DICHOTOMOUS DISORDER MODEL FOR SINGLE LIGHT-HARVESTING COMPLEXES

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Photosynthetic organisms conserve the captured energy of solar radiation into stable chemical forms. To do so, they have evolved specialized systems of pigment–protein complexes consisting of light-harvesting antennas and reaction centres. Photosynthetic antennas contain remarkably dense arrangements of light-absorbing pigments held by the protein scaffold, and their function is to absorb light and funnel the excitation energy to the reaction centre. Decades of experimental and theoretical research resulted in a detailed understanding of the energy migration pathways within the photosynthetic apparatus. The key parameters determining the excitation relaxation and transfer are inter-pigment coupling and energetic disorder or non-equality of excitation energies at equivalent pigment sites due to the interaction with the disordered protein scaffold. Circularly symmetric light-harvesting antennas from purple bacteria present a beautiful example of the interplay between these parameters. The spectral signature of this interplay could be observed with the single-molecule fluorescence microscopy techniques. The results of these measurements were interpreted with an intuitively clear dichotomous model of disorder of pigment site energies.

Keywords: photosynthetic, light-harvesting, antenna, energetic disorder, single-molecule

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Photosynthetic organisms conserve the intermittently available energy of impinging solar radiation into various stable chemical forms that can be utilized by an organism at its convenience. To do so, plants, algae, and photosynthetic bacteria have evolved specialized molecular machineries sharing a common architectural motif among different organisms: the photosynthetic apparatus consists of light-harvesting antenna complexes and reaction centres. Antennas absorb light, and the excitation energy is funnelled through the network of light-harvesting complexes to the reaction centre, where charge separation takes place and leads to the creation of energy-rich compounds and transmembrane proton gradient required for ATP synthesis [1].

Remarkably, although the quantum efficiency of the absorbed energy conversion to charge separation varies among organisms, overall it is very high and in some cases nears 100% [2]. Also, the initial energy transfer among different pigments within individual light-harvesting complexes and among different complexes takes place on an ultrafast time scale of femtoseconds to picoseconds [3]. This efficiency and speed result from specific arrangements of the light-absorbing pigments held by the protein scaffold. The intricacy of the mutual pigment arrangement is demonstrated by the fact that despite a very tight packing of pigments in the light-harvesting complexes, their fluorescence is not quenched. Concentration quenching is a phenomenon of the decrease of fluorescence quantum yield at a high concentration of fluorophores in a solution. For example, the fluorescence of chlorophyll a is completely quenched at a concentration of 0.3 M [4]. At the same time, the local concentration of pigments in a number of light-harvesting complexes from different

species approaches this limiting value. For example, in LHCII – the main peripheral light-harvesting complex in higher plants – the effective chlorophyll concentration is 0.25 M [5], and in the FMO complex from green sulfur bacteria the concentration of bacteriochlorophyll *a* is 0.1 M [6]. However, even at such a high concentration, the fluorescence of LHCII is not quenched because of optimized protein-mediated pigment positions and orientations.

Antenna systems from different organisms exhibit a remarkable diversity in terms of pigment number and composition as well as their structural arrangement. For example, LHCII is a trimeric pigment–protein complex with an asymmetric monomeric subunit. Each monomer, depending on the species, contains 13–15 chlorophylls *a* and *b*, and 3–4 carotenoids [1]. Fucoxanthin–chlorophyll (FCP) [8] and peridinin–chlorophyll protein (PCP) [9] complexes in diatoms and dinoflagellates contain an unusual 4:1 caroteinoid to chlorophyll stoichiometry, and carotenoids in these complexes contribute significantly to the light absorption. Phycobilisomes in cyanobacteria are peripheral light-harvesting complexes containing bilins, open chain tetrapyrrole pigments [10]. Different types of bilins comprise pigment–protein trimers that are organized in disks that, in turn, are assembled in rods. Green sulphur bacteria, photosynthesizing under extremely low light conditions, capture light by utilizing a gigantic assembly of bacteriophlorophylls (~200000) without the protein scaffold called chlorosome [11].

