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Journal of Photochemistry and Photobiology A: Chemistry 178 (2006) 271–280
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

A single chlorophyll in each of the core antennas CP43 and CP47 transferring excitation energies to the reaction center in Photosystem II of photosynthesis

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Available online 15 December 2005

Abstract

Trapping of pigment excitation energies in the core antenna by the reaction center (RC) in Photosystem II (PS II) is a process rate-limiting in the whole primary processes of photosynthesis until initial excitation-energy fixation by charge separation in the RC. It takes place from a single chlorophyll (Chl) in each of transmembrane protein–pigment complexes CP43 and CP47, which compose the core antenna separately attached to each of the two pigment strands 1 and 2 in the RC, respectively. Its excitation energies are transferred to the accessory Chl (B) or the adjacent pheophytin (H) in each of the strands. These features unique in PS II can be rationalized to have arisen as a byproduct of the requirement that the oxidized state P^+ of the central Chl pair P in the RC must have an exceptionally high redox potential for extracting an electron from water only in PS II. These features were clarified by reproducing the observed rate constant of excitation-energy trapping by the RC from the core antenna. Playing important roles here is the excitation spectrum of each pigment in the RC obtained by analyzing the absorption spectrum of the RC [K. Saito, K. Mukai, H. Sumi, Chem. Phys. Lett. 401 (2005) 122], on the basis of the observed pigment-energy arrangement therein. Here, the excited state B^* of B is lowest in the RC with H^* locating a little ($\sim$40 cm^{-1}) higher, while P^* is considerably ($\sim$180 cm^{-1}) higher in association with the very high redox potential of P^+, although only P carries an exciton as P^* on this Chl dimer in the RC.

Keywords: Photosystem II; Core antenna; Reaction center; Excitation-energy trapping; Accessory chlorophyll

1. Introduction

Photosynthesis is the ultimate energy source for all creatures on Earth. Main organisms for photosynthesis in green plants and algae are the Photosystem I (PS I), II (PS II) and the cytochrome b_6f complex, all of which are complexes of protein multisubunits penetrating the thylakoid membrane. In PS II, solar radiation energy harvested by the antenna system is utilized to extract an electron from water in its oxygen-evolving center. The electron is used to reduce a quinone to a hydroquinone in its reaction center (RC). The hydroquinone is released into the matrix space within the thylakoid membrane to be transferred to the cytochrome b_6f complex where the strong reducing power of the hydroquinone is utilized to pump protons against the transmembrane electrochemical-potential difference. Simultaneously with the proton pumping, an electron is transferred from the b_6f complex to PS I which penetrates the same thylakoid membrane. In the RC core of PS I, the electron is photoexcited to produce a strong reductant (NADPH), by which carbon dioxide is reduced to carbonhydrate in Carvin–Benson's dark-reaction cycle. Three-dimensional structures of both PS I and II were recently disclosed one after another in 2001 by X-ray crystallographic studies [1–3]. Such clarification has stimulated intensive researches for understanding initial light-reaction processes of photosynthesis on the standpoint of their relation to structure.

Proteins comprising both PS I and II scaffold pigments therein as active centers, which are mostly chlorophylls (Chls). Solar radiation energy is harvested as excitation of pigments in the antenna system of PS I and II. Pigment excitation energies in the antenna system are arranged in a funnel structure as to decrease toward the core antenna which encloses the RC. Excitation energies harvested flow down toward the core antenna along the funnel, and are trapped by the RC [4], where they are utilized to produce charge separation against the transmembrane electrochemical potential gradient along an electron-transfer chain of pigments as the initial energy fixation.

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doi:10.1016/j.jphotochem.2005.10.038

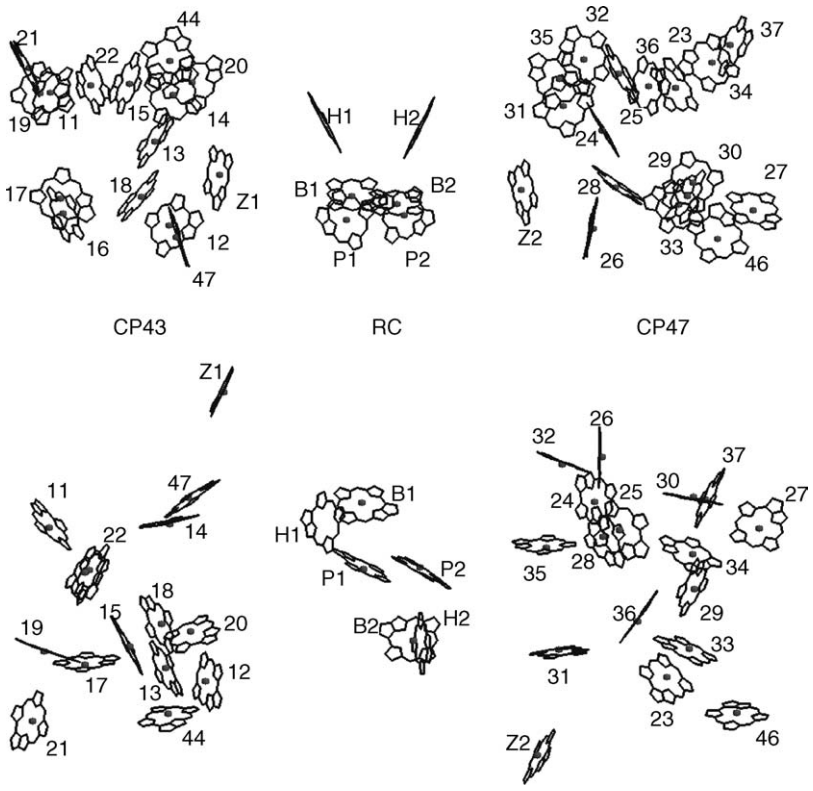

Fig. 1. Arrangement of pigments in the RC and Chls in the core antenna which is composed of CP43 and CP47 in PS II, obtained from the X-ray data in 1S5L.pdb associated with [15]. The upper and the lower halves are its projection to the direction parallel and perpendicular to the membrane plane, respectively. Numbering of Chls in the core antenna is in accordance with [15].

Shown in Fig. 1 is arrangement of pigments in the RC and that of Chls in the core antenna in PS II, where the core antenna is composed of CP43 and CP47 [2,3], each of which is a transmembrane protein-pigment complex. The present work is devoted to clarifying how different the pathway of excitation-energy transfer is from the core antenna to the RC in PS II in comparison with that in other photosystems in photosynthesis. As the first step of the clarification, it is important to see how peculiar the energetics in PS II is in comparison with other photosystems.

