Ultrafast Energy Transfer in LH2 Photosynthetic Antenna Conjugated with Artificial Fluorescent Dyes

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Abstract: Femtosecond transient absorption spectroscopy was carried out for energy transfer in photosynthetic purple bacteria LH2 antenna complex conjugated with artificial fluorescent dyes. Time constants of 3 ps and 18 ps were obtained by global analysis.
OCIS codes: (300.0300) Spectroscopy; (300.6530) Spectroscopy, ultrafast

1. Introduction

Harvesting solar energy could be one of the solutions for the energy problem that the humanity faces today, although its conversion efficiency is still quite low. Artificial adaptation of the highly sufficient photosynthetic reactions of plants, algae, and photosynthetic bacteria is recently getting considered seriously. The solar emission peaks around 500 nm covering the entire visible wavelength range of 400-800 nm and spreads into the ultraviolet and infrared range. Light-harvesting complex 2 (LH2) is the primary photoacceptor in the photosynthetic antenna system of the purple bacteria [1]. The chromophore of LH2 consists of carotenoids that absorbs light in the range of 400-550 nm and two types of bacteriochlorophylls B800 and B850 which absorb light at 800 nm and 850 nm, respectively. As can be seen in the absorption spectrum of LH2 shown in Fig. 1, there is a gap in the spectrum at the range of 620-750 nm, where the light absorbance is low. By attaching artificial dyes to LH2 that absorb light in the gap, it is possible to expand the available wavelength range, if the efficiency of dye→LH2 energy transfer is sufficiently high. In this study, Alexa Fluor 647, with maximum absorbance at ca. 650 nm with a molar extinction coefficient of ca. 2×10^5 L mol^{-1} cm^{-1}, was covalently bonded to LH2 (Fig. 1b). From steady state absorption and emission measurements, the quantum yield of the energy transfer was estimated to be ca. 0.85. To elucidate the dynamics of energy transfer in detail, femtosecond transient absorption (TA) measurement was carried out.

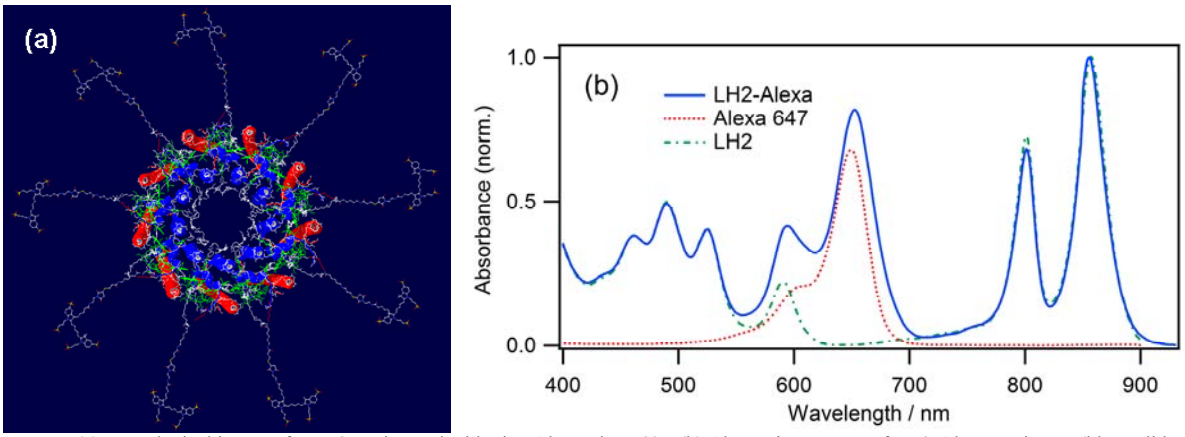

Figure 1. (a) Hypothetical image of a LH2 conjugated with nine Alexa Fluor 647. (b) Absorption spectra of LH2-Alexa conjugate (blue solid curve), Alexa Flour 647 (red dotted curve), and LH2 (green dotted and dashed curve).