Decades of experiments using various spectroscopic tools combined with theoretical efforts and structural analysis have led to a detailed picture of the excitation energy migration pathways within different kinds of photosynthetic complexes [12]. In the case of relatively large inter-pigment distances, the observed energy transfer dynamics could be straightforwardly interpreted based on the Förster theory of resonant energy transfer assuming a point dipole approximation and a weak coupling between interacting pigments [13]. However, such an approach is not applicable in a system of strongly coupled chromophores which is the case in many instances of light-harvesting complexes. The response of a multichromophoric assembly of tightly packed pigments with small inter-pigment distances has to be considered in terms of collective excitations or excitons of clusters of interacting pigments [14]. Excitation energy migration and relaxation is then treated in the framework of the generalized Förster [15], modified Redfield [16] or combined Redfield–Förster approach [17]. Key parameters in these descriptions are the excitation energies of individual pigments (site energies) and the coupling energies between pigments. Interaction of individual pigments with the scaffolding protein matrix modifies the site energies introducing thereby the so-called static disorder of pigment excitation energies. Essential is the coupling of electronic transitions to the fast nuclear motions (phonons) as it results in a homogeneous broadening of electronic spectra and relaxation of excitation within an exitonic cluster and energy transfer between clusters.

LH2, the peripheral light-harvesting complex from purple bacteria, has been one of the very well-studied examples of antenna complexes illustrating the inner workings of excitation energy transfer [18]. Unlike other antenna systems, LH2 features a symmetric cylindrical oligomeric structure with two rings of bacteriochlorophylls *a* (Bchl *a*) called B850 and B800 by the wavelengths of their maximal absorption. LH2 from the purple bacterium *Rps. acidophila* is an assembly of 9 equivalent *αβ*-apoprotein subunits each consisting of two transmembrane *α*-helixes holding 3 Bchls [19] (Fig. 1). The central Mg^{2+} ions of 2 Bchls in the subunit belonging to the B850 ring are coordinated by His residues of *α* and *β*-apoproteins. The Mg^{2+} ion of Bchl of the subunit belonging to the B800 ring is coordinated by carboxyl-*α*M1 of *α*-apoprotein. Bchl molecules in the B800 ring are perpendicular to the transmembrane *α*-helixes with the centre-to-centre distance of 21.1 Å yielding a weak coupling of 24 cm^{-1} [20]. Bchls in the B850 ring are perpendicular to Bchls in the B800 ring. The centre-to-centre spacing between pigments in the B850 ring is only ~9 Å resulting in a much stronger inter-pigment coupling of ~300 cm^{-1}. The consequence of this relatively strong inter-pigment coupling is that excitation is delocalized over a ring which is evidenced by its superradiance (larger radiative rate than that of a single Bchl) [21] and its absorption maximum red-shift to 850 nm relative to that of Bchl. The observed effects can be interpreted in terms
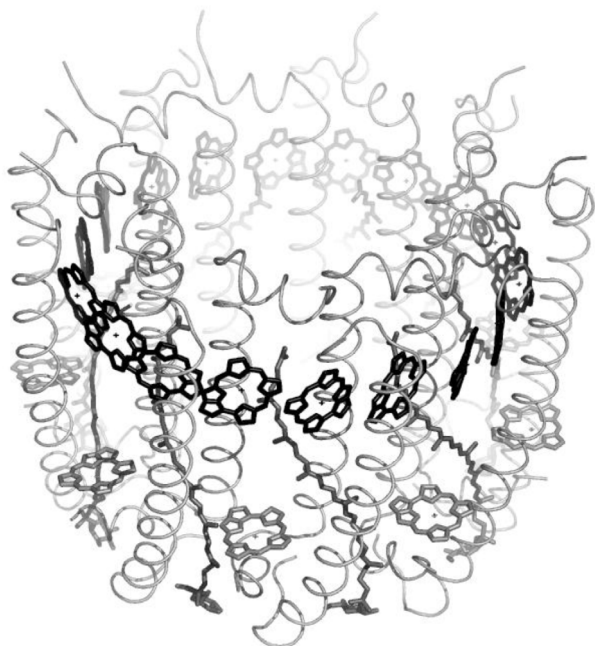
Fig. 1. The structure of LH2 from *Rps. acidophila*.