Photosynthesis is performed also in phototropic prokaryotes [4], although oxygen is not evolved therein, since an electron is extracted not from water, but from less stable substances such as hydrogen sulfides. Phototropic prokaryotes are equipped with only one photosystem for photosynthesis, according to which they are classified into two groups [5]. Solar radiation energies harvested by the antenna system are utilized to excite the electron in the RC for reducing a quinone to a hydroquinone in one group, and for producing a strong reductant (NADH) in the other group, as in PS II and in PS I of green plants and algae, respectively. The hydroquinone and NADH, thus, produced in the former and the latter, respectively, are utilized as in oxygenic photosynthesis of green plants and algae, that is, to pump protons against the transmembrane electrochemical-potential difference and to reduce carbon dioxide to carbonhydrate in Carvin–Benson's dark-reaction cycle, respectively. As understood from these functional differences, the photosystem in the former bacteria and PS II, and the photosystem in the latter bacteria and PS I have evolved from common ancestors.

Purple bacteria are among the former, for which the three-dimensional structure of both the RC [6] and the antenna system [7] has been clarified since 1984. Heliobacteria and green sulfur bacteria are among the latter, but the three-dimensional structure of their photosystems has not been clarified yet. When the three-dimensional structure of PS II was clarified in 2001, therefore, it has been anticipated that differences between oxygenic photosynthesis in green plants and algae, and anoxygenic one in phototropic prokaryotes will soon be clarified on the basis of the three-dimensional structure of the photosystems concerned. Unfortunately, however, such an anticipation has not been satisfied yet, since arrangement of pigments in the RC has turned out to be essentially similar between the photosystem in purple bacteria and PS II, in spite of the fact that they are opposite to each other in evolution of oxygen. Accordingly, such a difference in function between them must be rationalized from the standpoint of invisible differences in energy structure in the pigment assembly between them, not from that of visible differences in the three-dimensional pigment arrangement therein.

The key difference in the energy structure for distinguishing between the photosystem in purple bacteria and PS II should be derived from a feature that after excitation-energy trapping by the RC from the antenna system, the RC gets a redox potential sufficiently high to extract an electron from water in PS II, but in both the bacterial photosystem and PS I. Water is such a stable

substance that the redox potential for its oxidation is as high as ∼0.9 V at pH 6. To extract an electron from water, therefore, the excitation-energy trapping by the RC must lead to producing a substance therein whose redox potential is higher than ∼0.9 V. In the RC of PS II, such a substance is the oxidized state of the central Chl pair P which is produced as a result of charge separation occurring after the excitation-energy trapping by the RC. In PS II, the redox potential of the P^+/P couple in the RC amounts to ∼1.2 V, which is the highest in biological organisms [8]. In both the bacterial photosystem and PS I, it is only ∼0.5 V [8].

To accomplish such a high redox potential of the P^+/P couple in PS II, it is necessary that the positive charge of P^+ is screened neither by surrounding negative charges nor by easily-polarizable amino-acid residues in the protein matrix in the RC. This means that the surrounding of P in the RC is constructed to be very hydrophobic. As a byproduct in such a surrounding, the excitation energy of P cannot help being elevated in PS II. Such an expectation has in fact been confirmed by recent site-directed mutagenesis studies which have clarified that the excited state P^* of P is not lowest in energy in the PS II RC [9,10], differently in both the bacterial photosystem and PS I.

It is very interesting, then, which pigment gives the lowest excitation energy in the PS II RC. It was shown simultaneously by the mutagenesis studies in [9] that the lowest excitation energy therein is given by the accessory Chls, represented by B_1 and B_2 (called together B hereafter), which are located adjacent to the central Chl pair P in the two pigment strands 1 and 2, respectively, in Fig. 1. The same feature was pointed out already earlier than [9] by site-selective fluorescence-spectrum analyses [11], and it was derived recently also by pigment-modification studies [12] and by theoretical fitting of optical spectra [13]. Excitation energies intermediate between P and B in the PS II RC are given by pheophytins, represented by H_1 and H_2 (called together H hereafter), which are located next to B_1 and B_2 in the chain of P, B and H in the two pigment strands 1 and 2, respectively, as also seen in Fig. 1.

In both the bacterial photosystem and PS I, the central pair P of pigments in the RC constitutes a strong dimer with an intermolecular distance significantly shorter than others therein, with a center-to-center distance of 6–7 Å [1,6], especially called the special pair in the bacterial photosystem. The situation looks a little different in the PS II RC, since the intermolecular distance in the central pair of Chls, P_1 and P_2 in Fig. 1, is similar to other nearest-neighbor distances therein, at ∼8–10 Å depending on X-ray data of resolution at 3.5–3.8 Å [2,3,14,15]. This feature has let many people consider that excited states of the pigment assembly in the PS II RC might be multimers [16] on the basis of diagonalization of a Hamiltonian for the pigment assembly with assumed equal site energies without energy-broadening interactions [17,18]. In reality, energy broadening of these excited states brought about by interaction with static disorders and protein-matrix vibrations should be essential in judging whether they are multimers or not. In [19], therefore, that of each excited state was determined so as to reproduce the observed absorption spectrum of the PS II RC on the basis of the excitation energies of individual pigments experimentally determined in [9]. Thereby, the character of the excited states of the pigment assembly in the PS II RC was determined as a dimer for the excited state P^* of the central Chl pair P and monomers for excited states of other pigments. As a byproduct of such characterization, we obtained also the spectral forms of all the excited states of the pigment assembly in the PS II RC.

In both the bacterial photosystem and PS I, excitation energies in the core antenna are directly transferred to the central pigment pair P which constitutes a strong dimer with an excitation energy lowest among the excited states of the pigment assembly in the RC [4]. In the PS II RC, however, the excitation energy of the central pair P of Chls is not lowest, and the lowest excitation energy therein is given by the accessory Chl, B, although the pheophytin H has an excitation energy between B and P, as mentioned before. In PS II, the core antenna is composed of CP43 and CP47 shown in Fig. 1, and they are separately attached to the side of the pigment strands 1 and 2 in the RC, respectively. Pigments in the RC are arranged nearly in the two-fold rotational symmetry along the two strands 1 and 2, and Chls in CP43 and CP47 are arranged also nearly symmetrically in tune with the near two-fold rotational symmetry in the RC. In this situation, it seems reasonable to consider that the pigment strand of P_1, B_1 and H_1 traps pigment excitation energies from CP43, and that of P_2, B_2, and H_2 traps those from CP47.

