

超短パルスを用いたシアニン色素の多光子退色反応機構の解明
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Multiphoton photodegradation of indocyanine green in condensed phase

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Carbocyanine dyes have been extensively studied and synthesized for more than a century [1]. Among them, indocyanine green (ICG) is one of the most intensively investigated dyes and this near-infrared (NIR) laser dye has quite low quantum yields of isomerization and degradation from the S_1 state [2,3]. Thus, ICG molecules are used to detect specific cancers in human bodies [4].

Recently, we found that the quantum yield of ICG trans-to-cis photoisomerization was drastically increased by femtosecond NIR multiphoton excitation [5,6]. However, the photodegradation dynamics of ICG molecules has not been investigated thoroughly. In this paper, we reveal that the main photodegraded species are ICG fragments and the timescale of the photodegradation is 14 ps. We also reveal that the optical order of NIR electronic excitation changes from two to four with increasing the pump fluence.

Fig. 1 shows the transient absorption spectrum of ICG pumped by NIR femtosecond pulse (800 nm, 70 fs, 40 mJ/cm², 1 KHz) in ethanol. The details of experimental setup are described elsewhere [5]. In Fig. 1, transient signals observed around 560 nm, 790 nm, and 890 nm are assigned as transient absorption (TA) by ICG leuco forms, photobleaching (PB) of ICG in trans configuration, and TA by photo-produced cis isomers, respectively [6]. Note that leuco forms and cis isomers were produced within 2 ns [6] and the pump-probe delay for our transient absorption measurement was 2.5 ns.

Fig. 2 shows the NIR fluence dependence of absorbance change by ICG photoproducts and PB. In the fluence region lower than 3 mJ/cm², the absolute of absorbance change by PB was proportional to the pump fluence to the second power; in the leuco forms, it was proportional to the third power; and in the cis isomers, it was proportional to the fourth power. These results indicate that the main photodegraded species were produced by the NIR two-photon process and the species were not the leuco forms but the photo-fragments.

Fig. 3 shows the absolute ratios of absorbance changes in Fig. 2. ICG leuco forms and cis isomers were produced by NIR three-photon and four-photon processes, respectively. The absolute ratio of absorbance change (open circles, leuco forms/photobleaching) increased with the increase of the pump fluence to 4 mJ/cm². Then, the ratio decreased. On the other hand, the absolute ratio of absorbance change (closed squares, cis isomers/photobleaching) increased with the increase of the pump fluence to 10 mJ/cm² and leveled off thereafter. These results indicated that the optical order of the

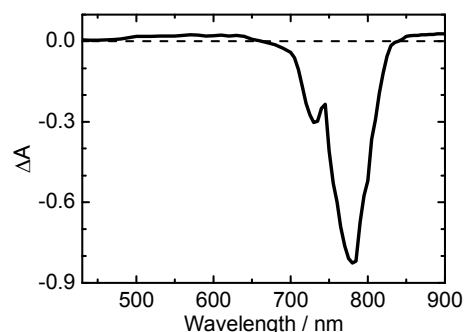


Fig. 1. Transient absorption spectrum of ICG in ethanol.

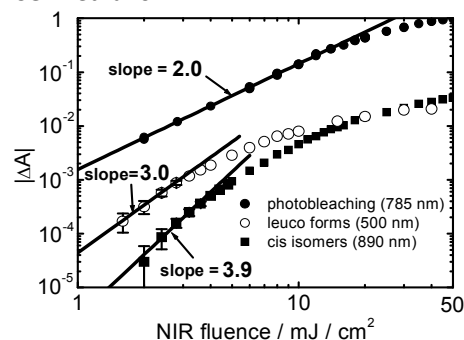


Fig. 2. NIR fluence dependence of absorbance change by ICG photoproducts.

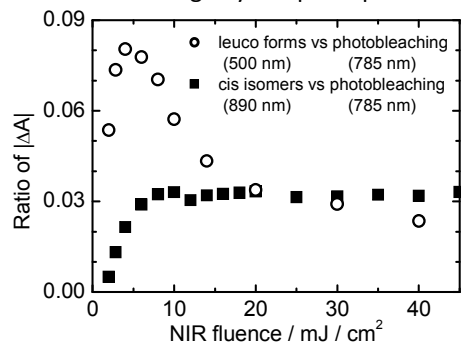


Fig. 3. Ratio of absorbance changes by ICG photoproducts to that of photobleaching.

electronic excitation by the NIR pump pulse in the main photodegradation reaction changed as $2 \rightarrow 3 \rightarrow 4$ with the increase of pump fluence. However, the results did not mean that the main photodegraded species were ICG leuco forms or cis isomers in the high fluence region. The absolute of the absorbance change by PB is much larger than those by the ICG photoproducts in Fig. 1 where the fluence was 40 mJ/cm^2 . This result indicates that the main photodegraded species were ICG fragments even in the high fluence region.

