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Saturation of Förster resonance energy transfer between two optically nonlinear cyanine dyes of small Stokes shift energies in polymer thin films

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We report the saturation of Förster resonance energy-transfer (FRET) between two optically nonlinear cyanine dyes in polymer thin films, where the energy donor and acceptor have small Stokes shift energies. Our combinations of dyes show the energy transfer rate of inversely proportional to the square of the distance between the energy donor and acceptor dyes. This result quite differs from the normal FRET results. From speculation based on the number of excited acceptor dye, our FRETs are saturated even at such a long distance approximately 10 nm between the energy donor and acceptor because of the optical excitation of acceptor dyes in addition to FRET process. © *2011 American Institute of Physics*. [doi:10.1063/1.3653228]

I. INTRODUCTION

Ultrafast all-optical switches based on optical nonlinearity will likely become crucial components of future generation high-speed optical communication networks.[1,2] For example, in semiconductor nanostructures, the optical nonlinearity of excitons plays an important role for their application. As another example, excitons in organic nonlinear optical materials have the principal advantages of ultrafast and efficient optical response, high processability, and high ease of preparing large-area films at low cost. Femtosecond optical dynamics has been investigated in various dyes.[3–8] In particular, the ultrafast response and high optical nonlinearity of excitons in cyanine dyes are attractive features for applications of ultrafast optical devices.[9]

For such devices, an increase in the exciton population decay rate that is essentially determined by the exciton oscillator strength has been required to eliminate the so-called pattern effects that are the change in the signal intensity and profile due to the superposition of the response by a previous pulse. To achieve ultrafast processing on the order of terabit/second, an additional process for ultrafast relaxation of excitons must occur. One of the approaches to increase the population decay rate is to use Förster-resonance energy-transfer (FRET).[10] Because of the simplicity of measurement and analysis, many experiments on FRET have been performed with material combinations that have large Stokes shift energies.[11,12] In the case of material combinations that have small Stokes shift energies, the applications in ultrafast devices are expected because of the shorter intraband relaxation times. However, since the excitation of only the donor dyes is difficult, the acceptor dyes are also excited, which will induce the saturation of the FRET at high transfer rate. In such cases, it is important to control the FRET rate by controlling the spectral overlap factor and the quantum efficiency of the energy donors. In this study, we investigate FRET dynamics in cyanine dye thin films with various distances R between the energy donor and acceptor dyes by changing the energy donor dyes. The combination with the smaller spectral overlap factor shows the behavior of a larger Förster radius, resulting from the larger energy relaxation rate of the donor dye. We discuss the photoluminescence (PL) characteristics, including the intensity and the decay profiles, in the samples on the basis of the relationship between R and the decay rate of donor dyes.

II. EXPERIMENT

We purchased the cyanine dyes for this study from Hayashibara Biochemical Laboratories, Inc., and we used them without further purification. We used $C_{25}H_{25}IN_2S_2$ (NK-126) and $C_{37}H_{37}N_2BF_4$ (NK-3336) for the energy donor molecules and $C_{47}H_{47}ClN_2O_2S$ (NK-4680) for the energy acceptor molecules. The chemical structures are shown in Fig. 1. Hereafter, we will refer to the NK-126, NK-3336, and NK-4680 molecules as D_1, D_2, and A, respectively. We fabricated the polymer thin films including the dye molecules with a solvent evaporation technique. A polyvinyl alcohol (PVA) was used as a matrix. The PVA is transparent for the absorption and PL regions of the dyes molecules, and the PVA has the excellent gas barrier properties,[13,14] which are important to reduce the photodegradation on the sample preparation and optical measurement. The methanol solution of dye molecules, which we varied from 8 to 200 μl, was cast in an aqueous PVA solution (10 wt%) of 1 ml. Then, the mixed solution of 50 μl was dropped on a glass plate. The solvent was evaporated at 70 °C for 30 min. The film thickness was not controlled and that was approximately 1 mm. The mean distance R between the energy donor and acceptor molecules was controlled by the density of dye molecules in the film. We maintained the ratio of the number of energy donor to acceptor molecules at unity. By measurement of the PL intensity varying the position of the

