Photosynthetic Light Harvesting

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17.1 Introduction

A prominent example of photobiology is light-initiated energy conversion—the process of photosynthesis. The photochemical energy transduction of photosynthesis starts with photoinitiated electron transfer reactions that occur on picosecond and longer time scales. Here we will focus on the photoinitiation process, which is called light harvesting. Sunlight is absorbed by chromophores such as chlorophyll bound at high concentration in proteins. Electronic energy transfer (EET) transmits the excitation energy to reaction centers wherein the electron transfer reactions are initiated. We recommend specialist reviews (Green and Parson 2003; Sundström et al. 1999; van Grondelle and Novoderezhkin 2006; Novoderezhkin and van Grondelle 2010; Scholes et al. 2011; Renger and Müh 2013; Cheng and Fleming 2009; Fassioli et al. 2014) for more detailed information on the biophysics of light harvesting. Here we will provide an introductory account in the context of photobiology.

Light-harvesting complexes are comprised of chromophores, light-absorbing molecules, usually bound into a protein scaffold. Photosynthesis is initiated by the absorption of light by the chromophores, which excites a molecule from the ground state to an electronic excited state. The excited state of a molecule like chlorophyll is short lived compared to usual biological processes, relaxing to the ground state with a time constant of about 4 ns in vivo (Connolly et al. 1982; Mullineaux et al. 1993). Before the molecule can return to its ground electronic state, the electronic excitation must be "harvested." That is, the excitation is transferred through space among the chromophores until it eventually reaches a reaction center where it initiates charge separation. That is the process of EET.

A map of the organization of light-harvesting complexes around reaction centers in a thylakoid membrane representative of higher plants or green algae (Croce and van Amerongen 2011) is shown in Fig. 17.1a. We show the reaction center from photosystem II, stripped of the protein scaffold in the lower part of Fig. 17.1a. Surrounding the reaction centers are major and minor chlorophyll-containing antenna complexes that bind, in total, about 200 chlorophylls per reaction center. Light harvesting involves the absorption of sunlight by any of these chlorophyll chromophores and subsequent transfer through space of that electronic excitation to the special pair of a reaction center. This process effectively concentrates the excitation at reaction centers so they can be cycled significantly more frequently than would be possible by direct excitation in sunlight—that is, the so-called antenna effect.

Light-harvesting complexes are not restricted to this particular design. Indeed, there is a wide variety of light-harvesting antenna structures in nature (Fig. 17.1b). They differ in the arrangements of chromophores as well as chromophore types. In addition to the various chlorophylls, other chromophores such as bilins and carotenoids tune the absorption spectra so that light can be harvested from the blue wavelengths all the way to the near-infrared, depending on the organism. All antenna complexes are able to convert the photogenerated excitations to charge separation with high efficiency (Blankenship 2002). Quantum efficiencies—the probability of converting an absorbed photon into a charge separated state—depend on antenna size, light conditions, and the organism. They are documented to be in the range 50–90 %, for example, the light harvesting to charge separation efficiency is in the range 84–90 % for photosystem II of higher plants (Jursinic and Govindjee 1977; Wientjes et al. 2013).

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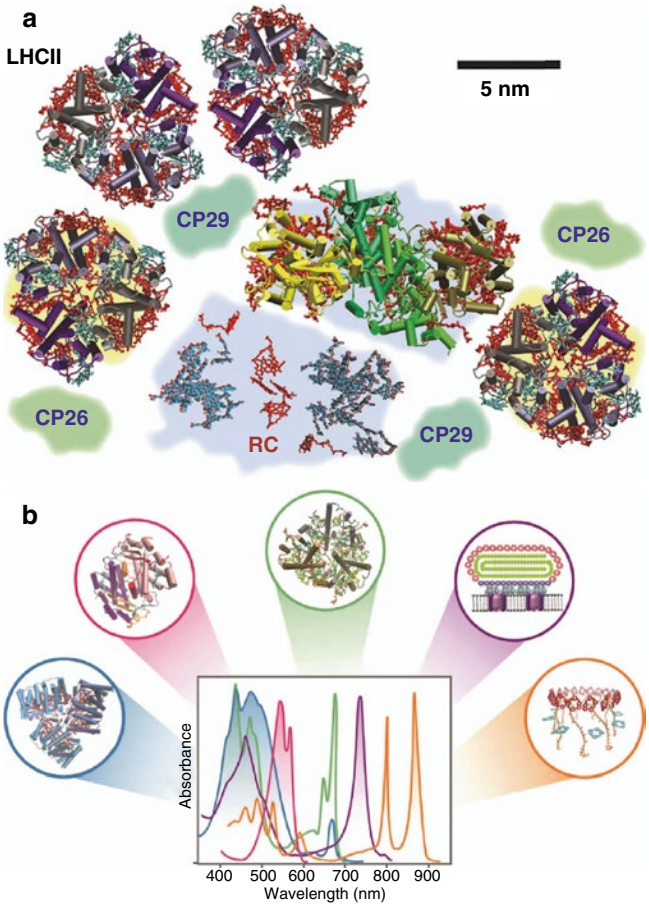

Fig. 17.1 (**a**) Structural organization of light-harvesting complexes and reaction centers in higher plants and green algae. Excitation energy captured by the LHCII and the minor peripheral light-harvesting complexes is transferred, via core light-harvesting complexes CP43 and CP47, to the reaction center where charge separation is initiated (Adapted from Scholes et al. (2011)). (**b**) Variation in light-harvesting antennae commonly encountered in photosynthetic organisms, which vary widely in their protein structure and the number and arrangement of pigments utilized. The molecular structures (with parent organisms in brackets) from left to right are peridinin-chlorophyll-protein or PCP (of *Amphidinium carterae*), phycoerythrin 545 (of *Rhodomonas* CS24), light-harvesting complex LHCII (of *Spinacia olearia*), schematic representation of a chlorosome (of *Chloroflexus aurantiacus*), and light-harvesting complex LH2 (of *Rhodopseudomonas acidophila*). Their respective absorption spectra, shown in matching colors, illustrate how different organisms have evolved to optimize their light-harvesting capabilities in different regions of the visible spectrum (Adapted from Scholes et al. (2012))

