

## Excitation energy transfer between J-aggregates in layer-by-layer alternate assemblies

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### Abstract

The layer-by-layer alternate assemblies incorporating two kinds of cyanine dyes have been fabricated by the alternate adsorption technique. In order to examine excitation energy transfer between J-aggregates, a thiocyanine dye has been employed as the donor and thiocarbocyanine dyes as the acceptor. It is confirmed that these dye combinations form the mixed J-aggregate in the alternate assemblies. From steady-state fluorescence spectra of the molecular assemblies, the occurrence of efficient energy transfer from the donor J-aggregate to the acceptor J-aggregate has been demonstrated. The experimentally obtained rate constant of energy transfer  $k_{ET}$  in the Stern–Volmer kinetics of the order of  $10^{13} \text{ nm}^2 \text{ molecules}^{-1} \text{ s}^{-1}$  is interpreted in terms of exciton migration and trapping in the mixed J-aggregate. The difference in  $k_{ET}$  between various combinations of cyanine dyes is not inconsistent with an exponential energy gap law. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Cyanine dye; J-aggregate; Alternate assembly; Energy transfer; Luminescence

### 1. Introduction

Remarkable optical properties of the J-aggregate of cyanine dyes, e.g. a sharp absorption peak J-band which is red-shifted from the monomer band, resonance fluorescence with ultra-short lifetime and large optical non-linearity, have been interpreted in the context of delocalization of Frenkel exciton over chromophores well arranged in one- or two-dimensional structure [1–7]. On the other hand, it has been known that exciton trapping in the chlorophyll aggregates plays an important role in the light-harvesting network of photosynthesis [8,9]. In connection with the photobiological processes, the detailed mechanism of exciton trapping and energy transfer in the J-aggregates attracts much attention [10]. The mixed J-aggregate of two kinds of cyanine dyes in the organized molecular assemblies seems to be a useful tool for constructing artificial photosynthesis system as well as novel imaging materials [3]. Considering that the rate and the efficiency of energy transfer are very sensitive to the geometry of the donor and acceptor molecules, luminescence properties of the molecular assemblies would be helpful to understand the structure of the mixed J-aggregate. We here call one J-aggregate whose J-band is located at

shorter wavelength a donor (J-)aggregate and another one an acceptor (J-)aggregate.

Decher et al. developed a novel method to fabricate the ultra-thin multilayers by means of the alternate adsorption of cationic and anionic polyelectrolytes (alternate adsorption technique) [11]. In the previous studies [12,13], we successfully applied this method to the preparation of the layer-by-layer alternate assemblies (alternate assemblies) incorporating the J-aggregate of anionic cyanine dyes. Furthermore, we observed the formation of the mixed J-aggregate of two different combinations of cyanine dyes: 3,3'-disulfopropyl-5,5'-dichloro-thiocyanine dye (dye I) and 3,3'-disulfopropyl-5,5'-dichloro-9-alkyl-thiocarbocyanine dye (dye II, ethyl; dye III, methyl) [13].

In this article, we have fabricated the layer-by-layer alternate assemblies by using the combination; dye I + 3,3'-disulfopropyl-5,5'-dichloro-9-phenyl-thiocarbocyanine dye (dye IV) and compared the results with those of the dye I + dye II and dye I + dye III combinations. On the basis of experimental observations, exciton migration and trapping in the mixed J-aggregate has been discussed.

### 2. Experimental

The molecular structures of cyanine dyes and poly(diallyldimethylammonium chloride) (PDDA) used in this

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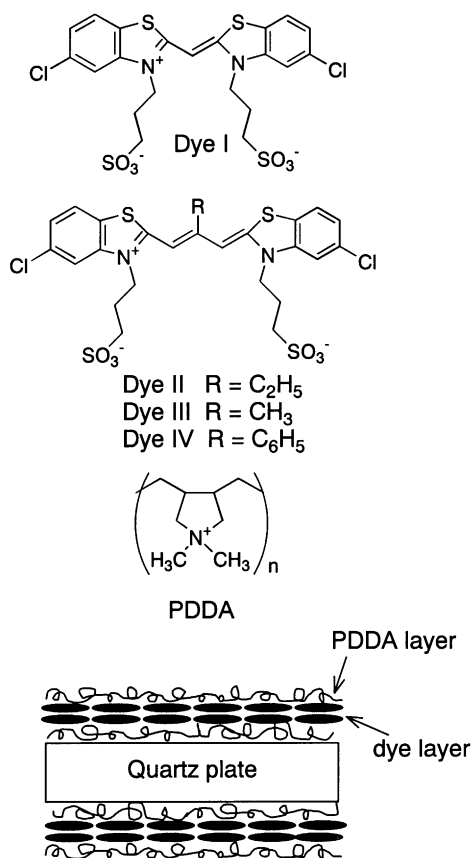


