

Lessons from nature about solar light harvesting

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Solar fuel production often starts with the energy from light being absorbed by an assembly of molecules; this electronic excitation is subsequently transferred to a suitable acceptor. For example, in photosynthesis, antenna complexes capture sunlight and direct the energy to reaction centres that then carry out the associated chemistry. In this Review, we describe the principles learned from studies of various natural antenna complexes and suggest how to elucidate strategies for designing light-harvesting systems. We envisage that such systems will be used for solar fuel production, to direct and regulate excitation energy flow using molecular organizations that facilitate feedback and control, or to transfer excitons over long distances. Also described are the notable properties of light-harvesting chromophores, spatial-energetic landscapes, the roles of excitonic states and quantum coherence, as well as how antennas are regulated and photoprotected.

Sunlight is the most abundant source of energy we have at our disposal. It plays the deciding role in net primary production on earth^{1–3} by promoting high-energy chemical transformations that otherwise proceed at negligible rates. Researchers must learn how to capture, transfer and store solar energy effectively because it is forecast to provide a significant fraction of the world's energy needs over the next century⁴. To utilize energy harvested from sunlight efficiently to promote photochemical reactions or to produce solar fuels, we must understand and improve both the effective capture of photons at a reactive site and the transfer of excitation energy. This would allow the design of molecular 'circuits' that can direct, sort and respond in sophisticated ways to excitation energy^{5–7}.

In this Review, by drawing parallels to photosynthetic light harvesting, we discuss the design principles for antenna systems that capture light. Light harvesting is important for the function of photosynthesis⁸ — for a variety of reasons — so exploring the operation of natural light-harvesting complexes provides an excellent platform for understanding how photo-excitation can be directed and amplified using assemblies of light-absorbing molecules^{9–12}.

It is not surprising that working out how nature has mastered the efficient capture of the Sun's energy has been the subject of research for over a century^{13,14}. This extraordinary chain of events is started and regulated by light harvesting. Energy from sunlight is captured by complexes that subsequently funnel it to reaction centres on a 10–100 picosecond timescale^{15–20}. More specifically, light harvesting relies on the process of electronic energy transfer moving electronic excitation energy — which is stored fleetingly (nanoseconds) by molecules in excited states — within networks of light-absorbing molecules (chromophores) to a target chromophore or trap^{21–25}. This timescale constrains the size of the chromophore arrays attached to the reactive site, or how far excitation energy can travel (exciton diffusion length) in organic films such as those comprising organic solar cells. The structural differences in antennas can be subtle between an arrangement of chromophores that optimizes trapping via energy transfer through the antenna, compared with an arrangement that works inefficiently, contains excitation traps or simply quenches the excited-state lifetime.

In the reaction centres, electronic excited states are converted to separated charges, and sequential electron transfers 'gear down' the

ultrafast dynamics of light-harvesting to relatively slow biological timescales. Later, energy is stored transiently as electro-chemical potential, trans-membrane charge-separated states that live for nanoseconds to milliseconds. That potential drives a complex network of processes facilitated by electron-transport chains and proton translocations that catalyse biochemical reactions to generate stored chemical potential.

The aim of this Review is to condense what has been learned from studies of natural light-harvesting complexes into a few important lessons that can aid the design of synthetic systems. Some of these design principles are not easily applied using current chemical synthesis procedures, yet they are fascinating and still under study. An example is the role that the protein plays by organizing the chromophores and tuning their 'site' energies in such a way that light harvesting is optimized. Other phenomena, such as the recent discovery¹² that quantum coherence is involved in the transport of electronic excitation, challenge our understanding of chemical dynamics.

Light-harvesting systems concentrate excitation

Natural solar-energy conversion in photosynthesis is one of the most important biological processes in which electronic energy-transfer plays a decisive role. The objective of photosynthesis is to produce biological energy, which is generated in direct ratio to photoinduced charge-separation reactions occurring in reaction-centre complexes. Notably, however, reaction centres are surrounded by many chromophores (often ~200) that are bound in light-harvesting complexes; these complexes contain a high concentration of molecular chromophores that absorb solar photons. The energy, stored in electronic excited states of the chromophores, is then transferred within and among light-harvesting proteins until it reaches a reaction centre (Fig. 1). The mechanism of this energy-transfer process at the heart of light-harvesting has been studied in considerable detail^{26–32}.

What advantage is gained by diluting the machinery that matters, the reaction centres that act as nature's solar cells, with proteins that simply capture sunlight and transport electronic energy? Augmenting a reactive site (for example, reaction centre) with a light-harvesting antenna enables it to attain a substantially (~100 fold) increased cross-section for light absorption. This means it

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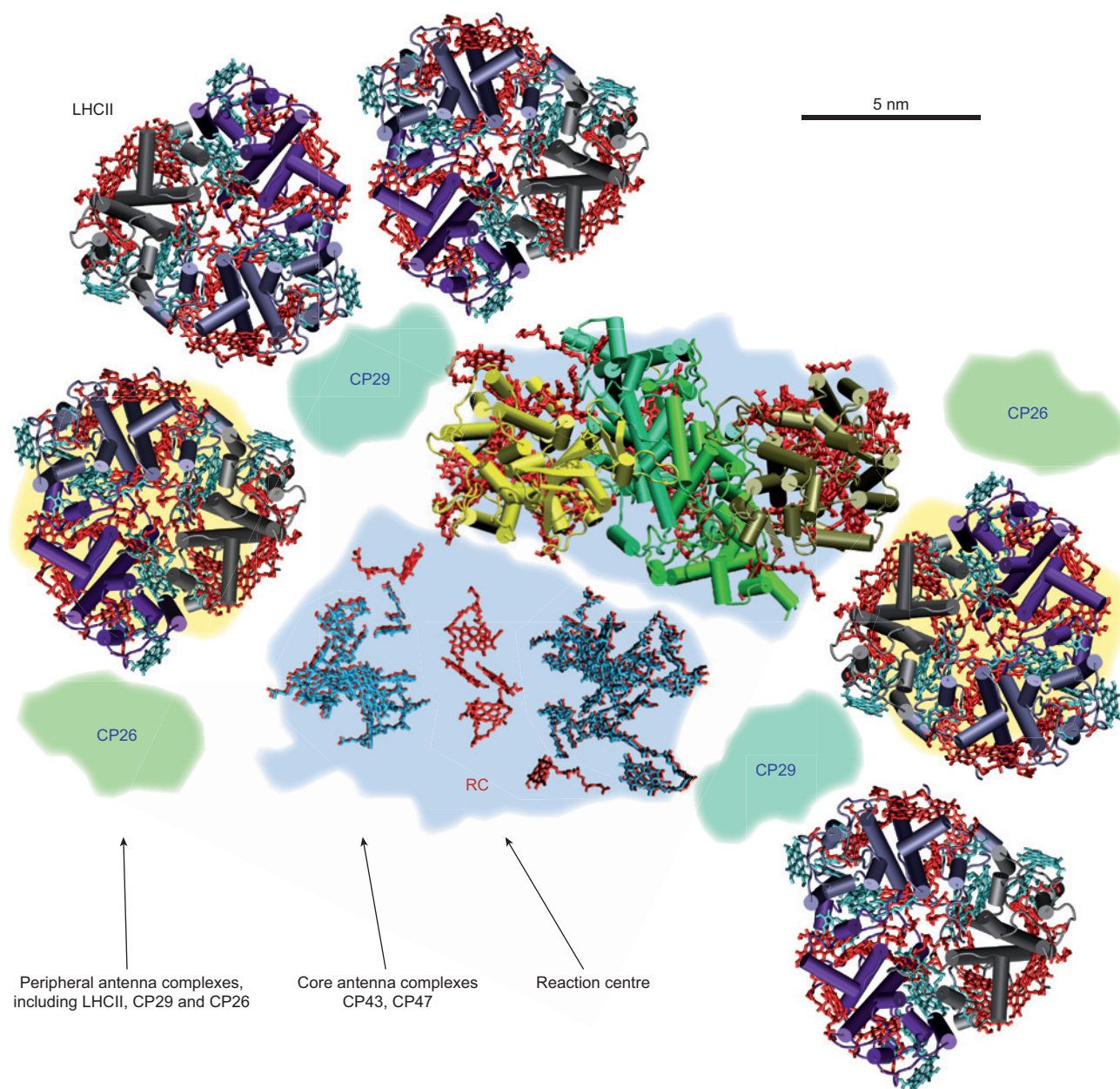