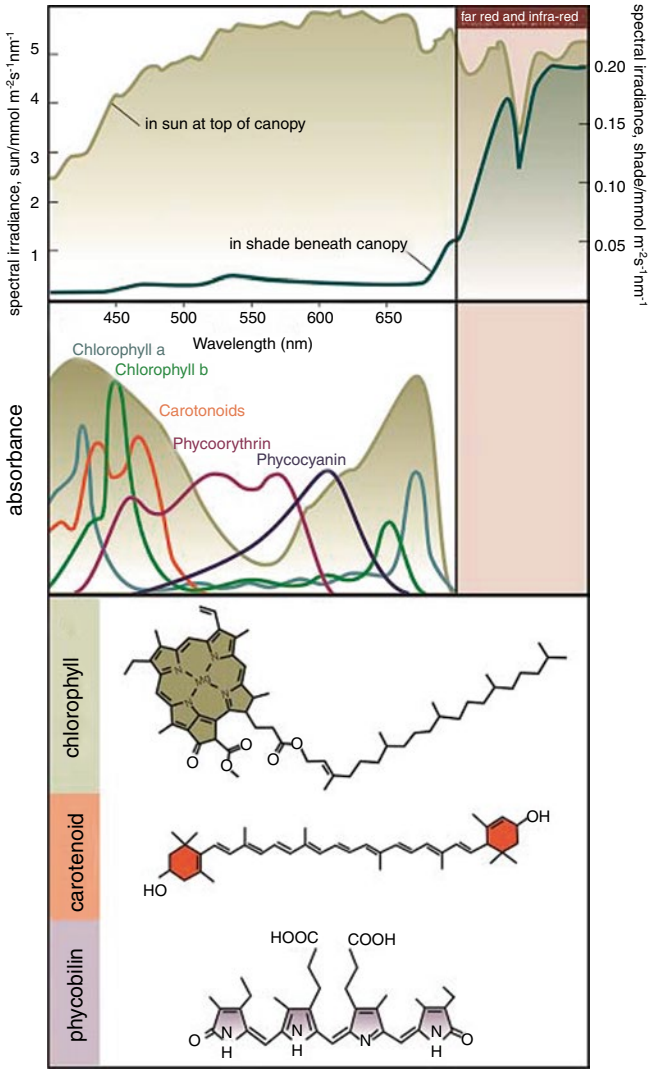

Fig. 17.2 (**a**) Spectral distribution of sunlight at the top of plant canopy and in the shade beneath it. (**b**) Action spectrum (illustrated as shaded spectrum) of photosynthesis for a higher plant (spectrum adapted from Campbell and Reece 2005) and absorption spectra of pigments involved in photosynthetic light-harvesting. (**c**) Schematic illustration of chlorophyll, carotenoid, and phycobilin structures

17.2 Light Quality and Pigments

The variation in the quality of light, or spectral composition, and the varying light intensity in different environments are vast, yet photosynthetic organisms have adapted to thrive in diverse conditions. The fluence rate at the top of the plant canopy can be over 100 times higher than in the shade beneath the canopy, when comparing in the visible part of the spectrum (Fig. 17.2a). Water provides a particularly interesting stratified environment based on available light. Blue light penetrates significantly deeper than red light in clear water (see Chap. 7).

An additional consideration is that not all wavelengths of light can support photosynthesis with the same efficiency, which is illustrated in the photosynthetic action spectrum (Fig. 17.2b; cf. Chap. 8). The action spectrum shows the yield of photosynthesis (e.g., oxygen production) as a function of excitation wavelength. It can be thought of as the relative effectiveness of different photon energies at generating electrons. The action spectrum reveals clearly the spectral cross section of light harvesting. Thriving in various light conditions requires diversification of light-harvesting complexes as well as nimble adaptation to prevailing conditions.

In all photosynthetic organisms, initial light absorption is performed by special organic pigments, which chemically and structurally can be broadly subdivided into three major groups: chlorophylls (Sects. 9.2, 9.3, 9.4, and 9.5), carotenoids, and phycobilins (Fig. 17.2b, c and Sects. 9.6 and 9.7). In green plants, for example, the action spectrum is in close agreement with the absorption spectrum of chlorophylls and carotenoids with prominent bands in the violet-blue and red region of the spectrum. The middle of the visible spectrum is reflected and transmitted, giving leaves their green color. So, why would plants evolve to reflect green light (Kiang et al. 2007)? Suggestions have been made that chlorophyll absorption is exactly complementary to bacteriorhodopsin, a purple pigment which was utilized in the earliest photosynthetic aquatic bacteria. It is believed that organisms that subsequently optimized their photosynthetic machinery relied on chlorophyll systems to capture available light after sunlight was filtered by bacteriorhodopsin. Reviews (Björn et al. 2009; Mauzerall 1973) have highlighted that biosynthetic pathways for metal porphyrins, which were utilized in electron transport, already existed prior to photosynthesis, and implementation of the existing precursor for the production of chlorins via porphyrins was a clear evolutionary advantage. Björn (1976) also suggested that the optimal absorption position for the light-harvesting pigment would be around 700 nm, as evidenced by the exclusive dominance of chlorophylls which use only the excitation energy from the red part of the spectrum to drive water-splitting and ferredoxin-reducing photochemistry. It is believed that this ability to efficiently absorb red light was the evolutionary driving force to select Chl *a* as the most abundant pigment in photosynthesis (Granick 1965; Björn et al. 2009). Later, as light did not present a limiting resource for photosynthesis in plants, lack of evolutionary pressure did not result in innovation of novel light-harvesting machineries which would utilize a wider part of the solar spectrum, and the family of chlorophyll pigments remains the most abundant in photosynthesis today.