Fig. 1. Molecular structures of PDDA and cyanine dyes (dyes I–IV) used in this study. The schematic structure of the alternate assembly is illustrated at the bottom.

study are illustrated in Fig. 1. 3,3'-Disulfopropyl-5,5'-dichloro-thiacyanine sodium salt (dye I), 3,3'-disulfopropyl-5,5'-dichloro-9-ethyl-thiacarbocyanine potassium salt (dye II), 3,3'-disulfopropyl-5,5'-dichloro-9-methyl-thiacarbocyanine triethylammonium salt (dye III) and 3,3'-disulfopropyl-5,5'-dichloro-9-phenyl-thiacarbocyanine triethylammonium salt (dye IV) were purchased from the Japanese Research Institute for Photosensitizing Dyes (Okayama). PDDA (MW = 40 000–50 000) and poly(sodium styrenesulfonate) (PSS, MW = 70 000) were obtained from Aldrich. These materials were used without further purification. The procedure of the alternate adsorption method has been already reported [12,13]. The alternate assembly was built up by immersing the quartz plate (10 mm × 30 mm × 1 mm in size) alternately for 30 min in a 1.0% (w/v) PDDA aqueous solution and in a mixed solution of cyanine dyes in water. In the combination of cyanine dyes, donor + acceptor; dye I + dye II, dye I + dye III, dye I + dye IV, the molar mixing ratio of [donor]:[acceptor] in the aqueous solution was varied from 1:0 to 0:1, while the total concentration was kept constant ( $5 \times 10^{-5}$  M). All the samples were prepared by repeating above cycle three times. The schematic structure of the alternate assembly is illustrated at the bottom of Fig. 1.

The amount of cyanine dyes incorporated in the alternate assemblies was determined by the following way. The sample plate was immersed in a 5 ml hot 0.1% (w/v) PSS aqueous solution for 15 min to dissolve dye molecules into the solution. The solutions were subjected to spectrophotometric analysis. In the absorption spectra, monomer bands of the donor and the acceptor were observed, from which dye concentrations were determined.

UV–VIS absorption spectra were recorded on a UV-2200 spectrophotometer (Shimadzu Seisakusho). Steady-state fluorescence spectra were measured with a PMA-10 detection system (Hamamatsu Photonics) with the excitation source of a 500 W xenon arc lamp whose wavelength was adjusted through a monochromator.

### 3. Results

The absorption spectra of dye I + dye IV assemblies with varying dye IV mole fractions  $\chi_{\text{dye IV}} = [\text{dye IV}] / ([\text{dye I}] + [\text{dye IV}])$  are shown in Fig. 2. The sharp peaks around 465 and 670 nm are assigned to the J-bands of dyes I and IV, respectively. The absorbance at the J-band of dye I decreases and that of dye IV increases with increasing  $\chi_{\text{dye IV}}$ . This means that the dye concentration in the alternate assembly is controlled by changing the ratio of [dye I]:[dye IV] in aqueous solutions. The peak position of the J-band is plotted as a function of  $\chi_{\text{dye IV}}$  in Fig. 3a. It is observed that the J-band of dye I is slightly blue-shifted on decreasing the concentration of dye I, which implies the change of the size of the J-aggregate [14]. The broader J-band at the lower concentration of the corresponding dye I is also a supporting evidence of the change of the aggregate size [3]. The J-band of dye IV is split into two bands at 600 and 660 nm for  $\chi_{\text{dye IV}}$  lower than 0.2. The 600 nm band is assigned to the dye aggregate because it is red-shifted from the monomer band of dye IV ( $\lambda = 566$  nm).