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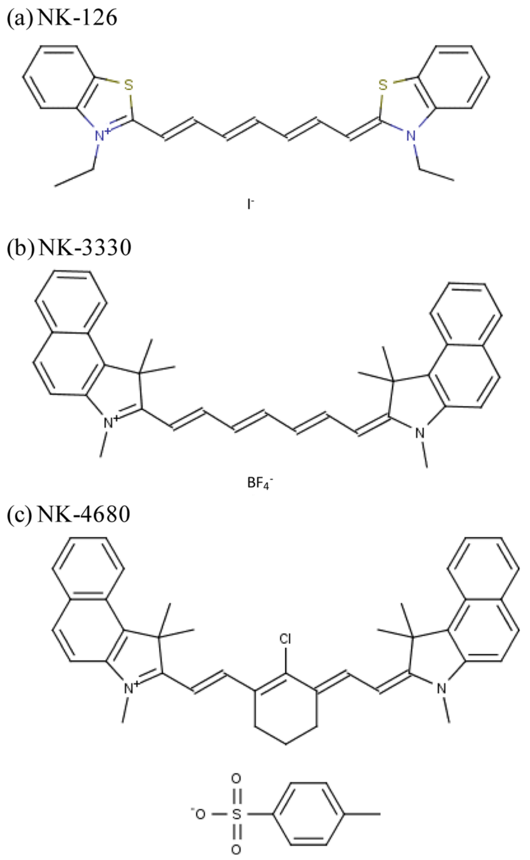

FIG. 1. (Color online) Chemical structures of the molecules.

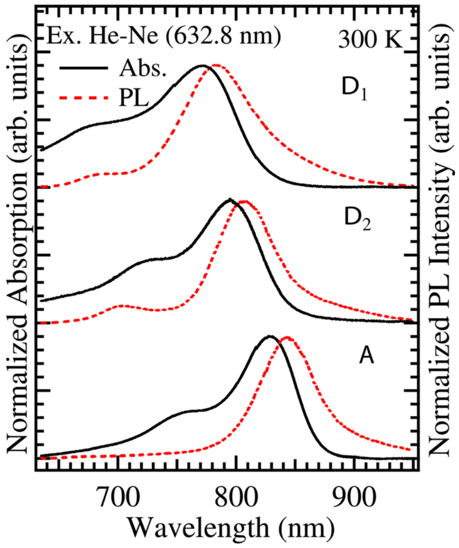

FIG. 2. (Color online) PL and absorption spectra for each dye thin film. All the spectra were normalized by the maximum peak intensity.

laser beam spot, we checked that the distribution of the molecules is almost homogeneous in the films.

The absorption and PL spectra were measured by using a 55-cm single monochromator with a resolution of 0.32 nm. The light source for the absorption spectra was a 100-W halogen lamp, and the excitation light for the PL spectra was the 1.959-eV (632.8-nm) line of a He-Ne laser. The transmitted and emitted lights were detected by using a liquid-nitrogen-cooled charge coupled device. Moreover, the PL decay profiles were measured with Hamamatsu Photonics C5680 streak camera system with a time resolution of 40 ps. In the time-resolved measurement, the excitation source was a mode-locked Ti:sapphire pulse laser delivering about 100-fs pulses with a repetition rate of 80 MHz. We used a 7-cm monochromator to reduce the laser spectral width from 40 to 4.5 meV in order to eliminate the contribution of the excitation light to the PL. When the Fourier limit was kept, the pulse width was consequently extended to approximately 900 fs. The excitation photon energy was 1.675 eV and the excitation density was kept at 0.88 μJ/cm^2.

III. RESULTS AND DISCUSSION

Figure 2 depicts the absorption (solid curves) and PL (dotted curves) spectra of the D_1, D_2, and A thin films. From the PL spectra of D_1 and D_2 and the absorption spectrum of A, we evaluated the spectral overlap factors with the following equation:[10,15]

$$J_n = \int F_{D_n}(\lambda) A_A(\lambda) \lambda^4 d\lambda, \tag{1}$$

where $F_{D_n}(\lambda)$ is the donor PL spectrum and $A_A(\lambda)$ is the acceptor absorption spectrum. The evaluated values of J are $J_1 = 1.38 \times 10^{13}$ and $J_2 = 1.17 \times 10^{13}$ for the $D_1 - A$ and $D_2 - A$ systems, respectively. Although a better overlap between the donor PL and the acceptor absorption is seen for the $D_2 - A$ system, the calculation presents that the $D_1 - A$ system has better overlap. This results from that the spectrum of D_1 is much wider than that of D_2. The ratio of the J_2 to J_1 is 0.845, which means the possibility that the FRET in the $D_1 - A$ occurs at longer R than that in the $D_2 - A$.

