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Control of optical properties in cyanine dye thin film fabricated by a layer-by-layer method

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We report the fabrication of cyanine dye molecule thin films by a layer-by-layer (LBL) method. In the LBL thin film, the photoluminescence properties can be controlled by the separation between the donor and acceptor dye molecule layers. While the distance dependence of the energy-transfer rate changes around 2 nm, which is comparable with the lengths of the molecules, the energy-transfer rate as evaluated from the photoluminescence decay time shows a maximum value of approximately 15 ns^{-1}. The thin films fabricated by the LBL method will be therefore applicable for ultrafast optical switches with higher repetition rate. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4866498]

I. INTRODUCTION

Energy transfer between dipoles has been an important topic in the discussion of exciton dynamics in semiconductor quantum dots and organic molecules.[1–11] Furthermore, precise control of the distance R between the energy donor and acceptor dipoles enables to clarify the change in energy-transfer rate k_{ET}, which is caused by changing in the dimensionality; k_{ET} in the Förster model considering the point-to-point interaction changes with R^{-6},[1] and k_{ET} in the plane-to-plane interaction changes with R^{-4}.[12] Hence, the precise control of R can clarify the actual exciton dynamics and be used to induce unique properties in the very short range region of R.

We have focused on the energy-transfer process to realize an ultrafast response, which can be applied to ultrafast optical devices operating at a high repetition rate of the order of Tbit/s, by using cyanine dye molecules in polymer thin films.[13] In general, while organic dye molecules can show an ultrafast response due to intramolecular relaxation,[3,14–19] they show slow exciton decay, which induces the so-called pattern effects. The ultimate goal of our study is to achieve not only ultrafast relaxation due to the intramolecular transition in a single cycle but also ultrafast exciton relaxation by the additional processes, including energy transfer. However, in our previous report using cyanine dye molecules mixed into polyvinyl alcohol (PVA) thin films, k_{ET} changed with R^{-2}. Because the thin films were fabricated by a solvent evaporation technique, there were two problems: (i) R was an average value and (ii) the surface roughness was large. The first problem makes the precise control of exciton response difficult, and the second causes a poor signal-to-noise ratio owing to surface scattering. To conquer these problems, we focused on the fabrication of the thin film by a layer-by-layer (LBL) method.[20,21] Precise control of R and the fabrication of thin films with a flat surface become possible with the LBL method. Therefore, in this work, we report the fabrication of polymer thin films with cyanine dye molecules by the LBL method. We discuss the photoluminescence (PL) dynamics and their dependence on R.

II. EXPERIMENT

$C_{25}H_{25}IN_2S_2$ (NK-126) and $C_{47}H_{47}ClN_2O_2S$ (NK-4680) were used in this study as the energy donor and acceptor molecules, respectively. Their chemical structures are shown in Fig. 1. When we chose the donor material, we focused on the intramolecular relaxation. If the energy separation between the excited and lowest states is large, the intramolecular relaxation requires several steps. Therefore, we considered a smaller Stokes shift to easily achieve ultrafast relaxation. We purchased cyanine dyes from Hayashibara Biochemical Laboratories, Inc. and used them without further purification. The glass substrates used for the LBL deposition were cleaned by immersion in fresh piranha solution (1/3 (v/v) mixture of 30% H_2O_2 and 98% H_2SO_4) for 60 min. The substrates were rinsed with water and used immediately after cleaning. The LBL assembly was performed by sequentially dipping the glass substrates in aqueous solutions of positively charged poly(diallyldimethylammonium chloride) (PDDA, $M_w = 400\,000$–$500\,000$) and negatively charged poly(acrylic acid) (PAA, $M_w = 1\,000\,000$). In the beginning of the sample preparation, adhesion layers of PAA/PDDA were deposited to enhance the binding of NK-4680 to the substrates. Finally, we covered the samples with PVA, which has excellent gas barrier properties,[22,23] to reduce the photo-degradation of the samples. PVA is transparent in the absorption and PL regions of the dye molecules.

