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Influence of the Architecture of Light-Harvesting Antennae on the Energy Transfer Efficiency and Rate: Probability Analysis

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Abstract—The high efficiency of natural light-harvesting systems is based on the optimal organization of various parts of photosynthetic antennae, carotenoids and porphyrins. The rate and efficiency of energy transfer inside an antenna and between the antenna and the reaction center were studied using probability analysis. The transfer rate and efficiency were found to depend on the antenna architecture. The most efficient antennae are those in which a maximal number of photosensitive elements are in direct contact with the reaction center, whereas the interaction with neighboring elements is minimal. The following types of antennae, in order of decreasing efficiency, were studied: parallel, ring, spherical, cluster, and sequential. Explicit expressions relating the average transfer route length and the fraction of energy received by the reaction center to the number of photosensitive elements and the efficiency of the elementary transfer event were derived. The spatial arrangement of photosensitive elements and the resistance of the antenna to damage of individual elements were taken into account.

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Photosynthesis is the main energy source in the biosphere. Notwithstanding the diversity of the structures and functions of light-harvesting systems, they have some properties in common: most of them are membrane proteins incorporating photosynthetic antennae surrounding the reaction center. Light-harvesting antennae are responsible for light absorption and electronic excitation transfer to a special pair of chlorophylls in the reaction center, where charge separation takes place, initiating further redox reactions.

The dynamics of electronic excitation migration and conversion in natural photosynthetic systems has been of interest to researchers for many years [1, 2]. The crystal structures of light-harvesting antennae from some bacteria have been determined by X-ray diffraction [3, 4]. All light-harvesting antennae are based on a network of interacting pigments (porphyrins) bound to other pigments (carotenoids) that extend the spectral range of absorbed light. This network usually has a ring structure [5]; however, the number of rings and their composition and arrangement are different in different bacteria. This raises the question of whether the structure of the antenna has an effect on the properties of a light-harvesting device, i.e., on the rate and quantum yield of energy migration from the antenna to the reaction center.

In recent year, much attention has been focused on the development of artificial photosynthetic systems [6, 7], including ones based on hierarchical molecular systems, dendrimers [8, 9]. Whereas the diversity of natural photosynthetic systems is limited by nature [10], the imagination of synthetic chemists knows no limit, so that artificial systems are highly various [11–13].

Different approaches are used for studying the energy transfer dynamics in photosynthetic systems, depending on the characteristic times of the process. The rates of energy transfer between the elements of the system are significantly different. Whereas energy transfer from carotenoid to porphyrin lasts no more than a few hundred femtoseconds, energy transfer between porphyrins takes a few picoseconds and that between two antennae, a few tens of picoseconds [5, 14]. This allows one to characterize energy transfer from carotenoid to porphyrin as a coherent process. Transfer between antennae is incoherent, which, together with the extreme complexity of biological systems, justifies the use of classical and semiclassical approaches to its description.

First attempts to describe the energy transfer dynamics in photosynthetic systems were based on the Förster theory [15], which considers energy transfer as an incoherent process. Applying the Förster theory to energy transfer in small systems gives results consistent with experimental data; therefore, it is also used for qualitative and semiquantitative consideration of large systems. The kinetic approach to analysis of energy transfer in photosynthetic systems is based on solution of the basic kinetic equation with the structure determined by the architecture of a photosynthetic system, and rate constants are calculated in terms of the Förster theory [16–18]. An analogous approach was used for model systems [11, 12], with the difference that the rate constants were used as model parameters.

More advanced methods of description of the energy transfer in photosynthetic systems are based on constructing the effective Hamiltonian of a porphyrin system [13, 19–24]. It is formulated either empirically, by fitting the matrix elements to spectral characteristics, or ab initio. The eigenvalues of this Hamiltonian determine the time characteristics of energy transfer. In the framework of this approach, matrix elements are represented as functions of the geometric parameters of an antenna, which makes it possible to consider the effect of the antenna architecture on the energy transfer characteristic [5, 24]. To consider the dissipation of energy to the protein surroundings, the density matrix representation is used [19].