The rate of excitation-energy transfer (EET) can be described by Förster's overlap integral between the fluorescence spectrum of the excitation donor and the absorption spectrum of the excitation acceptor [20], when the donor and the acceptor are well separated from each other in comparison with their physical sizes [21,22]. Since both CP43 and CP47 can be split out from the RC in PS II, their optical properties can individually be investigated. It has been observed [23,24] that the fluorescence spectrum of both CP43 and CP47 peaks just at the excitation energy of B determined in [9]. This means that excitation-energy trapping by the RC from the core antenna takes place mainly by resonant EET from CP43 to B_1 and that from CP47 to B_2. The excitation spectrum of both B_1 and B_2 in the RC has been determined in [19] in the course of characterization of the excited states in the pigment assembly in the RC. These informations will enable us to determine which pigments in CP43 and CP47 transfer excitation energies to B_1 and B_2, respectively, in the PS II RC, as done in the next section of the present work. Section 3 will be devoted to discussions on peculiarities of PS II in trapping of excitation energies from the core antenna and their initial fixation in the RC in comparison with those in the bacterial photosystem and PS I. Summaries are put as Section 4.

2. Excitation-energy trapping by the RC from the core antenna in PS II

Since the fluorescence spectrum of the core antenna peaks just at the absorption peak of B in the PS II RC, main acceptors in EET from the core antenna to the RC should be B in the RC. But, H is only ∼40 cm^{-1} higher than B, although the lowest exciton state on P is ∼180 cm^{-1} higher. The energy broadening of these states is ∼130 cm^{-1} for both B and H, and ∼120 cm^{-1} for P at room temperature [19]. Both B and H are located nearer to core-antenna Chls than P, as seen in Fig. 1. As also seen therein,

two Chls Z_1 and Z_2 in the RC are so remote from the central part of the RC where charge separation takes place for initial excitation-energy fixation. Therefore, they do not participate in excitation-energy trapping by the RC from the core antenna. Looking at these situations, the rate constant of the excitation-energy trapping from the core antenna can be considered to be estimated by taking into account not only the resonant EET to B, but also the near resonant EET to H, in each of the pigment strands 1 and 2 in the RC.

The rate constant of excitation-energy trapping by the RC has been observed to be not smaller than $(\sim 25\,\mathrm{ps})^{-1}$ from CP47 at room temperature [25]. Although that from CP43 has not been observed yet, it should have a magnitude similar to that from CP47, since CP43 and CP47 are attached nearly symmetrically to the pigment strands 1 and 2, respectively, in tune with their near two-fold rotational symmetry in the RC. It will be shown in this section that these magnitudes of the rate constant, together with the excitation spectra of both B and H in the RC, and the observed fluorescence spectra of the core antenna, enables us to determine core-antenna Chls which transfer excitation energies to the RC at room temperature.

We first determine the necessary condition for such Chls by reproducing the rate constant of the EET not smaller than $(\sim 25\,\mathrm{ps})^{-1}$ under an assumption that they give rise to the observed fluorescence spectra of the core antenna. Thereby, we can determine a single Chl transferring excitation energies from each of CP43 and CP47 to the RC. We will show, subsequently, that it must satisfy also the sufficient condition.

In the excitation-energy trapping by the RC from the core antenna, energies in CP43 are trapped by B_1 or H_1 in the pigment strand 1, and those in CP47 are trapped by B_2 or H_2 in the pigment strand 2. These pigments (B_1, H_1, B_2 and H_2) are monomers as acceptors in the excitation-energy trapping. Let us represent the excitation (i.e., absorption) spectrum of one of them as $A_j(E)$ as a function of excitation energy E for $j = B_1$, H_1, B_2 or H_2, whose position vector is represented by $\boldsymbol{R}_j$. Taking the spectrum as normalized to unity, by $\int A_j(E)\,\mathrm{d}E = 1$, we put its transition dipole $\boldsymbol{\mu}_j$ aside.

Donors in this EET are Chls which give rise to the peak of observed fluorescence from the core antenna at room temperature. Since such core-antenna Chls have not been identified yet, we have considered two possibilities of either a monomer or a dimer. The latter was considered to be possible only on a pair of Chls with a sufficiently large intermolecular EET interaction shown concretely in the next third paragraph.

Let us first consider that the fluorescence peak of the core antenna is brought about by a monomer, whose position vector and transition dipole are represented by $\boldsymbol{R}$ and $\boldsymbol{\mu}$, respectively. In this case, EET for the excitation-energy trapping by the RC takes place from the monomeric donor in the core antenna to a monomeric acceptor at the position vector $\boldsymbol{R}_j$ with the transition dipole $\boldsymbol{\mu}_j$. Distances between any Chl in the core antenna and any pigment in the RC, except remote Chls Z_1 and Z_2, are larger than ∼20 Å in the structure of PS II determined by X-ray crystallographic studies. In this situation, the matrix element of the EET mentioned above can adequately be approximated by the electrostatic interaction between these two transition dipoles [20–22], as:

$$J(\boldsymbol{R}_j, \boldsymbol{R}) = (\varepsilon|\Delta\boldsymbol{R}_j|^3)^{-1}\left[\boldsymbol{\mu}_j\cdot\boldsymbol{\mu} - 3\frac{(\boldsymbol{\mu}_j\cdot\Delta\boldsymbol{R}_j)(\boldsymbol{\mu}\cdot\Delta\boldsymbol{R}_j)}{|\Delta\boldsymbol{R}_j|^2}\right], \tag{2.1}$$

with $\Delta\boldsymbol{R}_j = \boldsymbol{R}_j - \boldsymbol{R}$, where ε represents an appropriate dielectric constant, which can be approximated by that at a frequency corresponding to the excitation energy in the EET. In the present work, ε was taken at 2.4 [$=(1.55)^2$] by accepting a value taken in [26–28]. The magnitude of the transition dipole was taken at the square root of $21.0D^2$ for a Chl and $16.0D^2$ for a pheophytin, which were measured in solution [29]. The direction of the transition dipoles was regarded as that connecting the two nitrogens on the pyrrole rings I and III of the chlorin macroring, and its position was regarded as the midpoint between these two nitrogens for both a Chl and a pheophytin, whose position has been determined by X-ray crystallographic studies [3,14,15]. The position vectors $\boldsymbol{R}_j$ and $\boldsymbol{R}$ were measured at the position of the transition dipoles determined above.

