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We report an increase in exciton decay rates because of long-range interaction based on surface charge between cyanine thin films. The dependence of the decay rate on the spatial separation between the cyanine molecule layers shows that the rate is almost constant, which is different from the well-known energy transfer process. The rate is hardly affected by the fluctuation of the film thickness, which is an advantage of using cyanine or organic molecules. © *2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4959191]

I. INTRODUCTION

Ultrafast all-optical switches are a key device for future high-speed optical communication networks.[1,2] In particular, optical switches based on saturable absorption have been extensively studied using various materials including semiconductor quantum dots,[3–6] quantum wells,[7–10] and organic materials.[11–13] Such switches require both large intensity modulation and ultrafast response, which has been a key issue. While the modulation magnitude depends on a decrease in the absorbance because of the state filling effect,[14] the ultrafast signal decay in nanostructured semiconductors relates to several factors, e.g., the intersubband transition,[15–18] spin relaxation,[7,19–21] and carrier tunneling.[22–24] In contrast, nonradiative intramolecular relaxation in organic molecules has been identified as another candidate for ultrafast device application.[25–29] In these results, while the ultrafast response for the single cycle operation was reported, the first excited state or the lowest exciton state works as a reservoir state. If the decay rate of this state is less than the repetition rate of the input pulse, then saturation of signal processing will occur. This effect makes operation at a high repetition rate of the order of THz difficult. Therefore, an additional mechanism to increase the decay rate of the reservoir state is required.

The resonant energy transfer was focused on as a method for increasing the decay rate,[30–36] in particular, on the cyanine molecule thin films.[37,38] The energy transfer causes ultrafast relaxation of the lowest excited states with a decrease in the distance between the energy donor and the acceptor molecules, which enables high repetition operation without the pattern effect. In contrast, our approach, which uses cyanine molecules to enhance the exciton decay rate, exhibited a different-from-usual dependence of the energy transfer rate on the donor-acceptor distance. In our previous study, we were able to fabricate high quality layer-by-layer (LBL) thin films, in which the exciton dynamics could be precisely measured.[39] Therefore, in this study, we clarify the mechanism of the increase in the exciton decay rate in the cyanine molecule thin films. While the exciton decay rate increases with different cyanine layers of the thin films, the rate for separation is almost constant. The origin of the increase is discussed with respect to the result of the separation dependence.

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(a) DTTCI
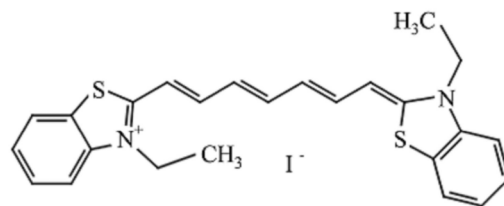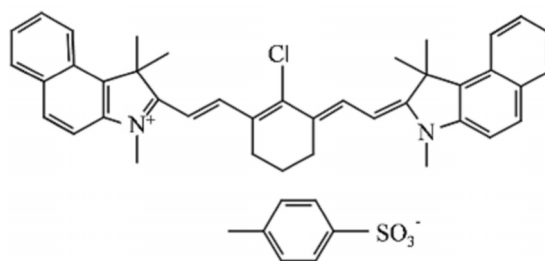
(b) PSA1411

FIG. 1. Chemical structures of cyanine molecules of (a) DTTCI and (b) PSA1411.

II. EXPERIMENT

We used two types of commercial cyanine molecules 3,3'-diethylthiatricarbocyanine iodide (DTTCI) and 2-[2-[2-Chloro-3-[2-(1,3-dihydro-1,1,3-trimethyl-2H-benz[e]indol-2-ylidene) ethylidene] -1-cyclohexen-1-yl]ethenyl]-1,1,3-trimethyl-1H-benz[e]indolium4-methylbenzenesulfo nate (PSA1411). The chemical structures are shown in Fig. 1. We used them without further purification. The cyanine dye thin films were fabricated by a layer-by-layer (LBL) method.[40–42] Previously, we reported fabrication of the LBL thin films with improved signal-to-noise ratio in pump-probe measurement.[39] The polymer layer consists of two layers of positively charged

FIG. 2. The absorption spectra of the D-P, DTTCI, and PSA1411 thin films indicated by the solid, dotted, and dashed curves, respectively.

