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Light-Harvesting in Photosynthesis

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A brief survey is given on the elementary reactions of photosynthesis, with an emphasis on the functional separation into reaction centers that perform, after excitation, an ultrafast charge separation across the photosynthetic membrane, and light-harvesting complexes that absorb light and transfer the excitation energy to the reaction centers. The basic concepts are compared to those of photovoltaics.

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1. Introduction

For a visitor from outer space, photosynthesis and its seasonal changes are probably the most obvious signs of life on earth. Light is absorbed in the process and its energy used to fix about 10^{11} t of carbon per year in the form of carbohydrates that directly or indirectly maintain most life on earth. The total flux of solar radiation on top of the atmosphere and at an altitude of 90° amounts to 1.4 kW m^{-2}. Of this, ≈ 1 kW m^{-2} reaches the surface of the earth on a clear day, and of this 0.5 kW m^{-2} fall into the spectral range that can be used for photosynthesis (350 to 1050 nm), corresponding to a photon flux of ≈ 2 mmol m^{-2} s^{-1}.

The light climates experienced by life on earth can, however, deviate considerably from the unperturbed solar spectrum (Fig. 1). These deviations reflect both the abiotic and the biotic environmental conditions. Important parameters are the intensity, the spectral composition, and their variations in time. Lower solar altitudes change mainly the total light flux. Clouds and overgrowing vegetation reduce the light flux, but also change the spectral quality of the light. The water droplets of clouds absorb infrared light and scatter preferentially blue and UV light, while overgrowth by green plants absorbs mainly blue and red light.

The spectral modifications are even more pronounced in aqueous environments, where often only a narrow band can pass whose position depends on the water depth, its turbidity, the presence and type of phytoplankton and macroalgae and, in coastal waters, the contents of yellow-brownish organic matter from decaying vegetation. Most of these parameters can, furthermore, change in time: rhythmically with the seasons or daily cycles, or irregularly with the weather conditions. It was and is a major challenge for photosynthetic organisms to adjust to these ever changing light conditions. It involves the competition with other photosynthetic organisms for the prevailing light and, equally important, the protection from excess light: they have to optimize between starvation and being scorched.

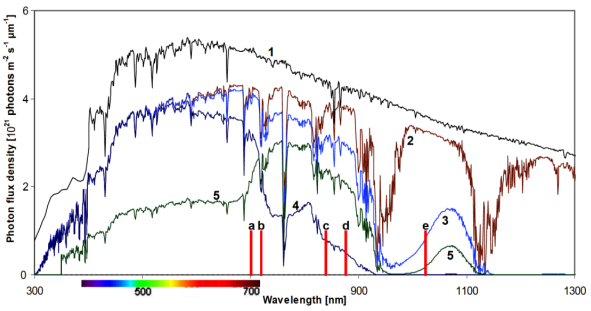

Fig. 1. Spectral distribution of light at different terrestrial and aquatic conditions, and positions of longest-wavelength absorbing complexes in different organisms. 1: top of atmosphere, 2: earth surface, clear sky, 3: 5 cm clear water, 4: 40 cm clear water, 5: 10 cm water containing green algae; (*a*) green plants, algae or cyanobacteria without (*a*) or with long-wavelength components (*b*), green bacteria (*c*), purple bacteria containing BChl *a* (*d*) or BChl *b* (*e*). Adapted from Kiang et al. [1]; the author thanks N. Kiang for providing the data files for this figure.

2. Modular organization and separation of light harvesting and energy transduction

The general solutions that have evolved for coping with the conflicting demands posed by the light climates are (a) a functional division of the productive photosynthetic apparatus into light-harvesting and energy transduction (Fig. 2), (b) a multi-level protection system against light-induced damage, and (c) an adaptive regulatory and repair system. This short overview will focus on topic (a).