Blue-green light is absorbed by phycobilins (Fig. 17.2b) and coincides with the action spectrum of red algae and cyanobacteria. These organisms can live in deeper waters where the longer wavelength light used by green plants is already filtered out. Owing to the high nitrogen content of phycobiliproteins, their production can be very costly whenever nitrogen is limiting. Thus, in the interest of energy conservation, higher plants, which are exposed to an abundance of light when growing on land, do not utilize phycobiliproteins for the capture of green light (Björn et al. 2009).

Considering the enormous variety of photosynthetic organisms, the diversity of chromophores utilized for light harvesting is not that large. There are certainly far fewer chromophore types than LHC "designs." So what structural and functional characteristics have led to the optimization of these classes of pigments? The basic structure of a chlorophyll molecule is similar to the heme part of hemoglobin, containing a porphyrin-like ring structure, coordinated to a central magnesium atom (Fig. 17.2c). The structural variation among the different chlorophylls originates from the differences in side-chain substitutions on the ring, which ultimately affect the absorption characteristics of the different pigments. The yellow-orange carotenoid chromophores, which display a triple peak in the 400–500 nm region, coinciding with chlorophyll Soret band absorption, are bicyclic and based either on α-carotene (one β and one ε ring) or β-carotene (two β rings). The open-chain tetrapyrrole bilins resemble a split porphyrin structure that has been twisted into a linear conformation.

All the pigments are based on π-electron systems, cyclic or linear, and they are all characterized by exceptionally high molar extinction coefficients, typically on the order of 1×10^5 M^{-1} cm^{-1}. In linear conjugated molecules, such as carotenoids and π-conjugated polymers, scaling laws predict that the dipole strength of the lowest allowed electronic transition will be correlated to the length squared (Tretiak et al. 1999). However, conformation disorder manifest as bond twists and conjugation interruptions is expected at normal temperatures, leading to the plateauing of the scaling at lengths corresponding to 10–15 double bonds (Scholes and Rumbles 2006).

We have so far only considered pigments as separate entities whose primary attribute is absorption strength, but as we are going to find out in the next sections, pigments are only pieces to a big puzzle. The construction of artificial light-harvesting model systems has been hindered by both the development of suitable pigments and the formation of the scaffolding that would circumvent the challenges of organizing large numbers of constituent chromophores. Recent advances have explored the path of developing an architectural platform of multichromophore biohybrid complexes that synergistically combines the bioinspired as well as synthetic building blocks for the formation of versatile assemblies for light harvesting (Reddy et al. 2013; Yang et al. 2013). The rationale behind the design of these biohybrid architectures is that synthesis of the framework structure to accommodate a large number of chromophores in an organized manner is extremely challenging. These limitations are overcome, as the bioconjugate utilizes the framework created by the analogue of a native photosynthetic light-harvesting peptide. The native chromophores, bacteriochlorophylls and their derivatives, on the other hand, have often limited synthetic malleability, but recently developed bacteriochlorins (Yang et al. 2013) are very stable towards diverse reaction conditions and can be tailored in a variety of ways, allowing for wavelength tuning, overcoming limitation that natural systems face in terms of a reduced coverage of the solar spectrum. It was also shown that these oligomeric biohybrid architectures that contain such bacteriochlorins exhibit energy

transfer yields to the native-like BChl *a* target sites on the order of 90 % (Reddy et al. 2013). Key advances in the field of artificial photosynthetic model systems will depend on the realization that in these large molecular assemblies, the role of constituent chromophores expands from primary energy absorbers to efficient energy conduits. Synergetic interactions between parts of light-harvesting assemblies will further dictate the desirable spectral features of participating chromophores. Some aspects of the photophysics governing these constraints will be discussed in the following sections.

17.3 Physical Principles of Antenna Architecture

There is a remarkable variation in antenna structures (Hohmann-Marriott and Blankenship 2011) (Figs. 17.3 and 17.4), but they show some basic principles in common with regard to the architectural assembly of chromophores (Fig. 17.4). Most antenna complexes are realized through pigment-protein associations, where the protein backbone allows for chromophores to be held in precise positions, predetermining the separation and relative orientation of these light-harvesting molecules. The advantage of a three-dimensional arrangement compared to a simple one-dimensional model is illustrated in Fig. 17.3. The efficiency of transferring excitation energy between two remote pigments, assuming equal ratio of donors and traps, in 1D is much smaller, compared to higher dimensional systems owing to the properties of random walks. This statistical problem has been researched in the 1960s, where the model consisted of an infinite lattice of unit cells defined with N points of which $(N-1)$ are occupied by a chlorophyll molecule, while one is represented by a trap (Pearlstein 1966, 1967; Robinson 1967; Montroll 1969). Calculations by Montroll (1969) assumed equal probability of excitation at any nontrapping chlorophyll, and steps were taken to near-neighbor lattice points only. For the limit of $N \to \infty$, the number of steps, n, required to reach the trap was evaluated as follows:

$$\langle n \rangle = \begin{cases} \dfrac{N^2}{6} & \text{linear chain} \\ \pi^{-1} N \log N & \text{square lattice} \\ 1.5164 N & \text{single cubic lattice} \end{cases} \tag{17.1}$$

A downhill energetic ordering of chromophores greatly biases the random walk. This principle is often referred to as an energy funnel, Fig. 17.3c, illustrating how high-energy pigments funnel excitation to energetically lower lying chromophores. In this downhill energy transfer model, excitation moves from the periphery towards the reaction center, and each step is associated with a small loss of energy as heat. The energy cost of the built-in irreversibility in the process is

