http://dx.doi.org/10.5012/bkcs.2014.35.3.703

Ultrafast Energy Transfer in Chlorosome Probed by Femtosecond Pump-Probe Polarization Anisotropy†

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Received September 25, 2013, Accepted October 18, 2013

Key Words : Chlorosome, Light harvesting complex, Energy transfer, Pump-probe polarization anisotropy

Energy transfer in photosynthetic light harvesting complexes (LHCs) has attracted much interest because of its technological potential in solar cell applications and a recent proposal that quantum coherence might play a role in achieving energy transfer of extraordinarily high efficiency.[1] Among various natural photosynthetic LHCs, chlorosomes are the largest and the most efficient LHCs found in nature.[2] Chlorosomes consist of bacteriochlorophyll (BChl) *c*, *d*, *e*, and *f* molecules self-assembled into supramolecular J-type aggregates without any protein, which is in contrast to other pigment-protein LHCs. This unique architecture allows us to easily synthesize chlorosomes and their chemically modified analogs, which can be used as building elements of artificial photosynthesis.[3] On the other hand, the large size of chlorosome prevents the determination of its supramolecular structural organization at the molecular level, and the exact arrangement of BChl molecules in chlorosome is still in controversy with the proposed models of curved lamellar structures and/or multi-layered rolls.[4,5]

Pump-probe polarization anisotropy probes the time evolution of the transition dipole orientation of photoexcited molecules in real time using a pair of linearly polarized laser pulses separated by a time delay. In particular, when the measurement is performed for an ensemble of molecules, the average orientation of the transition dipoles of individual molecules is obtained. Therefore, this technique has been mainly used for measuring the rotational diffusion dynamics of molecules, but it can also effectively probe the dynamics of excitation energy transfer in multi-chromophore systems such as conjugated polymers and photosynthetic LHCs.[6] Especially, pump-probe polarization anisotropy is one of the methods that can uniquely detect electronic coherence created among the excited states, which is considered to play an important role in efficient energy transfer of molecular aggregates, in the form of coherent oscillations superimposed on its decay.[7]

Previously, pump-probe polarization anisotropy has been applied to various types of chlorosomes.[8,9] From those studies, two major decay components were identified on the time scales of ~1 ps and ~10 ps. These kinetic components were attributed to layer-to-layer (or roll-to-roll) energy transfer and/or energy transfer from chlorosome to the baseplate. However, although it was reported that ultrafast energy transfer occurs on sub-ps time scale in chlorosomes,[9,10] any faster decay dynamics of polarization anisotropy have not been reported yet, partly due to limited time resolution (> 100 fs) of the previous studies. In this work, in order to probe the dynamics of excitation energy transfer on ultrafast time scale, we apply pump-probe polarization anisotropy to chlorosome from *Chlorobaculum* (*Cba.*) *limnaeum* using the laser pulses of 15 fs duration.

The details of the pump-probe polarization anisotropy experiment performed at room temperature are described in the Supporting Information (SI). Figure 1(a) shows the wavelength-resolved polarization pump-probe signals measured with the polarizations of pump and probe pulses parallel ($S_{\parallel}$) and perpendicular ($S_{\perp}$) to each other. Then, we integrated each of these signals with respect to the probe wavelengths in the range of 710-750 nm and obtained the integrated polarization pump-probe signals shown in Figure 1(b). From these polarization pump-probe signals, we obtained the transient polarization anisotropy, $r(T)$, using the following formula as shown in Figure 1(c):

$$r(T) = [S_{\parallel}(T) - S_{\perp}(T)] / [S_{\parallel}(T) + 2S_{\perp}(T)] \quad (1)$$

The transient anisotropy exhibits an initial value, $r(0)$, of 0.30 at $T = 0$ fs and rapidly decays to 0.27 within 100 fs. The anisotropy decay was fit by a single exponential with the time constant of 25 ± 9 fs. We were not able to identify any distinct coherent oscillation superimposed on the decay, mainly due to limited signal-to-noise ratio of our transient anisotropy signal along the population time T.

We note that $r(0)$ is lower than 0.4, which is the theoretical maximum value of polarization anisotropy for a two-level system. The polarization anisotropy value reflects the degree of order of the transition dipole orientations of constituent chromophores in a multi-chromophore system; therefore,

†This paper is to commemorate Professor Myung Soo Kim's honourable retirement.