Figure 1 | Structural organization of light-harvesting complexes and reaction centres in higher plants and green algae. The layout of the proteins comprising photosystem II (PSII) supercomplex¹³⁵ is templated on the electron-density map reported by Barber and co-workers (shaded regions)¹³⁶. To illustrate what the proteins resemble, atomic resolution structural models of the peripheral light-harvesting complex LHCII (pea¹³⁷) and the core of PSII (cyanobacterium¹³⁸) are drawn. Excitation energy captured by the LHCII and the minor peripheral light-harvesting complexes (including CP29 and CP26) is transferred, via core light-harvesting complexes CP43 and CP47, to the reaction centre (RC, red) where charge separation is initiated.

is more frequently converted to an excited state and, as a consequence, it can perform multiple turnovers (for example, photochemical reactions) in a fraction of a second. For example, fluorescence-based sensors are sensitive because the fluorescent signal can be detected with single-event precision — but the limitation is the infrequent absorption of light that activates the sensor. This has been obviated by connecting the sensor to many light-absorbing molecules that can each capture the input light then transfer their electronic excitation to the sensor, hence providing amplification³³. Absorption amplification means that the capture radii for weak incident light is increased both spectrally and spatially. The ability to concentrate excitation energy aids chemical reactivity initiated by energy pooling³⁴ and photophysical processes such as triplet up-conversion³⁵.

Excitation concentration by photosynthetic light-harvesting antennas particularly helps organisms thrive in low light conditions. Light levels are reported as irradiance in units $\mu\text{E m}^{-2} \text{s}^{-1}$ ($\text{E} = \text{Einstein} = 1 \text{ mol photons}$). During the day, irradiance is on average a few hundred $\mu\text{E m}^{-2} \text{s}^{-1}$ and it can peak at over 1,000 $\mu\text{E m}^{-2} \text{s}^{-1}$. Low light conditions for culturing photosynthetic organisms are considered to be $\sim 50 \mu\text{E m}^{-2} \text{s}^{-1}$, which is still considerably brighter than a typical office space. At an extreme, the irradiance from a full Moon on a clear night is $<0.001 \mu\text{E m}^{-2} \text{s}^{-1}$. Efficient and environment-customized light-harvesting allows some organisms to inhabit unusual ecological niches. One of the popular champions of photon scavenging reported so far is a bacteriochlorophyll-*e* containing green sulfur bacterium found in the Black Sea at a depth of 80 metres³⁶. At that depth solar irradiance

is estimated to be merely $\sim 0.003\text{--}0.01\ \mu\text{E m}^{-2}\text{ s}^{-1}$. Under such conditions primary production is very low (doubling times are in the range of 3–26 years), but it is remarkable that it occurs at all. A single bacterium receives only $\sim 300\text{ photons s}^{-1}$ in this habitat, whereas $\sim 10^{16}$ photons s^{-1} are incident on one medium-sized leaf of a plant sitting on your windowsill.

Most catalytic events in photosynthesis, such as quinone reduction and water oxidation, require multiple turnovers, that is, multiple consecutive photo-induced electron-transfer events at a single reaction centre. The photoexcitation rate of a reaction centre must therefore exceed a certain threshold otherwise stored energy is lost by charge recombination. Poisson statistics dictate that the antenna size per reaction centre depends on available light. Indeed, it has been found that some purple bacteria develop more expansive antenna systems when cultured under low light conditions (Fig. 2), and this influences the ratio of light-harvesting antennas to reaction centres needed to concentrate excitation energy at the optimal rate³⁷. When the quantity of interest is simply the quantum yield of charge separation, it was found that minimum functional areas could be identified that reflect the representative ratio of peripheral light-harvesting complexes to reaction centres (defined by the dashed squares in Fig. 2). However, long-range connectivity does affect other diffusion-related properties, for instance the first passage time of excitation to an available reaction centre.

Spectroscopic requirements of light-harvesting molecules

The building blocks of light-harvesting antennas are chromophores — molecules that can be selected for their size, shape, energy gap, absorption strength, spectral features or functionality. The size, shape and absorption strength of molecules determine how they interact with each other³⁸. The transition energies of the chromophores and shapes of their absorption and fluorescence spectra, together with how the molecules are assembled, decide the energy landscape.

The chromophores used for photosynthetic light-harvesting include chlorophylls, linear tetrapyrroles, and carotenoids such as β -carotene and lutein in plants, but also fucoxanthin and peridinin in some algae. They have exceptional molar extinction coefficients, typically $\sim 100,000\text{ M}^{-1}\text{ cm}^{-1}$. As a consequence, the absorbance for 675 nm light incident normal to the thylakoid membrane of a single complex of light-harvesting complex II (LHCII) — the major light-harvesting antenna of higher plants and green algae — containing 42 chlorophylls (24 chlorophyll-*a* plus 18 chlorophyll-*b*) is ~ 0.1 . That means 20% of the incident light at 675 nm can be captured by a single monolayer of protein. It is remarkable that such highly effective pigment–protein structures have been assembled despite limited synthetic versatility — the chromophores derive from the same biosynthesis pathways as other molecules such as haem. In the biological context, the chromophores are not solely selected for their optical properties, but also for their functional compatibility with the rest of the system³⁹.

Why is it not desirable to employ one giant three-dimensional molecule instead of an assembly of several molecules in the same volume? The issue here boils down to dielectric screening and electron–electron interactions. Screening of the transition density by other electrons in the system leads to size-saturation of the transition dipole⁴⁰. We speculate that it is probably better to couple several molecules through strong dipole–dipole interactions, weakly screened because of the ‘space’ between the molecules, than extend a many-electron system through space. Semiconductor nanocrystals, for example, can occupy the same volume as LHCII, but their lowest exciton transition has only $\sim 10\%$ of the absorbance strength compared with LHCII⁴¹.

What are the rules for engineering molecular chromophores with high extinction coefficients? Scaling laws are known for linear chromophores such as polyenes, carotenoids and π -conjugated polymers⁴². The lowest allowed electronic transition of

linear chromophores exhibits dipole strength dependent on length squared. However, under normal temperature conditions, the scaling plateaus at lengths of about 10–15 double bonds due to a combination of effects. They include conformational disorder that twists the bonds and breaks conjugation, dephasing and electron–electron screening. Polymethine dyes are examples of linear chromophores that have been extensively studied to optimize their optical properties by modifying donor–acceptor functionalization at each end of the π -electron system⁴³.