Energy transduction takes place in reaction centers (RCs), which upon excitation induce an ultrafast, stepwise charge separation across a membrane that generates an electrochemical potential (Fig. 3) [2]. RCs are monophyletic, they are variants of a single prototype from which they evolved over the past $\approx 3 \times 10^9$ years. They use chlorophylls (Chls) as redox components and can, therefore, absorb light by themselves. Most of the light absorption takes place, however, in light-harvesting complexes (LHC) [3]. The core LHC are near the RC and co-regulated. The peripheral LHC that do most of the light-harvesting are polyphyletic: there are at least 6 inde-

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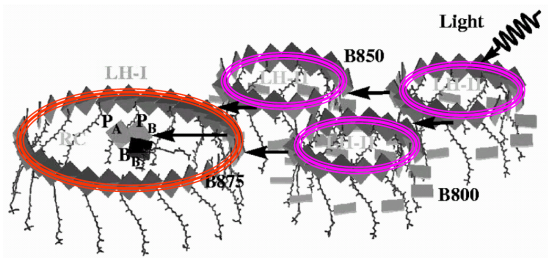

Fig. 2. Delocalized model of energy transfer in purple bacteria. LH-II is the peripheral LHC, LH-I the core LHC with the RC in the center. Colored rings indicate excitonically coupled Chls, thereby reducing the number of transfer steps and speeding up the Förster transfer [4–6]. Only the pigments are shown, the protein is omitted. Adapted from R.J. Cogdell, Glassgow.

pendently evolved types of LHC, and they contain Chls, carotenoids (Cars) and linear tetrapyrroles, phycobilins (PB) as chromophores that cover the entire visible and NIR spectrum. No single photosynthetic organism is capable of efficiently harvesting the full spectrum. Rather, a variety of photosynthetic organisms has evolved that are adapted to the various light climates by using characteristic pigment combinations. The functional division of the productive part of the photosynthetic apparatus into RC and LHC has a number of advantages.

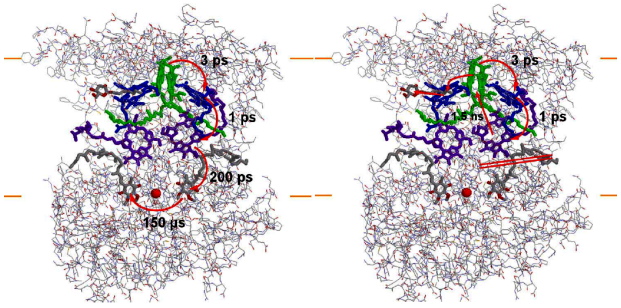

Fig. 3. Productive (left) and protective electron transport in reaction centers of purple bacteria. Adapted from Wachveitl and Zinth [7] and Angerhofer et al. [8].

(a) LHC reduce the biosynthetic investment: while RCs require about 165 amino acids (aa) per chromophore, even the most "expensive" LHC, biliproteins, require only 60–100 aa per chromophore. In green plants this is reduced to ≈ 15 aa, and the chlorosomes of green bacteria are almost devoid of protein.

TABLE

Light-harvesting effect of antennas on the turnover rates (s^{-1}) and saturation of RCs. The estimate assumes a turnover time of 10 ms, and a densely packed single layer of the complexes.

	Clear sky, solar altitude 90°		Ocean, 120 m depth	
	2000 μmol photons s^{-1} m^{-2}		0.05 μmol photons s^{-1} m^{-2}	
	Turnover rate (s^{-1})	RC saturation	Turnover rate (s^{-1})	RC saturation
RC only	1	0.01	25×10^{-6}	0.5×10^{-6}
core complex	50	0.5	0.001	25×10^{-6}
complete PS system	≤ 500	saturation	0.025	0.5×10^{-3}

(b) LHC enhance the absorption cross-section of RC. In a single-layer of RC, each would only receive ≈ 1 photon per second at maximum sunlight. Considering the turnover time of RC in the range of ≈ 0.01 s, this would correspond to 1% saturation, and even much less under reduced light (Table). By coupling hundred or more chromophores of the LHC to the RC, this situation is greatly improved.

(c) LHC broaden the spectrum of light absorption. RCs contain only Chls as chromophores, and only few of them. There absorptions cover, therefore, only a small fraction of the spectrum, which may not even match the prevailing light conditions. Consider, for example, an alga in clear oceanic water. At a depth of several meters, only a narrow band of light will be available that peaks, depending on the turbidity, between ≈ 460 and 550 nm. Chl *a*, the RC pigment of almost all oxygenic photosynthetic organisms, has two absorption maxima at ≈ 430 and ≈ 680 nm; this constitutes a considerable mismatch. In this case, antennas in the blue-green spectral region are advantageous, containing carotenoids, biliproteins, or a variety of Chls (Figs. 1, 4).