of the excitonic model of a circular pigment aggregate [22]. Within the framework of this model, an ideal B850 ring is characterized by an excitonic manifold of 18 energy states, with 16 states being pairwise degenerate. In a perfect ring excitation is delocalized over the whole ring. Because of the symmetry, only the low lying $k = \pm 1$ states are optically allowed, and this results in a redshifted absorption spectrum. This, however, is an oversimplified description since α-apoprotein and β-apoprotein-associated Bchls in the B850 ring are at non-equivalent sites, and their electronic excitation energies differ. A more realistic model of a ring of coupled dimeric subunits results in both low lying $k = \pm 1$ and higher lying $k = \pm 8$ states being optically allowed, which was, indeed, experimentally observed as an additional absorption band at 780 nm in a B800 ring-lacking LH2 mutant [23]. However, even this more sophisticated model of a ring of dimeric subunits does not allow interpreting all spectroscopic data of the B850 ring. For example, a low-temperature absorption spectrum of LH2 exhibits an 870 nm peak corresponding to a transition situated lower in energy than the 850 nm maximum [24]. To reproduce the experimental observations more adequately the excitonic model has to recognize possible non-equality of pigment site energies at equivalent sites – a phenomenon termed static

energetic disorder [12]. The existence of energetic disorder stems from the fact that pigments interact with an intrinsically disordered protein matrix and that this interaction exerts a somewhat different effect on pigment excitation energies at different sites. Incorporation of energetic disorder into the model reduces the extent of the excitation delocalization over the ring, lends some oscillator strength to all transitions in the excitonic manifold and lifts the degeneracy of the excitonic states. Experimentally the presence of energetic disorder was indirectly asserted as a limiting factor for the exciton delocalization and thus superradiance [39], and through its effect on the excitation energy migration in the B850 ring measured in time-resolved studies [25]. On the other hand, the presence of energetic disorder, its changes over time due to slow conformational changes of protein, and its influence on the spectral signature through a subtle interplay with fast nuclear motions have been demonstrated more directly with the aid of single-molecule spectroscopic methods that became available relatively recently [26].

Since the seminal demonstration of single-molecule detection by Moerner in 1989 [27], single-molecule microscopy has evolved into a toolkit of methods to study diverse biological systems in ways unattainable with more traditional bulk techniques [28]. The defining feature of a single-molecule approach is that it involves the measurement and/or manipulation of separate molecular entities, thereby circumventing ensemble-averaging of potentially different responses from individual molecules. This allows the detection of possible heterogeneities and the observation of the real-time dynamics of molecular interactions and parameters of interest.

Less than a decade after the first experiments, the single-molecule approach was used to monitor light-induced temporal changes of the fluorescence quantum yield and heterogeneity of this behaviour among individual LH2s from *Rps. acidophila* [29, 30]. Since then single-molecule spectroscopy methods were used to study light-harvesting systems from different organisms, including purple bacteria [31], higher plants [32], green sulfur bacteria [33] and cyanobacteria [34]. A series of works was dedicated to studying the room-temperature spectral dynamics of the light-harvesting complexes from different species of purple

