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Citation: *The Journal of Chemical Physics* **126**, 194705 (2007); doi: 10.1063/1.2730815

View online: <http://dx.doi.org/10.1063/1.2730815>

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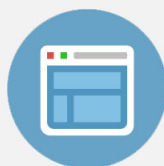
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# Exciton energy transfer between optically forbidden states of molecular aggregates

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(Received 18 July 2006; accepted 20 March 2007; published online 17 May 2007)

3-ethyl-2-[3-(3-ethyl-2(3*H*)-benzoxazolylidene)-1-propenyl]benzoxazolium iodide (dye I) and pseudoisocyanine bromide are employed to form *H* aggregates as donors and *J* aggregates as acceptors. The energy of an *H* band of the *H* aggregates is higher than that of a *J* band of the *J* aggregates. It was confirmed that excitation of the *H* band does not emit fluorescence by comparison of excitation spectra of dye I *H* aggregates with that of dye I monomer. Absorption, fluorescence, and excitation spectra of spin-coated films of *H* aggregates mixed with various quantities of *J* aggregates have been observed. Excitation spectra probed at the *J* band are found to have a component of the *H* band. Fluorescence spectra originated from excitation of the *H* band are extracted and qualitatively analyzed. It is confirmed that excitation of the *H* band causes to emit fluorescence of a *J* band of the *J* aggregates. These phenomena show that exciton energy can transfer from the lowest energy in electronic states of the *H* aggregate, which state is optically forbidden, to electronic state of the *J* aggregate. © 2007 American Institute of Physics.

[DOI: [10.1063/1.2730815](https://doi.org/10.1063/1.2730815)]

## I. INTRODUCTION

Molecular dyes are known to form a variety of aggregates such as dimers, *J* aggregates, *H* aggregates, and so on. When molecular dyes form *J* and *H* aggregates consisting of *N* molecules, molecular aggregates have *N* eigenelectronic states that spread into an energy region  $|4V|$  with a center at an electronic state of the monomer dye. Here, *V* is the transfer interaction energy for nearest-neighbor aggregated molecules. The lowest and the highest energy states in *J* and *H* aggregates, respectively, occupy more than 80% of total oscillator strength. The rest of the oscillator strength almost goes to the third and the fifth lowest and highest states in *J* and *H* aggregates, respectively. The corresponding spectra to the transition from the ground state to the coherently superposed states in *J* and *H* aggregates due to the optically allowed state are called *J* and *H* bands, respectively. Total transition dipole moments of the other odd number states are not exactly zero but negligibly small and that of even number states are exactly zero. Electronic states of *J* and *H* aggregates except those exhibiting the *J* and *H* bands are practically optically forbidden states.

Exciton energy transfer between optically allowed states

in molecules and molecular aggregates has been studied extensively.<sup>1-3</sup> When donors and acceptors locate close to each other with a mutual distance not much larger than the size of delocalized electron distribution, exciton energy transfer occurs in nonradiative process mediated by a virtual photon. This process is explained in terms of the Foerster mechanism.<sup>4,5</sup> According to the Foerster mechanism, exciton energy transfer ratio is proportional to the overlapped area between the fluorescence spectrum of a donor and the absorption spectrum of an acceptor. On the other hand, it has been reported in Ref. 6 that the exciton energy transfer takes place when a density of states (DOS) of donor aggregates overlaps with that of acceptor aggregates. This indicates that the exciton energy transfer between optically forbidden states is taking place in the system.