FIG. 3. Normalized transmittance change signals observed in D-P, DTTCI, and PSA1411 thin films. Solid curves show the results of fitting. The inset depicts the signals measured in the short-time region, where the signals are not normalized.
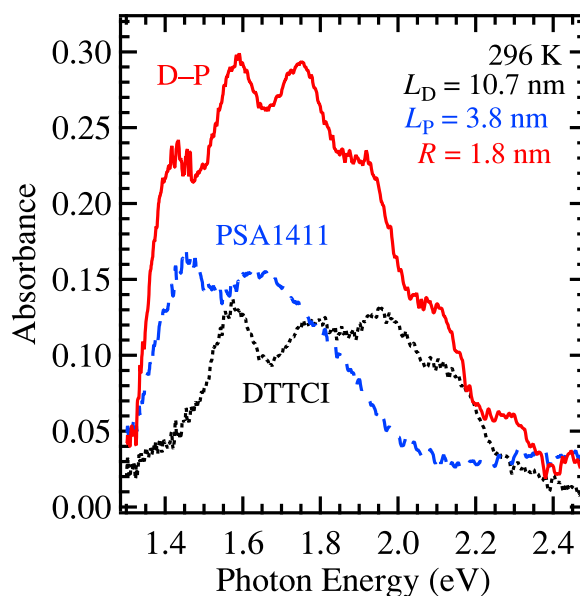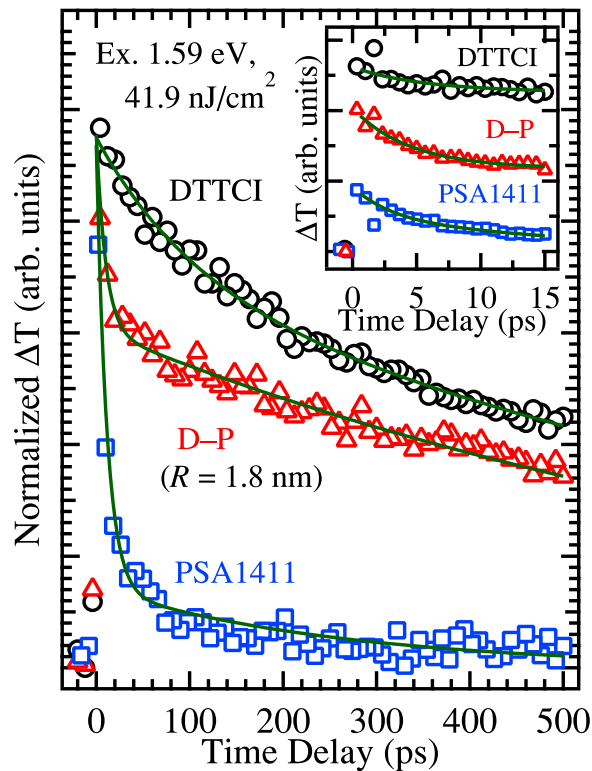
poly(diallyldimethylammonium chloride) (PDDA) and negatively charged poly(acrylic acid) (PAA), with an accuracy of 1.2 nm.[39] At the beginning of sample fabrication, the adhesion layer of (PAA/PDDA)$_3$ was deposited to enhance the binding of PSA1411 molecules to the substrate, where the subscript indicates the number of pairs of PAA and PDDA layers. The bottom PSA1411 layer is adsorbed to the adhesion layer on the substrate with a dipping time of 4 min, followed by the adsorption of the top DTTCI layer with a dipping time of 10 s. The thicknesses of the DTTCI L_D and PSA1411 L_P layers were 10.7 nm and 3.8 nm, respectively. Hereafter, we refer to the thin films consisting of the DTTCI and PSA1411 layers as D-P thin films. The separation R between the DTTCI and PSA1411 layers was controlled by the layer number of the PAA/PDDA. Finally, we covered the thin films with poly(vinyl alcohol) (PVA) by spin coating. The PVA has excellent gas barrier properties, which results in the suppression of photodegradation.[43,44] Thin films of the DTTCI and PSA1411 molecules were fabricated as reference samples. The layer thicknesses of the polymers and cyanine molecules were measured by a spectroscopic phase modulated ellipsometer.

The absorption spectrum was measured using a 100-W halogen lamp and a spectrometer with a resolution of 6 nm. The transient response was measured using a time-resolved transmission-type pump-probe technique. The light source used was a mode-locked Ti:sapphire pulse laser with a pulse width of approximately 90 fs and a repetition rate of 80 MHz. The pump and probe powers

TABLE I. The decay rates of the DTTCI, PSA1411, and D-P thin films evaluated by Eq. (1).

