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HYPOTHESIS

Why Is Electron Transport in the Reaction Centers of Purple Bacteria Unidirectional?

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Abstract—Although the two electron-transfer branches in the reaction centers (RC) of purple bacteria are virtually symmetric, it is well known that only one of them is functionally active (the A-branch). The mechanisms of functional asymmetry of structurally symmetric branches of the electron transport system are analyzed in this work within the framework of the theory of bimolecular charge-transfer complexes (CTC). CTC theory is shown to provide an explanation of this phenomenon. According to the CTC theory, the dominance of one branch is required to implement the CTC state in special bacteriochlorophyll pairs of RC, in which more than 30% of the excited electron density in the CTC is shifted toward one of the bacteriochlorophyll molecules. This causes a significant increase in the efficiency of further electron transfer to the primary quinone acceptor as compared to a system with two absolutely symmetric electron transfer branches. Specific features of dielectric asymmetry near the RC special pair are discussed. It is emphasized that a strong CTC is able to provide effective trapping of electronic excitation energy from antenna chlorophyll, which is a main function of the RC. Hypothetical stages of CTC formation in other classes of photosynthesizing bacteria during evolution are discussed.

Key words: purple bacteria, reaction center, excitation energy trapping, charge-transfer complexes, unidirectional electron transport

PROBLEM

In the reaction center (RC) complexes of purple bacteria, only one of two virtually symmetric electron transfer branches is active (the A-branch). This branch incorporates bacteriochlorophyll (BChl) $P870_L$, BChl $P800_L$, and bacteriopheophytin-760 (numerical indices show the absorption peak wavelength) [1, 2]. Many groups of researchers have tried to reroute the electron transport pathway in RC through the alternative B-branch. To attain this goal, one to three amino acid residues in the vicinity of chromophores $P870_L$ and $P870_M$ (the so-called special pair of RC BChl) were modified giving rise to formation/disruption of hydrogen bonds of these molecules with RC polypeptides (see [3-7], for reviews, [1, 2]). To provide deeper insight into the mechanisms of RC functioning, this problem is considered in this work within the framework of the theory of molecular charge-transfer complexes (CTC) [8]. The principles of CTC theory were elucidated by photochemists and photophysicists in the late 1960's on the basis of a large body of experimental data on binary molecular complexes formed either by preliminarily excited molecules (CTC) or during photoexcitation of one of two molecules of the resulting pair (excimers). According to many photochemists, this was a rare case in which a theory had been completely developed and described in many monographs, and then was shelved, scrapped, and even discarded.

In this work, the principles of the CTC theory developed in [8] are applied to the processes of electronic excitation trapping and charge transfer in the RC of purple bacteria.

CERTAIN PROPERTIES OF CHARGE-TRANSFER COMPLEXES (CTC)

Binary CTC (in general, a CTC may include more than two molecules) have the following characteristics [8].

a) There should be energy coupling between molecules A and B. The intermolecular binding energy should be significantly larger than the energy of molecular oscillations. Usually, the intermolecular binding energy is the exchange energy of two closely located molecules. If this

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Abbreviations: CTC) charge-transfer complex; RC) reaction center; P_2, P_2^*) special pair of RC in ground (S_0) and singlet excited (S_1^*) states, respectively; BChl) bacteriochlorophyll; *e*) electron charge; EE) electronic excitation.

interaction is stronger, the molecules contact each other or even form a chemical bond.

b) Molecules A and B may be identical or different.

c) At least one of the CTC molecules should be aromatic, i.e., capable of absorbing photons. Otherwise, the rates of the resulting processes are not fast.

