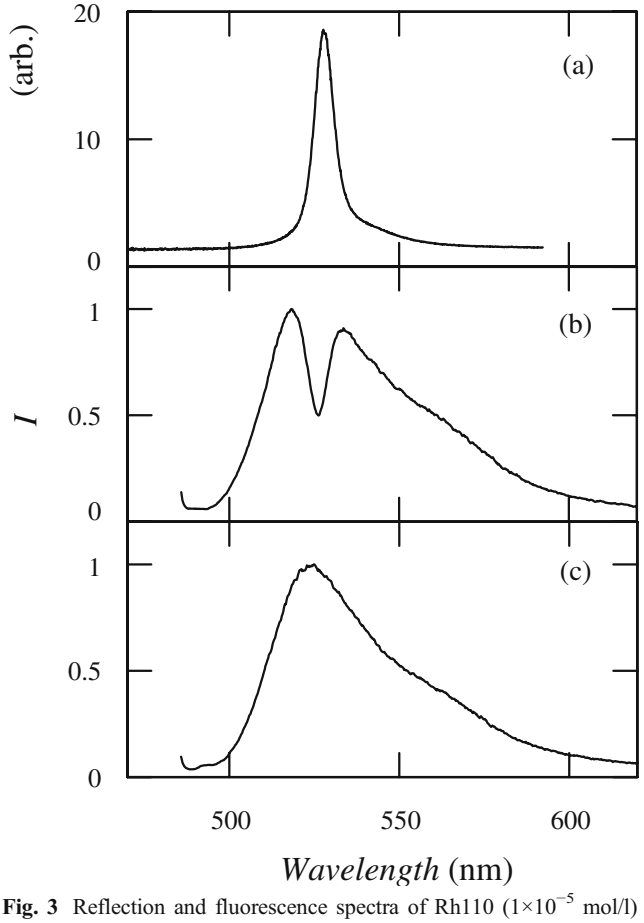


**Fig. 3** Reflection and fluorescence spectra of Rh110 ($1\times10^{-5}$ mol/l) dopant in CS91 suspension ($\phi$=0.0701). **a** Reflection spectrum with NaCl ($2\times10^{-5}$ mol/l); **b** fluorescence spectrum with NaCl ($2\times10^{-5}$ mol/l); **c** fluorescence spectrum with NaCl ($4\times10^{-5}$ mol/l)

A comparison of Fig. 3b and c clearly indicates that the fluorescence depletion at 535 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 of the cell [27]. When Fig. 3c is compared with Fig. 2a, the fluorescence band shape of Rh110 dopant in CS91 suspension is almost the same as that in aqueous solution, whereas a slight peak shift to the red side is observed. This result is consistent with our previous report [16], and the shift could be explained by light scattering of the CS91 spheres at the blue side. As for CS91 suspension ($\phi$=0.003) doped with Rh110 ($1\times10^{-5}$ mol/l), approximately 3% of Rh110 dyes were adsorbed on the colloidal particles (about 36 Rh110 molecules on a single silica sphere) by the examination of centrifuged supernatant of the suspension. The adsorption of dyes onto colloidal or silica-gel surfaces has been studied extensively [22, 28–30]. Emission from aggregate dimers of dyes on the silica surfaces reported so far may also be the cause for the red shift in the spectrum.

The photon trapping efficiency as mentioned above, i.e., the valley depth of the depletion is quantified from the fluorescence spectra by a method as shown in Fig. 4. Two fluorescence spectra of Rh110 dopant in CS91 suspension ($\phi$=0.0701), in the crystal state (with $2\times10^{-5}$ mol/l of NaCl, 30 min after mixing) and in the liquid state (with $4\times10^{-5}$ mol/l of NaCl), are overlapped with each other at the red-side tail (at approximately 550–600 nm). The difference in the fluorescence intensities ($I$) is divided by the fluorescence intensity ($I'$) in the liquid state at the Bragg-peak wavelength ($\lambda_p$=535 nm). Thus, obtained value of $I/I'$ is the photon trapping efficiency; the greater the value of $I/I'$, the higher the trapping efficiency. When silica suspension of $\phi$=0.002 is doped with $2\times10^{-6}$ mol/l of RhB

