Exciton dynamics as a function of excitation intensity and double-pulse excitation in cyanine molecule thin films: Toward low-power optical switches

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ABSTRACT

Exciton decay dynamics can be optically controlled by changing the excitation conditions, particularly, the excitation intensity. In this study, we report how the exciton dynamics in cyanine thin films depend on the excitation intensity and sequence. The excitons in these films have two decay components, and the ratio of the population of the fast decay component to the total population depends on the excitation intensity. Conversely, sequential excitation by a second optical pulse does not alter this ratio. Although the total excitation power is comparable, the change in the dynamics by the second pulse is different from the simple increase in the excitation power. Therefore, the sequential excitation by the second pulse can be a key point for realizing low-power optical switches.

I. INTRODUCTION

The control of exciton and carrier dynamics using ultrashort optical pulses has been important for understanding material properties and designing devices such as ultrafast optical switches. For example, increasing the excitation intensity induces various phenomena, including exciton (carrier) annihilation due to collision and interaction with phonons[1–9] and interaction with the optical field, such as Rabi oscillations.[10–16] These phenomena occur in both organic and inorganic materials. Therefore, it is essential to clarify how the excitation intensity affects the decay dynamics of the elementary excitations. Another approach to the study of the decay dynamics of the elementary excitation is the double-pulse method, which is useful for controlling coherent phenomena, including coherent phonons,[17–20] coherent plasmons,[21,22] and quantum beats,[23–25] because only the elementary excitations that maintain coherence can be controlled. However, the decay dynamics of elementary excitations by the second pulse is modified by the accumulation of the elementary excitations generated by the first pulse. Therefore, we must clarify the difference between the simple excitation intensity dependence and the decay dynamics measured by the double-pulse method. In particular, the accumulation effect, leading to the so-called pattern effect,[26–28] has hindered the realization of ultrafast optical switches.

Recently, an enhanced exciton decay rate was reported in double-layer cyanine thin films.[29,30] To realize ultrafast optical switches, it is important to understand the phenomenon induced by an increase in the excitation intensity and that induced by the sequential excitation. Therefore, in this study, we investigate how the excitation intensity and sequence affect the decay dynamics of excitons in the single- and double-layer cyanine thin films, where the single-layer sample shows the intrinsic exciton dynamics and the double-layer sample shows the modified exciton dynamics. The exciton dynamics have two decay components, and the population of each component depends on the excitation intensity. Furthermore, the variation of the decay rates also differs in the two measurement method. On the basis of these results, we discuss room-temperature exciton dynamics as a function of excitation intensity, as well as temporal pulse separation in the double-pulse measurement. We also discuss how these phenomena may be used to control exciton dynamics.

II. EXPERIMENT

We used two types of commercially available 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-methylbenzenesulfonate (PSA1411). Figure 1 shows the chemical structures. The cyanine molecule thin films were fabricated by using the layer-by-layer method. The details of the sample preparation are available in Ref. 31. The DTTCI and PSA1411 layers were 10.7 and 3.8 nm thick, respectively. Hereafter, we refer to the double-layer thin film consisting of one layer each of DTTCI and PSA1411 as the DP thin film. The separation R between the DTTCI and PSA1411 layers was 1.8 nm. Finally, to suppress photodegradation, the thin films were covered by spin coating with poly(vinyl alcohol) to serve as a gas barrier.[32,33] The DTTCI and PSA1411 thin films were fabricated as reference samples.

The transient signal was measured by using a transmission-type time-resolved 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 energy was tuned to 1.59 eV, which is the exciton energy in the DTTCI thin film. To eliminate the pump-beam contribution to the probe beam, the pump and probe beams were orthogonally polarized. The pump beam was chopped at 2 kHz to modulate the intensity of the probe beam transmitted through the sample. The transmitted probe light was detected by a Si photodiode, and the intensity was amplified by a lock-in amplifier. In the double-pump measurements, the two pump pulses had the same polarization and intensity. Hereafter, the pulse exciting the samples at zero (positive) time delay is referred to as the first (second) pulse. All measurements were made at room temperature.