bacteria as a signature of the underlying conformational changes [26, 31, 35–37]. The experiment involved excitation of the B800 ring and observation of the fluorescence signal after the fast energy transfer to the B850 ring. Therefore, the study was essentially concerned with the dynamics of the B850 ring. This work led to the discovery of notable (up to a few tens of nanometres) fluorescence spectral jumps between long-lasting states of the constant spectral maximum position, and these jumps were also found to be reversible. The frequency and size of the jumps correlated with the excitation intensity, suggesting that at least in part they were excitation light-induced. It was further observed that the shifts of the spectral maximum position were accompanied by changes of the spectral line shape: the red-shifted spectra featured a pronounced short-wavelength wing, while both the red and the blue-shifted spectra were found to be broader than those with the intermediate values of the peak wavelength. Based on the modified Redfield theory, changes of the spectral peak position were interpreted to be due to the abrupt changes of the realization of energetic disorder of Bchls in the B850 ring that in turn were suggested to be associated with slow conformational movements of the protein scaffold leading to the variation of the protein effect on electronic pigment transitions. The specific spectral line shapes associated with different spectral peak positions were accounted for by a subtle interplay between the static energetic disorder and fast nuclear motions in the case of different exciton delocalizations. The model successfully reproduced different spectral occurrences, however, since realizations of the static disorder were generated from a Gaussian distribution at random, the calculation could not be used to reproduce the real-time spectral dynamics.

An alternative model of static disorder was suggested by Valkunas et al. [38, 39] to offer a simpler and intuitively more accessible picture of microscopic changes underlying the observed spectral dynamics. Each Bchl in the B850 ring was assumed to reside in only two possible states with different electronic transition energies associated with only two assumed conformational states of the protein. A transition between these states can occur either in the ground or excited electronic states (Fig. 2). The rate of the inter-state transition then consists
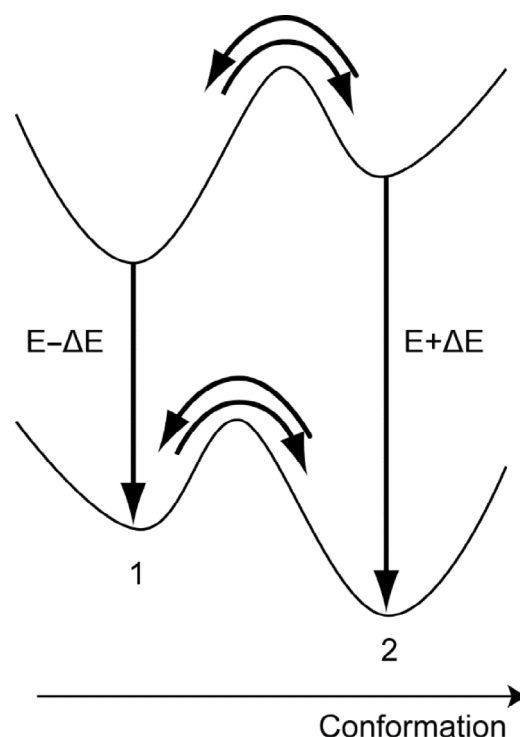

Fig. 2. A model of conversion between conformational states with different excitation energies.

of two parts: the part dependent on the inter-state energy barrier in the ground state and the part dependent on the excitation by means of transition in the excited state or the ground state because of the local heating after radiationless relaxation. The light-dependent part of the transition rate is expressed through the populations of different excitonic states and the participation coefficients of different pigments in those excitonic states. Fluorescence spectral evolution is then modelled by generating the initial realization of the static disorder randomly, diagonalizing the one-exciton Hamiltonian, and calculating the resulting transition rate constants for all pigments; pigment transition probability between states is assumed to decay exponentially with time, and since transitions occur randomly, equating transition probabilities of different pigments to a set of random numbers, a pigment with the shortest waiting time can be found; the energy state of that pigment is changed, and the fluorescence spectrum with the new realization of energetic disorder is calculated using the modified Redfield theory; this calculation sequence is repeated a number of times thereby generating spectral dynamics.