d) In accordance with (a)-(c), the process of CTC formation proceeds in two stages:

$$[A \approx B] + \text{photon or exciton} \rightarrow [A \approx B]^* \xrightarrow{K_{CTC}} [A^{-\delta e} \approx B^{+\delta e}]^*,$$

where $[A \approx B]$, $[A \approx B]^*$, and $[A^{-\delta e} \approx B^{+\delta e}]$ is the molecular complex in the ground, excited, and CTC states, respectively; *e* is the electron charge; $+\delta e$ and $-\delta e$ is the parameter of electron density excess/deficiency in the two molecules producing the CTC state, respectively, ($\delta < 1$); K_{CTC} is the rate constant of formation of the CTC state.

e) A CTC can be strong or weak. In quantum mechanical theory, a CTC is described by the following Ψ-function [8]:

$$\alpha\, \Psi\, [A^{-e} \approx B^{+e}] + \beta \Psi\, [A^{+e} \approx B^{-e}]\ ,$$

where $\delta = \alpha - \beta$ is the parameter of CTC strength. A strong CTC satisfies the condition $\delta = \alpha - \beta > 0.3$; + and – correspond to the presence/absence of the whole electron (*e*) in the molecule, respectively.

CTC states with δ close to 1 have been experimentally obtained in photochemical systems. Therefore, the CTC-forming molecules were ionized. However, the electronic energy of this state was gradually converted into the energy of polarization of surrounding molecules (formation of a polaron coat) and dissipated to heat.

CTC Properties Relevant to the Problems of Reaction Centers of Purple Bacteria

f) CTC are formed in media with high dielectric permeability coefficient $\{\varepsilon(\nu)\}$, particularly, within the frequency range (ν) comparable with the inverse lifetime of the CTC itself. Otherwise, the electrostatic attraction forces of opposite charges ($+\delta e/-\delta e$) may cause their recombination.

It should be noted that at a frequency of 10^2 Hz the $\varepsilon(\nu)$ value of water is 80. At this frequency, within a half-period time, the water clusters may partially decay and undergo repolarization. Perhaps the majority of these clusters undergo rearrangement or even complete collapse, because there is a significant mutual compensation of electric charges of hydrogen and oxygen atoms, giving rise to a substantial decrease in the local values of $\varepsilon(\nu)$. However, at electric field frequencies of about 10^{10} Hz and within the optical range, the value of $\varepsilon(\nu)$ is 4.5 [9] and 1.7, respectively. Note that within the optical frequency range the value of $\varepsilon(\nu)$ is virtually equal to the squared light refraction index.

g) Absorption spectra of CTC are broadened and shifted toward a longer wavelength as compared to the absorption spectra of the monomeric molecules. Absorption spectra of strong CTC are split into two bands, both the split magnitude and the amplitude ratio being quantitatively calculated theoretically from the angle between the dipole transition moments of the two molecules. For example, in the case of coaxial/orthogonal mutual orientation of these moments, one of two bands is degenerated and the long-wavelength/short-wavelength band is observed alone [8, 10].

h) Strong CTC are formed only if the CTC-forming molecules are electrically asymmetrical. This requirement can be met if the energy levels of the S_1^* excited states of two molecules differ from one another. In the case of identical molecules, this requirement is met if they are bound at different sites or as a result of local difference in the dielectric permeability at the sites of CTC formation.

i) Strong CTC are characterized by constant values of electric dipoles, which are significantly longer ($p = 3$-6 Å) than in monomeric molecules ($p \cong 1$ Å). This is very important, because neighboring molecules and atomic groups located at the distance of the dipole length are exposed to the dipole electric field of a strong CTC.

j) Strong CTC are effective electron donors because their excited energy-rich electron is partially transferred from one molecule to another at a distance of several angstroms, thereby facilitating its further detachment. Dye molecules in the S_1^* excited states may also contribute to electron donation reactions, strong CTC of dye molecules being very effective electron donors.