More rigid, cyclic, π -electron systems have the advantage that conformational disorder can be avoided. Polycyclic aromatics have absorption bands with notably high extinction coefficients, up to $410,000\text{ M}^{-1}\text{ cm}^{-1}$ in the case of the tetracene $^1\text{B}_g$ band⁴⁴. However, this most intense band of the polycyclic aromatics is always a higher excited state, not the first or second absorption band, because of the rules deciding the angular momentum decomposition of electronic levels of these molecules⁴⁵. Squaraines are examples of small organic molecules with very high extinction coefficients of their lowest electronic transition — up to $\sim 250,000\text{ M}^{-1}\text{ cm}^{-1}$ has been reported⁴⁶.

In addition to absorption strength, spectral width of absorption bands needs to be considered. It is often advocated that broad spectra are desirable for chromophores constituting the active layer of organic solar cells because a greater spectral cross-section of the solar spectrum can be harvested. However, it is only if the device absorbs all incident light that this argument holds, otherwise it makes no difference for light capture if the absorption band of a single chromophore is broad or narrow. There must be a good reason why primary light-harvesting chromophores tend to have sharp absorption bands and little vibronic structure. Most likely the advantage is that energy transfer among like chromophores is most efficient when vibronic bands are weak, the absorption band is narrow, and the Stokes shift is small. That is easily rationalized by Förster theory.

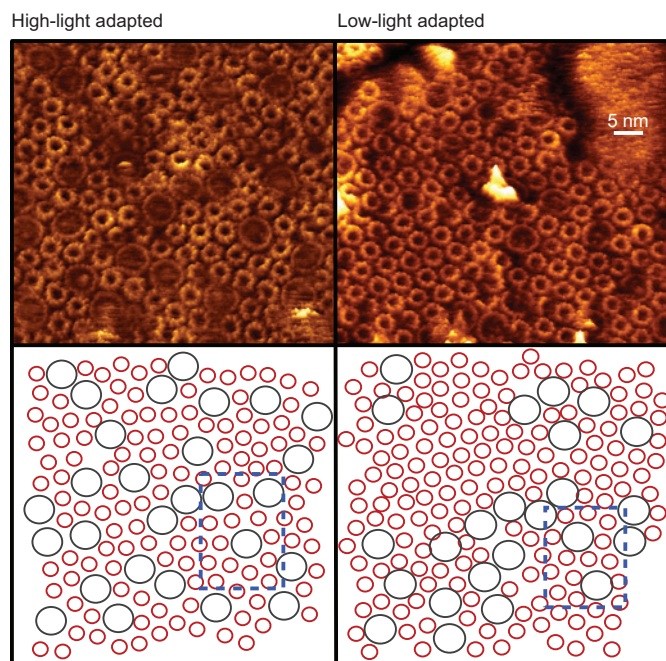


Figure 2 | Antenna complexes matter more in low light conditions.

Atomic force microscopy images of photosynthetic complexes in the photosynthetic membrane of *Rhodospirillum rubrum* grown under high (left) and low (right) light¹³⁹. The large rings are LH1–reaction centre complexes and the small rings are LH2. The decrease in ratio of LH1 reaction centres to LH2 for low-light-adapted bacteria is highlighted in the lower schematic diagrams. Figure adapted with permission from ref. 37, © 2009 Elsevier.

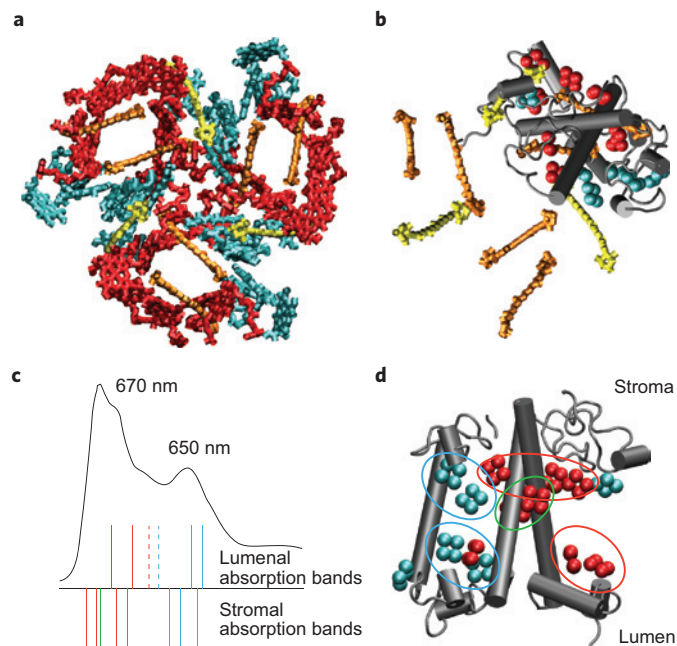


Figure 3 | Structure and spectroscopy of the major light-harvesting complex of higher plants, LHCII. **a**, View from the luminal side of the membrane of the LHCII trimer, showing only the chromophores. Chlorophyll-*a* is coloured red and chlorophyll-*b* is blue. The two lutein (orange) and one violoxanthin (yellow) carotenoids are shown (the neoxanthin is omitted for clarity). **b**, Stromal view highlighting a single LHCII complex showing the chromophore positions. Only the central nitrogen atoms of each porphyrin ring are drawn. **c**, Absorption spectrum of the LHCII trimer (77 K) with assignments of the positions of electronic absorption bands drawn as sticks according to the model proposed by Schlau-Cohen and colleagues⁵⁹. Solid lines denote exciton states, where excitation is coherently shared in the groups of chromophores circled in part **d**. Localized absorption bands are drawn as dashed lines. **d**, Side view of one LHCII complex.

Spatial and energetic landscapes

Early work established that excitation energy cascades among chromophores to sensitize reaction centres⁴⁷, but it was not known to what extent the organization of these pigments matters. Under certain dimensional and concentration conditions, excitation is efficiently quenched by randomly distributed traps⁴⁸, and models in that spirit are well suited for understanding the morphology dependence of exciton diffusion in photosynthesis⁴⁹ as well as systems like conjugated polymers⁵⁰. At a more detailed level we must ask what concentration of chromophores is optimum. Are there ideal arrangements of molecules with respect to each other, and how can chromophores with different absorption energies best be organized to capture a broad spectral cross-section of light and funnel energy through space to the final energy acceptor? The answers to these questions define the spatial and energetic landscape of the antenna.

Studies of the fluorescence emission from solutions of organic dyes showed that the fluorescence quantum yield is drastically reduced at high dye concentration⁵¹. For example, in the case of chlorophyll-*a* in ether solvent, the fluorescence is almost completely quenched at a concentration of 0.1 M. Nevertheless, chlorophyll is present in LHCII at a concentration of approximately 0.25 M and up to 0.5 M in photosystem I (PSI). Clearly it is remarkable that no concentration quenching is found for these antenna complexes. As already suggested by Beddard and Porter⁵², the organization of these molecules in the protein scaffold is not random and must be a crucial factor in obviating concentration quenching in photosynthetic complexes while enabling the chromophores to be employed at high local

concentration to optimize energy transfer. The arrangement and choice of chromophores also needs to avoid quenching by charge transfer. For example, reaction centres and antenna systems are constructed from the same basic chromophores, but the molecular dimer in reaction centres, the special pair, is a potent electron donor.