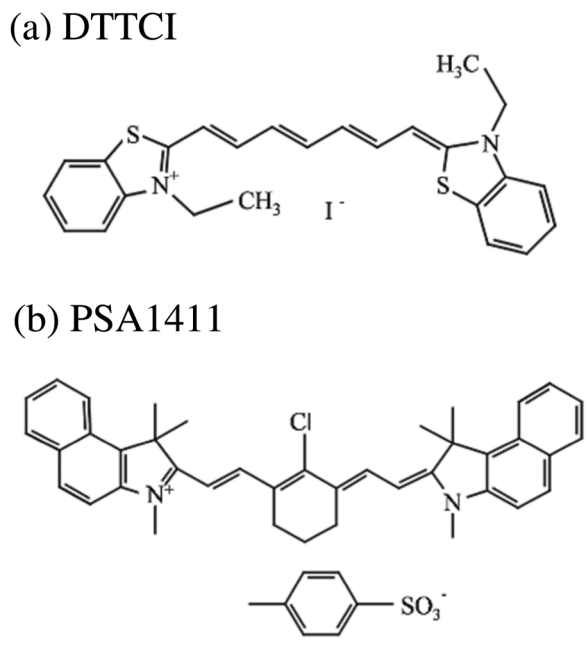

FIG. 1. Chemical structures of cyanine molecules (a) DTTCI and (b) PSA1411.

III. RESULTS AND DISCUSSION

We start by discussing the response due to the first and second pulses. Figure 2 shows the transmission-change signals measured by the double-pulse method in the DTTCI, DP, and PSA1411 thin films. The dynamics in the PSA1411 thin film is the reference. Each signal is normalized by the intensity at the zero delay. The pump-pump separation Δ_{pump} of 250 ps corresponds to a 4 GHz repetition rate. As previously reported,[30] the fast relaxation component appears in the DP thin film and does not originate from the response of the PSA1411 layer. The fast relaxation in the DP thin film originates from interactions between excitons in the DTTCI and those in the PSA1411 molecules.

We now discuss the factors in the two decay components modified by the second pulse. To analyze the time-domain signal, we fit the data in Fig. 2 with a double-exponential function

$$\Delta T(t) = C_1 e^{-k_1 t} + C_2 e^{-k_2 t}, \quad (1)$$

where t is the time delay, C_1 and C_2 correspond to the population of each component, and k_1 and k_2 are the decay rates. In this function, the first and second terms are related to the fast and slow decay components, respectively. The fitting results are indicated by

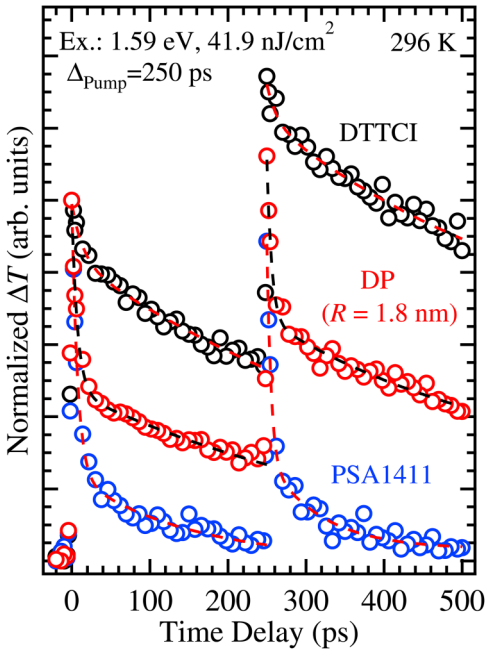

FIG. 2. Time-resolved transmission-change signals in the DTTCI, DP, and PSA1141 thin films by the double-pulse method. The open circles and dashed curves indicate the experimental results and fitting curves, respectively.

the dashed curves in Fig. 2. To fit the responses due to the second pulse, a constant baseline is added to Eq. (1). The parameter values resulting from these fits are listed in Table I. The distribution of excitation within the fast and slow decay components is firstly discussed. The ratio of C_1 to $C_1 + C_2$ gives the ratio of the exciton population of the fast decay component to the total exciton population and is plotted as a function of k_1 and k_2 in Figs. 3(a) and 3(b), respectively. The closed and open circles correspond to the values by the first and second pulse, respectively. The population ratio changes with k_1 and k_2, but the change caused by the second pulse is very small.