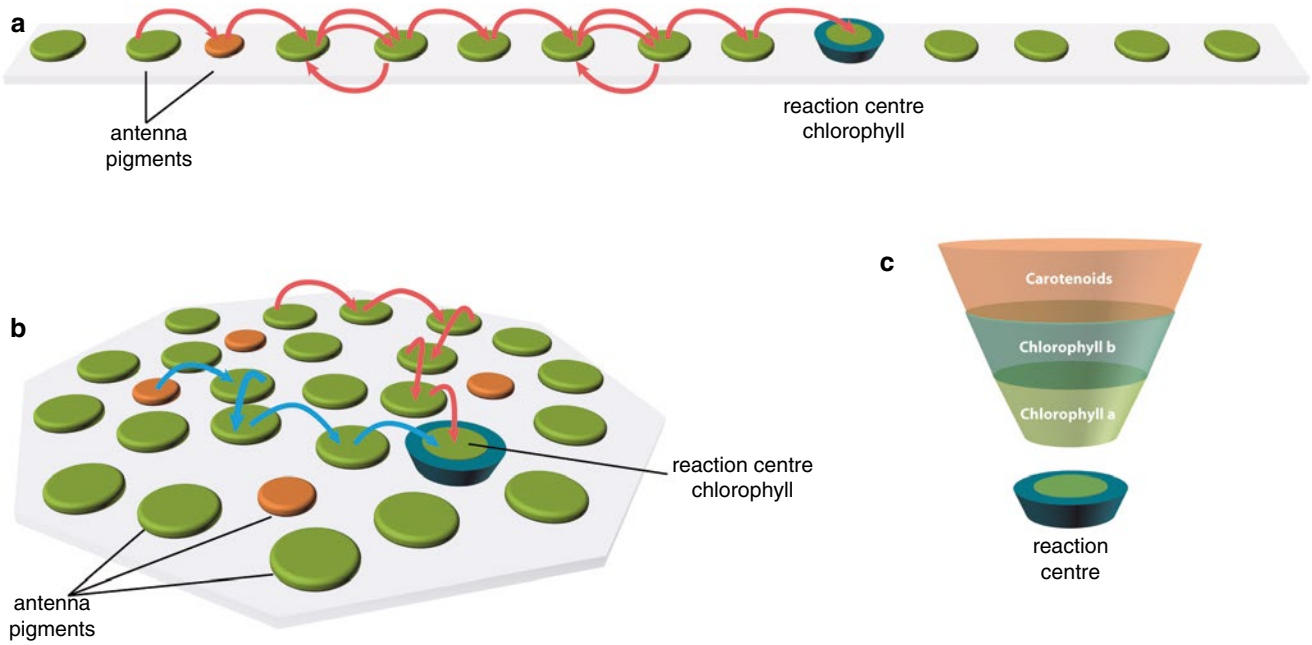

Fig. 17.3 Schematic illustration of excitation transfer paths taken in an inefficient one-dimensional arrangement model (**a**), where far more steps are necessary for the shuttling of the energy to the reaction center, as compared to when the light-harvesting chromophores rely on a three-dimensional spatial distribution (**b**). The funnel analogy of a photosynthetic antenna, where higher-energy pigments at the periphery are excited first and subsequently deliver the excitation energy to red-absorbing chromophores in the proximity of the reaction center