Spectroscopic ellipsometry was used to accurately determine the layer thickness of the polymers and dye molecules. The measurements were performed using a spectroscopic phase modulated ellipsometer in the spectral range from 1.5 to 4.0 eV. The absorption spectra were measured by using a 100 -W halogen lamp and a spectrometer with a resolution of

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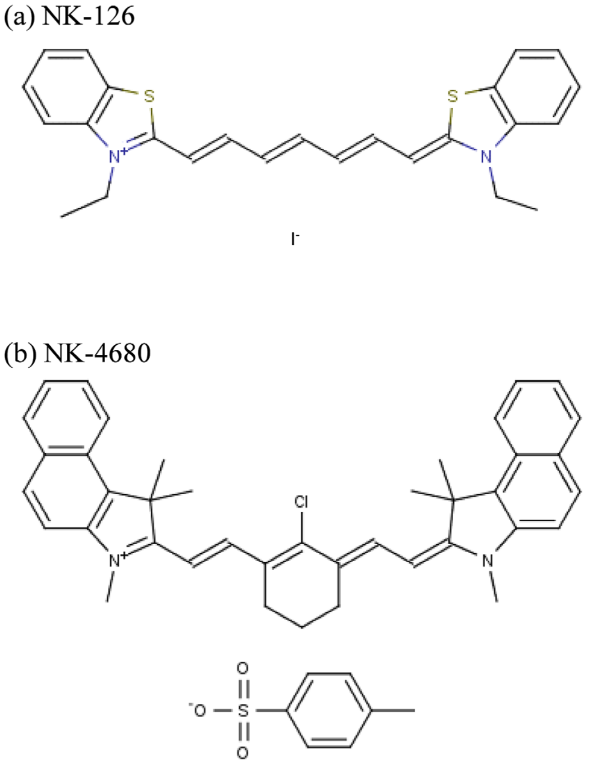

FIG. 1. Chemical structures of molecules. NK-126 ($C_{25}H_{25}IN_2S_2$): energy donor, NK-4680 ($C_{47}H_{47}ClN_2O_2S$): energy acceptor.

6 nm. For the conventional PL measurements, the 632-nm line of a He-Ne laser was used as the excitation light source, and the emitted PL was detected with the same spectrometer as in the absorption measurements. The PL decay profiles were measured with a Hamamatsu Photonics C5680 streak camera system with a time resolution of 40 ps. In the time-resolved measurements, the second harmonic light of the output from an optical parametric oscillator, which provided 140-fs optical pulses with an 80-MHz repetition rate, was used as the excitation light with energy of 2.1 eV so as not to excite the acceptor molecule.

III. RESULTS AND DISCUSSION

Figure 2 shows the total layer thickness of the $(PAA/PDDA)_n$ LBL films plotted as a function of number of bilayer n, which was determined by spectroscopic ellipsometry. Here, $n = 0.5$ indicates a single PDDA layer. The sample structure with $n = 2$ is schematically shown in the inset. A linear dependence of the layer thickness on n is clearly observed. Therefore, the average thickness of one bilayer of PAA/PDDA was estimated to be 1.056 ± 0.103 nm from a least-square fitting (dotted line).

Next, to clarify the adhesion of the dye molecules, we measured the dependence of absorption spectrum of the acceptor molecule thin film on the dipping time, as shown in Fig. 3(a). The samples were fabricated with different dipping times of the acceptor molecule. While the value of the optical density does not depend monotonically on the dipping time, the value shows a trend of increasing with increasing dipping time. Figure 3(b) summarizes the dipping time dependence of the thickness (open circles) and the optical density at the lower-energy-side absorption-band around 1.46 eV (closed triangles). The results indicate that the film thickness of both the donor and acceptor molecules can be controlled by the dipping time.

