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On the efficiency of the long wavelength minor bacteriochlorophyll groups in the vicinity of reaction centers

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ABSTRACT

The role of minor chlorophyll and bacteriochlorophyll groups in excitation delivery to reaction centers and subsequent trapping in them was analyzed by means of PC-modeling. The analysis of general type of photosynthetic units and, in particular, those resembling typical photosystems of purple bacteria, has revealed some types of structures in which the presence of minor BChl fractions in the vicinity of reaction centers did increase the efficiency of the useful energy trapping. In some cases the spectral range of optimal energy conversion is broadened.

1. Introduction

Many photosynthetic organisms possess small chlorophyll (Chl) and bacteriochlorophyll (BChl) spectral fractions. Their absorption peaks are usually shifted to longer wavelengths relative to those of the major antenna /B/Chls and RC special pairs. So, they form potential holes and thus focus electronic excitations (EEs). As it concerns plants, one may find extensive material devoted to various long-wavelengths Chl complexes especially in photosystem-1 of higher plants and cyanobacteria (see in more detail in [1–3]). Unfortunately, yet the position of these minor groups is not reliably established within the membrane architecture of rather complex plant photosystems. Therefore the problems of minor fractions in plants are omitted in this paper. Antenna systems of many purple bacteria have very complex spectra [4,5]. In recent publications [6,7] a noticeable spectral diversity was established even in their "homogeneous" spectral BChl fractions, like b850. So, one may expect that purple bacteria may also contain minor BChl groups.

Many authors speculated about the role of minor fractions mostly in plant photo-system-1 (see in reviews [2,8]). Some of them argued that electronic excitation (EE) focusing in minor pigment groups may increase the net efficiency of photosynthesis. However, the alternative consideration was also suggested. According to Karapetyan et al. [8] "Long-wave chlorophylls of PS-1 slow down the capture of energy by P700". In fact, the positive effect of long wave-lengths groups inevitably must be weakened by corresponding decrease of the rate constants on the excitation way from /B/Chl minor fraction/s/ to the RC accepting pigments.

In this study, the physico-mathematical modeling was undertaken which enabled to estimate qualitatively the joint action of the above mentioned competing factors in general and in some particular models of the whole photosynthetic units.

2. Description of the general model

The general analytical model is shown in Fig. 1A.

Homogeneous bulk /B/Chl is represented in Fig. 1 by two groups marked as $\{\mathbf{1}^*\}$ and $\{\mathbf{2}^*\}$ (hereafter * signifies the number of EEs in corresponding BChl group) which include 24 remote and 6 neighboring to RC molecules respectively. Note, the same model with 72 and 18 molecules in $\{\mathbf{1}^*\}$ and $\{\mathbf{2}^*\}$ states as well as that with three consecutive BChl-*a* groups containing 60, 24 remote and 6 adjoining molecules have yielded practically similar QY_e dependences versus spectral shifts of their minor groups. EEs in $\{\mathbf{1}^*\}$ and $\{\mathbf{2}^*\}$ groups have the same energy as those in the RC special pair $\{\mathbf{4}^*\}$. The spectral position of minor BChl-m molecules (state $\{\mathbf{3}^*\}$) and consequently the energy magnitude of its EEs was scanned. This model may be presented mathematically as the set of balance differential equations.

$$d\{\mathbf{1}^*\}/dt = -(k_{1,2} + k_{g1})\{1^*\} + k_{2,1}\{\mathbf{2}^*\} \quad (1a)$$

$$d\{\mathbf{2}^*\}/dt = -(k_{2,1} + F^+(\Delta\nu)k_{2,3} + k_{2,4} + k_{g2})\{\mathbf{2}^*\} + k_{1,2}\{\mathbf{1}^*\} + F^-(\Delta\nu)k_{3,2}\{\mathbf{3}^*\} + k_{4,2}\{\mathbf{4}^*\} \quad (1b)$$