Absorption spectra of the dye I + dye II and the dye I + dye III assemblies have been reported in our former

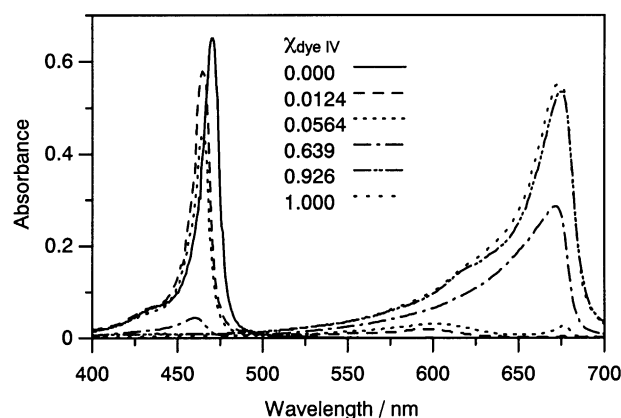


Fig. 2. Absorption spectra of the dye I + dye IV alternate assemblies with various mole fractions of dye IV.

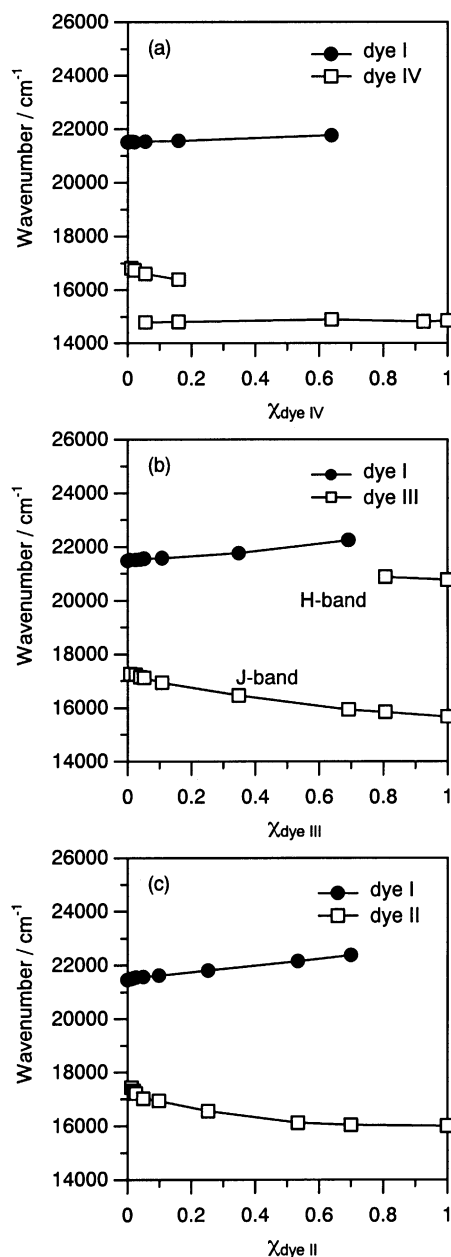


Fig. 3. Dependence of the peak position of the J-band on the mole fraction of dye IV (a), dye III (b), dye II (c).

paper [13]. The J-bands of dyes II and III appear around 625 and 630 nm, respectively, in addition to the J-band of dye I at about 465 nm. Variations of the peak positions of the J-bands with  $\chi_{\text{dye III}}$  or  $\chi_{\text{dye II}}$  are given as a reference in Fig. 3b and c, respectively. The J-bands of dyes I–III tend to be blue-shifted on decreasing the concentration of corresponding dyes.