In the case that excitation-energy trapping by the RC takes place from a dimer of Chls in the core antenna, we represent the position vectors of two Chls composing the dimer by $\boldsymbol{R}_a$ and $\boldsymbol{R}_b$, with transition dipoles $\boldsymbol{\mu}_a$ and $\boldsymbol{\mu}_b$, respectively. The excited states of the dimer are composed of a lower and an upper exciton state, and the excitation energy associated with the fluorescence peak of the core antenna should be attributed to the lower exciton state. It will be shown later that a dimeric donor is not appropriate in reproducing a rate constant of the EET not smaller than $(\sim 25\,\mathrm{ps})^{-1}$. As a situation most efficient in the EET from the lower exciton state, therefore, we consider that the two Chls composing the dimer have a same excitation energy, where the exciton state is constituted by an amplitude of $\pm 1/\sqrt{2}$ for the excited state of each Chl comprising the dimer. As emphasized also in [21,22] for EET from B to P within the RC, the matrix element for the EET from the lower exciton state in the core antenna to the monomeric RC Chl at the position vector $\boldsymbol{R}_j$ with the transition dipole $\boldsymbol{\mu}_j$ is given by:

$$J(\boldsymbol{R}_j; \boldsymbol{R}_a, \boldsymbol{R}_b) = \frac{[J(\boldsymbol{R}_j; \boldsymbol{R}_a) \pm J(\boldsymbol{R}_j; \boldsymbol{R}_b)]}{\sqrt{2}}, \tag{2.2}$$

with $J(\boldsymbol{R}_j; \boldsymbol{R}_i)$ for $i = a$ or b in Eq. (2.1). Concerning the ± in Eq. (2.2), we take either + or − signs according to the magnitude of the right-hand side of Eq. (2.2) becoming as large as possible, in order that the EET from the exciton state becomes as efficient as possible.

From what pair of core-antenna Chls should we calculate the rate constant of EET to the RC? This dimer case should occur for a pair with a sufficiently large intra-pair EET interaction. Its magnitude can be estimated also by an approximation of transition–dipole interaction in Eq. (2.1), but the dielectric constant ε therein should be taken at a value much nearer to unity than 2.4 taken in Eq. (2.1) [19]. Moreover, broadening of the excitation energy of each Chl determined in the RC is at most $\sim 130\,\mathrm{cm}^{-1}$ at room temperature [19]. Taking into account these features, we have calculated the rate constant of EET to the RC from a pair of Chls with the intra-pair EET interaction larger

than ∼100 cm^{-1} for $\varepsilon = 1$, where the exciton splitting within the pair becomes considerably lager than ∼130 cm^{-1}, with a value larger than ∼200 cm^{-1}.

With $J(\boldsymbol{R}_j)$ representing $J(\boldsymbol{R}_j; \boldsymbol{R})$ for the monomeric donor or $J(\boldsymbol{R}_j; \boldsymbol{R}_a, \boldsymbol{R}_b)$ for the dimeric donor, the rate constant of EET from the donor in the core antenna to the acceptor at the position vector $\boldsymbol{R}_j$ in the RC is given by Förster's formula [20] of:

$$k = \frac{2\pi}{\hbar} J(\boldsymbol{R}_j)^2 \int A_j(E) F(E)\, \mathrm{d}E, \tag{2.3}$$

derived from Fermi's Golden Rule, where $A_j(E)$ represents the normalized absorption spectrum of the acceptor mentioned before, and $F(E)$ represents the observed fluorescence spectrum of either CP43 or CP47, also normalized to unity as $\int F(E)\, \mathrm{d}E = 1$.

By decomposing the absorption spectrum of the RC, its components contributed from B and H in the RC has been determined in [19] as a Gaussian form, with j = B and H, of

$$A_j(E) = (2\pi W^2)^{-1/2} \exp\left[\frac{-(E - E_j)^2}{(2W^2)}\right], \tag{2.4}$$

with

$$W^2 = W_\mathrm{S}^2 + \lambda \hbar\bar{\omega} \coth\left(\frac{\frac{1}{2}\hbar\bar{\omega}}{k_\mathrm{B}T}\right), \tag{2.5}$$

where W represents the width of the peak at energy E_j, and Eq. (2.5) represents that W^2 is composed of the static part W_S^2 due to inhomogeneous broadening brought about by static disorder and the remaining temperature-dependent part due to protein-matrix vibrations with an average energy quantum $\hbar\bar{\omega}$ in association with their reorganization by energy λ [30].

The average energy quantum $\hbar\bar{\omega}$ was taken at 50 cm^{-1}, as observed uniformly in many proteins [31,32]. Remaining parameters have been determined for maize and cyanobacterium *Synechocystis* PCC 6803 in [19], given by:

$$\left.\begin{array}{l} W_\mathrm{S} \approx 80\,\mathrm{cm}^{-1} \text{ and } \lambda \approx 22\,\mathrm{cm}^{-1}, \text{ for Synechosystis PCC 6803} \\ W_\mathrm{S} \approx 84\,\mathrm{cm}^{-1} \text{ and } \lambda \approx 25\,\mathrm{cm}^{-1}, \text{ for maize} \end{array}\right\}, \tag{2.6}$$

for both B and H at $E_j \approx 14663$ and 14706 cm^{-1}, respectively, in the RC. Here, B = B_1 or B_2, and H = H_1 or H_2, in tune with EET to the RC from CP43 or CP47, respectively.

To give $F(E)$ in Eq. (2.3), the fluorescence spectrum of the core antenna observed at room temperature [23,24] was fitted by a Gaussian shape [33] of

$$F(E) = (2\pi W_\mathrm{f}^2)^{-1/2} \exp\left[-\frac{(E - E_\mathrm{f})^2}{(2W_\mathrm{f}^2)}\right], \tag{2.7}$$

with

$$\left.\begin{array}{l} E_\mathrm{f} \approx 14665\,\mathrm{cm}^{-1} \text{ and } W_\mathrm{f} \approx 157\,\mathrm{cm}^{-1}, \text{ for CP43} \\ E_\mathrm{f} \approx 14640\,\mathrm{cm}^{-1} \text{ and } W_\mathrm{f} \approx 166\,\mathrm{cm}^{-1}, \text{ for CP47} \end{array}\right\}. \tag{2.8}$$

Eqs. (2.4) and (2.7) enable the integration in E in Eq. (2.3) to be performed into

$$k = \frac{2\pi J(\boldsymbol{R}_j)^2/\hbar}{[2\pi(W^2 + W_\mathrm{f}^2)]^{1/2}} \exp\left[-\frac{(E_j - E_\mathrm{f})^2}{2(W^2 + W_\mathrm{f}^2)}\right]. \tag{2.9}$$

Here, W is obtained from Eq. (2.5), where the set of W_S and λ given in Eq. (2.6) are a little different between *synechosystis* PCC 6803 and maize. Calculated values of k are not different more than six percent between the two cases. Accordingly, only values of k calculated with the set of W_S and λ for *synechosystis* PCC 6803 will be shown below.