Fig. 4 shows the schematic diagram of the newly found multiphoton reaction paths of ICG molecules in ethanol. The timescales of the relaxation processes from the electronic excited states investigated by us and other groups are also described [2,3,5,6]. The timescale of ICG photodegradation from electronic excited states higher than S_1 state has not been investigated. In the following, we investigated the relaxation process from high-order singlet states to the ground state of the photodegraded species by pump-probe measurement on PB.

Fig. 5 shows the absolute change by PB at 785 nm as a function of pump-probe delay. The pump fluence was 10 mJ/cm^2 . Under the femtosecond NIR irradiation of 10 mJ/cm^2 , the fragments were mainly produced by the NIR four-photon process as indicated above. With the increase of the delay time, the absolute of the absorbance change decreased. The temporal profile was reproduced well by the model function consisting of three exponential decay components and a constant background. The time constants of the three decay components were 1.4 ps, 14 ps, and 485 ps. The time constants of 1.4 ps and 485 ps were consistent with the lifetimes of ICG molecules at the S_n and S_1 states, respectively. The lifetime of ICG molecules at singlet electronic excited states higher than the S_n state was shorter than that at S_n state of 1.4 ps [6]. Thus, the decay component of 14 ps was thought to represent the relaxation dynamics from the singlet system to other electronic systems or the dynamics at electronic excited states outside of the singlet system of trans configuration. In this study, we observed photoproducted ICG leuco forms, cis isomers, and fragments. The timescales for leuco form production and cis isomer productions were $< 10 \text{ ps}$, and $1\text{-}2 \text{ ns}$, respectively [6]. Moreover, the singlet system for the ICG cis isomer is expected to be similar to that for the ICG trans isomer [6,7]. Thus, newly found decay component of 14 ps should represent the relaxation dynamics in the multiphoton photodegradation process from the S_k state of the trans singlet system.

References [1] W. West, *Photograph. Sci. Eng.* 18 (1974) 35. [2] S. H. Ashworth et al., *J. Chem. Phys.* 104 (1996) 5761. [3] H. Gratz et al., *J. Photochem. Photobiol. A: Chem.* 128 (1999) 101. [4] T. Sugie et al., *Cancers* 2 (2010) 713. [5] M. Fuyuki et al., *Chem. Phys. Lett.* 499 (2010) 121. [6] M. Fuyuki et al., *J. Photochem. Photobiol. A: Chem.* 252 (2013) 152; *RSC Adv.* 3 (2013) 7313. [7] M. Wittmann and A. Penzkofer, *Appl. Phys. B* 65 (1997) 761.

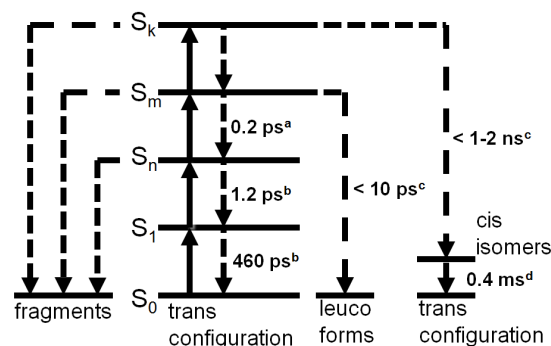


Fig. 4. Newly found ICG multiphoton reaction pathways. Arrows with straight line represent NIR pumping. Arrows with dashed line represent relaxation processes. ^aref. 5, ^bref. 2, ^cref. 6, ^dref. 3.

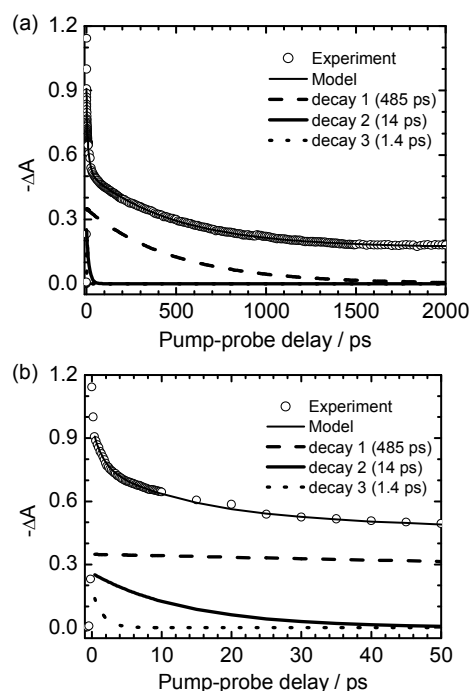


Fig. 5. Absorbance change by ICG photobleaching at 785 nm as a function of pump-probe delay. (b) Magnified view of (a). The pump fluence was 10 mJ/cm^2 .