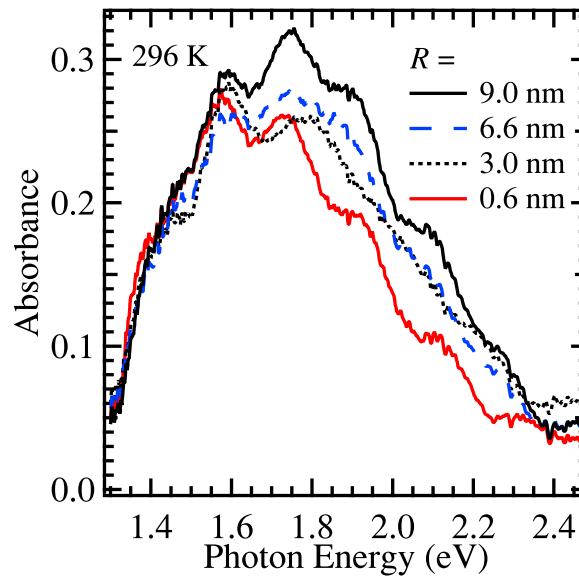|	k_1 (10^{-3}/ps)	k_2 (10^{-3}/ps)
DTTCI	199.6	0.9770
PSA1411	316.4	3.798
D-P (R = 1.8 nm)	227.0	1.136

FIG. 4. The absorption spectra in the D-P thin films fabricated with various R values.

were kept at 41.9 and 3.14 nJ/cm^2, respectively. The pump energy was tuned to 1.59 eV, the exciton energy in the DTTCI thin film. In order to eliminate the pump-beam contribution to the probe beam, the pump and probe beams were orthogonally polarized to each other. The pump beam, chopped at 2 kHz, modulated the intensity of the probe beam transmitted through the sample. The probe intensity was detected by a Si photodiode and amplified by a lock-in amplifier. All measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

In Fig. 2, the absorption spectra of the D-P, DTTCI, and PSA1411 thin films are depicted by the solid, dotted, and dashed curves, respectively. R in the D-P thin film was 1.8 nm. The absorption peaks observed at 1.63 eV and 1.45 eV for the D-P thin film originate from the lowest exciton transition of the DTTCI and PSA1411 molecules, respectively. Moreover, the absorbance value in the D-P thin film indicated by the solid curve almost agrees with the numerical summation of the absorption spectra of the DTTCI and PSA1411 thin films. Therefore, overlapping the DTTCI and PSA1411 molecule layers without resolving during the fabrication process is possible.

The effects of the PSA1411 layer on the exciton dynamics of the DTTCI molecules were demonstrated by measuring the time-resolved transmission-change signals, as shown in Fig. 3, where the open circles, open squares, and open triangles indicate the experimental results observed at 1.59 eV in the DTTCI, PSA1411, and D-P thin films, respectively. Each signal is normalized at the maximum intensity. Furthermore, the results in the short-time region from 0 to 15 ps are shown in the inset. Here, the signals are not normalized so that the intensity can be compared. All profiles consist of two components: a fast component is attributed to intramolecular decay, and a slow component is attributed to exciton decay.[39] Because the fast component observed in the PSA1411 thin film is slower than the temporal pulse shape, the fast component is a result of not the coherent artifact but the intramolecular decay. Both the intramolecular and exciton decay rates of the DTTCI molecules seem to be enhanced by stacking the DTTCI layer on the PSA1411 layer, which was not observed by stacking the layers of a single type molecule.[39] In order to evaluate these decay rates, fitting with double exponential function was performed as follows:

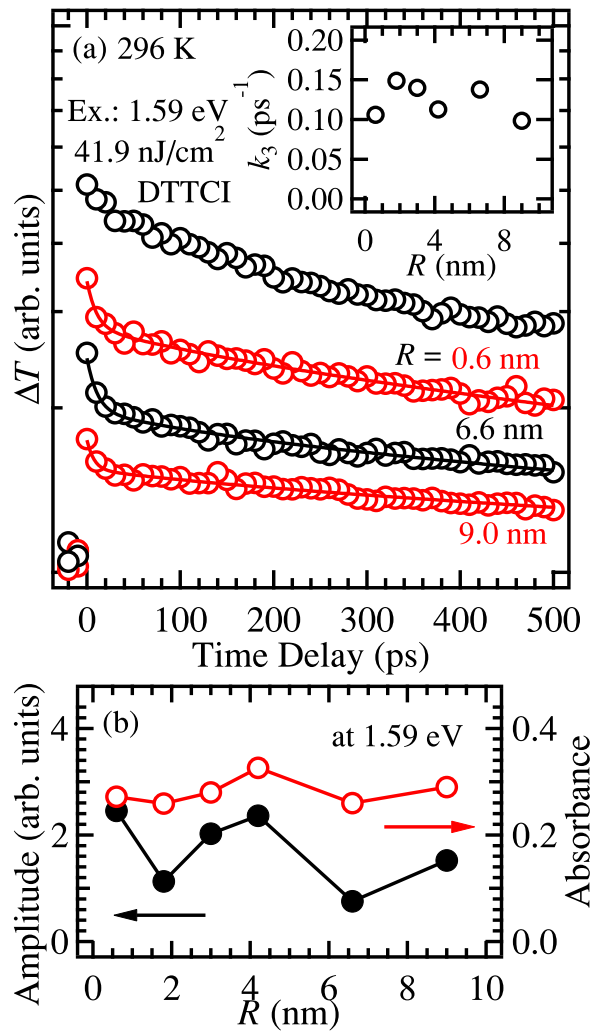$$I(t) = C_1 \exp[-(k_1 + k_2)t] + C_2 \exp(-k_2 t), \tag{1}$$