SPECIAL PAIRS OF REACTION CENTERS AS STRONG CTC

According to the literature, the special pair of the RC (P_2) has CTC characteristics, at least in purple bacteria [11-13]. For example, in BChl *a*-containing sulfur and non-sulfur purple bacteria, the P_2 absorption band is significantly broader and red-shifted compared to the corresponding absorption band of BChl *a* monomer *in vivo* (at 800 nm). This finding is fully consistent with the theory of the band splitting into two bands at 870 and 800 nm. It follows from a high value of energy of interaction between $P870_L$ and $P870_M$ that the magnitude of the band splitting should be considerable [10]. Therefore, these molecules are thought to form strong CTC. In accordance with the theory, the areas under absorption bands at 870 and 800 nm account for 86 and 14% of the total absorption capacity of P_2, respectively. This is due to a small angle between the molecules. The dominant contribution of the 870-nm band is of considerable functional importance, because this band mediates effective migration of electronic excitation (EE) energy from light-harvesting BChl *a* molecules to P_2. Usually, the absorption peak of the antenna molecules in the P_2 vicinity is at 880 nm because of strong interaction between them. This interaction should be strong enough to provide superfast intermolecular leaps of EE migration. It is very improbable that the monomer BChl *a* absorption peak is shifted to 870 nm only as a result of interaction with polypeptides. Indeed, if a BChl *a* monomer with absorption band at 800 nm were incorporated in an RC instead of P_2, the resulting RC would be virtually unable to accept the EE energy migrating from antenna BChl-880.

As noted above, formation of a strong CTC requires electrical asymmetry between the CTC-forming molecules. Several factors may cause this asymmetry. It was shown in classical works of Boxer et al. ([14, 15] and references therein) that a gradient of local dielectric permeability across the gap between $P870_M$ and $P870_L$ molecules is the main contribution to the electrical asymmetry *in vivo*. It seems that this gradient is built in natural systems by amino acid residues of different polarity. Hydrogen bonds also significantly contribute to local values of $\varepsilon(\nu)$. It was shown in [3] that modification of the hydrogen bond network in a mutant RC is able to cause displacement of the unpaired electron from its natural position at $BChl_L$ to the alternative $BChl_M$. Perhaps, asymmetrical location of a carotenoid molecule in the RC relative to $P870_M$ and $P870_L$ is also a factor of dielectric asymmetry of the special pair.

It should be noted that according to the system of notation used in this work, condition $\delta > 0$ corresponds to the presence of a negative charge δe at $P870_L$, whereas $\delta < 0$ indicates that negative charge is located at $P870_M$.

ACTIVITY RATIO OF A- AND B-BRANCHES IN RC *in vivo*

This problem has been studied by many researchers. For example, Boxer et al. suggested that the ratio of rate constants of electron transfer along the branches A and B is determined by the energy barrier parameters (height and width) for electron tunneling [14]. The possibility of energy control of the electron transfer efficiency ratio in these branches was discussed theoretically by Parson et al. [16]. However, these authors failed to notice that the CTC concept alone is sufficient both for explaining the dominant role of the A-branch in purple bacteria and for planning genetic engineering experiments designed to modify this ratio. Consider these possibilities within the framework of the CTC theory in more detail.

1. Consider the B-branch in RC of purple bacteria. The question is whether it can be activated or not. If the direction of the dielectric permeability gradient in the vicinity of the special pair were changed to the opposite one by replacing the amino acid residues mentioned above and/or by forming/breaking hydrogen bonds near $P870_M$ and $P870_L$, the condition $\delta < 0$ would be observed and the photoexcited electron from the CTC state would be transported along the B-branch. However, this would result in the loss of the A-branch, which has been selected during evolution and has preferable contacts with quinones Q_A and Q_B.

2. Can the two branches be active simultaneously? To attain this goal, the dielectric characteristics in the vicinity of P_2 should be symmetric. Therefore, in Eq. (1) the following condition should be observed: $\alpha \cong \beta$. However, in this case the parameter $\delta \to 0$, the CTC is not strong, and its dipole amplitude is rather small. It should be expected that in complexes of this type excited electrons P_2^* are distributed virtually equally between the A- and B-branches of the RC, but the total rate of electron trapping by these branches is significantly decreased because preliminary partial charge separation provided by a weak CTC is not sufficiently effective.