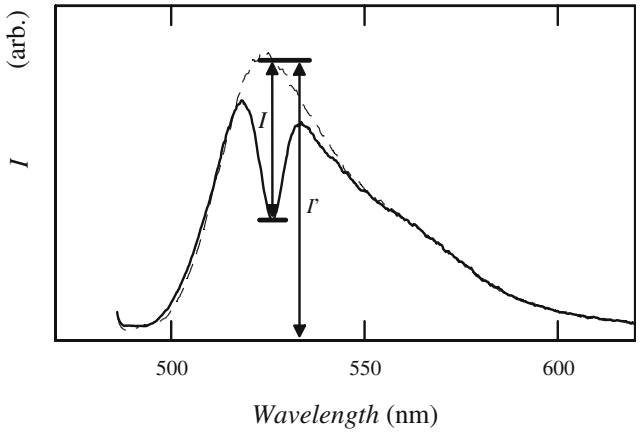


**Fig. 4** Fluorescence spectra of Rh110 ($1\times10^{-5}$ mol/l) dopant in CS91 suspension ($\phi$=0.0701). *Solid curve*: with NaCl ($2\times10^{-5}$ mol/l) and 30 min after mixing, *broken*: with NaCl ($4\times10^{-5}$ mol/l). $I$: attenuated intensity, $I'$: original intensity at the Bragg peak wavelength

dye, approximately 75% of RhB dyes were found to be adsorbed on the silica spheres (about 80 RhB molecules on a single silica sphere). Therefore, the mean distance between RhB dyes on CS91 sphere surface is shorter than that in aqueous solution. In this study, however, 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.

## Enhancement of transfer efficiency of electronic excitation energy from Rh110 to RhB

The efficiency of electronic excitation energy transfer from photo-excited Rh110 to RhB 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 Rh110. In this study, the enhancement of transfer efficiency of electronic excitation energy from Rh110 to RhB was examined in three different NaCl concentrations, because the size of colloidal crystals changes according to the NaCl concentration in the suspension as mentioned before. 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. In addition, as a reference experiment, the volume fraction of the silica spheres in the suspension was changed to 0.0370. In this case, the Bragg-peak wavelength is shifted to the red side at $\lambda_p$=650 nm, beyond the fluorescence band of the Rh110 dye.

Figure 5a,c shows the reflection spectra, and Fig. 5b,d shows fluorescence spectra of the dyes in CS91 suspension. Figure 5a,b is the spectra when the Bragg peak is matched ($\lambda_p$=535 nm, $\phi$=0.0701) with the donor fluorescence band, whereas Fig. 5c,d is that when the Bragg peak is mismatched ($\lambda_p$=650 nm, $\phi$=0.0370) with the fluorescence band. The NaCl concentration was changed depending on the CS91 volume fraction because the critical concentration of the crystal melting increases according to the increase in the volume fraction. In Fig. 5b, when the Bragg peak wavelength is matched with the donor fluorescence band, the acceptor RhB fluorescence intensity with crystals is clearly larger than that without crystals. On the other hand when the Bragg peak wavelength is mismatched with the donor fluorescence band as shown in Fig. 5d, the acceptor RhB fluorescence intensities are almost the same irrespective of the presence of the crystals.