Figures 3(c) and 3(d) show the ratio of the decay rate by the second pulse to that by the first pulse as a function of k_1 and k_2, respectively. The closed and open circles show the ratio of k_1 and k_2, respectively. Although the increase in the ratio of k_1 clearly depends on k_2 indicated by the closed circles in Fig. 3(d), the increase in the ratio of k_2 does not depend significantly on k_1 and k_2 indicated by the open circles in both of Figs. 3(c) and 3(d). These results demonstrate that the slow decay rate is the material intrinsic value, while the fast decay component depends on the material and other parameter values. Hence, the slow component causes the pattern effects. This is important to consider the applications.

We now discuss what the instantaneous high density of excitation causes. To clarify the difference between the sequential excitation (double pump) and a simple increase in the excitation intensity, the transmission-change signals for several excitation intensities in the DTTCI thin film are shown in Fig. 4(a). With increasing the excitation intensity, the fast component seems to be enhanced. Note that the signal strength decreases at $16I_0$, where I_0 is the lowest excitation intensity. These data were fitted with Eq. (1), and the results are summarized in Figs. 4(b) and 4(c). In the analysis, the coherent artifact was eliminated. Here, C_1 (C_2) ratio means $C_1/(C_1 + C_2)$ [$(C_2/(C_1 + C_2)$]. As shown in Fig. 4(b), with increasing the excitation intensity, the C_1 ratio (i.e., the population of the fast component) increases, whereas the C_2 ratio decreases. Considering the very slight decrease in the C_1 ratio shown in Figs. 3(a) and 3(b), the increase in the C_1 ratio suggests the difference of the excitation process from the double-pulse excitation. If all molecules within the beam spot are excited by the first pulse, the response to the second pulse will decrease because fewer ground-state molecules are available for excitation. However, the result for the pump-intensity dependence shows that less than

TABLE I. Parameter values as determined by fitting Eq. (1) to data shown in Fig. 2 for DTTCI, DP, and PSA1411 thin films.

	C_1	k_1 ($\times 10^{-1}$/ps)	C_2	k_2 ($\times 10^{-2}$/ps)	Baseline
DTTCI 1st	0.154	0.695	0.835	0.181	
DTTCI 2nd	0.100	0.811	0.682	0.263	0.540
DP 1st	0.501	1.348	0.470	0.226	
DP 2nd	0.445	1.650	0.441	0.314	0.227
PSA1411 1st	0.749	1.328	0.240	0.674	
PSA1411 2nd	0.445	1.650	0.441	1.447	0.033

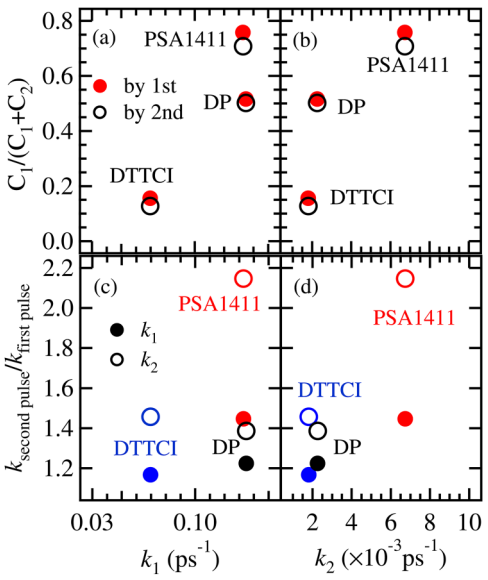

FIG. 3. Ratio of C_1 to $C_1 + C_2$ in the DTTCI, DP, and PSA1411 thin films as a function of (a) k_1 and (b) k_2. The closed and open circles show the ratio of the response to the first and second pulse, respectively. The ratio of decay rate by the second pulse to that by the first pulse as a function of (c) k_1 and (d) k_2. The closed and open circles show the values related to the variation of k_1 and k_2, respectively.