RC complexes with such characteristics were indeed obtained by target-oriented mutagenesis of *Rhodobacter capsulata*. Up to three amino acid residues were replaced in mutants of this bacteria [17, 18]. In [17] it was shown that the rates of electron transfer along the A- and B-branches in these mutants are comparable to one another, and the charge fractions entering these alternative branches are 23 and 62%, respectively. However, the overall rate constant of the two electron flows $(15\ \text{psec})^{-1} \cong 6.7\cdot10^{10}\ \text{sec}^{-1}$ is one fifth of the rate constant in the wild-type A-branch $((3\ \text{psec})^{-1} \cong 33\cdot10^{10}\ \text{sec}^{-1})$. Even replacement of BChl-800 by bacteriopheophytin in the A-branch changed the electron transfer rate in the branch [19].

Perhaps such a decrease in the electron transfer rate was also due to the specific mechanism of EE trapping at the RC special pair. This mechanism was theoretically predicted in [20] and recently confirmed experimentally in [21]. According to this mechanism, exposure of the RC special pair of purple bacteria to an electric field of a strong CTC dipole induces polarization of mobile hydrogen atoms of bound water molecules or NH_2-groups of proteins in the special pair vicinity. Indeed, of all atoms, only hydrogen can be displaced or rotated within the time interval comparable with the CTC lifetime (about 100 fsec). This process is associated with energy dissipation (at least 40-50 meV), thereby hindering significantly back migration of EE from P_2^* to antenna BChl *a* and facilitating the primary EE trapping by the CTC state of P_2^*. In addition to the universal background polarization of fixed electrons, the processes of reorientation of pairs of hydrogen atoms in water molecules induced by the electric field of the CTC state of P_2^* determine the dielectric permeability coefficient value during the CTC lifetime (i.e., within tens of femtoseconds after RC excitation). It should be noted that changes of parameter ε(ν) on a time scale of about 100 fsec (i.e., about three orders of magnitude shorter than in classical works of Boxer et al. [14, 15]) are of particular importance within the framework of the concept considered in this work. It was shown in [14, 15] that electrical asymmetry of the RC plays a significant role in the reaction of electron transfer from bacteriopheophytin to quinone Q_A (i.e., on a time scale of about 200 psec [11-13]). However, the time interval of about 100 fsec is too short for any changes in the protein conformation or even atomic group polarization. Apart from universal minimal background electron polarization along interatomic bonds, only polarization of light hydrogen atoms containing uncompensated charges contributes to the ε(ν) spectrum within this time range.

Thus, to provide effective functioning of the RC in purple bacteria, the primary electron donor should be represented by a strongly bound (i.e., asymmetrical) pair of BChl *a* molecules or their structural analogs. In photosynthesizing organisms *in vivo*, this is achieved by asymmetry of the closest protein surrounding of the special RC pair P_2 [13, 14]. However, in modified RC this can be implemented by incorporating different molecules (e.g., BChl *a* and bacteriopheophytin or even other porphyrins) into the CTC position favorable for electron donation to A-branch. Using this approach, it was shown in [22, 23] that if RC P870 is replaced by bacteriopheophytin *a*, the charge separation efficiency in such RC is 50%. According to [24, 25], such a substantial decrease in the activity of artificial heterodimers can be attributed to a significant difference in the redox potentials of BChl *a* and bacteriopheophytin *a* (up to 150 mV). In my opinion, it would be more correct to compare the energy levels of corresponding CTC states rather than redox potentials of CTC-forming molecules. If the red-shift requirements for the P_2 absorption spectrum and electrical asymmetry in favor of the A-branch were observed, such heterodimers would provide a basis for effective functioning of artificial reaction centers.