The purpose of the present paper is to confirm that the exciton energy transfers between optically forbidden states. For this purpose, *H* and *J* aggregates are employed for donors and acceptors, respectively. *H* and *J* aggregates have optically forbidden states at the lower and higher energy sides of DOS, respectively. When *H* band is excited, *H* aggregates do not emit fluorescence since exciton energy at *H*

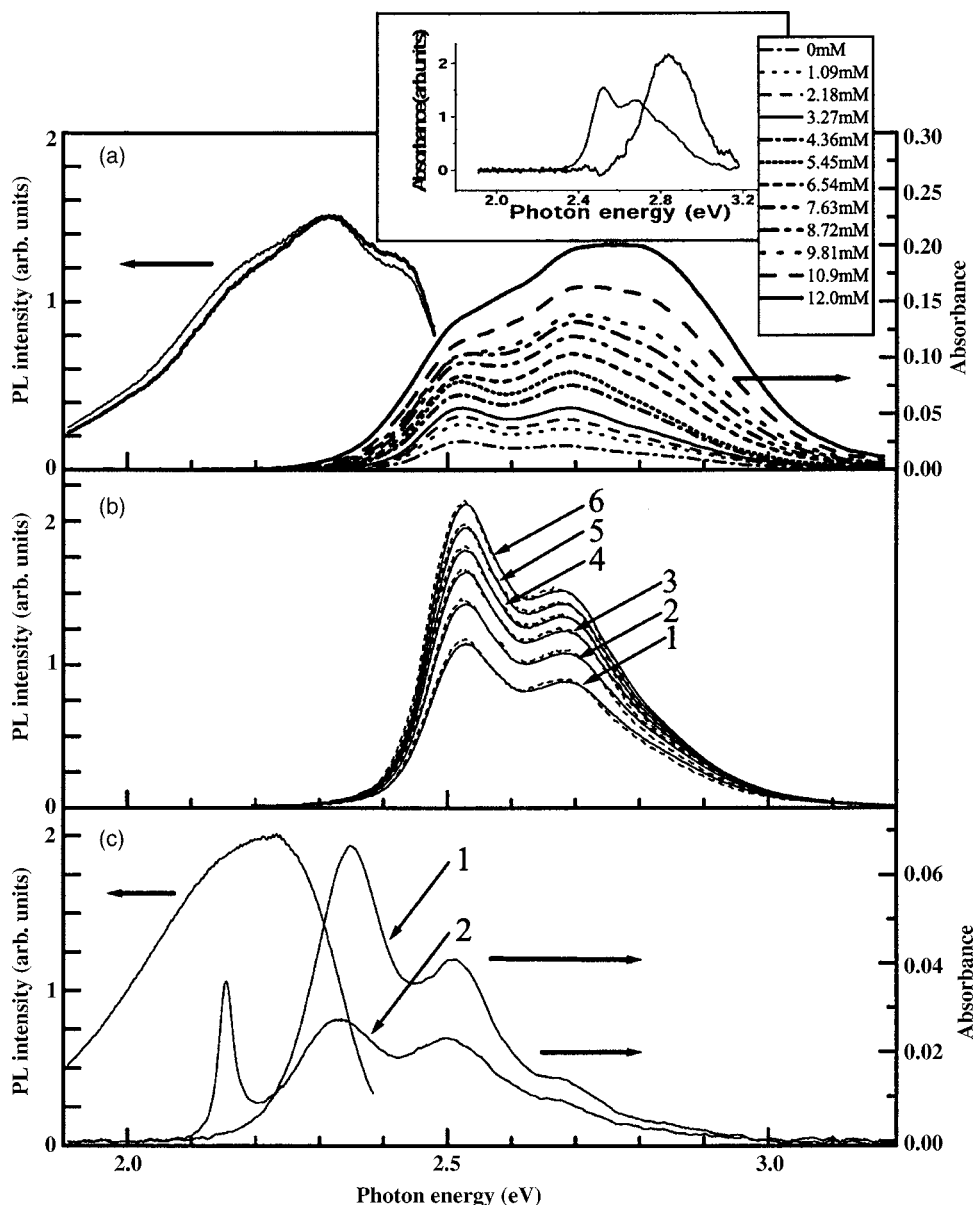


FIG. 1. (a) Absorption spectra of spin-coated film of various molar fractions of dye I. Fluorescence spectra of the film of the largest (thin line) and the lowest (thick line) molar fractions of dye I. The result of the singular value decomposition of successive absorption spectra is shown in the inset. (b) Excitation spectra of the film of the largest (solid line) and the lowest (broken line) molar fractions of dye I probed with various photon energies: (1) 2.10, (2) 2.14, (3) 2.17, (4) 2.21, (5) 2.25, and (6) 2.29 eV. (c) Fluorescence and absorption spectra of spin-coated film of (1) PIC monomer and (2) PIC *J* aggregates.

