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超短パルスを用いたシアニン色素の新規反応経路の開拓と制御
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New photoreaction paths of indocyanine green in condensed phase

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The control of chemical reaction by light is one of the central themes of chemistry.　The recent development of the ultrafast laser technique has enabled researchers to observe elementary step of chemical reactions and control reaction dynamics in the femtosecond timescale [1].　In this study, we report newly found photo-isomerization path involving multiphoton excitation process and the intermediate states of the process investigated by two-color two-pulse excitation.

The potential barrier on the electronic excited state is one of the main factors which determine the reaction dynamics.　The potential barrier on the S_1 state of dye has been reported to hinder the isomerization [2].　The potential barrier is thought to be lower at higher electronic excited state [3], and the electronic excitation to S_n state, which is reached by the second harmonic (SH) of the fundamental pulse resonant to $S_1 \leftarrow S_0$ transition, increases the efficiency of trans-cis isomerization at model dyes, such as DODCI and DTTCI [3].

Recently, we found that the main trans-cis reaction path of indocyanine green (ICG) involves not one-photon but two-photon process of SH pulse corresponding to four-photon process of fundamental (NIR) pulse resonant to $S_1 \leftarrow S_0$ transition.　We also found that four-photon process of NIR pulse is involved in the main pathway under NIR irradiation condition.

Figure 1 shows the transient absorption spectrum of ICG pumped by fundamental femtosecond pulse (800 nm, 70 fs, 50 mJ/cm^2, 1 KHz) in ethanol.　The details of experimental setup are described elsewhere [4].　In figure 1, transient signals observed around 560 nm, 790 nm, and 880 nm are assigned as transient absorption (TA) by ICG leuco-forms, photo-bleaching of ICG in trans configuration, and TA by photo-produced cis-isomer, respectively [5].　Note that cis-isomer itself is produced within 2 ns [4] and the pump-probe delay time for our transient absorption measurement is 2.5 ns.

Figure 2 shows the NIR fluence dependence of absorbance change by cis-isomer.　It is clear from the figure that, although the saturation occurs with increasing the NIR power, the absorbance change is proportional to the NIR fluence to the forth power in the low power region.　This result is consistent with the fact that the absorbance change is proportional to the UV fluence to the second power as shown in figure 3.　These results clearly indicate that the highest electronic excited state (denoted by S_k) involved in the main trans-cis isomerization path is higher than S_0 by NIR four-photon energy.

Figure 4 shows the schematic diagram of trans-cis isomerization process derived from the observed results. Here we discuss the reason for the reaction paths to shift from single-photon processes to four-photon process.　In our study, femtosecond pulses were used and the pump photon flux during
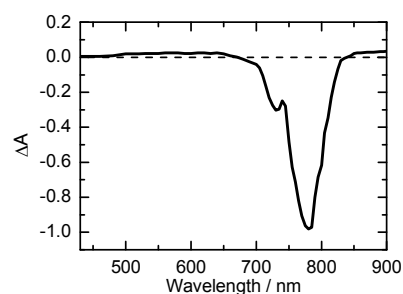

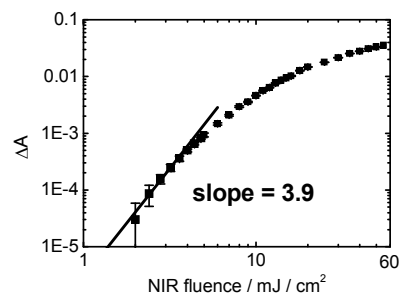Figure 1. Transient absorption spectrum of ICG in ethanol.

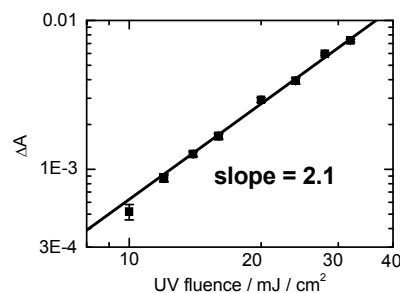Figure 2. NIR fluence dependence of cis-isomer production.