As well as through concentration, energy transfer can be optimized by careful consideration of the microscopic arrangement of chromophores. For example, energy transfer is extremely distance-dependent⁵³. Typical interchromophore centre-to-centre distances of neighbouring molecules are consequently close (~6 to 25 Å) — so energy-transfer rates are fast in light-harvesting complexes. However, if the chromophores are positioned too close to each other in certain orientations, then non-fluorescent dimers can serve as excitation sinks that deplete excitations. Hence, while a crude optimization of light harvesting involves maximizing the concentration of chromophores in the volume of a light-harvesting complex, a critical consideration is how to avoid concentration quenching. Similarly, conjugated polymer films that exhibit minimal concentration quenching are best suited for studies of electroluminescence⁵⁴. It is noteworthy that those materials consist of a maximal concentration of effective chromophores ('effective' because chromophores are ill defined along conjugated polymer chains⁴¹), which has implications for quantifying energy transfer in these systems⁵⁵. It has also been shown that the concentration of light-harvesting molecules can be regulated without requiring intimate control of their organization by incorporating the chromophores into a host matrix, such as a zeolite⁵⁶.

In the quest for discovering the design principles guiding chromophore arrangement for optimal light-harvesting, it has been thought that long-range molecular ordering can be important⁵⁷. Ordering is indeed found for chlorosomes (green sulfur bacteria) and the light-harvesting complexes of purple bacteria — suggesting the utility of cylindrical and circular assemblies — but recent structural data indicate that most light-harvesting complexes do not contain symmetrically ordered chromophores. Theoretical models can explain why order is not necessary, for example Buchleitner and co-workers examined random networks of chromophores and found that a few highly optimal configurations can always be found simply by statistical sampling⁵⁸; LHCII is one such example (Fig. 3). A number of studies have investigated the pathways of excitation energy flow within this pigment-protein complex^{28,29,59–61}.

One factor assisting the rapid and directional transfer of excitation to the reaction centre is the three-dimensional organization of light-harvesting complexes. We can classify these structural organizations into three types (Fig. 4) differentiated by the position of the peripheral light-harvesting complexes relative to the reaction centre, which is always membrane-bound. Figure 4 shows a cross-section of the organization described in Fig. 1, where light harvesting and energy trapping occur in the plane of the photosynthetic membrane. Higher plants, green algae, and purple photosynthetic bacteria are examples of this common motif. Compelling images of such a layout in purple photosynthetic bacteria have been captured using atomic force microscopy^{62,63} (Fig. 2).

The Förster spectral overlap suggests how energy transfer can be directed by spatially organizing molecules with specific transition-energy gaps: energy is directed towards the acceptor chromophore whose absorbance has the most overlap with the donor's fluorescence⁶⁴. This control of energy transfer is achieved with the penalty of energy loss associated with the energy gradient (the stored excitation energy diminishes with each downhill energy-transfer step), but it can provide high quantum yields of long-range energy trapping, as has been demonstrated, for instance, in dendrimer macromolecular antenna systems⁶⁵. Indeed, gradient-directed energy transfer has been a paradigm in supramolecular antenna systems⁶⁶. This kind of energy funnel is employed in phycobilisomes, the light-harvesting antennas found in cyanobacteria and red algae, shown located on the stromal side of the photosynthetic membrane in

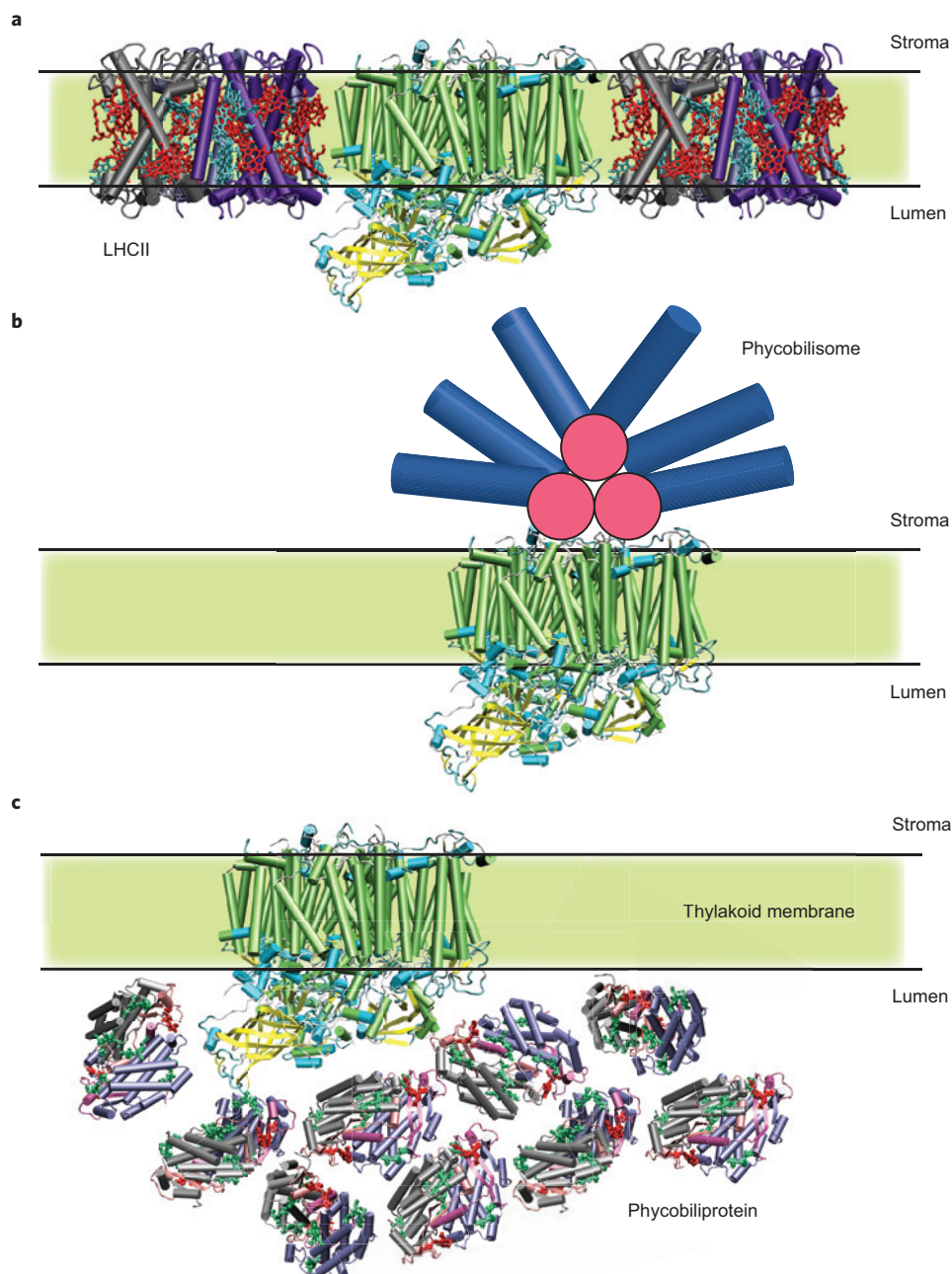


Figure 4 | Organization of light-harvesting antenna complexes relative to the photosynthetic membrane. Examples shown are representative of: **a**, Higher plants and green algae. **b**, Cyanobacteria and red algae. **c**, Cryptophytes. See text for further discussion.

Fig. 4b. They are about 50 nm end-to-end, and are extraordinary examples of self-assembled protein subunits^{67–70}. Similarly, the chlorosome of green sulfur bacteria sits on the stromal side of the membrane^{71,72}. Figure 4c shows the arrangement of phycobiliprotein antenna complexes in the thylakoid lumen⁷³, which is unique to a class of algae called cryptophyceae.