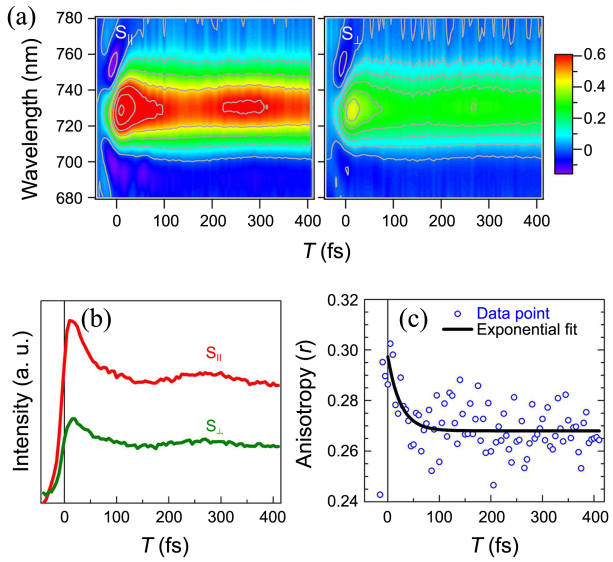

Figure 1. (a) Wavelength-resolved polarization pump-probe signals, $S_{\parallel}$ (left panel) and $S_{\perp}$ (right panel), measured with the polarizations of pump and probe pulses parallel and perpendicular to each other, respectively. (b) Wavelength-integrated polarization pump-probe signals, $S_{\parallel}$ (red line) and $S_{\perp}$ (green line). (c) Transient anisotropy $r(T)$ (empty dots) obtained from $S_{\parallel}$ and $S_{\wedge}$ and its fit by an exponential decay and an offset (black line).

more random orientations of the transition dipoles would give a lower anisotropy value. The initial anisotropy value lower than 0.4 is commonly observed in conjugated polymers.[11] Like conjugated polymers, chlorosomes have significant structural disorder and defects, resulting in an assembly of coherent domains (where the exciton is delocalized) of various sizes. As a result, chlorosomes will have a broad distribution of excitation energies (manifested as a broad absorption band in Figure S1 in the SI). Such large static heterogeneity can cause rapid localization of initial excitation into coherent domains of large sizes (and thus lower energies). If such localization is faster than the time resolution of our experiment (15 fs), the initial value of transient anisotropy would be low as in our data.

The 25-fs decay component of the transient anisotropy has never been identified for chlorosomes, partly due to limited time resolution (> 100 fs) of the previous studies. Considering that the decay component is much faster than the processes of layer-to-layer or roll-to-roll energy transfer processes, which occur on the time scale of picoseconds, it must be related with energy transfer within a BChl layer. From an atomistic calculation for model chlorosomes consisting of BChl molecules forming multilayered rolls, a similarly fast decay of transient anisotropy was observed.[12] This theoretical result proposes that the initial step of energy transfer occurring in a BChl layer of chlorosome is of ultrafast nature, probably due to strong electronic coupling between BChl monomer units. The time scale of the anisotropy decay observed in this work is also in good agreement with ultrafast line shape dynamics (20-30 fs) revealed in the 2D spectra of chlorosomes using two-dimensional electronic spectroscopy.[10,13] In those studies, the fast line shape dynamics were attributed to downhill energy transfer through a ladder of exciton states of various energies. Specifically, it was suggested that such ultrafast energy redistribution of initial excitation can occur only within and/or among coherent domains in the close proximity in the same BChl layer, mainly from smaller domains (of high energies) to larger ones (of low energies).

In conclusion, by using pump-probe polarization anisotropy, we measured the ultrafast energy transfer dynamics in chlorosome from *Cba. limnaeum*. The 25-fs decay can be attributed to energy transfer within and/or among coherent domains in individual BChl layers of chlorosome.

Acknowledgments. This work was supported by Institute for Basic Science (IBS) [CA1401-01]. This work was supported by an Inha University Research Grant (INHA-48581). This work was partially supported by Grants-in-Aid for Scientific Research (A) (No. 22245030) as well as on Innovative Areas "Artificial Photosynthesis (AnApple)" (No. 24107002) from the Japan Society for the Promotion of Science (JSPS).

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