CTC IN OTHER GROUPS OF PHOTOSYNTHESIZING ORGANISMS

Within the scope of the concept suggested in this work, it would be interesting to consider the processes of energy trapping and primary charge separation in RC of green bacteria, because the special RC pair in these organisms (P840) is a symmetric homodimer. Green bacteria contain about 70 molecules of BChl *a* (B-805) and about 1000 molecules of BChl *c* (C-750) per RC [11]. This is about 30 times larger than the BChl *a* content per RC in purple bacteria (e.g., *Rhodospirillum rubrum*). High antenna BChl content in green bacteria is widely thought to be associated with low insolation level in the habitat of these bacteria. However, it is interesting to elucidate whether or not this situation is due to a relatively low efficiency of RC functioning in green bacteria. In other words, large antenna size might be required to compensate for low efficiency of EE trapping by weak CTC states of symmetrical P840 pairs, because according to [26], the special pairs P840 are symmetrical homodimers.

It would be also interesting to consider the processes of energy trapping and primary charge separation in RC of heliobacteria, which contain 35 molecules of antenna pigment per BChl *g*-based special pair [11]. According to the literature, the special RC pairs in heliobacteria are homodimers. In the context of the concept suggested in this work, it should be expected that special RC pairs in heliobacteria produce strong CTC, probably due to asymmetry of the protein surrounding of P_2.

The requirements for energy assimilation efficiency per RC in higher plants are significantly more demanding. These requirements are satisfied by a significantly higher than in purple bacteria rate of electron transfer from the rate-limiting external sites of the electron transport chain (≅50 and ≅10 *e*/sec, respectively). It should be noted that the rate-limiting stages of electron transport can be determined from the light curves of photosynthesis saturation. Although antenna complexes of some higher plant species contain up to 600-800 molecules of chlorophyll (Chl) *a* and Chl *b* per RC [27], effective EE trapping in RC of these plants can probably be achieved only if special pairs P700 and P680 form sufficiently strong CTC. However, this suggestion should be thoroughly scrutinized.

EVOLUTIONARY ASPECT OF ORGANIZATION OF CHARGE-TRANSFER COMPLEXES IN PHOTOSYNTHETIC REACTION CENTERS

According to contemporary paleobotanical findings, fossil cyanobacteria are attributed to 3- to 3.5-billion-year-old geological layers. It can be assumed that in prehistoric times ancestors of contemporary cyanobacteria lived in an environment enriched with energy-rich chemical compounds but at low illuminance. If this assumption were true, further evolution of these ancestor species would strive for the following ecological and functional advantages.

a) To increase the efficiency of solar radiation utilization, the pigment system of these organisms could be rearranged to displace the main long-wavelength absorption band from the range inherent in Chl *a* (near 670-685 nm) to the spectral region containing a larger number of solar photons. The shift to the longer-wavelength spectral range was facilitated by the fact that these bacteria do not mediate water oxidation and oxygen evolution.

b) The efficiency of interaction between antenna pigments and RC should be increased to the highest possible level.

It can also be suggested that the following stages of evolution were passed by the hypothetical ancestors of cyanobacteria to meet these goals.

1. A fraction of the genes responsible for Chl *a* biosynthesis mutated giving rise to BChl *c* genes. The absorption maximum of the protein complex of this pigment *in vivo* is at 750 nm. However, the efficiency of inductive-resonance EE energy migration from the antenna pigment C750 to such high-energy RC pairs as P700 or P680 is rather low. As a result, there was a trend toward a continuous increase in the relative content of this pigment. In chlorosomes of some species of green bacteria, this value reached 1000 antenna BChl molecules per RC.

2. The next stage of evolution was determined by a new conversion of genes. As a result, biosynthesis of Chl *a* or BChl *c* was replaced by biosynthesis of BChl *a*. Thus, the absorption spectrum of the P_2 pairs of RC complexes of these bacteria was shifted to the near IR range (800-890 nm), thereby matching the absorption bands of antenna pigments at the level of EE migration. For example, in contemporary green bacteria there is an effective energy migration "funnel" C-750 → BChl-805 → P-840.