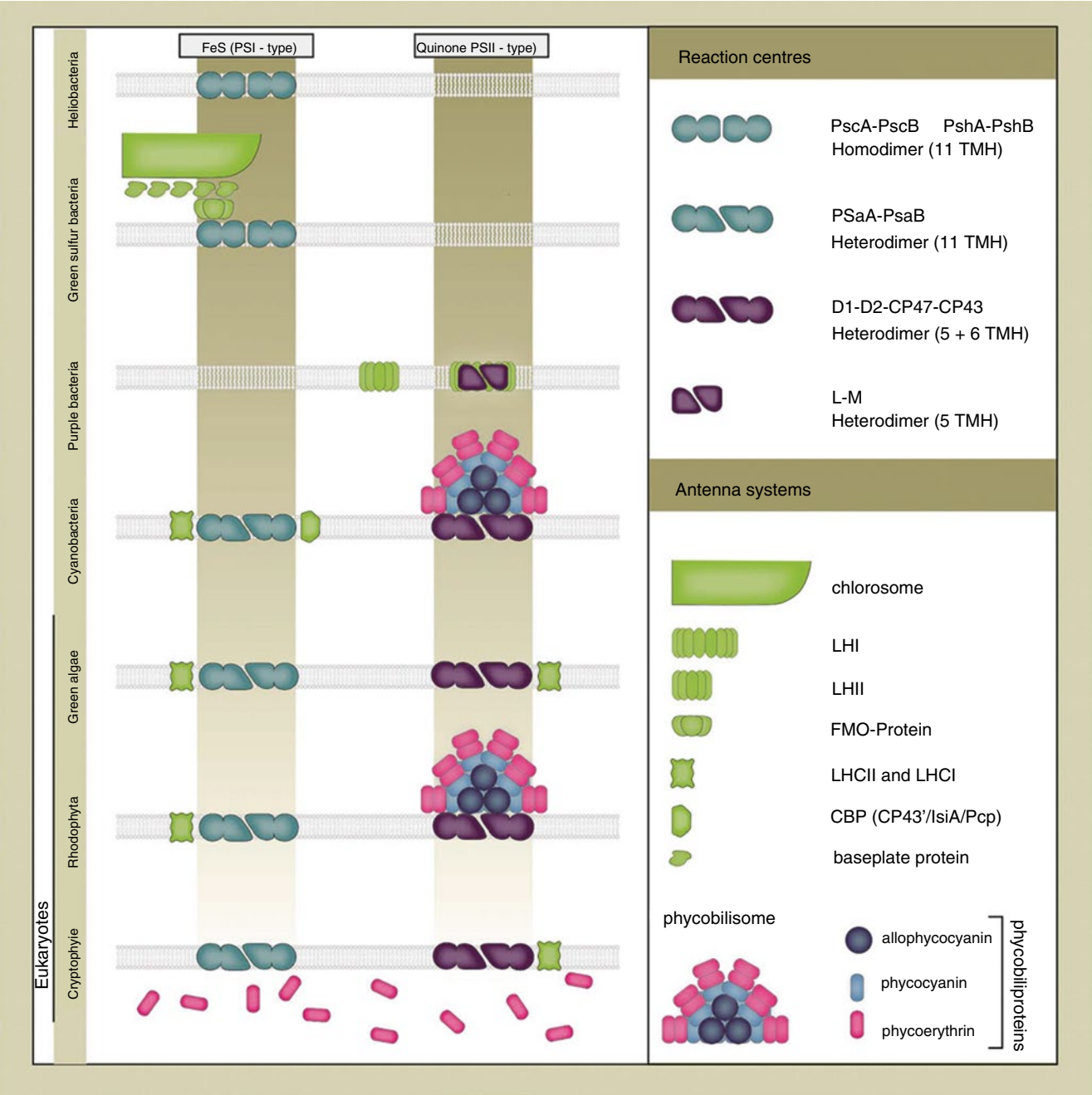

Fig. 17.4 Light-harvesting machinery of some photosynthetic organisms. Abbreviations: *TMH* transmembrane, *LH* light harvesting, *LHC* light-harvesting complex, *CPB* chlorophyll-binding protein

justified, as the net outcome is the concentration of the excitation energy at the reaction center.

Photosynthetic cells generally contain hundreds of thousands of reaction centers and tens of millions of antenna pigment molecules. Often, we think of an elementary unit, a photosynthetic unit (PSU), mentioned above, which represents a set of antenna associated with a particular reaction center, defined by a stoichiometric ratio between the total number of those two components. Theoretical treatments of membranes have focused on either treating all pigments individually, relying on a random walk process, or by grouping them in pools and only treating the interactions between the elementary units. On a microscopic level, describing the interaction among N pigments in a light-harvesting complex would require precise knowledge of the structural details, including the position, orientation, and relative distances. The kinetic properties would have to be evaluated by solving the rate matrix for the system of N coupled states.

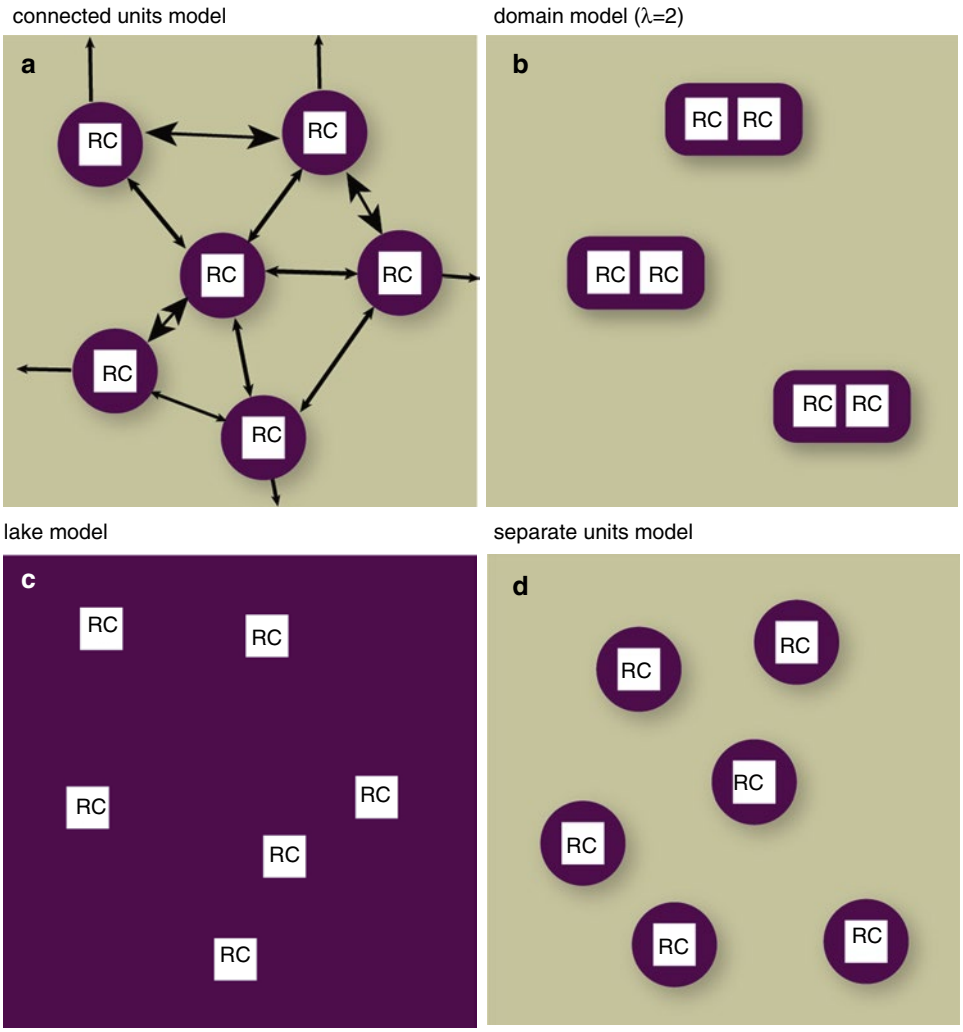

Fig. 17.5 Models of antenna organization. (**a**) Connected units, (**b**) Domain model. In the extreme cases of the separate units (puddle) model (**d**), antenna pigments are associated exclusively with a single RC, whereas in the lake model (**c**) energy absorbed by individual antenna pigments is equally likely to be transferred to any RC (Adapted from Bernhardt and Trissl (1999))