In the present work, we use an extremely simplified approach in which the energy transfer is considered as random walks on a network of connected elements [12, 25]. This seemingly simple approach makes it possible to find a one-to-one correspondence between the energy transfer rate and efficiency, in the one hand, and the most general properties of the photosynthetic system structure, on the other hand. This approach also allows one to find the optimal arrangement of light-sensitive elements in the system. Since energy transfer along the antenna is accompanied by dissipation, the type of antenna architecture has a significant effect on which fraction of the photon energy is received by the reaction center, i.e., on the quantum yield.

DESCRIPTION OF THE MODEL

The energetic characteristics of the elements of a photosynthetic system are such that excitation migration between porphyrins in the same antenna is reversible and that from the antenna to the reaction center is irreversible. Therefore, it is natural to call the reaction center an energy acceptor. The antenna porphyrins are hereafter referred to as light-sensitive elements (LSEs). Porphyrins will be called neighboring if energy transfer between them is possible. Inasmuch as one photon excites only one LSE, all excitation energy is concentrated in this element at the initial instant of time. Therefore, the population of this LSE is 1. To consider the energy dissipation, we assume that each energy transfer event between any neighboring LSEs occurs instantaneously with the efficiency p, and the $(1 - p)$ fraction of energy dissipates. Energy transfer from a given LSE to all neighboring LSEs occurs with equal probability; therefore, the population Q of a given LSE after the $(i + 1)$th transfer event is

$$Q_{i+1} = p \sum_{\text{neighboring LSE}} \frac{q_i}{n_i} - Q_i, \tag{1}$$

where q_i are the populations of the neighbors of the given element, and n_i is the number of neighbors of each of these elements. The fact that the energy of a given LSE is uniformly transferred to all neighboring LSEs is equivalent to summation over all unbranched energy transfer routes taking into account their statistical weights. Thus, the process of energy transfer to the acceptor can be represented by summation over all transfer routes leading to the acceptor. Then, the fraction of energy received by the acceptor is

$$Q = \sum_{N = N_{\min}}^{\infty} p^N \sum_{j=1}^{j_{\max}} \left(\prod_{n=1}^{N} \theta_{j,n} \right)^{-1}, \tag{2}$$

where N is the route length, θ_n is the number of neighbors of the nth LSE met along this route, and j is the number of the route of length N. The Q value is determined only when the initially excited LSE is specified; therefore, it is also necessary to specify the efficiency averaged over the antenna. The excitation of each LSE in the antenna is equiprobable; therefore, the average efficiency $\langle Q \rangle$ is determined by the equation

$$\langle Q \rangle = \frac{1}{M} \sum_{i=1}^{M} Q_i, \tag{3}$$

where Q_i is the efficiency in the case of excitation of the ith LSE and M is the total number of LSEs.

In addition to the energy transfer efficiency, the rate of this process is an important characteristic of the photosynthetic system. It depends on two main factors: the architecture of the antenna and the rate of the elementary event of energy transfer between two LSEs. The second factor reflects the nature of the LSE and is not discussed hereafter. To characterize the efficiency of the antenna in time, let us introduce two parameters: the minimal $L_{\min}$ and average $\bar{L}$ route lengths. The former is defined as the minimal number of elementary events of energy transfer required for at least a small portion of energy to be received by the acceptor. The average route length is the sum of route lengths taken with the weights proportional to the energies transferred along these routes:

$$\bar{L} = \frac{\sum_{N = N_{\min}}^{\infty} p^N N \sum_{j=1}^{j_{\max}} \left(\prod_{n=1}^{N} \theta_{j,n} \right)^{-1}}{\sum_{N = N_{\min}}^{\infty} p^N \sum_{j=1}^{j_{\max}} \left(\prod_{n=1}^{N} \theta_{j,n} \right)^{-1}}. \tag{4}$$

The $L_{\min}$ and $\bar{L}$ values are determined for particular initially excited LSEs. It is also expedient to introduce the corresponding lengths averaged over the entire antenna ($\langle L_{\min} \rangle$ and $\langle \bar{L} \rangle$).