The fluorescence spectra of the dye I + dye IV assembly are shown in Fig. 4. The excitation wavelength is 410 nm where only dye I aggregate is excited. In Fig. 4, we can see strong resonance fluorescence of the dye I aggregate at 470 nm in the absence of dye IV ( $\chi_{\text{dye IV}} = 0$ ). How-

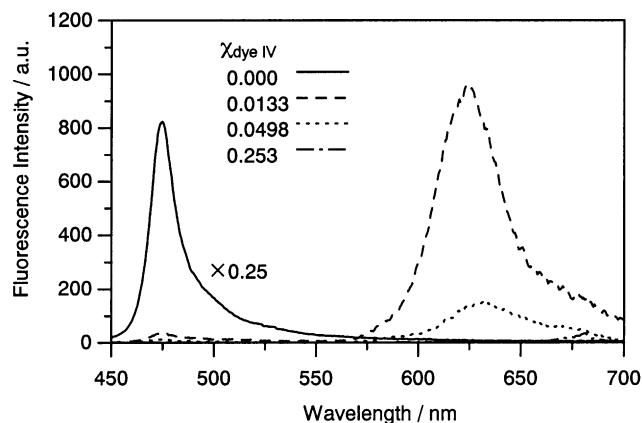


Fig. 4. Fluorescence spectra of the dye I + dye IV alternate assemblies with various mole fractions of dye IV under the excitation with 410 nm light.

ever, resonance fluorescence of the dye I aggregate is almost completely quenched and that of the dye IV aggregate (620–680 nm) is sensitized in return when small amount of dye IV is mixed in the alternate assembly. These observations demonstrate efficient energy transfer from the donor aggregate (dye I) to the acceptor aggregate (dye IV). Similar observations in the dye I + dye II and the dye I + dye III assemblies have been reported [13]. In order to treat the fluorescence quenching quantitatively, the normalized fluorescence intensity has been introduced by the spectral area of resonance fluorescence divided by the absorbance at the excitation wavelength. Fig. 5a shows the plots of the normalized fluorescence intensity of the donor aggregate and the acceptor aggregate as functions of  $\chi_{\text{dye IV}}$ . It is clear in this figure that the donor fluorescence is rapidly quenched and the acceptor fluorescence is sensitized in return by excitation energy transfer. However, due to relatively large errors, an estimation of the maximum value of the acceptor fluorescence is rather difficult. The normalized intensities of the donor and the acceptor aggregates in the dye I + dye III and the dye I + dye II assemblies are also given in Fig. 5b and c, both of which demonstrate efficient energy transfer from the donor aggregate (dye I) to the acceptor aggregate (dyes III, II).

## 4. Discussion

### 4.1. Stern–Volmer analysis of energy transfer

In the previous papers [15,16], we have classified the structure of the mixed J-aggregate into four types according to their spectral properties: separate type (S-aggregate), homogeneous aggregate of amalgamation type (HA-aggregate), homogeneous aggregate of persistence type (HP-aggregate), mosaic type (M-aggregate).

In this study, we have observed that the mixed J-aggregates, dye I + dye II, dye I + dye III, dye I + dye IV are

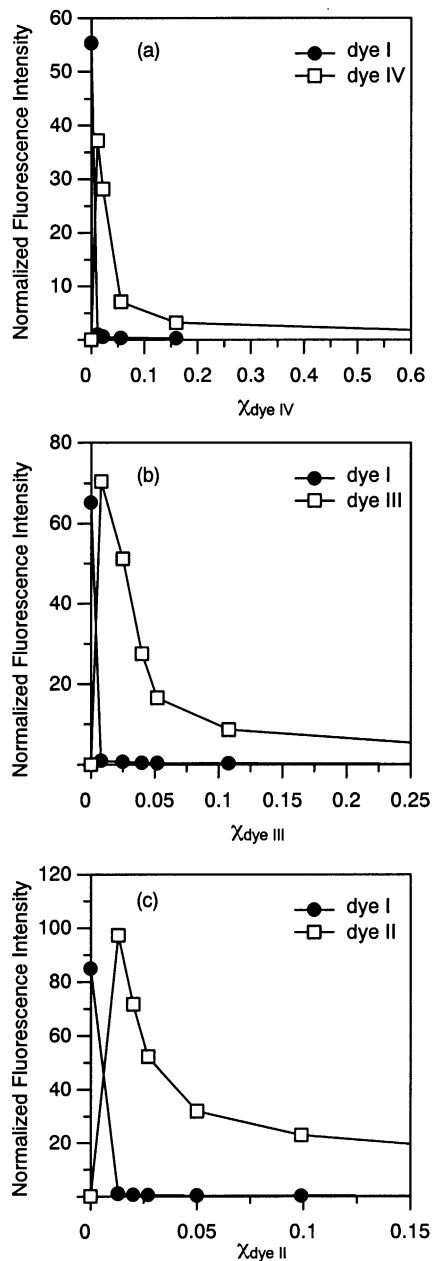


Fig. 5. Plots of the normalized fluorescence intensity of the donor (dye I) aggregate and the acceptor aggregate against the mole fraction of dye IV (a), dye III (b), dye II (c).