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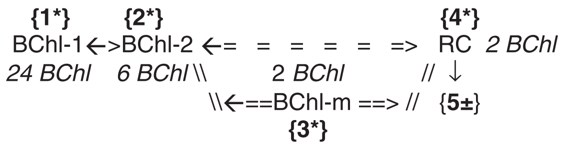

Fig. 1. The dynamic and compostion scheme of a general model of a photosynthetic unit. The mark <-> signifies statistically preferred EE transfer.

$$d\{\mathbf{3}^*\}/dt = -(F^-(\Delta\nu)k_{3,2} + F^-(\Delta\nu)k_{3,4} + k_{3,5} + k_{g3})\{\mathbf{3}^*\} + F^+(\Delta\nu)k_{2,3}\{\mathbf{2}^*\} + F^+(\Delta\nu)k_{4,3}\{\mathbf{4}^*\} \quad (1c)$$

$$d\{\mathbf{4}^*\}/dt = -(k_{4,2} + F^+(\Delta\nu)k_{4,3} + k_{4,5} + k_{g4})\{\mathbf{4}^*\} + k_{2,4}\{\mathbf{2}^*\} + F^-(\Delta\nu)k_{3,4}\{\mathbf{3}^*\} \quad (1d)$$

$$d\{\mathbf{5}^*\}/dt = k_{3,5}\{\mathbf{3}^*\} \quad (1e)$$

$$d\{\mathbf{6}_\Sigma g\}/dt = k_{g1}\{\mathbf{1}^*\} + k_{g2}\{\mathbf{2}^*\} + k_{g3}\{\mathbf{3}^*\} + k_{g4}\{\mathbf{4}^*\} \quad (1f)$$

The following rate constant values were used in general case.

2.1. Antenna molecules

It was reliably proved that BChl molecules are very dense in vivo, so inter-chromophore distances between closest neighbors are about 10 Å [2,4,8]. Correspondingly, the magnitudes of the rate constants between groups {**1***} and {**2***} were taken with a good surplus as,

$$K_{1,2} = 10^{12}\,\mathrm{s}^{-1}; \quad k_{2,1} = 4k_{1,2} = 410^{12}\,\mathrm{s}^{-1}$$

(note, their multiplications by 2 or 0.5 change our results by no more than 0.15%).

The rate constants for intra-molecular wasteful losses were taken [9] as:

$$K_{g1} = k_{g2} = k_{g3} = 1.5 \times 10^9\,\mathrm{s}^{-1}.$$

The rate constants for EE transfers between minor BChl-m and its neighbors were:

$$K_{2,3} = F^+(\Delta\nu)3 \times 10^{11}\,\mathrm{s}^{-1}, \quad k_{3,2} = 3k_{2,2} = F^-(\Delta\nu)9 \times 10^{11}\,\mathrm{s}^{-1}.$$

$$K_{4,3} = F^+(\Delta\nu)35 \times 10^9\,\mathrm{s}^{-1}; \quad k_{3,4} = F^-(\Delta\nu)35 \times 10^9\,\mathrm{s}^{-1}$$

where $35 \times 10^9\ \mathrm{s}^{-1}$was adopt from [1,5]; $F^+(\Delta\nu)$ and $F^-(\Delta\nu)$ are normalized Foerster-type integrals which account of the overlapping of fluorescence spectrum of donor molecule and absorption spectrum of acceptor molecule (see the procedure in [10]); $\Delta\nu$ is the difference between absorption peak of the bulk BChl and its minor fraction BChl-m divided by the absorption peak.

The distance between antenna BChls and RC special pair plays the most important role in EE migration. In plants and in purple bacteria it is of the order of 20 [8] and 40 Å [4,5] respectively which justifies the use of Foerster theory [11] for EE migration between BChl-m and RC in this model.

