

# Multiphoton reaction of DTTCI observed by femtosecond pump–probe and two-pulse correlation measurements



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## ABSTRACT

To understand the elementary steps of chemical reactions, unimolecular reactions are important and considered to be model reactions. We carried out pump–probe and two-pulse correlation (2PC) measurements of the multiphoton-induced reaction of DTTCI (3,3'-diethyl-2,2'-thiatricarbocyanine iodide), a kind of cyanine dyes, under the red-tail excitation condition and found that both photoisomerization and photodegradation were caused by a two-photon process and the reaction time for photoisomerization was approximately 0.5 ns. Excitation dynamics was examined by 2PC measurements and the temporal character of the intermediate state was analyzed.

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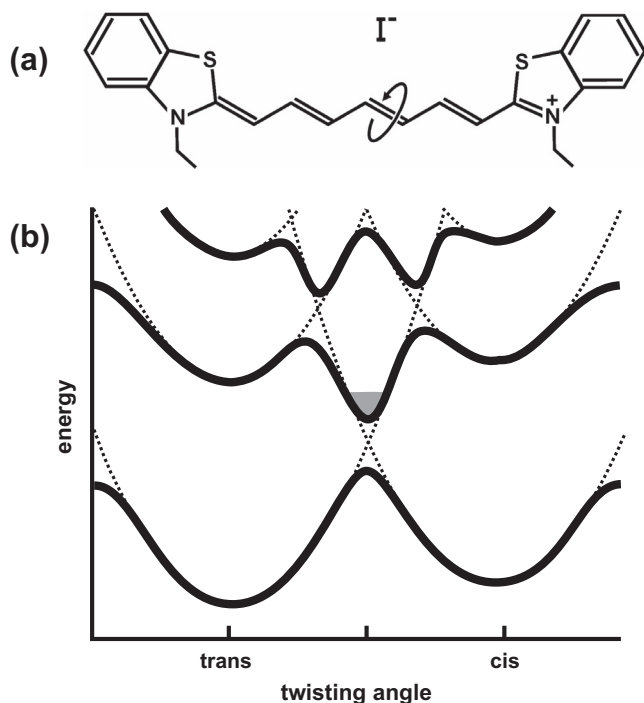
## 1. Introduction

Unimolecular reactions, such as photodissociation and photoisomerization, are important to understand the elementary steps of chemical reactions, and substantial effort has been dedicated to reveal the reaction mechanisms [1–5]. Photochemical reactions initiated by multiphoton absorption, i.e., multiphoton chemical reactions, are essentially different from conventional photochemical reactions because the character of the populated state depends on the optical order of the excitation process and new photochemical reaction channels are opened through the excitation of reaction intermediates. In this regard, knowledge of the contribution of the multiphoton process to photochemical reactions is necessary to exploit new photochemical reaction pathways, and the multiphoton process is expected to play a vital role in the optical control of chemical reactions. For instance, the photochromic reaction efficiency of a diarylethene derivative is strongly dependent on the optical order of the excitation process [6–8] and under femtosecond excitation, the main reaction pathway for the photoisomerization of indocyanine green (ICG), a cyanine dye, is higher than a three-photon process [9–11].

Cyanine dyes, such as DTTCI (3,3'-diethyl-2,2'-thiatricarbocyanine iodide) depicted in Fig. 1(a), are one of the model compounds for studying trans-to-cis photoisomerization. As the well accepted model, their photoisomerization process proceeds through the twisting around the central C–C bond in the conjugated chain as shown in Fig. 1(a) [12,13]. Fig. 1(b) shows a typical energy diagram concerned with the photoisomerization of cyanine dyes [14–18]. The photoisomerization process is briefly explained as follows. When the dyes in the thermodynamically stable trans conformation are excited to the excited singlet ( $S_1$ ) state, the relaxation to the potential minimum called sink region (shaded area in Fig. 1(b)) occurs through the twisting motion [12,13]. Then, molecules in the sink region undergo nonradiative transition back to the electronic ground state. On the ground state potential, molecules either relax back to the trans conformation or form a cis-isomer [19,20]. DTTCI is a cyanine dye that shows an absorption peak at 760 nm and the isomerization occurs by photoexcitation to the  $S_1$  state [21,22]. Photoisomerization products, however, are usually observed when the molecules are excited on the blue side of the absorption band [22,23]. Based on the models of Rulliere [18] and Velsko and Fleming [17], the results mean that the barrier lies along the reaction coordinate, namely twisting angle for isomerization in the  $S_1$  state and the excess energy is insufficient for isomerization by photoexcitation at the photon energy lower than the peak of absorption band [16]. Thus, it was considered that by photoexcitation at the red tail of its absorption band, DTTCI would be suitable for the study of multiphoton reactions in the  $S_1 \leftarrow S_0$  res-

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**Fig. 1.** (a) Molecular structure of DTTCI. (b) Schematics of the potential energy curves for DTTCI as a function of the twisting angle around the central C–C bond. The shaded area represents the sink region of  $S_1$  state.

onance condition while suppressing the reaction signal produced by the one-photon process.

