

A Regulation of Energy Flow in Purple Bacterial Photosynthetic Antennas

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Abstract: Ultrafast energy transfer dynamics in photosynthetic antennas were investigated by femtosecond pump-probe measurements. Photo-excited carotenoids with short-polyene chains efficiently transfer energy to bacteriochlorophylls, while the energy rapidly dissipates to carotenoids in antennas containing longer carotenoids.

OCIS codes: (260.2160) Energy transfer; (320.7150) Ultrafast phenomena

1. Introduction

Carotenoids (Cars) are naturally occurring photosynthetic pigments that play the two important roles of light-harvesting (LH) and photo-protection in photosynthesis of plants, algae, and bacteria [1]. Cars absorb sunlight in the blue-green regions of the spectrum and efficiently transfer it to nearby bacteriochlorophyll *a* (Bchl *a*). The S_0 ground state of Cars has A_g^- symmetry assuming that their linear polyene backbone has C_{2h} point group symmetry. The lowest singlet excited state, S_1 ($2^1A_g^-$), is optically forbidden, therefore the S_2 ($1^1B_u^+$) state is the lowest optically allowed state. The ultrafast spectroscopic measurements on purple bacterial LH complexes proposed that the singlet-singlet excitation energy transfer (EET) from Car to Bchl *a* involves two pathways of $S_2 \rightarrow Q_x$ and $S_1 \rightarrow Q_y$. The overall efficiency of Car \rightarrow Bchl *a* EET has been reported to be 30~100% depending strongly on number of conjugated double bonds n of the Cars involved [1]. Recently, we reported a new EET pathway of Bchl *a* $Q_x \rightarrow$ Car S_1 in LH1 from *Rhodospirillum (Rsp.) rubrum* S1 involving the Car, spirilloxanthin (Spx) with $n=13$ [2]. The reverse EET pathway of Bchl *a* $Q_x \rightarrow$ Car S_1 in LH2 has been also confirmed by broadband two-dimensional electronic spectroscopy [3]. The $Q_x \rightarrow S_1$ EET is rather efficient (40 %) in LH1 from *Rsp. rubrum* S1, whereas this channel is almost closed in LH2 from *Rhodobacter (Rba.) sphaeroides* 2.4.1, containing spheroidene (Sph) with $n=10$ [4]. These results imply that the EET of $Q_x \rightarrow S_1$ depends on n . In this study, the reverse EET dynamics in LH2 complexes containing Car with different n were investigated by femtosecond pump-probe spectroscopy.

2. Experimental

Femtosecond pump-probe measurements were carried out using a mode-locked Ti:Sapphire laser system [5]. Excitation pulses were obtained from an optical parametric amplifier. A white continuum probe pulse was generated using a 5.0 mm sapphire plate. The instrument response function was determined to be less than 100 fs. The isolated LH2 complexes were dispersed in 20mM Tris-HCl buffer with detergents to avoid aggregation. The samples were circulated in a 1.0 mm optical path length flow cell. All measurements were performed at room temperature.

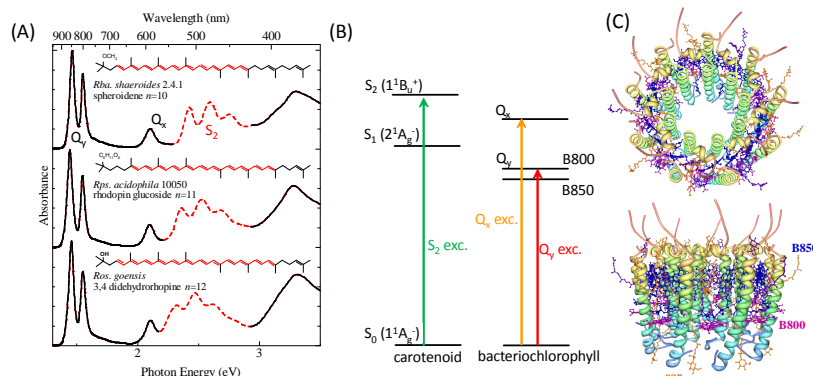


Fig.1. (A) Steady-state absorption spectra of LH2 complexes. Insets show the chemical structures of carotenoids contained in antenna complexes. (B) Energy diagrams of carotenoid and bacteriochlorophyll *a*. (C) The crystal structure of LH2 from *Rps. acidophila* 10050.

Table 1. The obtained EET rates of each pathway in LH1 and LH2.