The protein is the scaffold that controls organization of the chromophores in light-harvesting complexes, but it is not solely a structural framework. Specific interactions between chromophores and amino acids shift spectra substantially, leading to quite marked spectral inhomogeneity⁶¹. For example, half the spectral shift of bacteriochlorophyll-*a* absorption in the B850 band of LH2 — the peripheral antenna complex of purple bacteria — in *Rhodospirillum rubrum* is attributed to specific pigment–protein interactions⁷⁴. Fine-tuning of bacteriochlorophyll-*a* site transition energies results in the allowed exciton transition maximum being anywhere in

the range from 800 to 850 nm, depending on the species of purple bacteria⁷⁵, from *Roseobacter denitrificans* to *Rhodospirillum rubrum*. A further striking example of how the protein itself can influence energy transfer was recently predicted by quantum chemical calculations⁷⁶. The heterogeneous dielectric environment of a protein is found to modify electronic couplings between chromophores, leading to changes in energy-transfer times of a factor of two compared with those in the presence of a continuum dielectric environment like that of a liquid solution. The ‘scaffold’ has remarkable potential to influence energy transfer beyond that decided by the chromophore arrangement.

Excitonic states are assembled for light harvesting

It turns out that many of the most fascinating energy-transfer phenomena are found in multichromophoric systems. Energy transfer from one chromophore to another is promoted by electronic

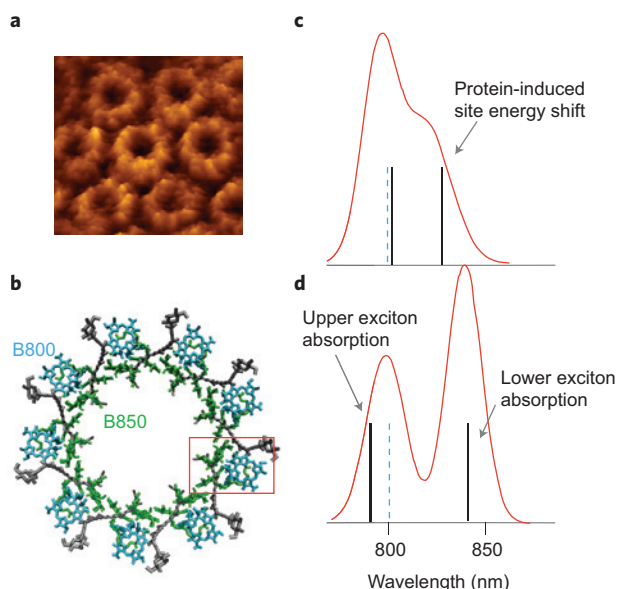


Figure 5 | How electronic coherence creates chromophores.

a, Enlargement of a section of the image in Fig. 2 showing a group of LH2 complexes. **b**, Structural model of the chromophores in the LH2 complex of *Rps. acidophila*. Reproduced with permission from ref. 37, © 2009 Elsevier. **c,d**, Simulated absorption spectrum for the LH2 sub-unit (containing one B850 dimer, and one B800 monomer, indicated by the red box in part **b**, with no coupling (**c**) and electronic coupling (**d**) between the molecules. The B800 absorption band is indicated by the dashed line. (C. Smyth, F. Fassiolli and G. D. Scholes, unpublished results.)

coupling between their transition densities. However, when this electronic interaction is large compared with spectral line broadening, the excitation can become coherently shared among the molecules to form Frenkel (or molecular) excitons^{41,77}. The new absorption bands produced by the exciton effect can be put to use: rather than employing different chemical types of chromophore molecules, it has been found that delocalized excitons, controlled mainly by the relative positions and orientations of neighbouring chromophores, can also be used to form an energy-transfer funnel.

The complex LH2 is one of the most widely studied photosynthetic antenna proteins^{17,20,26}. It provides good examples of how excitons modify light harvesting. Purple bacteria biosynthesizes one kind of light-harvesting chromophore (for example, bacteriochlorophyll-*a*), but they also engineer excited states using collective properties of more than one molecule. The crystal structure of LH2 reveals two symmetric rings of bacteriochlorophyll-*a* chromophores⁷⁸. The chromophores in the B850 ring (associated with the 850-nm absorption band) interact strongly with each other; their nearest-neighbour electronic couplings are $\sim 300 \text{ cm}^{-1}$, which is more than ten times that between the molecules in the B800 ring (associated with the 800-nm absorption band)^{79,80}. In the case of purple bacteria, the absorption spectrum of bacteriochlorophyll-*a* is shifted from 800 nm to 850 nm partly by interactions with the protein described in the previous section, and partly by the electronic interactions among the molecules in the B850 ring of LH2 (Fig. 5). These electronic interactions essentially produces a new chromophore that provides the gradient that directs energy flow from B800 to B850 (ref. 27).

The lessons from this example are that when molecules are positioned closely to each other, interchromophore electronic interactions are strong enough that the quantum mechanical superposition principle causes excitation to be shared coherently, resulting in significant shifts in absorption resonances, redistribution of dipole strength among transitions, and changes in orientation of transition dipoles. These delocalized states can be used to increase or decrease

absorption or emission probabilities. The advantage of increased absorption cross section at a particular wavelength is obvious, but it may also be desirable to minimize radiative loss from the lowest level(s) of a manifold of exciton states, depending on how the molecules are oriented.

Exciton states seem to be present to some extent in all photosynthetic light-harvesting complexes, and they clearly help manipulate energy-transfer pathways^{26,29}. The implications of exciton delocalization for energy transfer are more profound than simple spectral tuning to provide an energy gradient, and hence construction of a 'downhill' energy-transfer route. It is the way the B850 exciton states act as energy acceptors for excitation in the B800 ring that makes a difference — increasing the energy-transfer rate by a factor of ten over expectations from Förster theory²⁷. The reason for this improvement is not at all obvious from far-field spectroscopy — that is, absorption and fluorescence — and was elucidated through the development of generalized Förster theory that accounts for how excitonic states transfer excitation^{27,81–84}. Many studies have investigated the extent of and consequences for electronic delocalization in the B850 ring of LH2^{85–90}.

Quantum-mechanical delocalization even seems to play a role in energy transfer in very large and apparently structurally disordered antenna complexes. For example, PSI consists of an Fe–S reaction centre surrounded by an intrinsic core antenna comprising around 100 chlorophyll-*a* molecules, in turn surrounded by peripheral light-harvesting complexes (for example, LHCI)^{91,92}. Although the Förster model can justify the overall dynamics and quantum efficiency of energy transfer to the reaction centre in PSI (ref. 92), more sophisticated treatments of energy transfer find there is a role played by pockets of strongly coupled chlorophylls within the PSI antenna⁹³. These quantum-coherently interacting groups of molecules serve as effective donor–acceptor states⁸¹, which are found to diminish the number of sites that need to be explored when the excitation undergoes a random walk through the antenna, and decrease the likelihood that excitation will be inadvertently trapped at a defect site in the antenna. Interestingly, it was concluded from this study that the most important optimization in PSI is the energy-transfer step that traps energy at the reaction centre, rather than overall design of the antenna. Although coherence is involved in the PSI core antenna light-harvesting, it is probably not a critical optimization.