(d) The modular architecture allows for quantitative variations of LHC and RC. Depending on the light conditions, their proportion can be adapted in almost all photosynthetic organisms. Trees have, for example "sun leaves" and "shade leaves" in regions exposed to high and low light, respectively. The number of LHC per RC is maximized in the shade leaves, but reduced in sun leaves, thereby allowing the RC to work in an optimum range irrespective of the light intensity.

(e) Many organisms also allow for qualitative changes of the antenna system. The most striking example is

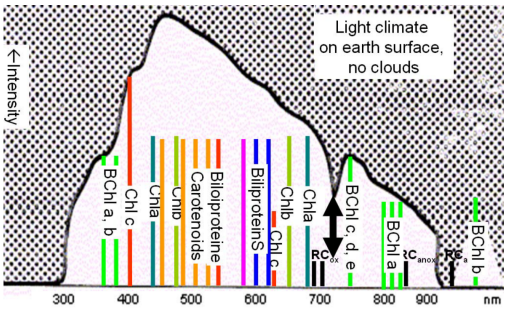

Fig. 4. Coverage of solar spectrum with photosynthetic light-harvesting pigments.

probably the complementary chromatic adaptation of cyanobacteria (Fig. 5) where the LHCs are reversibly restructured with differently absorbing biliproteins whose absorptions match the color of the light [9].

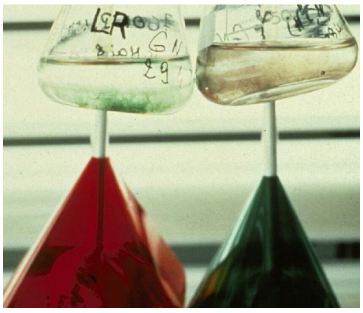

Fig. 5. Complementary chromatic adaptation of the cyanobacterium, *Fremyella diplosiphon*. When grown under red light (left), the LHC contains mainly the blue-green (= red-absorbing) phycocyanin. The same culture produces LHC rich in the red (= green-absorbing phycoerythrin when it is grown under green light). The picture was provided by Nicole Tandeau de Marsac, Institut Pasteur, Paris.

(f) In oxygenic photosynthesis, two photosystems work in series, which requires a current matching of the electron flow through both systems. Part of this regulation is by a rearrangement of the LHC such that excitons are preferentially funneled to one or the other photosystem's RC. Since also part of the electron flow can be changed from linear (producing the reductant, NADPH, and the energy-rich triphosphate, ATP, at a ratio of 2:3) to cyclic (producing only ATP), this also allows for an adaptation to the relative metabolic needs of the two products of photosynthesis.

(g) Any overload of the photosynthetic system can lead to severe damage. LHC are involved in the adaptation to excess light by non-productive internal conversion of excited states into heat. This process, called non-photochemical quenching, involves various protective mechanisms that are only partly understood. One example is the chemical transformation of the light harvesting carotenoid, violaxanthin, into the quenching carotenoid, zeaxanthin. Quenching also takes place in RC, by triplet energy transfer to carotenoids (Fig. 3).

3. Light-harvesting proceeds with high quantum efficiency at the expense of energy efficiency

Light-harvesting proceeds generally with quantum efficiencies near 100%. Long-range transfer proceeds by the Förster mechanism, which is often assisted by excitonic coupling that decreases the number of transfer steps. Short-range transfer by electron exchange (the Dexter mechanism) is particularly important with carotenoids. The primary charge separation in RC takes place within <10 ps, and is nearly irreversible under non-saturating conditions due to a carefully optimized reaction sequence (Fig. 3). With excited lifetimes of Chls in the range of 5 ns, this corresponds to quantum efficiencies >98%. Since charge separation starts from the lowest excited singlet state, ^1S, of the primary donor, this energy sets a low-energy limit for photosynthesis. In oxygenic photosynthesis, the primary donors of both photosystems absorb at $\lambda_{RC} \approx 700$ nm, in special cases at $\lambda_{RC} \approx 720$ nm. Excitons generated by the absorption of photons with $\lambda < 700$ nm in the LHC are transferred to the RC with quantum efficiencies near 100%, but at the cost of downgrading them to energies corresponding to λ_{RC} (170 kJ mol^{-1} for $\lambda_{RC} = 700$ nm). Assuming clear skies and that all photons < 700 nm are absorbed by the LHC, this amounts to an energetic efficiency of light capture of 77%. RCs of anoxygenic photosynthesis absorb at longer wavelengths (≈ 840, 870 or 980 nm). They have, accordingly, also LHC that absorb down to these wavelengths, thereby sampling a larger fraction of the solar spectrum, but with a reduced overall energetic efficiency (65% for $\lambda_{RC} = 980$ nm).