In this study, we examined the multiphoton-induced reactions of DTTCI, such as photoisomerization and/or photodegradation by red-tail excitation, using a femtosecond near-infrared (NIR) pulse. Pump–probe transient measurements revealed that the isomer and the leuco form were generated through the two-photon process and the reaction time for the photoisomerization was 0.5 ns. The photoisomerization process was investigated by two-pulse correlation (2PC) measurements, in which the sample was excited by two pump pulses (pump–pulse pair) and pump-induced change was monitored by a probe pulse as a function of the interval between the two pump pulses [9,10,24–27]. Through this technique, knowledge of multiphoton excitation dynamics was obtained from a correlation peak profile. We analyzed the two-photon excitation process and the temporal behavior of the intermediate state.

## 2. Experimental

Details of 2PC experiments were described elsewhere [9,10,27]. Briefly, the light source was a Ti:sapphire regenerative amplifier (Spectra-Physics, Spitfire Pro); repetition rate, 1 kHz; wavelength, 794 nm; duration, 120 fs; and pulse energy, 1 mJ. The output pulse was separated into three pulses. One was used to generate a white light continuum as the probe pulse by irradiation of a water flow cell. The remaining two pulses were used as the pump pulse for 2PC measurements and one of the two pump pulses was used as the pump pulse for conventional pump–probe measurements. The pump pulses were subjected to ON/OFF modulation with a mechanical chopper at 500 Hz. The two pump pulses and one probe pulse were focused on a sample after passing through the optical delay lines. The sample was a free jet of DTTCI (0.5 mM) in methanol with a thickness of approximately 0.3 mm to minimize thermal effects on the sample. The transmitted probe pulse was detected by a photomultiplier after passing through a

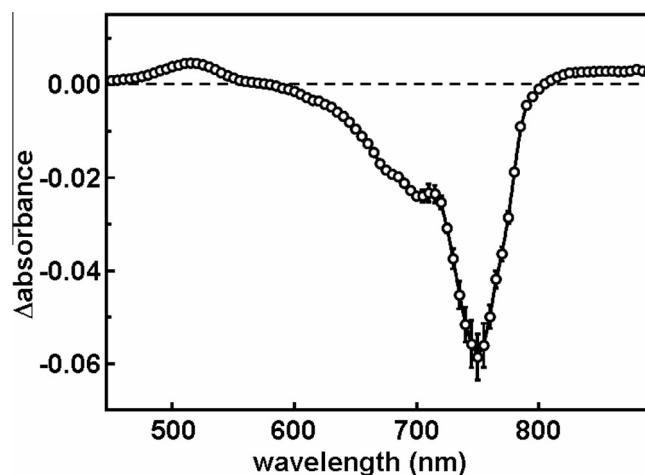
polarizer and a monochromator. The pump-induced transmission change of the probe pulse was measured as a function of pump pulse interval by a lock-in amplifier.

## 3. Results and discussion

Fig. 2 shows a transient absorption (TA) spectrum obtained by a single NIR pump pulse ( $46 \text{ mJ/cm}^2$ ) at the probe delay time of 5 ns, at which the  $S_1$  state of the trans conformation fully relaxed because the  $S_1$  state lifetime was reported to be 1.22 ns [28]. Three transient signals were observed: a photo-bleaching band at around 760 nm and long-lived TAs at around 500 nm and longer than 820 nm. The TA observed at around 820 nm was assigned to the absorption of the cis-isomer ground state, as described below. In a previous research by Fouassier et al. [13], the cis-isomer absorption was observed as a broad peak at around 800 nm and therefore, TA observed at around 820 nm was assigned to the red tail of the cis-isomer absorption peak whose main part was immersed with the strong photo-bleaching band at around 760 nm. Although  $T_n \leftarrow T_1$  absorption is also thought to be a candidate for the origin of the transient absorption [21], cyanines were known as molecules in which the formation of the triplet state is small or negligible [20]. Even if the triplet state were generated, the  $T_n \leftarrow T_1$  absorption peak would appear at around 860 nm [29] and be longer than the relevant wavelength (820 nm). Thus, the contribution of triplet state to TA at around 820 nm could be ruled out.

In the visible region, TA ranging from 450 nm to 560 nm was attributed to a leuco form that had a partly substituted conjugated chain, based on a report of the photogeneration of a leuco form of indocyanine green (ICG). ICG has a similar structure to DTTCI and the same conjugated chain length as DTTCI, and the generated leuco form has an absorption at around 540 nm [30]. Regarding the triplet species, its contribution was ruled out based on the reason described above [20]. Although the short-lived 520 nm absorption is well known in DTTCI [31], to our knowledge, this long-lived absorption at around 520 nm is observed for the first time in this work. For further investigation of this long-lived species, accurate measurements of lifetime and transient vibrational spectra and theoretical treatment based on quantum chemistry are necessary. Then, in this study, we focused on the photoisomerization process from trans to cis conformation observed at around 820 nm and conducted experiments to reveal the reaction rate and the order of the optical process for the generation of the cis-isomer.

Fig. 3 shows temporal profiles of transient signal intensities for the probe delay time of 0–5 ns at the wavelengths of 520 nm (TA



**Fig. 2.** Transient spectrum of DTTCI observed at the delay time of 5 ns. Solid line is a guide for the eyes.

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