FIG. 5. (a) The transmittance change signal of D-P thin films of various R values. The top profile shows the signal of the DTTCI thin film. Solid curves show the results of fitting with Eq. (2). The inset indicates k_3 plotted as a function of R. (b) The signal amplitude at 0 ps (closed circles) and the absorbance at 1.59 eV (open circles) are plotted as a function of R.

where C_1 and C_2 are the intensities and k_1 and k_2 are the intramolecular and exciton decay rates, except in the D-P thin film. The evaluated k_1 and k_2 are listed in Table I.

The origin of the enhancement of k_1 and k_2 in the D-P thin film was elucidated, by measuring the dependence on R. The absorption spectra of the D-P thin films with various R values are shown in Fig. 4. While the absorbance at 1.59 eV, the lowest exciton transition of the DTTCI molecules, is almost constant for R, the absorbance at 1.75 eV increases with an increase in R. This increase was also observed in our previous work.[38] The reason for this increase is not yet clear; however, it may relate to the distance from the substrate. Considering that the absorbance at 1.59 eV is hardly changed by R, the thicknesses of the DTTCI and PSA1411 layers are nearly constant.

Figure 5(a) depicts the pump-probe signals observed in the D-P thin films for various R values. The profile of the DTTCI thin film is shown at the top for reference. It is noted that the longitudinal axis is a logarithmic scale. Here, the profiles are not normalized. In Fig. 5(b), the signal amplitude at 0 ps and the absorbance at 1.59 eV are plotted as a function of R by the closed and open circles, respectively. The signal amplitude corresponds to the variation of the absorbance originating from fluctuations in the thickness, which indicates that the amplitude of the transient signals observed by the pump-probe technique is proportional to the number of excited molecules.

In contrast, all signals observed in the D-P thin films show the fast component. The possible origins of this fast component are the energy transfer and surface charge. While the decay rate due to the energy transfer depends on R, that due to the surface charge does not depend on R. We analyzed the signals by a triple exponential function, as follows:

$$I(t) = C_1 \exp[-(k_1 + k_2)t] + C_2 \exp(-k_2 t) + C_3 \exp[-(k_2 + k_3)t], \tag{2}$$

where C_3 and k_3 are the coefficient and the energy transfer rate, respectively. The solid curves in Fig. 5(a) show the results of this fitting. The evaluated k_3 is plotted as a function of R in the inset of Fig. 5(a); k_3 is nearly constant independent of R. Usually, the energy transfer rate because of the point-to-point interaction described by the Förster model is proportional to R^{-6}.[30,33] Moreover, in bilayer structures, the rate because of the plane-to-plane interaction is known to be proportional to R^{-4}.[32,35] Therefore, the energy transfer is not the major factor for the fast response.

Here, we consider that the increase in the exciton decay rate originates from the surface charge, because the electric field due to the surface charge does not depend on the distance. The important point is that the increase in the decay rate was not observed in only the bilayer structure of a type of cyanine molecule;[39] the existence of the different cyanine molecule layer is a key point. When the extended dipole[45] is formed between excitons in the DTTCI and PSA1411 layers in the D-P structure, the exciton lifetime changes with the relationship between the directions of polarization. In particular, the lifetime decreases in the case of parallel direction. Thus, the stack of different cyanine molecule layers induces the surface charge, whose field increases the exciton decay rate. This mechanism is hardly affected by the fluctuation of L_D, which is an advantage of the fabrication process towards mass production.

IV. CONCLUSION

The exciton dynamics in double-layered cyanine thin films has been studied by a time-resolved transmission-type pump-probe technique. The fabrication of the D-P thin films with R was confirmed by the absorption spectra. While k_1 and k_2 in the D-P thin film increased by more than those of the DTTCI thin film, k_3 hardly depends on R. As the possible origin of the increase in the exciton decay rate, we considered the electric field due to surface charge. Our results demonstrate that the increase in the exciton decay rate as a result of the surface charge can be used for ultrafast all-optical switches operating at high repetition rates.

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