For the unperturbed solar spectrum, the amount of light-harvesting would increase well into the IR with increasing cut-off wavelengths of the RC, in spite of the decreasing energetic efficiency. This situation can, however, change near strong and broad absorption bands that are prominent, in particular, in aquatic conditions. Even a small water column of only few cm shows strong absorptions in the NIR spectral range (Fig. 1). Red-shifts in these regions would decrease the total amount of energy harvested. It seems reasonable, therefore, that groups of organisms have evolved whose longest-wavelength absorbing complexes cluster right at the high-energy edge of these NIR absorptions (red bars in Fig. 1).

The situation becomes more complex in the presence of competing photosynthetic organism. An example is again shown in Fig. 1. In the shade of green algae most of the visible light is blocked, with a steep increase of light intensity > 700 nm. In this case, already a small shift into the IR would be advantageous, and under these conditions there have indeed cyanobacteria been found that contain such pigments [10]. They either contain chlorophylls that are red-shifted, compared to Chl *a*, or a Chl *a* pool that is red-shifted by a special environment (see below). In *Acaryochloris marina*, LHC and RC contain Chl

d by which their absorptions are red-shifted by ≈ 25 nm. A search for other Chl d containing organisms has not only uncovered several new species, but also one that contains the even more red-shifted Chl f [11]. It remains to be seen if this is also functional in the RCs, thereby red-shifting λ_{RC} to ≈ 735 nm.

There are many other examples on how special light conditions are met by organisms with appropriate pigmentation. In clear oceanic waters where the intensity maximum of the light is at ≈ 470 nm, algae containing c-type Chls benefit from their intense Soret band at ≈ 450 nm [12]. *Prochlorococcus* is another example where a small shift of a specialized pigment can be advantageous. They contain [8-vinyl]-Chls a and b whose Soret bands are, *in vivo*, red-shifted by only 8–10 nm compared to those of Chl a and Chl b, respectively. This shift seems, nonetheless, to allow low-light adapted strains to grow at depths reaching 200 m where only a narrow band of blue light is available [13]. Light in the blue region is also harvested by biliproteins with urobilin chromophores, these are particularly abundant in cyanobacteria of the *Synechococcus* group that have been isolated from the open ocean [14]. Yet another group of blue-light absorbing pigments are carotenoids. They are present in all photosynthetic organisms as protective pigments, but their light-harvesting efficiency is generally poor because of their short excited state lifetimes ($\approx$ 1 ps). However, haptophytes, dinoflagellates and some other algae contain the longer-lived (≤ 150 ps) carotenoids, fucoxanthin or peridinin, as main light-harvesting pigments [15]. All of the aforementioned organisms contribute substantially to marine photosynthesis that provides about 50% of the global biomass production.

4. Light energy can be supplemented by thermal energy

Photosynthesis occurs at ambient temperature ($\approx$300 K) whose thermal energy is small compared to that of the light energy. For oxygenic photosynthesis ($\lambda_{RC} \approx 700$ nm) it amounts to only $\approx 2\%$, and for bacterial photosynthesis up to 3%. Although these values seem negligible, there are conditions where thermal upconversion seems relevant. This is most pronounced in situations where photosynthetic organisms with similar pigmentation compete for light. If, for example, light < 700 nm is largely depleted under a dense canopy of green vegetation, organisms capable of using the residual light > 700 nm have a clear advantage.