Due to the different natures of the LSEs and acceptor, the efficiencies of elementary events of energy transfer between two LSEs and between LSEs and the acceptor can be different (hereafter, designated as p and

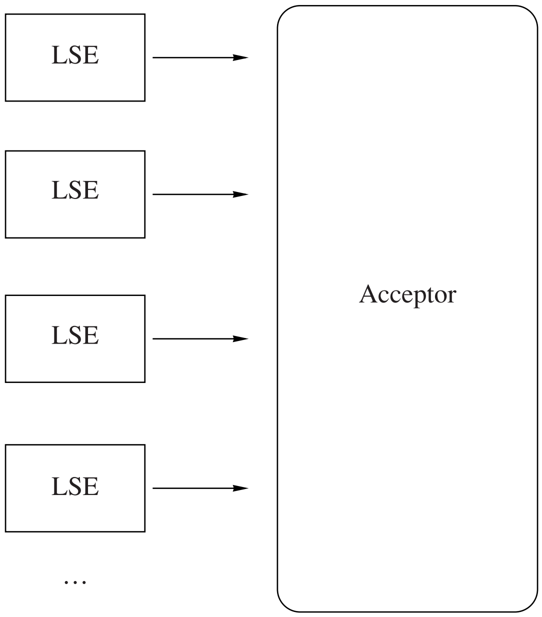

Fig. 1. Parallel antenna architecture.

P, respectively). This fact influences the efficiency of the antenna as a whole. To consider this effect, the above approach is applicable. It is worth noting that, for any route, energy transfer between LSEs and the acceptor occurs only once. This means that, in every summand of Eq. (2), the multiplier p^N should be replaced by $p^{N-1}P$. Thus, the refined formula for determination of the antenna efficiency will differ from Eq. (2) only in the presence of the multiplier P/p before the sum. It is evident that the $L_{\min}$ and $\langle L_{\min}\rangle$ values are independent of p and P and depend only on the antenna architecture. The $\bar{L}$ and $\langle \bar{L}\rangle$ are also independent on these parameters since, to determine them, the numerator and denominator in Eq. (4) must be multiplied by the same quantity P/p. These considerations allow us to simplify further calculations.

DIFFERENT TYPES OF THE ARCHITECTURE OF ANTENNAE

Type 1: Parallel Architecture

In this case, the excitation of any LSE leads to the same result: the acceptor receives a fraction of the light quantum energy P, and the $(1 - P)$ fraction dissipates. The average and minimal route lengths are equal to unity (Fig. 1).

$$Q_m = \langle Q\rangle = P,$$
$$L_{\min} = \bar{L} = \langle L_{\min}\rangle = \langle \bar{L}\rangle = 1. \tag{5}$$

Type 2: Sequential Architecture

Let a chain contain an infinite number of LSEs (then each has two neighbors) and the LSEs be numbered beginning from the acceptor (Fig. 2). If photon leads to excitation of the mth LSE, then the ultimate population of the acceptor unit according to Eq. (2) is

$$Q_m = P\sum_{i=0}^{\infty} p^{m+2i-1}2^{-m-2i}\nu(m, i), \tag{6}$$

where $\nu(m, i)$ is the number of routes of length $(m + 2i)$. This quantity has the following properties:

$$\nu(m, 0) = 1, \quad \nu(m, 1) = m,$$
$$\nu(m, i) = \nu(m+1, i-1) + \nu(m-1, i). \tag{7}$$

With the use of these relations, it can be shown that

$$\nu(m, i) = m\frac{(m+2i-1)!}{i!(m+i)!}. \tag{8}$$

Then, the ultimate population of the acceptor unit according to Eq. (6) is

$$Q_m = \frac{P}{p}\left(\frac{p}{1+\sqrt{1-p^2}}\right)^m. \tag{9}$$

If the number of LSEs in such an antenna is finite, Eq. (9) ceases to be valid. Unfortunately, we failed to find an analytical expression for a finite antenna. However, our numerical estimates allow us to state that the efficiencies Q_m for the infinite and finite antennae are almost the same if the number of elements exceeds 20 and there are no less than five LSEs between the initially excited LSE and the last element of the finite antenna. Therefore, further analysis of the properties of the sequential antenna is based on Eq. (9).