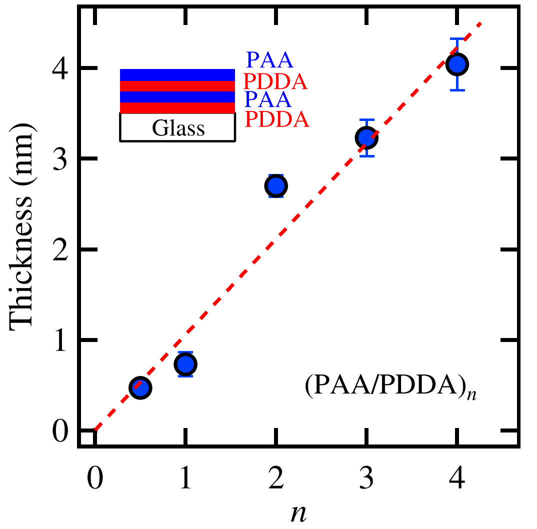

FIG. 2. Thickness of $(PAA/PDDA)_n$ bilayers determined by spectroscopic ellipsometry as a function of n. Dotted line denotes the result of least-square fitting of experimental data. Inset shows schematic of sample structure with $n = 2$.

Figure 4 shows the dependence of the PL spectrum of the thin films on R, where the donor and acceptor layers

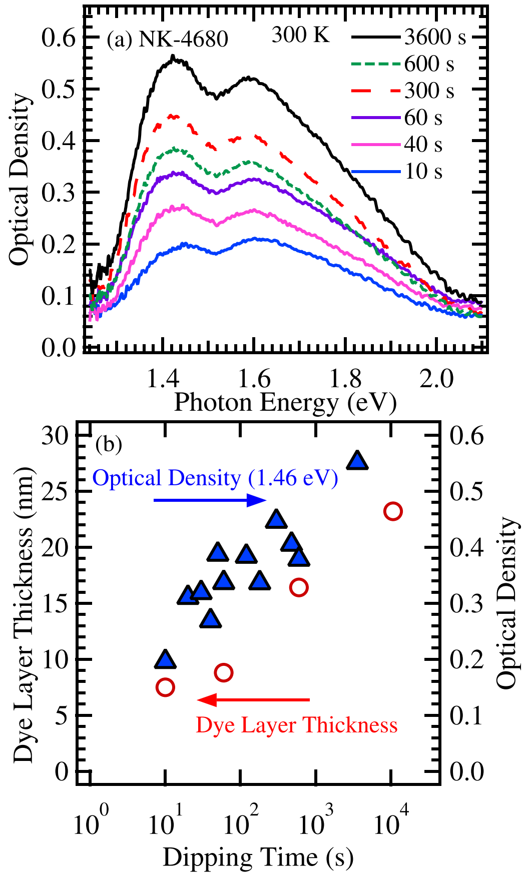

FIG. 3. (a) Dependence of absorption spectrum of acceptor molecule on dipping time. (b) Dependence of the dye layer thickness and optical density at 1.46 eV on dipping time indicated by circles and triangles, respectively.

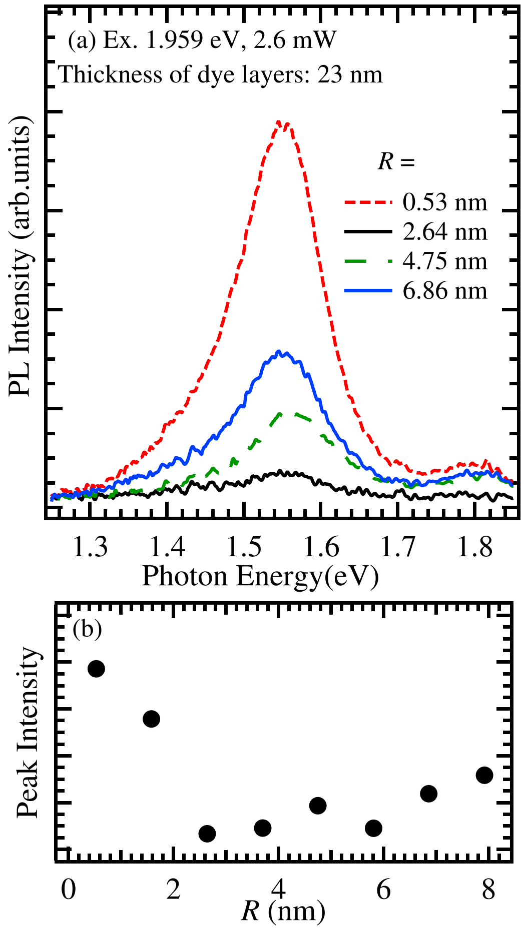

FIG. 4. (a) Dependence of PL spectrum in samples with donor and acceptor layers on R. Observed PL originates from donor molecules. (b) PL peak intensity plotted as a function of R.