Quantum coherence affects the energy-transfer mechanism

Decades ago, careful measurements of the electronic absorption spectra of molecular crystals showed that Davydov splitting⁹⁴ — which reveals molecular exciton states — could be easily observed or hidden according to the magnitude of electronic coupling compared with spectral line broadening⁹⁵. Curiously, photosynthetic light-harvesting complexes generally conform to an intermediate case where the electronic coupling between chromophores is similar in magnitude to coupling to the environment and to the disorder in site energies^{26,86}. Therefore, researchers expect quantum-mechanical effects to influence dynamics in these systems. Recently some theoretical studies have concluded that this situation is desirable for optimum excitation transport^{96–98}. Predictive theories are most easily formulated when one energy scale outweighs all others, which is not the case in the intermediate coupling regime.

It is common to think of the dynamics of energy transfer in terms of the evolution of populations — probabilities that excitation has reached the various 'sites' (chromophores) in a light-harvesting complex. Quantum coherence introduces correlations among wavefunction amplitudes at different sites in the complex. To account for those correlations, the dynamics need to be described in terms of the evolution of both the populations and coherence accounting for quantum superpositions (Box 1). The result is that interference effects can change the way those probabilities evolve with time. Historically, coherent evolution in energy-transfer dynamics

has focused on donor–acceptor (two site) systems⁹⁹, but the results are much richer in the case of multichromophoric systems, which makes the study of light-harvesting complexes so fascinating.

An important advance was made recently that has stirred renewed activity in the study of quantum coherence — the ability to detect evidence for electronic superpositions and their evolution using two-dimensional electronic spectroscopy experiments^{59,100–105}. An example of a cross-peak indicating electronic coherence is shown in Fig. 6. The system studied was the PC645 antenna protein of the cryptophyte alga *Chroomonas* sp. strain CCMP270 (sample at ambient temperature). We highlight the same cross peak reported in previous work¹⁰², DBV₊–MBV, (where DBV relates to dihydrobiliverdin and MBV, mesobiliverdin) but now better resolved¹⁰⁵. The periodic appearance and disappearance of the cross peak as a function of the waiting time between the pump pulse sequence and the probe is caused by the evolving phase determined by the energy difference between the two electronic states that participate in the superposition¹⁹.

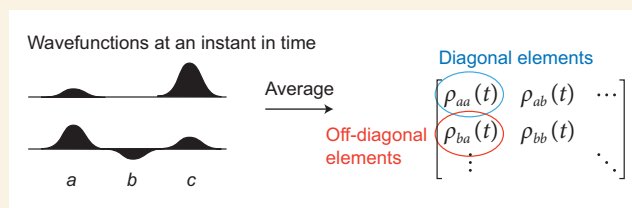
It is not known whether coherent quantum dynamics is critical to make energy transfer highly efficient in large systems. Nevertheless, coherence presents opportunities for controlling energy transfer in multichromophoric assemblies^{106,107} because of the ways it modifies the random hopping mechanism assumed in the Förster model. For long length (and time) -scale energy transfer, or exciton diffusion, we can gain some insight by comparing a classical random walk to a quantum random walk¹⁰⁸. For normal diffusion it is known that the mean-squared displacement of the walker (the localized electronic excitation) increases linearly with time. Quantum random walks are considerably more complicated¹⁰⁹.

In the limit of ballistic wave-like diffusion of excitons on a periodic lattice, an exponential speed-up is possible. The migration of Frenkel excitons is traditionally considered wave-like because of the way the phase of the exciton at each molecular site changes as the exciton translates, but this limit does not apply to photosynthetic systems owing to their spatial and energetic disorder, which modifies quantum transport significantly¹¹⁰. Recent work has found that exciton diffusion lengths are increased in molecular organic semiconductor films with crystalline order¹¹¹. That may be a good example of a case where the classical random walk is modified by quantum effects in the crystalline domains, despite the prevalent disorder. In realistic situations with disorder it is unclear whether quantum corrections to classical random walks help ‘speed up’ energy transfer, but they certainly modify the pathways traversed by excitation.

Within a light-harvesting antenna, electronic excitations evolve according to a finely tuned interplay between the electronic interaction generating quantum superposition states, and the coupling to an environment (protein backbone and solvent) that destroys such superpositions. The experiments show that quantum coherent contributions to excitation dynamics do not decohere as fast as originally thought, possibly owing to a combination of slow and spatially correlated fluctuations of the environment¹¹². An important, though subtle, result of coherent sharing of excitation during dynamics is that the averaging over the bath fluctuations is changed¹¹³, by the same process that causes exchange narrowing of absorption bands in molecular aggregates²³. That diminishes the ‘frictional drag’ on the excitation that is related to polaron formation in competition with energy transfer^{114–117}.

Coherence arises when the electronic coupling between the chromophores is comparable to, or larger than, other energy scales in the system such as disorder and electrostatic coupling to fluctuations in the surroundings¹¹⁸. The consequent challenges for theoretical description of the dynamics have been reviewed recently^{22,119}. The electronic coupling between molecules can be tuned over orders of magnitude simply by the separation and orientation of chromophores⁵³. Hence, regardless of the decoherence-inducing coupling to the environment, arrangements of chromophores can typically be found where coherent quantum effects can exist

Box 1 A bird's eye view of quantum dynamics



At some instant in time t_0 , imagine we can freeze the system and calculate wavefunctions that tell us how electronic excitation is distributed as amplitudes on different chromophores, labelled a , b and so on. These wavefunctions show how excitation is coherently shared at this instant in time for each state of the system.

To follow the evolution in time — energy-transfer dynamics and excitation sharing — we need to consider a suitable statistical average of the quantum states represented by these wavefunctions. The density matrix provides a quantum-mechanical representation of probabilities (populations, for example ρ_{aa}) and coherences (for example ρ_{ab}).

The way the diagonal elements of the density matrix change with time tells us about the kinetics of energy transfer from molecule to molecule (population transfer). The off-diagonal elements contain information about the coherence between different chromophores. In averaging over all the pathways that can be taken during the dynamics (because we do not know which one was actually taken), we find that the slightly different ways the wavefunctions change with time causes them to interfere destructively when we take the average (like adding waves of different frequency)¹⁴⁰. That decoherence diminishes the quantum corrections to the dynamics. The surviving coherence, collected in the off-diagonal density matrix elements, introduces quantum-mechanical corrections to energy-transfer dynamics caused by coherent sharing of excitation as it moves through the antenna complex.

because electronic couplings are comparable to other energy- and timescales characterizing the system. That ratio is advocated to be optimal for energy transfer, but there is a limit to how large the coupling between chromophore transitions and the environment (line broadening) can be, because large interchromophore electronic couplings are usually accompanied by low-lying charge-transfer states and therefore quenching.

It is the realization that a biological process, normally understood to operate in a classical, thermodynamic limit, is able to utilize quantum-mechanical superposition states and interferences that is most tantalizing. That recognition implies we can harness ‘quantum weirdness’ in other nanoscale systems, including chemical materials, outside of pristine laboratory conditions. The biological and practical implications of these experimental observations are currently a matter of debate and intense investigation. From a practical perspective, the presence of coherent quantum dynamics opens the door for assemblies to be designed wherein energy transfer can be partially directed to a desired outcome, even at room temperature, by exploiting quantum attributes built into the system Hamiltonian, essentially by the choice and arrangement of chromophores.