Numbering of Chls in the core antenna is different in the three X-ray crystallographyic studies in [3,14,15]. We take hereafter the numbering in [15] shown in Fig. 1, simply because the publication of [15] is the latest although resolution in positional determination is almost the same among them at 3.8 Å in [3], 3.7 Å in [14] and 3.5 Å in [15].

Calculation of Eq. (2.9) were first performed for a pair of core-antenna Chls which can be considered as a candidate of a dimer by the criterion mentioned earlier. In this case, we could not obtain a value not smaller than (∼25 ps)$^{-1}$ as the rate constant of EET to the RC from any pair of core-antenna Chls. Calculated from the X-ray data in [15], for example, the largest rate constant from each of CP43 and CP47 are given by:

1. From a pair of Chl15 and Chl44 in CP43 to B_1 in the RC; (1240 ps)$^{-1}$.
2. From a pair of Chl29 and Chl33 in CP47 to B_2 in the RC; (333 ps)$^{-1}$.

Let us check positions of these Chls in Fig. 1. We have seen, thus, that any pair of Chls which can be regarded as a candidate of a dimer in the core antenna do not satisfy the condition as a donor which has been observed to transfer excitation energies to the RC with a rate constant not smaller than (∼25 ps)$^{-1}$.

Next, let us assume that a monomeric Chl in the core antenna transfers excitation energies to the RC, contributing to the fluorescence spectrum of the core antenna. Let us first investigate CP47 from which the rate constant of EET to the RC has been observed to be not smaller than (∼25 ps)$^{-1}$. Three largest values of k calculated by Eq. (2.9) are similar between [15] and [3] for pigment arrangement, being given by:

1. From Chl31 in CP47 to H_2 in the RC; (20 ps)$^{-1}$ in [15], (29 ps)$^{-1}$ in [3].
2. From Chl31 in CP47 to B_2 in the RC; (40 ps)$^{-1}$ in [15], (38 ps)$^{-1}$ in [3].
3. From Chl35 in CP47 to H_2 in the RC; (57 ps)$^{-1}$ in [15], (57 ps)$^{-1}$ in [3].

Let us check positions of these Chls in Fig. 1

Corresponding values of k for pigment arrangement determined in [14] are significantly different from those written above in both the magnitude order and their magnitudes themselves, as:

1. From Chl35 in CP47 to H_2 in the RC; $(61\,ps)^{-1}$ in [14].
2. From Chl31 in CP47 to H_2 in the RC; $(65\,ps)^{-1}$ in [14].
3. From Chl31 in CP47 to B_2 in the RC; $(359\,ps)^{-1}$ in [14].

These rate-constant values derived from the pigment arrangement determined in [14] do not satisfy the observation-based requirement that there must exist CP47 pigments which transfer excitation energies to the RC with a rate constant not smaller than $(\sim 25\,ps)^{-1}$. In this situation, we must consider that the pigment arrangement determined in [14] cannot be relied for reproducing the EET from CP47 to the RC. Both [15] and [3] indicate that only Chl31 in CP47 satisfy the requirement, enabling us to understand that in CP47 only Chl31 can transfer excitation energies to the RC with a rate constant larger than $(\sim 25\,ps)^{-1}$ at room temperature. Other Chls in CP47 cannot do so.

Next, let us proceed to see the situation in CP43 from which excitation energies are transferred to B_1 or H_1 in the RC. The value of the rate constant of this EET should be similar to that from CP47 to B_2 or H_2 in the RC, that is, not smaller than $(\sim 25\,ps)^{-1}$, from near symmetrical arrangement of pigments between CP47 and CP43 toward the pigment strands 2 and 1 in the RC, respectively. Three largest values of k calculated by Eq. (2.9) for pigment arrangement in [3,15] are given by:

1. From Chl14 in CP43 to B_1 in the RC; $(35\,ps)^{-1}$ in [3], $(42\,ps)^{-1}$ in [15].
2. From Chl20 in CP43 to H_1 in the RC; $(36\,ps)^{-1}$ in [3], $(38\,ps)^{-1}$ in [15].
3. From Chl14 in CP43 to H_1 in the RC; $(48\,ps)^{-1}$ in [3], $(41\,ps)^{-1}$ in [15].

Let us check positions of these Chls in Fig. 1. All of them seem to satisfy the requirement for transferring excitation energies to the RC with a rate constant not smaller than $(\sim 25\,ps)^{-1}$. The fourth largest one definitely does not satisfy the requirement, giving $(438\,ps)^{-1}$ from Chl12 in CP43 to B_1 in the RC in [3], and $(69\,ps)^{-1}$ from Chl47 in CP43 to B_1 in the RC in [15]. From the pigment arrangement in [14], we get:

1. From Chl14 in CP43 to H_1 in the RC; $(35\,ps)^{-1}$ in [14].
2. From Chl14 in CP43 to B_1 in the RC; $(50\,ps)^{-1}$ in [14].
3. From Chl47 in CP43 to B_1 in the RC; $(158\,ps)^{-1}$ in [14].

Here, only the first and the second largest values by Chl14 seem to satisfy the requirement as in [3,15], but Chl20 does not even appear in the list above.

In CP43, only Chl14 satisfies the requirement in the pigment arrangement determined in any of [3,14,15]. Chl20 definitely does not satisfy the requirement in the pigment arrangement determined in [14], although it seems to satisfy it in that determined in both [3,15]. For CP43, we conclude, accordingly, that Chl14 can surely transfer excitation energies to the RC with a rate constant not smaller than $(\sim 25\,ps)^{-1}$. It is less probable that Chl20 can additionally do so. Moreover, if this pathway of EET from Chl20 to H_1 in the RC is also comparably probable in CP43, it breaks the symmetry between CP47 and CP43 toward the RC, since a similar pathway definitely does not exists from CP47 to the RC. In these situations, we conclude that Chl20 in CP43 probably do not transfer excitation energies to the RC, together with other Chls except Chl14 in CP43.

Thus, we found only Chl14 in CP43 and only Chl31 in CP47 as satisfying the necessary condition that they can transfer excitation energies to the RC with a rate constant observed, if they emit the same fluorescence as observed for CP43 and CP47, respectively.