form a film with a thickness of 23 nm. The PL originates from the donor molecules. The reason for the disappearance of the acceptor molecule PL is unknown, and this tendency was also observed in previous reports using quantum dots.[10,12] In the case that the luminescence centers are sandwiched by the polymers, the PL seems to disappear. Since the dye molecule at the top layer covered by PVA film can emit the PL, covering by charged polymer leads to the PL disappearance. Hence, we considered that the charged polymer may modify the electronic states in the dye molecules, which changes the dye molecules to optically inactive. In the region $R > 2$ nm, the intensity of PL band of the donor molecule, which locates around 1.55 eV, decreases with decreasing R. This weakened PL results from the energy transfer from the donor molecule to the acceptor. On the other hand, in the region $R < 2$ nm, the PL intensity increases with decreasing R.

To elucidate the origin of the increase in the PL intensity and clarify the energy-transfer dynamics, we measured the time-resolved PL spectrum using a streak camera. Figure 5 shows the PL decay profiles observed in the main PL region 1.55–1.65 eV in the samples with various R values. The top profile was measured in the single layer donor thin film. All profiles consist of two components: fast and slow decay. The fast component originates from the energy transfer, and the slow component is attributed to spontaneous emission decided by the dipole moment of the exciton in the dye molecule. To evaluate the energy transfer rate, the signals were fitted with a double exponential function shown below

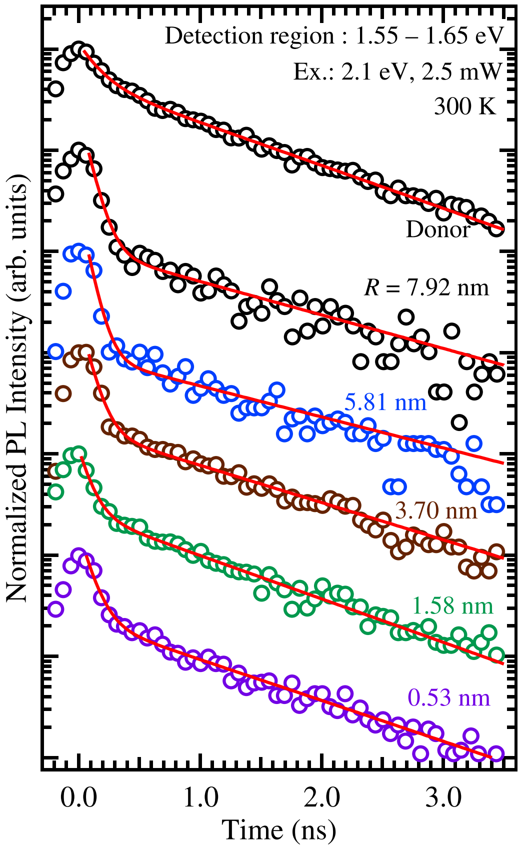

FIG. 5. PL decay profiles observed in samples with various R values. Top profile was measured in the donor thin film for reference. Solid curves are fitting results.

$$I(t) = C_1 e^{-k_{\mathrm{D}} t} + C_2 e^{-(k_{\mathrm{ET}}+k_{\mathrm{D}})t}, \tag{1}$$

where k_{D} indicates the slower PL decay rate due to the exciton relaxation, and C_1 and C_2 are constants. Although the donor in the PVA film showed a decay profile that could be fitted by a single exponential function in our previous report,[13] the PL decay profile observed in the donor thin film fabricated by the LBL method demonstrates two components. Considering that the donor molecule has the absorption and PL line widths, this appearance of second component in the donor PL decay profile is attributed to the energy transfer between the donor molecules because the in-plane density is much higher than that in the previous work.