Natural antennas are regulated, photoprotected and robust

Photosynthesis is highly regulated. Reaction rates need to be juggled to cope with daily and seasonal light variation as well as environmental stresses that limit CO₂ fixation^{120,121}. Indeed, even the most rapidly growing plants use less than half the excitations absorbed by light-harvesting complexes¹²². A sophisticated hierarchy of ‘safety

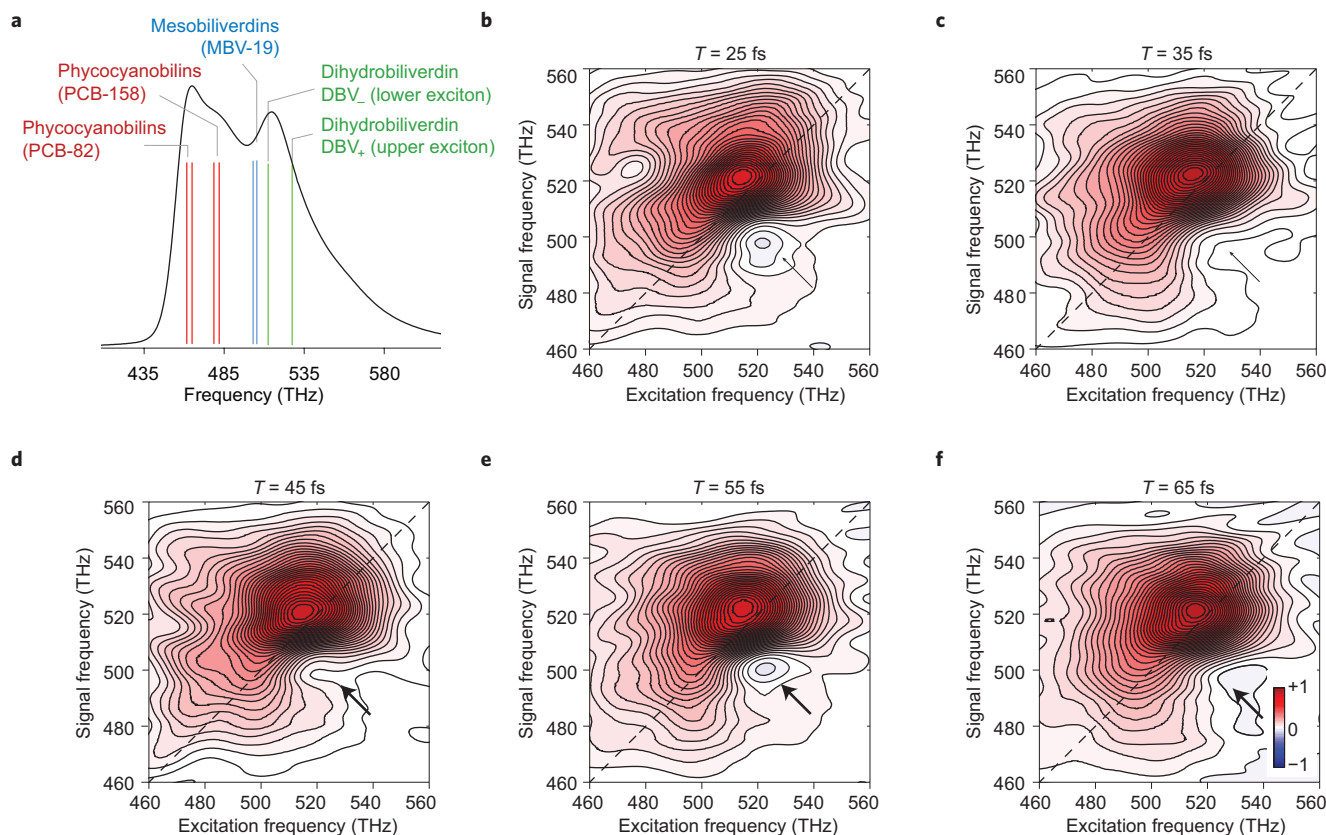


Figure 6 | Two-dimensional electronic spectroscopy for the detection of quantum coherence¹⁰⁴. **a**, Absorption spectrum of the cryptophyte light-harvesting antenna complex PC645 from *Chroomonas* sp. strain CCMP270. **b–f**, Two-dimensional electronic spectra of PC645 (ambient temperature, 12 fs near-transform limited laser pulses). The appearance and disappearance of a cross-peak as a function of the waiting time, T , between the pump pulse sequence and the probe caused by electronic coherence is indicated by an arrow. These data¹⁰⁵ were recorded with a new experimental set-up that has >25 times better signal-to-noise and 10 times faster acquisition time than the set-up used to study this antenna complex previously¹⁰². 1 eV = 240 THz. DBV, dihydrobiliverdin; MBV, mesobiliverdin. Part **a** reproduced with permission from ref. 102, © 2010 NPG.

valves, triggered by pH changes in the thylakoid lumen, are used to dissipate excess excitation and to re-route electrons¹²³. Organic molecules are highly susceptible to photodamage, so an integrated approach to photoprotection of synthetic antenna systems is desirable. A model example has been reported recently¹²⁴.

The solar irradiance can change by orders of magnitude during the day. At low light conditions photosynthesis can be limited, thus light harvesting is crucial. But under bright sunlight — or even quite moderate light flux — excitations are harvested much faster than the frequency that reaction centres ‘reset’ after doubly reducing the final electron acceptor in the reaction centre that stores the photogenerated potential (in type-II reaction centres a quinone serves this function). The excess excitations could form triplet states and, in turn, singlet oxygen that devastates biological molecules. It is not surprising, then, that various mechanisms have evolved to dissipate excess excited states (both singlets and triplets).

First of all, in virtually all photosynthetic light-harvesting complexes, the chlorophylls occur in combination with carotenoids. For instance in LHCI, each monomeric subunit contains two luteins in the centre, a neoxanthin and a violaxanthin (see Fig. 3) in addition to the chlorophylls. The carotenoids in the complex fulfil multiple functions: (1) the two central luteins constitute an essential structural element; (2) carotenoids have an essential function in light-harvesting; photons absorbed by the allowed visible transition (the S_2 state) are transferred mainly to chlorophyll-*a* on a femtosecond timescale^{125,126}; (3) triplets formed on the chlorophylls (predominantly on chlorophyll-*a*) are quenched very efficiently by the carotenoids¹²⁷; and (4) the carotenoids in most light-harvesting complexes

play a role in a process called non-photochemical quenching that operates under high light conditions, and which allows the light-harvesting antenna to switch into a state in which most of the excitation energy is dissipated as heat^{120,128–130}.

These functions, and certainly (3) and (4), are essential in natural photosynthesis. A protein-based photosynthetic apparatus does not survive when chlorophyll triplets accumulate. The reason is simple: chlorophyll triplets react very effectively with oxygen to produce singlet oxygen, an extremely reactive species. In contrast, carotenoid triplets are too low in energy to produce singlet oxygen, and as a consequence triplet–triplet energy transfer from chlorophyll to carotenoid protects the photosynthetic apparatus. This protection is extremely efficient: in all plant light-harvesting systems it is almost impossible to detect a chlorophyll triplet at room temperature even under conditions in which the excited state lifetime is long and a substantial amount of carotenoid triplet is being formed.