Figure 3(a) shows the image map of the normalized PL spectra for various Rs with a step of 1 nm in the $D_1 - A$ samples. It is noted that the abscissa axis is the energy scale. The solid curves indicate the PL spectra of D_1 and A for reference. The PL spectrum of the $D_1 - A$ sample clearly depends on R: The PL intensity of the A dye is superior to that of D_1 one with R less than 10 nm. Moreover, the energy position of the PL peak of the $D_1 - A$ samples decreases as R decreases for $R \leq 10$ nm. The energy peak position shift may originate from the reabsorption and/or FRET between A dyes. In order to clarify the R dependence of the PL intensity ratio, Fig. 3(b) plots the peak intensity ratio of D_1 to A as a function of R. For $R \leq 9$ nm, this ratio is less than unity, showing that the A contribution dominates below 9 nm.

Figures 4(a) and 4(b) plot the same quantities as Figs. 3(a) and 3(b), respectively, for the case of $D_2 - A$ samples. Figure 4(a) shows that the main contribution to the PL peak changes from D_2 to A for the $R \leq 14$ nm. Moreover, the energy position of the PL peak of the $D_2 - A$ samples decreases as R decreases $R \leq 14$ nm. Figure 4(b) shows that the peak intensity ratio of D_2 to A is less than unity for $R \leq 14$ nm, showing that the A contribution dominates below 14 nm. This result indicates that the combination of D_2 and A results in a longer distance FRET (14 nm) than that of D_1 and A (9 nm). However, it seems to be inconsistent with the relation of the spectral overlap factors.

In order to investigate the origin of this inconsistency and to determine the energy transfer rate k_{ET} from D to A molecules by the PL time evolution, we measured the R dependence of PL decay profiles in the two systems. We firstly show the time-resolved PL spectra in Fig. 5. The upper and lower spectra depict the emission from the $D_1 - A$ and $D_2 - A$ molecules, respectively. The time window of these spectra is 250 ps. The values of R are 4 nm and 5 nm for the $D_1 - A$ and $D_2 - A$ molecules, respectively. Although the PL from the donor dyes shown in Figs. 3 and 4 seem to be almost zero in the region of R less than 7 nm, the time-resolved PL spectra show the slight intensity in the donor PL regions indicated by the arrows. Therefore, the donor PL excited by the pulse laser intensities can be analyzed by the time evolution profiles even $R < 7$ nm.

The data points in Figs. 6(a) and 6(b) show the measured PL decay profiles in the $D_1 - A$ and $D_2 - A$ samples, respectively. The laser profile is shown at the bottom in Fig. 6(a). To eliminate the contribution of A PL, we extracted each profile from the streak image in the PL region from 1.58 to 1.65 (1.62) eV in the $D_1 - A$ ($D_2 - A$) system. The top profile in each figure exhibits the PL decay profile of the donor dye, for reference.

The evaluated decay rates k_{D} of the excitons in D_1 and D_2 are 0.62 and 1.77 ns^{-1}, respectively. The critical FRET distance depends on $k_{\mathrm{D}}J_n$, and the values of $k_{\mathrm{D}}J_n$ are 0.857 and 2.07 for the $D_1 - A$ and $D_2 - A$ systems, respectively. Hence, the critical R in the $D_2 - A$ is longer than that in the $D_1 - A$ due to larger k_{D}, so that the $D_2 - A$ system shows the energy transfer at longer R.

For evaluation of the energy transfer rate, we performed a fitting with a double exponential functional form as follows:

$$I(t) = C_1 e^{-k_{\mathrm{D}}t} + C_2 e^{-(k_{\mathrm{ET}}+k_{\mathrm{D}})t}, \qquad (2)$$

where C_1 and C_2 are constants. The solid curves in Figs. 6(a) and 6(b) show the results of this fitting.

Figure 7 shows the k_{ET} determined from Eq. (2) as a function of R for the $D_1 - A$ (open circles) and $D_2 - A$