2.2. Reaction center

It was assumed for simplicity that just the primary electron expel from excited RC special pair ({**4***} → {**5±**}) is irreversible and thus EEs in {**5±**} state account for the useful quantum yield (see verification of this assumption in the next paragraph). Corresponding rate constant was taken as $k_{4,5} = (3\ \mathrm{ps})^{-1}$ and that for wasteful EE losses in {**4***} state, $k_{g4} = (300\ \mathrm{ps})^{-1}$ [12].

The values of rate constants for EE transfer between antenna group {**2***} and reaction center {**4***} ($k_{2,4}$ and $k_{4,2}$) were either zero, or were varied in a wide range.

3. General model, results

3.1. Model in Fig. 1

All above mentioned rate constant magnitudes were included into the (1a–f) set of balance equations and it was solved with the aid of special PC-program RKGS [13].

Molecules of four groups {**1***}–{**4***} were initially excited proportionally to the numbers of molecules in each group (see BChl quantities in Fig. 1).

3.2. Series A: $k_{2,4} = 0$, $k_{4,2} = 0$

The direct EE migration between antenna groups {1*}, {**2***} and RC {**4***} is eliminated. The spectral position of the absorption peak of minor group {**3***} was gradually shifted in both directions. The dependence of the useful quantum yield (QY_e) value versus this shift is shown in Fig. 2 by curve 1. The useful quantum yield QY_e (EE trapping in {**5±**} state) reached maximum when the spectral shift $\Delta\nu$ aspired to about 0.3 portion of the width of BChl-*a* absorption band. Note, it is close to BChl-*a* Stokes shift which is equal to about 0.35 portion of the width of BChl-*a* absorption band [14].

Fig. 2 shows that the maximum of QY_e value occurred to be nearly the same when the minor group {**3***} contained two or four BChl molecules, as well as in the case when the RC trapping constant was increased twofold. Thus, in this simplified general structure the presence of a group of minor BChl-m, which formed the potential hole of about 130 cm^{-1}, did increase the efficiency of EE trapping by RCs.

3.3. Series B: $k_{4,2} = 3\,k_{2,4} \neq 0$

The channel of direct EE migration between antenna group {**2***} and RC {**4***} was activated. For $\Delta\nu = 0$ when $F^+(\Delta\nu) = F^-(\Delta\nu) = 1$, the values of these rate constant pairs are presented in the legend of Fig. 3.

The data in Fig. 3 prove that the positive effect of EE focusing vanishes, as the direct migration channel between the major bulk

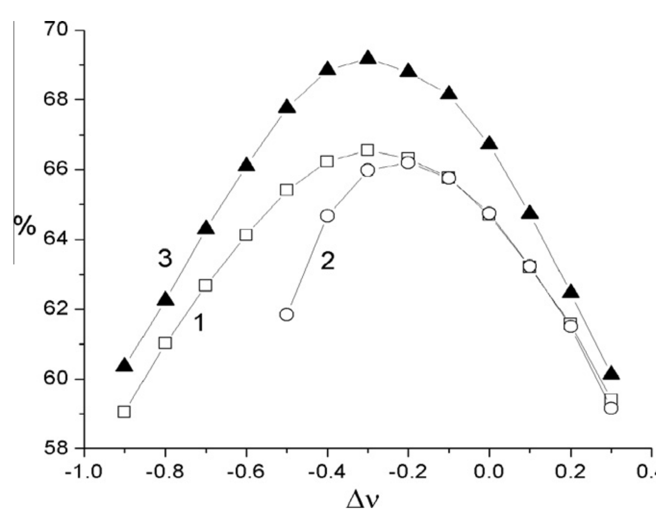

Fig. 2. The value of the useful quantum yield, QY_e versus the spectral shift ($\Delta\nu$) of the absorption band of BChl minor fraction. Series A. Curve 1: basic data; curve 2: BChl-m is doubled (contained four molecules); curve 3: RC trapping constant $k_{4,5}$ was multiplied by two. $\Delta\nu$ is expressed in the portions of the BChl absorption band.