The sophistication and complexity of microscopic models can be circumvented by resorting to simplifying assumptions (e.g., energy transfer within the elementary unit is infinitely fast or the pigments are isoenergetic). That sort of global approach has previously been discussed by Bernhardt and Trissl (1999) by contrasting the "puddle" and the "lake" arrangement (Fig. 17.5). The separate units in the "puddle" model are completely isolated from one another, and their excitons are localized to that specific PSU. The other extreme is illustrated by the "lake" model, where reaction centers are embedded in a matrix of antenna pigments where excitons are free to visit any of the reaction centers. Upon encountering a reaction center that is closed to photochemistry, the energy could be transferred to a reaction center that is open, eventually leading to trapping. This model is applicable to many purple bacteria (Blankenship 2002).

A couple of variations of the intermediate case also exist, where exchange of excitons can occur between different PSUs to a certain degree. In the connected units model, developed by Joliot and Joliot (1964), the puddles are interconnected to a certain degree, but the degree of energy transfer between pigments in different puddles is less probable than between chromophores within the same puddle. In the domain model (Paillotin et al. 1979; Den Hollander et al. 1983), which is mathematically more sophisticated, a group of PSUs with a specific number of RCs are localized in a puddle (mini-lake). This scenario seems to be more obvious for dimeric aggregation of RCs, something observed in green photosynthetic bacteria, where more than one RC associates with a single chlorosome antenna complex well separated from other peripheral antennae (Blankenship 2002).

Fluorescence techniques have been developed to further elucidate these statistical models of PSU organizations. Relationships between the photochemical and fluorescence yields with respect to the fraction of open/closed reaction centers may distinguish between the extremes of a lake and puddle arrangement. Closure of a trap results in the removal of one of the decay pathways, prompting the increase in the fluorescence yield. In the puddle arrangement, the fluorescence intensity linearly increases with the fraction of traps that are

closed, but the relationship in the lake model is a bit more complicated, demonstrating a nonlinear increase of emission as the traps are progressively closed. This shows that in the lake model the diffusion of excitation is strongly facilitated with the final goal of the capture of that energy by an open trap, leading to comparatively lower emission yields in the lake arrangement as compared to the puddle architecture.

Today, our view of the PSU has become considerably more sophisticated, as detailed biochemical and biophysical information on specific complexes have become available. This has enabled the elucidation of the energy transfer events that occur within the PSU. High-resolution crystal structures have been elucidated for several light-harvesting complexes and that has inspired sophisticated models for energy transfer (van Grondelle and Novoderezhkin 2006; Cheng and Fleming 2009; Scholes and Fleming 2006; Renger and Müh 2013). Most recently, models that even include atomistic details of the protein environment have been reported (Olbrich and Kleinekathöfer 2010; Olbrich et al. 2011; Shim et al. 2012; Curutchet et al. 2011).

17.4 Energy Transfer Mechanism

Perrin in 1927 noted the phenomenon of energy transfer while undertaking fluorescence quenching experiments. Observations suggested that interactions between molecules in solution occurred over distances greater than their diameters and in the absence of collisions. It was realized that these interactions that lead to transfer of electronic excitation energy were derived from the Coulombic coupling between transition dipole moments of the molecules. Dipole-dipole coupling has an inverse distance-cubed dependence ($1/R^3$, where R is the center-to-center separation of donor and acceptor chromophores), so it can act to transfer energy between molecules separated by up to several nanometers.

The model was further clarified with the vision of Theodor Förster who realized that in solution, excited molecules undergo multiple collisions with the surrounding matrix, leading to phase decoherence before incoherent energy transfer can occur (Förster 1946). What this means is that spectral lines are quite broad for molecules in solution (or similar condensed phases) and therefore energy is conserved even when transferred between two chromophores with different spectra as long as the fluorescence spectrum of the donor overlaps to some extent with the absorption spectrum of the acceptor chromophore; see the shaded gray region in Fig. 17.6a. We now have a much better understanding of the origins of spectral line broadening; see Sect. 2 of Oh et al. (2011) and references cited therein. These details are significant in more sophisticated theories for energy transfer, but we will not cover that subject here.

Spectral overlap is much less probable for molecules in the gas phase at low temperature because the vibronic transitions are sharp lines, not broad bands. Nevertheless, the gas phase vibronic transitions of donor and acceptor chromophores can be an important ingredient in Förster theory. That is, vibronic progressions in the donor fluorescence spectrum and acceptor absorption provide an important contribution to the spectral overlap (energy conservation during energy transfer), especially when the two chromophores are different. For example, energy transfer from a green- to a red-absorbing molecule is enabled because of the donor fluorescence transitions to vibrations in its ground electronic state and/or acceptor absorption transitions to vibronic levels in the acceptor excited state. The Förster spectral overlap sums over all the ways these energy-conserving coupled transitions can happen.

Förster's interest in the topic of energy transfer was sparked by realizing that energy capture in photosynthesis was much more efficient than would be predicted assuming that photons were directly absorbed by the reaction centers. The highly efficient energy transfer between closely spaced chromophores was described in terms of a "hopping process," where excitation migrates through an antenna complex in a random walk fashion and each step is promoted by weak electronic coupling between the transition dipole moments of the light-harvesting chromophores.