To render the necessary condition to the necessary-sufficient one, it might seem necessary to check also the sufficient condition that Chl14 in CP43 and Chl31 in CP47 really emit the same fluorescence as observed for CP43 and CP47, respectively. In reality, it is not necessary, since we have shown that it is only one Chl in each of CP43 and CP47 that satisfies the necessary condition mentioned above. If they do not satisfy the sufficient condition mentioned above, there would be in each of CP43 and CP47 no Chl which can transfer excitation energies to the RC with a rate constant not smaller than $(\sim 25\,ps)^{-1}$, in contradiction to the observation. We conclude, thus, that Chl14 in CP43 and Chl31 in CP47 transfer excitation energies to the RC with a rate constant not smaller than $(25\,ps)^{-1}$ at room temperature. We can say, as a prediction in the present work, that they must emit the same fluorescence as observed for CP43 and CP47, respectively, with a peak energy and a width given by Eq. (2.8).

It could be considered that the fluorescence spectrum at room temperature is emitted nearly equally from plural excited states in the Chl assembly in each of CP43 and CP47. In this case, not only Chl14 in CP43 and Chl31 in CP47, but also other Chls must participate in the EET for the excitation-energy trapping by the RC from the core antenna, contributing to its fluorescence spectrum. Since it is with a rate constant much smaller than $(\sim 25\,ps)^{-1}$ that such Chls can transfer excitation energies to the RC, we cannot reproduce as a whole the rate constant of the EET observed to be not smaller than $(\sim 25\,ps)^{-1}$ in this case. We consider, therefore, that this case can be excluded.

As the main result of the present investigation, shown by arrows in Fig. 2 is the pathway of EET from the core antenna for the excitation-energy trapping by the RC in the pigment arrangement in the PS II core. It is composed of EET from Chl31 in CP47 to B_2 or H_2 in the RC and that from Chl14 in CP43 to B_1 or H_1 in the RC, located nearly symmetrically between CP47 and CP43 toward the RC. Rate-constant values of these EETs, estimated by k of Eq. (2.3), are also shown therein.

3. Peculiarities of PS II in excitation-energy trapping and initial fixation

It has been argued in [34] that orientations of three Chls in each of CP43 and CP47 in the pigment arrangement determined in [14] have been optimized for achieving a high efficiency in EET for excitation-energy trapping by the RC from the core antenna. In the numbering of Chls in [15] shown in Fig. 1, the number of these Chls is 12, 14 and 20 in CP43, and 26, 31 and 35 in CP47. It has been clarified in the present work that excitation-energy trapping by the RC from the core antenna takes place predominantly by EET from Chl14 in CP43 and from Chl31 in

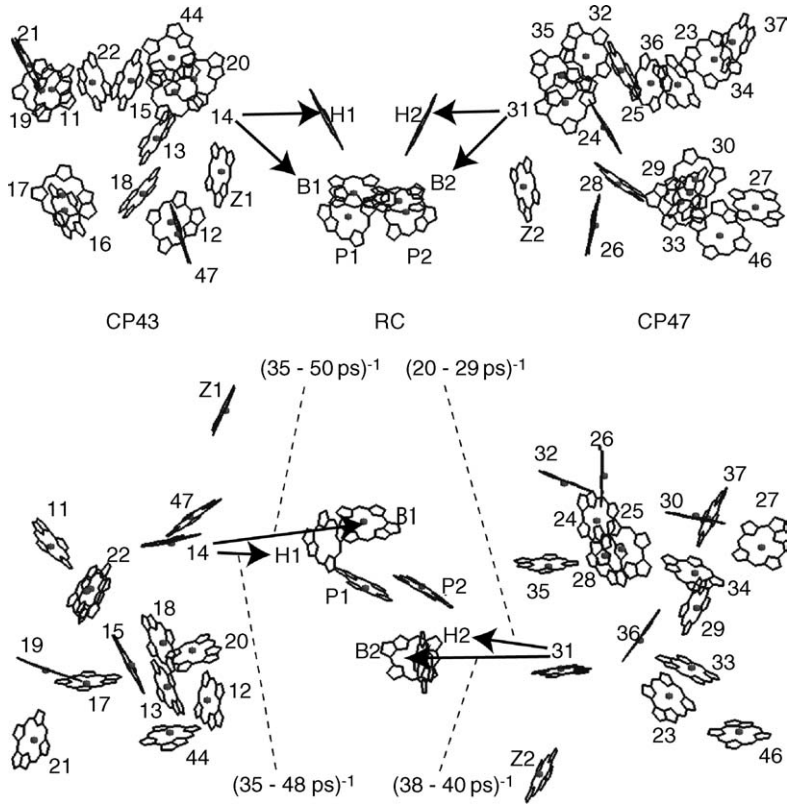

Fig. 2. The most probable pathway of EET for the excitation-energy trapping by the RC from the core antenna composed of CP43 and CP47, added by arrows to Fig. 1. Only Chl14 in CP43 and only Chl31 in CP47 participate in the EET, to B_1 or H_1 in the pigment strand 1 and to B_2 or H_2 in the pigment strand 2 in the RC, respectively, nearly symmetrically between CP47 and CP43 toward the RC. Rate-constant values of these EETs, estimated by k of Eq. (2.3), are also shown therein.

CP47 to the RC. It is reasonable that these two Chls are included in the six Chls mentioned in [34].

Clarification of Chls which transfer excitation energies to the RC, performed in the present work, enables us to picture the light-reaction processes in PS II until initial excitation-energy fixation in the RC, as follows. Solar radiation energies are harvested by the antenna system as excitations of pigments therein. They are transferred among pigments in the antenna system along the excitation-energy funnel toward the core antenna, and are first thermalized in the core antenna before they are trapped by the RC, as in other photosystems [35]. The thermalization time has been estimated to be several ps in PS II [28]. After trapped by the RC, excitation energies are quickly thermalized among pigments in the RC before the charge separation takes place as the initial excitation-energy fixation therein. The thermalization time in the RC has been estimated to be sub-picoseconds [36,37], and the time for the charge separation therein is not shorter [38,39]. These situations show that excitation-energy trapping by the RC from the core antenna is a process rate-limiting, hence, most important, in the whole light-reaction processes in PS II until the initial excitation-energy fixation in the RC. It is this rate-limiting process that we have clarified as taking place by EET from Chl31 in CP47 to B_2 or H_2 in the RC and EET from Chl14 in CP43 to B_1 or H_1 in the RC, nearly symmetrically between CP47 and CP43 toward the RC.