According to Eq. (3), the antenna efficiency averaged over all LSEs is

$$\langle Q\rangle = \frac{\sum_{i=1}^{M} Q_i}{M} = \frac{P}{p}\frac{\sum_{i=1}^{M}\left(\frac{p}{1+\sqrt{1-p^2}}\right)^i}{M}$$
$$= \frac{P}{M(1+\sqrt{1-p^2}-1)}\left(1-\left(\frac{p}{1+\sqrt{1-p^2}}\right)^M\right). \tag{10}$$

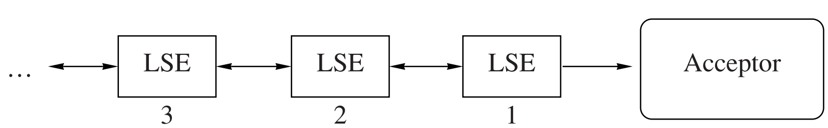

Fig. 2. Sequential antenna architecture.

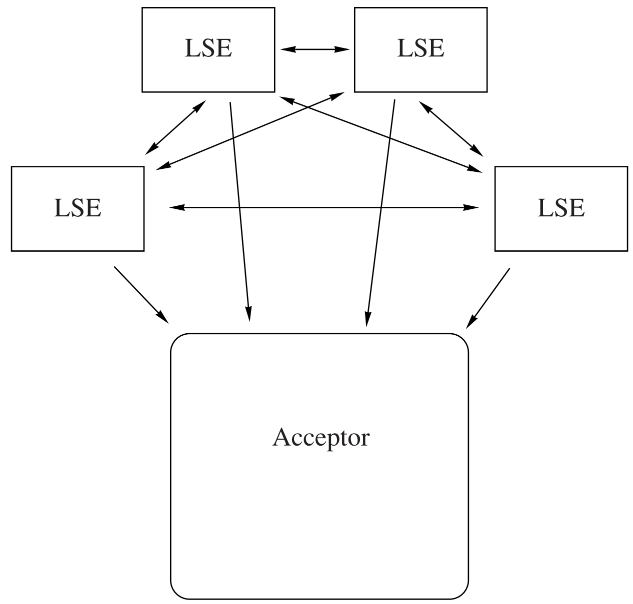

Fig. 3. Cluster antenna architecture.

It is evident that the minimal route length $L_{\min}$ when the mth element is excited is m. Then,

$$\langle L_{\min}\rangle = \frac{1}{M}\sum_{m=1}^{M} m = \frac{M+1}{2}. \tag{11}$$

The average route length is determined by Eq. (4):

$$\bar{L} = \frac{\sum_{i=0}^{\infty} p^{m+2i}2^{-m-2i}m\frac{(m+2i-1)!}{i!(m+i)!}(m+2i)}{\sum_{i=0}^{\infty} p^{m+2i}2^{-m-2i}m\frac{(m+2i-1)!}{i!(m+i)!}} = \frac{m}{\sqrt{1-p^2}}. \tag{12}$$

This means that the average length along the entire antenna can be determined by the equation

$$\langle\bar{L}\rangle = \frac{1}{M\sqrt{1-p^2}}\sum_{m=1}^{M} m = \frac{M+1}{2\sqrt{1-p^2}}. \tag{13}$$

Type 3: Cluster Architecture

This type is possible only in artificial photosynthetic systems. In nature, it is not encountered because of geometric limitations: porphyrins are too large to form clusters (Fig. 3).