Förster summarized his theory in an expression for the energy transfer rate from the donor to the acceptor, which is dependent on the center-to-center separation R, expressed in units of cm; the relative orientation of their transition dipoles (κ) (Fig. 17.5c); and the Förster spectral overlap integral, J_F (Fig. 17.6b). The rate is (Braslavsky et al. 2008):

$$k^{\text{Förster}} = \frac{1}{\tau_D} \frac{9{,}000(\ln 10) k^2 \phi_D J_F}{128\pi^5 N_A n^4} \frac{1}{R^6} \qquad (17.2)$$

where ϕ_D is the donor quantum yield, τ_D the excited state lifetime of the donor (in same units as $1/k$), n is the refractive index of the surrounding medium, and N_A (in units of mol^{-1}) is Avogadro's number. The Förster spectral overlap (J_F), which has the units of $M^{-1}\,\text{cm}^3$ or $M^{-1}\,\text{cm}^{-1}\,\text{nm}^4$, is derived from the overlap of the area-normalized donor emission spectrum ($F_D(\lambda)$) and the absorption spectrum of the acceptor expressed in extinction coefficients, $\varepsilon_A(\lambda)$ [$M^{-1}\,\text{cm}^{-1}$]. The expression for the Förster spectral overlap integral J_F is as follows:

$$J_F = \int_0^\infty F_D(\lambda)\varepsilon_A(\lambda)\lambda^4 \mathrm{d}\lambda \qquad (17.3)$$

An example calculation for the overlap integral J_F has been illustrated in Fig. 17.6b for the case of phycoerythrin 545 (PE545) (donor) and chlorophyll *a* (acceptor). Note that

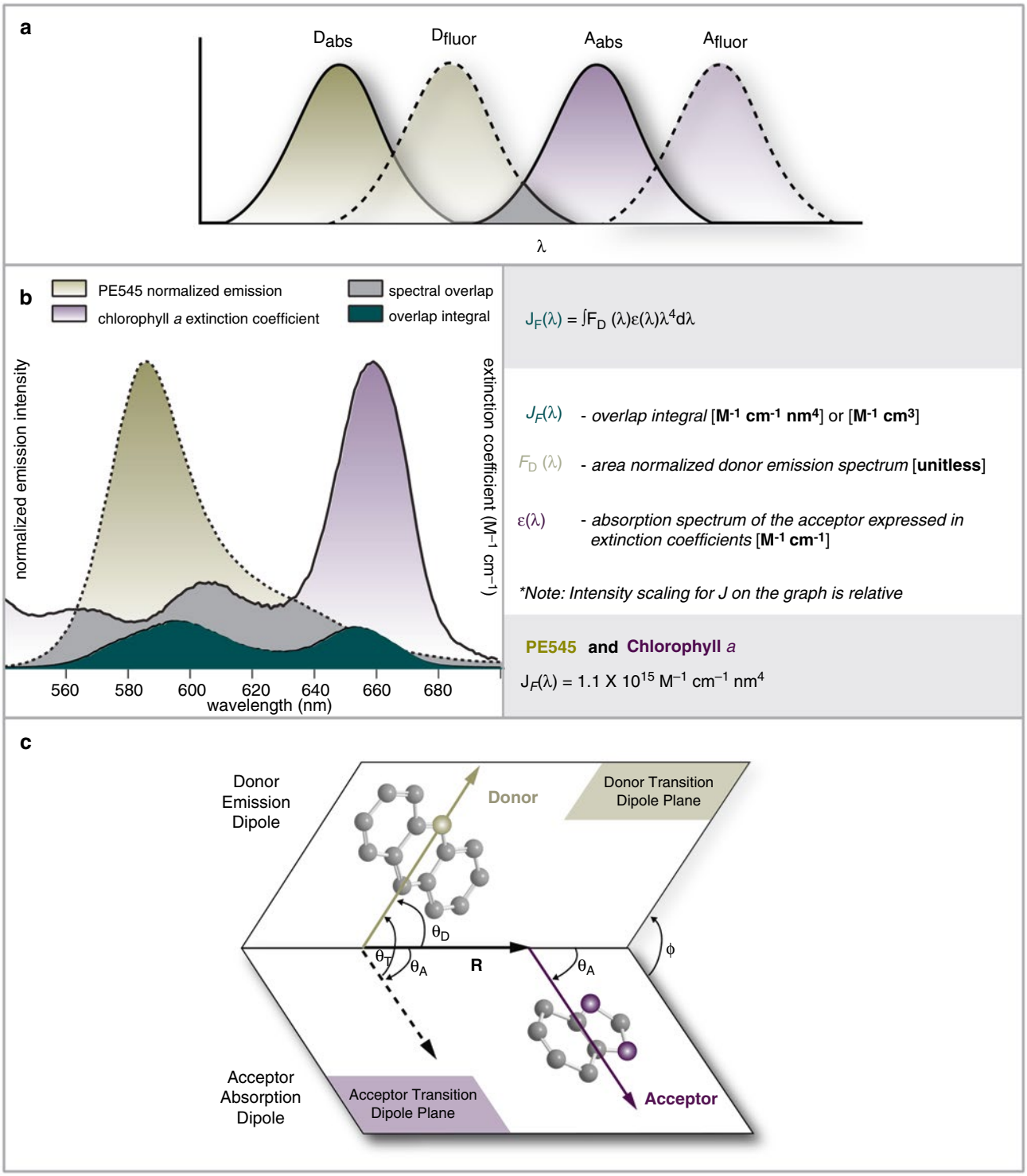

Fig. 17.6 (**a**) Spectral overlap of the donor emission and acceptor absorption required for Förster resonance energy transfer. (**b**) Calculated overlap integral between the emission of phycoerythrin 545 (PE545) and chlorophyll *a*. (**c**) Schematic representation of the angles used for calculating the orientation factor between two dipoles

the scaling for J_F on the graph is arbitrary, as the two *y*-axes are used for the donor and acceptor spectral intensities.