Figure 3. UV fluence dependence of cis-isomer production.

the irradiation was more than 10^7 times higher than those in previous studies using cw laser [5]. Thus, the number ratio of ICG molecules excited to high electronic states, such as S_k, by NIR multiphoton processes to those excited to S_1 by NIR one-photon process should be much larger in our study than in previous studies. According to Rulliere-Velsko-Fleming model that is generally applicable to symmetrical carbocyanine dyes, the energetic barrier against photoisomerization is lower at higher singlet electronic excited state [3]. As a result, the amount of cis-isomer produced in the new reaction path via S_k state overcame the amount of cis-isomer produced in the conventional path via S_1 state and the new reaction path became the main reaction path in our study.

For further understanding of multiphoton process in the new photo-isomerization path, we measured UV-NIR two-pulse correlation (2PC) on the absorbance change at 880 nm (cis-isomer) as shown in figure 5(a). The 2PC trace shows clear pump-pump interval dependence. Figure 5(b) shows the UV pump fluence dependence of the cross term. In the figure, the results of the least square fit to a model function are also shown. The model function was a convolution between the time profiles of pump pulses and exponential decay functions corresponding to the relaxations at intermediate states. Both in positive and negative NIR-UV delay regions, the traces are well reproduced by the combination of two decay components. The time constants of the decay components are 1.0 and 0.1 ps, respectively. The former time constant is consistent with the lifetime of S_n state of ICG molecule reported as 1.2 ps [6]. This lifetime reflects the intramolecular deactivation from S_n state to vibronic S_1 state. The relaxation of vibronic S_1 state is slower than the intramolecular deactivation of S_n state for dye molecules [8]. Figure 6 shows the initial amplitude of the fast decay component (0.1 ps). The initial amplitude is almost proportional to the UV pump fluence. This result indicates that the fast decay component represents relaxation dynamics on S_n state. The vibrational relaxation on S_n state should be responsible for this fast decay component.

In the presentation, the multiphoton processes in the production of ICG leuco-forms as well as the photoproducts from other dye molecules will be also described.

References

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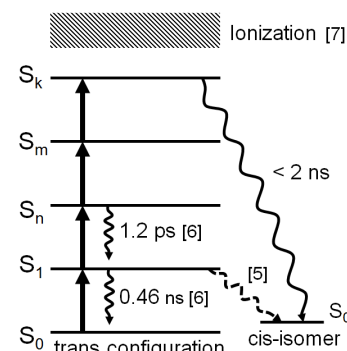
Figure 4. Newly found trans-cis reaction pathway via S_k. Arrows with straight line represent NIR pumping. Conventional pathway is shown with an arrow with dashed line from S_1.
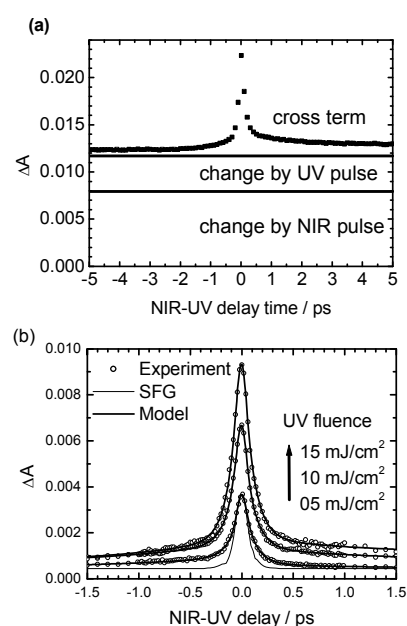

Figure 5. NIR-UV two-pulse correlation trace of absorbance change by cis isomer; (a) The NIR and UV pump fluences are 10 and 15 mJ/cm^2, respectively. In figure 5(b), 2PC traces of the cross term are drawn. The thin and thick lines represent the NIR-UV SFG signal from BBO crystal and the results of the least square fit to the model function, respectively.
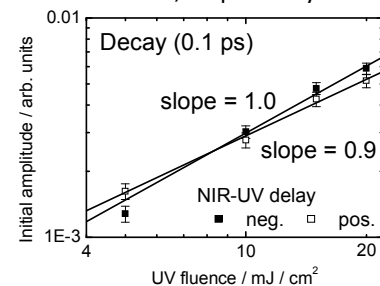

Figure 6. Initial amplitude of the decay component with the time constant of 0.1 ps in figure 5(b).