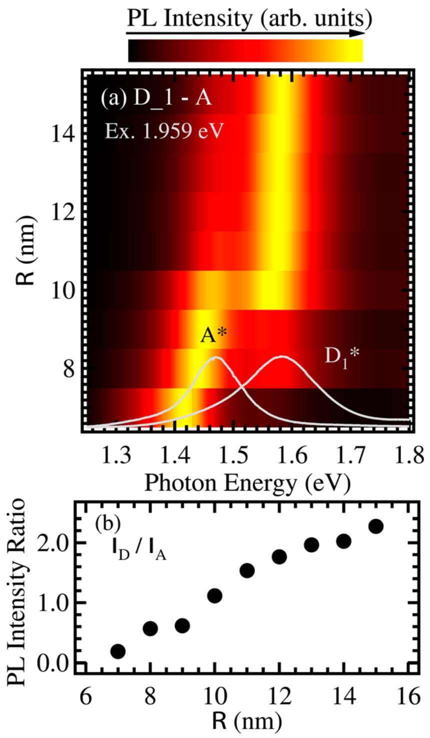

FIG. 3. (Color online) (a) Image map of the PL spectra of the $D_1 - A$ thin films for various Rs; the brightness is proportional to the PL intensity. The solid curves show the PL spectra of D_1 and A dye thin films for reference. (b) PL intensity ratio of the D_1 and A energy regions.

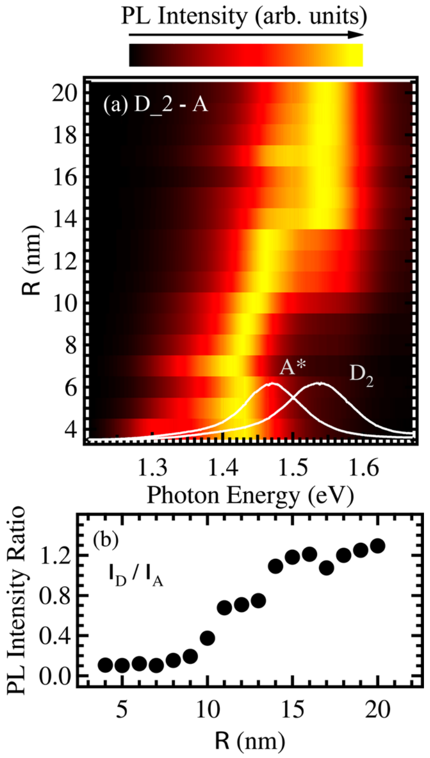

FIG. 4. (Color online) (a) Image map of the PL spectra of the $D_2 - A$ thin films for various Rs; the brightness is proportional to the PL intensity. The solid curves show the PL spectra of D_2 and A dye thin films for reference. (b) PL intensity ratio of the D_2 and A energy regions.

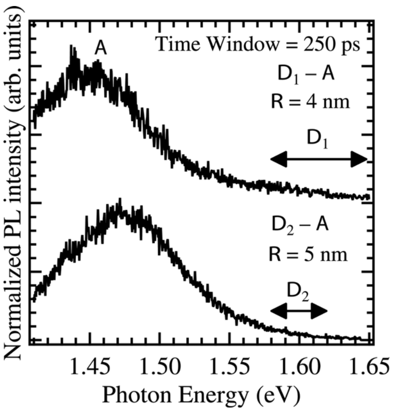

FIG. 5. Time resolved PL spectra in the $D_1 - A$ (upper) and $D_2 - A$ (lower) systems. The arrows indicate the donor PL regions.

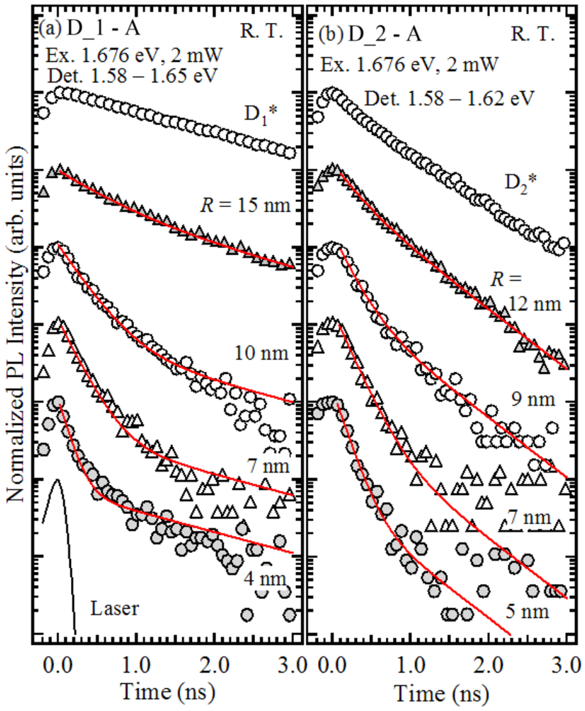

FIG. 6. (Color online) Data points show the R dependence of the PL decay profile in the (a) $D_1 - A$ and (b) $D_2 - A$ systems. The curves at top indicate the profiles of the donor thin films. The solid curves show the fitting results from Eq. (2), and the laser profile is shown at the bottom of (a).