characterized by the two J-bands in absorption spectra whose peak positions tend to be blue-shifted with decreasing mole fraction of the corresponding dyes. Therefore, they may be called a partitioning type (P-aggregate) which belongs in general to the M-aggregate as two kinds of dyes seem to be mixed like a mosaic pattern but partitioning of the donor J-aggregate by the acceptor J-aggregate and vice versa are evident. A schematic structure of the P-aggregate has been given in the Fig. 13 of [13]. This is somewhat similar to the ‘statistical dilution’ of the J-aggregate proposed by Lanzafame et al. [17].

It is obvious that excitation energy transfer depends on the structure of the mixed J-aggregate. In the case of the P-aggregate, the donor aggregate and the acceptor aggregate are not isolated but mixed each other. Therefore, the molecular exciton created inside the donor aggregate could transfer excitation energy to the acceptor aggregate (fluorescence quenching and sensitization). To describe excitation energy transfer in the mixed J-aggregate, we have employed the Stern–Volmer kinetics as an approximation [18,19].

$$\frac{I_0}{I} = 1 + K[A] \quad (1)$$

where  $I_0$  and  $I$  are the normalized fluorescence intensity of the donor aggregate in the absence and the presence of the acceptor aggregate,  $[A]$  is surface density of the acceptor molecules ( $\text{molecules nm}^{-2}$ ),  $K$  denotes a Stern–Volmer constant ( $\text{nm}^2 \text{molecules}^{-1}$ ), from which one can estimate the rate constant of energy transfer  $k_{\text{ET}}$  ( $\text{nm}^2 \text{molecules}^{-1} \text{s}^{-1}$ ) by

$$K = k_{\text{ET}}\tau_{\text{D}} \quad (2)$$

where  $\tau_{\text{D}}$  (s) is the fluorescence lifetime of the donor aggregate in the absence of the acceptor. Since dye I aggregate is a common donor in this study, the fluorescence lifetime of pure dye I aggregate,  $\tau_{\text{D}} = 120 \pm 10$  ps, has been used [13].

Fig. 6 summarizes the Stern–Volmer plots for the dye I + dye IV assembly, together with those of the dye I + dye II and the dye I + dye III assemblies as reference. It should be noted that these plots cover only a small  $\chi$ -region where the concentration of the acceptor is fairly low ( $\chi_{\text{dye II}} = 0\text{--}0.14$ ,  $\chi_{\text{dye III}} = 0\text{--}0.15$ ,  $\chi_{\text{dye IV}} = 0\text{--}0.25$ ). Such limitations are unavoidable because of too weak intensity of the donor fluorescence at high acceptor concentration. Although experimental data points are scattered, they are approximately fitted to the straight line for each dye assembly. The slopes obtained from least square fitting are summarized in Table 1, together with the rate constant  $k_{\text{ET}}$ . It is noticed in Table 1 that the Stern–Volmer constants are in the order of  $10^3 \text{ nm}^2 \text{molecules}^{-1}$  and, thus,  $k_{\text{ET}}$  are in the order of  $10^{13} \text{ nm}^2 \text{molecules}^{-1} \text{s}^{-1}$ . As a result, the rate of energy transfer  $k_{\text{ET}}[A]$  is in the order of  $10^{12} \text{ s}^{-1}$ . This value is in the same order as those reported by Kobayashi for energy transfer rate in the J-aggregate of pseudoisocyanine (Pic) [20].