One way to use this light while maintaining λ_{RC} at 700 nm is the thermally-assisted uphill transfer of excitation energy from pigments absorbing at $\lambda_{LHC} > \lambda_{RC}$. Such low-energy pigments are, indeed, found in most photosynthetic organisms [16, 17]. The current limit for red-shifted LHC containing Chl a is 738 nm, in photosystem I of the cyanobacterium *Spirulina platensis*. In BChl b containing purple bacteria ($\lambda_{RC} \approx 980$ nm), the LHC absorb at 1020 nm, and there is a BChl a containing purple bacterium ($\lambda_{RC} \approx 870$ nm) with an LHC absorbing at 963 nm [18]. The mechanism for this transfer is unclear, but it is likely that the ultrafast charge separation in the RC helps out-competing the energetically and entropically favored back transfer to these LHC.

5. Photosynthesis and solar cells

Global photosynthesis fixes per year $\approx 10^{11}$ t of carbon in the form of carbohydrates, and has provided in the past the fossil fuel we are using. Since these deposits are limited, the technical harvesting of solar energy is an option that is increasingly exploited. In this section, some general concepts of the natural and technical systems shall be briefly compared, as well as emerging hybrid techniques.

The primary steps in photosynthesis are photovoltaic, that is, a light-induced charge separation across a membrane. Although the biomass yield of photosynthetic organisms is generally $< 1\%$ [19], charge separation proceeds with near to 100% quantum efficiency. The resulting membrane potential is used in a cyclic process to generate the high-energy compound, ATP, or in a linear process to drive an uphill redox process, the reduction of NADPH by water. Both products are moderately stable high-energy compounds that drive the immediate cellular metabolism, or are converted to long-term storage products such as starch or oil. Silicon based solar cells and dye-sensitized solar cells also generate a photocurrent, but the short-term storage to buffer supply and demand over hours or days, is a major challenge. Besides smart grids, water reservoirs or rechargeable batteries, the electrolytic production of hydrogen is an option [19]. There are, *vice versa*, efforts to generate hydrogen photosynthetically by coupling the photosynthetic electron transport to hydrogenases or nitrogenases [20–22].

Both silicon and dye-sensitized solar cells are, in the terminology of photosynthesis, RC-only systems. The currently installed large-scale silicon-based photovoltaic fields are most efficient under clear skies, some use surface modifications to increase capturing of diffuse light. If they are supplemented by light-harvesting systems, these are generally macroscopic devices like mirrors that, unlike natural LHC, also rely on direct insolation. Concentrators based on internal reflection are an attempt to cope with diffuse light [23]. Interestingly, this principle is also used in leaves, where the optical pathlength, and thereby the absorption, is increased several fold by an appropriate architecture.

Light-harvesting can also be enhanced on the microscopic scale by metallic nanoparticles. LHC from algae and photosynthetic bacteria gave up to 18fold fluorescence enhancement, mainly by plasmonic enhancement of absorption, when coupled to silver nanoparticles [25]. Implementation of this principle would require control over distance and relative orientation of the two components. By controlled changes of these parameters, this hybrid system might even be capable of quenching excess energy. Reversible distance control is, in principle,

available, even by light [26]. It is presently unclear if this combination also enhances the light-harvesting efficiency per unit volume, when the spatial demands are compared to that of plant light harvesting systems, or the compact packing of Chls in chlorosomes [27].

Current semiconductor cells are single band-gap systems that, like photosynthesis, downgrade the energy of exciting photons to that of the low-energy band-gap ($\approx$ 1100 nm). Multi-junction cells are under development [28]; and dye-sensitized solar cells (DSSCs). with different dyes can be layered; both are conceptually an advantage compared to oxygenic photosynthetic organisms where two photosystems work in sequence, but operate at almost the same wavelengths ($\approx$ 700 nm). Alternatively, it has been proposed to couple the water-splitting photosystem II ($\lambda_{max} \approx 700$ nm) with a bacterial system ($\lambda_{max} \approx 870$ nm) [19]. An advantage of the existing natural system is the individual regulation of the two photosystems and the accessibility of the intermediate electron carriers, thereby allowing for flexible current matching. Communities of photosynthetic organisms may be considered a biological equivalent to multi-junction devices. Pierson et al. [29] have shown that in a marine microbial mat, the different types of phototrophs are layered in a way that the upper layer uses light $\leq$ 700 nm, and the lower layer sequentially the NIR light down to 1020 nm.

Last but not least shows the current diversity of photosynthetic organisms that very likely no single technology will be capable of efficiently harvesting the sun in the different light climates on earth.

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