The transition rate constants between different energy states of the pigments and the excitation energy difference between the states were adjusted by fitting the averaged fluorescence spectrum, the distribution of spectral peak positions, the occurrence of spectral changes of different magnitude, and the distribution of time delays between the large spectral changes observed in the single-molecule measurement of LH2 fluorescence spectra. The resulting rate constant values were 0.0037 and 0.0074 s^{-1} for the transitions in the ground state and 0.18 and 0.37 s^{-1} for the transitions in the excited state for 2.5 μW excitation power. The rate constants in the excited state were expectedly found to increase with the excitation power.

The obtained fits reproduced the experimental observations reasonably well except that the model fell short of realistic prediction of the red-shifted spectral occurrences observed in the experiment with comparable frequency as the spectral jumps in the opposite direction. The authors argued that this shortcoming might be due to the way the disorder realizations were generated. The strongly red-shifted states are obtained if a few neighbouring pigments are in a low energy state – this causes a significant localization of the excitation on those pigments and results in an additional redshift due to the enhanced electron–phonon coupling. However, localization of the excitation on a pigment according to the calculation increases the probability of its spectral change, making the formation of the clusters of neighbouring red pigments unlikely. Consequent are infrequent red-shifted spectral occurrences. It is therefore obvious that although intuitively appealing and able to capture some of the experimental features, the dichotomous model of energetic disorder requires additional degrees of sophistication to describe a broader set of experimental observations.

Summarizing, the investigation of photosynthetic light-harvesting systems with various spectroscopic tools accompanied by theoretical modelling has led to a detailed understanding of the energy transfer and conversion in the antenna systems. Important for a fundamental understanding of the photosynthetic function, this information can also be used in the creation of improved artificial systems. On the other hand, the interpretation of the excitation energy transfer in the photosynthetic apparatus has served as a platform to test and develop theories with a possibly broader scope of application. In that sense, bacterial light-harvesting rings presented an example with a rich energy transfer dynamics occurring in different regimes. In addition to exhaustive studies using conventional ensemble techniques, these systems were also scrutinized using single-molecule approaches. The latter revealed hitherto undiscovered effects whose interpretation served as an additional test but called for a further adjustment of the existing theories.

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DICHOTOMINIS NETVARKOS MODELIS PAVIENIAMS ŠVIESĄ SUGERIANTIEMS KOMPLEKSAMS

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Santrauka

Fotosintetiniai organizmai transformuoja ir išsaugo sugertą saulės šviesos energiją stabilios cheminės energijos pavidalu. Tam padaryti evoliucijos metu jie išvystė specializuotas pigmentų-baltymų kompleksų sistemas, sudarytas iš šviesą sugeriančių antenų ir reakcijos centrų. Fotosintetinės antenos sudarytos iš tankaus pigmentų tinklo, laikomo baltymo karkaso, o jų funkcija yra sugerti šviesą ir nukreipti sužadinimo energiją į reakcijos centrą. Dešimtmečiai eksperimentinio ir teorinio darbo leido atskleisti detalų energijos pernašos paveikslą fotosintetiniame aparate. Pagrindiniai parametrai, lemiantys sužadinimo energijos relaksaciją ir pernašą, yra tarppigmentinės sąveikos stiprumas ir energetinė netvarka arba pigmentų, esančių ekvivalentiškose padėtyse, sužadinimo energijos netapatumas dėl sąveikos su netvarkia baltymo matrica. Cilindriškai simetriškos šviesą sugeriančios antenos iš purpurinių bakterijų yra geras šių parametrų sąveiką iliustruojantis pavyzdys. Spektrinė šios sąveikos reprezentacija buvo aiškiai stebima naudojant pavienių molekulių fluorescencijos mikroskopiją. Šių matavimų rezultatai buvo interpretuoti naudojant intuityviai lengvai suprantamą dichotominį energetinės netvarkos modelį.