We have hitherto studied luminescence and excitation energy transfer in the LB films incorporating the donor J-aggregate and acceptor molecules either in the monomeric state or in the aggregated state [19,21]. In the LB films incorporating the J-aggregate of *N,N'*-dioctadecyl-oxacyanine perchlorate (S9: donor) doped with the sulfur homologue, *N,N'*-dioctadecyl-thiacyanine perchlorate (S11: acceptor) in the monomeric state, we have obtained a Stern–Volmer constant of  $1720 \text{ nm}^2 \text{molecules}^{-1}$  (room temperature) for [S11] of  $10^{-3}\text{--}10^{-1} \text{ molecules nm}^{-2}$  [19], which seems to be in the same order as those given in Table 1. According to

Table 1  
The summary of  $K$ ,  $k_{ET}$  and  $\Delta E$  for the mixed J-aggregates

Cyanine dye	$K$ ( $10^3 \text{ nm}^2 \text{ molecules}^{-1}$ )	$k_{ET}$ ( $10^{13} \text{ nm}^2 \text{ molecules}^{-1} \text{ s}^{-1}$ )	$\Delta E$ ( $\text{cm}^{-1}$ )
dye I + dye II	$2.5 \pm 0.3$	$2.1 \pm 0.3$	5490
dye I + dye III	$1.7 \pm 0.2$	$1.4 \pm 0.2$	5740
dye I + dye IV	$1.1 \pm 0.1$	$0.9 \pm 0.1$	6600

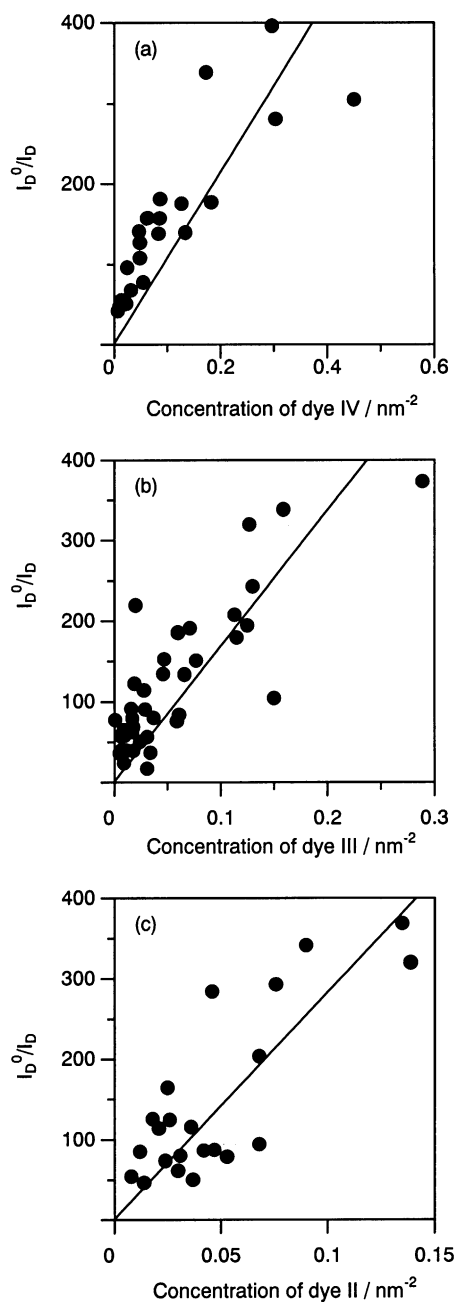


Fig. 6. Stern–Volmer plots of the normalized fluorescence intensity of the donor aggregate in (a) the dye I + dye IV, (b) the dye I + dye III and (c) the dye I + dye II alternate assemblies.