1/8 of the molecules in the beam spot are excited at I_0. This result indicates that saturation of the signal intensity does not occur in the double-pump measurement.

Moreover, the decay rates k_1 and k_2, which are normalized to their values for the lowest excitation intensity I_0, are plotted in Fig. 4(c) by closed and open circles, respectively, as a function of excitation intensity. With increasing the excitation intensity, k_1 increases and remains almost constant above $5I_0$. The plot has the fluctuation, in particular, the point at $2.8I_0$ largely drops. This fluctuation originates from the contribution of the coherent artifact to the signal. As mentioned above, the artifact was eliminated in the analysis; however, multiple reflection in the sample causes the noise. Thus, when the excitation intensity is small and the signal intensity is weak, the scattered light distorts the signal. While the absolute value of k_1 in the low excitation power region may include the ambiguity, the increase and decrease in the ratio with the increase in the excitation intensity were clearly shown in the signals. Therefore, this trend can be discussed. Conversely, k_2 decreases very slightly and may even be said to be constant. Considering that both k_1 and k_2 slightly increase in response by the second pulse [cf. Figs. 3(c) and 3(d)], this result is controversial; the increase in k_1 and k_2 by the second pulse does not originate from high density excitons.

The same measurements were made for the DP thin film, as shown in Figs. 5(a)–5(c). Although there are several measurement errors, the tendency of the dependence on the excitation intensity is similar to that for DTTCI thin film, except for k_1; the signal

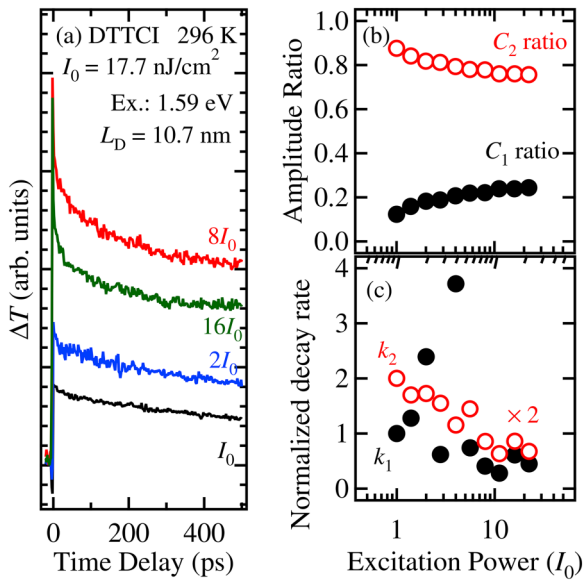

FIG. 4. (a) Dependence of time-domain signal on the excitation intensity in the DTTCI thin film. (b) C_1 ratio and C_2 ratio as a function of excitation intensity. (c) k_1 and k_2 as a function of excitation intensity. The values are normalized by the respective value at I_0.

intensity at $16I_0$ decreases, the C_1 ratio (C_2 ratio) decreases (increases), and k_2 decreases with increasing the excitation intensity. This indicates that while the decay rates in the DP thin films are modified, the dependence of the dynamics on the excitation intensity is based on the characteristics of the DTTCI molecule. While the increase in the excitation intensity modifies k_1, the

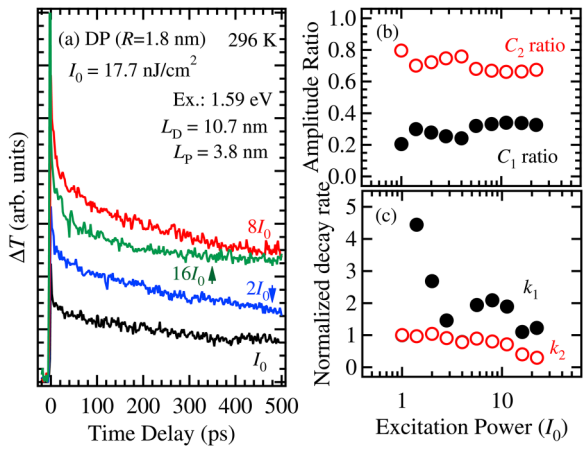

FIG. 5. (a) Time-domain signal in the DP thin film. (b) C_1 and C_2 ratios as a function of excitation intensity. (c) k_1 and k_2 as a function of excitation intensity and normalized by the respective value obtained at I_0.