2. Experimental methods

The laser system used in this work has been described in detail previously[2]. The output of a femtosecond Ti:Sapphire laser (Tsunami, Spectra-Physics) pumped by the SHG of a cw Nd^{3+}:YVO_4 laser (Millennia V, Spectra-Physics) was regeneratively amplified with 1 kHz repetition rate (Spitfire, Spectra-Physics). The amplified pulse was equally divided into two pulses by a beam splitter and sent to a pair of non-collinear optical parametric amplifiers (TOPAS-White, Light Conversion). The pulse centered at ca. 650 nm with a pulse duration of 17 fs

generated from one of the TOPAS-White was used as the pump pulse. White-light supercontinuum was generated from a 1 mm thick CaF plate by focusing the beam centered at ca. 1000 nm generated from the other TOPAS-White. The signal and the reference pulses were detected with multichannel diode array systems (PMA-10, Hamamatsu) and sent to a personal computer for further analysis. Spectra were calibrated for group velocity dispersion numerically based on the optical Kerr measurement between the pump pulse and the white-light continuum.

Alexa Fluor 647 with maleimide group (Invitrogen) was conjugated to the SH group attached to the lysine residue of the α-polypeptide of LH2 (*Rhodopseudomonas acidophila*). The number of the dyes conjugated to a single LH2 is estimated to be nine and the hypothetical image of LH2-Alexa conjugate is shown in Fig. 1a. Although in this figure, nine Alexas are homogeneously stretched out from the C-terminal region, the actual configuration could be distributed randomly around LH2.

3. Results and discussion

The TA spectra of LH2-Alexa conjugate excited at 650 nm are shown in Fig. 2 in the time range of femtoseconds to nanoseconds. Immediately after the photoexcitation, ground state bleach and stimulated emission of Alexa appears in the range of 590-750 nm. The TA spectrum that peaks at 455 and 515 nm is assigned to the excited state absorption of Alexa by comparison with that of the free Alexa Flour 647. These features decay in the picosecond time scale and simultaneously taken over by new TA and stimulated emission at 840 and 860nm, respectively, which can be assigned to B850 bacteriochlorophyll. The weak bleach at 800 nm could be that of B800, while any feature related to the carotenoid was unobservable.

The global analysis was carried out with double exponential functions and the obtained time constants for the energy transfer were ca. 3 ps and 18 ps with relative ratio of approximately 1:2. This result indicates that Alexas are not homogeneously organized as shown in Figure 1a but distributed in different configurations with different transfer efficiencies. It can be expected that, if Alexa could be attached only to the ideal configuration, energy transfer will occur with the shortest time constant. The photosynthetic membrane of most purple bacteria contains two types of light-harvesting complexes, LH1 and LH2. LH1 surrounds the reaction center (RC) and LH2 transfers energy to the RC by way of LH1. The time constant for intercomplex LH2→LH2 energy transfer is considered to be a few picoseconds, while that of LH2→LH1 is 3-5 ps and the final LH1→RC transfer is 35 ps [1]. It can be said that the time constants for Alexa→LH2 energy transfer is comparable to those in the natural photosynthetic membrane.

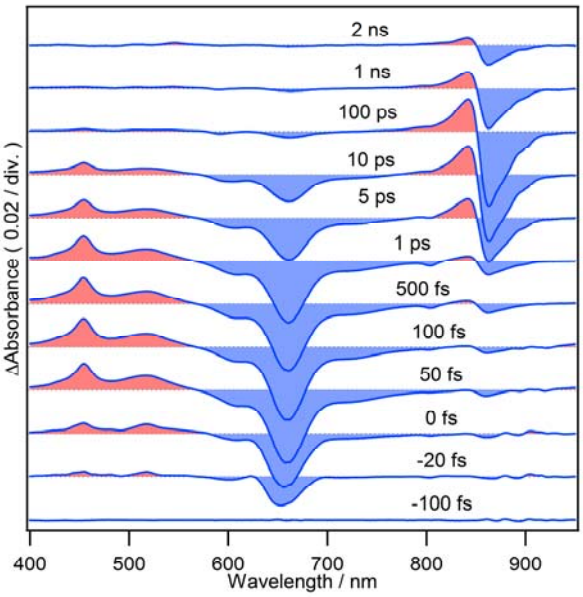

Figure 2. Femtosecond transient absorption (TA) spectra of LH2-Alexa conjugate from femtosecond to nanosecond time range excited at 650 nm with pulse duration of 17 fs.

4. References

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