band rapidly relaxes to the lowest state of *H* aggregates that is optically forbidden. If *H* aggregates locate close to *J* aggregates with a mutual distance not larger than its physical size and if DOS of *H* aggregates at the low energy side overlaps with DOS of *J* aggregates at the high energy side, excited *H* band would cause *J* aggregates to emit fluorescence at the *J* band through exciton energy transfer between optically forbidden states.

## II. EXPERIMENT

Two kinds of cyanine dye and polyvinylalcohol (PVA) are used for film-forming materials. One cyanine dye is 3-ethyl-2-[3-(3-ethyl-2(3*H*)-benzoxazolylidene)-1-propenyl]benzoxazolium iodide (dye I) used as a donor, and the other cyanine dye is pseudoisocyanine bromide (PIC) used as an acceptor. Dye I (NK-85) and PIC were purchased from Hayashibara Biochemical Laboratories, Inc. (Okayama, Japan). To prepare a donor sample, 10 mg PVA was dissolved in 2 ml distilled water

and 1 ml methanol at 90 °C. Dye I's with about  $10^{-3}$  and  $10^{-5}$  mol were added into the solution for aggregated sample and for monomer sample, respectively. For the combination of donor and acceptor, various moles of PIC up to  $10^{-2}$  mol were added to the aggregated sample of dye I. PICs of 12 and 3 mg were added with 10 mg PVA into 2 ml distilled water for *J* aggregate and monomer of PIC sample, respectively. All solutions were spin coated on a fused-quartz microscope-cover glass at 3000 rpm. Absorption spectra were measured with Shimadzu spectrophotometer model UV-3100, and fluorescence and excitation spectra with Hitachi fluorometer model F-4500.

## III. RESULTS AND DISCUSSION

Absorption spectra with various molar fractions of dye I are shown in Fig. 1(a). The absorption spectrum of the smallest molar fractions of dye I agrees with that of dye I monomer. A zero phonon line of electronic state of dye I monomer is at 2.53 eV. With an increase of the molar fractions of dye

I, absorption spectra of the higher energy part around 2.85 eV grow. In order to extract the growing absorption peak, singular value decomposition method is applied to successive absorption spectra in Fig. 1(a). Two spectral components are obtained and are shown in an inset of Fig. 1(a). One is an absorption spectrum for dye I monomer, another is that for an extracted absorption peak with a maximum at 2.85 eV. Because the extracted absorption peak is blue-shifted, the extracted peak is expected to be an *H* band. Fluorescence spectra of the largest and the smallest molar fractions of dye I, with excitation energy of 2.95 eV, are shown in Fig. 1(a). Both fluorescence spectra have maxima at 2.30 eV and show good agreement with each other. In general, excitation of an *H* band does not contribute to emit fluorescence. In order to investigate whether excitation of the extracted peak emits fluorescence or not, excitation spectra of the largest and the smallest molar fractions of dye I probed by fluorescence with various energies have been observed, as shown in Fig. 1(b). Excitation spectra of the smallest molar fraction of dye I, which correspond to that of dye I monomer, are normalized to have the same area with that of the largest molar fraction one. These spectra substantially coincide with each other. Excitation spectra of the largest molar fractions of dye I do not include the extracted peak at 2.85 eV. Thus, it is concluded that excitation of the extracted peak at 2.85 eV does not lead to the emission of fluorescence. Therefore, the extracted peak is concluded to be an *H* band of aggregated dye I. The result shows that DOS of *H*-aggregated dye I spreads from *H* band at 2.85–2.53 eV.