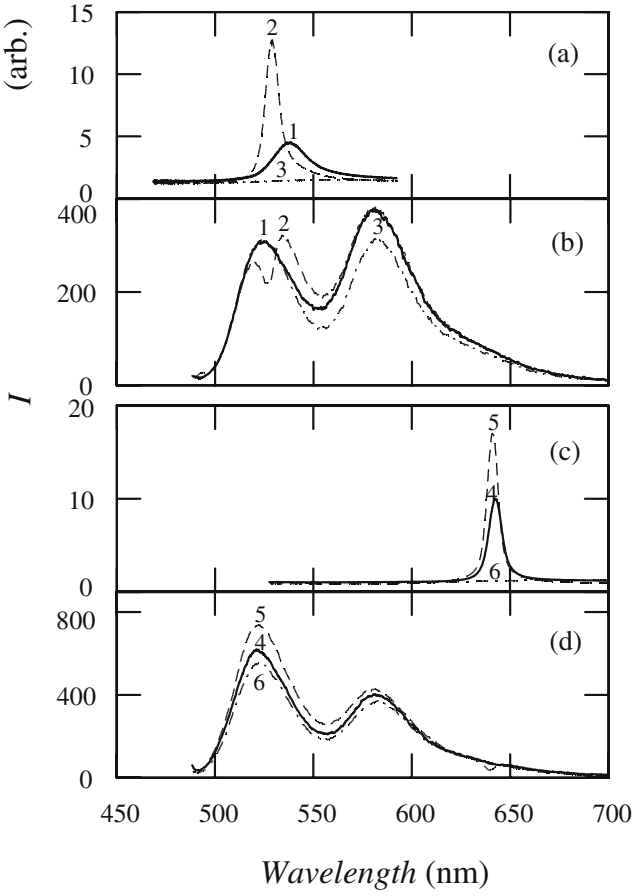


**Fig. 5** Reflection and fluorescence spectra of Rh110 ($1\times10^{-5}$ mol/l) and RhB ($2\times10^{-6}$ mol/l) dopants in CS91 suspension. **a** Reflection spectra ($\phi$=0.0701); **b** fluorescence spectra ($\phi$=0.0701); **c** reflection spectra ($\phi$=0.0370); **d** fluorescence spectra ($\phi$=0.0370). NaCl concentration in mol/l: (1) 0; (2) $2\times10^{-5}$; (3) $5\times10^{-5}$; (4) 0; (5) $4\times10^{-6}$; (6) $1\times10^{-5}$

These facts indicate that the enhancement of transfer efficiency of electronic excitation energy is caused by the colloidal crystals. For the quantitative discussion, spectra in Fig. 5b,d are normalized to unity at the donor Rh110 fluorescence intensity maximum as shown in Fig. 6a,b, respectively. Figure 6a clearly shows the increase in the acceptor RhB fluorescence intensity by 20% in the presence of crystals, whereas in Fig. 6b no increase in the RhB fluorescence intensity is observed even in the presence of crystals. This enhancement value of 20% is considered to be the minimum because the Bragg peak wavelength for the suspension with large crystals appeared at the blue side than that for the small crystals as shown in Fig. 5a. In Fig. 6a,b, the fluorescence band of Rh110 in the absence of crystals does not fit that of Rh110 + RhB in the presence of crystals at the red tail of approximately 550 nm. This indicates the participation of efficient reabsorption of Rh110 fluorescence by RhB, whose absorption peak locates at 553 nm, at the red tail of Rh110 fluorescence band. Consequently, the efficiency of electronic excitation energy transfer from

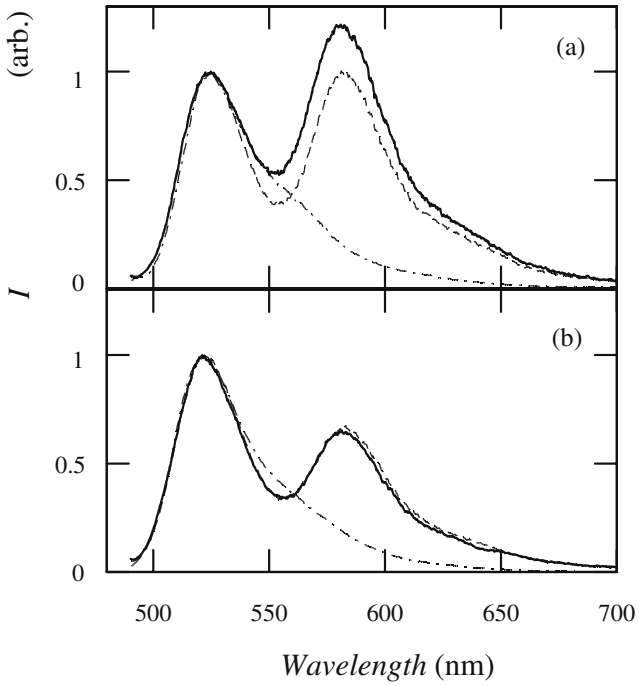


**Fig. 6** Normalized fluorescence spectra of Rh110 ($1\times10^{-5}$ mol/l) and RhB ($2\times10^{-6}$ mol/l) dopants in CS91 suspension. **a** $\phi$=0.0701, **b** 0.0370. *Solid curve*: without NaCl and 30 min after mixing; *broken-line curve*: with NaCl: (**a** $5\times10^{-5}$ mol/l, **b** $1\times10^{-5}$ mol/l); *dash-dottedcurve*: Rh110 dopant only in CS91 suspension with NaCl ($4\times10^{-5}$ mol/l)

Rh110 to RhB is enhanced by the photon trapping of the colloidal crystals.