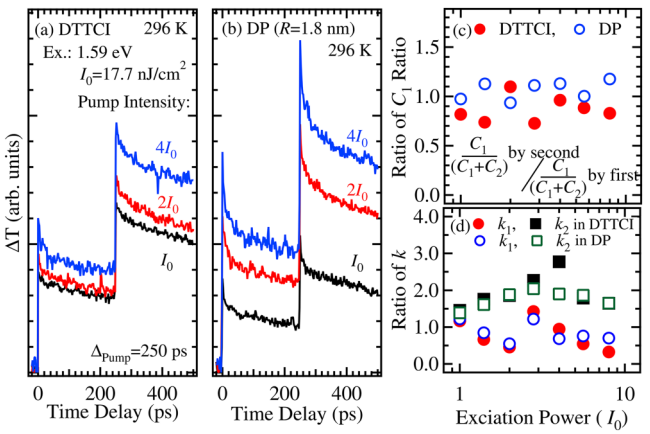

FIG. 6. Transmission change for several excitation intensities as measured by the double-pulse method in (a) DTTCI and (b) DP thin films. Δ_{pump} = 250 ps. (c) Ratio of the C_1 ratio for the second pulse to that for the first pulse in the DTTCI and DP thin films plotted as a function of excitation intensity. (d) Ratios of decay rates k_1 and k_2 plotted as a function of excitation intensity.

second pulse modifies k_2 more than k_1 in Figs. 3(c) and 3(d). This difference should be understood for designing devices.

The dependence of the parameters on the excitation intensity is caused by the interaction with the adjacent excited molecules. As the excitation intensity increases, the C_1 ratio (distribution to the fast component) increases. If the absorption saturation, causing the increase, decreases for some reason, the transmission change would not increase. However, as shown in Figs. 4(a) and 5(a), the transmission change increases, at least for excitation intensities less than $8I_0$. Thus, the decrease in the intramolecule decay due to the increase in the excitation intensity is not the main reason for the increase in the C_1 ratio. A possible explanation is the increase in interactions between adjacent excited molecules similar to the phenomenon of stimulated emission.[5] This increase causes the variation of k_1. For the DP thin film, k_1 is modified by the interaction with the PSA1411 molecules. In other words, the decrease in k_1 measured between $4I_0$ and $8I_0$ in Fig. 4(c) may correspond to the decrease between I_0 and $4I_0$ in Fig. 5(c). Considering that k_1 in the DP thin film is almost independent of R,[29,30] k_1 may almost reach the maximum value in the double-layer structure of the DP sample.

We now turn to the details of the exciton dynamics due to the second pulse. Figures 6(a) and 6(b) show the transmission change for the several excitation intensities measured by the double-pump method in the DTTCI and DP thin films, respectively.

To clarify the effect of the second pump, we analyzed the transmission change by fitting the data with the double-exponential function. We first discuss the change in the ratio of the populations in the two decay components. The ratio of the C_1 ratio for the second pulse to that for the first pulse in the DTTCI and DP thin films is plotted as a function of excitation intensity in Fig. 6(c). Both ratios are essentially constant. These ratios increase in both thin films with increasing the excitation intensity, as shown

in Figs. 4(b) and 5(b). This indicates the difference of the excitation process. As mentioned above, the first pulse does not excite all molecules within the laser spot. Therefore, while the second pulse efficiently excites the molecules in the ground state, which are not excited by the first pulse, a simple increase in the excitation power includes some loss of the power in the excitation process.