In Fig. 6(a), the evaluated k_{ET} was plotted as a function of R. The dotted line indicates k_{ET} in the donor thin film. Because of the energy transfer from the donor to the acceptor, k_{ET} increases up to twice the value of single donor layer at around $R = 5$ nm. k_{ET} shows a slight dependence on R. The appearance of R dependences in the PL intensity (Fig. 4) and k_{ET} demonstrates that the exciton dynamics can be controlled by changing R in the LBL thin films. However, k_{ET} decreases with decreasing R, which is opposite to the

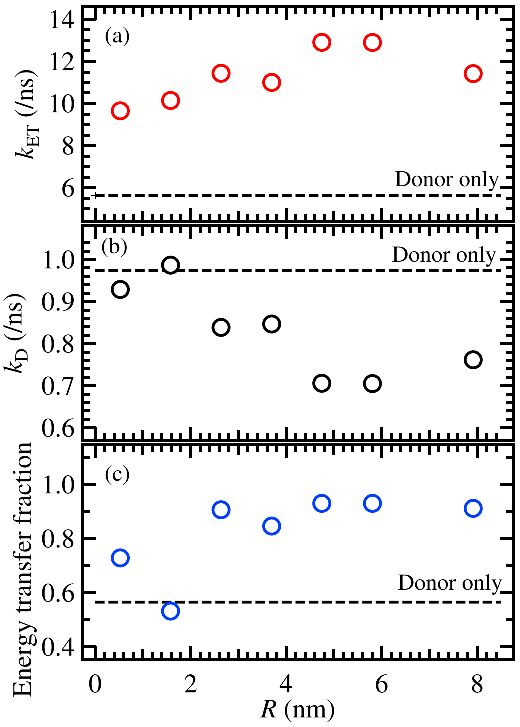

FIG. 6. (a) R dependence of k_{ET}. (b) R dependence of k_D. Dotted line indicates rate measured in donor thin film. (c) $C_2/(C_1+C_2)$ for each value of R was plotted as energy transfer fraction.

usual R dependence. Usually, k_{ET} increases with decreasing R. For instance, as mentioned earlier, k_{ET} caused by the point-to-point interaction depends on R^{-6} in the Förster model,[1] and k_{ET} in the plane-to-plane interaction shows dependence on R^{-4}.[12]

To consider the R dependence of k_{ET}, we focused on the decay rate of the donor molecules, which is plotted as a function of R in Fig. 6(b). The dotted line indicates the decay rate in the donor thin film. While the exciton in the donor dye molecule relaxes slower than the intrinsic rate in the case of $R > 2$ nm, k_D increases with decreasing R. The increasing k_D clearly denies the possibility of the so-called back transfer which is the energy transfer from the acceptor to the donor.

Furthermore, we focused on the amount of energy transfer. In Fig. 6(c), the value of $C_2/(C_1+C_2)$ as the fraction of energy transfer was plotted as a function of R. This value indicates the ratio of the excitons decaying by spontaneous emission and by energy transfer. Hence, in the region $R > 2$ nm, 90% of the excitons in the donor molecules excited by the optical pulse relax by energy transfer, nonradiatively. However, in the region $R < 2$ nm, it drops to less than 80%. Our results also deny the possibility of Stern-Volmer-type quenching. We next considered the different interactions between the donor and acceptor molecules. Namely, when the donor molecule approaches within 2 nm of the acceptor, the electron in the donor experiences a repulsive force from the acceptor molecule. This repulsive force prevents energy transfer. Therefore, because some of the excitons relax in the donor molecules, the PL intensity increases and k_{ET} decreases. The distance of 2 nm is almost comparable with the length of the donor molecule. This will be the key distance for the energy transfer in the LBL thin film.

IV. CONCLUSION

Cyanine dye molecule thin films were fabricated by the LBL method, and the distance between the donor and acceptor dye molecule layers was controlled by the thickness of the polymer layers. We found that R can be controlled within approximately 1 nm, and that the thicknesses of the dye layers vary with the dipping time. The PL intensity and k_{ET} change with R, and the dependences in the region $R < 2$ nm differ from those in the region $R > 2$ nm. Because the energy transfer is suppressed in the region $R < 2$ nm, k_{ET} decreases by approximately $10\,\mathrm{ns}^{-1}$. However, the maximum k_{ET} by fabricating thin film by the LBL method indicates the possibility of application for the ultrafast all-optical switches with higher repetition rate. The performance may be enhanced by optimizing the molecules and the donor/acceptor ratio.

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