Möbius and Kuhn [22], Eq. (1) has been rewritten in the form

$$\frac{I_0}{I} = 1 + \frac{N_{1/2}}{N} \quad (3)$$

where  $N$  is the number of donor molecules per acceptor molecule in the S9(J) + S11 LB film and  $N_{1/2}$  the value of  $N$  for  $I = I_0/2$ . By assuming the surface area per S9 molecule,  $\sigma_D = 0.6 \text{ nm}^2$  ( $1.2 \text{ nm} \times 0.5 \text{ nm}$ ) [23] and  $K = 1720 \text{ nm}^2 \text{ molecules}^{-1}$ ,  $N_{1/2} = 2900$  has been obtained [19]. This means that molecular exciton can visit about 3000 donor molecules, occasionally reaching the vicinity of a S11 molecule. Provided that the surface area per dye I molecule in the alternate assembly is almost the same as S9 molecule in the LB film ( $1.2 \text{ nm} \times 0.5 \text{ nm}$ ),  $N_{1/2}$  amounts to about 1800 (dye I + dye IV), 2800 (dye I + dye III), 4200 (dye I + dye II), respectively. These estimations are not unreasonable if we note that the P-aggregate is reduced to the combination of the donor J-aggregate and the acceptor molecules in the monomeric state in the low acceptor concentration limit. In this sense, efficient energy transfer is possible in the P-aggregate.

$k_{ET}$  increases in the order (dye I + dye IV) < (dye I + dye III) < (dye I + dye II). The energy gap law in excitation energy transfer has been discussed by Yomosa [24]. Parameter  $k_{ET}$  is dependent of the energy gap  $\Delta E$  between the energy donor and the acceptor. In the conventional exponential energy gap law [25,26],  $k_{ET}$  is proportional to

$$k_{ET} = (\text{const.}) \exp(-\Delta E) \quad (4)$$

The  $\Delta E$ -values estimated from the peak position of the J-band are included in Table 1. The energy gap increasing in the order (dye I + dye II) < (dye I + dye III) < (dye I + dye IV) would bring about the decrease in  $k_{ET}$  by Eq. (4) (Fig. 7).

#### 4.2. Exciton migration in the mixed J-aggregate

To account for efficient energy transfer in the J-aggregate, several theoretical approaches based on certain new concepts have been proposed; coherent exciton domain [19,22], soliton propagation [27,28], excitonic fast and nearly lossless energy transfer [29,30]. According to Kuhn and co-workers, we have assumed that excitation energy transfer occurs by exciton migration and trapping inside the mixed J-aggregate

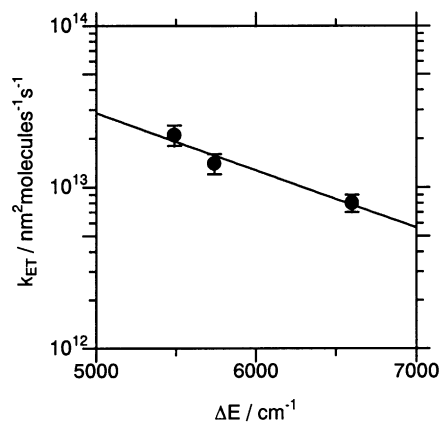


Fig. 7. Exponential energy gap law between  $k_{ET}$  and  $\Delta E$  for dye I + dye II, dye I + dye III and dye I + dye IV alternate assemblies.

[19,22]. Then, the ratio ( $I_0/I$ ) is recast into the following form [22,31]:

$$\frac{I_0}{I} = 1 + \tau_D \frac{\langle H \rangle [P]}{\langle t \rangle [B]} \nu \theta \quad (5)$$

where  $[B]$ ,  $[P]$  denote surface densities of the donor molecules and the acceptor molecules, respectively. Parameters  $\nu$  and  $\theta$  are coherent size of the donor aggregate and trapping efficiency of exciton by the acceptor, respectively, and  $\langle t \rangle$  and  $\langle H \rangle$  denote average time and average number of exciton hopping before trapping. According to Kuhn and Kuhn [32,33],  $\langle H \rangle / \langle t \rangle$  is related to the 'velocity of exciton migration'  $v_m$  and the average distance  $h$  of the donor molecules in the J-aggregate.

$$\frac{\langle H \rangle}{\langle t \rangle} = \frac{v_m}{h} \quad (6)$$

Eq. (1) is related to Eqs. (3) and (5) by the following way:

$$N = \frac{[B]}{[P]} \quad (7)$$

and

$$N_{1/2} = \tau_D \frac{\langle H \rangle}{\langle t \rangle} \nu \theta \quad (8)$$

Therefore,  $k_{ET}$  in Eq. (1) is equal to

$$k_{ET} = \frac{\langle H \rangle}{\langle t \rangle} \frac{1}{[B]} \nu \theta = v_m \frac{1}{h} h^2 \nu \theta = v_m \delta \theta \quad (9)$$

$$\delta = h \nu \quad (10)$$

Here,  $\delta$  denotes a coherent length of donor exciton.