Absorption spectra of PIC monomer and its *J* aggregate are shown in Fig. 1(c). A zero phonon line of an electronic state of PIC monomer is at 2.35 eV and *J* band appears at 2.15 eV. It is concluded that DOS of *J*-aggregated PIC spreads from 2.15 eV (*J* band) to 2.68 eV. Therefore, DOS of *H*-aggregated dye I overlaps with that of *J*-aggregated PIC in a region between 2.53 and 2.68 eV. It is expected that excitation of *H* band causes to emit fluorescence of *J* band through exciton energy transfer between DOSs of both aggregates.

In order to study the exciton energy transfer between optically forbidden states, spectroscopy for *H* aggregate spin-coated film mixed with various molar fractions of *J* aggregates has been performed. Absorption spectra of spin-coated thin film made of the largest molar fractions of dye I mixed with various molar fractions of PIC (mixed sample) are shown in Fig. 2(a). It is clearly seen that absorbance of *J* band originated from *J*-aggregated PIC increases with the molar fraction of PIC above 10 mM. Fluorescence excitation spectra of the mixed sample probed at fluorescence peak of *J* band (2.13 eV) have been measured, as shown in Fig. 2(b). Excitation spectra in Fig. 2(b) are consisted of three components; the *H* band, dye I monomer, and PIC monomer. After these spectra were analyzed by multiple regression method, partial regression coefficients for each state are obtained. It is obvious that the excitation of the *H* band results in emitting fluorescence of *J* band. Therefore, it is qualitatively concluded that the exciton energy transfers from optically forbidden state of the *H* aggregate to electronic states of the *J* aggregate.

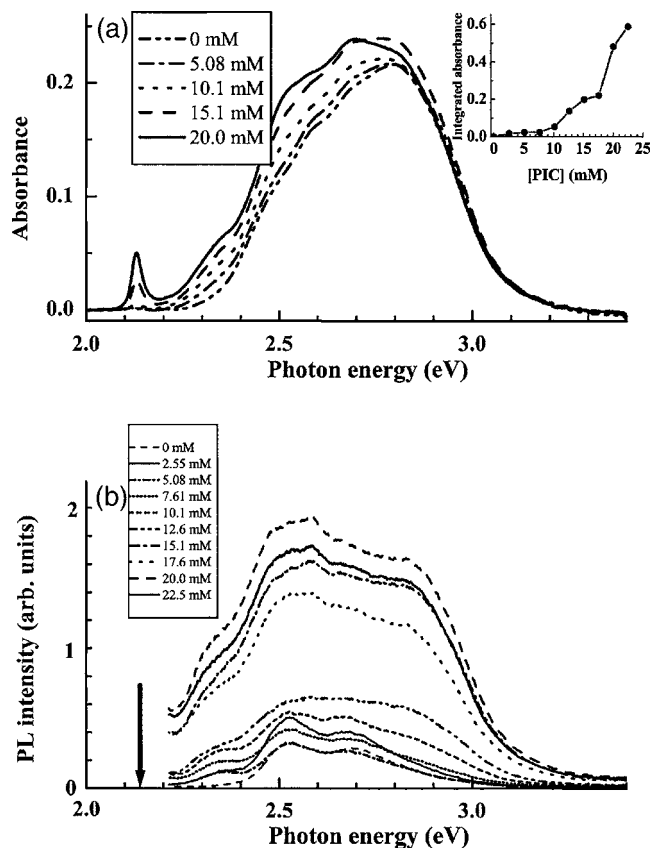


FIG. 2. Absorption spectra of spin-coated film of the largest molar fractions of dye I mixed with various molar fractions of PIC. The inset shows integrated absorbance (IA) over the spectral region between 2.10 and 2.17 eV as a function of PIC molar fraction. (b) Excitation spectra of the same sample probed at 2.13 eV.