In the cluster, energy can be transferred between any two LSEs and between any LSE and the reaction center. Let a cluster contain M elements. The characteristic feature of this cluster is that excitation of any element leads to the same result. Calculations analogous to the above allow us to obtain the following results. Upon the excitation of one (any!) LSE, the reaction center receives the following fraction of energy:

$$Q = P\sum_{i=0}^{\infty} p^i M^{-1-i}\mu(i), \tag{14}$$

where $\mu(i)$ is the number of routes of length $(i + 1)$, which is independent of the number m of the initially excites LSE. It follows from the antenna architecture that

$$\mu(i) = (M-1)^i; \tag{15}$$

then,

$$Q = P\sum_{i=0}^{\infty} p^i M^{-1-i}\mu(i) = P\sum_{i=0}^{\infty} p^i M^{-1-i}(M-1)^i = \frac{P}{M}\frac{1}{1-\frac{p(M-1)}{M}} = \frac{P}{M-pM+p}. \tag{16}$$

The average efficiency of the antenna is Q.

As in the case of the parallel architecture, the minimal route length is equal to unity:

$$L_{\min} = \langle L_{\min}\rangle = 1. \tag{17}$$

The average route length is the same for all LSEs: according to Eq. (4), it is

$$\bar{L} = \langle\bar{L}\rangle = \frac{P\sum_{i=0}^{\infty} p^i M^{-1-i}(M-1)^i(i+1)}{P\sum_{i=0}^{\infty} p^i M^{-1-i}(M-1)^i} = \frac{M}{M(1-p)+p}. \tag{18}$$

Type 4: Ring Architecture

This type of antenna (Fig. 4) is most typical of natural photosynthetic systems. As in the cluster antenna, all LSEs in the ring antenna are equivalent. The above equations allow us to obtain

$$Q = P\sum_{i=0}^{\infty} p^i 3^{-1-i}\mu(i), \tag{19}$$

where $\mu(i)$ is the number of routes of length $i + 1$. To calculate $\mu(i)$, let us note that $\mu(i) = 2\mu(i-1)$ and $\mu(0) = 1$. Hence,

$$\mu(i) = 2^i, \tag{20}$$

$$Q = \langle Q\rangle = \frac{P}{3-2p}. \tag{21}$$

As in the previous case,

$$L_{\min} = \langle L_{\min} \rangle = 1. \quad (22)$$

Using Eq. (4), we obtain

$$\bar{L} = \langle \bar{L} \rangle = \frac{P\sum_{i=0}^{\infty} p^i 3^{-1-i} 2^i (i+1)}{P\sum_{i=0}^{\infty} p^i 3^{-1-i} 2^i} = \frac{3}{3-2p}. \quad (23)$$

A close analogue of the ring architecture is a spherical one. If the LSEs are arranged around the acceptor as the carbon atoms in fullerene and each LSE has three neighbors, we obtain

$$Q = \langle Q \rangle = \frac{P}{4-3p}, \quad L_{\min} = \langle L_{\min} \rangle = 1, \quad \bar{L} = \langle \bar{L} \rangle = \frac{4}{4-3p}. \quad (24)$$

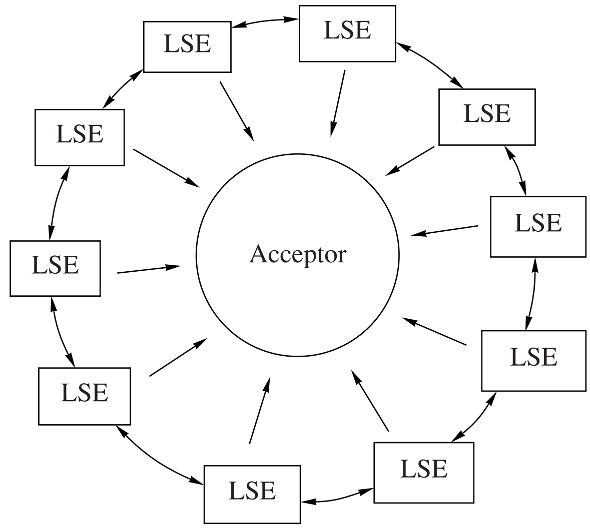

Fig. 4. Ring antenna architecture.