## Colloidal crystal size and the energy transfer efficiency

It should be mentioned that the enhancement of electronic excitation energy transfer efficiency is observed even when the colloidal crystal size is small and the depletion in the fluorescence spectrum is absent. In Fig. 5b, the photon trapping efficiency ($I/I'$) for the suspension with large colloidal crystals at the slight NaCl additive concentration is calculated to be approximately 43%, whereas that with small colloidal crystals in exhaustively deionized condition is 0%. Interestingly, the fluorescence intensity of the energy acceptor RhB is almost the same for both cases, though the values themselves are larger when compared with that in the absence of crystals. Therefore, the enhancement of electronic excitation energy transfer is considered to be caused by the presence of the colloidal crystals irrespective of their size and the value of photon trapping efficiency ($I/I'$). This is because the large depletion in the fluorescence spectrum is attained by the number of crystals whose crystal layers are aligned perpendicular to the observation direction.

In the suspension with large colloidal crystals, the contribution of heterogeneous crystals formed on the cell wall are large [16]. The crystal layers of these heterogeneous crystals are aligned parallel to the cell wall, i.e., perpendicular to the observation direction in the measurement of reflection spectra. On the other hand, when the suspension is exhaustively deionized and the colloidal crystal size is small, the photon trapping is still efficient in spite of the absence of the depletion in the fluorescence spectrum. Actually, though it is small, a Bragg reflection peak is observed for the small crystals in Fig. 5a. The fluorescence of energy donor Rh110 emitted from inside the cell is directed to all directions and the photon is trapped by many small crystals in random orientation. These small crystals give only small $I/I'$ value because the fraction of crystals whose layers are aligned perpendicular to the observation direction by chance is not large.

## Enhancement of energy transfer efficiency by colloidal particles

Interestingly, the enhancement of transfer efficiency of electronic excitation energy is observed even in colloidal suspension without crystals when the efficiency is compared with that in aqueous dye solution without colloidal spheres. A comparison of the fluorescence spectrum of Fig. 2c (Rh110+RhB, in aqueous solution) and the spectra of Fig. 6a,b (in colloidal suspension) indicates that the latter gave the larger fraction of RhB fluorescence. Furthermore, a comparison of the spectrum of Fig. 6a ($\phi$=0.0701) with that of Fig. 6b ($\phi$=0.0370) indicates that the former gave the larger fraction by 33%. That is, the larger the volume fraction of colloidal spheres, the larger the RhB fluorescence fraction, i.e., the larger transfer efficiency of electronic excitation energy.

It is considered that the enhancement is due to the multiple light scattering of the colloidal spheres. The colloidal particles in the measurement cell cause light scattering, and hence the effective optical path length increases. This multiple scattering induces the same effect as the photon trapping. In fact, the fluorescence lifetime of Rh110 is 4.7 ns in CS91 suspension ($\phi$=0.0701) by a single photon counting (SPC) measurement, and it is longer than that of 4.4 ns measured in water. The multiple scattering increases the possibility of reabsorption of Rh110 fluorescence by RhB dyes in the suspension. It should be mentioned as a matter of course that the further enhancement of electronic excitation energy transfer will be attained by the crystal formation of the colloidal particles in the suspension as discussed before.

## Mechanism of electronic excitation energy transfer

When Rh110 and RhB dyes are dispersed homogeneously in solution, the average distance between donor and acceptor dyes is calculated to be approximately 50 nm for

the dye concentrations of this work. 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 ($R$); it can be calculated using Eq. 3 [23].

$$E = 1 \Big/ \left[1 + (R/R_0)^6\right] \tag{3}$$

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 include in our experimental condition of the dye concentrations because $R$ is estimated to be approximately 50 nm; the radiative (trivial) mechanism should be dominant in our case. 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 condition; the crystallinity of colloidal crystals does not likely affect the adsorption of dyes.

## Conclusion

When a suspension of colloidal crystals is irradiated with an external 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. 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 is enhanced by 20% at the minimum. 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. In addition, the transfer efficiency of electronic excitation energy in the colloidal suspension was larger than that in aqueous solution. This result is attributed to the multiple light scattering of the colloidal spheres.

**Acknowledgments** Drs. M. Komatsu and M. Hirai of Catalyst & Chemical Ind. (Tokyo, Japan) are thanked deeply for providing the sample of CS91 spheres. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research (B), 16350124, 2004.

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