Next, we discuss the variation of the decay rates. Figure 6(d) shows the ratio of k_1 excited by the first pulse (solid circle) and k_1 excited by the second pulse (open circles) in the DTTCI and DP thin films. Furthermore, a ratio similar to that of k_2 in the DTTCI and DP thin films is shown by the closed and open squares, respectively. Although the data include a fragment, both samples show a similar dependence on excitation intensity. When the excitation intensity increases, the decay rate, in particular, k_2, can be a controllable parameter, this is different from the simple increase in the excitation intensity.

Δ_{pump} is also an important parameter to control the dynamics in both coherent and incoherent controls. Thus, we discuss the response by the second pulse as a function of pulse separation in the DP thin film, as shown in Fig. 7(a). Δ_{pump} was varied from 50 to 250 ps. The transmission change due to the second pulse for $\Delta_{pump} = 50$ ps is larger than that for $\Delta_{pump} > 150$ ps. Figures 7(b) and 7(c) show the results of the fitting by Eq. (1). The ratio of the C_1 ratio in Fig. 7(b) is almost constant for Δ_{pump}. This property is similar to that in Fig. 6(c).

Moreover, the ratios of k_1 and k_2 decrease with increasing the excitation intensity and with decreasing Δ_{pump}. From Fig. 6(b), we see that a decrease in Δ_{pump} corresponds to the increase in the excitation intensity. The tendency of the results in Fig. 7(c) is similar to that of Fig. 6(d) for intensities greater than $4I_0$. Therefore, in the double-pulse method, change in Δ_{pump} has an effect similar to change in the excitation intensity, thus suggesting that the sequential excitation opens the way for optical switches with low power consumption. On the other hand, focusing on the time response, the ratios of k_1 and k_2 are less than unity in the case of $\Delta_{pump} = 50$ ps, which indicates that the fast decaying component by the second pulse becomes slower than that by the first pulse. However, k_2 by the second pulse in the Δ_{pump} range larger than 100 ps is larger than that by the first pulse. This increase in k_2 is an advantage for the switching operation. Therefore, Δ_{pump} between 100 and 200 ps is better for the switching operation in our molecule combination.

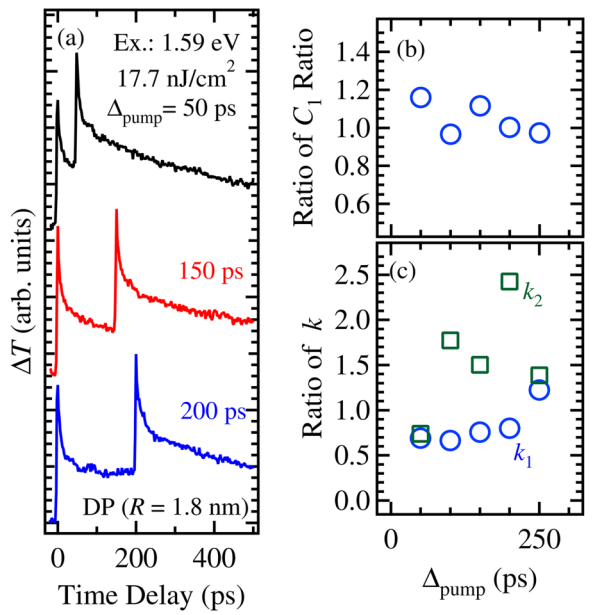

FIG. 7. (a) Transmission change for several Δ_{pump} in the DP thin film. (b) Ratio of the C_1 ratio as a function of Δ_{pump}. (c) Ratio of decay rates as a function of Δ_{pump}.

IV. CONCLUSION

We investigate the exciton dynamics as a function of excitation intensity and double-pulse excitation. The change in exciton dynamics due to the increase in the excitation intensity differs from the change induced by the second pulse. As the excitation intensity increases in the single pulse measurement, the population distribution to the fast decaying component increases, and the decay rate of the component varies with the intensity. On the other hand, in the case of the double pulse measurement, while the population distribution is almost constant for changing the excitation intensity and Δ_{pump}, the decay rate of a slow decaying component is changed by the second pulse. Our results indicate that the sequential excitation can reduce power consumption in the optical switching operation.

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