	$S_2 \rightarrow Q_x$	$S_1 \rightarrow Q_y$	$Q_x \rightarrow S_1$
<i>Rba. sphaeroides</i> 2.4.1 (LH2)	$(166 \text{ fs})^{-1}$	$(2.1 \text{ ps})^{-1}$	-
<i>Rps. acidophila</i> 10050 (LH2)	$(130 \text{ fs})^{-1}$	$(18 \text{ ps})^{-1}$	$(262 \text{ fs})^{-1}$
<i>Ros. goensis</i> (LH2)	$(216 \text{ fs})^{-1}$	$(40 \text{ ps})^{-1}$	$(177 \text{ fs})^{-1}$
<i>Rsp. rubrum</i> S1 (LH1)*	$(111 \text{ fs})^{-1}$	-	$(75 \text{ fs})^{-1}$

*The EET rates in LH1 from *Rsp. rubrum* S1 was reported in Ref 2.

3. Results and Discussion

Figure 1 shows the steady-state absorption spectra of three different LH2 complexes. The absorption bands ranging from 2.1 eV to 3.0 eV are originated from the S_0 - S_2 transition of Cars, depending on n . Bchl a has three distinct absorption bands at 3.3 eV (Soret), 1.9 eV (Q_x), and 1.4 eV (Q_y). Two absorption bands of Q_y originate from the two different Bchl a molecules assemblies of LH2 (called as B800 and B850 shown in Fig. 1(C)) [1]. Figures 2(A)-(C) represent the photo-induced absorption (PIA) spectra, taken at 0.5 ps upon excitation either to S_2 , Q_x , or Q_y . The PIA spectra of all LH2 complexes excited into S_2 contain the S_1 - S_n and T_1 - T_n transient absorption and ground state bleaching signals of Cars. In the PIA spectra after excitation into Q_x of Bchl a , the S_1 and T_1 transient absorption and the ground state bleaching of Cars were also observed, owing to the reverse $Q_x \rightarrow S_1$ energy transfer [2,6]. To clarify the transient signals due to Cars in the PIA spectra, the difference spectra between the Q_y and Q_x excitations were examined. The Q_y state of Bchl a is lower lying than S_1 of Cars (Fig. 1(B)), thus the $Q_y \rightarrow S_1$ EET is negligible. In the difference spectrum (lower panels of Figs. 2(A)-(C)), the transient signals due to Cars, the S_1 and T_1 transient absorption and the ground state bleaching, obviously depend strongly on n . Table 1 and Fig. 2(D) summarized the EET rates and efficiencies of each pathway in the LH2 complexes determined by the analysis of the kinetic traces of the transient signals. The LH2 complexes containing the short carotenoid ($n=10$) efficiently transfer the absorbed energy to Bchl a , and then Car \rightarrow Bchl a EET efficiencies decrease with n . On the other hand, the reverse Bchl \rightarrow Car EET is negligible in LH2 containing the short carotenoid ($n=10$), while the reverse EET becomes efficient (40%) with n . In conclusion, the ultrafast EET dynamics between Cars and Bchl a in the LH2 complexes have been investigated by femtosecond pump-probe measurements. The results suggest that LH2 containing the short carotenoid has an efficient light-harvesting function, while that the long polyene carotenoids bound to LH complexes regulate an excess energy of Bchl a .

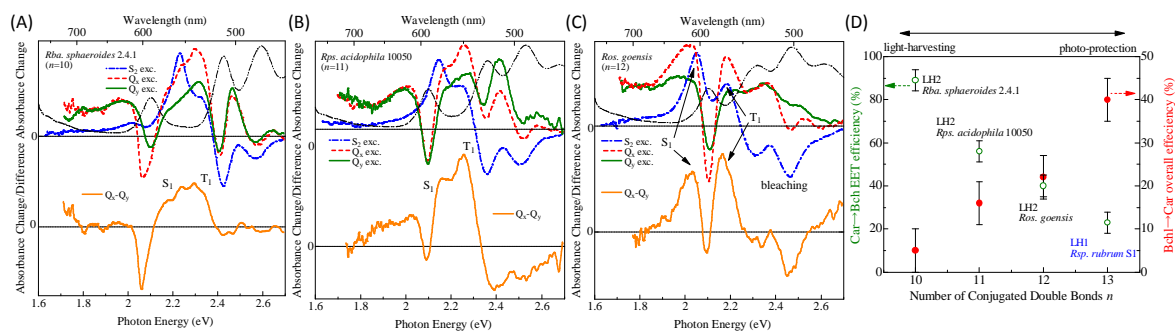


Fig. 2. (A)-(C) PIA spectra of the LH2 complexes upon excitation either to S_2 , Q_x , or Q_y , taken at 0.5 ps. Lower panels represent difference spectra between Q_x and Q_y excitations. (D) EET efficiencies of Car \rightarrow Bchl and Bchl \rightarrow Car as a function of n .

4. References

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