In order to confirm the exciton energy transfer quantitatively, fluorescence spectra of mixed sample that is excited by light with 2.95 eV were observed, as shown in Fig. 3(a). Excitation energy at 2.95 eV is employed to excite the *H* band most since fluorescence of *J* band is caused by the excitation of three states, *H* band, dye I monomer, and PIC monomer, and a fraction of contributions from these states depends on molar fraction of PIC, as indicated in Fig. 2(b).

Fluorescence intensity at 2.13 eV shown in Fig. 3(a) increases with an increase of the PIC concentration in parallel with the increase of the absorbance of *J* band shown in Fig. 2(a). Thus, fluorescence at 2.13 eV is assigned to *J* band. Therefore, these spectra support qualitatively that excitation of the *H* band induces emission from the *J* band. To discuss the fluorescence from *J* band caused by the excitation of *H* band quantitatively, contribution of fluorescence spectra originated from the *H* band will be extracted from fluorescence spectra in Fig. 3(a). For this purpose, fluorescence spectra excited at 2.53 eV and excitation spectra probed by light with 2.25 eV were observed, as shown in Figs. 3(b) and 3(c), respectively. Probe energy of 2.25 eV is employed because emission of fluorescence from *J* band is negligible at 2.25 eV and excitation energy of 2.53 eV is employed so as not to excite the *H* band as much as possible. Contribution from the *H* band to the excitation spectra is less than 0.1%. It is confirmed that the excitation of *H* band does not lead to



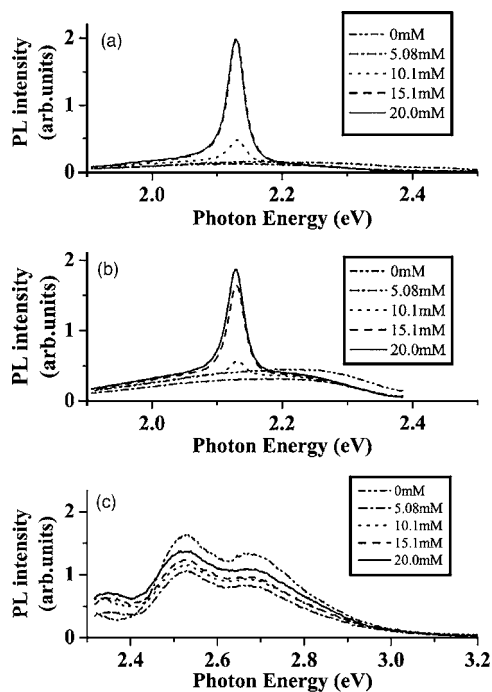


FIG. 3. (a) Fluorescence spectra of mixed sample at each molar fraction of PIC dye. Excitation energy is 2.95 eV. (b) Fluorescence spectra of mixed sample at each molar fraction of PIC dye. Excitation energy is 2.53 eV. (c) Excitation spectra of mixed sample at each molar fraction of PIC dye probed by fluorescence at 2.25 eV.

emission of fluorescence at 2.25 eV. This evidence supports the neglect of contribution of *H* band to fluorescence spectra. Fluorescence spectra shown in Fig. 3(b) are composed of three fluorescence spectra; *J* band, dye I monomer, and PIC monomer. Compared to fluorescence spectra shown in Fig. 3(a), a distinguished feature of fluorescence spectra shown in Fig. 3(b) consists of fluorescence spectra originated from dye I monomer and PIC monomer. Fluorescence of *J* band is considered to be originated partially from *J* aggregates that are excited by exciton energy transfer between optically allowed states, which is consistent with the Foerster model. In order to subtract the contribution of excitation of dye I monomer and PIC monomer from fluorescence spectra shown in Fig. 3(a), fluorescence spectra shown in Fig. 3(b), which is considered to be free from contribution of excitation of the *H* band, are used. After fluorescence spectra in Fig. 3(b) are normalized to have the same spectral area in the energy range larger than 2.20 eV with those in Fig. 3(a), these spectra are subtracted from fluorescence spectra shown in Fig. 3(a). The result is shown in Fig. 4. The area of fluorescence spectra in Fig. 4 is shown in the inset of Fig. 4. It is obvious that fluorescence of *J* band caused only by the excitation of the *H* band increases in proportion to absorbance of *J* band. This confirms again that exciton energy transfer takes place between optically forbidden states of *H* aggregates to *J* aggregates.