3. However, the evolution to even more effective systems continued (*the best is the enemy of the good*). It is well known that the red spectral limit of an optimum photoelectrical energy conversion system driven by solar radiation at sea level in various geographical regions ranges from 1000 to 1040 nm [28].

For example, at the level of the Earth's surface, the fractions of incident solar light that are physiologically active in contemporary plants (<730 nm) and purple bacteria (<930 nm) are 45 and 65%, respectively. Therefore, it was necessary to provide a further shift of the long-wavelength absorption band of BChl toward the IR region. This problem was solved by Nature not only at the expense of new changes in molecular structure, but also by synthesizing new proteins. These proteins were designed to provide stronger binding to chlorophyll molecules both in antenna ensembles and in P_2 pairs of RC. Based on the same BChl *a* molecule, purple bacteria developed new spectral forms of chlorophyll–protein complexes with mutually coordinated spectra: antenna forms B880 and B890 and RC pairs P870 and P890. Given the fact that the monomer BChl *a* absorption peak in neutral media is at 770 nm, these spectral shifts can be regarded as a record. Another evolutionary invention was to modify the chemical structure of the main pigment of photosynthesis (BChl *b* instead of BChl *a*). The absorption maximum of antenna complexes in contemporary photosynthetic bacteria containing BChl *b* (e.g., *Rhodopseudomonas viridis* or *Blastochlorii*, according to the new classification) is shifted to 1020 (!) nm. However, even in this "evolutionary experiment", Nature failed to provide a coordinated shift of the absorption band of the P_2 pair. In these bacteria the RC special pair absorption peak is only at 960 nm. Therefore, the EE energy level in the antenna pigment BChl-1020 is about 60 meV lower than the EE energy level of the RC.

Because the RC complexes of contemporary purple bacteria contain strongly bound BChl *a* pairs and because excitation of these pairs gives rise to strong CTC states, the processes of EE energy migration back to antenna BChl in these bacteria are effectively inhibited. As a result, the relative amount of antenna pigment in contemporary purple bacteria is substantially reduced (≅30 BChl *a* per RC). A new mechanism of adaptation emerged in these bacteria living in areas with low levels of insolation. This mechanism includes activation of biosynthesis of BChl *a* and special proteins capable of associating up to 200 additional BChl *a* molecules per RC. These additional protein–BChl complexes are called B800 + B850. This mechanism is undoubtedly more progressive than the processes in the chlorosomes of green bacteria.

Perhaps, chemical structure and functional organization of antenna pigment ensembles and special RC pairs in extracellular chlorosomes of contemporary green bacteria and in contemporary BChl *b*-containing purple bacteria are examples of only partially successful intermediate stages on the infinitely long way to perfection.

As far as the inactive B-branch of electron transport in the RC of purple bacteria is concerned, it was suggested by V. P. Skulachev [29] that it is a rudimentary structure inherited from evolutionary ancestors (cyanobacteria). According to recent X-ray diffraction data, two chlorophyll molecules of photosystem 1 RC in cyanobacteria are simultaneously involved in electron transport. In addition, they also play an important role of bridges for effective EE migration from bulk light-harvesting pigments to RC pairs [30]. Because these bridges are close to the special pair, they significantly increase the rate and quantum efficiency of energy migration (according to the inductive resonance theory, energy migration rate is a R^{-6} function of distance R [31]). Perhaps both P800 and bacteriopheophytin a_M of the B-branch will be extinct after the next several millions of years of evolution, unless they fulfill certain functions that are presently obscure (e.g., triplet–triplet energy migration between RC chlorophylls and carotenoid [32]).

The consistency of the hypothesis suggested in this work could be experimentally tested by correlation analysis of quantum yields of the primary charge separation in RC complexes of a large variety of bacterial mutants, including strains differing from each other in dielectric and energy asymmetry between special pair molecules. According to the concept suggested in this work, such asymmetry should have a decisive effect on the efficiency of special pair transition to strong or weak charge-transfer complexes.

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