Non-photochemical quenching is a protection mechanism that is switched on under high light conditions when the photosynthetic electron-transfer machinery gets saturated and the probability of recombination of charge-separated states increases. These recombinations may again lead to triplet states and cause damage. In plants, non-photochemical quenching is switched on by the build-up of a trans-membrane proton gradient that, in intense light, can happen in a few tens of seconds^{120,128}. Consequently, such quenching must be on account of some physical mechanism that allows one or more of the light-harvesting complexes to switch into a quenching state. Currently, two mechanisms for the quenching event are heavily discussed. The first is proposed to operate in one of the minor

light-harvesting complexes of PSII, CP29, where a charge separation has been observed between a chlorophyll and the carotenoid zeaxanthin, followed by rapid recombination¹³¹. In intact thylakoids under non-photochemical quenching conditions, signals reflecting the formation of carotenoid radicals have also been observed¹³². The second is proposed to operate in LHCII, where, under conditions that mimic the quenching state, a major fraction of the chlorophyll excitons were observed to decay through energy transfer to one of the luteins in the heart of the complex, thereby populating the lutein S_1 state that subsequently decays on a picosecond timescale¹³³. Two-photon fluorescence excitation experiments on LHCII and plants in different quenching states, in which the carotenoid S_1 state was selectively excited, indeed demonstrated an increased interaction between the luteins and their surrounding chlorophylls with increased levels of quenching¹³⁴. It is not impossible that both mechanisms operate in parallel. It is remarkable that both 'switches' require a conformational change to modulate the interaction between the carotenoid and the chlorophyll. That interaction controls the switch between light harvesting and quenching.

Inspiration and opportunities

Photosynthetic light-harvesting complexes are sophisticated multi-chromophoric assemblies used to regulate and concentrate photo-excitations under wide-ranging incident irradiances for delivery to reaction centres. They provide wonderful model systems for the study of energy-transfer mechanisms in well-defined structures. From those studies, several broad lessons have been learned that have been described in this Review. There still remains an interesting question though, what are photosynthetic antenna complexes optimized for?

The next step seems to be elucidating how we can write a blueprint to 'make something' based on what we have learned from photosynthetic complexes. Despite the thousands of studies reported on energy transfer, researchers have not really established clear design principles except for the use of an energy gradient. However, most photosynthetic light-harvesting complexes do not incorporate a substantial internal energy gradient directing energy flow, that is, only one of two chemical types of chromophores are used. As a starting point we propose that we should define functional components, chromophore groups that perform a function like rectification, amplification, or feedback, and work out the rules describing how these components interact with each other. In Box 2 we give a general strategy for designing an antenna, starting with the specification of the application.

Finally we conclude with a list of some specific issues that require further clarification and study:

A goal would be to design and to synthesize a well-defined antenna unit that comprises 6–10 chromophores and a structural framework. However, as already mentioned, it is surprising that we do not have a clear direction for preparing these units. An antenna complex is part of a larger system, and it is the optimal function of that larger entity that dictates the role of the antenna. Therefore optimization of the antenna in isolation is not sufficient, though even that presents a considerable challenge. What we first need to think about is what the antenna will do. That will help define input and output.

Chromophores with large absorption strengths that can be conveniently incorporated into the synthetic protocol need to be designed. Optical properties that are conformation dependent can be suppressed by locking the molecules to a rigid molecular framework that defines the synthetic light-harvesting complex. That might also help reduce decoherence if environment fluctuations have a correlated component. From the perspective of theory, we should consider more carefully the nature of molecules that comprise the electronic system, given a 'real' molecule's intrinsic complexity compared with notional 'two-level systems' usually considered in theoretical prescriptions.

Box 2 Design steps for constructing an antenna system

A. Define the application, which will decide the scope of the antenna. For example, will the antenna 'wire' an input excitation to an output, or will the entire antenna capture light and focus the excitation energy to one or more points (traps)?

B. Decide the spectral capture and amplification needed. This will define the chromophore variety, number and concentration requirements.

C. Define the spatial and spectral energy landscape. The number of paths connecting input to output should be considered.

D. Juggle energy scales to produce optimal resonance conditions. This involves considering the following energy scales and setting them to be approximately equal:

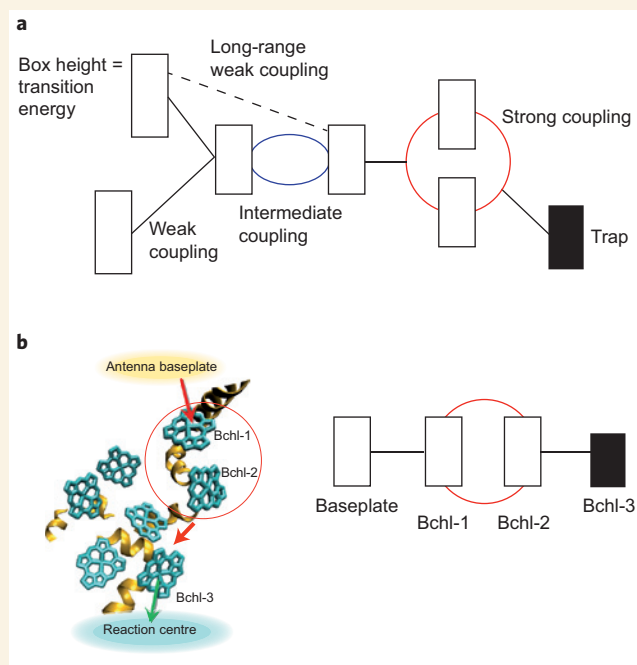
D1. The electronic coupling between nearest-neighbour chromophores.

D2. Homogeneous line-broadening (defined by the reorganization energy).

D3. Site energy differences and/or the grouping of chromophores with similar transition energies.

D4. Disorder (inhomogeneous broadening).

D5. The environmental relaxation time (that is, it is not only the fluctuation amplitude caused by the environment that matters, but also the timescales of those fluctuations).



To aid the design process we need to break the problem down into components and connectivities, like an electrical circuit, as shown in part **a** of the figure. This energy-transfer circuit diagram defines the energy landscape of the antenna. To gather an understanding for such a circuit we must first understand the operation of 'components', like the pair of chromophores interacting in the intermediate coupling regime, and work out how they interact with other components. We already know a lot about strongly coupled chromophores.

The example in **b** illustrates the energy-transfer 'rectifier' identified in the Fenna-Matthews-Olson complex¹⁴¹ between the baseplate and bacteriochlorophyll-*a* (Bchl) molecules 1–3. It would be worthwhile to identify other energy transfer motifs in order to build up a catalogue of components.

Theoretical studies working out how chromophores should be arranged are crucial. One difficulty here is that quantum corrections to the energy-transfer dynamics are not intuitive. Indeed, it is not clear how sensitive is the operation of antenna complexes to the precise organization of chromophores. Valuable future studies will include working out how to increase the length scale over which quantum effects influence dynamics. At present this issue is challenged by the complexity of information reported by experimental studies of large systems.

Realizing the importance of the environment and its role in decoherence and transport, we should elucidate design principles for synthetic structural scaffolds or matrices. To aid advances in this direction, we need experiments to probe the relevant environment response more directly.

Insights are needed into how regulation and photoprotection can be introduced and made reasonably sophisticated, for instance, feedback and control loops to change antenna function on various timescales and levels of change. The design of artificial light-harvesting systems should also take into account the operating environment because incident light levels dictate the optimum antenna size.

To sum up, there are a number of outstanding questions about mechanistic details of energy transfer, especially concerning how the electronic system interacts with the environment and what are the precise consequences of coherence. Nonetheless, a clear framework exists on which light-harvesting systems can be designed. We suggest that the circuit concept introduced in Box 2 will aid the conception of sophisticated assemblies where the flow of excitation is directed and regulated.

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Additional information

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