We have attempted a qualitative estimation of the coherent size of the donor aggregate from the spectral absorption linewidth [3,34].

$$\frac{\omega_{1/2}(M)}{\omega_{1/2}(J)} = \sqrt{\nu} \quad (11)$$

Table 2

Coherent size  $\nu$  of donor (dye I) aggregate estimated from the J-band width (Eq. (11))<sup>a</sup>

dye I + dye II		dye I + dye IV	
$\chi_{\text{dye II}}$	$\nu$	$\chi_{\text{dye IV}}$	$\nu$
0.000	13.8	0.000	14.6
0.013	12.0	0.012	12.6
0.050	10.2	0.056	11.0
0.253	4.2	0.639	4.2
0.700	1.9		

<sup>a</sup> The width of dye I monomer band in aqueous solution  $\omega_{1/2}(M) = 1950 \text{ cm}^{-1}$  was used.

where  $\omega_{1/2}(M)$  and  $\omega_{1/2}(J)$  are the linewidth of monomer band and J-band of dye molecules. The  $\nu$  of dye I aggregate in the dye I + dye II and the dye I + dye IV assemblies are summarized in Table 2. Considering the limits and errors of Eq. (11), together with the former work of Kuhn [32], we may assume  $\nu$  of about 10.

By using  $\nu = 10$ ,  $h = 1.2 \text{ nm}$  [23], and  $\theta = 0.1-1$ , as well as  $k_{ET} = 10^{13} \text{ nm}^2 \text{ molecules}^{-1} \text{ s}^{-1}$  from Table 1, a crude estimation of  $v_m = (0.8-8) \times 10^{12} \text{ nm s}^{-1}$  is obtained. This value is not so different from  $v_m = 2 \times 10^{12} \text{ nm s}^{-1}$  of Kuhn and Kuhn [32,33]. These considerations would suggest that the coherent exciton extending over about 10 donor molecules (dye I) (coherent size  $\sim 10^1$ ) could move over 1800–4200 molecules on an average (incoherent size  $\sim 10^3$ ), before excitation energy transfer to the acceptor aggregate (dyes II–IV). A possibility of the hierarchical structure of the J-aggregate: coherent size, incoherent size, physical size, has been raised by Möbius and Kuhn [22], Yonezawa [3,35], Sundström et al. [10], and recently, thoroughly discussed by Kobayashi and co-workers [20,36,37].

Finally, we should mention that  $v_m h$  of  $(1-10) \times 10^4 \text{ cm}^2 \text{ s}^{-1}$  is not so different from a typical value of the diffusion coefficient  $D$  of molecular organic solids [38]. Exponential energy gap law (Eq. (4)) reflecting the dependence of exciton trapping efficiency  $\theta$  on the energy gap  $\Delta E$  is not inconsistent with excitation energy transfer by exciton migration and trapping in the mixed J-aggregate.

## 5. Conclusions

In the present paper, we have reported excitation energy transfer in the mixed J-aggregate of two kinds of cyanine dyes incorporated in layer-by-layer alternate assemblies. For the combinations dye I + dye II, dye I + dye III, dye I + dye IV, the mixed J-aggregate is formed in the alternate assembly, whose structure is classified into partitioning type. The fluorescence spectra of these assemblies show efficient energy transfer from the donor aggregate (dye I) to the acceptor aggregate (dyes II–IV). The rate constant of energy transfer  $k_{ET}$  determined by Stern–Volmer analysis is in the order of  $1 \times 10^{13} \text{ nm}^2 \text{ molecules}^{-1} \text{ s}^{-1}$ . The difference of

$k_{ET}$  between various combinations of cyanine dyes can be understood in terms of the trapping efficiency  $\theta$ . As  $\theta$  is an exponentially decreasing function of the energy gap  $\Delta E$  between the donor aggregate and the acceptor aggregate,  $k_{ET}$  decreases with increasing  $\Delta E$ . It is concluded that exciton migration inside the donor aggregate considerably enhances energy transfer in the P-aggregate.

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