(closed circles) systems. The dotted line indicates the decay rate of the exciton in the acceptor dye. The abscissa axis is logarithmic scale. As R decreases, k_{ET} increases in both systems. In order to clarify the R dependence, we performed a fitting with a function with a form of R^{-x} for the data with $R \leq 5$ nm to eliminate the affect of saturation. The solid curve indicates the fitting result for the $D_1 - A$ system. The curve show that k_{ET} is proportional to $R^{-2.0}$ for the $D_1 - A$ system. For the $D_2 - A$ system, the number of data points is too small for the reliable fitting, the fitting was not performed. However, the gradient is more moderate than that of the $D_1 - A$ system. This indicates that the index of the R dependence is less than two for the $D_2 - A$ system. It is well known that k_{ET} due to the dipole-dipole interaction is proportional to R^{-6}. Moreover, in the bilayer structure, the FRET process from one energy donor to all the energy acceptors in the layered structure is proportional to R^{-4}.[16] Therefore, our results showing k_{ET} proportional to R^{-2} deviate from the usual FRET results; next we discuss the reason for this deviation from an aspect of the population.

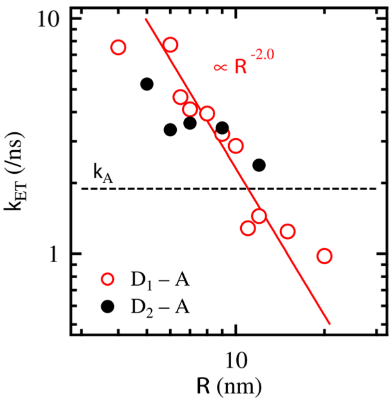

FIG. 7. (Color online) R dependence of k_{ET}. The abscissa axis is logarithmic scale. The solid curve demonstrates the result of fitting with R^{-n}. The dotted line indicates the decay rate of the exciton in the acceptor dye.

Here, we discuss the origin of the R^{-2} dependence. In the $D_1 - A$ ($D_2 - A$) system, k_{ET} is faster than k_A in the region of $R < 10$ (12) nm. In addition, the ratios of the optical densities of D_1 and A and D_2 and A at 1.676 eV are 2.73 and 0.95, respectively. Our samples have equal numbers of donor and acceptor dyes, and the acceptor dyes are also optically excited. The optically excited acceptor dyes cannot receive the energy transfer from the donor dyes. In the case of the $D_2 - A$ system, the number of the optically excited acceptor dye is slightly larger than that of the donor dyes, and k_{ET} is larger than k_A. The nearest neighbor acceptor dyes around the donor dyes are almost excited by the optical and FRET processes, so that FRET process with larger R acceptor also occurs. Therefore, the FRET is almost saturated around $R = 15$ nm in the $D_2 - A$ systems with larger critical R. On the other hand, in the $D_1 - A$ system with $R < 10$ nm, although k_{ET} is larger than k_A, the number of the optically excited acceptor dye is less than that of the donor dyes. Therefore, the $D_1 - A$ system can show the larger k_{ET} even though the nearest neighbor acceptor dyes are partially excited. Namely, when k_{ET} is larger than the k_A, the saturation of the FRET process occurs. Moreover, the ratio of the optically excited acceptor and donor dyes determines the increase in k_{ET}. There is a possibility that the formation of an aggregate as described by the extended dipole moment model[17] is the origin of the R^{-2} dependence.[18] However, we confirmed that the aggregate was not formed in the high-density mixture solvent, so that the saturation of the FRET is main reason for the R^{-2} dependence.

IV. CONCLUSION

We investigated the FRET dynamics in dye combinations with small Stokes shift energies. We found that the combination of the dyes with the smaller spectral overlap factor J showed as larger critical R than the one with the larger J. The difference in critical R originates from the difference in the exciton decay rate in the energy donor dyes. Moreover, the energy transfer rate k_{ET} is inversely proportional to the square of the distance between the energy donor and acceptor dyes R (that is, $k_{ET} \propto R^{-2}$) for both combinations. From speculation based on the number of excited acceptor dye, our FRETs are saturated even at long distances between the energy donor and acceptor because of the optical excitation of acceptor dyes. Our results indicate that the ultrafast optical switches based on excitons in cyanine dyes with small Stokes shift energies using FRET can be created with further optimization and that optimization of the ratio of the dye numbers should enable even faster operation. Therefore, the results of $k_{ET} \approx 10$ ns^{-1} suggests the possibility of 10 Gbps operation.

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