The lowest excited state in the PS II RC is located on B_1 and B_2 in the pigment strands 1 and 2, respectively, although the excited state of each of H_1 and H_2 is located a little ($\sim$40 cm^{-1}) higher. The lower exciton state on the dimeric pair P of P_1 and P_2 is $\sim$180 cm^{-1} higher, on which the positive charge is produced as a result of the initial excitation-energy fixation by charge separation in the RC. Both B_1 and B_2 are nearer to the pair P than H_1 and H_2, respectively. EET from a pair of B_1 and H_1 to that of B_2 and H_2 between the pigment strands 1 and 2 can be estimated to take $\sim$20 ps by using the excitation spectra of these pigments determined in [19]. In these situations, it seems reasonable to consider that observed sub-picosecond thermalization of excitation energies after trapping by the RC from the core antenna takes place only among pigments in each of the strands 1 and 2. After the thermalization, the initial fixation of excitation energies by charge separation begins from the excitation of B_1 when the trapping took place from CP43, and from the excitation of B_2 when the trapping took place from CP47.

As a result of the initial excitation-energy fixation, however, charge separation takes place only along the pigment strand 1, producing initially $P^+B_1^-$ which subsequently makes a transition to $P^+H_1^-$ [40]. A similar one-sided formation of the charge separated state along only one of the pigment strands in the RC is seen also in the bacterial photosystem [6]. There, excitation energies in the core antenna are first transferred to the special pair P, which works as the connecting tuber of the two strands.

In bacterial photosynthesis, therefore, formation of the excited state P^* of P can induce straightforwardly to charge separation only along one of the pigment strands in the RC [41]. In the PS II RC, however, charge separation begins from formation of the excited state either B_1^* or B_2^* of B_1 and B_2 in the pigment strands 1 and 2, respectively, with similar energies. Excitation energies are transferred from both CP43 and CP47 to the pigment strands 1 and 2 in the RC, respectively, with similar rate constants not smaller than $(\sim 25\,\text{ps})^{-1}$. Accordingly, it seems reasonable to consider that charge separation as the initial excitation-energy fixation will takes place with similar rate constants irrespective of whether it starts from the formation of B_1^* or B_2^*. It appears, then, to be clarified how such similar rate constants are realized, when the initial excitation-energy fixation takes place as charge separation only along the pigment strand 1.

The similar rate constants cannot be obtained if the first event following the formation of B_1^* or B_2^* is such a charge separation as either $P^+B_1^-$ or $B_1{}^+H_1^-$ along the pigment strand 1 and as either $P^+B_2^-$ or $B_2{}^+H_2^-$ along the pigment strand 2, respectively. In this case, it would take an additional long time for both $P^+B_2^-$ and $B_2{}^+H_2^-$ along the pigment strand 2 to be changed into charge separation along the pigment strand 1. It means that B_1^* induces neither $P^+B_1^-$ nor $B_1{}^+H_1^-$ along the pigment strand 1 and B_2^* induces neither $P^+B_2^-$ nor $B_2{}^+H_2^-$ along the pigment strand 2, in contradiction to proposals by several investigators [10–13,40]. Moreover, it has been observed that the primary charge-separated state $P^+H_1^-$ along the pigment strand 1 occasionally recombines into the spin-triplet state $^3B_1^*$ on the accessory Chl [42], although with a small rate, differently in the bacterial RC where the spin-triplet state is form on the special pair P. If B_2^* induces either $P^+B_2^-$ or $B_2{}^+H_2^-$ along the pigment strand 2, these charge-separated states would not recombine into the spin-triplet state $^3B_1^*$ on B_1 on the pigment strand 1, resulting in a situation which has not been observed. In this respect, too, production of either $P^+B_2^-$ or $B_2{}^+H_2^-$ from B_2^* can be excluded from consideration.

To realize the similar rate constants, the excitation energies must first be transferred to P also in PS II, since P is located at the connecting tuber of the two strands of pigments [39], as in bacterial photosynthesis. The excited state P^* of P is $\sim 180\,\text{cm}^{-1}$ higher than both B_1^* and B_2^*. Therefore, it would energetically be disadvantageous for both B_1^* and B_2^* to transfer their excitation energies to P^*, even if from P^* the charge separated state $P^+B_1^-$ can easily be produced only along the pigment strand 1 in the RC as in bacterial photosynthesis. To overcome such disadvantage, it plays important roles that coupling between P^* and both B_1^* and B_2^* is due to EET facilitated without wave-function overlap between donor and acceptor, and it has a magnitude as large as several dozens of wave numbers, as estimated from the pigment arrangement in the RC. In this situation, we are naturally led to quantum-mechanical virtual mediation by P^* as a mechanism by which both B_1^* and B_2^* induce the charge-separated state $P^+B_1^-$ only along the pigment strand 1 with similar rate constants between them [39]. This mechanism is essentially the same as the superexchange mechanism originally proposed in magnetism [43]. In this mechanism, P^* is not really produced in the mediation, and both PB_1^* and PB_2^* are unistep converted into the charge-separated state $P^+B_1^-$ by tunneling through the high-energy P^* state at all temperatures. Its rate constant is larger than that for really producing P^* from both B_1^* and B_2^* [39]. The reason why both PB_1^* and PB_2^* are not unistep converted into the charge-separated state $P^+B_2^-$ along the pigment strand 2 is considered to be that $P^+B_2^-$ is higher in energy than $P^+B_1^-$, as in the bacterial system [44].

In PS II, this superexchange mechanism for formation of $P^+B_1^-$ from both B_1^* and B_2^* must be adopted for the initial excitation-energy fixation by charge separation. It is because P^* could not help being elevated in energy higher than both B^* and H^* as a byproduct of the requirement that the redox potential of P^+ must be set as high as 1.2 V only in PS II. At a glance, therefore, this mechanism seems unique to PS II. It is very interesting, however, to note that such a superexchange mechanism works also in purple-bacterium *Rhodopseudomonas* (*Rps.*) *viridis* for the initial excitation-energy fixation in the RC at low temperatures below ∼50 K [45]. In purple-bacterium photosynthesis, excitation energies of the core antenna called LH1 are trapped by the special pair P of bacteriochlorophylls in the RC to form its excited state P^* at room temperature. Subsequently, P^* induces the charge separation initially between P and the adjacent accessory bacteriochlorophyll B_1 along the pigment strand 1 [6]. The excited state P^* is lowest in energy in the pigment assembly in the RC, but in *Rps. viridis*, the lowest excited state $LH1^*$ of the core antenna LH1 [46] is still lower than P^* by $\sim 150\,\text{cm}^{-1}$, similarly to the relation between B^* and P^* in the PS II RC. In purple bacteria, however, LH1 has a nearly circular form [7], enclosing the RC with a radius of several dozens of angstroms from P which is located in the center of the RC. In this situation, coupling for EET from $LH1^*$ to P is as small as only several wave numbers, being estimated from the structure of LH1 [7]. It is due to this smallness of the EET coupling between $LH1^*$ and P that the superexchange mechanism for the initial excitation-energy fixation manifests itself only at low temperatures in bacterial photosynthesis, in comparison with the situation in PS II.

