Energy Transfer Dynamics of Photosystem II Dimer Revealed by Femtosecond Transient Absorption Spectroscopy

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Photosynthesis has been supplying energy to almost all of the life on Earth. Elucidation of the reaction dynamics and mechanism in natural systems is an important issue for the advanced utilization of the light energy in the artificial systems. Photosystem II core complex (PSII-CC) is one of the representative natural systems of the membrane-protein complex, which plays a crucial role in primary processes in photosynthetic reaction, i.e., light harvesting, charge production and oxidation of water. PSII-CC consists of antenna polypeptides CP43 and CP47, which contain 13 and 16 chlorophyll *a* (Chl) molecules, and D1/D2-cytb559 reaction center (RC) polypeptides. Correlation between the excellent photofunctional dynamics and the precise structure of PSII-CC is quite important problem to be clarified.[1] Although the typical PSII takes a dimeric form, detailed functionalities of the dimer have not yet been elucidated. In the present work, we have investigated the role of the dimer by comparing the dynamics of PSII monomer and dimer by femtosecond transient absorption (TA) spectroscopy.[2]

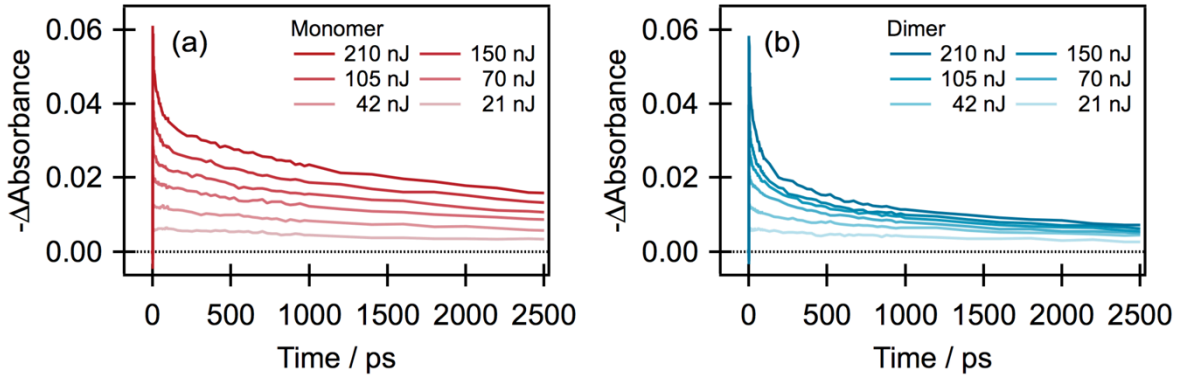

Figure 1. Time traces of transient absorbance of PSII-CC (a) monomer and (b) dimer probed at 676 nm with various excitation intensities of 21-210 nJ (excitation wavelength: 640 nm).

Figure 1 shows time traces of transient absorbance of PSII-CC monomer and dimer probed at 676 nm (bleaching signal of the ground-state Chl) with various excitation intensities. Fast recovery of the bleaching signal of the ground-state was pronounced with increasing excitation intensities which is attributable to singlet-singlet annihilation. Although no significant difference was observed in weak excitation intensity conditions, rapid recovery of the bleaching signal is more clearly observed at higher excitation intensities for the dimer, indicating that energy transfer between subunits (the monomer) takes place in the dimer.

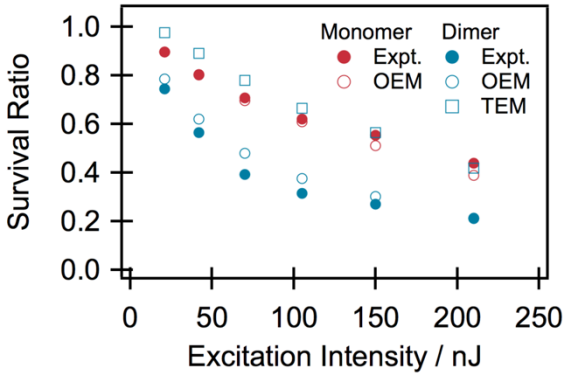

Figure 2. Calculated (open circles and squares) and experimentally obtained (closed circles) survival ratio of Chl excitons.

To quantitatively elucidate the dynamics in detail, we have estimated the decrement of exciton. Figure 2 shows survival ratio of excitons, S_{Ratio}, which is defined as numbers of excitons after the annihilation divided by that of the initially excited ones. Smaller value of S_{Ratio} indicates more effective quenching of excitons by the annihilation. The experimental S_{Ratio} is the ratio of bleached ground state absorbance before and after the annihilation (Fig. 1 closed circles). S_{Ratio} was also calculated based on binomial theorem, i.e., the probability for the production of j excitons in a single PSII-CC particle, P_j ($0 \leq j \leq n$), can be calculated as $P_j = {}_n\mathrm{C}_j a^j (1-a)^{n-j}$. Here a is the initial ratio of excited Chls against all the Chls, n is the number of Chls in a single particle (n=35 for the monomer and n=70 for the dimer). If excitons in a single PSII-CC particle decrease to one exciton by annihilation, survival ratio can be calculated as $S_{\mathrm{Ratio}} = \Sigma P_j / \Sigma j P_j$ (one exciton model, OEM, Fig. 2 open circles). The remaining exciton induces charge separation (CS) in the RC, thus, S_{Ratio} is also the ratio of produced CS state against the number of initial excitons. In the case of PSII-CC dimer, two CS states can be produced from two remaining excitons, because a dimer contains two RCs (two excitons model, TEM, Fig. 2 open squares). For both monomer and dimer, OEM reproduces the experimental results significantly well. This indicates that only one CS state remains after annihilation in spite of two RCs being involved in PSII-CC dimer. Efficient annihilation might reflect that dimer has better protection ability to quench excess energy. We will also discuss the energy transfer dynamics of beta-carotene at the conference.

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References:

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