The other key ingredient in Förster theory, indeed all theories for energy transfer, is the electronic coupling. As mentioned above, in Förster theory the electronic coupling is assumed to be a transition dipole-dipole coupling, so it depends on $1/R^3$ and the orientation factor, κ:

$$\kappa = \hat{\mu}_D \cdot \hat{\mu}_A - 3\left(\hat{\mu}_D \cdot \hat{R}\right)\left(\hat{\mu}_A \cdot \hat{R}\right) \qquad (17.4)$$

where $\hat{\mu}_D$ and $\hat{\mu}_A$ represent transition dipole moment unit vectors of the donor and the acceptor, respectively, whereas $\hat{R}$ is the unit vector of the centre-to-centre separation of the transition dipole moments. The vectors and angles used to define the orientational factor are illustrated in (Fig. 17.6c), and the geometric graphic of κ^2 is summarized in the following expression:

$$\begin{aligned}\kappa^2 &= \left(\cos\theta_T - 3\cos\theta_D \cos\theta_A\right)^2 \\ &= \left(\sin\theta_D \sin\theta_A \cos\phi - 2\cos\theta_D \cos\theta_A\right)^2\end{aligned} \tag{17.5}$$

Despite the general success of Förster theory, numerous studies employing high-resolution structural models, ultrafast spectroscopy, and quantum chemical calculations indicate that only a few cases of energy transfer within photosynthetic light-harvesting complexes can be correctly characterized by conventional Förster theory. Chromophores in light-harvesting systems are generally found at very high concentration (up to 0.6 M in pigment-protein complexes), with a high degree of architectural organization. Even though pigment distances have been optimized to minimize electron transfer, which requires overlap of molecular wave functions, it is expected that the interaction energies of neighboring chlorophylls, located 0.5–2 nm apart, would vary widely and that the variation in the coupling strength would have a direct impact on the quantum mechanical characteristics of energy transfer kinetics. That has motivated developments that extend the original Förster theory (Beljonne et al. 2009; van Grondelle and Novoderezhkin 2006; Ishizaki and Fleming 2012; Cheng and Fleming 2009).

There are three principle ways that energy transfer theories need modification to predict energy transfer in light-harvesting complexes. First, electronic coupling must be calculated without invoking the dipole approximation, because of the close intermolecular separation described above. Second, the presence and role of molecular exciton states as excitation donors and acceptors need to be considered. That is usually done using generalized Förster theory (GFT) (Scholes and Fleming 2000; Mukai et al. 1999; Jang et al. 2004) or modified Redfield theory (Yang and Fleming 2002; van Grondelle and Novoderezhkin 2006). Third, solvent screening of the electron coupling should be considered (Scholes et al. 2007; Curutchet et al. 2011). More subtle, yet highly interesting, corrections are needed to account for dynamical effects of coherence (Scholes 2010; Ishizaki and Fleming 2012; Lambert et al. 2013).

The electronic coupling between the donor and acceptor chromophores, which promotes electronic energy transfer processes in photosynthetic light harvesting, can be partitioned into a long-range coulombic contribution (sometimes also referred to as electrodynamic interaction), V^{ed}, and a short-range term, V^{ioo}, which is dependent on interchromophore orbital overlap (Scholes 2003; Olaya-Castro and Scholes 2011) and becomes very significant below 5 Å. The coupling term, V^{total}, at all separations can be expressed as the sum of the two contributions:

$$V^{total} = V^{ed} + V^{ioo} \tag{17.6}$$

In Förster theory, the weakly coupled chromophores are assumed to be well separated compared to their size, so that the short-range term V^{ioo} is neglected, and the Coulombic coupling can be approximated as a point dipole-dipole interaction. This model that centers on the localized donor-acceptor states is, for example, applicable to the weakly coupled B800 ring of purple bacterial LH2 (Krueger et al. 1998). The main problem with the dipole-dipole approximation is that it works well only when the separation between chromophores is large compared to the size of those molecules (or if the molecules and their arrangement are symmetric, like a "sandwich" dimer of anthracene molecules). When the dipole approximation fails, we need to account more realistically for the shape of the transition densities of the chromophores when we calculate the Coulombic coupling between them. A straightforward approach is to use the transition density cube (TDC) method developed by Krueger and co-workers (Krueger et al. 1998). How and why this is useful is reviewed elsewhere (Scholes 2003; Scholes and Fleming 2006).

Interchromophore orbital overlap effects V^{ioo} influence the electronic coupling when molecules are very close. The main case where they matter is when the transitions on the molecules—de-excitation of the donor and excitation of the acceptor—are spin forbidden (Andrews et al. 2011). Triplet-triplet energy transfer and the closely related energy transfer from triplet chlorophyll to sensitize singlet oxygen are processes in photosynthesis mediated by V^{ioo}.

17.5 Summary and Further Reading

We recommend specialist reviews for more detailed information on the biophysics of light harvesting (Green and Parson 2003; Sundström et al. 1999; van Grondelle and Novoderezhkin 2006; Novoderezhkin and van Grondelle 2010; Scholes et al. 2011; Renger and Müh 2013; Cheng and Fleming 2009; Fassioli et al. 2014). One of the topics that has generated great interest recently is the question of coherence in light harvesting. In other words, is the incoherent hopping model, where excitation energy jumps randomly from molecule to molecule, sufficiently accurate to capture the details of light harvesting? It is clear this model does not work when chromophores are relatively strongly electronically coupled. We suggest the interested reader to refer to these reviews—and references cited therein—for more information (Fassioli et al. 2014; Scholes et al. 2011, 2012; Cheng and Fleming 2009; Ishizaki and Fleming 2012; Huelga and Plenio 2013).

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