In PS II and the purple-bacterium photosystem, the final excited states achieved in the excitation-energy funneling is B^* in the former and $LH1^*$ in the latter. Both of them are unistep converted into the charge separated state in the RC by the superexchange mechanism, without real production of the excited state P^* of the central pigment pair in the RC, although only at low temperatures in the latter. Trapping of excitation energies in the core antenna by the RC followed by their initial fixation therein is most important in the initial processes of photosynthesis [35]. It is interesting to note that in this most important process the mechanism mentioned above has been conserved as common between PS II and the purple-bacterium photosystem in spite of apparent differences in pigment arrangement in the antenna system. Thus, we can satisfy ourselves, also from the standpoint of the mechanism, that both PS II and the purple-bacterium photosystem have evolved from common ancestors [5].

In PS I, both the RC pigments and the core-antenna ones are scaffolded in a single large transmembrane protein. The lowest excited state in the pigment assembly in the RC core is located on the central Chl pair called P700 therein [1]. Therefore, pigment

excitation energies in the core-antenna part should be trapped by P700 for subsequent charge separation for their initial fixation. Curiously, however, in the core antenna there exist excited states of Chls whose energies are ∼100–200 cm^{-1} lower than P700, called red Chls [1,47]. Excitation energies are first thermalized in the core antenna also here, and hence initially pooled in the red Chls therein before trapped by the RC. Also in PS I, therefore, the excitation-energy trapping by the RC from the core antenna has been constructed to be up-hill. It can be shown [48] that to overcome this situation, the mechanism of unistep superexchange virtual mediation at an intermediate state plays important roles in the excitation-energy trapping by the RC also in PS I at all temperatures, although the pathway working here is considerably different from those in the bacterial photosystem and also in PS II mentioned above. Thus, we have seen that the mechanism in the process of excitation-energy trapping from the core antenna and subsequent fixation by the RC has been conserved to be unistep superexchange commonly among PS I, PS II and the bacterial photosystem in the course of evolution, since this process is most important in the initial processes of photosynthesis.

4. Summary

The absorption spectrum of the RC in PS II has been decomposed into contributions from accessory Chls B (i.e., B_1 and B_2 in Fig. 1), pheophytins H (i.e., H_1 and H_2), the central Chl pair P (i.e., P_1 and P_2), and remote Chls Z (i.e., Z_1 and Z_2) in [19]. The decomposition is based on pigment excitation energies determined by site-directed mutagenesis studies in [9,10]; the excitation energy of B is lowest in the RC, although the next lowest one given by H is only ∼40 cm^{-1} above B^*. Excited states of P are excitons on the Chl dimer [19], but even its lower exciton state P^* is ∼180 cm^{-1} higher than B^*. Such arrangement of pigment excitation energies peculiar in the PS II RC has arisen as a byproduct of the requirement that the oxidized state P^+ of P must have an exceptionally high redox potential for extracting an electron from water only in PS II. Pigments P_1, B_1 and H_1 and those P_2, B_2 and H_2 are arranged nearly in the two-fold rotational symmetry, constituting pigment strands 1 and 2 in the RC, respectively, where P is working as a connecting tuber of the two strands. The core antenna surrounding the RC is composed of CP43 and CP47 in PS II. They are separately attached to the side of the pigment strands 1 and 2 in the RC, respectively, and Chls therein are arranged also nearly symmetrically in tune with the near two-fold rotational symmetry in the RC. In this situation, we consider that the pigment strand 1 traps pigment excitation energies from CP43, and the pigment strand 2 traps those from CP47.

The fluorescence spectrum of both CP43 and CP47 at room temperature peaks at the excitation energy of B in the RC [23,24]. This means that pigment excitation energies of the core antenna are transferred to B in the RC and also to H which is only ∼40 cm^{-1} above, but not to P. The rate constant of such EET should be given by Förster's formula of Eq. (2.3) where Förster's overlap integral is composed of the observed fluorescence spectrum of CP43 or CP47 as the EET donor and the absorption spectrum of B or H as the EET acceptor. The latter has been obtained by the decomposition of the absorption spectrum of the RC. The rate constant for such EET at room temperature is not smaller than $(\sim 25\,ps)^{-1}$ from CP47 [25], and it should have a similar value also from CP43 from the symmetry mentioned above. By equating the Förster's rate constant to this value, we can obtain that such EET occurs from a single Chl in each of CP43 and CP47 at room temperature. It is Chl14 in CP43 and Chl31 in CP47 in the numbering of Chls in [15], as shown in Fig. 2 with rate-constant values of such EET estimated by the formula.

After such EET from the core antenna to the RC, pigment excitation energies are initially fixed by charge separation in the RC. The charge separation has been observed to take place only along the pigment strand 1, initially as $P^+B_1^-$, then to $P^+H_1^-$. The EET from the core antenna to the RC takes place both from CP43 to the pigment strand 1 and from CP47 to the strand 2, with similar rate constants. In each of the pigment strands, the charge separation begins from formation of B^* which is nearest to P with the lowest energy in the RC. Production of the initial charge-separated state $P^+B_1^-$ along the strand 1 from B_2^* on the strand 2 must be mediated by the lower exciton state P^* on P located midway between B_1 and B_2. The mediation at P^* becomes quantum-mechanically virtual in the superexchange mechanism, tunneling though the high-energy P^* state by a large EET coupling [39]. Its rate constant is larger than that for real production of P^*. From the symmetry mentioned earlier, production of $P^+B_1^-$ from B_1^* on the strand 1 and that from B_2^* on the strand 2 should take place with similar rate constants. A similar value of the rate constant can be obtained only by a similar mechanism, without accidental coincidence. This means that production of $P^+B_1^-$ from B_1^* on the strand 1 is also virtually mediated by P^* on P in the quantum-mechanical superexchange mechanism, without real production of P^*. Calculating by the general theory in [41], in fact, we can show [39] that the rate constant of the initial excitation-energy fixation by this superexchange mechanism reproduces well both the magnitude and the temperature dependence of the rate constant [38] observed by direct lowest-edge excitation in the RC-absorption band.

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