#### IV. SUMMARY

The exciton energy transfer between optically forbidden states has been examined. Dye I aggregates are employed as

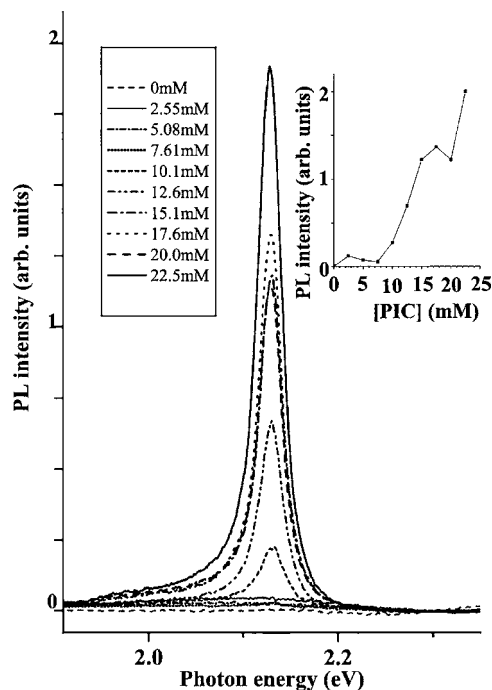


FIG. 4. Extracted fluorescence spectra originated from excitation of the *H* band. The inset indicates the area of the spectra as a function of molar fractions of PIC dye.

donors, which have the *H* band. *J* aggregates of PIC are employed as acceptors, which have the *J* band. It is concluded that the *H* band does not emit fluorescence and it contributes to the fluorescence from *J* band in mixed sample. This phenomenon is not explained by Foerster mechanism because there is no overlap between fluorescence spectrum of the *H* band and absorption spectrum of the *J* band. Consequently, these evidences show that the exciton energy can transfer between optically forbidden states when DOSs of donor aggregates and acceptor aggregates overlap each other. Separation dependence between *H* aggregate layer and *J*-aggregate one in Langmuir-Blodgett film would give us more information about the mechanism of exciton energy transfer discussed here.

#### ACKNOWLEDGMENTS

The authors would like to express thanks to Kawaguchi Optical Industries for the preparation of the fiber tips. The work is partly supported by Research for the Future of Japan Society for the Promotion of Science (ISPS-RFTF-97P-00101).

- <sup>1</sup>T. Kobayashi, *J-Aggregates* (World Scientific, Singapore, 1996).
- <sup>2</sup>A. A. Muentert, D. V. Brumbaugh, J. Apolito, L. A. Horn, F. C. Spano, and S. Mukamel, *J. Phys. Chem.* **96**, 2783 (1992).
- <sup>3</sup>T. Tani, T. Suzumoto, K. Kemnitz, and K. Yoshihara, *J. Phys. Chem.* **96**, 2778 (1992).
- <sup>4</sup>J. T. M. Kennis, A. M. Streltsov, H. Permentier, T. J. Aartsma, and J. Amesz, *J. Phys. Chem. B* **101**, 8369 (1997).
- <sup>5</sup>R. Monshouwer, I. Ortiz de Zarate, F. van Mourik, and R. van Grondelle, *Chem. Phys. Lett.* **246**, 341 (1995).
- <sup>6</sup>K. Mukai, S. Abe, and H. Sumi, *J. Lumin.* **87-89**, 818 (2000).