RESULTS AND DISCUSSION

The above probability analysis of the energy transfer dynamics in different photosynthetic systems makes it possible to characterize this dynamics by several quantities, the efficiency and route length averaged over the antenna $\langle Q \rangle$ and $\langle \bar{L} \rangle$, respectively—being the most important among them. For the sake of convenience, the results are summarized in the table.

The probability analysis of energy transfer showed that the architecture of the antenna significantly influences the transfer efficiency and rate. As intuitively predicted, the probability analysis shows that the most efficient antennae are those in which a maximal number of LSEs are in direct contact with the reaction center and the interaction with neighbors is minimal. In order of decreasing efficiency, the antenna types can be arranged as follows: parallel, ring, spherical, cluster, and sequential. A drawback of the sequential architecture, untypical of the other types, is that the efficiency of the antenna sharply decreases when even one contact between two LSEs is damaged and becomes zero when the connection between the first LSE and the reaction center is broken. The other types of antennae are more tolerant to damage. For example, the damage of even any three contacts in an antenna of the spherical type does not exclude any of the LSEs from light harvesting. The cluster antenna is evidently most stable to destruction.

The efficiency of the sequential antenna is also significantly affected by the probability of energy transfer between two LSEs. Indeed, at p rather close to unity, the Taylor expansion near $p = 1$ gives

$$\langle Q \rangle = \frac{P}{M(1+\sqrt{1-p^2}-p)}\left(1-\left(\frac{p}{1+\sqrt{1-p^2}}\right)^M\right) \approx \frac{P}{p}\left(1-\frac{M+1}{\sqrt{2}}\sqrt{1-p}\right); \quad (25)$$

Comparison of antennae with different architectures

Type	Number of LSEs	Average antenna efficiency $\langle Q \rangle$	Average transfer chain length $\langle \bar{L} \rangle$
Parallel	M	P	1
Sequential	M	$\frac{P}{M(1+\sqrt{1-p^2}-p)}\left(1-\left(\frac{p}{1+\sqrt{1-p^2}}\right)^M\right)$	$\frac{M+1}{2\sqrt{1-p^2}}$
Cluster	M	$\frac{P}{M(1-p)+p}$	$\frac{M}{M(1-p)+p}$
Ring	M	$\frac{P}{3-2p}$	$\frac{3}{3-2p}$
Spherical	M	$\frac{P}{4-3p}$	$\frac{4}{4-3p}$

i.e., the deviation of the efficiency from the maximal one is proportional to $\sqrt{1-p}$, whereas, for the other types of antennas, it is proportional to $(1 - p)$. Thus, the parallel arrangement of LSEs is more favorable. However, it should be taken into account that the parallel arrangement of a large number of LSEs leads inevitably to interactions between them and to a change in the type of antenna architecture. However, the use of a large number of LSEs is necessary for efficient light absorption and conversion. To resolve this contradiction, either the size of reaction centers should be decreased or the spherical arrangement of LSEs should be used, leading thereby to some loss in transfer efficiency but also to a significant gain in absorption efficiency due to the fact that the spherical surface can accommodate a large number of LSEs.

Natural light-harvesting antennae are mainly of the ring type. In particular, the LH1 antenna of the photosynthetic unit of purple bacteria is a ring consisting of 32 porphyrin fragments [5]. The architecture of the antenna of the photosynthetic complex of cyanobacteria is intermediate between a cluster and a ring and consists of 96 porphyrin rings [24]. The total number of porphyrin fragments per reaction center varies from 50 to several hundreds. Notwithstanding large sizes of photosynthetic complexes, the total quantum yield of the photosynthetic process varies from 80 to 95% [5]. This fact points to an extremely high efficiency of the elementary event of energy transfer in biological systems. In particular, for the LH1 antenna [5] to have an efficiency of 80%, P according to Eq. (21) should be $P = p = 0.923$.

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